Contribution of Point Source Inputs of Phosphorus from a Bunker Silo in a Small Agricultural Watershed in Southern Ontario, Canada

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.

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Abstract

Nutrient losses from agricultural operations contributes to the issue of eutrophication of freshwater systems. Although many studies have been conducted on diffuse nutrient losses from fertilizer application, there is a paucity of studies on point source phosphorus (P) loss from bunker silos. Furthermore, the build-up of legacy P in the landscape from historical land management practices can create critical source areas of P that contribute to P loads long after those practices cease. The goal of this thesis is to quantify the contribution of a dairy farm (dominated by bunker silo losses) to watershed P losses, and to monitor P concentrations in surface and groundwater across a riparian zone to characterize the sorption potential of its sediments and infer whether the riparian zone may be acting as a sink for P, or a source of previously retained (legacy) P to the stream. Stream discharge was monitored continuously throughout the study, and automatic water samplers were deployed in the stream above, and below the bunker silo to analyze soluble reactive P (SRP), total dissolved P (TDP), and total P (TP) on an event basis. The riparian zone was equipped with a series of nested wells and piezometers along a three transects to monitor groundwater P levels, and to determine the hydraulic conductivity of the riparian groundwater. A transect was also installed on the unaffected side of the transect as a reference. The farmyard contribution to watershed P losses over a one-year period was 32% (SRP) and 22% (TP). Cumulative loads over the entire study suggest that the farmyard P losses were 21.2 kg/ha SRP and 120 kg/ha TP. Peak P concentrations occurred during snowmelt and thaw events and were smaller during periods of baseflow. However, after the bunker silo was refilled in mid-summer months, both SRP and TP were considerably elevated. Large amounts of P were found to be stored in the riparian soil, however, estimated contributions of riparian P to the overall loads were negligible. This may be a result of missed flowpaths during site set-up, or an occurrence of upwelling of P in the streambed. The results of this research suggest that this particular farmyard bunker silo contributes large amounts of P to the adjacent stream on an annual basis. This study should be used as a starting point for future studies examining livestock farmyard nutrient losses.

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Chapter 1

Introduction and Problem Statement

Agricultural intensification over the past several decades has led to substantially higher levels of phosphorus (P) and nitrogen (N) in groundwater and surface water bodies, and is a contributor to eutrophication (Hoffmann et al., 2009; Scalenghe et al., 2002). The problem of nutrient loss in agriculture is not a new phenomenon. The USEPA (1988) attributed nonpoint source pollution from agriculture as the major source of contamination in lakes and streams, and this continues to be the case today in many areas, such as the Lake Erie watershed (IJC, 2014). Nutrients may be supplied from excess fertilizer or manure application in fields, but can also come from livestock farms through leaching from bunker silos or runoff from feedlots or manure storage. Indeed, many efforts have been focused on quantifying and reducing diffuse nutrient loss from cropped fields over wide areas, with less research emphasis placed on 'point' sources on livestock farms such as bunker silos or manure storage. Consequently, the relative importance of these 'point' sources relative to diffuse sources from fields remains unclear. The few studies that have been done on this subject have shown that livestock farming and the use of bunker silos contribute significant nutrient loads to freshwater ecosystems with little consideration to mitigate (Gebrehanna et al., 2014; Haigh, 1999; Holly et al., 2018). Despite the considerable efforts placed on conservation practices in fields across North America, Sharpley et al. (2013) pointed out that efforts to improve agricultural water quality through conservation programs have experienced little success. Some of this is due to insufficient farmer adoption, some due to the presence of legacy nutrients in the landscape, but some may also be due to the fact that there may be significant nutrient sources in the landscape (such as bunker silos) that have been overlooked. Thus, there is a need to understand the contribution of bunker silos to nutrient losses from watersheds, both in terms of magnitude and the timing of losses.

Although there is a paucity of information on the role of bunker silos in nutrient losses from agricultural watersheds, there is a general awareness that they are a potentially high nutrient source. Consequently, land management features such as riparian zones are used to mitigate losses because these zones permit a remarkably diverse set of environmental and biogeochemical processes that can control nutrient losses. Although these landscape units can effectively reduce nutrients in runoff, these zones can become enriched with nutrients over time and consequently become ineffective. Thus, an improved understanding of riparian zone function in livestock-impacted areas is needed. This thesis explores the contribution of a bunker silo to watershed P loads and evaluates the role of an adjacent riparian zone in modifying runoff chemistry.

Chapter 2 Literature Review and Thesis Objectives

2.1 Eutrophication & Nutrient Reduction Targets

Phosphorus is an element that is essential to life. In freshwater systems, it is often the limiting nutrient that controls the growth of algae and other aquatic plants (Schindler, 1978). When an excess of P is introduced into a system, the pace at which algae grows substantially increases, often leading to eutrophication, which is problematic. Thus, the importance of properly managing or mitigating nutrient loss from agricultural watersheds should not be overlooked.

The issue of eutrophication is not a new issue. Indeed, Hasler (1947) observed the implications of excessive additions of nutrients from domestic and agricultural drainage, including the loss of salmonid fishes, an increase in coarse fish, compositional species changes of plankton, and the occurrence of blue-green algal blooms from 37 lakes around the world. Although eutrophication is not a new issue, there has been an increase in the frequency of algal blooms in many freshwater systems both within North America and globally (Carpenter et al., 1998). The eutrophication of freshwater lakes has significant ecological and economic implications (Sharpley et al., 1994). Consequences of eutrophication can include depletion of dissolved oxygen, increased incidents of fish kills, reductions in species diversity and harvestable biomass, formation of potentially toxic or harmful algal blooms, and water treatment problems (Smith & Schindler, 2009). Moreover, eutrophication has implications on the economic growth. One U.S. study evaluated potential annual value losses in several categories (recreational water usage, waterfront real estate, spending on recovery of threatened and endangered species, and drinking water), and found that the combined economic costs were ~$2.2 billion annually (Dodds K et al., 2009). Indeed, eutrophication can have a severe impact on the economy and the ecological make up of freshwater systems.

To combat these issues, the Great Lakes Water Quality Agreement (GLWQA), a bi-national agreement between the United States and Canada, formalized in 2012, agreed to work towards a reduction of excess nutrient loading to Lake Erie. The GLWQA set a goal to reduce total phosphorus (TP) entering the western and central basins of Lake Erie by 40%. Given that much of the inputs to Lake Erie originate from agricultural sources (IJC, 2014), reducing P loss from agricultural operations is a key step in improving the quality of water entering Lake Erie.

2.2 Phosphorus in Terrestrial Ecosystems

2.2.1 The Phosphorus Cycle and Forms of Phosphorus

The global P cycle has four main components: (i) the exposure of bedrock material from tectonic uplift that contains P bearing rocks and minerals that are slowly weathered due to natural forces; (ii) the supply of particulate and dissolved P to receiving soils and rivers through the process of physical erosion and chemical weathering; (iii) the transport of P from soils to bodies of water; and (iv) the deposition and sedimentation of P in lake or river beds (Ruttenberg, 2003). In comparison with other essential components of organic matter, P is cycled on a geologic time-scale, and has very low atmospheric returns (Walker & Syers, 1976). The weathering of continental bedrock, specifically apatite – the most abundant primary-P mineral – is the largest natural contributor of P to soils. During the weathering process, soluble P is made available for terrestrial plant uptake and is returned to the soil through decayed litterfall (Ruttenberg, 2003). When the breakdown of primary minerals occur, P eventually transitions into the pool of SRP. This pool is ultimately adsorbed to soil or bound to other mineral forms (Smeck, 1985). Soluble reactive P in solution that has adsorbed to mineral compounds can be desorbed, and can again become bioavailable for plant uptake (Kleinman et al., 2011), or lost to surface water bodies. Humans have disrupted the natural cycle of P by mining P-bound minerals and producing fertilizers that are applied to agricultural lands to improve crop yields. Unfortunately, humans have applied P at a greater rate than it can be used by plants, which has led to a build-up of P in agricultural soils (Haygarth et al., 2014). This 'legacy' P is significant because it can supply P to runoff, which can eventually enter rivers and lakes.

Phosphorus may exist in soils as organic or inorganic P. Organic P is found in undecomposed residue, microbes, and within organic matter throughout the soil, such as parent material, while inorganic P (P_i) is often bound to aluminum (Al), iron (Fe), and calcium (Ca) compounds and may be available for plant uptake (Sharpley et al., 2003). The presence of Al and Fe are common indicators of P_i, and many studies have focused on their interactions (Sallade & Sims, 1997; Scalenghe et al., 2002; Shenker et al., 2005). Phosphorus is primarily held on the oxides of clay particles in soils through adsorption-desorption reactions, governed by equilibria exchange. Depending on soil type and pH, relatively insoluble forms of P are often rapidly fixed becoming unavailable for plant uptake.

Although P is held by the metallic oxides of clay particles, this previously held P can be released when oxygen is absent and Fe^{3+} is reduced to Fe^{2+}. Sallade and Sims (1997) incubated soils from agricultural drainage ditches for a 21-day period in anoxic conditions. They observed an decrease in redox potential and pH, and a positive correlation between the increase of Fe and SRP. Their results showed the substantial amount of P that can be desorbed from Fe oxides during short periods of flooding.

Phosphorus may be lost in runoff in either dissolved or particulate forms. Dissolved P forms are lost through desorption (Fe, Al) and dissolution (Ca) reactions. Dissolved P can also be released from plant material (Sharpley et al., 1992; Sharpley et al., 2003). In contrast, particulate forms of P are lost through erosive processes as the P is attached to soil particles. In Ontario, roughly 80% of P lost from agricultural fields is as particulate P in loam soils (Plach et al., 2019). When P lost in agricultural runoff ends up in receiving water bodies, the dissolved P is immediately available for aquatic plants, whereas particulate P can only become available to plant uptake with a change in chemistry in anaerobic environments (Sharpley et al., 2003).

2.2.2 Agricultural Phosphorus Management

As a limiting nutrient in aquatic and terrestrial vegetation, the demand for P in agriculture is high, leading to high rates of fertilizer application. Indeed, the global P demand in fertilizers in 2015 was 41.2 million tonnes, with 5.04 million tonnes used in North America (FAO, 2017). Phosphorus can be delivered to freshwater systems diffusely or directly, through point sources. Many studies have focused on diffuse sources of nutrient pollution in agriculture, as it has proven difficult to manage. Although it is important to manage edge of field losses such as surface runoff or tile drainage, point sources of nutrient pollution must also be considered. Historically, the 'point' P sources that have been emphasized have been septic systems and urban runoff, and less emphasis has been places on farmyards. Because farmyards receive precipitation that 'runs off', they are still considered to be 'diffuse' sources. However, because there are zones within farmyards that contain very rich P sources (e.g. bunker silos and manure storage), these zones actually behave more like 'point' sources in the landscape. Many livestock farmers have manure storage lagoons to contain the P in the landscape. However, bunker silos are not as carefully managed. Unfortunately, seepage occurs from bunker silos, creating effluent with high levels of nutrients that can be lost to the environment and perturb aquatic systems.

2.2.3 The Role of Bunker Silos in Agriculture and How They Function

Bunker silos are a vital part of any livestock operation, as they store silage in an easy to access manner that will be the main source of food for the livestock. The production of silage involves several stages, aiming to finish with a product that has retained an optimal nutrient balance. The fermentation of harvested crop ensures the preservation of large amounts of silage that will be used over winter months. This is achieved by transitioning silage from an aerobic to an anaerobic state, ultimately lowering the pH to somewhere between 3.5 – 5, inhibiting putrefying bacteria (Gebrehanna et al., 2014). However, during this stage of fermentation, nutrient-rich effluent is produced that can travel to receiving soils and waters, causing an excess of nutrients within them. Effluent production is difficult to manage, as untreated effluent is rich with N and P, has a high biological oxygen demand, and has a low pH that can damage concrete and steel structures (Fransen & Strubi, 1998; Gebrehanna et al., 2014; D. I. Jones & Jones, 1994). Given the nutrient-rich effluent from silage, some farmers have employed wetlands adjacent to bunker silos to mitigate potential water quality issues. However, the efficacy of these features in attenuating nutrients is not known. It is therefore important to further understand the effects that bunker silo effluent can have on receiving soils and streams, and the potential for treatment wetlands to mitigate these losses.

2.2.4 Importance of Riparian Zones in Agricultural Systems

Riparian buffer strips or zones are wetlands adjacent to streams and ditches that are found extensively in agricultural systems, serving a crucial role in protecting our freshwater ecosystems and providing important ecosystem services by helping keep rivers and lakes from accumulating high amounts of chemical constituents. Riparian zones link upland terrestrial environments to aquatic ecosystems and include important ecological processes that are a regulated by the larger environmental landscape surrounding the riparian zone (Naiman et al., 1993). Furthermore, vegetation found in riparian zones regulates various aspects and processes within it, including light and temperature regimes, nourishment of aquatic and terrestrial biota, regulation of flow and nutrients from upland areas, and provide a variety of ecosystem services that maintain biodiversity within riparian soils (Décamps & Naiman, 1990).

The land-water interface that separates upland terrestrial environments from aqueous ecosystems is a hotbed of biogeochemical activity. Riparian zones typically cover a small portion of the landscape, but play a significant role in filtering nutrients and other contaminants from groundwater and surface runoff (Dahl et al., 2007). Moreover, their ability to retain the nutrients that pass through their soils increases their importance, especially in agricultural environments, where nutrient loading is often of concern. In catchments dominated by agriculture, it is common to see fields flanked by narrow riparian zones that are situated adjacent to a small stream or drainage ditch.

Given the great potential of riparian zones to retain nutrients in agricultural runoff, these zones are sometimes situated next to 'point' sources such as bunker silos or manure storage to 'treat' runoff before it enters receiving waters. Although riparian zones have great potential to retain nutrients, their efficacy differs both spatially and temporally. The ability of a riparian zone to reduce P is dictated by flowpaths and biogeochemical reactions that occur within them (Hoffmann et al., 2009).

2.3 Flow Paths within Riparian Zones

The efficacy of a riparian zone at attenuating nutrients in runoff can be impacted by the flowpaths through which water travels through the riparian area. There are several flowpaths within riparian zones that regulate the physical and biogeochemical processes that control retention mechanisms and the flux of nutrients that may enter. Two major flowpaths include (1) diffuse shallow groundwater flow, and (2) overland flow (Hoffmann et al., 2009).

Diffuse groundwater flow represents areas where local and or regional groundwater flow passes through the riparian sediment and into the stream. However, the composition of riparian sediments, and the hydrologic conditions within the sediment dictate the rate of flow (Devito et al., 2000). Subsurface geology is also an important factor that can impact groundwater flow through riparian soils (Vidon & Hill, 2004). Heavily compacted peat, for example, will have significantly lower flow rates, slowing the flow of groundwater, and potentially increasing nutrient retention within the riparian sediments. Conversely, a sandy loam soil will have a higher hydraulic conductivity, increasing groundwater flow rates. Hydraulic conductivity and hydraulic head control factors such as the flow path and direction, and the residence time of groundwater and associated solutes (Hoffmann et al., 2009).

Overland flow has much shorter residence times within a riparian zone when compared to groundwater flow, as water travels above the surface and flow velocity is generally driven by slope and the roughness of the vegetation. However, if the overland flow rate is high enough or vegetation is submerged beneath the floodwaters, particulate P can be carried though the riparian zone and into the receiving water body (Dorioz et al., 2006). Nutrient loading is also heavily influenced by antecedent moisture conditions of soils. Saturated soils are often quicker to generate overland flow (Hively et al., 2005). Hively et al. (2005) also notes that high intensity, short duration summer rain events generate overland flow very quickly, especially in barnyards and cow paths, where nutrient rich runoff may accumulate, amplifying nutrient concentrations. Although diffuse groundwater discharge is an important pathway for nutrient loading, there are several other pathways that can facilitate P loading in agricultural systems.

Floodplain inundation has also been shown to contribute significant loads of P to surface waters (Hoffmann et al., 2009). Both pathways can contribute significant loads of P to surface waters. The inundation of floodplains during extreme precipitation events or wet seasons (fall wet-up/spring snowmelt) can play a major role in nutrient losses. Desorption of P in anaerobic environments can occur when levels of soil P are high, which is common with well established, long-term buffer zones (Hoffmann et al., 2009; Uusi-Kämppä, 2005). Riparian zones play an important role in filtering nutrients before they can enter freshwater ecosystems. This becomes critical in agricultural environments where nutrient loads can be substantial and are easily lost to the environment if poorly managed.

2.4 Biogeochemical Processes and Retention Mechanisms of Phosphorus in Riparian Zones

Retention mechanisms in riparian zones are governed by a variety of physical and biogeochemical processes, and are influenced on a spatiotemporal scale. These processes include sediment deposition, sorption and precipitation, reduction oxidation processes, plant uptake, and biological mineralization-immobilization dynamics. Furthermore, different forms of nutrients that enter riparian zones will interact with it differently. For example, particulate P may enter a riparian zone through overland flow, or wind-blown sediments, while dissolved P can enter through groundwater flow. Some elements of a riparian zones are better at retaining P than others, however, if managed correctly, coupling elements such as width and slope can greatly increase the amount of P that is retained.

The sedimentation of PP can occur in riparian zones during precipitation events, overland flow, and floodplain inundation. However, several aspects control the amount of sedimentation that occur within a riparian zone during times of overland flow, like the volume of flow and flow velocity, infiltration rates of soils, vegetation type and density, slope, and width of riparian zone (Hoffmann et al., 2009). Residence time of surface runoff plays a major role in determining retention potential. Kronvang et al. (2007) determined that a residence time of ~7 days was necessary to retain 50% of the bioavailable P in a constructed wetland in the Central Swiss Plateau in an agricultural catchment. Infiltration can also enhance P retention of finer sediment associated P particles that become entrapped within the soil profile of the riparian zone, and reduce runoff volumes and sediment transport capacity (Hoffmann et al., 2009). Furthermore, dense vegetation cover will result in an increased hydraulic roughness of a riparian zone, resulting in decreased flow velocity that will in turn increase the potential for sedimentation and ultimately P retention. The form of P being transported in runoff governs the likelihood of the P reaching freshwater. Particulate P, for example, is much more likely to become deposited within the riparian zone than P in the dissolved form during overland flow due to the roughness of the vegetation, which slows the velocity of water and thus its carrying capacity for sediments (Cooper et al., 1995). Indeed, this is a major reason why riparian and vegetated buffer strips have been recommended as a best management practice to mitigate P loss from agricultural fields.

Riparian zone vegetation can play a vital role in sequestering nutrients. Although nutrient accumulation in non-woody biomass may only result in short-term retention, long term accumulation in woody biomass is possible (Naiman & Decamps, 1997). The difference between woody biomass and non-woody biomass is the life cycles. In cool, temperate climates, non woody biomass typically dies during colder winter months, and can release P that it has previously taken up, whereas woody vegetation has a much longer lifespan, and will retain a larger amount of P for much longer. Harvesting of riparian vegetation can be a way to remove substantial amounts of P, and initiate further P uptake. Richardson and Marshall (1986) showed P uptake in a fen peatland of 2 – 5 kg/ha yr^{-1}. Furthermore, harvesting plant biomass in riparian zone wetlands can enhance species diversity (Verhoeven et al., 1983), and increase its P retention ability through plant uptake.

Indeed, there are a number of physical features that can enhance a riparian zone's ability to function as a filtration system for nutrient runoff. Perhaps the most important features include the slope, soil type, width, and vegetation type within a riparian zone. An experimental field study conducted by Abu-Zreig et al. (2003) found that wider riparian areas were able to retain larger amounts of P, and that 31-89% P retention occurred in 2-15 meter wide riparian zones, respectively. Wider riparian areas do not always equate to higher rates of P retention, despite the fact that they result in longer solute residence time and give more time for biogeochemical reactions to occur. Unfortunately, riparian zones are often too narrow, so that a maximum crop yield can be met. The slope of a riparian zone can also affect its retention efficiency, as gentler slopes are able to retain more P than steeper ones (Abu-zreig et al., 2003) by allowing a greater residence time and minimizing erosive forces. Vegetation such as dense grasses are most effective in retaining P, largely because it slows down surface runoff and encourages deposition or permits adsorption and biological uptake (Osborne and Kovacic, 1993). Given that P is readily adsorbed by the oxides of clay particles, riparian zones with greater clay content can more readily adsorb P. Furthermore, the age of a riparian zone may also play a role in its retention efficiency. Sharpley et al. (2013) discusses legacy P and a riparian zones ability to retain additional P inputs when the vegetation and soils have been saturated with P from previous and historical land management. Areas within riparian zones that have accumulated large amounts of legacy P can become potential hotspots of P release during overland flow or flooding. However, the presence of other minerals such as Fe and Al oxides can affect biogeochemical reactions during times of overland or groundwater flow.

A positive correlation exists with the presence of Fe and Al oxides and the sorption capacity of P, especially in groundwater recharge areas, where Fe and Al oxides often accumulate. The specific surface areas of these amorphous inorganic minerals are quite large, and are therefore a suitable host for P sorption, rather than more crystalline forms (Darke &

Walbridge, 2000). Darke and Walbridge (2000) established that P sorption varied seasonally, however, found that sorption peaked in the spring and early summer, when agricultural runoff was concentrated with fertilizers. Moreover, higher concentrations of Fe and Al in summer, rather than winter months, were attributed to seasonal flooding and deposition of the amorphous oxides, or perhaps a change of Fe and Al chemistry brought on by flooding and anaerobic conditions. Phosphorus retention efficiency in riparian zones is governed by the Equilibrium P Concentration (EPC_0), where the concentration sorption and desorption are equal. If inputs of solutes have P concentrations higher than the EPC, soils will sorb P and act as a sink, however, if solutes have P concentrations that are lower than the EPC desorption of P occurs and will act as a source of P (Froelich, 1988; Hoffmann et al., 2009). This is important in the case of riparian zones, as they have the ability to shift between sources and sinks as conditions change (e.g. oxic/anoxic conditions) or runoff quality changes.

In addition, the potential of sediment P to be resuspended during hydrological events is high, and any P that has sorbed to the sediment may be released. The inundation of floodplains is normally not a regular occurrence, however, will typically happen during large snowmelt events, or precipitation events in the early spring. Deposition of riverine sediment in riparian floodplains is a way of P retention during inundation, however, the anoxic environment creates ideal conditions for reductive dissolution of Fe^{3+} oxides to Fe^{2+}, and the subsequent desorption of phosphates to the solutes within the anoxic zone (Hoffmann et al., 2009).

Riparian zones are important landscape features, found at the interface between fields or farmyards and streams or ditches on farms. While these zones have the potential to treat runoff before it enters receiving waters, their efficacy can vary substantially in space and time. It is unclear if these zones are able to retain P from high input land uses such as bunker silos, or if these zones may in fact release the previously stored P to runoff passing through them.

2.5 Thesis Objectives

Much of the research done on agricultural nutrient loss has focused on diffuse pathways, and a knowledge gap exists on the importance of small 'point' sources such as bunker silos on agricultural nutrient losses. The purpose of this research is to provide an improved understanding of the role of bunker silos on P loss in the environment, and the efficacy of riparian zones at attenuating those losses. The specific objectives of this thesis were to:

1) Quantify the contribution of a dairy farm (dominated by bunker silo losses) to watershed P losses over a one-year period, and
2) Monitor P concentrations in surface and groundwater across a riparian zone, and characterize the sorption potential of its sediments to infer whether the riparian zone may be acting as a sink for P from the bunker silo or as a source of previously retained P to the stream.

Chapter 3 Materials and Methods

3.1 Study Site

The study was conducted in the Hopewell Creek watershed on a dairy farm, located ~15 km northeast of Waterloo, just outside of Maryhill, Ontario (Figure 3.1). The area of the Hopewell Creek watershed is 72 km^2, however, the specific drainage area of the study site (subwatershed within the Hopewell Creek watershed) was roughly 14 km^2. Water from this drainage area flows into Hopewell Creek, a small tributary to the Grand River, which subsequently drains into Lake Erie.

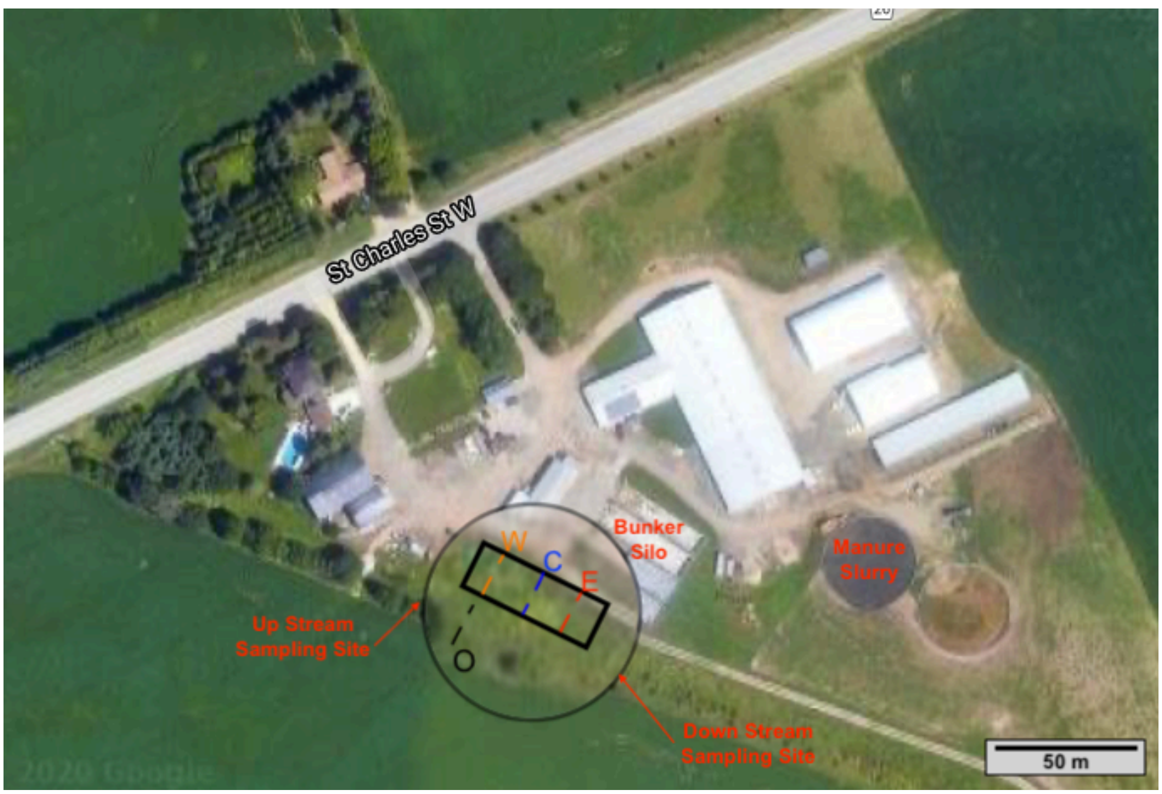

Figure 3.1: The location of the farmyard and bunker silo relative to the riparian zone and stream are shown. The locations of the monitoring transects and the stream sampling locations are also shown in orange (west transect), blue (center transect), red (east transect), and black (opposite transect).

The area receives a mean annual precipitation of around 900 mm (17% as snowfall) and experiences a cool, temperate climate. Thirty-year mean air temperatures range from -6.5°C and 20 °C in January and July, respectively (Environment Canada, 2019). The soil types within the watershed are dominated by Humic gleysols, and are classified texturally as loam/silt loam over a loam till. There is a common presence of ferric iron concentrations within the soils (Presant & Wicklund, 1971). Land use within this catchment is predominantly agricultural (46%) and forested (41%), with very little residential areas (9%) (Irvine et al., 2019). Agricultural land use in the contributing area is primarily corn, soy and winter wheat rotation row crops. At the base of the 14 km^2 sub-watershed, there is a dairy farm (Figure 3.1) with 250 cows. Although there is pasture for the cows on this farm, this pasture is located downstream of the specific study site.

A small section of riparian zone and a section of the stream located adjacent to the dairy farm (Figure 3.1) were selected for study. The cattle barn is located ~100 meters from the study site, and manure is pumped into a storage lagoon just over 100 meters from the study site. No cattle access the stream. A bunker silo is located within 15-20 meters adjacent to the study site, situated between the stream and the cattle barn, and has been at that site for approximately 15 years. The storage capacity of the bunker silo is roughly 2600 m^3 that can hold ~ 630 cubic feet of feed on a dry matter basis; however, all bunkers are not always filled to capacity. The bunker silo is refreshed annually in late July to early August. Following this time, approximately 2.3 tonnes of silage are used to feed livestock on a daily basis, slowly reducing the storage of material held in the silos throughout the year. Three of the four bunkers store corn silage, while the remaining bunker stores alfalfa (haylage). All silage is treated with a bacterial inoculant to enhance fermentation after storage. A residential property is located near the stream but does not contribute significant quantities of runoff or nutrients to the stream.

Soil characteristics within the riparian zone, determined visually, varied across the study site. Locations in closest proximity to the bunker silo had a top layer of loamy soil, followed by a layer of coarse gravel, then a sandy clay loam at depths greater than roughly 1 meter. Locations further from the road had less of a gravel layer, and instead had a thicker layer of loamy soil that transitioned into a sandy clay textured soil at depths of roughly 1 – 1.5 meters. Surface soils were classified as loamy to silty loam.

Two concentrated overland flow paths (east and west transects) were evident within the studied section of the riparian zone, which received direct surface inputs from the bunker silo. These flow paths were in small elevation depressions and were often saturated with runoff, whereas the zone between these flowpaths was slightly higher in elevation (center transect), exhibited drier characteristics and did not receive any direct inputs from the bunker silo. The riparian zone vegetation consisted of mixed grass species with no trees or wooded vegetation, and had mean slope of 5.3%.

Figure 3.2: Flooded riparian zone after snowmelt and precipitation event (a), and late fall during drier conditions (b). Bunker silo with silage (c), and bunker silo opening (d)

3.2 Experimental Design

To determine the contributions of the farmyard (dominated by bunker silo effluent), water chemistry in a stream adjacent to the bunker silo was monitored ~50 m upstream (Up) and ~30 m downstream (Down) of the farmyard (total length of study reach ~110m) over a one-year period (Jan 2018 – Jan 2019) and combined with streamflow to determine annual P loads and yields.

To examine the role of a riparian wetland situated between the silo and stream in modifying runoff chemistry, a 30 m long, 12 m wide section of the riparian zone was selected for detailed study. Three transects were installed across the riparian zone, running between the bunker silo and the stream, and an additional transect was installed on the opposite side of the creek (unimpacted/opposite; Table 1, Figure 3.1). The east and west transects were installed along the concentrated flowpaths from the bunker silo (described above), whereas the center transect was installed in the zone between the east and west transects that did not receive direct inputs from the bunker silo. Shallow groundwater was monitored along these transects, along with soil biogeochemistry to assess potential P retention or release from the riparian zone.

3.3 Field Methods

Streamflow was estimated at 10-min intervals using continuous measurements of water depth by a pressure transducer (U20, Onset Ltd., barometrically corrected) and a rating curve that was developed over a one-year period and spanned a wide range of flow conditions. Stream gauging to develop the rating curve was done using a Hach FH950 flow mate (Hach Ltd., USA). Pressure transducers were installed both up and downstream of the bunker silo; however, it was found that the difference in flow between the two stream sections (100 m apart) was negligible and within the range of error of the measurements. Consequently, only streamflow from the downstream logger is used in this thesis and streamflow inputs from the riparian zone are assumed to be negligible.

Stream samples were collected both up and downstream of the farmyard (Figure 3.1) over a one-year period from January 2018 – January 2019. Sampling was focused around precipitation and melt events, although periodic baseflow samples were collected at least bimonthly. Stream samples were collected using automated water samplers (ISCO 6712, AVENSYS Ltd.), at sampling intervals of 1-6 hours depending on storm intensity and duration, ensuring that samples were collected throughout the storm hydrograph to permit the determination of event mean nutrient concentrations. Sampler tubing was suspended within the water column so that samples were collected within the water column, and not from the water surface, or stream bed. Samples were collected in 1L plastic bottles that were acid washed in 10% concentrated H_2SO_4 and triple rinsed with deionized water, however, only 500 mL of sample was collected at each sampling interval. Ice, or ice packs were added to the ISCO bottle storage areas during longer storm events during summer months (refreshed daily) to ensure the preservation of samples in higher temperatures. At the conclusion of sampling event, samples were collected within 24 hours and transported back to the laboratory for immediate filtration and analysis or preservation.

A network of piezometers and wells was installed within the riparian zone (Figure 3.1). Each nest had a well with a depth of 75 cm, and a set of piezometers with depths of 25, 50, 75, and 100 cm, with 150 cm deep piezometers in the middle locations. Wells and piezometers were made with polyvinyl chloride (PVC) pipe (1.5-2” ID). Wells (2”) were slotted along the entire length of the pipe and triple-wrapped in nylon screening to reduce the amount of sediment to enter the slots, while piezometers (1.5”) were slotted for 20 cm, centered around their specific depth, and similarly triple-wrapped in screening.

Water levels in the wells and piezometers were monitored to infer the direction of groundwater flow using electronic water level measuring tape (Cole Parmer Ltd. USA). Groundwater samples were collected from nested wells and piezometers (Table 3.3.1) with a peristaltic pump and clean (triple rinsed with deionized water) tygon tubing within 24 hours of storm events during the spring, summer and fall seasons for the determination of groundwater P concentrations. Before samples were taken, wells and piezometers were purged to ensure that a fresh groundwater sample was collected. Following the collection of groundwater, samples were taken back to the laboratory for immediate processing. Antecedent moisture conditions were determined visually during the collection of stream and groundwater samples, as soil moisture probes were not installed throughout the riparian zone.

TRANSECT	LOCATION	PIEZOMETER DEPTHS (CM)
EAST	Up	Well, 25, 50, 75, 100
EAST	Middle	Well, 25, 50, 75, 100, 150
EAST	Down	Well, 25, 50, 75, 100
CENTER	Up	Well, 25, 50, 75, 100
CENTER	Middle	Well, 25, 50, 75, 100, 150
CENTER	Down	Well, 25, 50, 75, 100
WEST	Up	Well, 25, 50, 75, 100
WEST	Middle	Well, 25, 50, 75, 100, 150
WEST	Down	Well, 25, 50, 75, 100
OPPOSITE	Up	Well
OPPOSITE	Down	Well

Table 3.3.1 Description of piezometer depths at each nest of wells and piezometers throughout each transect. All wells were installed at 75 cm depths. Transect locations are shown in Figure 3.1. Locations along transect refer to location in the riparian zone, with “Up” located at the upland edge of the riparian zone, adjacent to a gravel road, “Down” located at the riparian zone-stream interface, and “Middle” located halfway between these points within the riparian zone.

Soil samples were collected using an Oakfield sampler in July 2019 for various analyses, including water extractable phosphorus (WEP), total phosphorus (TP), and phosphorus saturation index (PSI) to determine how saturated soils were with P, and their potential for P release (lab methods described in the following section). Additional samples were collected to determine bulk density using standard techniques (300 ml soil tins for each soil horizon, done in triplicate). Samples for soil chemistry were collected at 13 locations throughout the riparian zone – at each nest of wells and piezometers, up and down stream of the affected area, and on the opposite side of the stream from the affected area, and were collected as close to the wells and piezometers as possible without disturbing the area surrounding them (~20 cm away from each pipe). A total of 52 samples were collected. Each sampling location was sampled at depths of 0-5 cm, 5-15 cm, 15-30 cm, and 30-45 cm. Composite samples (n=5 samples per depth composite) were collected for the soil chemistry to ensure a true representation of the sampling area and stored in large Ziplock bags at 4C until they could be processed in the lab (dried at 30C within 24 h to preserve them). Soil sampling occurred after the groundwater sampling campaign ended so that the soil around the wells and piezometers were left undisturbed during their use. Furthermore, the soil was sieved to < 2 mm in the laboratory, as per the standard method (Pierzynski, 2000).

The hydraulic conductivity (K_{sat}) of the riparian soil was measured at multiple depths at each sampling location. Hvorsley (1951) slug tests were performed by purging the pipe and measuring the rate of its recharge with the use of a pressure transducer (U20, Onset Ltd.). Loggers recorded in five-minute intervals, and were left in the pipes until a full recharge occurred. The K_{sat} measurements were combined with measurements of hydraulic head to estimate a riparian groundwater flux using Darcy's Law (Dingman, 2015) on four dates (two wet, and two dry conditions). Groundwater estimates were multiplied by the groundwater P concentrations on each date to estimate a groundwater P load to the stream. These estimates were compared with instantaneous changes in P loads in the stream to determine if the groundwater phosphorus flux could account for the observed differences in P load in the stream.

A survey of the study site was conducted using a differential GPS to obtain the topography of the riparian zone and bathymetry of the stream. GPS points were taken at the top, and surface elevation at every well and piezometer that was installed. Results of this survey were used to generate cross sectional figures of the transects within the riparian zone, and were also used for the calculations of hydraulic gradients.

3.4 Laboratory Methods

All water samples were immediately processed upon arrival at the Biogeochemistry Lab at the University of Waterloo. A 50 mL subsample from each sample was filtered using 0.45 μm cellulose acetate filters (Delta Scientific) and frozen for preservation until analyzed for SRP. A 50 mL unfiltered subsample was acidified to 0.2% H_2SO_4 for total phosphorus (TP) analysis. The acidified subsample was digested with acid (H_2SO_4) and potassium persulfate ($K_2S_2O_8$) in an autoclave (EPA/600/R-93/100, Method 365.1), and subsequently analyzed colorimetrically (Bran Luebbe AA3, Seal Analytical, Method no. G188-097 for TP).

Standard laboratory methods (Pierzynski, 2000) were used for WEP analysis, where 5g of dried soil that was previously sieved to 2 mm was extracted with 50mL of deionized water and shaken for one hour. Samples were then syringe filtered through 0.45 μm cellulose acetate filters (Delta Scientific) and analyzed for SRP colorimetrically (Bran Luebbe AA3, Seal Analytical, Methods 103-93 (SRP).

Phosphorus Sorption Index (PSI) was calculated for soils at each locations at varying depths following the method outlined by Sims (2009). The PSI can be used as an estimate of a soil's maximum P sorption capacity (Sims, 2009). A 1g sample of soil was shaken with 20 mL of of monobasic potassium phosphate (KH_2PO_4) solution (75 mg/L P) for 18 hours and syringe filtered through 0.45 μm cellulose acetate filters (Delta Scientific) before being analyzed colorimetrically (Bran Luebbe AA3, Seal Analytical, Methods 103-93 (SRP) (Pierzynski, 2000). Soil extracts were analyzed with 10% duplicates and the relative precent difference between duplicates was ≤ 5%. All samples were analyzed colorimetrically using the Bran Luebbe AA3, Seal Analytical with a detection limit of 0.001 mg/L for SRP and 0.01/L mg for TP.

3.5 Data Analyses

Events were delineated based on stream hydrograph responses. To delineate individual events, baseflow was first separated from event flow using the Ecohydrology package (R Statistics). Events commenced when the hydrograph rose above baseflow and ended when flow returned to baseflow. Where two successive events occurred (prior to the first event returning to baseflow), events were combined into a single larger event. Although baseflow was separated for the delineation of events, flow estimates for each event contained the total streamflow that occurred during that event as baseflow and event flow cannot be easily differentiated chemically. In this thesis, "baseflow" refers to periods of runoff occurring between events and does not include the portion of events that is baseflow.

For each event, flow-weighted mean concentrations (FWMC) of SRP and TP were determined using the methods of Williams et al. (2016), and P loads (mg/event) were determined by multiplying the total flow for the event (L) by the FWMC (mg/L) at both the upstream and downstream stream monitoring locations in the stream. For events that were missed due to equipment failure (or small events not captured by autosamplers), two interpolation techniques were used. Regressions were used to determine relationships between discharge and flow weighted mean concentrations (FWMC) or loads of SRP and TP at both the upstream and downstream locations. The R^2 values that were generated for the model regressions were 0.75 for the upstream flow load relationship, and 0.68 for the downstream flow load relationship (Figure 3.3). To ensure that subtle differences in slope in the discharge-load relationships at each site did not bias the interpolation method, a second approach was used and compared to the regressions. The ratio of the FWMC between the up and downstream locations was determined for all observed events and this same ratio was applied to downstream events for events that were predicted from flow (gap filled) for the upstream location. The interpolated events are compared in Figure 3.3. An average of the two predicted values was used in load estimates. For events sampled by one sampler but missed by another due to equipment failure, the ratio of FWMC was used. Baseflow nutrient concentrations were determined using linear interpolation between the routinely collected baseflow samples.

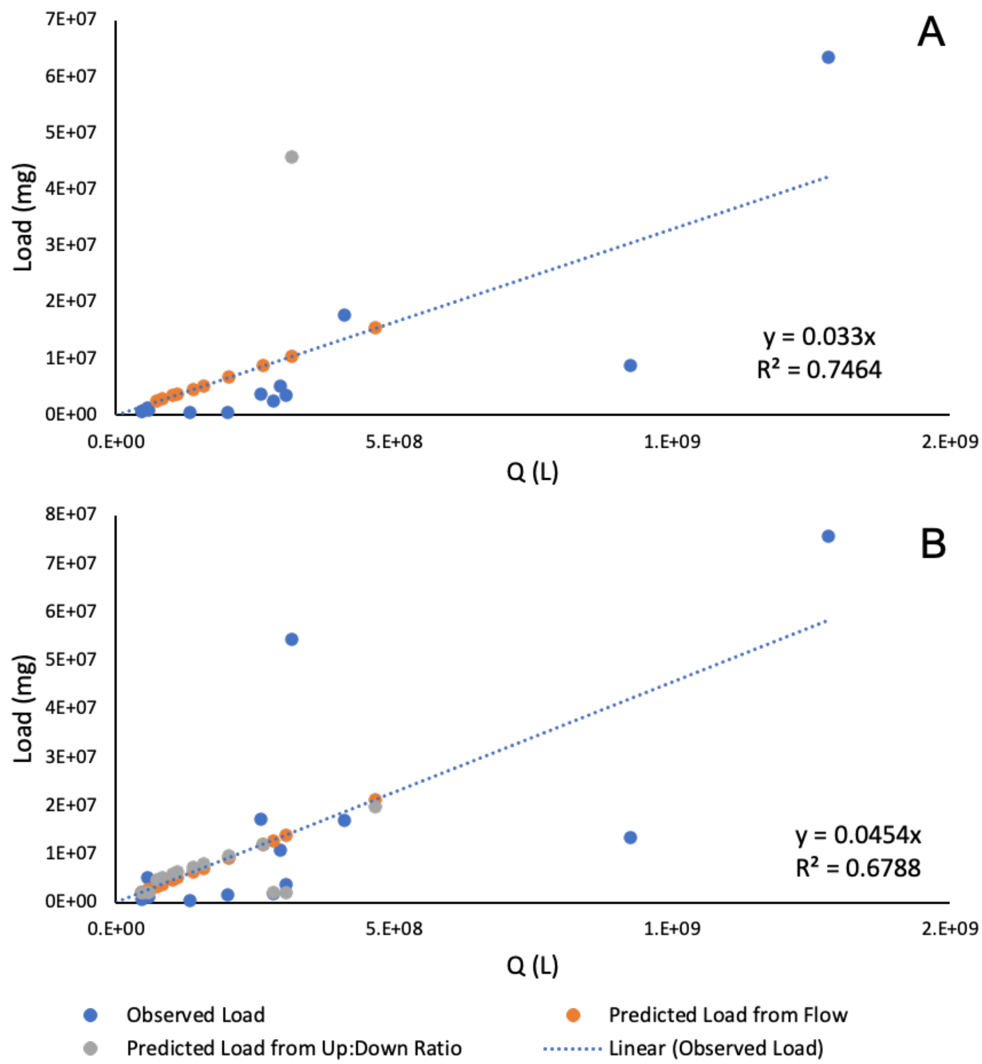

Figure 3.3 Event streamflow (L/event) and load (mg/event) relationships upstream (a), and downstream (b) with observed loads (blue), those predicted from streamflow-load relationships (orange) and those predicted from the ratio of the FWMC between the upstream and downstream locations after the upstream P load had been predicted from flow (grey).

Concentrations of P in the stream were not normally distributed and could not be transformed to achieve a normal distribution. Thus, non-parametric statistics are used in this thesis. Differences in SRP and TP concentrations between the upstream and downstream locations of the stream were tested using a Kruskal-Wallis test using R. This was done for the entire study period, but also separately for the periods before and after the bunker silo was refreshed (August 2019). Kruskal-Wallis tests were done in R to determine whether statistical differences were present in soil characteristics within the impacted and non-impacted areas of the riparian zone. A significance level of 0.05 was applied to all Kruskal-Wallis tests that were conducted for this thesis.

Chapter 4 Results

4.1 Meteorological and Hydroclimatic Conditions over the Study Period

Overall, 2018 was a dry year, with air temperatures that were slightly warmer than normal. Total annual precipitation received during the study period was 762.7mm (Figure 4.1), 17% less than the typical 30-year means for the region (916.3 mm, Environment Canada, 2020, Figure 4.2). Seasonal air temperatures generally resembled 30-year normals throughout the study period, with annual maxima and minima temperatures observed in the summer and winter, respectively (Figure 4.2). However, the study year was warmer than normal. For example, the observed temperatures in December (-1.4°C) were nearly 2°C warmer than the 30-year normal (-3.3°C) and summer temperatures during the study period were also slightly higher than the 30-year normal, with the biggest difference observed in September (17.1°C, 2.6°C warmer than the 30-year normal, Figure 4.2).

Total stream runoff over the study period was 2.03×10^{12} mm, producing a runoff ratio of (discharge/precipitation = 0.65). Much of this flow occurred during the non-growing season (Figure 4.1) A total of 20 events were observed over the study period, of which 5 were very large events (Figure 4.1, Table 4.1). The largest events observed were associated with snowmelt or mid-winter thaws. One event in particular was notable: the February 20th event was the highest recorded flow throughout the study period, with an observed maximum flow rate of ~1.9×10^4 m^3/s (Figure 4.1), enough flow to flood the riparian zone (Figure 3.2 a). This event coincided with major flooding throughout the Grand River watershed (GRCA, 2018).

Streamflow throughout the remainder of the year was relatively low, with a highest observed flow of ~8.8 x10^2 m^3/s (June 4), between the months of June – September.

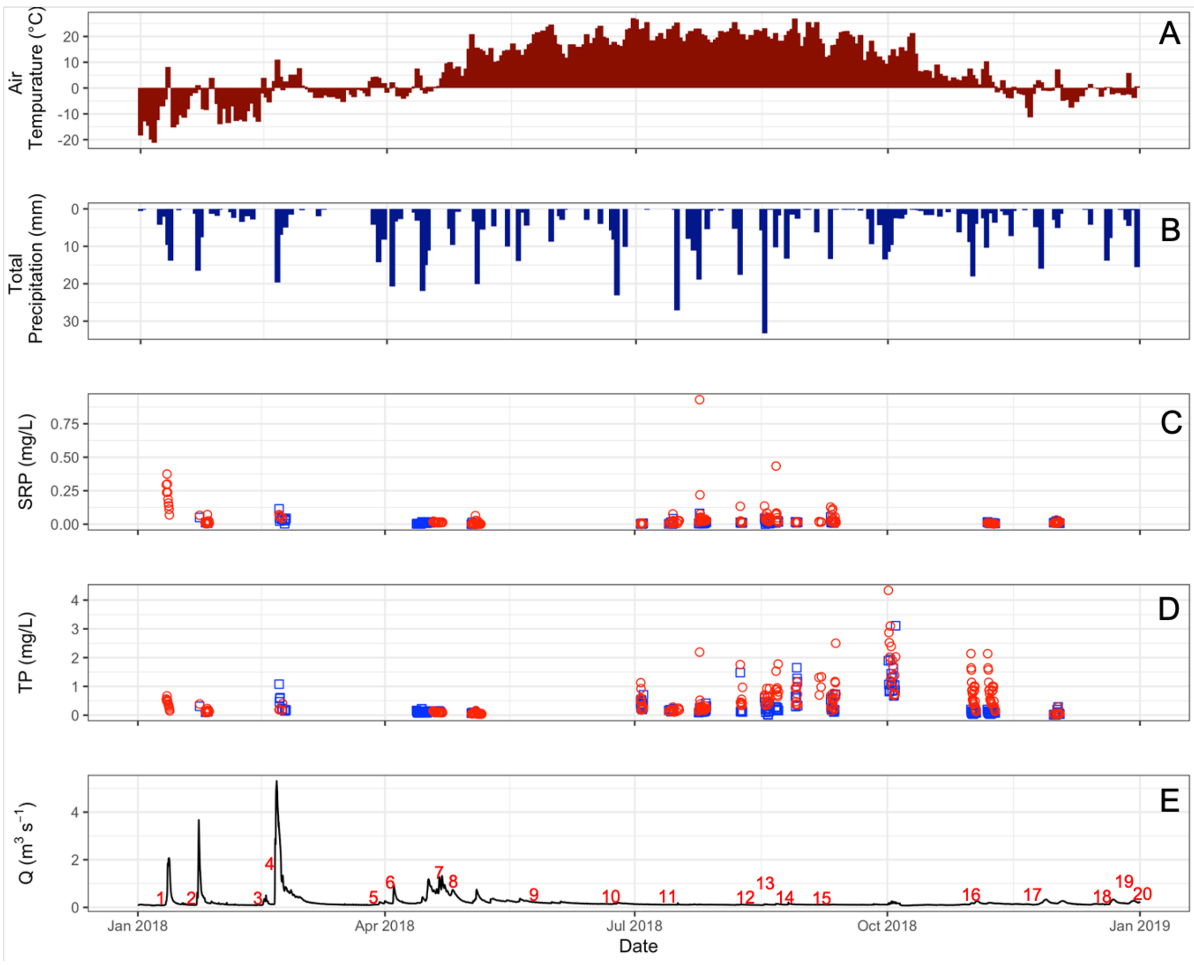

Figure 4.1: Precipitation (a), air temperature (b), stream concentrations of SRP (c) and TP (d), and streamflow with sampling events numbered in red (e) over the study period. Phosphorus concentrations are shown both upstream (blue) and downstream (red) of the bunker silo and farmyard.

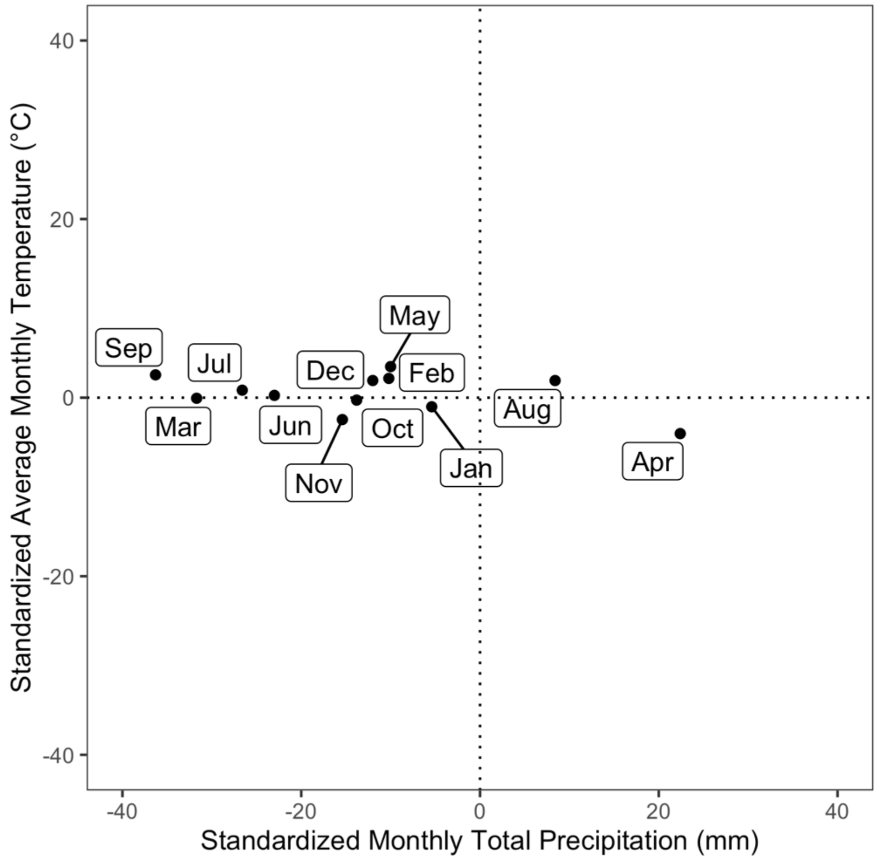

Figure 4.2: Standardized mean monthly temperature (y-axis) and monthly total precipitation (x-axis) for 2018. Shows that 2018 was drier than 30-year normals, with the exception of April and August

Event	Dates	Runoff (mm)	SRP UP FWMC (mg P/L)	SRP Down FWMC (mg P/L)	TP Up FWMC (mg P/L)	TP Down FWMC (mg P/L)
1	01/10 – 01/20	22.6		0.172		0.347
2	01/22 – 02/05	29.3	0.043	0.042	0.278	0.264
4	02/19 – 03/12	91.5	0.049	0.059	0.501	0.215
6	04/12 – 05/01	65.9	0.009	0.015	0.125	0.108
7	05/02 – 05/09	14.4	0.002	0.008	0.065	0.065
11	07/13 – 07/19	4.3	0.014	0.019	0.164	0.180
12	08/15 – 08/20	3.3	0.015	0.047	0.240	0.588
13	08/20 – 08/25	4.1	0.021	0.090	0.230	1.017
14	08/26 – 08/30	3.3	0.014	0.015	0.863	0.677
15	09/29 – 10/08	7.3			1.245	1.725
16	10/29 – 11/18	20.2	0.009	0.006	0.093	0.753
17	11/24 – 12/14	21.8	0.011	0.012	0.062	0.062
Median Baseflow			0.014	0.037	0.32	0.43
Median Pre Silo Fill			**0.014**	**0.019***	**0.164**	**0.180***
Median Post Silo Fill			**0.014**	**0.037**	**0.235**	**0.715**

Table 4.1: Flow weighted mean concentrations of SRP and TP, up and down stream of the bunker silo for each captured event. Median concentrations for the periods before and following the refreshing of the bunker silo (annual fill) are down.**Event 1 is not included because the upstream autosampler did not collect samples due to equipment failure. The inclusion of this large event for the downstream location skews the comparison of the two sites.*

4.2 Stream Nutrient Concentrations and Loads Up and Downstream of Bunker Silo and Farmyard

Statistical differences were found in instantaneous soluble reactive P concentrations, and ranged from <0.001 – 0.11 mg/L at the upstream site and 0.005 – 0.93 mg/L, at the downstream site (Figure 4.1). Total P concentrations ranged from 0.01 – 3.4 mg/L , and 0.02 – 4.3 mg/L, up and down stream, respectively. Concentrations peaked during snowmelt and thaw events early in 2018 and were smaller during baseflow periods. However, both SRP and TP were considerably elevated at the downstream location in the mid-summer months in 2018 after the bunker silos had been filled with fresh silage (Figure 4.1, 4.3).

Flow weighted mean concentrations varied for the 20 events measured throughout the study period, and were most often greater downstream from the farm than upstream (Table 4.1). Indeed, for all events, SRP loads were greater downstream when compared to upstream, with the exception of event two (January 22, 2018), where upstream concentrations were slightly higher (Figure 4.3). There were several events where TP concentrations were slightly higher up stream, notably more in the early spring snowmelt period (Table 4.1). However, TP concentrations during the late summer and early fall months were all higher at the downstream location (Figure 4.3, Table 4.1). Moreover, concentrations at the downstream location tended to be greatest during very low flow conditions and were more dilute at higher flows (Figure 4.4). In contrast, concentrations of P at the upstream location tended to be positively related to flow (Figure 4.4).

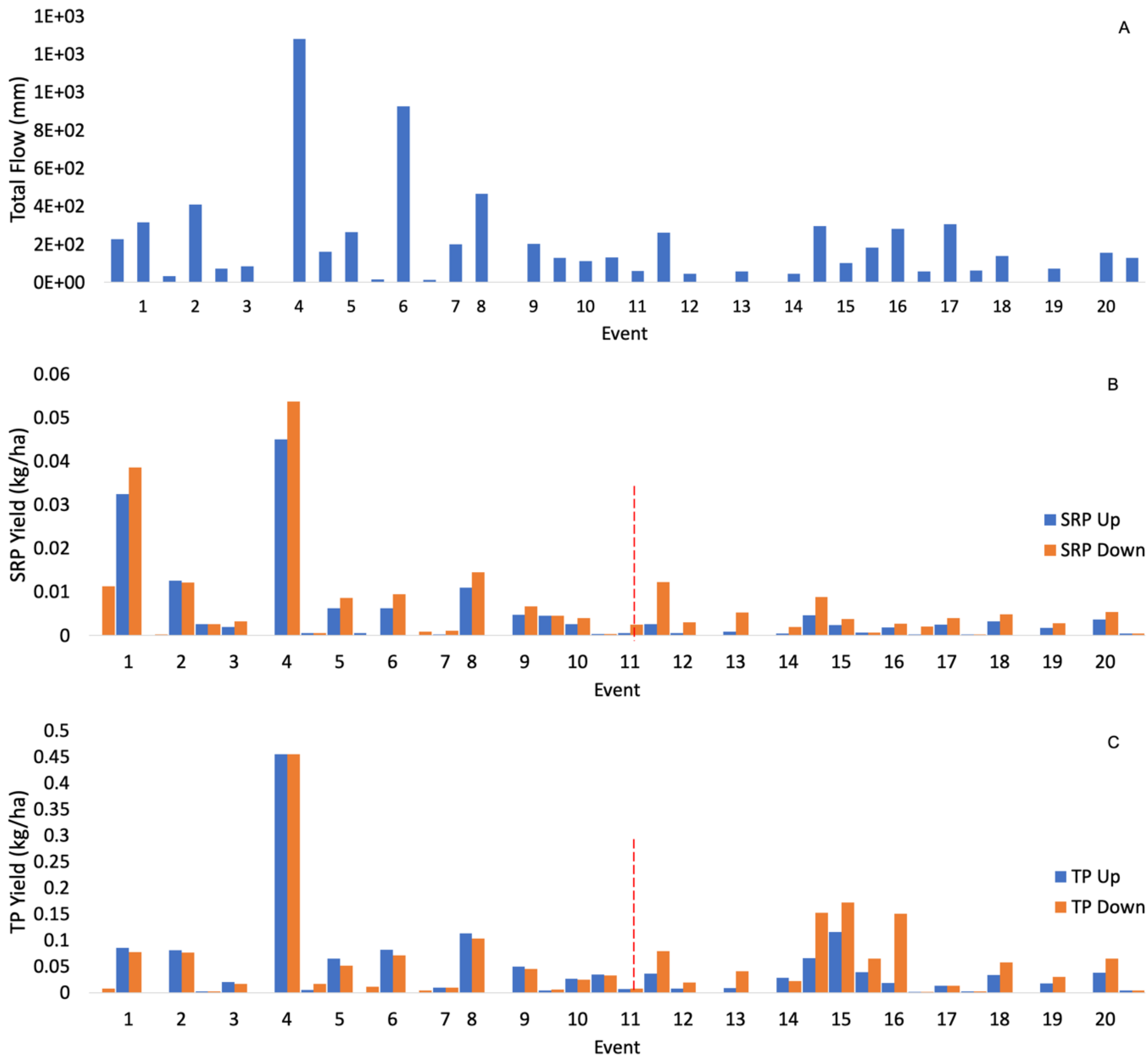

Figure 4.3: Total streamflow for each event (a), and yields of SRP (b) and TP (c) for events occurring over the study period. The time at which the bunker silo was refreshed is shown using a dashed vertical line. Yields are shown above (blue) and below (orange) the bunker silo and farmyard.

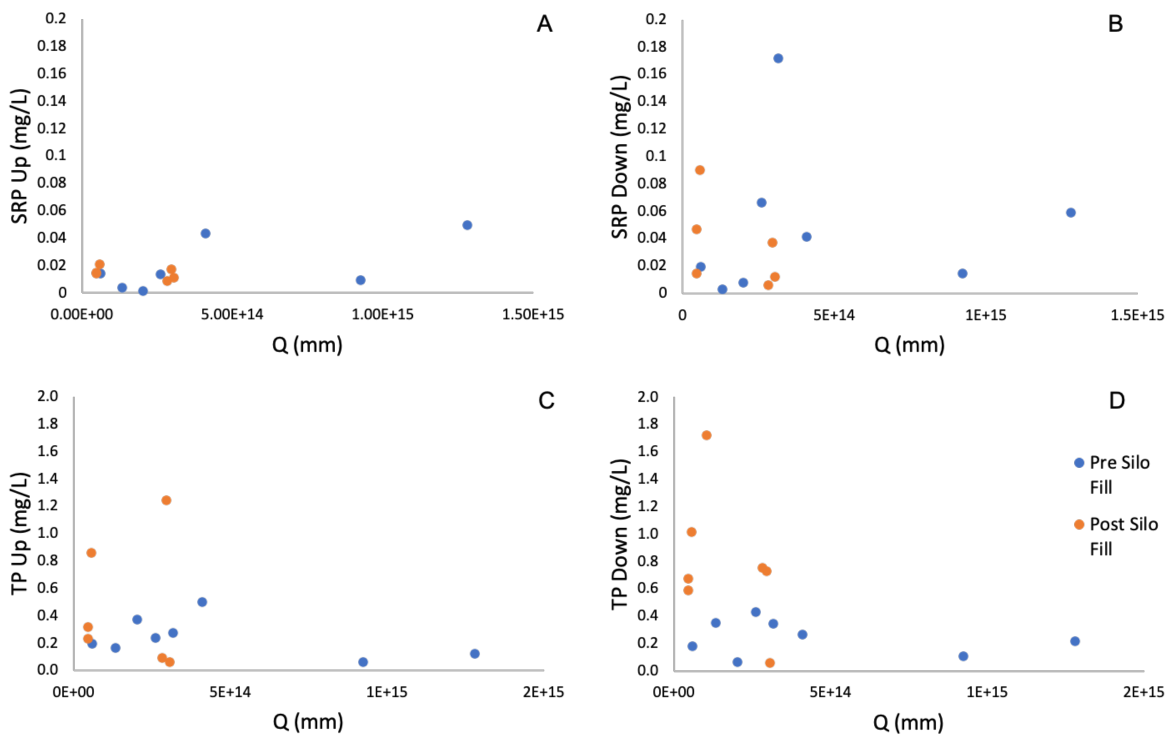

Figure 4.4: Comparison of total streamflow per event (mm) and flow weighted mean concentrations (mg/L) of SRP (a,b) and TP (c,d) at the upstream (a,c) and downstream (b,d) locations.

As noted earlier, differences in streamflow were negligible between the up and downstream locations and thus, the same stream discharge values were applied to both locations and multiplied with the observed nutrient concentrations at each location to generate a load for that location. Seasonal variations in load contributions are apparent, with the higher flow events that were associated with winter snowmelt (Figure 4.1) contributing the greatest loads (Figure 4.3). Of the total losses of P over the study period, 84.6% and 79.3% (SRP/TP), were associated with event flow, whereas 15.4% and 20.7% (SRP/TP) were associated with baseflow (between-event) conditions. Of the events occurring over the study period, events one (January 10 – 20) and four (February 19 – May 12) were the largest contributing events, spanning roughly 40 days, and collectively adding 0.16 kg/ha, or 43% of the total SRP yield throughout the study period, and 1.07 kg/ha, or 31% of the total TP yield for the study period.

Cumulative totals of annual SRP and TP losses revealed statistically greater overall yields downstream of the bunker silo (0.23 kg SRP/ha, 1.90 kg TP/ha) than upstream of the bunker silo (0.16 kg SRP/ha, 1.48 kg TP/ha), indicating that the farmyard supplied P to the stream over the 100 m reach. Indeed, 32% of annual SRP and 22% of annual TP lost from the 14 km^2 contributing area was supplied by the 0.05 km^2 farmyard. The annual yields at the downstream location are shown weighted for the entire contributing area (14 km^2). However, if the differences between the up and downstream locations ($3.29 \times 10^2 - 2.23 \times 10^2 = 1.06 \times 10^2$ kg SRP; $2.68 \times 10^3 - 2.08 \times 10^3 = 5.99 \times 10^2$ kg TP) are expressed in kg/ha of farmyard area (5 ha), the farmyard lost 21.2 kg/ha SRP and 120 kg/ha TP.

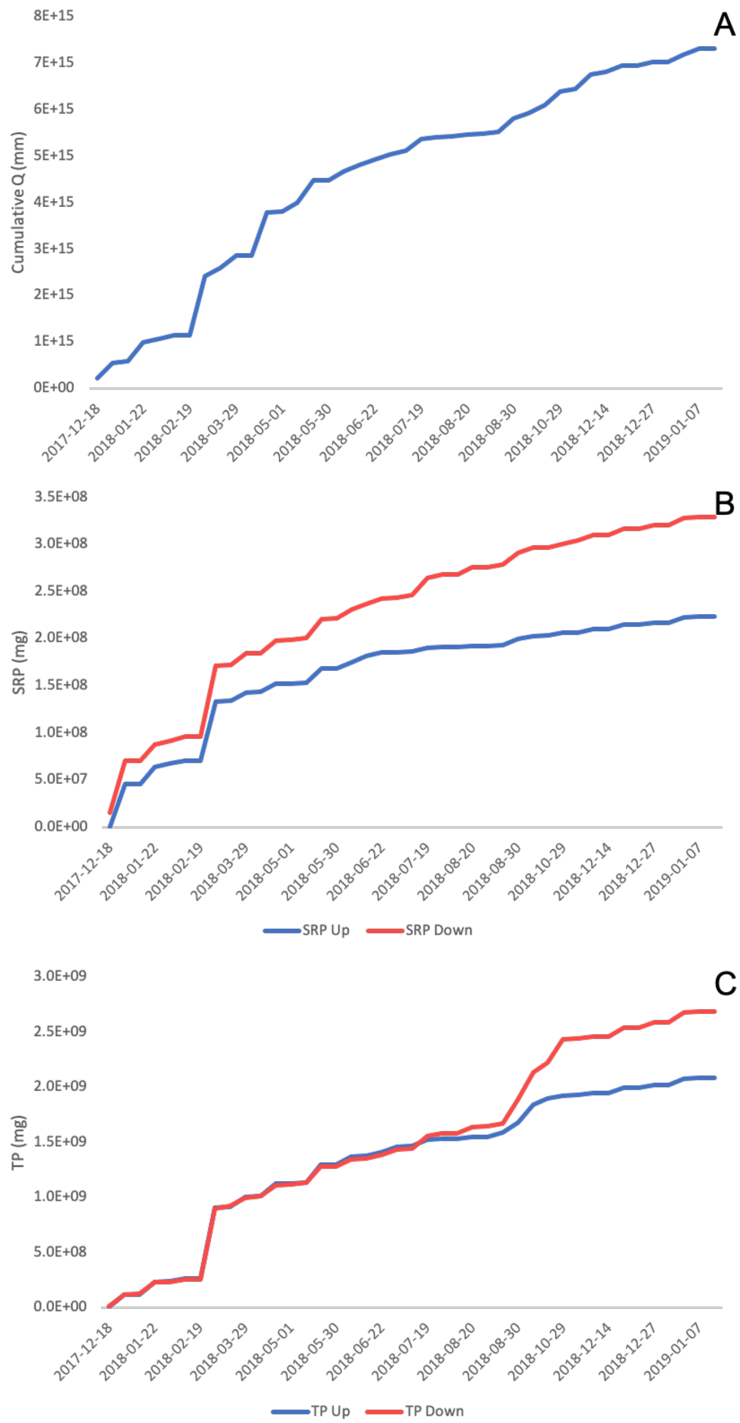

Figure 4.5: Cumulative mm of stream runoff (a), and loads of (b) SRP and (c) TP. Phosphorus loads at the upstream (blue) and downstream (red) locations are shown.

4.3 Riparian Zone Soil Characteristics and Phosphorus Content

4.3.1 Soil Hydrophysical Characteristics

As noted in Chapter 3, soils above 1m were loamy in texture whereas a layer of sandy clay loam was found at approximately 1 m depth. Bulk densities of the soil gradually increased with depth between the surface (0.92 g/cm^3 at 0-5 cm) and the subsurface (1.31 g/cm^3 at 30-45 cm) (Table 4.2).

Depth (cm)	Mean Bulk Density (g/cm^3)	Median Water Extractable P (kg/m^2) West Transect	Median Water Extractable P (kg/m^2) Center Transect	Median Water Extractable P (kg/m^2) East Transect	Total WEP (kg) for Riparian Zone Section (360 m^2)
0-5	0.92	185.02	39.53	100.41	38993.5
5-15	1.08	208.25	39.49	294.61	65081.1
15-30	1.27	364.86	273.57	303.81	113068.1
30-45	1.31	191.56	372.63	2.29	67977.4
Total (summed over depths)		949.67	725.22	701.11	285119.9

Table 4.2: Soil bulk density and water extractable phosphorus pools in the top 45 cm of soil. An estimated water extractable phosphorus pool (kg) for the entire 360 m^2 buffer strip (top 45 cm only) is provided.

Hydraulic conductivity varied both spatially across the site but also with depth. Generally, K_{sat} decreased with depth (Table 4.3) although this was not always the case. Spatially, K_{sat} was much greater in the west transect (orders of magnitude) compared to the east and center transects (Table 4.3).

		K_{sat} (m/s)		
Location	**Depth (cm)**	**West Transect**	**Center Transect**	**East Transect**
Up	25	No data	No data	7.31E-03
Up	50	No data	No data	2.15E-03
Up	75	6.96E-02	3.39E-04	6.71E-04
Up	100	4.26E-02	2.74E-04	9.75E-05
Middle	100	1.56E-02	No data	3.49E-04
Middle	150	1.70E-02	1.44E-03	3.20E-04
Down	100	8.15E-03	No data	No data
Geometric Mean Across Depths and Locations		2.29×10^{-2}	5.12×10^{-4}	6.97×10^{-4}

Table 4.3: Approximate saturated hydraulic conductivities for riparian soils. Tests were not done on all piezometers. Missed piezometers are shown with “no data”.

4.3.2 Phosphorus Characteristics in the Soil

Phosphorus content in the soil (WEP) and phosphorus sorption index (PSI) differed spatially throughout the riparian zone, both with depth and proximity to the bunker silo. Statistical differences in water extractable SRP (Figure 4.6) and TDP (Figure 4.7) are apparent between the impacted and non-impacted transects of the riparian zone. Indeed, the east and west transects presented more variable values than the center and opposite transects. In the affected east and west transects, WEP typically decreased with depth at all locations, with the exception of the west transect down location, where, at a depth of 15-30 cm WEP increased considerably. The locations closest to the bunker silo in the east and west transects exhibited higher levels of WEP at the surface than locations further away.

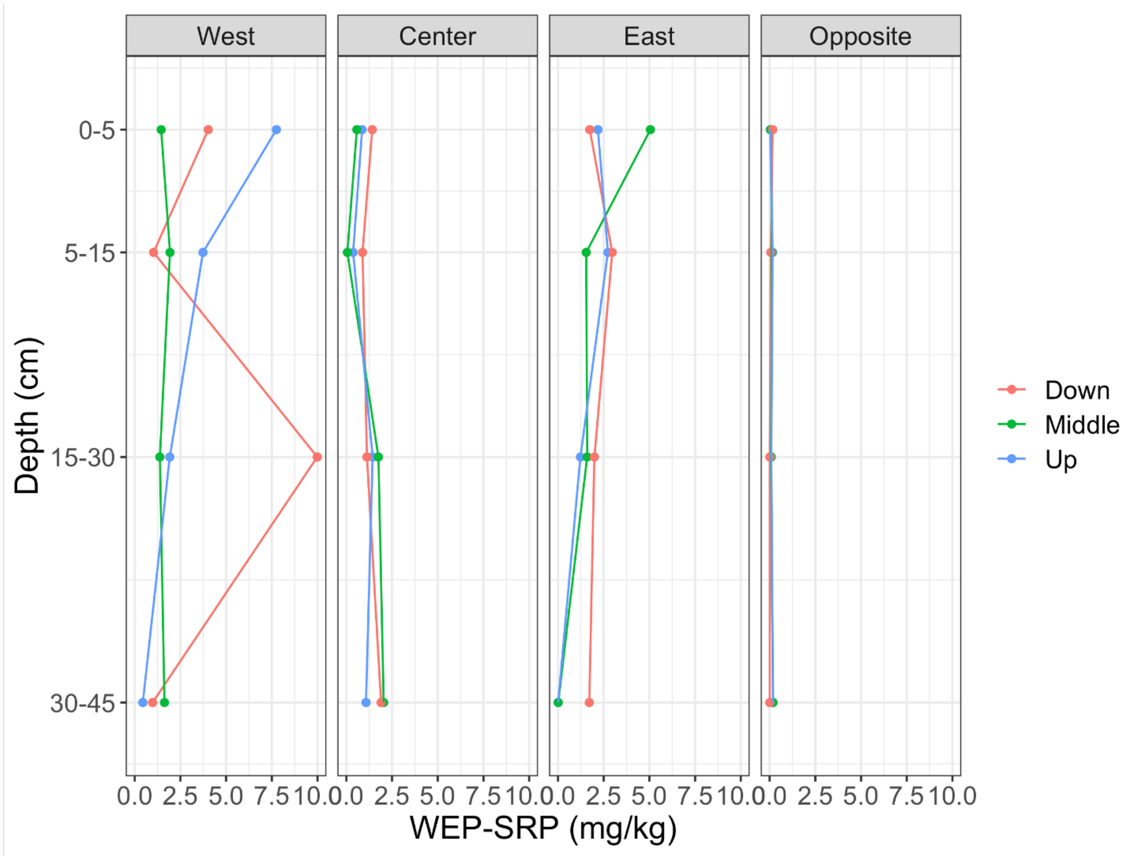

Figure 4.6: Water extractable P as SRP (mg/kg) for each sampling location (up, middle, down position), and transect (west, center, east, and opposite) within the riparian zone.

A comparison of water extractable SRP and TDP values yielded fairly similar results, indicating that levels of non-reactive P (TDP-SRP=NRP) are low within the study area. However, slightly higher TDP values were observed within the opposite transect, where NRP values were higher than the transects in the affected area. For example, mean water extractable NRP values in the non-impacted transect were 0.47 mg/kg, whereas mean NRP in the affected transects were 0.28 mg/kg. However, the water extractable P was a small proportion of the total P in riparian soils (Figure 4.8). Total P concentrations of the soil on the affected side were all statistically higher than the unaffected side of the riparian zone, which never exceeded 1000 mg/kg.

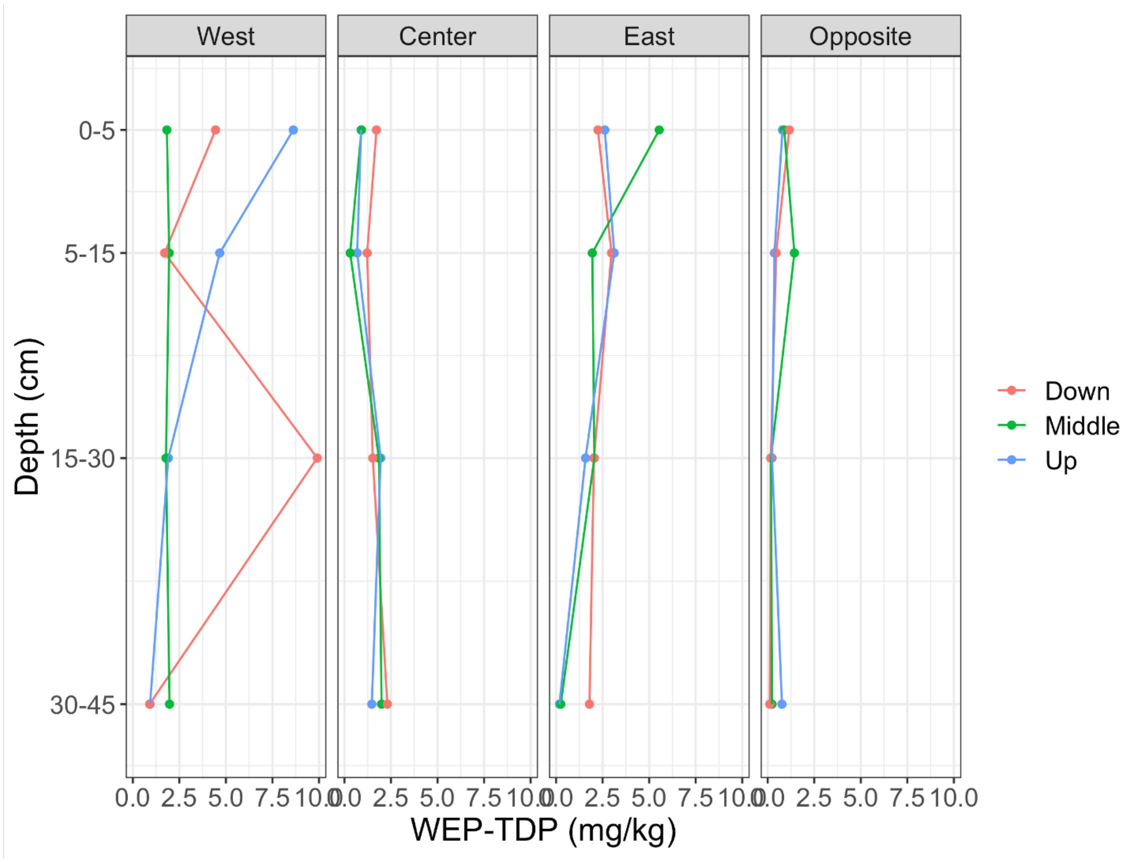

Figure 4.7: Water extractable P as total dissolved P (TDP) (mg/kg) for each sampling location (up, middle, down positions), and transect (west, center, east, and opposite) in the riparian zone.

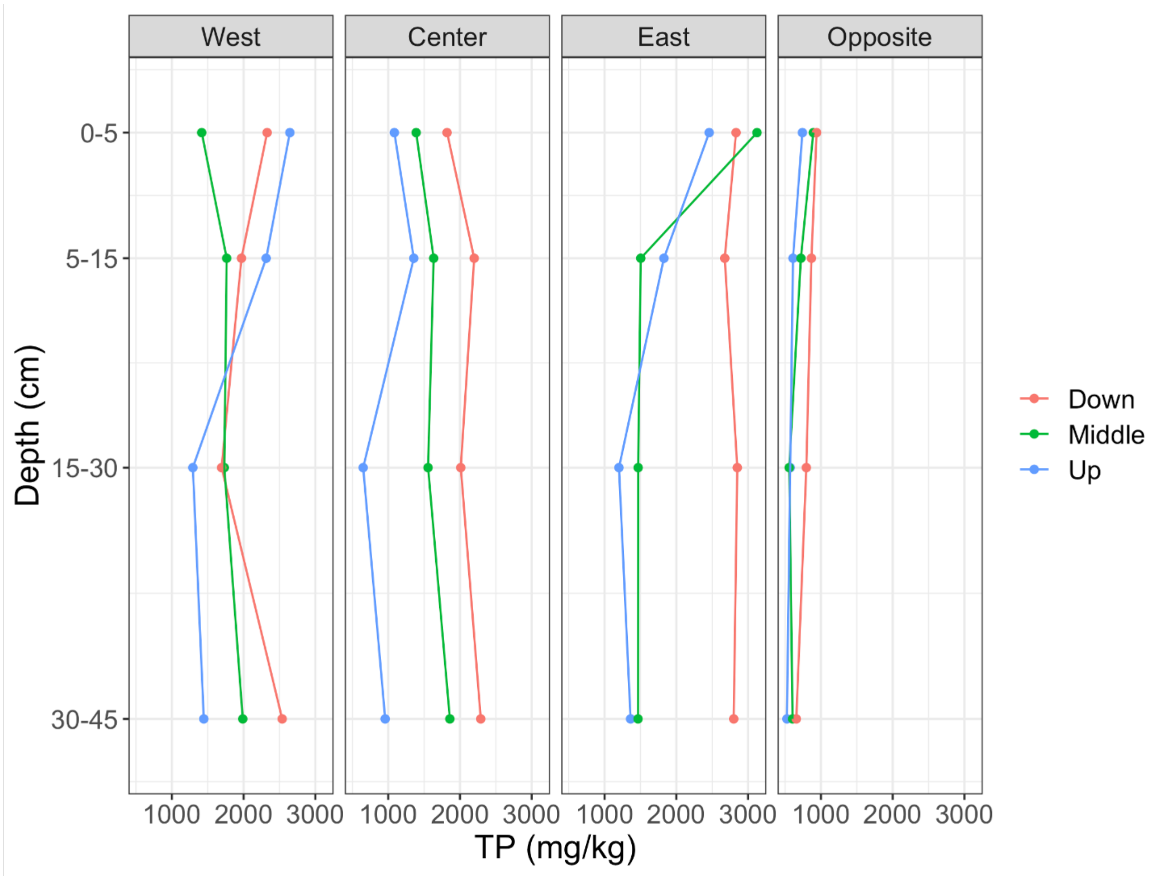

Figure 4.8: Total P (mg/kg) for each sampling location (up, middle, down position), and transect (west, center, east, and opposite) in the riparian zone.

The index of phosphorus sorption (PSI) in the soils varied spatially across the riparian zone, and were found to be statistically different between the impacted, and non-impacted transects. Lowest values of PSI (i.e. soils with less sorption potential or nearly saturated with P) were observed nearest to the surface, and the sorption potential (PSI) generally increased with depth, although this was not always the case, particularly at the downstream locations (shown in red, Figure 4.9). PSI in the affected area of the riparian zone was considerably lower than PSI on the opposite (unaffected by bunker silo) side of the stream. Locations in closer proximity to the bunker silo (e.g. soils at upland position) all had reduced PSI relative to other positions within the riparian zone. This was especially true at the West and East transects, which received direct inputs from the bunker silo. Notably, soils in the middle position, particularly in deeper soils on the affected side of the riparian zone also had substantially lower PSI (i.e. likely more saturated) than elsewhere in the riparian zone.

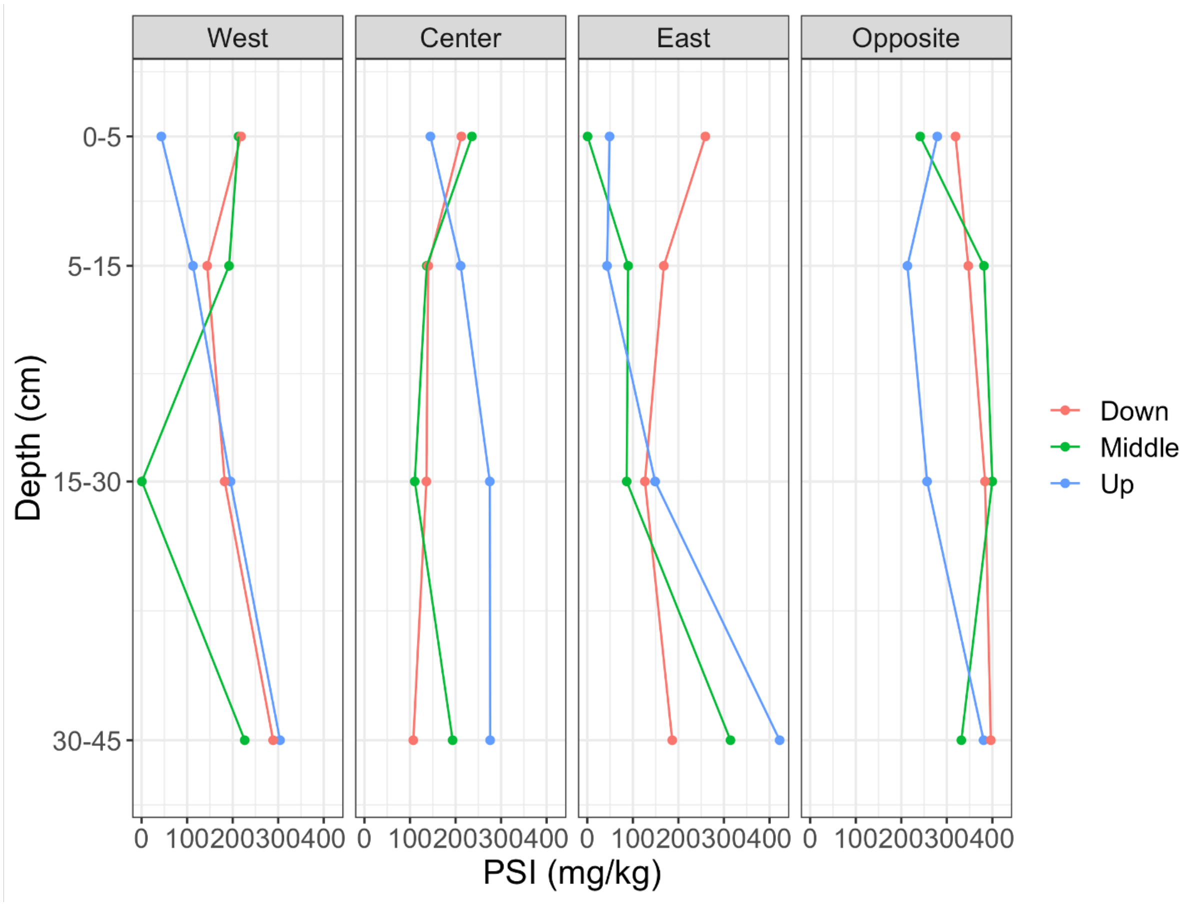

Figure 4.9: Phosphorus Sorption Index (mg/kg) for each location (up, middle, down), and transect (west, center, east, and opposite) in the riparian zone.

4.4 Flow and Nutrient Concentrations and Fluxes in Shallow Groundwater in the Riparian Zone

Periodic measurements of phosphorus concentrations in bunker silo effluent (grab samples of the direct liquid outputs from the silo itself, taken on 2-3 occasions) demonstrate very high SRP concentrations (94.3 mg/l SRP). Groundwater concentrations of P were considerably lower than this, but still highly elevated along the most directly impacted transects (i.e. west and east transects that received direct inputs of effluent) (Figure 4.10). Phosphorus concentrations in riparian groundwater differed with proximity to the bunker silo and farmyard and to a lesser extent with depth. Indeed, groundwater SRP concentrations in all transects were highest at the upslope riparian zone locations and decreased with distance from bunker silo (Figure 4.10; 4.12 – 4.14). In addition to varying with proximity to the P source, groundwater SRP concentrations also differed among the transects. The highest mean SRP values were observed in the west transect, and to a lesser extent in the east transect, whereas the center transect had lower mean SRP concentrations. Although groundwater P concentrations in the center transect were lower than those in the west and east transects, they were still higher than those in non-impacted areas of the riparian zone, such as those observed on the opposite site of the stream (0.005 – 0.18 mg/l SRP). Soluble reactive P concentrations generally decreased with depth in most locations, except for in the west transect, at the upslope location, where higher average SRP values were observed in the 50 cm piezometer (Figure 4.10). A comparison of seasonal median P concentrations in groundwater with soil water extractable P showed a positive relationship (Figure 4.11).

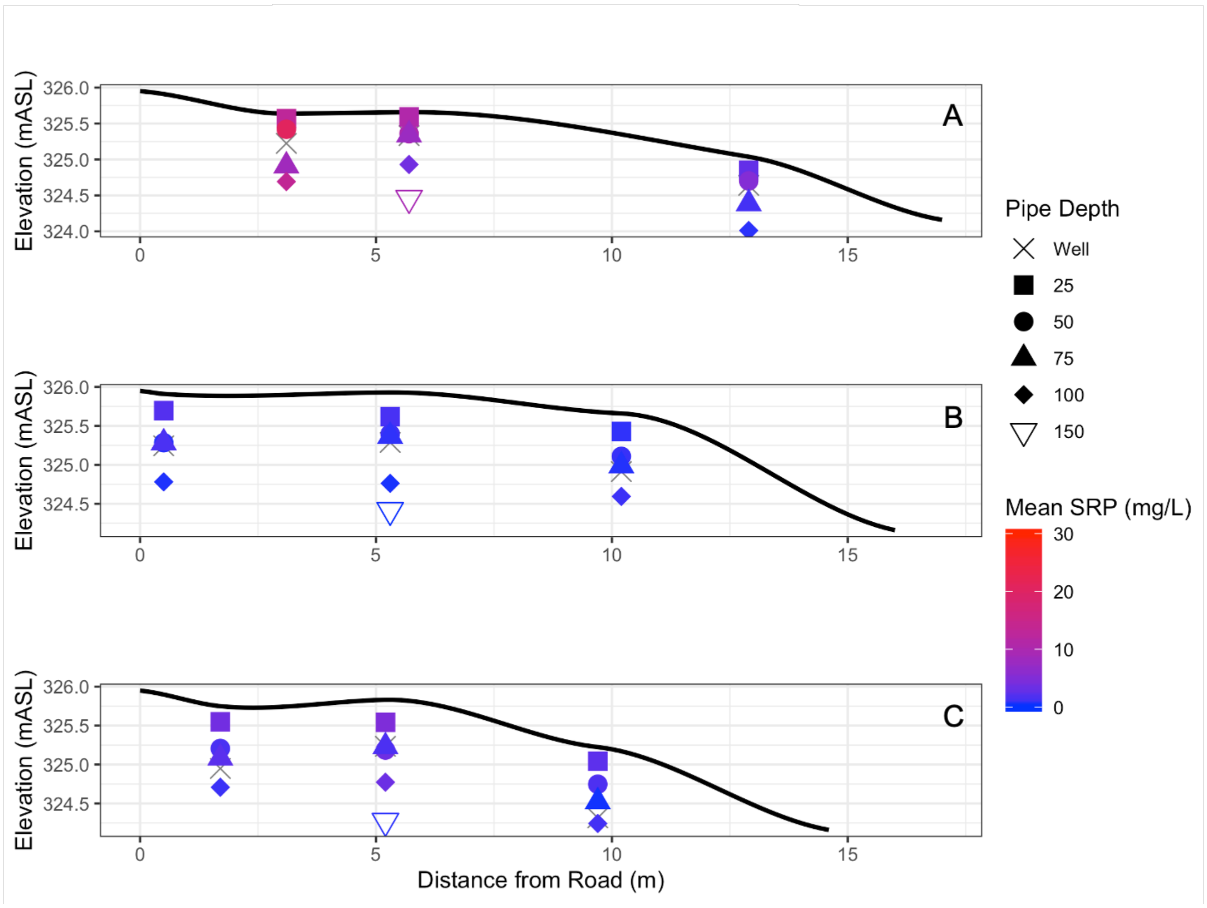

Figure 4.10: Mean groundwater SRP concentrations in the (a) west, (b) centre and (c) east transects, with each piezometer depth depicted (shape), along with concentration magnitude (color).

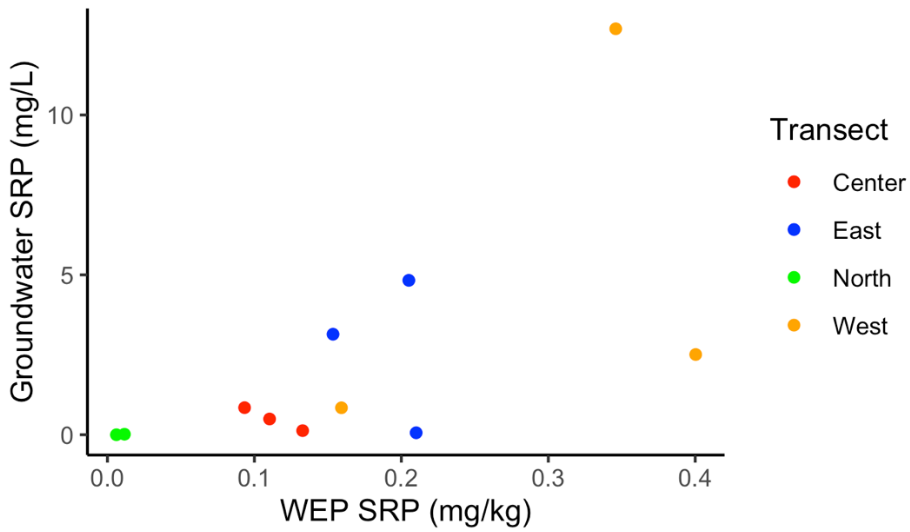

Figure 4.11: Median SRP concentrations in groundwater compared with water extractable P (WEP) in the soil at each nest location.

Temporal differences in groundwater concentrations occurred throughout the study period, both with antecedent moisture conditions and water table position, and, before and after the bunker silo was refreshed in summer 2018. Indeed, groundwater SRP concentrations increased under wetter antecedent moisture conditions and following precipitation and snowmelt events (Figures 4.12 – 4.14). Mean groundwater SRP concentrations also increased after fresh crop had been ensiled in the bunker silo in August. Mean concentrations of SRP in groundwater were 0.85 mg/L and 5.43 mg/L, pre and post silo fill, respectively (Figure 4.10). Groundwater concentrations of SRP in the riparian zone peaked in a November event, which was the first significant flush after the silo was refreshed (between events 15 and 16).

Routine measurements of groundwater hydraulic head throughout the riparian zone indicate that groundwater consistently exhibited a lateral flow direction towards the stream under both wet and dry conditions (Figures 4.12-4.14), although flow appeared to move "downward" in the west transect at the upland location, before it moved laterally across the remainder of the riparian zone. Hydraulic head data in the near-stream piezometers (Figures 4.12-4.14) also suggests that groundwater is upwelling from below and entering the stream. However, deeper piezometers are needed throughout the riparian zone to confirm this.

Under dry conditions (Figure 4.14), the water table was frequently deeper than the depths of the wells in the center transect, resulting in fewer groundwater samples from the center transect during summer months. Wetter conditions (Figures 4.12, 4.13), however, generated higher water tables that regularly flooded the east and west transects, sometimes resulting in ponding of effluent rich runoff in those transects. Phosphorus concentrations in shallow groundwater following the refreshing of the bunker silo were much greater under wet antecedent conditions than dry. Moreover, the elevated concentrations of SRP in groundwater at depth in the west transect coincide with the direction of water movement, indicating that some of the SRP from the bunker silo is being transported into the riparian groundwater system.

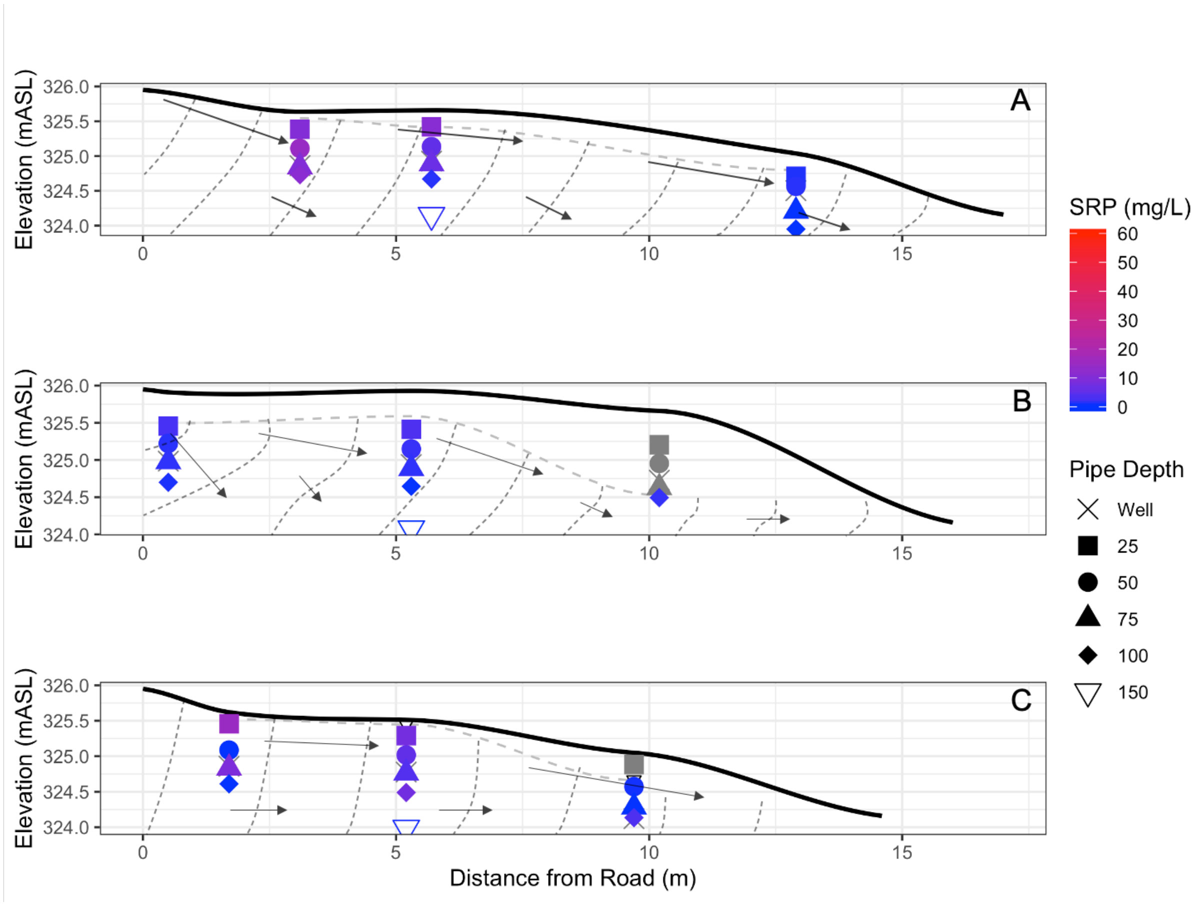

Figure 4.12: Soluble reactive P concentrations and flow path directions for October 4, 2018, during moderately wet antecedent moisture conditions in the (a) west, (b) centre, and (c) east transects.

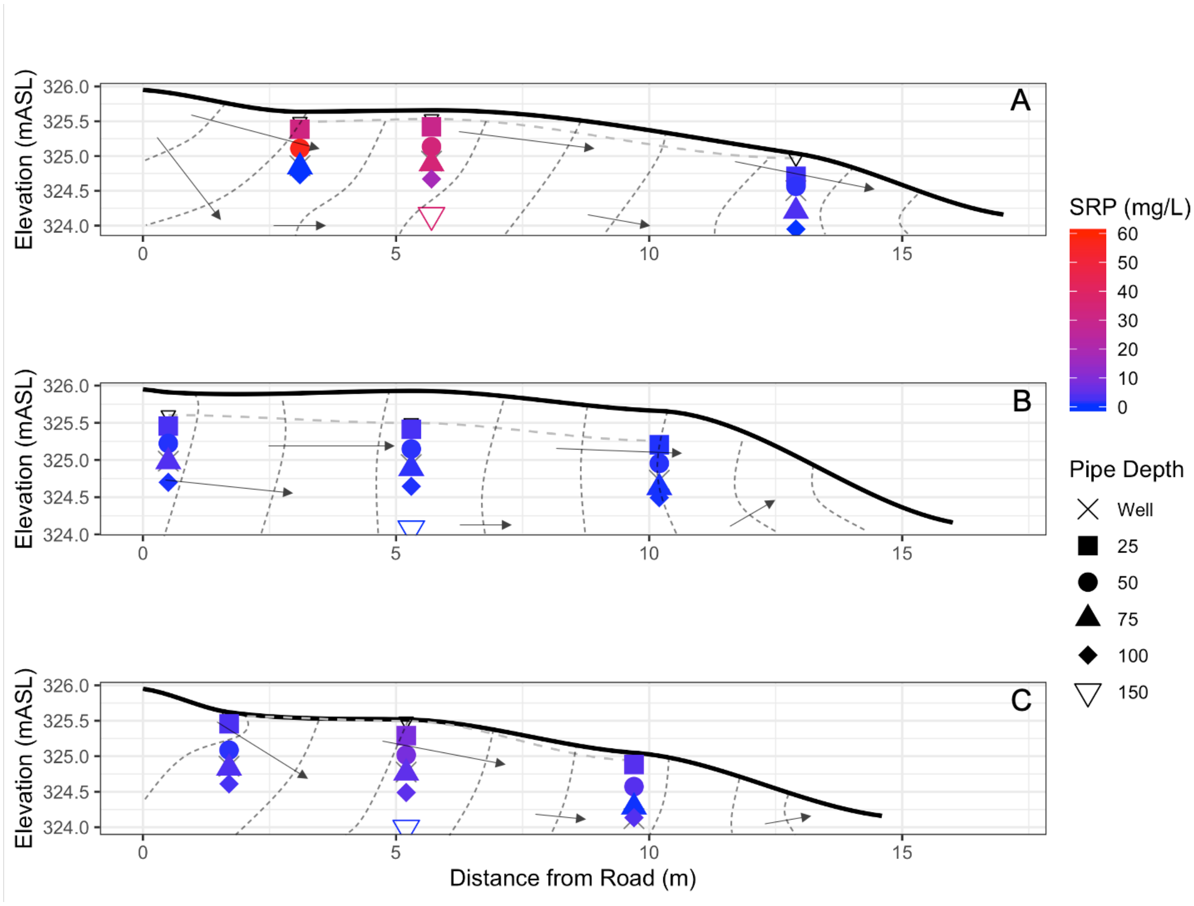

Figure 4.13: Soluble reactive P concentrations and flow path directions for November 11, 2018, during wet antecedent moisture conditions in the (a) west, (b) centre, and (c) east transects.

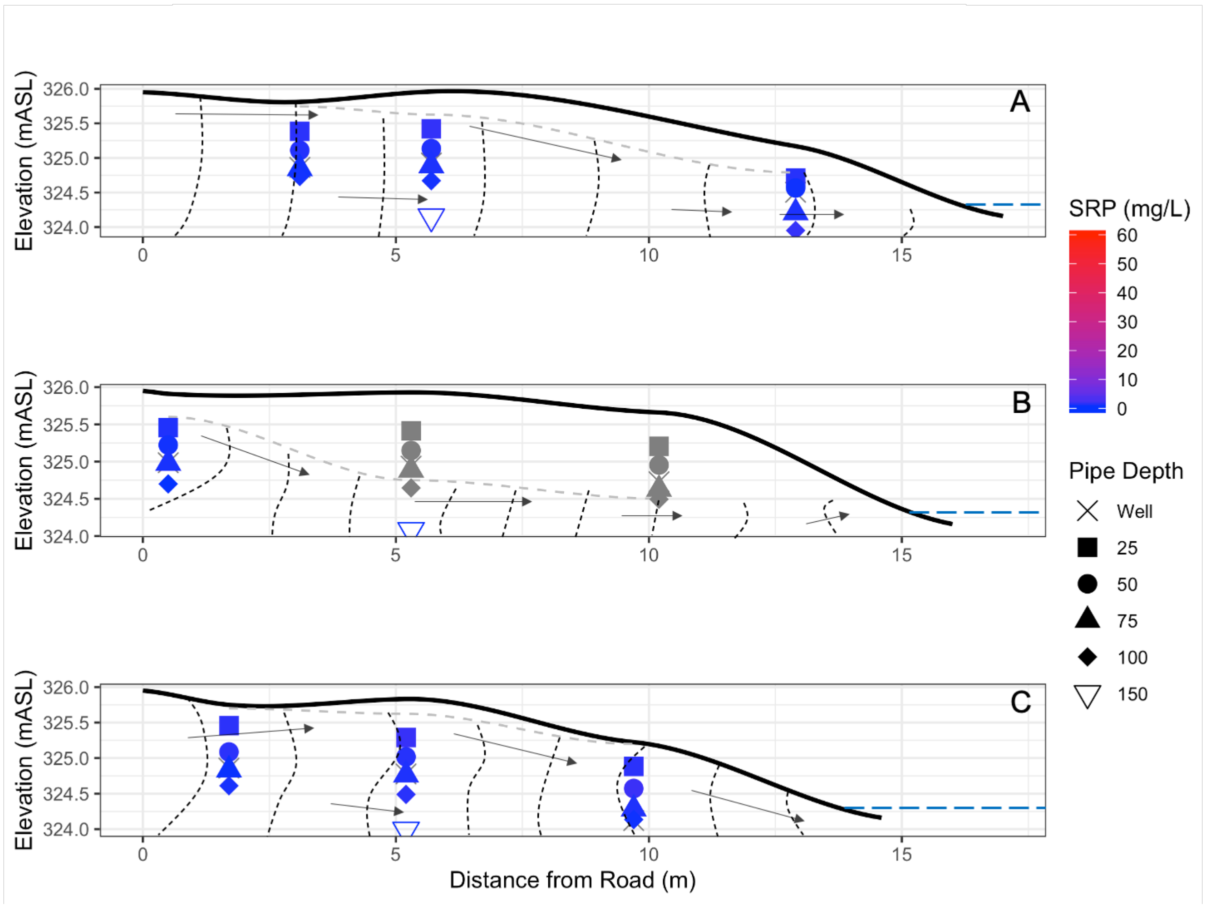

Figure 4.14: Soluble reactive P concentrations and flow path directions for August 21, 2018, with dry antecedent moisture conditions, after a summer rainstorm in the (a) west, (b) centre, and (c) east transects.

A rough estimate of a groundwater flux (water and P) was calculated to determine the potential contribution of shallow riparian groundwater to the P loads to the stream. This was done on four events after the bunker silo was refreshed (Table 4.4). Although water tables were higher during wet antecedent conditions, and groundwater fluxes were greater during these periods (e.g. October 3, 2018), drier summer months contributed higher percentages of groundwater SRP to stream loads than wetter periods in the fall (Figure 4.4), when there was likely more of a dilution effect under greater flow conditions. Table 4.4 shows the percent of each load that was influenced by groundwater flow, and demonstrates that on days with lower flow, a higher percentage of SRP contributed to stream loads. However, although summer months with higher flow exhibited slightly higher percentages of overall loading, the estimated contribution of groundwater SRP (based on estimates made using Darcy's Law) was negligible and could not account for the observed increases in stream P loads. No direct surface runoff from the silo was observed on any of the dates in Table 4.4.

Date/ Event	Groundwater Flux Estimated Using Darcy Equation (L)	Stream Discharge (L)	Stream Load at Downstream Location (mg)	Observed Change in P Load along Riparian Reach (mg)	Estimated groundwater P flux (mg) using median groundwater P concentration	Estimated groundwater P flux (mg) using highest groundwater P concentration
2018-08-08/Baseflow	$2.9x10^4$ (0.0004)	$8.4x10^7$	$1.7x10^7$ (SRP)	$1.4x10^7$	$3.1x10^4$ (0.002)	$6.2x10^4$ (0.002)
2018-08-21 13	$7.2x10^4$ (0.0004)	$2.1x10^8$	$5.1x10^6$ (SRP)	$3.9x10^6$	$5.6x10^4$ (0.011)	$1.3x10^5$ (0.014)
2018-10-03 15	$1.1x10^5$ (0.0002)	$5.2x10^8$	$5.3x10^6$ (SRP)	$1.9x10^6$	$1.1x10^5$ (0.02)	$9.3x10^5$ (0.06)
2018-10-31 16	$1.5x10^4$ (0.0002)	$3.8x10^6$	$3.8x10^6$ (SRP)	$1.3x10^6$	$9.6x10^3$ (0.003)	$2.9x10^4$ (0.007)

Table 4.4: Estimates of the groundwater flux from the riparian zone estimated using Darcy's Law, compared with the total volume of measured stream flow (L) for the corresponding event. Groundwater flow and P fluxes are shown as a percentage of the stream flow and stream P load in brackets beside the flux estimate. The observed change in P Load along the riparian reach was estimated by subtracting the P load at the upstream location from the P load at the downstream location.

Chapter 5 Discussion

The results of this study add to the existing body of literature that shows that nutrient losses can occur from bunker silos, and discusses the potential effectiveness of riparian zones in mitigating these losses. This work highlights the importance of proper management of point sources of agricultural nutrients to mitigate losses to the environment. These results also shed light on further research that should be conducted to better understand the complex relationship that bunker silo effluent can have with riparian soils, and various factors that contribute to their nutrient losses.

5.1 Importance of Hydroclimatic Variability and Antecedent Wetness Over the Study Period

Phosphorus dynamics were likely impacted as a result of drier conditions throughout the study period when compared to 30-year normals. Due to the dry study year, there were likely lower overall nutrient losses from the farmyard than there would have been in a wetter year. Although the overall year was dry, there were wet periods during the year that were notable. One important hydrologic event to note occurred on February 19-22, where over 25 mm of rain was observed on a melting snowpack. These conditions caused substantial flooding in the affected area of the riparian zone and other parts of the catchment, and the entire riparian zone was submerged (Figure 3.2a). Soluble reactive P and TP concentrations recorded during the event were all higher downstream of the bunker silo, indicating a possible desorption of P from the flooded riparian soils. Gburek & Sharpley (1998) displayed the importance of upland hydrologic conditions and P release in saturated soils, or soils with high water tables, and observed elevated levels of P release from soils with wet antecedent moisture conditions during precipitation events. Wet antecedent moisture conditions often lead to lower infiltration capacity in soils (Blackburn, 1975), and likely resulted in the increased losses to the stream. Unfortunately, the extreme flooding damaged the autosampler at the upstream location and consequently, the precise contribution of the riparian zone to the overall stream load can only be estimated. Although there may have been direct inputs from the bunker silo, no obvious direct leachate from the bunker silo was observed and the P was likely flushed from the riparian zone instead. This event demonstrates the significance of 'hot spots' and 'hot moments' Vidon et al. (2010), where flooded riparian zones, or a rise in water table can increase the potential for nutrient losses., and riparian zones that are saturated with P can become *critical source areas*.

Phosphorus concentrations in stream samples rose during high flow (thaw events, snowmelt, and spring storms); however, they sometimes exhibited higher concentrations during smaller precipitation events throughout the latter part of the study period, particularly following the refresh of the bunker silo in August 2018. The fact that groundwater P concentrations increased in the autumn of 2018 as conditions became wetter, indicates that the bunker silo P is indeed mobilized under wetter conditions. However, the apparent negative relationship between flow and stream P concentrations suggests that there is a limited supply of P to the stream that is diluted under high flow conditions rather than a source that is mobilized with wetter antecedent conditions (Jarvie et al., 2010), which suggests that the groundwater does not provide an unlimited source of P, irrespective of flow conditions or the

P saturation in the riparian zone. It was hypothesized that the riparian zone in this study would become a source of P to the stream during high flow periods, mobilizing previously retained P. Although there are indeed greater P concentrations in groundwater in the fall of 2018 following antecedent conditions and the refresh of the silo, these may be somewhat limited temporally. However, baseflow after the refresh mad a big difference to the loads, and could be attributed to the chronic leakage of effluent post silo refresh.

Irvine et al. (2019) reported that the snowmelt period for the same study site represented the greatest P losses over the study period. The same was true here. Macrae et al. (2007) also reported for a nearby site that the greatest losses occurred in a few extreme events but that most losses occurred in "event" flow rather than baseflow. The current study has shown that although events indeed account for the majority of P losses, especially snowmelt, there are also small, chronic losses that occur in baseflow at this site, after the bunker silo was refreshed.

5.1.1 Spatiotemporal Variations in Stream Water

Inputs of P loads varied throughout the study period and were affected by numerous factors. Although P concentrations and loads in stream water were greater following events than during baseflow, a more dramatic shift in P concentrations and loads was apparent following the bunker silo replenishment, where increased P loads were observed. First flush events from bunker silos are highly contaminated and is recommended by the Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA) to be collected and contained to decrease losses to the environment (Clarke & Stone, 2005). Although a riparian zone is present at the field site to capture the effluent, downstream loading of TP increased in the days following, indicating elevated levels of nutrients produced by the fresh silage (Figure 4.3) and demonstrating that the riparian zone was not able to capture all of the P.

Total P loads up and downstream were fairly even throughout the study period until the replenishment of silage in the bunker silos, when downstream loads spiked considerably. Conversely, SRP loads were consistently higher downstream throughout the study period, further demonstrating the significance of legacy P in releasing chronic losses of P. The significance of legacy P has been documented previously in the literature (Sharpley et al., 2013). This work demonstrates the significance of small wetlands receiving inputs from bunker silos in contributing chronic losses of SRP due to their legacy P build up.

5.1.2 Spatiotemporal Variations in Groundwater

Temporal variations in groundwater SRP levels were largely influenced by the production of silage effluent. After the bunker silo was replenished mid-summer, groundwater SRP increased significantly. However, significant increases cannot be attributed solely to the bunker silo replenishment. Many of the larger precipitation events that were sampled (with the exception of a few snowmelt events), occurred during the second half of the study period. These precipitation events flush silage effluent into the receiving riparian zone and influenced P concentrations. Moreover, it is important to note that the higher number of sampled events in the second half of the study period likely influenced, and perhaps skewed the observed groundwater concentrations.

Groundwater concentrations also varied spatially, with higher observed concentrations in the east and west transects. The concentrated flowpaths through these transects received most of the runoff generated from the barnyard, thus influencing the spatial variability of SRP. Runoff often pooled in these flowpaths, especially in the upper location of the west transect. This pooling of runoff and effluent is a major reason why the highest observed groundwater concentrations were sampled from this location. Furthermore, visual observations throughout the study period observed the most pooling and saturation through the west transect.

5.2 Relative Contributions of Farmyard to Overall Stream Loads

Contributions of P from the farmyard in this study were substantial. Irvine et al. (2019) observed yields from the same watershed (0.15 kg SRP/ha, 0.94 kg TP/ha) that were higher than those of other surrounding watersheds (e.g. 0.1 kg SRP/ha, 0.70 kg TP/ha), however, it was unclear as to whether the higher yields were a result of inputs from the farmyard. This study can confirm that although the watershed losses are primarily driven by cumulative losses from the upstream 14km^2 watershed, a substantial proportion (32% of SRP, 22% of TP) come from the farmyard. Thus, the farmyard yields (dominated by the bunker silo) likely explain the majority of the differences in yields between this study site and other surrounding watersheds with comparable field land use and management.

Phosphorus yields observed during the current study are considerably larger than those observed by Irvine et al. (2019) (nearly double the SRP and double the TP). This may have been due to having a wetter 2018 winter with a greater number of freeze-thaw cycles as well as the substantial February flood event, whereas in Irvine's study year, the winter was cold and the snowmelt period was long and driven by radiation melt.

Although storm and melt events accounted a large proportion of the P fluxes, P concentrations were highest during lower flows during the study period, with the exception of some snowmelt sampling days. During higher flows, SRP from point sources can be diluted (Jarvie et al., 2010), which is likely what occurred during this study. Jarvie et al. (2010) found that intensive livestock farming on heavy clay soils can increase stream TP dramatically. Higher TP concentrations were observed downstream of the bunker silo in our study, especially post silo fill (Figure 4.4), and could be attributed to the presence of clay soils within the riparian zone that receives chronic effluent runoff from the adjacent bunker silo. Jarvie et al. (2003) found P had negative relationship with flow, and that concentrations are strongly influenced by point sources of effluent that are diluted under high flow conditions. Furthermore, the study found that diffuse sources were positively correlated with flow, and observed increased P concentrations with increased flow (Jarvie et al., 2003). Our study revealed similar results, where in most cases high flow conditions were associated with diluted P concentrations.

Although many studies have been done on farmyard P runoff (Dunne et al., 2005; Edwards & Withers, 2008; Neumann et al., 2002), direct contributions of P from bunker silo effluent have not been considered. Given their importance in the current study, future studies should consider comparing losses from point source bunker silo losses to diffuse edge of field losses. Controlling losses from these high P sources in the landscape can considerably improve our ability to reduce P losses from fields. Future studies should examine the density of farms such as the one from this study in the landscape to determine the potential overall impact of controlling bunker silo effluent to minimize P loss throughout the Great Lakes region. The occurrence of these soils are hot sources of P and controlling these losses would be a large step forward. However, if critical source areas like these cannot be identified in the landscape then controlling their losses may not make a large difference overall.

5.2.1 Role of Soil Properties and Characteristics on Phosphorus Dynamics

Soil properties such as PSI had a substantial effect on the riparian zones ability to adsorb bioavailable P. Low PSI hindered the soils ability to retain excess P from barnyard runoff, resulting in less sorption of P in riparian soils, especially in wet antecedent moisture conditions. The general pattern of an increase of PSI with depth in the east and west transects suggests that deeper soils are more likely to sorb excess bioavailable P within the soil solution. However, hydraulic conductivity of the riparian soils decreased with depth, resulting in more movement of soil solution through the shallow subsurface. Furthermore, the much higher PSI values on the unaffected side of the riparian zone suggest that silage effluent significantly reduces the soils PSI.

Water extractable P gave an indication of the potential P release from riparian soils. The higher values of recorded WEP at shallower depths suggest that the soil is more capable of desorption during precipitation events, or flooding. This is especially true for the east and west transects that were often flooded and/or saturated at the surface. Similarly to PSI, the unaffected side of the riparian zone showed stark contrasts to WEP values. The much lower values indicate that the runoff of silage effluent into the receiving riparian zone impacts the soil WEP, that ultimately leads to increased release of SRP to the soil solution (Figure 4.11).

Soil type within the riparian zone also had an impact on P dynamics facilitation of P flux to the stream. The coarse textured soils within the upper layers of the riparian zone that had low PSI, and likely a high degree of P saturation are prone to leaching SRP into the soil solution, as is shown in Andersson et al. (2013). However, as soil type changes with depth to a finer sandy clay loam, the soil likely has a higher retention efficiency, as PSI increases, and WEP decreases. The finer sandy clay layer acts as an aquitard to the shallow and deep soils, influencing a dominant lateral groundwater flow (Mengis et al., 1999).

Results showed that the riparian zone contribution to the overall load was negligible. However, several factors should be noted. Variation in hydraulic properties of soil should be considered when analyzing the K_{sat} data. Hydraulic conductivity between the east and west transect were three orders of magnitude apart, and SRP loads from the two transects also had large differences. Large differences in K_{sat} within a riparian transect are not uncommon. Elmes & Price (2019) recorded a four order of magnitude difference in K_{sat} within sandy/silty upland soils, differences that are similar to those in this study. Characterization of the structure of an aquifer is extremely difficult, but important for contaminant tracing studies (Sudicky, 1986). Although the results from this study show a negligible addition of SRP from groundwater sources, sufficient characterization of the riparian zones subsurface structure may not have been adequate. Ways to improve accuracy of flux measurements could include the addition of a higher spatial density of piezometers throughout the riparian zone to better characterize the sites subsurface structure. Translatory flow, described by Lischeid et al. (2002) as the displacement of pre-event water from shallow soil pore spaces due to increased pressure from infiltrating water, could be a factor influencing SRP lost from the riparian zone that wasn't sampled. If pre-event water within shallow soil pores throughout the west transect (which received the majority of bunker silo effluent) had a high SRP concentration, then translatory flow may indeed be a missing contributing factor to P loading.

5.3 Efficacy of Riparian Zone in Mitigating Phosphorus Transport Between the Bunker Silo and Stream

The affected area of the riparian zone in this study has received a chronic supply of silage effluent for 15 years. The complex interactions and biogeochemical P transformations make it difficult to determine whether the affected riparian area is a contributor of P to the freshwater stream, or a sink to the P that it receives. However, there are several factors that should be examined to indicate the overall health and ability to function.

Sorbed P to riparian soil has the potential to be mobilized under wet conditions. This was evident in the February 20 event, where elevated levels of TP were recorded at the downstream location (Figure 4.1). Further evidence of the release of previously bound P to the soil solution is apparent in Figure 4.12, where SRP concentrations reached as high as 57.05 mg/L. The nutrient loss that occurred during these two events is similar to what is explained in Macrae et al. (2010), where antecedent moisture conditions were a driving factor in nutrient export in the Strawberry Creek Watershed, a neighboring catchment to the one in this study. However, perhaps a more important factor to consider, and a possible driving force behind the build up of P in the riparian soils, is the role of legacy P.

Legacy P is a result of historical inputs of P over long periods of time and has proven to be a potential source long after nutrient sources ceases – in some cases even decades after (Kleinman et al., 2011). The elevated levels of nutrient inputs and consistently higher loads of P measured downstream demonstrate that the results of this study indicate the presence of legacy P in the affected area of the riparian zone is highly likely. Furthermore, the high degree of soil P saturation (Figure 4.6, 4.7 & 4.9) in the riparian soils also suggest a legacy P build up from historical (and continued) inputs. Legacy P stores have been noted in the literature as being very important to P loss (Jarvie et al., 2013; Sharpley et al., 2013; Zhu et al., 2018). In our study, the soils in the center transect and near stream locations of each transect are not yet saturated with P (Figure 4.9), which suggests there is room for the riparian zone to sorb more P. Moreover, high groundwater P recorded during the study implies that at least some of that P is being remobilized and being flushed into the stream. The fact that groundwater flux estimates could not account for the observed P increase at the downstream sampling location could be a result of (a) insufficient piezometer depths and transects causing incorrect groundwater flux estimates, or (b) another pathway of P that was unaccounted for (e.g. An upwelling from below the stream bed). The elevated levels of P in the riparian groundwater and soils suggest that even if the bunker silo was removed, the riparian zone may supply P to the groundwater, and subsequently the stream, long after its removal, as is the case in many critical source areas with legacy P (Jarvie et al., 2013). The data from this study indicates that the riparian zone mitigates some of the P from the bunker silo, but not all, and that more effective removal is needed.

The affected riparian zone could be considered a hotspot for P accumulation, as runoff from the bunker silo and barnyard often pool and deposit sediment in its soils, similarly reported in other publications (Sharpley et al., 2013; P. Vidon et al., 2010). Antecedent moisture conditions and the presence of legacy P in the riparian zone lead to the question of whether it acts as a source of P to the freshwater environment, or as a sink. The study results demonstrate the ability for the riparian zone to be both a source, and a sink for P. Hot spots and hot moments, defined in McClain et al. (2003) are areas that exhibit high rates of reaction relative to adjacent areas, and high reaction rates in a short period of time when compared to longer periods in the same area, respectively. Our hypothesis that the affected riparian zone could be a re-occurring hot spot that experiences hot moments is reflected in the data. Wet antecedent moisture conditions and periods of thaw and/or snowmelt led to elevated P levels in groundwater and downstream water samples (Figures 4.3, 4.5). Biogeochemical reactions within the riparian soils may be a result of converging hydrological flow paths – barnyard and bunker silo effluent runoff, and riparian zone groundwater – where materials necessary for reactions to occur meet (McClain et al., 2003).

5.4 Limitations

Several limitations existed during this study, or became apparent during data analysis. Infrequent stream water samples were collected during the initial data collection phase of the study as a result of equipment failure, and lack of experience at the specific field site. During the February 20 event, ISCO samplers were activated too close to the stream, and were tipped over as a result of high flow, resulting in a loss of samples. Furthermore, battery failure was a frequent problem until new batteries were purchases and installed with solar panels to ensure a constant power source. While modelling P loads, it became evident that any samples taken under a stream discharge of 410 m^3/h were too high to be believable, likely as a result of sucking up stream sediments that were stirred up while the ISCO purged its sampling lines, and were not representative of the true SRP levels within the water column.

Sudicky (1986) outlines the importance of spatial variability of hydraulic conductivity. The extreme level of detail of the hydraulic conductivity measurements taken in that study demonstrates the increased accuracy and confidence of tracking solutes through groundwater. Increased detail of hydraulic conductivity measurements in our study would have helped better determine the SRP groundwater inputs into the stream.

Pressure transducers used to determine stream levels that were used with the rating curve to determine stream discharge failed on October 5, 2018. As a result of the failure, stream discharge of a nearby stream, with very similar hydrographs was paired with our discharge data to fill in the missing discharge (October 6 – December 31, 2018). This occurred as a result of the pressure transducer's memory filling up. More frequent data dumps would have avoided the loss of stream discharge data.

5.5 Next Steps

This research has shown that point source pollution in agriculture is still a problem that exists with little prevention on small scale operations. Although many regulations exist within smaller scale operations Ontario wide in terms of fertilizer application to mitigate edge of field losses (Nutrient Management Act, 2002), there are less stringent policy and regulations surrounding nutrient losses from bunker silo effluent on small farms. Nutrient loading from bunker silos on small scale farms may be negligible, but cumulative effects of the hundreds of dairy farms scattered across southwestern Ontario add to the growing problem of eutrophication of our freshwater ecosystems. Strategic plans, and policy implementation that advance mitigation efforts to limit nutrient losses from bunker silos, but are also fair to small scale farming operations, is critical.

Several management options that are currently in place for larger scale operations could work on smaller scales. Collection and containment of bunker silo effluent is an option that would decrease losses to the environment, and can be recycled as fertilizer (Clarke & Stone, 2005). The Ontario Ministry of Agriculture, Food, and Rural Affairs suggests a dilution factor of 1:1 bunker silo effluent to water, and to follow liquid manure spreading guidelines to spread the material as fertilizer (Clarke & Stone, 2005). Moreover, OMAFRA suggests that any seepage collection tanks should be installed at least 200 ft. from any surface water. At our study site, the bunker silo was constructed within 200 ft. of the stream, and would need a collection tank to be installed ~50 ft. from the bunker silo. Other options to limit nutrient losses do exist. In-silo effluent absorbents can be used to minimize effluent production, and have been shown to reduce production as much as 85% (R. Jones & Jones, 1996).

Although this research confirmed that bunker silos are a source of nutrient loss, there are many questions left unanswered, where future research opportunities exist. Future site specific research might consider analyzing stream bed sediments to determine their current SRP levels and their chemical composition and mineralogy. Stone and Mudroch (1989) found that the chemical composition and mineralogy of sediments are the controlling factors of P adsorption/desorption, and suggested that the size of particle had no effect on P adsorption. It would also be important to install more nested wells and piezometers at a higher density of depths and surface distance. This would allow for a more detailed and accurate groundwater flux estimation, and minimize the potential of missing an important layer within the subsurface.

Higher frequency of stream and groundwater sampling events in a multi-year future study would also increase our understanding of the specific environment.

Chapter 6 Conclusion

The aim of this research was to quantify the contribution of P losses from a dairy farm bunker silo over a one year period, to monitor P concentrations in surface and groundwater across a riparian zone, and characterize the sorption potential of its sediments to infer whether the riparian zone may be acting as a sink for P, or a source of previously retained legacy P to the stream.

This research has shown that significant losses of nutrients from bunker silos is evident on a spatiotemporal scale. In particular, the loss of SRP to the freshwater stream occurred mostly as overland or translatory flow. Soluble reactive phosphorus spiked during one storm in particular (event 4), where downstream SRP and TP levels were much higher than upstream levels. This was a precipitation event on melting snow. Moreover, after fresh silage had been added to the bunker silo, the following month saw a large spike in cumulative TP loads.

Characterization of sorption potential of the riparian sediments was done and an inference as to whether the riparian zone acted as a source of P to the stream was made. The results showed that elevated levels of WEP existed throughout the affected area of the riparian zone, with the highest levels occurring in the west transect. Furthermore, the soil appeared to be quite saturated with P, as a reflection of the low PSI results within the affected riparian zone. Although the riparian soils exhibited elevated levels of WEP, paired with relatively low PSI values, the estimated contribution of P to the stream that this study calculated was negligible. The lack of evidence of riparian zone P contribution from these data leaves the question as to whether the riparian zone has a flowpath that was missed when installing the nested wells and piezometers, or if an upwelling of P is occurring in the stream bed.

Several management options were identified and explored as potential mitigating strategies in reducing losses of bunker silo effluent. The need for increased policy and regulation on smaller scale livestock farming operations in southern Ontario was suggested, as cumulative farmyard losses may account for substantial additions of P into freshwater systems. However, before implementation such as these are applied, further research should be completed to ensure effective, but fair policies are made. Collection and containment systems may be one such implementation to reduce effluent losses. These systems would not only reduce direct effluent losses, but serve as a source of nutrient rich fertilizer that farmers could use on future crops. This practice has been previously explored as a method of reducing nutrient pollution (Kemppainen, 1987; Purves & McDonald, 1963). Site specific management options might include installing a collection and containment system, however, removing the affected area of the riparian zone and backfilling with fresh soil or slag could be beneficial to reduce P loading in the future.

This thesis has been beneficial in improving our understanding of how riparian zones interact with direct losses of bunker silo effluent. Furthermore, the research collected during this study has shown that southern Ontario livestock farms and nutrient losses from bunker silo effluent remains an unresolved issue. Although many management practices are in place, much of the focus on controlling nutrient losses in agriculture is on edge of field losses, while direct inputs – like those of bunker silos – are generally thought to be under control. To improve water quality and eutrophication in freshwater systems, it is important to spend more efforts on controlling point sources like these. As diffuse sources of nutrient pollution like edge of field losses are difficult to manage, point sources should, in theory, be easier to control. This research should be used as a starting point for future studies like this to further our knowledge of bunker silo nutrient dynamics within riparian zone soils in southern Ontario.

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