The use of a filter product to remove phosphorus from surface runoff in agricultural fields

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 fields are the largest sources of phosphorus (P) entering the Great Lakes in North America. Research has suggested that multiple conservation practices (CPs) used together (stacked) are an effective way to reduce the amount of P losses individual fields; however, some P loss still occurs. Advancements in the chemical removal of P have provided landowners with an opportunity to capture P that has leaves fields in runoff before it enters local waterways and act as a final polishing agent. A commercially available phosphorus sorbing material (PSM) in the form of a geotextile filter was installed on two well managed fields in midwestern Ontario (ILD and LON) to determine its efficacy in removing dissolved reactive P (DRP), total P (TP) and total suspended solids (TSS) from surface runoff, thereby reducing edge of field P losses. Laboratory tests on unused and used filter material were also conducted to try to determine the sorption potential, amount of P stored in the filter and the mechanisms of P removal. During the two-year study period, the filter removed 0.018 kg/ha of DRP, 0.4 kg/ha of TP and 8.75 kg/ha of TSS at the ILD site. In contrast, the filter at LON released 0.22 kg/ha of DRP and 0.15 kg/ha TP, but removed 37 kg/ha of TSS. The filter most effectively removed P within 8 months of filter installation, suggesting that time was a critical factor impacting performance, among others. Laboratory tests on unused (new) and used (field) filter material indicated that the raw filter material had a large potential to adsorb DRP under controlled conditions, and that this potential was smaller in used material from LON but not ILD. The extraction of P from used filter material indicated that the filters retained approximately 200 mg/kg of DRP at each site (0.0027 kg/ha at ILD and 0.0022 kg/ha at LON) with the majority of this P held in more soluble form likely associated with the metal oxides/clay filter components. This suggests that previously retained P has the potential to be rereleased from the filter. Additionally, the amounts of P held in the filter material calculated via lab tests was considerably lower than the amount removed through the water samples calculations suggesting that some of the P removed by the filter did not stay inside the material. The results of this study demonstrate that P has the potential to be chemically removed at the edge-of-field, but the efficacy of filters as a CP differs in both space and time. This thesis has shown how an edge-of-field filter for surface runoff can be implemented in a field setting in midwestern Ontario, and has identified and which factors are most important to determining the efficacy of this practice.

Acknowledgements

Dedication

To members of the Carlow, Murphy, O'Brien and Payne families living and deceased from whom I take great inspiration. I come from a long history of farmers and land stewards and it is a pleasure to continue that work in a small way.

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Chapter 1

Introduction and Problem Statement

Phosphorus (P) is an important nutrient for crop growth but also has the potential to run off and create environmental problems in water bodies. Natural mobilization of P is slow and low solubility phosphates and their rapid transformation to insoluble forms make the element the most common growth limiting nutrient in plant species including algae (Schindler 1974; Smith, 2000). A few of the significant sources of excess P to water bodies include agricultural runoff from fields, municipal discharge, including wastewater treatment, and industrial effluents (Karageorgiou et al., 2007). However, the largest sources of phosphorus to aquatic systems are from agriculture and urban activities (Carpenter et al., 1998). In aquatic ecosystems, P can result in fish kills, the development of toxic algal blooms as well as reduced biodiversity and oxygen levels (Carpenter et al., 1998). Algal blooms have been documented in water bodies across the globe including the Baltic Sea, the Gulf of Mexico and Lake Winnipeg in Canada.

The Great Lakes region of North America has seen a number of large algal blooms due in part, to the density of agricultural land on both the American and Canadian side of the lakes (Carpenter et al., 1998). Lake Erie is of special concern for algae growth as it is the outlet for major US and Canadian rivers such as the Thames, Sandusky, and Maumee in addition to its natural shallow depths and warm temperature relative to the other lakes (Carpenter et al., 1998). Lake Erie also provides drinking water for some 11 million people on both sides, including the cities of Toledo, Ohio and London, Ontario for which a clean water supply is vital (Lake Erie LaMP, 2011). Nonpoint sources of P, such as those from agricultural runoff, have been more difficult to quantify, control and remediate over the years when compared to point sources (Sharpley, 2016). Though P loss from individual fields may be low, the sheer number of farms contributing runoff to the Lake Erie basin means a large amount of P is entering the lake every time a hydrologic event occurs (Maccoux et al., 2016). Excessive use of fertilizer and manure in agriculture has caused a nutrient imbalance in soils which has been identified as a leading cause of water contamination in agricultural watersheds (Vitousek et al., 2009; Su et al., 2011). Some reasons for this large role include the application of more fertilizer than needed for crop growth as well as soil erosion by wind and water (Carpenter et al., 1998). From an agricultural perspective, the losses of small amounts of P are minimal compared to the amount applied to fields; however, these relatively small loses from thousands of fields are enough to cause eutrophication (Dils and Heathwaite, 1999). Recognizing the problem, The International Joint Commission created target goals for the reduction of P entering Lake Erie by 40% from 2008 levels. (IJC, 2014). In attempting to reach these goals, multiple different strategies have been employed by both countries, most specifically targeting the agricultural industry.

For a number of years, it has been recommended to farmers that they should implement conservation practices (CPs) in their fields to both control nutrient losses and increase soil health. A few of the most commonly used CPs include; crop rotations with wheat, planting cover crops during the non growing season, and nutrient management plans for manure or synthetic fertilizers. The use of such CPs are the main strategy landowners have in order to reduce the amount of nutrients being delivered to waterways from non-point sources such as agricultural fields (Bosch

et al., 2013). Which CPs will be most effective on specific farms will depend on factors such as climate, soil type and topography (Macrae et al., 2021). Since both surface and subsurface runoff can be sources of P from agriculture, multiple CPs may be needed to target both routes of P loss. Other studies have pointed to the need for the adoption of CPs that are effective during snowmelt that can reduce sediment and P losses in areas where snowmelt is a hydrologic driver in the non-growing season (Su et al., 2011). Individual studies have shown the beneficial nature of any number of these practices, but a number of modelling studies have concluded that implementing one practice may not enough to reach reduction targets (Bosch et al., 2013). Thus, to reach reduction targets either every farm must do one practice or a large portion of farms must do multiple practices (Smith et al., 2015a; Scavia et al., 2019), specifically targeting the non-growing season.

In addition to traditional field management strategies, newer P removal technologies have begun to be implemented. Typical P removal structures include large amounts biproduct or rocks rich in Ca, Fe and Al in fields with high levels of soil test P (Bryant et al., 2012; Penn et al., 2020). These materials can be placed in large ditch style filters (Bryant et al., 2012) edge of field filters (Penn et al., 2017) or long flow through beds (Penn et al., 2020). These phosphorus sorbing material (PSMs) have shown success in controlled environments of wastewater treatment plants and laboratory tests (Sovik and Klove, 2005; Renman and Renman, 2010; Herrmann et al., 2014). However, few filter-based P removal studies have been conducted in field settings under variable climatic and flow conditions. Little is known about their efficacy during the non growing season, despite the fact that P loss is dominant during this period in cool, temperate regions. In addition, little is known about the performance of PSMs at reducing edge of field losses when used in conjunction with stacked agronomic CPs including conservation till and small soil test P.

Finding a strategy or suite of strategies that can best remove P from runoff during the non growing season is of utmost importance to meeting P reduction targets set out in the International Joint Commission. Practices that are particularly effective at removing dissolved P are especially important as other practices frequently are ineffective in trapping this form, and DRP is a highly bioavailable form of P. This thesis explores the efficacy of a PSM at reducing edge of field P losses from fields that already employ a suite of stacked CPs, to determine if commercially available PSMs can be used in conjunction with other CPs to reduce P losses in runoff. This work can provide guidance to policy makers setting standards for Ontario agriculture and P losses.

Chapter 2

Review of Literature

Losses of P from agricultural systems are controlled by a number of factors including both source and transport pathways from field to waterways. This literature review will first discuss the P cycle, where P is found and how it moves in agricultural landscapes. Then, this review will discuss how agricultural losses, the primary source for P in the Great Lakes basin, have been employing agronomic CPs to reduce P loads. The use of geotextiles and other filters for all industries and then specifically in agriculture will be discussed, including the chemistry of trapping and removing P as well as the types of filters and design that have been implemented in other locations. The economics of removing P from individual agricultural fields will also be discussed. Lastly, this review will list the objectives of the thesis.

2.1 Phosphorus cycle and use

Phosphorus is a mineral essential for all life as it forms the base of the ATP molecule and is used in the formation of DNA/RNA (Smith, 2000). The majority of P found in nature occurs in sedimentary rock deposits and is composed of various calcium phosphate compounds (Samreen and Kausar, 2019). On human time scales- P is a one-way flow system, unlike other minerals such as nitrogen (N) which moves through a cycle (Withers et al., 2015). Rock phosphate is mined for the creation of synthetic P fertilizers such as monoammonium phosphate (MAP) and diammonium phosphate (DAP) with the majority of mining occurring in China, Morocco (Western Sahara) and the United States (Gorazda et al., 2013; Samreen and Kausar, 2019). The creation of such fertilizers began in the mid 1800's from a process of mining P rich rocks to remove the P and put it in a granular form that can be land applied (Samreen and Kausar, 2019). Later it was discovered that treating the P rich rock with phosphoric acid resulted in an increase in the amount of soluble P that is available for plants (Smith, 2000). Of all the rock phosphate that is mined in the world approximately 95% is used as fertilizer in the agricultural industry (Samreen and Kausar, 2019). A major source of inefficiency within the P mining system is that only 10% of the mined rock P is consumed (Cordell et al., 2009).

The P rich fertilizer is then spread onto fields, transported in runoff through wind or water erosion and is swept into rivers and eventually lakes where it settles to the bottom and can remain in sediments (Smith, 2000). Along the pathway, P can be stored in a number of places including both terrestrial and marine plants, bound to soil particles, in dissolved forms and both inorganic and organic forms (Smith, 2000; Jarvie, et al., 2002). A small amount of atmospheric deposition does occur with P but is not considered a major source (Smith, 2000). Another potential source, soluble phosphates released by the weathering of calcium P rocks like apatite is usually rapidly immobilized (fixed) into insoluble forms (Smith, 2000; Samreen and Kausar, 2019). P rarely exists in a gaseous form unlike Carbon (C), Nitrogen (N) or Sulfur (S) so the major pathway for its release is from weathering (Smith, 2000). With no volatilization and with usually very low leaching losses, erosion and runoff are by far the most important sources of the nutrient carried in inorganic and organic particulates by streams to the ocean (Smith, 2000). The end phases of P in the cycle are land surfaces, incineration, deposited in a landfill or released into water (Withers et al., 2015). True waste in the cycle occurs when P reaches the oceans where it is no longer

recoverable on human time scales (Withers et al., 2015). The P cycle has been described as inefficient because of the large number of losses along the pathway from the production and use of P based products that are not reused (Gorazda et al., 2013; Withers et al., 2015). In the food production process, from seed to consumer, 80% of the P used is lost to the environment; which shows the need for a more sustainable system (Samreen and Kausar, 2019). Phosphorus has no substitute but can be reused many times, so to fix the broken cycle, P needs to be used more efficiently and recycled across all sectors (Withers et al., 2015). Opportunities to close the P cycle by reducing P losses and capturing any unavoidable losses and reusing them for fertilizers are being explored in many jurisdictions across the globe (Gorazda et al., 2013). Any reduction in losses that can be achieved before P reaches its final end point in the oceans aides in making the P cycle more efficient.

2.1.1 Forms of phosphorus in runoff and soil

Phosphorus in soil may be present in both organic and inorganic forms, but phosphorus in runoff is operationally defined as either dissolved (TDP) or particulate (PP), and the two forms are differentiated based on the filtration of the water sample using a 0.45 micrometer filter (Jarvie et al., 2002). Total P (TP) is the sum of TDP and PP. Dissolved P may be further subdivided into "reactive" (DRP) and non-reactive P (DUP), using the Murphy and Riley (1962) phosphomolybdic acid methodology. DRP is most often thought of as just lone orthophosphate molecules and very bioavailable while DUP is most likely dissolved P in organic forms (Li and Brett, 2013). Dissolved P is estimated to be 10-40% of all P in runoff from cultivated soils (Sharpley et al., 1992). Particulate P includes P that is associated with organic matter, sediments or minerals (Elrashidi et al., 2005). Particulate P comes in many forms and can be loosely bound in exchangeable forms, moderately bound to organic matter and detritus or more tightly bound to metals like Ca and Fe (Van der Grift et al., 2018). Water from bare soils, runoff during large storm events or water rich in organic matter and metals are more likely to contain large amounts of PP compared to other conditions due to erosion of soils (Van der Grift et al., 2018). In a typical agricultural system, there is a large amount of interaction and shifting between these forms of P (Jarvie et al., 2002). As all of these forms of P are operationally defined by lab testing, these are simply the most commonly accepted fractions and terms (Li and Brett, 2013).

Within soils, P can be found in organic and inorganic forms. Inorganic fractions of P can be held by a range of mechanisms. The portion of P in any given form differs widely by field depending upon soil type and source of P. Soils high in clay content have a high P sorption capacity because of large surface area to volume ration which allows more greater contact between runoff and soil (Parfitt, 1979; Darch et al., 2015). Organic P is mostly released from decomposing plant and animal matter but needs to be transformed by soil microbes in order to be used by plants (Haygarth and Jarvis, 1997). Inorganic P is associated with Ca, Al and Fe oxides and clay particles with the pH of soils dictating which is most common (Hinsinger, 2001). One of the most difficult aspects of P control in agricultural systems is the fact that geochemical conditions in soils such as pH, chemical composition and redox potential along flow paths can result in changing P forms or even sorption or dissolution (Domagalski and Johnson, 2011).

There are a number of laboratory tests to determine agronomic P levels (i.e. soil P available to crops) or how likely P loss from soils is, which include Bray-P, Olsen-P or Mehlich 3 P (Wang et al., 2015; Zopp et al., 2019). Another classification of soil-based P, water extractable P (WEP),

is P that is most at risk of being lost during a runoff event because it can easily be removed from soil with water (Wang et al., 2015).

2.1.2 Additional phosphorus sources from agricultural systems

The main source of P into agricultural soils are, synthetic fertilizers like MAP or DAP, and animal manure which accounts for about 60% and 25% of P applied to USA fields respectively (Smith, 2000). Phosphorus applied to soils are involved in multiple complex reactions that remove it from the solution and incorporate it into other less soluble or insoluble labile and stable compounds (Smith, 2000). If applied too frequently, P from these sources can build up in the topsoil of fields and bind with clay particles, organic matter or metal oxides all of which are easily erodible (Sims et al., 1998). This build-up of nutrients over longer periods of time results in legacy P and can cause major challenges in terms of reducing concentrations in runoff (Sharpley et al., 2013). Globally, as a result of an increase in agricultural production and fertilizer use in emerging economies, the average soil P levels in surface soils has increased 3 times from 6 to 21 kg/P/ha between 1961-2007 (Schipanski and Bennett, 2012; Withers et al., 2015). Specifically, in Canada, for the period of 1961-2013 the country used 2% of the worlds P fertilizer only behind USA, China, India and Brazil (Lu and Tian, 2017). An increase of P fertilizer usage in Canada by 10-49% was observed when comparing the time periods of 2002-2006 to 2010-2014, much of which was imported (Powers et al., 2019). This trend is coupled with a 4% decrease in the total farmed acres in Canada from 2006-2011 which indicates more P being applied to fewer fields (Canadian Ag Census, 2016). Manure is another source of P to soils which is widely used in Ontario especially on farms with livestock operations. Manure generally has a low N:P ratio, that when applied to crops trying to reach N goals can quickly lead to P build up in soils (Withers et al., 2015). Unlike synthetic fertilizer, manure can vary in nutrient content based on diet and animal source and thus is easier to over apply on one nutrient or another. With synthetic fertilizer it is easier to get a custom blend of all the nutrients a specific field needs to reduce the risk of overfertilization however this depends on consistent soil sampling and good field management. Van der Salm et al., (2017) showed that after 17 years of matching fertilizer P to plant uptake the plant available P in the topsoil declined over the study period, which suggests more is needed in order to keep P levels at recommended marks. Farmers are often reluctant to reduce fertilizer or manure input due to fear of crop yield decline or change soil characteristics. Evidence shows, however, that although P rates in soil do decline in years with lower fertilizer applications, they do not negatively impact yield immediately and regular soil testing can catch any problems before they cause large impacts (Ribey and O'Halloran 2016).

An additional source of P to soils comes from plants. The majority of P stored in plants is in the orthophosphate form, with much of this being water extractable P (Noack et al., 2012). Phosphorus from plant residue especially can easily be leached into soils and is in a form that can be taken up by the next crop on the field (Noack et al., 2012). Early studies in P loss have shown that common agricultural crops such as soybeans and corn contribute large amounts of P from both living tissues and after harvest residues to soil (Sharpley, 1981; Schreiber, 1999). Foyjunnessa et al., (2016) showed that a large portion of P that is released by plant residues comes from the root region. Decomposing plants can provide P to future crops, microbe populations, or remain within the soil in various forms waiting until conditions change (Espinosa et al., 2017). Incorporation of plant residue after harvest increases the amount of P in soil pools and can increase the amount of

P in subsequent crops (Noack et al., 2014). In colder climates, plants left on fields over the non growing season such as winter wheat or cover crops can act as a source of P. Non frost tolerant cover crop species such as oats and red clover released more DRP during simulated winter freeze thaw cycles than the hardier winter wheat (Lozier and Macrae, 2017). A study from Roberson et al., (2007) also demonstrated that cash crops such as alfalfa release increased amounts of dissolved P after under going freeze-thaw cycles. Crops of all kinds release P in both living and residue forms and these can be made worse by freezing conditions. Other smaller source of P to soils do exist such as rainfall, which can contain between 0.01-0.06 mg P/L, a level that is generally negligible in the overall agricultural P budget (Smith, 2000).

One of the most important sources for P removal is its incorporation into plants during their growth. For agriculture, P is an important source of nutrients for plants, especially for young tissues, in which it promotes everything from root growth to flowering. A large amount of P is removed from the soil by crops and once they are harvested the field must be replenished with P for use by the next crop (Domagalski and Johnson, 2011). Estimating P values in plants can be done by using the C:P ratio which generally occurs in 500:1. Agricultural crops typical to the Great Lakes region include corn, soybeans and wheat and these crops remove P from the soil they grow in at various rates. In order to meet these crops needs, the fertilizers described above are often used to provide the nutrients or manure from animal sources. Phosphorus additions to soils from fertilizers are easily sorbed to P-binding sites but there are only so many sites in soils for P to be held (Schipanski and Bennett, 2012). If more P is applied than the crops can take up during a growing season, the excess remains in the soils and is more susceptible to being lost (Schipanski and Bennett, 2012). Plant uptake of P can be impacted by soil condition and tillage practice but it most prominently controlled by the fertilizer application rates. Corn grown in soil with high rates of N fertilizer took up larger amounts of P from the soil because the plants grew larger and needed more nutrients of all types than those receiving lower fertilizer rates (Al-Kaisi and Kwaw-Mensah, 2007). Another study showed that a wheat crop was able to incorporate 6-15% of the P released by a previously planted legume's stubble (Espinosa et al., 2007). Understanding soil test P values and their meaning for crops is especially important for P because unlike other nutrients such as N, plants do not always benefit from additional P applications. In the case of corn, a critical value of P can be mathematically determined for optimum growth and when fertilizer applications go above this value corn no longer benefits in terms of yield and there is a larger risk for losses (Gagnon et al., 2020).

2.2 Runoff generation and phosphorus movement

A considerable pathway of P loss from agricultural systems, in both dissolved and particulate forms, is runoff from agricultural fields (Withers et al., 2015). Erosion and soil runoff are the largest causes of P losses in agricultural systems along with animal waste (Gorarzda et al., 2013). Phosphorus can be moved by water through agricultural systems in two primary ways: surface runoff and subsurface runoff through tile drains. Both occur after rainfall or snowmelt on the surface of a field and thus, hydrology is the most critical factor in determining how P will move through the field (Hygarth and Jarvis, 1999). Surface runoff consists of water leaving the top of the field without infiltrating into the soil and moving into drains or creeks (Ryden et al., 1973), and may occur either as infiltration excess (i.e., when the precipitation rate exceeds the infiltration capacity), or as saturation excess (i.e., when soils are saturated and no additional water can

infiltrate. The addition of tile drains into agriculture allows for water to be more quickly removed from fields by transporting it to ditches, which allows for earlier planting in spring among other agronomic benefits (Smith et al., 2015b). The amount and intensity of rainfall along with soil characteristics and management determines whether tile runoff will occur during an individual period of rain (Sims et al., 1998; Haygarth et al., 1998). Tile drains aim to limit the number of times the field is waterlogged, improve soil aeration and limit the amount of soil compaction which aides in crop production (Dils and Heathwaire, 1999). Land cover, soil P content, topography and agronomic practices are some of the most important factors for determining when and where P loss in surface runoff will occur (Lemunyon and Gilbert, 1993: Weyers et al., 2021). Increasing land cover reduces the amount of P released from surface soil by limiting the amount of soil that comes in direct contact with rainfall and lowering the total amount of surface runoff generated (Elrashidi et al., 2005; Weyers et al., 2021). Specifically, on agricultural fields, increased land cover can be achieved by leaving the residue of the previous crop (corn and bean stalks) or adding cover crops in the NGS (Elrashidi et al., 2005). Practices such as reduced tillage and cover cropping can reduce the amount of surface runoff on a field by promoting more infiltration into soils and tile drains and reducing the impact on rainfall directly on the soil surface (Dodd and Sharpley, 2015; King et al., 2015). King et al., (2015) demonstrated that tile drains can increase the total amount of water lost by 10-25% because more of the annual rainfall turns into subsurface flow relative to the amount stored, evaporated or transported.

The pathway with which water leaves a field has an impact on the type and amount of P contained within it. Often there are higher values of TP and DRP in surface runoff due to recent fertilizer applications that were placed on top or shallowly incorporated into soils (Dils and Heathwaite, 1999). Specifically, surface runoff was shown to contained more PP and higher TP compared to tile runoff which contains higher portions of DRP and less PP (Haygarth et al., 1998; Van Esbroeck et al., 2016). The likely reason for more particulate P in surface runoff is from larger discharge values in surface runoff which can result in more erosion while dissolved P is more often controlled by chemical processes (Sharpley and Smith 1995; Haygarth and Jarvis 1997). Given that soil test P levels tend to be higher in soil layers closer to the surface, the risk of losing this P via surface runoff is greater (Sims et al., 1998). Nutrients reach tile drains via a downward movement of P in the soil by leaching over time through the profile, or by preferential flow through macropores which includes wormholes, cracks and root channels (Sims et al., 1998). However, this vertical movement of P through soils is not as likely to occur if fertilizer and manure are applied appropriate rates and times because the sorption capacity in surface soils is high (Dils and Heathwaite, 1999). Duncan et al. (2017, Pease et al., 2018 and Plach et al., 2019) all found positive relationships between soil test P and P concentrations in tile drain effluent; however, there as substantial variability in the data that was most likely related to field-specific hydrology . Phosphorus movement downward in soil profile is more likely in organics soils with low Fe and Al levels, sandy soils and unsaturated structures soils with high clay content (Dils and Heathwaite, 1999). In some older studies, tile drains have been shown to; reduce the amount of P in runoff from fields (Bengtson et al., 1988) and cause an increase in P in runoff (Calvert 1975) with the difference likely coming down to soil type and management system but generally values were thought to be negligible (Sims et al., 1998). Though in recent years, high concentrations of P in tiles have been both documented and shown to be a result of runoff water bypassing the soil and entering tile drains directly through macropores (Williams et al., 2017; Grant et al., 2019). The concentrations of DRP and TP in tile drains are varied in response to storm melt events, seasons

and on field management (Macrae et al., 2007). Other important factors for P management and water movement in tile drained fields include tile depths, quantity and spacing in between them (Sims et al., 1998). In general, tile drains have low levels of nutrient loss during baseflow levels but can be a source of high P during large discharge periods (Dils and Heathwaite, 1999). Previous work in midwestern Ontario has shown that tile drains can contribute less P than surface runoff but make up more flow than surface runoff does, though this may differ depending on soil type (Lam et al., 2016; Van Esbroeck et al., 2017).

Phosphorus entering groundwater does occur, though is generally not a major concern for agricultural losses, as its concentrations are statistically less than any other portion (Domagalski and Johnson, 2011). When all the P applied to a field is not used by plants, or chemical conditions do not favour P sorption, it has the potential to be transported deeper in the ground and moved into aquifers (Domagalski and Jonhson, 2011). Studies have shown P rich groundwater can contribute to eutrophication in some regions but are an unlikely factor in midwestern Ontario (Meinikmann et al., 2015).

2.2.1 Hotspots and hot moments

Anywhere that water moves in agricultural systems nutrients can move as well. One way to deal with P losses is to identify and provide controls over flow pathways which directly move high P loads into surface waters (Dils and Heathwaite, 1999). Phosphorus losses most often occur from areas where high amounts of surface runoff exist on the same fields with elevated soil P values (Gburek and Sharpley, 1998). This situation would be a hotspot, a specific area of a watershed where P concentrations are always high (Lawrence et al., 2010). Hotspots tend to occur in areas that have been repeatedly over fertilized, or areas that are consistently prone to erosion (Sims et al., 1998). High concentrations of both total and dissolved P in a surface runoff event can be most directly related to recent nutrient applications (fertilizers or manure), the moisture content of the soil before the event, and the intensity of the rainfall during the event (Haygarth and Jarvis, 1997). The occurrence of hotspots are mostly controlled by the amount of electron donors and acceptors, soil redox conditions, hydrology and the specific degradation or transformation of each potential contaminant (Lawrence et al., 2010). Phosphorus saturation in soils is also a potential risk with consistent overapplication of manure or fertilizer making high concentrations of P in surface runoff extremely likely (Sims et al.,1998). Phosphorus losses can be most effectively managed in these areas by focusing on controlling soil P and fertilizer/manure inputs in the zones that are most likely to produce surface runoff, the hotspots (Elrashidi et al., 2005). Bosch et al., (2013) note that the most effective way to reduce loads of P into Lake Erie are to target the use of CPs to high nutrient input areas that would be considered hotspots. As a result of being smaller in area, hotspots can be isolated from hydrological transport pathways. However critical source areas develop when P hot spots have active hydrological connectivity to the stream channel (Sharpley et al., 2011). This critical source area is much more likely to lose P than other hotspots and need to be managed with specific practices like erosion controls (Elrashidi et al., 2005).

Another factor in P movement are hot moments which are times of the year when high concentrations of P in runoff are reported (Andrews et al., 2011). This is generally caused by climate and precipitation patterns in specific areas that cause more runoff during certain seasons. Heavy precipitation or snowmelt events or seasons tend to cause more erosion and runoff rates providing both more nutrients and means to transport those nutrients to waterways (Vidon et al.,

2010). Additionally, hot moments can also occur after fertilizer applications, when soils are under anoxic conditions and when mineral dissolution is releasing P (Vidon et al., 2010). Hot moments can often involve anoxic conditions, mineral dissolution releasing P, and hydrological controls on soil biogeochemistry (Lawrence et al., 2010). The greatest risk for P loss is during storms immediately following fertilizer applications which gives a transport mechanism to the hot moment (Williams et al., 2017). The occurrence of specific hot moments is likely controlled by the soil redox conditions P transported via heavy storms overland flow during hot moments can account for a significant amount of the yearly P losses (Vidon et al., 2010). For surface runoff, hot moments can be started by recent fertilizer applications, the moisture of the soil before an event and the intensity of the rain during that event (Haygarth and Jarvis, 1997). Ontario results demonstrate that hot moments for P transport tend to be the non growing season from October to April for both tiles and surface runoff (Van Esbroeck et al., 2016). The non growing season provides mixed precipitation of snow and rain with the fact that no crops are on the field providing the right opportunity for P losses. In contrast, studies conducted in the Chesapeake Bay region of the USA showed that hot moments for dissolved P occurred during the summer and fall, most often during heavy summer storms (Zhu et al., 2012). Storm events are more likely to cause erosion of ditch banks and soil surfaces,hotspots however, remained similar between the two regions with areas of most concern those with high soil test P levels and (Penn et al., 2007; Zhu et al., 2012). Determining when hot moments occurring and where are hot spots are important to selecting the right CP that could help limit the losses (Zhu et al., 2012; Canga et al., 2016).

2.2.2 Seasonality of phosphorus movement

The transport of P varies depending upon seasonal conditions, especially in midwestern Ontario. The types of P moving are also impacted by season with more dissolved P moving during frozen soil conditions and more particulate bound P moving during non-frozen conditions (Zopp et al., 2019). Previous research has shown that in this region, the majority of P is moved during the non-growing season from November to April (Van Esbroeck et al., 2016). In these months, rainfall and snowmelt are important processes for driving nutrient movement (Su et al., 2011). With milder temperatures in winter occurring more often, many soils remain unfrozen during the non growing season which means there is a higher amount of P and sediment loss (Su et al., 2011). A thicker snow layer over soils provides insulation and prevents it from becoming frozen but a late season snow and mild conditions can leave the soil exposed to cold temperature and lead to freezing (Su et al., 2011). Frozen soils are more often experienced in the Canadian Prairies and Northern States of Minnesota and Wisconsin than in midwestern Ontario (Costa et al., 2019; Zopp et al., 2019). With changing climate previously cold environments with majority snowmelt driven runoff are now experiencing more rain on snow events which can lead to lower DRP losses but higher TP losses compared to either rain of snow only events (Hoffman et al., 2019). The summer months tend to have drier soils and less frequent precipitation meaning less flow and thus less nutrient movement.

Many factors contribute to P loss during cold conditions but the largest sources come from on field practices right before or during the non growing season. This includes any cover crops left on the field over the winter which have the potential to release P, especially non frost tolerant species (Lozier and Macrae, 2017). Even cash crops such as Alfalfa can see increased P loss as a

result of undergoing periods of freezing meaning that more P is released from these plants or residues during the cold non-growing seasons (Roberson et al., 2007). Ogaard (2015) showed that even after multiple freeze thaw cycles, cover crops did not cause a major spike of water extractable P in the spring, being only15-40% depending on the species with oilseed radish releasing the most and rye the least. In the Canadian prairies, Costa et al., (2019) found that during snowmelt events, most nutrients were released from plants during the first 5 hours of contact with surface runoff. Additionally, this work showed that the more freeze thaw cycles a crop experienced the more P that is released, with 5 cycles causing 9 times more P release (Costa et al., 2019). Manure and fertilizer applications directly on frozen soils lead to the most P loss because the P can not adsorb to the soil, timing nutrient applications to warm soils conditions is key for reducing losses in the non growing season (Grant et al., 2019; Stock et al., 2019). The risk of P lost during freezing conditions is 185 times higher for actively growing plants such as fall cover crops than from stubble of a previous crop (Elliot, 2013). Consistently one of the most important factors to determine P loss potential from any soils during cold conditions is the soil test P value and thus any factor than can reduce soil test P will also reduce P loss (Satchithanantham et al., 2019; Zopp et al., 2019).

2.3 Conservation practices for phosphorus management

Work to reduce point sources of P into the Great Lakes in the 1960's, largely from industrial waste and wastewater, were successful at reducing algal blooms but overtime non point source of P to the lakes, mostly from agriculture, became the main driver of the blooms (Great Lakes Commission, 2012). As a result, CPs were implemented more often as a balance between facilitating crop growth and reducing the amount of P in runoff. CPs are land operations with a goal of protecting the health and quality of soil and water and are important mechanisms that reduce movement of nutrients and sediment from non point sources (Lenke et al., 2011; Bosch et al., 2013). CPs are categorized into two varieties, structural changes, and management changes (Rao et al., 2012; Bosch et al., 2013). Structural CPs involve the building of physical features including WASCOBs, berms and edge of field filters, all of which require additional maintenance costs as well as its initial building cost (Rao et al., 2012). A management CP is a strategy that can be introduced by a landowner on a continuous basis either seasonally or daily like a nutrient management plan or conservation tillage practices (Rao et al., 2012). Factors that influence the performance of these CPs are the physical geography of the land they are applied on, the hydrologic process at play and the general climate in the area (Rao et al., 2012). To better organize the large number of CPs Tomer et al., (2013) provides a conservation pyramid approach with four layers that categorizes them by location in the field and role in removing P.

The first layer of P reduction is what can be done within the soil (Tomer et al., 2013). These practices including reduced tillage, crop rotations, and nutrient management that can help build soil health and keep P within the soil for plant use. The first of these strategies is the use of conservation tillage, which includes the practices of strip-till and no-till. The practice of no-till eliminates all forms of tillage and a crop is planted into the ground next to the remnants of the previous year's crop. Strip tillage is a more recent development in which only the piece of land that will be seeded into in the spring is tilled leaving the space between the rows untouched (Lemke et al., 2011). From 2006 to 2011 there was an increase of 23.8% of land seeded in Canada into no-

till soils and for the first time on record in 2011 no-till systems accounted for more than half of all the seeded land in the country (Stats Canada Census of Agriculture 2011). While better for soil structure and organic matter concentrations no-till practices have been shown to increase dissolved P concentrations in surface runoff 1-2 times when compared to rotational till systems but often results in reductions in TP and sediment loss (Gaynor and Findlay 1995; Ulen et al., 2010; Smith et al., 2015; Dagnew et al., 2019). However, other work has shown that no till systems in heavy clay soils increased P in both surface and subsurface runoff as a result of the large macropores that can form direct pathways to tile drains (Findlay, 1995; Sims et al., 1998). Tillage practices also impact P loss with no-till leading to more TP loss during frozen conditions but less TP loss during non frozen conditions as compared to conventional tillage (Zopp et al., 2019). Specifically, a fall tillage can lower the amount of P loss due to winter manure applications compared to no-till soils because of great surface area of soil is exposed after tillage (Stock et al., 2019). No-till conditions have also been shown to trap snow within standing crop residue and thus lead to more runoff from snowmelt later in the season (Schneider et al., 2019).

Another common strategy is the use of fertilizer management, which includes a broad suite of practices. Placing fertilizer in subsurface bands next to seed while planting instead of broadcast spraying them over the fields was shown to reduce the amount of DRP in runoff by 60% in a soil tank study and TP loads by up to 30% on a watershed scale (Grant et al., 2019; Dagnew et al., 2019). A 4R nutrient management plan can also be developed for individual fields which uses soil tests and yields to develop a customized plan to apply the right kind of fertilizer at the right rate, time of year and location in the field. Crop rotation and cover crops are other ways of reducing P concentrations in runoff within soils. A study by Smith et al., (2015) shows that a corn-soy-wheat-oat cover crop rotation was able to reduce both soluble and total P concentrations by over 80% compared to a corn-soy rotation. Two studies conducted a modelled adoption of cover crops by a large portion of farms in a Southern Ontario watershed returned a decrease of 20-30% and 10% of total P losses if multiple fields in a watershed switched to the practice respectively (Dagnew et al., 2019; Hanief and Laursen, 2019). The increased rate of soil cover from any material including crop residue and cover crops results in a decreased volume of runoff which in turns lowers P transport by helping reduce the energy of rainfall hitting a bare soil surface (Elarshidi et al., 2005).

The second layer of CPs are in field structural changes such as grassed waterways and controlled drainage which act to control water movement within fields (Tomer et al., 2013). Buffer strips and grassed waterways provide an opportunity for surface runoff to be filtered by running through vegetated areas before entering waterways. Modelling work by Hanief and Laursen, (2019) showed that the adoption of grassed waterways along the Grand River watershed could result in a decrease of 17% of TP. Smith et al., (2015) found that grassed waterways caused more than twice the soluble P concentrations in runoff while only providing a small decrease in TP concentrations. Grassed waterways and buffer strips tend to reduce only sediment bound P and offer little control of the dissolved portion of P because they allow for gravity to drop out sediments but don't contain the materials needed for chemical sorption of the dissolved P (Sharpley et al 2004). Controlled drainage systems allow for the storage of water within tile drains during the dry summer seasons in order to keep the water table high and limit P losses during this season. A 5-year comparison study showed that controlled tile drainage resulted in a 12% reduction in TP loss compared to a free drainage tile system with the majority of the reductions come from trapped particulate P (Tan and Zhang, 2011). Other research on controlled drainage systems showed no

significant difference in DRP and TP loads but a 25-39% reduction in total tile drain flow (Saadat et al., 2018). Grassed waterways are most often used in fields with lots of topography and controlled drainage is most effective in very flat locations (Tan and Zhang, 2011; Smith et al., 2015). Controlling water within in a field is an important step to slow soil erosion and reduce P in runoff.

The third tier is the control of water below fields which can be accomplished by detention basins and wetlands which can contain and store water (Tomer et al., 2013). Ponds and detention basins allow a place for water to remain while sediments, and P attached to them, settle out. A multi year study on a constructed retention pond system showed that it was able to increase in TP concentration in every year, proving itself to be a sink for P (Uusheimo et al., 2020). However only 4-7% of TP was retained by the pond each year while much larger amounts of suspended solids, 25-40%, were left in the pond (Uusheimo et al., 2020). Wetlands are able to provide more nutrient reduction in agricultural runoff including both N and P. A large surface wetland with a 2-day retention time saw a 59% TP removal rate (Lu et al., 2009). However, a similar study on an agricultural wetland resulted in a 25% P removal rate (Braskerud 2002). The ability of a wetland to remove P is closely tied with the amount of plant growth in the wetland and thus can vary seasonally but usually represent long-term storage of P (Richardson and Craft 1993; Lu et al., 2009). Constructed wetlands built to interrupt surface runoff in an agricultural landscape were able to remove 24-66% of TP, which depended upon the biogeochemical makeup of the runoff and the most dominant form of P (Mendes et al., 2018). The soil redox conditions and the supply of ions that sorb P in the runoff were the key biogeochemical factors in the constructed wetland but depending on conditions and season these structures could turn from a sink for P to a source (Mendes et al., 2018). Keeping agricultural runoff in a wetland or pond for a period of time allows for some P reduction and reduced erosion.

The final tier of field conservation is the management of the riparian area. These practices include buffer strips along drains and P removal structures like filters and bio reactors (Tomer et al., 2013). These CPs are the last line of defense to capture any nutrients the previous categories let pass through before they leave the field. These practices generally occur on the marginal land around the edge of fields, especially those close to waterways. Riparian buffer areas have the ability to remove some P from the runoff through sedimentation as well as plant uptake of dissolved P but most successfully retain particulate bound P (Hoffmann et al., 2009). Edge-of - field buffer strips are best able to remove sediments and nutrients with low, shallow and diffuse flow (Lee et al., 2003; Dabney 2006). Soil type and length of buffer were found to be significant factors in dissolved P removed by edge of field buffer strips with 8-15 m width being most effective while slope was not a major factor (Abu-Zreig et al., 2003; Darch et al., 2015). Edge of field buffer strips, even just 2m in width, can reduce dissolved unreactive P by 60-70% but are less effective on DRP (Darch et al., 2015; Smith et al., 2015). Owens et al., (2007) suggest that vegetated buffers may release more soluble P than they capture as a result of their ability to trap larger sediments leaving any P associated with those sediments susceptible to release. The difficulty with these structures is their ability to receive runoff water from multiple different sources (overland, tile, groundwater) that all have different chemistries and require different strategies to remove P and other pollutants (Hoffmann et al., 2009). Additionally, wetlands rely on plant mass to remove P and also perform the strongest during the spring but in the fall season as vegetation begins to die, they may contribute to P release (Lu et al., 2009). Cold climates cause

additional stress to the buffer area through the release of DRP from freeze-thaw cycles and the reduced vegetation cover in the winter season (Schwer and Clausen, 1989). Total P retention in riparian buffer areas is higher in the growing season and less so during snow-melt periods (Schwer and Clausen, 1989). Updated research from Satchithanantham et al., (2019) found that riparian DRP sorption was not significantly different in summer runoff events compared to snowmelt runoff events in Manitoba but this has not been demonstrated in all regions. The research showed that the DRP removal in riparian zones is more controlled by adsorption processes in areas with the right chemical conditions and soil test P versus biological processes which require growing plants (Satchithanantham et al., 2019

Beyond grass, a woodchip bioreactor installed to filter tile drains was able to remove 28-64% of TP and 35-89% of DRP with increased performance when spiked with spent wastewater treatment filter material (Gottschall et al., 2016). Another woodchip-based bioreactor with an extra bed biofilm filter was able to remove 26% of TP loads and 19% of DRP (Sarazen et al., 2020). A filter box filtering tile drainage water was able to remove 28% of TP but had no effect on the DRP in the runoff (Bauwe et al., 2019). The edge of field filter design used in the Bryant et al., (2012) study resulted in a removal of 22% of the TDP load when accounting for filter bypass over the entire study period. Filters and bioreactors mimic and enhance the P removal the impacts of buffer strips, while often taking up smaller portions of land.

Impact studies of CPs have also been conducted on a watershed basis with the use of agricultural water models. Dagnew et al., (2019) found great P reductions on a subwatershed scale but the model used the assumption that 100% of the farms within the watershed implemented particular CPs, something that would be incredibly difficult to achieve in real life. Other modelling work, using the common SWAT model, shows the need for aggressive implementation of multiple CPs to significantly reduce P loading into Lake Erie (Bosch et al., 2013). To meet targets either every farm must adopt one CP or only half the farms in an area may need to adopt several CPs on the same field (Dagnew et al., 2019). The combination of cover crops, subsurface placement of fertilizer at the correct rates, and filter strips saw a reduction in both TP and DRP by more than 50%, which would meet current targets if adopted by 55% of fields in the watershed (Dagnew et al., 2019). Lemke et al., (2011) conducted a paired watershed study comparing water quality from one watershed with a number of CPs implemented and the other with few; in 7 years of monitoring there were no significant changes to TP, DRP or TSS yield. The most likely cause of not seeing noticeable results is that not enough fields in the subwatershed ended up using CPs and because it takes a long time for results of implementing the practices to be observable (Lemke et al., 2011; Schoumans et al., 2014). The strategy of stacking multiple CPs at a single site may work best because it combines surface and subsurface targeted CPs to get the most benefit in terms of reduction in P loss (Lemke et al., 2011). Overall, the maximum benefits of CPs are achieved with a combination of well tested in-field strategies and edge of field buffers that are maintained overtime (Dabney et al., 2006; Lemke et al., 2011). Exploring the layers of the conservation pyramid it is clear that there is a gap in many commonly used CPs were there are not many that specifically target DRP and runoff that occurs during the non-growing season.

2.4 Phosphorus removal structures

P removal structures are an example of the final tier of the conservation pyramid which is the riparian control of nutrients when used in agricultural systems. These structures are designed to capture and remove the remaining portion of P left in field runoff and work best in conjunction with other on land CPs (Penn et al., 2017). Phosphorus removal structures can be placed in the least productive areas of fields on the edges limiting the amount of land needed. Structures can range in size and material but all have the goal of chemical removing P from runoff before it enters waterways. In addition to treating agricultural runoff, P removal structures have seen success treating wastewater, mine drainage, and other nutrient rich solutions in a variety of landscapes (Penn et al., 2017). Material used inside the structures are classified as phosphorus sorbing material (PSM).

2.4.1 Phosphorus sorption chemistry

The main mechanism for P removal in these structures are the chemical removal or transformation of phosphate molecules. Orthophosphate anions in solution can combine with various cations to form stable and low solubility phosphate mineral phases (Baker et al., 1998). Ca, Fe, Mg and Al all have a strong ability to bind with P and are the main ions used in most P removal structures (Barca et al., 2012). P Removal can occur by physical, chemical sorption, biological or crystallization floatation processes with the PSM dictating which is used (Karageorgiou et al., 2007). In sorption specifically, P removal can occur as ligand exchange (adsorption), precipitation, lattice diffusion and anion exchange (Sparks, 2003). P removal can be nearly instantaneous in most systems because of how quickly the chemical reactions between P and other ions occur, though there is the potential for some additional removal over longer periods of time (Szabo et al., 2008). The P sorption process occurs in two steps; the first is a quick reaction while the second occurs at a much slower rate and often involves surface precipitation (Canga et al., 2016). Szabo et al., (2008) found that most of the P removal in flow through experiments occurred in the first 10-20 minutes of pushing water through the PSM. As a result of the non cyclic nature of P pathways in the environment, P sorption to ions of any kind is considered to be one of the most important P sequestration mechanisms (Richardson and Marshall 1986; Reddy et al., 1995; Hoffmann et al., 2009). All P sorption reactions are heavily dependent upon the pH of the system. Primarily, solution pH dictates which type of phosphate anion will be more present and what types of ions will be most actively binding with them (Penn et al., 2017). Lower pH systems (5-7) tend to favour P sorption by iron and aluminum while higher pH levels (8-10) make P removal through Ca precipitation (Penn et al., 2017). In general, competing modes of P removal tend to decrease the effectiveness of both options and it is best to choose one mode of action when using a PSM.

2.4.1.1 Calcium and phosphorus interactions

Materials that provide Ca ions allow for the removal of P through a precipitation reaction. The main form of Ca-P, formed by the adsorption of phosphates to calcium is hydroxyapatite (HAP) which is the most stable form (Chen et al., 2016). The Ca-P precipitation reaction follows a second order dependence upon the initial concentration of P in the system as shown in (Manimel Wadu et al., (2013). Cao et al., (2007) found that the precipitation of Ca-P's mostly occurred during the

first hour of them being in contact with each other and after that hour mark there was little additional changes in the P concentration of the system. The precipitation reaction requires high pH (above 8) in order to occur as Ca-P solubility greatly decreases with rising pH, however the reaction itself involves the release of H+ ions which cause a decrease in pH (Baker et al., 1998; Cao et al., 2007). Newly formed Ca-P begin as amorphous precipitates and over time and by passing through numerous intermediate stages develop into the final form HAP. In a system either Ca or P could be the limiting agent for the reaction but success has been found at keeping a 1:2 ratio of P to Ca and Ca concentrations near 100 mg/L (Kim et al., 2006; Klimeski et al., 2012; Chen et al., 2016). In agriculture it is very likely that P is the limiting element, especially if fields are managed using any CPs keeping P loads in runoff low. If the Ca concentration or the pH decreases over this time, the dissolution of Ca-P associations can occur because they are unstable and fully reversible until forming HAP (Klimeski et al., 2012; Chen et al., 2016). Exactly which type of Ca-P has formed in a material can be determined by XRD analysis which also shows how strong they are and can aide in determining how likely newly removed P is to be released (Herrmann et al., 2014). In general P removal mechanism involving precipitation like Ca-P generally need more contact time in order to have success in reducing P loads and this must be taken into account when designing systems using this process (Penn et al., 2020). In order to see removal through the Ca-P mechanism, materials rich in easily releasable Ca are needed.

One Ca based PSM is steel slag, which is the remnants of steel processing, composed of mainly Fe and Ca oxides with a mix of other compounds where the amounts of each vary depending on where the slag is produced (Barca et al., 2012). The two main types are Basic Oxygen Furnace (BOF) which is mostly Ca based and Electric Arc Furnace (EAF) which is mostly Fe based, a single steel plant usually only produces one (Barca et al., 2012). The exact makeup of steel slag is an important factor in determining P removal ability so much so that a model developed to estimate P removal ability of a specific steel slag mix could not predict removal ability of another sample from the same steel plant (Penn et al., 2012). A steel slag ditch filter system was able to remove 37% of dissolved P load while a subsurface filter bed was able to remove 55% of dissolved P (Penn et al., 2020). Since steel slag can contain both Ca and Fe oxides P removal occurs both through the Ca-P precipitation and the ligand exchange onto Fe or Al material and which occurs depends heavily on specific conditions such as pH (Barca et al., 2012). Barca et al., (2012) also noted that sometimes there is not always enough Ca molecules in slag to cause enough Ca-P precipitation reactions to occur, in that case excess Ca in the water being treated can make up the difference.

Gypsum is a calcium sulfate compound found in calcium rich rocks such as limestone. The gypsum molecule ($CaSO_4.2H_2O$) is relatively soluble in water and can easily dissolve into calcium, sulfate, and hydrogen ions (Klimchouk, 1996). The compound can be used as a soil amendment applied directly to fields or in geotextile filters placed in areas of high runoff (Favaretto et al., 2012). The calcium in gypsum molecules have a strong ability to combine with orthophosphates and form various Ca-P compounds, which makes it an excellent choice for use in agriculture settings (Grubb et al., 2012; Chen et al., 2016). If in disequilibrium, like in most natural settings, the calcium ions released by the dissolution of gypsum combine with the phosphorus ions dissolved in the runoff to eventually form HAP reducing the amount of dissolved P in the system (He et al., 2018). Some of the most important factors for gypsum dissolution in systems are the grain size, salts in solution and the absence of common ions (Klimchouk, 1996). Land applied

gypsum can have additional benefits such as lower TP values seen in runoff and control P loss from high P fields (King et al., 2016; He et al., 2018). Once adsorbed to the Ca, the P will remain insoluble as long as some part of the gypsum remains present (Bryant et al., 2012) and not be a concern for leaching out back into the environment. Gypsum is best used in high P concentration soils and runoff because of its ability to remove P from soils it can easily decrease plant available P, depriving crops of vital nutrients (Favaretto et al., 2012). Land application of gypsum can cause excess calcium to bind clay particles in the soil more tightly resulting in increased tile runoff on a field scale leading to some loss of productivity which can be mitigated by using it in an edge of field filter (Watts and Dick, 2014). Even at a field high soil test P, King et al., (2016) noticed that gypsum application did not remove all the P in runoff and needs to be implemented alongside other P reducing techniques in order to see the greatest benefit. Phosphorus sorption isotherms done on gypsum were able to show that its maximum P adsorption occurred in a solution of 2400mg/L where the gypsum adsorbed 24.7mg/g of material (Grubb et al., 2012). The calcite molecule ($CaCO_3$) can also provide P removal but unlike Ca-P precipitation reactions, the P-$CaCO_3$ reaction is more of an adsorption process which means it is not as stable (Karageorgiou et al., 2007). Crushed limestone can also provide calcium for P removal and when combined with silica sand to make a filter material removed 88% of available P in solution when left for 10 hours (Baker et al., 1998).

2.4.1.2 Iron, aluminum and phosphorus interactions

The other most used mechanism for P removal is the iron and aluminium process. There are many different ways for these ions to remove P from solution but the most common are through precipitation and ligand exchange reactions (Wang et al., 2021). Iron and Al metal ions have the ability to form metal-P hydroxides which sorb or entrap P and precipitate out of solution (Devlin et al., 2017). In ligand exchange reactions, a phosphate ion replaces a hydroxyl group on an iron oxide compound and becomes incorporated into the structure (Szabo et al., 2008; Liu et al., 2018). The ligand exchange reaction for P removal requires less contact time with water and material than precipitation reactions (Penn et al., 2020). Like Ca, removal of P with Fe or Al is reliant on both P and metal concentrations as well as the pH of the system. Low pH (< 5) is ideal for the removal of P via iron processes (Mendes, 2020). Keeping a low pH is especially important when using the ligand exchange process because of the release of hydroxyl groups which cause the pH to rise which makes P removal more difficult (Liu et al., 2018). P removal efficiency using Fe rich materials is highly dependent upon the ions in solution, specific Fe species, and other factors including pH (Wang et al., 2021). One way to force this iron reaction is through an electrode treatment system where an iron anode releases Fe molecules which are then oxidized and combine with phosphate ions to precipitate out of solution (Tran et al., 2012). The electrode is used with a low voltage direct current to form ions of the metals that would be more reactive with phosphate molecules (Devlin et al., 2017). In field systems, there are a number of different sources or Fe and Al including steel slag, iron rich sand and lab made metal salts. These materials can either be added to P rich runoff or wastewater, placed inside a filter, or used in separate treatment tanks as electrodes for water treatment.

In a tank electrode study, Devlin et al., (2017) found that 70-80% of the soluble P in stream samples could be removed. There was no significant difference between the performance of the Fe or Al except under high flow rates where Al performance decreased significantly, suggesting

both metals are suitable for normal P removal strategies (Devlin et al., 2017). A flow through experiment in peatland columns found that wastewater influent maintained higher P removal compared to DRP lab standard solutions with increased retention when the columns were spiked with high concentrations as a result of the Al and Fe ions in the wastewater (Ronkanen et al., 2016). The study also showed that adding additional Al into peat soils can increase P removal, especially if the peatland experiences anoxic conditions where Fe bound P can be released (Ronkanen et al., 2016). In a constructed wetland system, Fe rich steel slag (27% Fe) was able to remove 70-90% of DRP (Ayaz et al., 2012). The steel slag had much higher P removal values than the other materials like gravel and marble stone tested which contained less than 5% Fe (Ayaz et al., 2012). EAF steel slag that was rich in iron and of various sizes was found to be able to remove 20-60% of P in applications ranging from filter beds to golf course drainage systems and pond filters (Penn et al., 2016). A study using bio-filters of vegetation stacked upon a core of sand to filter waste water. Two types of sand were used, a loamy sand with low iron soil and a Fe rich Skye sand. Though no significant difference in TP load reduction was observed in the one-year study, the researchers hypothesize that the iron rich sand would last longer as a filter material because of its strong ability to adsorb phosphate (Glaister et al., 2014). Another study using iron and aluminum rich sandy loam soil found that it was only able to retain 6% of the P passed through the column (Sanford and Larson, 2015). This was much lower P retention than Ca rich steel slag, which also had a high P sorption capacity than the iron rich sand (Sanford and Larson, 2015). The Fe and Al removal process of P has found success in a number of different settings but has many requirements that would make it difficult to use in uncontrolled environments.

2.4.1.3 Potential interference in phosphorus sorption reactions

When P removal structures are used in uncontrolled environments, a number of different compounds can interfere with the chemical mechanisms for P removal described above. Magnesium, like Ca^{2+}, is a dominant cation found in calcareous soils that can also undergo precipitation reactions with P (Manimel Wadu et al., 2013). Though not a strong cation for P precipitation on its own, when present, Mg^{2+} has the ability to block the Ca-P precipitation reaction and cause the creation of more soluble Ca-Mg-P compounds (Manimel Wadu et al., 2013). Cao et al., (2007) showed the presence of Mg^{2+} significantly inhibited the formation of HAP and caused the formation of more water-soluble amorphous forms of Ca-P know as (ACP). The Mg^{2+} ion interferes in the precipitation reaction be becoming incorporated into the structure of the Ca-P and preventing its formation into HAP (Cao et al., 2007). In general, the higher the amount of Mg present in soils the larger amount of water-soluble P will be present in that soil (Manimel Wadu et al., 2013). After 24 hours of shaking Cao et al., (2007) found that 65% of the calcium and 75% of the P added to the system still remained in solution when magnesium was added with it much higher than the control without the added Mg^{2+}. In laboratory testing, after shaking for 24 hours, about 65% of the Ca and P molecules remained in their solo states when magnesium was added into the mix and precipitation rates decreased by 96% (Cao et al., 2007). Typical Mg^{2+} concentrations in soils amended with manure were enough to interfere with gypsum abilities to reduce P in the soil surface (Cao et al., 2007). The presence of Mg^{2+} is not always detrimental for P removal, a beneficial slow-release fertilizer called struvite ($MgNH_4PO_4$-$6H_2O$) can be produced, but is limited in systems already high in calcium (Ye et al., 2011). Often when MAP is applied to calcareous soils high in exchangeable magnesium the struvite molecule tends to be produced.

Calcium and Mg^{2+} compete for the same binding sites and the two ions make it difficult for each to successfully removal P in uncontrolled environments.

Carbonate ions are another source of concern for the formation of Ca-P compounds. Carbonate can be substituted for phosphate ions in the structure which will reduce the crystallinity of the HAP and reduce the rate of Ca-P precipitation especially in alkaline water (Cao et al., 2007; Barca et al., 2012). Carbonate can also block and compete with Ca for P binding sites in addition to causing the precipitate of $CaCO_3$ limiting any P removal (Cao et al., 2007). Rock that is rich in $CaCO_3$, such as opoka, has been shown to have low P removal abilities compared to other sources of Ca^{2+} because the calcium carbonates do not dissolve as easy (Hylander et al., 2006). Oxidizing the Opoka rock to transform some of the $CaCO_3$ to CaO produced a material called Polonite that was able to remove more than 10 times more P due to CaO being more reactive (Hylander et al., 2006). Other carbon compounds such as carboxylic and phenolic groups from organic matter, of which plenty is present in agricultural systems, can complete with P for the binding sites of metal hydroxides and potentially prevent some P removal (Szabo et al., 2008). Smith et al., (2008) demonstrated that the addition of organic matter reduced the amount of P that can be removed in a system. In a study of multiple materials that were mixed with increasing amounts of peat showed that the higher the OM content the lower the P sorption capacity as a result of OM competing with P for binding sites and releasing already sorbed P (Xu et al., 2006). Further, Penn et al., (2020) saw an underperformance of steel slag filters as a result of high concentrations of bicarbonate in runoff water which caused $CaCO_3$ to precipitate instead of Ca-P. Klimeski et al., (2012) suggest that the presence of humic substances can prevent Ca-P precipitates from forming due to their ability to form other complexes with Ca^{2+} ions. As strong as metal ions like Ca^{2+} and Fe^{2+} can be for P removal, they compete with other compounds for binding sites when trying to remove P in uncontrolled environments.

2.4.2 Testing methods for PSM efficacy

In order to test the effectiveness of P removal structures in the lab setting two experiment methods are commonly used; batch tests, and flow-through tests. The batch tests involve combining a small portion of the material with a lab made solution of known P concentration in a test tube or jar which is then mixed for a period of time ranging from minutes to hours (Szabo et al., 2008; Penn and McGrath, 2011). The simple jar tests allow for preliminary results of the effectiveness of filter materials at removing P and can be adapted into a more formal isotherm to determine maximum sorption capacity (Xu et al., 2006; Penn and McGrath, 2011). Batch experiments are a critical first step to determine the potential a material has to remove P prior to using it (Mendes, 2020). In order to reach equilibrium within the batch test, 6 times more P was needed in the initial concentration compared to the same material in a flow through experiment (Penn and McGrath, 2011). Batch experiments in the lab tend to overestimate the ability of a material to retain P as well as lifetime of effective P removal as a result of the large amounts of P added to them (Jenssen and Krogstad, 2003; Renman and Renman 2010; Herrmann et al., 2014). Batch tests tend to show strong P removal because they are conducted in controlled environments with long contact times, vigorous mixing and a stable pH value (Szabo et al., 2008). The concentrations used in batch tests are often over 10 mg/L of P which is far beyond likely concentrations the material would experience in agricultural runoff.

Flow-through experiments take a select amount of removal material and allow water to be pumped through the material at a consistent rate and samples to be taken from the effluent for testing (Hylander et al., 2006; Canga et al., 2016). This system requires more equipment including a pump, large beakers and filters as well as a large amount of space to house the set up. These types of experiments more often use real world runoff or wastewater samples to test in the set up and allowing for the testing of other parameters such as flow rate, time and grain size (Canga et al., 2016). The results of these experiments are used to inform wastewater treatment plants or others looking for P control on which specific product under which conditions will remove P. A few studies have shown that the use of flow through experiments are preferred over batch tests for P sorbing materials because the set up is more similar to real world conditions (Szabo et al., 2008; Penn and McGrath, 2011). A flow through test conducted in a lab with appropriate concentrations in addition to field testing is the preferred method to determine the correct P removal material and design for a specific situation (Drizo et al., 2008). Penn et al., (2016) were able to develop a model to determine a PSM's ability to remove P which is validated with flow through experiments and in field experiments while not relying on batch tests. As a result of inconsistencies with lab testing, field scale studies should be completed before declaring one type of material suitable for P removal.

2.4.3 Factors impacting PSM performance

The design of P removal structures is extremely important to their functionality and efficiency. Structures can range from industrial sized wastewater treatment tanks to small geotextile filters to filter beds and bioreactors (Hylander et al., 2006; Penn et al., 2017). The type of P, dissolved or particulate bound, to be targeted for removal needs to be determine before designing a structure as that influences the mix of chemical and physical removal processes needed. The goal of these structures is to remove as much P as possible whilst using a minimal amount of material with low cost and a small footprint (Devlin et al., 2017). As shown in Buda et al., (2012), the best P removal structures will be those which score the best on 4 criteria; low cost, high availability, low toxicity to soil and water, and potential for reuse of the material as a fertilizer/soil amendment. Penn et al., (2020) provided more specific guidelines on designing PSM suggesting there must be an effective material in large amount, enough contact time and flow rate through the material, as well as an ability to rejuvenate or replace the material when needed. Other factors for effective P removal structure design take into account such as grain size, P concentration and flow rate.

The grain size of the material used in P removal structures is an important factor for determining how effective such a structure will be for P retention and release. Grain sizes that are larger than 2 mm create heterogeneous material while those less than 2mm form homogenous materials (Canga et al., 2016). Heterogeneous materials cause variations in velocity of water moving through the material and reduce the chance that water will interact with the specific ions in the filter for P removal (Canga et al., 2016). Smaller grain sizes provide larger surface areas for more interaction between phosphate and metal ions. Smaller grain sizes also increase the solubility of compounds needed for P removal, such as gypsum in water, as much as 20% for a decrease of grain size from 2mm to 0.3mm (Klimchouk, 1996). Gypsum that was ground to a smaller size resulted in 3 times more P sorption as a result of its increased surface area by 4 times (Kordlaghari and Rowell, 2006). Lyngsie et al., (2014) also demonstrate that material with a small grain size ranging from 0.05-0.5 mm result in 90% retention of P. Canga et al., (2016) conducted an

experiment using several different materials were grain sizes ranged from 1.6 to 3.3 mm and found that the smaller sized materials removed the most P. Chen et al., (2016) found that using nano gypsum particles results in more P removal because of its greater surface area and increased solubility in the smaller form. In a column experiment a coarse steel slag with a size of 0.25-4 mm removed 3 times as much P as a very coarse slag which had a grain size of 2-7mm (Hylander et al., 2006). These studies show that a small material grain size (less than 3 mm) is the most effect for P removal in all types of PSM.

The initial concentration of P is a critical component of P removal structures efficacy. Solutions containing higher amounts of P have a greater chance of successful removal because there are more P ions available. In general, the higher the concentration of P in a solution the more that can be removed; even small changes in initial concentrations can increase the materials P removal ability (Adam et al., 2005). Greater concentrations of P flowing into a material can further promote the dissolution of chemical compounds, such as gypsum, providing more binding sites for P molecules and facilitating suitable pH conditions (Herrmann et al., 2014). If targeting dissolved forms of P for removal, high concentrations of dissolved P are critical for the metal cation adsorption process to begin. Several studies have shown how products that work well at removing P from high concentration solutions but did not perform well with low concentrations (Penn et al., 2017). The best performing PSM tend to be those that are installed at sites which experience runoff with DRP concentrations larger than 0.2 mg/L (Mendes, 2020). Long periods of time with low levels of DRP in runoff reduces the ability of the material to sorb P because an equilibrium can form between the P sorbed in the filter and the P in the runoff (Penn et al., 2014; Penn et al., 2017). If lower concentrations are expected, the material needs to be designed in a way that increase the likelihood that P will reach a metal ion or settle out in sediment.

The movement of water through a P removal structure is an important factor in determining P removal ability. In some systems, flow rate can be controlled by increasing the pumping speed while other systems simply rely on the flow of water naturally through a filter. In a controlled system, an increase in water velocity through a gypsum-based filter would result in a higher dissolution rate and thus more Ca being released and theoretically, more P being removed (Klimchouk, 1996). However higher flow rates can overwhelm structures which would lead to a decrease in filter retention time and thus the efficiency (Buda et al., 2012). A common finding in research is that P removal efficiency tends to be higher at low flow rates (more than 60% efficiency) but much lower at higher flow rate (less than 25% efficiency) (Buda et al., 2012; Penn et al., 2017). A slower flow rate would result in a longer residence time of water within the filter material and more contact between particles in both the water and material. Laboratory and field studies of P removing material suggest that more retention time leads to larger amounts of P removal (Penn et al., 2017). The hydraulic conductivity of the filter bed used in the Bryant et al., (2012) study limited the ability of the filter to allow the flow through of water during high flow events and thus reduces its effectiveness in storm events. If shorter contact times are used, a possible way of increasing P removal is the use of mixing (Szabo et al., 2008). High intensity mixing allows less P removal material to be added and for it to last long while still reaching removal thresholds though is most plausible in contained treatment tank structures (Szabo et al., 2008). The transport of water through the filter material is the key to removal of P because the interaction between material and phosphate molecules are so important (Canga et al., 2016). Mendes, (2020) suggests that material which experiences event driven runoff and have large

swings in flow rates are less effective than those that experience steady runoff at a consistent pace and can shift from P sinks to P sources over time.

2.4.4 Structural design for PSM

Geotextiles are permeable textiles used in combination with soil, rock, or any geotechnical related material with the goal of letting water pass through and trapping soil and sediments (Rollin and Lombard, 1998; Watson and John, 1999). The textile portion can be a synthetic fabric like polyester or polyethylene or organic material such as cotton or palm (Rollin and Lombard, 1998; Tauro et al., 2018). Textiles can also be woven together in a lattice type pattern or bonded together by heat or other processes leading to a non-woven structure (Koerner and Koerner, 2015). The key features for effectiveness are the percentage cover, ability to hold water, weight when wet, and ability to adhere to surface topography (Tauro et al., 2018). The geotextile can be filled with different materials depending upon what the user is wanting to filter; heavy metals, P and N, or sediments among others. It is very difficult for a filter to stop clay and silt particles because they can become suspended in water with just 0.01 m/s of flow and are often too light for gravity forces to settle (Rollin and Lombard, 1998). This can make removing sediment bound P difficult because it is most often associated with such fine particles. Any particles that make it through the filter will either travel downstream still suspended in the water or will be trapped within the material of the filter (Rollin and Lombard, 1998). Filtration performance depends on factors such as porosity, wettability and permeability being larger than the soil around the filter and these factors can be altered by changing geotextile opening size and material mix inside (Rolling and Lombard, 1998; Koerner and Koerner, 2015). Canga et al., (2016) note that the use of geotextile filters for the removal of P at agricultural sites that tend to be already low in P concentrations remains a challenge because of a limited supply of P. The ultimate goal of a filter is to be operated in an unsupervised manner for a set time before it will need to be replaced or replenished (Herrmann et al., 2014).

Another option is leaving P sorbing material in free standing filter beds or drainage ditches with runoff water being directed to pass through them. These set ups are larger in size and require more material than the geotextile filters. A ditch filter was constructed in the Bryant et al., (2012) study where truckloads of gypsum and sand were placed into a central filter bed that was fed by tile runoff from several fields in the area. Even with high initial concentrations of TDP in the water the filter was only able to remove 22% of the P load accounting for all flow conditions (Bryant et al., 2012). Another ditch system was constructed in Penn et al., (2020) to filter P from tile drainage where runoff leaving the tile drains were then passed through a ditch system filled with tons of steel slag with similar levels of performance. In a system created to filter wastewater, Kholoma et al., (2016) designed a filter bed system where materials could be layered on top of each other in water tight beds where the wastewater is forced to flown down the bed and through the material. Another filter bed type study used sloped wetland beds that were lined with PVC and filled with P removal materials to filter dairy barnyard runoff (Hill et al., 2000). Constructed wetlands are another design frequently used for P removal with some using PSM calcite, limestone while others simply relying use PSM and rely on gravity and biological processes for removal (Penn et al., 2017). Constructed wetlands see a wide range effectiveness from 20-90% DRP and in general have longer residence times compared to filter beds (Penn et al., 2017). There are several different design options for PSM with the main goals of each to provide sufficient material and contact time with water in order for the chemical reactions to occur and remove P.

2.4.5 Potential for failure with PSM

Even when trying to control the above factors to create the most efficient P removal structure, one of the most common results in studies testing these materials were failures and an underperformance of expectations. The majority of the studies on the P removal technologies tend to have been lab based with fewer amounts of in field examples (Buda et al., 2012). Penn et al., (2017) did a review of 40 different filter material set ups and determined there was an average P removal rate of just 33%, which is lower than lab testing showed in many cases. A review by Koerner and Koerner, (2015) discussed the four main categories of geotextile filter failures, these were improper design, use in unusual soil types, trying to filter liquids other than water and incorrect installation of materials. These categories when able to explain a number of issues of P removal structure failure but did not explain all underperformance issues. Klimeski et al., (2012) noted that Ca rich materials have a tendency to retain a lot of P under ideal lab conditions but not in real world conditions where other materials, factors and low P concentrations are present. In addition, P-binding capacities of materials that are calculated from laboratory saturation curves can overestimate performance by the material in the field (Herrmann et al., 2014). Postila et al., (2017) found that both slag and phoslock filters had worked well in lab tests but both were not successful at retaining P in the field. This could be caused by many factors but the most likely causes were a low pH, too large grain size material, and a short retention time (Postila et al., 2017). Johansson Westholm (2006) shows that most of the studies conducted with P removal materials have been done in lab settings with few making it to a field scale study. Every P removal structure requires specific in order to work effectively. A significant problem experienced by a number of filter material studies was the bypass of the filter by runoff water during major P loss events (Pionke et al 2000; Buda et al., 2012; Bryant et al., 2012). Large amounts of water can overwhelm P removal structures designed to slow down water and reduce P removal. The efficiency of a PSM will reduce over time as a result of becoming P saturated and a decrease in sorption sites until it reaches a point where it can no longer sorb P (Mendes, 2020). Penn et al., (2020) details that a steel slag filter needed to be replaced every 4-6 months in order to keep up effective P removal levels, suggesting leaving material longer than that leads to underperformance. The lifetime of any PSM is dependent on the P load of the site, the P sorption capacity of the material and how water flow throughs the system (Mendes, 2020). When placed in outdoor conditions, these structures are no longer in controlled environments and changes in pH and concentrations occur more often making the risk of failure higher.

2.5 Economics of removing phosphorus

The economics of P removal structures and strategies are important to consider when determining overall effectiveness and evaluating their potential use. A large number of the studies testing P removal structures have not taken into account the costs and benefits of such a system or the opportunity costs in comparison to other P management strategies (Buda et al., 2012; Rao et al., 2012). It is critical to understand the economic impacts of P removal structures at the whole farm and watershed scale before implementing a widespread strategy (Buda et al., 2012). The types of costs associated with implementing P removal structure are planning, design and installation   as

well as the costs to maintain them over time. Sharpley et al., (1994) concluded that a main issue causing the difficulty of nonpoint source P management is the creation of P management strategies that benefit the environment, economics and agricultural productivity. One immediate challenge is the improved water quality from landowners adding a P removal structure produces a positive externality and social benefit with no direct payback to the adopter (Rao et al., 2012). More conventional CPs such as cover crops or conservation tillage can be done cheaply and provide weed suppression and reduced erosion among other benefits to help reduce the cost over the long term. To increase CP adoption large government grants, like those given out through the farm bill in the USA, have been shown to be only somewhat effective (Smith et al., 2015). Lemke et al., (2011) noted, the highest rise in CP adoption occurs during the years when the most money was available to landowners but some were unwilling to take on larger projects like wetlands or filter beds even if fully paid for. Providing the right financial incentives as well as expertise over time is key to encouraging uptake of P removal structures. To make P removing structures economical the cost of material must be low, it must have the ability to be reused and be placed at sites with high soil test P (Buda et al., 2012; Penn et al., 2020). Specifically, the ability to rejuvenate a material and reuse it after sorbing P is more cost effective than having to replace the material outright (Penn et al., 2017).

From the work of McDowell and Nash (2012), it is reported that of the P removal strategies studied, edge of field filters were the least cost effective. This is in part because an edge of field P filter provides no benefits to the landowner in terms of soil health, yield increases, or reduced inputs that could help offset the cost of frequent replacement. Even large-scale projects such as the in-ditch filter described in the Bryant et al., (2012) were not economically viable as it required a large amount of costly maintenance and repair work with the authors ultimately suggesting that this type of set up is not practical for use on the farm scale. Another ditch style filter described in Penn et al., (2020) details that it cost roughly 6000 dollars per kg of DRP removed which they described as an unacceptable price. A bottom-up filter system in a separate field was able to remove P for 525 dollars per kg which was also difficult to accepted (Penn et al., 2020). Gachango et al., (2015) reported that a surface flow constructed wetland was able to remove P at a cost of 55-1148 Euros per kg of P.

The most effective filters as described in (Buda et al., 2012) are the ones that have the ability to be reused as a soil amendment or fertilizer afterwards. Hylander et al., (2006) demonstrated that fine grain slag and polonite rich in P after use in filter beds caused barley to add a large amount of dry plant mass when used as a fertilizer. Though not every material can be used as a fertilizer; as shown with gypsum pellets saturated with P, did not increase water extractable P or Mehlich P in soils for crops to access and also did not reduce soluble P in runoff (Grubb et al., 2012). Another site with higher soil P using gypsum as a soil amendment reported a decrease in the P concentration but not a significant change in terms of P loads over the study period (King et al., 2016). When left on the field long enough, some P from the gypsum pellets will be sorbed onto soils but this is most effective in fine textured soils (Grubb et al., 2012). Watts and Dick, (2014) suggest that if the economic benefits outweigh the costs that gypsum can be a very important tool for P management in agricultural systems but suggests applying it as a soil amendment or directly into manure that will be land applied as the best strategies for its use. Struvite is a commercial fertilizer composed of Mg and P that is produced in some wastewater treatment centers, it is put into pellet form ready to be land applied (Ye et al., 2011). Other strategies for lowering costs

include the mixing of removal material with solution, which can result in savings by reducing the amount of material needed and how frequently it needs to be changed (Szabo et al., 2008). The common thread with the removal of P is that it is most easily captured in controlled environments such as wastewater treatment plants or treatment tanks because in agricultural fields very small amounts of P tend to be recovered (Withers et al., 2015).

2.6 Thesis objectives

Many of the P removal strategies are structures presented in this review do not always physically remove P from solutions which limits its potential for reuse and could lead to other environmental problems downstream. The effectiveness of a filter product to reduce hydrologic losses of DRP and TP as well as TSS from surface runoff from two well managed fields in Ontario over a 2-year period was studied. The objectives were to

1) quantify annual and seasonal P losses from surface runoff and tile drainage at the sites

2) quantify the amount of DRP and TP removed from surface runoff by the filter

3) determine if filter efficacy differs with age, flow volume, P concentration or P form (DRP and TP)

4) quantify the amount of P stored in the filter material after it had been in a field setting for 16 months and determine the form the P was retained in

5) compare the sorption potential of DRP in unused filter material with filter material that had been used at two sites

6) characterize ion concentrations (Ca^{2+}, SO_4^{-2}, CO_3^{-}, Mg^{2+}) in runoff samples and filter extracts to infer DRP removal mechanisms in the lab and field

Objectives 1-3 will be explored in Chapter 3 while objectives 4-6 will be discussed in Chapter 4.

CHAPTER 3

How low can you go? Can filters at the edge-of-field reduce phosphorus losses from agricultural fields that already use multiple conservation practices?

3.1 Introduction

Water quality in the Great Lakes region of North America is of great importance but has been on the decline with the rise of algal blooms since the 1990's (Great Lakes Commission, 2012). One of the leading sources of excess nutrients into the lakes is runoff from agricultural fields from both Canada and the United States, particularly into Lake Erie. Conservation practices (CPs) to reduce P losses to surface water bodies can be employed on fields and at the edges of fields, although on-field CPs (avoiding P loss) should be prioritized over treatment systems, which can be overwhelmed (Tomer et al., 2013). A binational agreement has set an ambitious target to reduce P loads entering the western Lake Erie basin by 40% of 2008 loads by the year 2025 (Great Lakes Commission, 2012). To achieve these targets, the use of multiple or 'stacked' CPs (e.g. cover crops, conservation tillage, 4Rs nutrient management) on fields has been suggested to be the most effective way to reduce P losses from individual fields, as using one strategy in isolation is likely not enough to reach reduction targets (Bosch et al., 2013). Even multiple on-field CPs may not be enough to meet the ambitious targets that have been set, as despite the use of multiple CPs on a given field, P losses are still observed (Plach et al., 2019). Thus, the application of CPs such as filters at the edge-of-field in addition to on-field CPs may offer opportunities to further reduce P losses in runoff.

Recent work has shown that edge-of-field P losses from fields in midwestern Ontario that employ multiple CPs are small (~0.5 kg/ha) in comparison to estimated loads from fields that do not employ multiple CPs (1-1.5 kg/ha) (Tan and Zhang, 2011; Williams et al., 2017; Plach et al., 2019). Although both surface runoff and tile drainage are important flowpaths in Ontario, the amount of water and P transported through each pathway varies with soil type and season, but with loam soil surface runoff is a substantial pathway for P loss (Van Esbroeck et al., 2016; Plach et al., 2019). Even research conducted on pasture land, considered as low intensity agriculture, shows that tile drains produced about half the P loads compared to surface runoff (Mittelstet et al., 2011). These results suggest that the largest pool of P to target for reductions is surface runoff, which can be intercepted at the edge of field by a filter.

Previously research in the Great Lakes region has shown that the majority of annual P loss from fields occurs during the non-growing season (Macrae et al., 2007; King et al., 2015; Pease et al., 2018; Plach et al., 2019), typically associated with surface runoff at fields with loam soils and undulating topography (Van Esbroeck et al., 2017). Unfortunately, some of the commonly used CPs such as cover crops and riparian zones are less effective during these periods (Hoffmann et

al., 2009; Darch et al., 2015; Kieta et al., 2018). Furthermore, CPs such as riparian zones tend to be implemented situationally, where farms have creeks passing through them, and can be more complex to apply due to farmer willingness and economic situation (Sharpley et al., 2003). Consequently, there is a gap in CPs that are effective during the critical loss time of the non-growing season that can remove dissolved reactive P (DRP), which is the most bioavailable.

Geotextile filters installed at field edges offer an alternative way to further reduce P concentrations in surface runoff. Such filters typically consist of a woven fabric exterior filled with porous media that can facilitate P removal. Examples of materials can be sand, woodchips, or rock with additional sources of metal ions suitable for removing phosphate including calcium, iron and aluminum (Rollin and Lombard, 1998; Devlin et al., 2017). The larger materials trap particulates, but the inclusion of metal ions facilitates sorption of dissolved P (Zhang et al., 2016). A commercially available brand of filters, Filtrexx®, aims to remove P by both chemical and physical processes, which is ideal for treating runoff at the edge of field. These filters offer an opportunity to further reduce P losses from fields that already employ multiple CPs, because they are less likely to become saturated with P or clogged quickly, and they are expected to function during the non-growing season.

The goal of this study is to determine the efficacy of a commercially available filter in reducing edge-of-field P losses in surface runoff from two working farms in midwestern Ontario, Canada that already employ multiple CPs. The specific objectives of this field-based study are: 1) to quantify annual and seasonal P losses from surface runoff and tile drainage at the two sites, 2) to quantify the amount of DRP and TP removed from surface runoff by the filter; and 3) to determine if filter efficacy differs with age (i.e., time since installation), flow volume, P concentration or P form (DRP and TP).

3.2 Study sites and methods

3.2.1 Study sites

This research was done on two working farms in midwestern Ontario that have been monitored since 2011: ILD (UTM 17T 472,219 mE, 4,767,583 mN) and LON (UTM 17T 466,689 mE, 4,832,203 mN) (Figure 1). These sites have been previously reported on by Van Esbroeck et al. (2016; 2017), Lozier et al. (2018) and Plach et al. (2018; 2019). The study took place over two water years (Oct 1 – Sept 30) from 2016-2018.
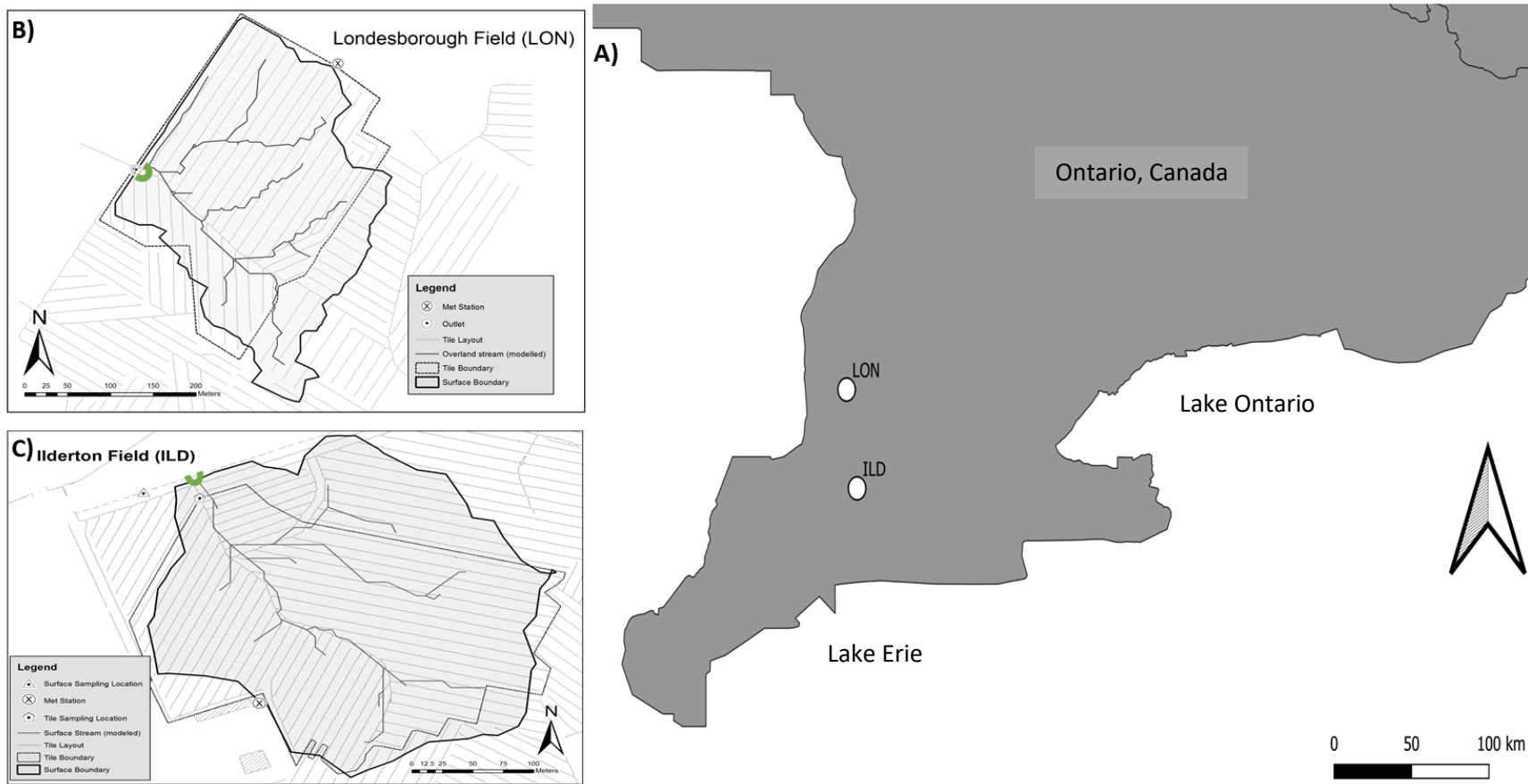
Figure 3.1 A) Locations of the two field sites in midwestern Ontario. The insets show the surface and tile drainage area for the B) LON and C) ILD sites with the location of the filter material shown in green semicircles.

Both sites have humid continental climates with warm summers and cool winters. The ILD site receives 1247 mm precipitation per year (17% as snow) and has a mean annual temperature of 8.2C whereas the LON site receives 1024 mm of precipitation (30% as snow) and has a mean temperature of 7.2C (ECCC, 2019). The 7.8 ha ILD site has hummocky topography with imperfectly drained soils of the Thorndale silt loam and Embro silt loam varieties (Hagerty and Kingston 1992). The 8.1 ha LON site has a gently undulating topography that is also imperfectly drained with Perth clay loam as its dominant soil type (Hoffman et al., 1952). Both fields are systematically tile drained at a depth of 90 cm (Figure 3.1). The fields have both followed a Corn-Soy-Winter Wheat rotation and have both been at the same stage of this rotation since 2011 (Table 3.1). Other CPs used by the farmers include conservation tillage (strip till at ILD and shallow (5cm) vertical till at LON) following wheat harvest with no-till during corn and soy rotations, the use of cover crops after winter wheat (oat at ILD, red clover or oat at LON), and 4R nutrient management strategies for fertilizer applications (Table 3.1). Fertilizer was applied at both sites in August of 2017 after the wheat was harvested and was the only amendment to the soils throughout the study period. Soil sampling was conducted at the sites in August 2017 with samples collected from 5 zones at ILD and 4 zones at LON. Five soil cores were taken in each zone and the depths of 0-2, 2-6 and 6-12 inches were homogenized across these 5 cores. All soil samples were sent to A&L Canada Laboratories Inc. in London, Ontario to be analyzed with with results presented in Table 3.2 as averages of the results of all of the zones. The methods for soil analysis include ENV-G-021 (modified from SM 4500-H+) for pH and AGR-G-001;(modified from western states laboratory proficiency testing program soil and plant analytical methods) for calcium. The sites are comparable in their soil organic matter content, pH, calcium content and soil fertility (Table 3.2). High levels of calcium at both locations and throughout all depths were measured during soil testing conducted during the summer of year 1 as seen in Table 3.2. Additional parameters tested during this period confirmed that the soil test P in the top 15 cm has remained consistent with the levels recorded over time and are ~ 15 +/- 5 mg/kg at LON and ~ 12 +/- 2 mg/kg at ILD.

Table 3.1 General farming practices for each site for the two years of the study.

	Year	ILD	LON
Crop	2016	Soybeans	Soybeans
	2017	Winter Wheat	Winter Wheat
	2018	Corn	Corn
Tillage	2016-2017	None	None

	2017-2018	Strip Tillage (Oct./2017 following P application)	Shallow Vertical Till (Oct. 2017 following P application)
Phosphorus Application Rate and Type	2016-2017	None	None
	2017-2018	Monoammonium phosphate granular 76 kg P ha^{-1} Liquid Dairy Manure 40 kg P ha^{-1}	Monoammonium phosphate granular: 123 kg P ha^{-1}
Application Method	2016-2017	None	None
	2017-2018	Broadcast	Broadcast
Cover Crops	2016-2017	Winter Wheat	Winter Wheat
	2017-2018	Oats	Oats

Table 3.2 Soil properties for the study sites showing means and ± 1 standard deviations for various depths after soil sampling in August 2017.

Parameter	Depth (inches)	ILD	LON
Organic Matter (mg/Kg)	0-2	4.86 ±0.43	4.99 ±0.67
	2-6	4.46 ±0.42	4.65 ±0.61
	6-12	4.04 ±0.42	4.2 ±0.82
pH	0-2	7.37 ±0.26	7.42 ±0.08
	2-6	7.42 ±0.25	7.4 ±0.29
	6-12	7.4 ± 0.23	7.6 ±0.07
Olsen-P	0-2	23.7 ±7.59	30.5 ±5.29

(mg/Kg)	2-6	15.6 ±1.49	15.5 ±2.06
	6-12	12.8 ±6.34	6.5 ±1.12
Total Calcium (mg/Kg)	0-2	3099 ±446	3234 ±362
	2-6	3178 ±295	3335 ±248
	6-12	3276 ±519	4060 ±612

Filtrexx® filters (embedded with NutriLoxx®) were installed at the field edges of both of the sites, where surface runoff exits the field and is monitored. The filters contain a combination of wood chips, clay and gypsum pellets encased in a mesh woven fabric sock measuring 16 inches in diameter. At the LON site, the material was wrapped in a semi-circle around a surface runoff outlet culvert in 3 different layers (Figure 3.2), whereas at ILD the material was placed in concentric circles stacked two layers high around a surface inlet that drained surface runoff from the field (Figure 3.2). Materials were installed in concentric circles to provide multiple opportunities for the filters to retain P in runoff. Roughly 25 feet of the geotextile material was used with a total estimated weight of 100 kg of material at each of the research sites (approximate cost of $400/site).
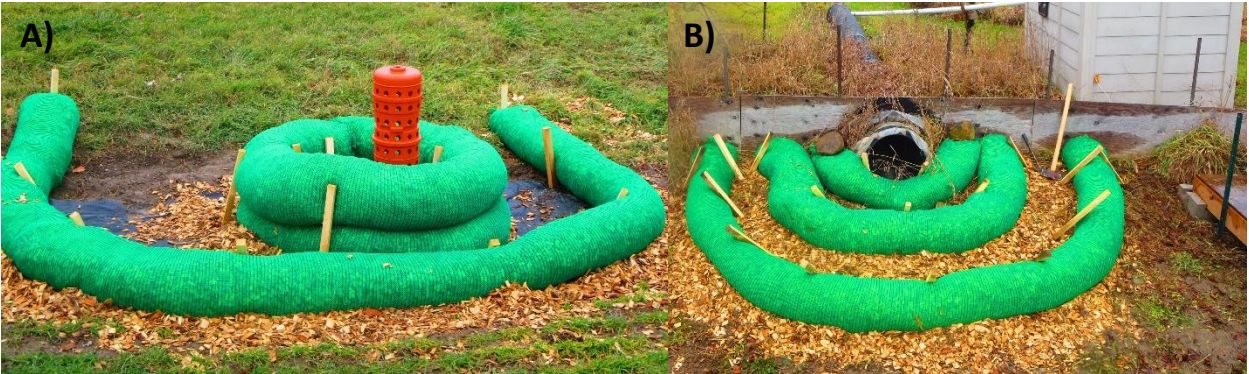
Figure 3.2 Filter material installation at A) ILD and B) LON.

3.2.2 Field and laboratory methods

Each site was equipped with a meteorological station to record rainfall (S-RGB-M002) and air temperature (S-THB-M002) (Onset Ltd.). Snowfall data was taken from Environment Canada Stations located closest to the sites, i.e., Wroxeter for LON and Strathroy for ILD. Snow accumulation was validated with on-site snow surveys before large runoff events using a transect sampling program in addition to measuring Snow Water Equivalent. The outlets for surface runoff

and tile drainage at each field were equipped with flow sensors (Flo-Tote 3, Avensys Canada) as well as water level loggers (U20, Onset Ltd.) for periods in which flow sensors failed. All measurements were taken at 15-minute intervals. Automated (Teledyne ISCO 6700, Avensys Canada) water samplers were placed before and after the filter material to collect high frequency samples throughout the duration of surface runoff events for the study period (Oct 2016 - Sept 30, 2018). The autosamplers were triggered when flow commenced, and collected samples at intervals between 30 min and 3 hours for surface runoff events and at 2 – 8 hours intervals in tile drainage (adjusted seasonally to span the entire event hydrograph, described in Van Esbroeck et al., (2016).

Water samples collected from the sites were retrieved from the field within 24h (summer) and 72h (winter) of collection and the samples were either frozen and stored for later analyses during busy seasons or promptly processed in the laboratory. A lab comparison of samples that were frozen prior to filtration against samples that were filtered prior to freezing did not reveal significant changes to DRP concentrations from these sites (Macrae and Plach, unpublished data). For each sample, a 50 ml aliquot was passed through a cellulose acetate 0.45 **µ**m pore size filter and analyzed for dissolved reactive P (DRP) (ammonium-molybdate ascorbic-acid, Method No. G-175-96 Rev. 13 for DRP., AAIII Bran Luebbe, Seal Analytical, Seattle USA) and major ion concentrations (DIONEX ICS3000) at the University of Waterloo in the Biogeochemistry Lab. A 100 ml unfiltered aliquot was digested using acid persulphate and subsequently analyzed for total P (TP) concentrations using colorimetric analysis at UW (EPA/600/R-93/100, Method 365.1 then Method no. G-188-097, AAIII Bran Luebbe, Seal Analytical). The detection limit for DRP and TP analysis was 1 µg/L and 10 ug/L, respectively. Analytical precision was determined on 10% duplicates and found to be ≤6% of reported values. A subset of unfiltered samples were analyzed for total suspended sediments (TSS), where ~100 ml of sample was passed through a 0.7µm pore size filter (Whatman 42), and the dry mass of material on the filter was obtained gravimetrically (dried at 105 °C for 1hrs).

3.2.3 Calculations of P loads

During the study period, a majority of surface runoff events before and after the filter as well as tile runoff were sampled at both sites (88% of surface events, 95% of total surface flow; 86% of tile events, 95% of tile flow). However, a few events were missed due to equipment failures in the tile and surface. For sampled events, P loading for the captured tile and overland flow events was calculated by multiplying the concentration of a discrete or composite sample, by the average flow rate for the sample interval, multiplied by the length of time the sample represented:

$$\text{Event Load} = \sum_{i=1}^{n} Ci \ Qp \ Ti \qquad\qquad [1]$$

Where Ci is the concentration (mg/L) of a discrete or composite sample. $\bar{Q}p$ is the mean discharge (l/s) for the interval between samples and Ti is the time interval (s) represented by the sample. Following the determination of event loading, the Flow-Weighted Mean Concentrations for events were calculated as:

$$FWMC = Event\ Load/\ \text{Event Discharge} \qquad\qquad [2]$$

For events without samples an estimated FWMC was calculated from a close event in size and season. To calculate the load from uncaptured events the following equation was used.

$$Event\ Load = Estimated\ FWMC * \text{Event } Discharge \qquad\qquad [3]$$

All surface flow was considered to be "event flow". However, for tile drainage, there were periods during which there was small rates of flow, between event peaks (i.e. baseflow). Baseflow conditions were generally considered to be flow at 2.5 L/s or less during periods with no rain. Sample P concentrations during baseflow periods were assumed to be 0.001 kg DRP/ha and 0.01 kg TP/ha, as has been observed consistently at these sites over an 8-year period, and verified by periodic grab samples collected throughout the study period. Total P loads for each season and water year were determined by summing both the event and baseflow. The mass of P retained by the filter was determined by subtracting the load below the filter from the load above the filter. A positive value denotes release by the filter and a negative value represents retention by the filter. The differences in the before FWMCs and after filter FWMCs of each of DRP, TP and TSS for all events were compared using a series of paired T Tests. For ILD the number of surface runoff events samples was 10 while the number at LON were 12 with 5 and 8 respectively for TSS. These were deemed significant at $p < 0.05$ and the results are presented in Table 3.4.

3.3 Results

3.3.1 Meteorological data

Meteorological conditions at the sites generally experienced the seasonal conditions typical for the region, although there were some departures from long-term average climatic conditions (Figure 3.3). At ILD, the 2016-2017 water year (957 mm) was 21% drier than normal while 2017-2018 (686 mm) was 44% drier than the long-term normal (1217 mm). At LON, the 2016-2017 water year (1034 mm) was 25% drier than average, whereas the 2017-2018 (980 mm) was 29% drier than the long-term normal (1372 mm). The driving force for these differences was low rainfall amounts in summer and fall at ILD and in summer at LON (Fig 3.3). The winter of 2016-2017 had higher air temperatures than the 30-year average at both sites and experienced a number of rain events. The air temperature fell closely to the average for the remainder of the study period at both sites. Throughout both 2017 and 2018, there were numerous freeze-thaw cycles and rain-on-snow events, which led to multiple runoff responses.

Meteorological conditions between the two sites were similar over the study period (Figure 3.3), although there were a few differences in temperature and precipitation between the two sites, which were located 80 km apart. Magnitudes of precipitation received by the two sites were most similar in the winter and spring when storms are larger in the region, but differed more in summer

and fall when storms are more localized (convective). Air temperature values were consistent across the sites, especially during melt events in the winter season, with the more southern site (ILD) experiencing slightly warmer temperatures.
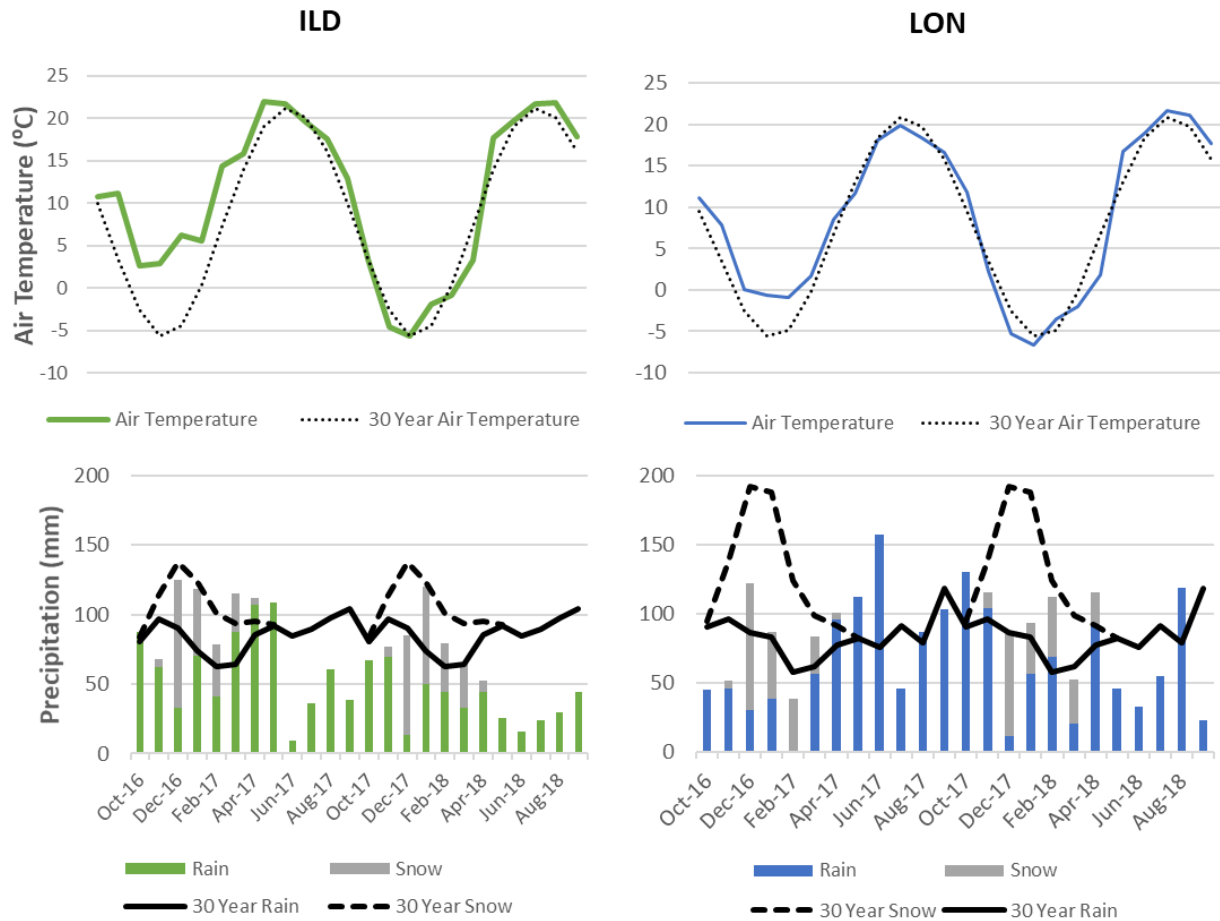
Figure 3.3 Average monthly air temperature (a) and precipitation (b) at the ILD and LON sites. Observed conditions are compared with the 30-year average (1981-2010).

3.3.2 Contribution of flowpaths to runoff and P loss

In order to obtain an annual P load leaving the field, both the tile drains and surface runoff pathways were monitored for flow and sampled throughout the study period (Figures 3.4, 3.5).
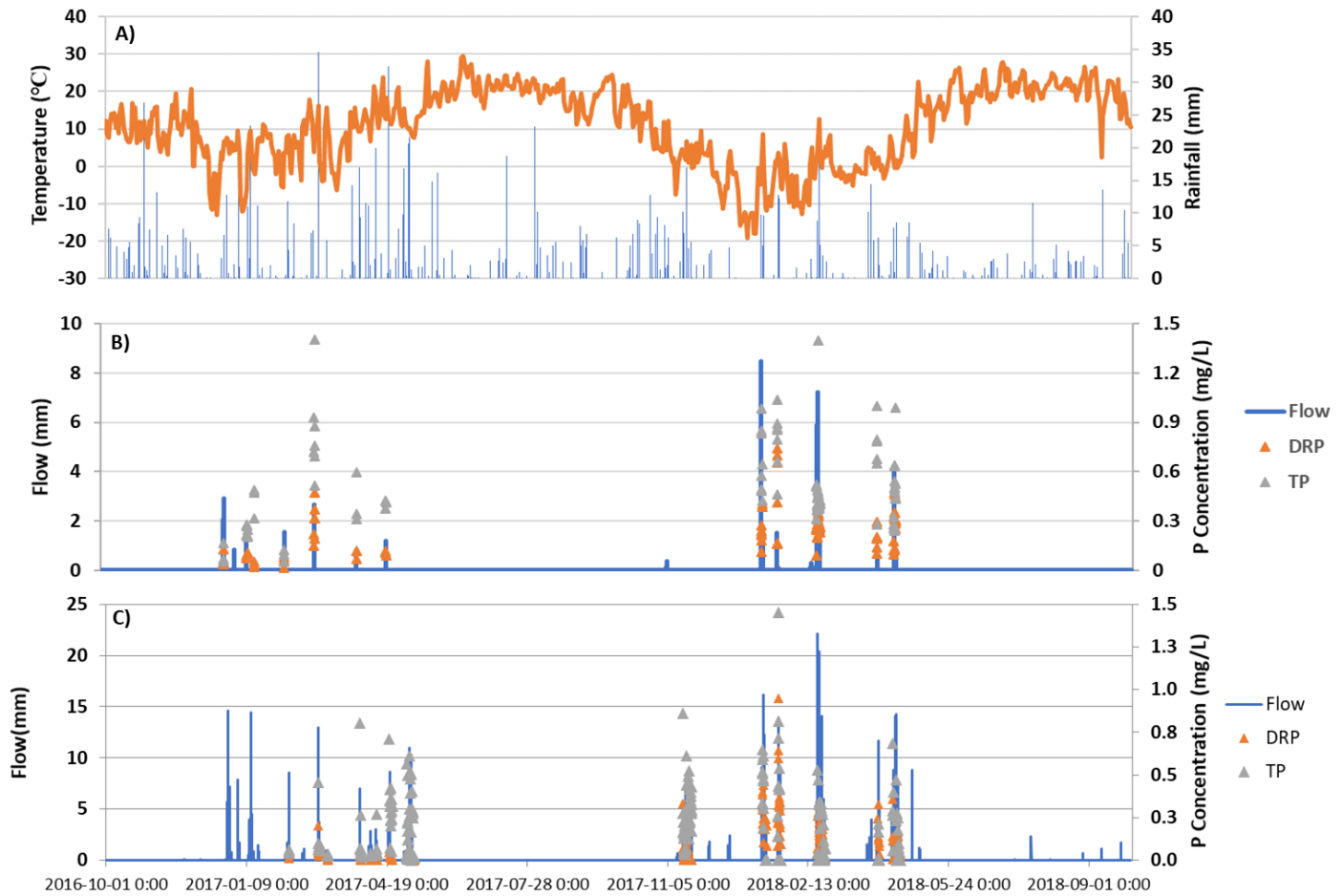
Figure 3.4 The graphs show the daily air temperature and rain A), flow and phosphorus concentrations for the surface runoff B) and tile drains C) for the study period at ILD.
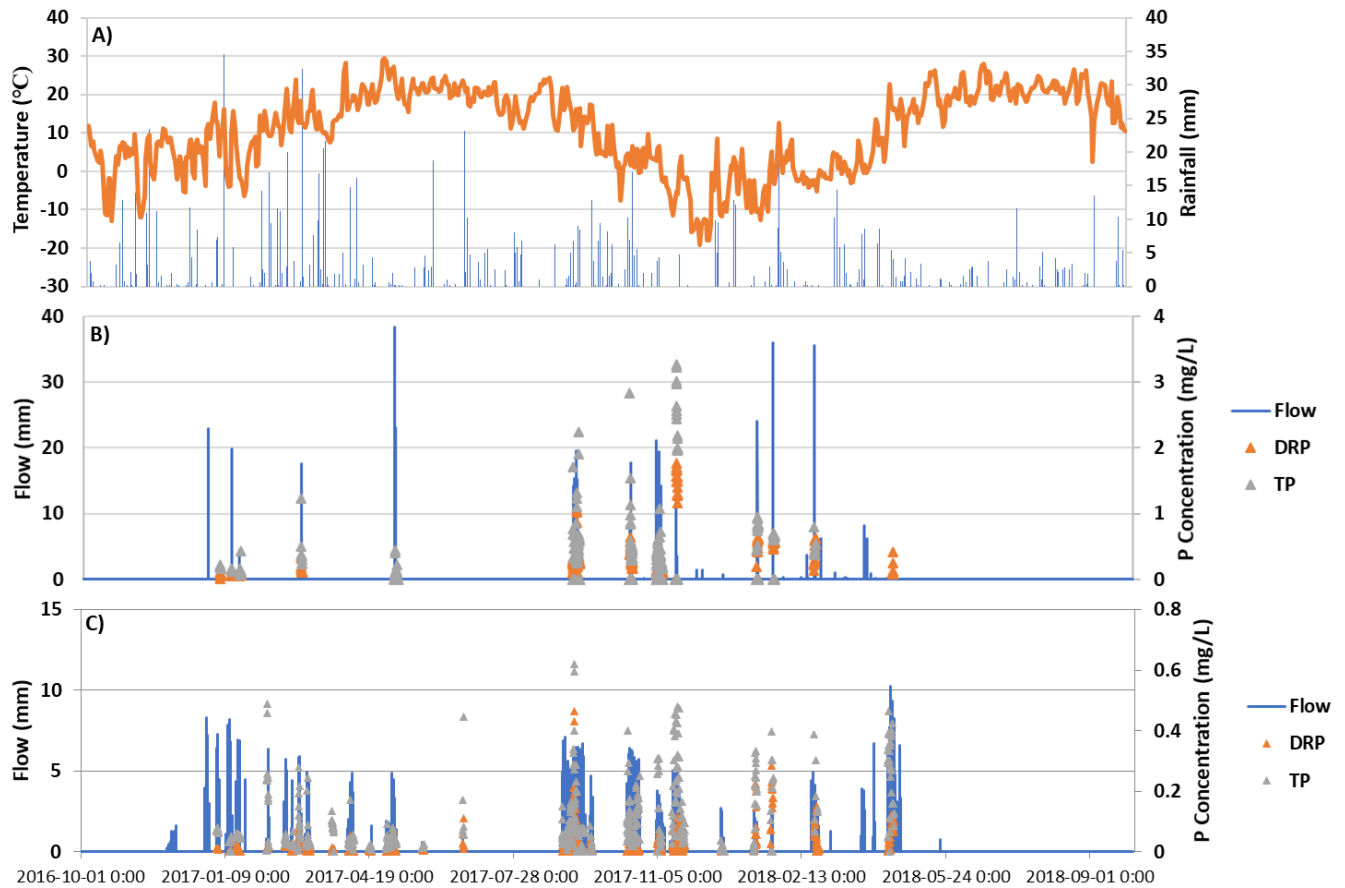
Figure 3.5 The graphs show the daily air temperature and rain A), flow and phosphorus concentrations for the surface runoff B) and tile drains C) for the study period at LON.

As was observed for meteorological conditions over the study period, similarities in distributions of tile flow and surface runoff were also similar between the two sites. Both sites experienced long dry periods during the summer and were very active during the NGS (Figures 3.4, 3.5). Single day rainfall totals of 20-30 mm were the most common causes of runoff events with slightly less rain being required to trigger winter events with snowmelt. Although tile drain responses were observed in the absence of surface runoff, all surface runoff events also experienced tile drainage. Starting in the fall of 2017, tile flow events began to last longer at the LON, coinciding with a plug of roots in the tile. However, once this was repaired in November 2017, the tile responses returned to more normal durations of flow. P concentrations were elevated during events compared to baseflow, and were greater in surface runoff compared to tile drainage at both sites. Most discrete samples fell between 0.1-2 mg/L for TP concentration, and between 0.001 – 1 mg/L for DRP concentration.

Total volumes of runoff from the LON site were similar for the two study years, whereas considerably more runoff occurred from the ILD site in 2017-2018 than in 2016-2017 (Table 3.3).

Notably, the LON site experienced dramatically more surface runoff than the ILD site in both study years (Table 3.3), as is typical for these sites (Plach et al., 2019).

Table 3.3 Discharge and phosphorus loads by year at ILD and LON for surface and tile drains. The percent of total for the yearly budget is provided in brackets. P loads represent losses prior to filter treatment. TP – DRP = dissolved unreactive P (DUP) + particulate P (PP).

	Pathway	Parameter	Year 1 ('16-17)	Year 2 ('17-18)
ILD	**Tile**	Discharge (mm)	243 (97)	609 (94)
		Load DRP (kg/ha)	0.04 (17)	0.51 (35)
		Load PP+DUP (kg/ha)	0.17 (69)	0.74 (52)
	Surface	Discharge (mm)	7 (3)	36 (6)
		Load DRP (kg/ha)	0.01 (5)	0.1 (7)
		Load PP+DUP (kg/ha)	0.02 (9)	0.08 (6)
	Total	Discharge (mm)	250	645
		Load (kg/ha)	0.24	1.43
LON	**Tile**	Discharge (mm)	427 (75)	332 (60)
		Load DRP (kg/ha)	0.09 (12)	0.07 (4)
		Load PP+DUP (kg/ha)	0.22 (30)	0.24 (13)
	Surface	Discharge (mm)	146 (25)	220 (40)
		Load DRP (kg/ha)	0.20 (27)	0.96 (53)
		Load PP+DUP (kg/ha)	0.23 (31)	0.53 (30)
	Total	Discharge (mm)	573	552
		Load (kg/ha)	0.74	1.8

Phosphorus loads from the sites were greater in 2017-2018 than in 2016-2017 (Table 3.3). These data represent P loads exiting the field, prior to treatment by the filter. The greater P loads in 2017-2018 coincide with a larger number of surface runoff events and more runoff in general (Figures 3.4, 3.5), and with a P application at the beginning of the 2017-2018 water year (Table 3.1). Runoff and P loss events occurred primarily during the winter and spring months and rarely occurred during the summer months (Figures 3.4,3.5).

Tile drains represented the predominant hydrologic pathways at both sites (>90% at ILD, 60-75% at LON). This was also true for P loads at the ILD site. However, at the LON site, surface runoff represented the dominant P pathway in both years (25% discharge, 57% of TP loss in 2016-2017; 40% discharge, 82% of TP loss in 2017-2018). The slightly higher proportion of water moving through the surface at LON in year two coincided with a tile blockage occurring in the first month and a half of that study year.

Differences in the form of P between surface runoff and tile discharge were also observed, where the majority of the DRP was lost from surface runoff events. Across both sites and years, DRP accounted for ~50-60% of the TP in surface runoff. In contrast, DRP only represented 20-30% of TP in tile drainage at ILD and 20% of TP at LON (Table 3.3).

3.3.3 Filter performance-events and chemistry

To evaluate the performance of the filter in reducing P losses from the site, concentrations of P were measured both before and after the surface runoff passed through the filter. Any events during which there was equipment malfunction (1 event at each site) were excluded from the comparison but two events where portions of the event bypassed the filter by overtopping it were included. Thus, a total of 10 events from ILD and 12 events from LON were selected for comparison (Table 3.4). These events accounted for 96% of the total surface runoff and 99% of the TP loss at the edge of the field.

Table 3.4 The performance of the filter material at each site for each sampled event before and after the filter as flow-weighted mean nutrient concentrations (FWMC) and yields in g/ha for P and kg/ha for TSS. Differences in yields after the filter compared to before are shown as percentages. A positive difference represents a release of P from the filter, whereas a negative change represents a retention of P inside the filter.

Site	Event	Date	Flow (mm)	FWMC DRP (mg/L) †,‡		Yield DRP (g/ha) †,‡			FWMC TP (mg/L)		Yield TP (g/ha)			FWMC TSS (mg/L) ‡		Yield TSS (kg/ha) ‡		
				Before	After	Before	After	Difference (%)	Before	After	Before	After	Difference (%)	Before	After	Before	After	Difference (%)
	1	Jan 12-13 2017	1.48	0.08	0.01	1.3	0.1	-1.1 (-90)	0.24	0.30	3.6	4.5	0.8 (23)					
	2	Jan 17-18	0.08	0.03	0.00	0.0	0.0	-0.03 (-98)	0.42	0.40	0.4	0.3	-0.02 (-6)					
	3	Feb 28-March 1	2.58	0.30	0.04	7.7	0.9	-6.8 (-88)	0.82	0.27	21.1	6.9	-14.2 (-67)					
	4	March 30-31	1.27	0.10	0.00	1.3	0.0	-1.3 (-99)	0.33	0.27	4.1	0.4	-3.8 (-92)					
	5	April 20-21	1.68	0.08	0.01	1.3	0.2	-1.2 (-88)	0.30	0.19	5.0	3.2	-1.8 (-36)					
	6	Jan 11-12 2018	12.92	0.26	0.26	34.0	34.0	-0.01 (-0.04)	0.63	0.61	82.1	79.4	-2.7 (-3)	29.47	12.57	3.8	1.6	-2.2 (-58)
	7	Jan 22-23	1.54	0.42	0.16	6.6	2.4	-4.1 (-63)	0.71	0.46	10.9	7.1	-3.8 (-35)	63.38	61.06	1.0	0.9	-0.1 (-4)
	8	Feb 19-23	15.17	0.28	0.26	41.8	39.9	-1.9 (-5)	0.38	0.30	58.1	45.2	-12.8 (-22)	51.52	16.05	7.8	2.4	-5.4 (-69)
	9	April3-4	1.12	0.19	0.13	2.1	1.5	-0.6 (-30)	0.70	0.56	7.9	6.3	-1.6 (-20)	162.49	108.23	1.8	1.2	-0.6 (-33)
	10	April 15-17	5.49	0.27	0.26	15.0	14.2	-0.8 (-5)	0.47	0.46	25.7	25.1	-0.6 (-2)	18.30	9.04	1.0	0.5	-0.5 (-51)
	Year 1	Oct '16-Sept '17	7.09			11.6	1.2	-10.3 (-89)			34.2	15.3	-18.9 (-55)					
	Year 2	Oct '17- Sept '18	36.25			99.6	92.1	-7.5 (-8)			184.6	163.1	-21.5 (-12)			15.5	6.7	-8.7 (-57)
ILD	Total	Oct-'16-Sept '18	43.34			111.1	93.3	-17.9 (-16)			218.8	178.4	-40.4 (-18)			15.5	6.7	-8.7 (-57)
	1	Jan 11-12 2017	22.36	0.07	0.07	14.9	14.8	-0.04 (-0.3)	0.13	0.16	27.9	36.4	8.5 (30)					
	2	Jan 17-18	5.94	0.03	0.03	2.0	1.8	-0.3 (-12)	0.07	0.06	4.3	3.3	-1.0 (-24)					
	3	March 1-2	15.92	0.16	0.15	23.4	21.5	-1.9 (-8)	0.47	0.37	67.2	53.7	-13.5 (-20)					
	4	May 5-6	60.67	0.01	0.01	8.8	6.0	-2.8 (-32)	0.13	0.08	78.2	49.2	-29.0 (-37)					
	5	Sept 5-10	41.22	0.36	0.60	148.8	246.5	97.7 (66)	0.60	0.88	246.8	361.3	114.6 (46)	79.05	47.84	32.4	19.6	-12.8 (-40)
	6	Oct 15-17	28.63	0.30	0.34	84.3	96.6	12.3 (15)	0.46	0.48	130.0	136.5	6.5 (5)	13.41	11.14	3.8	3.2	-0.7 (-17)
	7	Nov 2-3	19.94	0.13	0.51	26.5	100.5	74.0 (279)	0.31	0.68	61.4	134.0	72.7 (118)	59.01	46.88	11.7	9.3	-2.4 (-20)
	8	Nov 4-7	39.52	0.16	0.23	61.8	90.8	29.0 (47)	0.35	0.39	139.2	153.2	14.0 (10)	48.51	5.16	19.1	2.0	-17.1 (-89)
	9	Nov 16-19	15.60	1.62	1.70	250.7	264.3	13.6 (5)	2.74	2.79	425.7	432.6	6.9 (2)	56.39	32.81	8.8	5.1	-3.7 (-41)
	10	Jan 11-12 2018	41.11	0.53	0.56	217.2	230.6	13.4 (6)	0.83	0.74	338.8	303.7	-35.1 (-10)	22.41	22.00	9.2	9.0	-0.2 (-2)
	11	Jan 22-23	34.88	0.54	0.55	187.0	190.1	3.1 (2)	0.59	0.60	206.3	207.6	1.2 (1)	7.73	7.36	2.7	2.6	-0.1 (-5)
	12	Feb 19-21	40.73	0.33	0.34	131.8	139.0	7.2 (5)	0.48	0.41	193.8	167.9	-25.9 (-13)	4.91	3.25	2.0	1.3	-0.7 (-33)
	Event 1-4	Jan '17-May '17	104.89			49.1	44.2	-5.0 (-10)			177.6	142.5	-35.1 (-20)					
	Year 1	Oct '16-Sept '17	146.10			197.9	290.7	92.7 (47)			424.3	503.9	79.5 (19)			32.4	19.6	-12.8 (-40)
	Year 2	Oct '17- Sept '18	220.41			959.5	1111.9	152.4 (16)			1495.3	1535.6	40.3 (3)			57.2	32.5	-24.7 (-43)
LON	Total	Oct-'16-Sept '18	366.52			1157.4	1402.6	245.2 (21)			1919.6	2039.5	119.8 (6)			89.6	52.1	-37.5 (-42)

†Significantly different (<0.05) between the FWMC and Yield before and after the filter at ILD

‡ Significantly different (<0.05) between the FWMC and Yield before and after the filter at LON

Some consistent patterns in DRP and TP FWMC and yields before and after the filter were apparent across both sites. The first few events at both sites showed reductions in DRP ranging from 80-100 % at ILD to 8-30% at LON. Although these reductions are large when expressed as a proportion of the P loss per event, it is important to note that the yields during these events were small to begin with (Table 3.4). The efficacy of removal was larger for DRP than for TP during these initial events.

There was a notable change in filter performance at both sites after the filters had been in the field for some time. At both sites, filters were dry in the field for several months (i.e. during the growing season). At both sites, there was a reduction in filter removal efficacy; however, while the filter continued to remove P at the ILD site, increases in P were observed below the filter at the LON site (Table 3.4). This shift in removal efficacy was more apparent for DRP than it was for TP. The decline in removal efficacy occurred after 8 months of dry conditions at the ILD site, whereas the filter began to release P to runoff at the end of Year 1 (event 5) at the LON site (Table 3.4). Patterns observed were similar for DRP and TP at the sites.

The greater P losses from both sites, combined with the weaker performance of the filter in the second year, led to an overall lack of filter performance over the entire study period. After removing nearly all of the P passing through the filter in year 1 at the ILD site, the filter only removed 17% of the total DRP and 22% of the TP that passed through it over the entire study period. After a small positive start in P removal (10% of DRP and 20% of TP), the filter material at LON released DRP and TP for the remainder of the study, leading to an overall net increase (30% DRP and 11% TP) over the study period. Losses of P from the filter during the 5th event at the LON site alone were enough to cancel out any P reduction by the filter during the first four events and lead to a net release in Year 1.

In contrast to P loss, removal of total suspended sediments (TSS) was quite large at both sites. TSS was determined for surface runoff samples collected before and after the filter starting in the fall of 2017 and capturing half of the total runoff events at each site. Consistently, the filter was able to reduce TSS in samples, but the total amount removed varied among events. Over the events measured for TSS, the filter at LON removed roughly 37 kg/ha while the filter at ILD removed about 9 kg/ha (Table 3.4). This was approximately 50% of all the sediment that passed through the filter at each site during the measured events.

3.3.4 Drivers of filter performance

To better understand the performance of the filter and how (why) it may have changed over the study period, the performance of the filters in this study are examined as a function of time since installation, flow volume, and initial P concentration in runoff water.

3.3.4.1 Changes of filter performance with time
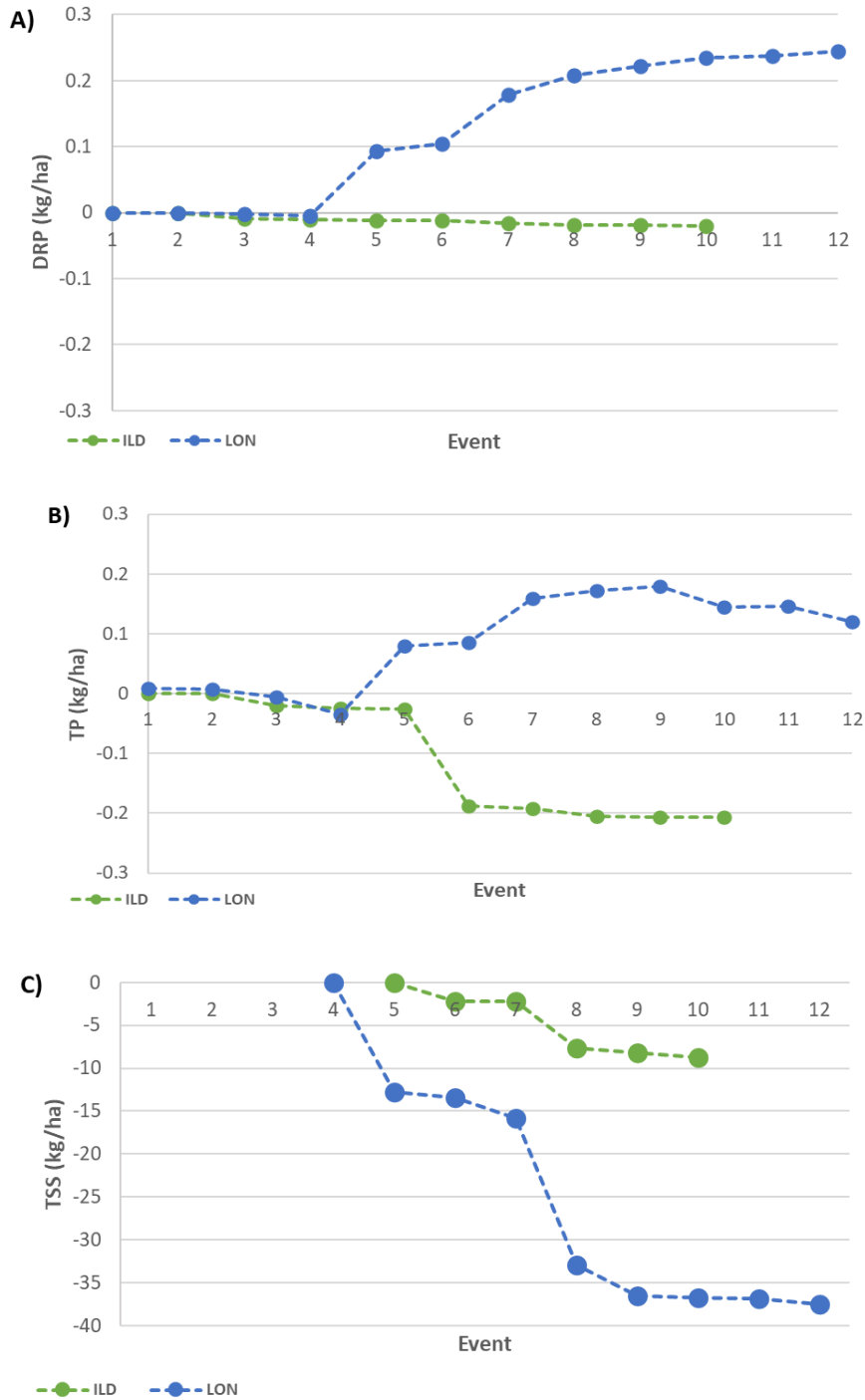
Figure 3.6 Cumulative P and TSS retention by the filter material over all events in the study period for A) DRP B) TP and C) TSS. Negative values indicate there is P/TSS retained by the filter while positive values indicate a release of P/TSS from the filter.

Small amounts of P removal were observed in the first 4 events at both sites (Figure 3.6). At ILD this removal continued for both DRP and TP over all events though the amount of removal decreased in events 6-10. In contrast, the filter at LON appeared to become a source of both TP and DRP after event 4 with only a few later events seeing a small removal of TP again. Figure 3.6 also shows the importance of individual events in overall filter performance. For example, for the ILD site, the TP reduction was so significant for Event 6 that it accounted for the majority of TP retention over the study period. At LON, the P released during event 5 is more than all P removed in previous events for both forms. However, over the course of the study more than double the amount of DRP was released compared to TP while at ILD TP removal was much higher than DRP removal.

For TSS, strong removal was observed at both sites and the filter's performance did not appear to decrease with time. Unlike for P, no single event at either site resulted in an increase in sediment after the filter. Further, after large reductions in TSS, subsequent events did not show TSS releases. Consistent with P, a few particular events (5 and 8) accounted for a large amount of the cumulative removal of TSS.
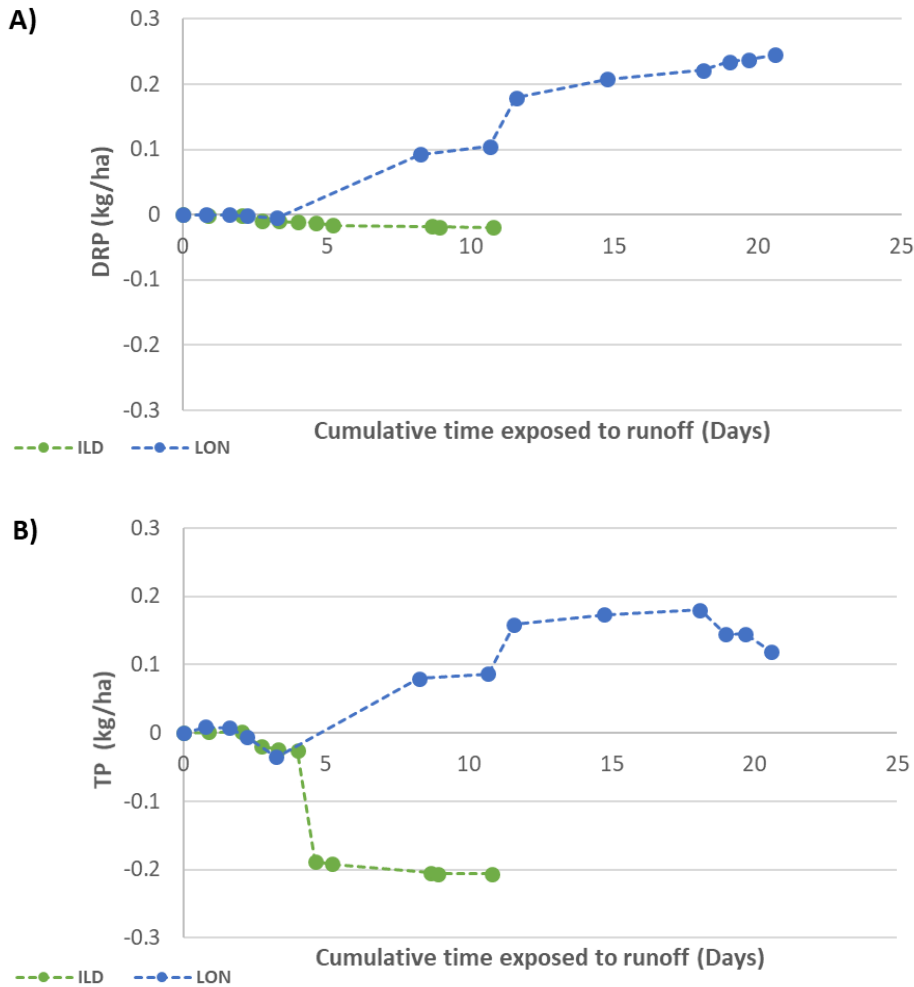
Figure 3.7 Cumulative P retention by the filter material over the cumulative time the filter material is exposed to runoff for A) DRP and B) TP. Negative values indicate there is P retained by the filter while positive values indicate a release of P from the filter.

Given that more runoff occurred at the LON site, the performance of the filters was also evaluated as a function of the amount of time (day) that each filter was exposed to runoff (i.e. allowing for a potential decomposition of the filter material) (Figure 3.7). Over the study period, the filter material at the LON site was in contact with runoff for almost twice the amount of time that the ILD material was. The duration of events is also relevant. At the ILD site, surface runoff during most events lasted less than a single day in length, with the longest event occurring over ~3 days. However, at LON, after initially experiencing small events, the remaining events were very large and all ranged from one to five days in length. Indeed, the decrease in filter performance at the LON site occurred following an event during which the filter material was beneath water for approximately five days. The material at LON decreased in its P removal ability after being exposed to 8 days of runoff whereas the ILD continued to reduce P after being exposed to 10 days of runoff, although not as effectively. These results suggest that the filter material could see

decreased performance as a result of prolonged time exposed to runoff during single events and over the course of its lifetime.

3.3.4.2 Changes of filter performance with flow
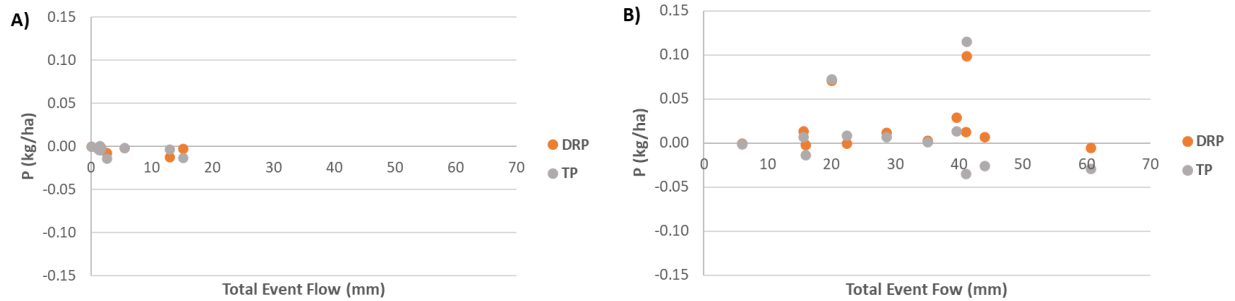
Figure 3.8 P retention by the filter material over the total flow of each event for A) ILD and B) LON. Negative values indicate there is P retained by the filter while positive values indicate a release of P from the filter.

Filter performance may also be impacted by the total volume of runoff passing through the filter during a runoff event (Figure 3.8). All of the events at ILD had less than 20 mm of total and all showed positive P removal. The majority of the events at LON were larger than 20 mm and most of events showed slight P release. The largest event at LON was one of the few able to remove P. However, both small and large events in terms of total flow volume were able to remove both DRP and TP.
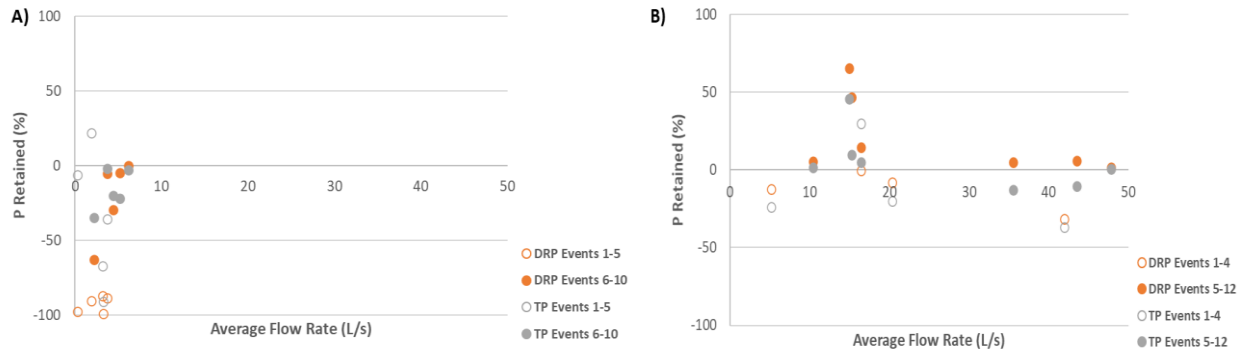
Figure 3.9 Percent of P retained by the filter over the average flow rate during that event for A) ILD and B) LON. Open circles represent events that occurred in the first 8 months of the study and full circle are events beyond 8 months. Negative values indicate there is P retained by the filter while positive values indicate a release of P from the filter.

In addition to total volume of flow during and event, how fast that water is moving could also impact filter performance by limiting the contact time between the runoff and the filter. An examination of individual average flow rates per event is presented in (Figure 3.9). Overall, the average flow rates during events at LON were much larger than those at ILD with all but one event at LON being above 10 L/s. Firstly, DRP removal at the ILD site was greatest under low flow velocities and least under large flow velocities. However, these higher P removal events with low average velocities also occurred in the first few months after filter installation and all of the event's velocities were very similar. In contrast, no difference was observed at the LON site with some smaller and larger average flow rate events seeing removal of P and a mid-flow rate event causing the most release of P.
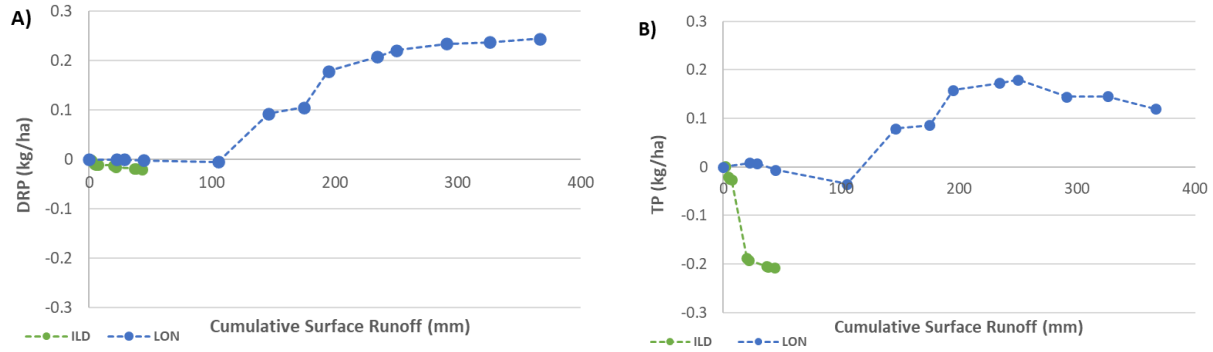
Figure 3.10 Cumulative P retention by the filter material over the cumulative surface runoff for A) DRP and B) TP. Negative values indicate there is P retained by the filter while positive values indicate a release of P from the filter.

Finally, filter performance was examined as a function of the cumulative surface runoff that had passed through it (Figure 3.10). Over the course of the study period, ILD received only 50 mm of surface runoff and saw small amounts DRP and TP removal at nearly every event. However, at LON, there was nearly 400 mm of surface runoff over the 12 sampled events. After small amounts of P removal during the first few events, once the filter passed 100 mm of surface runoff it was no longer able to remove DRP and only occasionally removed small amounts of TP.

3.3.4.3 Changes of filter performance with runoff P concentration
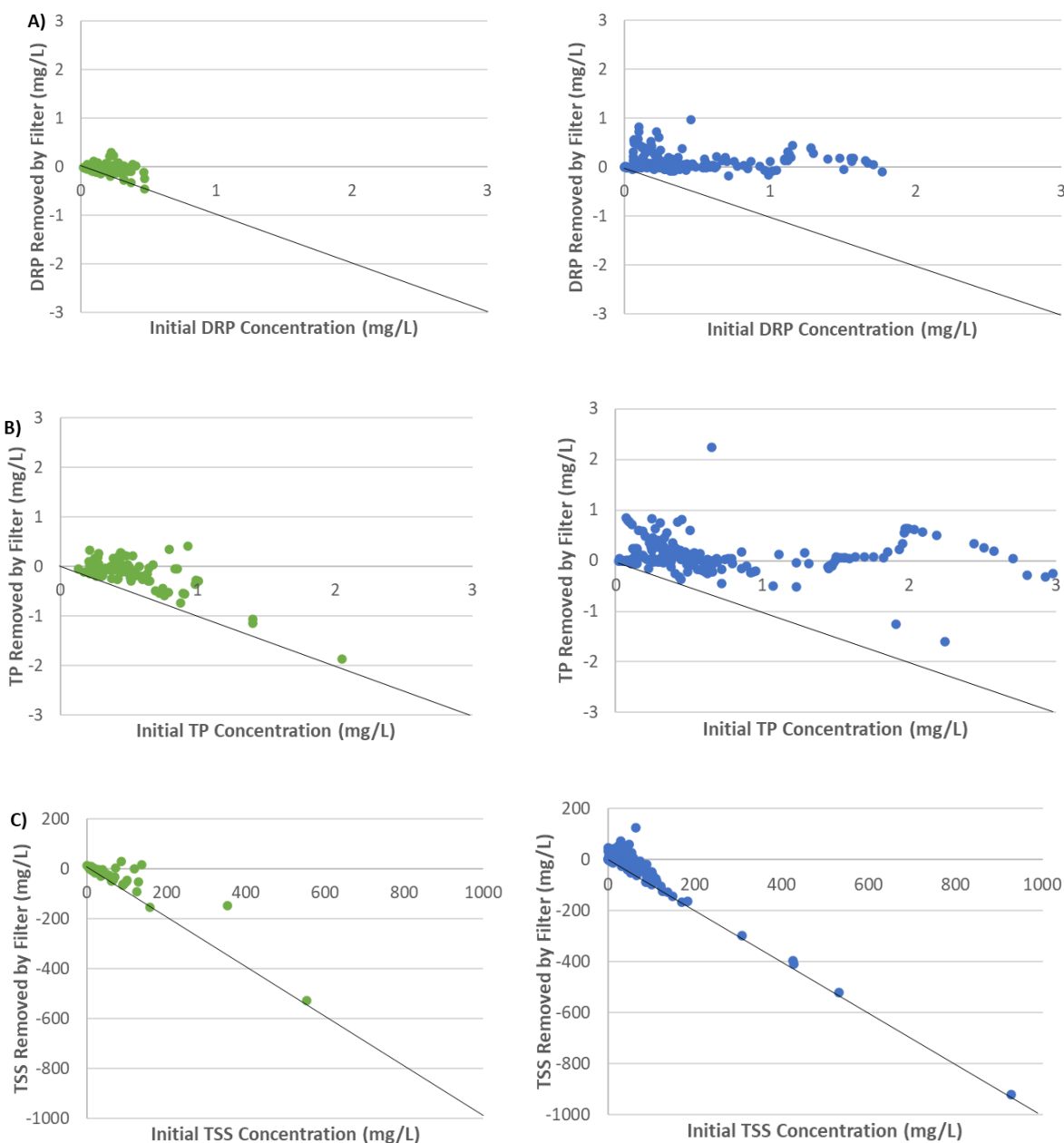
Figure 3.11 Concentrations in water samples for A) DRP B) TP and C) TSS at ILD in green and LON in blue. The graphs show the initial concentration in the sample before the filter against the amount of P/TSS removed by the filter (Before-After) at that same time. A positive value indicates release by the filter whereas a negative value indicates removal by the filter. The solid 1:1 line in each figure shows 100% removal by the filter.

Another possible driver of filter performance is the initial concentrations of P in the water entering the filter (Figure 3.11). At the ILD site, P removal generally increases with runoff P concentrations but nearly all samples fall below 0.5 mg/L of DRP and 1 mg/L of TP. At the LON site, there appears to be no positive relationship between P removal and runoff P concentration. At LON larger concentrations of DRP and TP were more likely to show a release of P than removal. Both sites show samples with P release of DRP and TP but this was much more frequent at LON. No clear threshold of initial concentration needed for effective removal of either TP or DRP is visible. In contrast, TSS removal did often increase with runoff TSS concentration at both sites. Figure 3.11 (c) shows that a number of samples, and the majority of those with high initial concentrations, fall along the line of complete sediment removal. Some lower initial concentration samples did not perform as well, falling short of perfect removal and even releasing sediment on occasion.

3.4 Discussion

The data presented in this chapter have shown that the filter at the edge of the field was able to remove DRP and TP in surface runoff at both sites, and, these reductions occurred during the most hydrologically active NGS when other P-reducing CPs may be less effective. However, the filter seemed to only be effective for a few months of the two-year study. In addition, there was a large difference between the performance of the filter at LON compared to ILD. Multiple factors could have influenced the performance of the filter materials. These results suggest that while filters have the potential to reduce P loss from individual fields, their efficacy differs in space and time and they should therefore be used with caution. Moreover, the filters may have a "lifespan" after which they begin to release previously-retained P.

3.4.1 Filter P removal ability and mechanisms

The filter material showed an ability to remove both TP and DRP from surface runoff. Over the entire study period the material at ILD removed roughly 20% of both DRP and TP while at LON the material resulted in a 21% and 6% increase in DRP and TP respectively. In terms of raw comparisons, this filter product performed on the lower end of other P removal materials. An in-ditch gypsum filter was able to remove about 65% of P entering the system, but when this was adjusted for water that bypassed the filter during storm events, the filter was able to remove 22% of total dissolved P (Bryant et al., 2012). A riparian buffer of 2m was able to retain 32% of TP, this increased to 54% with a 5m buffer (Abu-Zreig et al., 2003). An integrated filter bed and riparian buffer system saw a 40-50% removal of TP and 30-80% for DRP (Zak et al., 2018). There was a 59% TP removal from a construction wetland (Lu et al., 2009) while Braskerud (2002) only saw 21-24% P removal rate in a similar wetland. Boyer et al., (2011) showed materials such as slag and alum sludge have P removal rates of 20-50% for DRP. Slag rich in Ca can reduce P by 99% in filtration systems while slag with lower amounts of Ca only removes 12% (Barca et al., 2012). All of these systems are very different but seem to be producing similar results in terms of

P reductions across various materials and set ups. Importantly, very few of these systems reached a perfect removal of P in any form, most common were removal rates between 20-50%.

The mechanism for removal of the DRP from the filter in this study is likely a chemical interaction with Ca or adsorption onto metal oxides or clays. In the Filtrexx® filter, Ca is released when the gypsum pellets inside the material dissolve after interacting with runoff, similar to that shown in Zhang et al., (2016). Then the Ca is free to combine with the dissolved phosphate movinging in the runoff to form a Ca-P bonded compound (Barca et al., 2012). The Ca-P bond eventually results in a precipitation reaction, which most often occurs in pH ranges above 7 (Penn et al., 2011). The other method for removal is adsorption to Fe/Al oxides or clay particles. This reaction usually occurs through ligand exchange where the oxide or clay is adsorbed with phosphate via an oxygen bridge and is quicker than the precipitation reaction, and with clays especially, occurs most often at mid-range pH's (Penn and Warren, 2009). It is possible that after the first few successful events, the amount of calcium available for removal of P was low because of a decreased amount of gypsum in the filter. In addition, the number of free binding sites on the metal oxides and clay particles could have been filled early on leaving less options for P removal later in the study period. Other Ca based P removal products, such as steel slag, have shown P removal rates at 99% in filtration systems, but this is only achieved with high concentrations of both P and Ca (Barca et al., 2012). In typical field conditions steel slag filters were less successful in P removal reaching only about 30% in ditch filters (Penn et al., 2020) and around 10% removal in a wastewater treatment wetland (Postila et al., 2017). Fe and Al based removal studies in the field showed a 52% removal in a pilot study (Wang et al., 2021) with lab results showing near perfect removal (Jiang et al., 2013). It is critical to have a consistent source of Ca or metal oxide and clay binding sites for strong chemical removal of DRP in a filter system.

The main mechanism for the sediment and other forms of P (i.e., particulate P (PP) and/or dissolved unreactive P (DUP)) removal is likely a physical filtration or increased removal due to gravity as a result of slower runoff. This can occur by the wood chips and woven fabric of the filter preventing larger grained sediments from passing through the filter or causing them to settled inside the filter. Visually over time, it was clear that a large amount of sediment had built up in the filter material and it was observably heavier at the end of the study than when it was first installed, suggesting it was rich in sediment. It was demonstrated that even while the filter was reducing TSS by 50%, there was an increase in DRP at LON, demonstrating how uncoupled the removal of sediments is from the removal of DRP at these sites. In most events, the majority of TP reductions (60-99 %) are the result of decreased PP and DUP while only 1-40% are the result of decreased DRP. This is not true for every event but certainly most across both sites. At LON specifically every event but 1 that saw a release of TP saw a small decrease in PP and DUP, that was overwhelmed by the large amount of DRP being released. Four events at ILD saw the reverse where a small amount of PP and DUP was released from the filter but larger reductions in DRP were enough to keep an overall TP reduction for the event. This again shows the uncoupled nature of DRP reduction from PP and DUP reduction, with the later aligning closer with TSS reductions. Across both sites, 8 of 11 events showed both reductions in TSS and PP/DUP, but were often smaller reductions in P. This type of performance is also seen in riparian buffer systems, especially when narrow in width, where large particles settle out but the levels of TP do not decrease as

dramatically as TSS does (Abu-Zreig et al., 2003; Dabney et al., 2006; Hoffmann et al., 2009). The types of particles P attached to are often smaller in grain size like silts or clay are more difficult to settle out simply due to gravity, and thus more sediments can be removed compared to PP (Parfitt, 1979; Sharpley, 1980). PSM's that experience excess sediment load can lead to a shorten the lifespan of a filter by increasing P saturation or clogging it (Klimeski et al., 2012; Mendes, 2020). In addition, these results are similar to reductions shown from another filter where a lot of sediments were reduced but lower amounts of TP were removed (Choudhury et al., 2016). Szabo et al., (2008) found that with higher amount of TSS in runoff there was less efficient P removal by the material. This filter was able to remove roughly 50% of the TSS that passed through it but this could have led to reduced performance with P removal.

3.4.2 Factors influencing filter performance

Filter performance over time, based on flow rate and initial P concentration were all analyzed as potential contributing factors. The best predictor of filter performance was the time since the filter was installed. The filter did reduce both TP and DRP at both sites for the first 4-5 events which spanned a 5-month period (January-May 2017) after initial installation in October 2016. After this period, neither site was able to reduce P again at the level seen during the first few months and the filter at LON began to release DRP. As a result of the inequality of surface runoff received by the two locations during the study period, some of the impact may be masked by the overwhelming amount of runoff passing through the LON filter. A review of other PSM found that their efficiency decreases over time as a result of saturation of P sorption sites (Mendes, 2020). Other P removal structures, especially those in wastewater treatment plants, have shown the need to be refreshed or replaced after a certain period of time as they have reduced capacity (Szabo et al., 2008). Beyond wastewater treatment, the ability for P sorption has been shown to decrease over time in batch experiments with several materials including limestone and steel slag (Postila et al., 2017). A study by Penn et al., (2020) recommend replacing or rejuvenating steel slag filters every 4-6 months to ensure adequate P removal. This study did not replace the material in order to understand how long it could last. Time is most likely an indicator of filter performance because of the mechanisms for DRP removal being chemical reactions. There is only a finite supply of gypsum inside the filter and because it is water soluble, a large amount may have dissolved during the first few events leaving lower amounts of Ca available for P removal (Klimchouk, 1996). In addition, other studies have shown that if a decrease in the concentration of Ca is observed, there is the potential for more dissolution of already precipitated Ca-P compounds (Diaz et al., 1994; Adam et al., 2007). As time continued to progress the amount of free binding sites on clay particles or metal oxides would also become limited

Flow rate and volume played a role in the filter performance but likely not as significant as time. The extreme decline in P removal at LON occurred during events with high flow rates and large total volumes, more than double any values seen at ILD. This large amount of fast-moving water at LON may have overwhelmed the filter materials capacity to reduce P. Other studies have

shown P removal efficiency tends to be considered high (>60%) at lower flow rates while increasing flow rates decreases the performance down to <25% (McDowell et al., 2007; Penn et al., 2012). In this study, at flow rates less than 5 L/s ILD P removal was greater than 80% while the events at ILD with flow rates of 10 L/s saw reductions less than 30%. Lower flow rates, like those seen at ILD, allow for longer interaction time between the water and the filter material which could lead to more chemical removal reactions (Szabo et al., 2008). If contact time is low between material and runoff this can be offset but mixing the two together in order to increase the chance of those reactions occurring (Szabo et al., 2008). Dabney et al., (2006) showed an increase in P reduction within and edge of field filter that experience slow and diffuse flow. Another in field study showed low P removal ability from steel slag with a likely cause being a short retention time in the filter due to quick flow rates (Postila et al., 2017). Other research show that flow rate is a key factor for gypsum dissolution, which increases as the flow rate increases (Klimchouk, 1996). This suggests, because the Filtrexx® is a gypsum-based filter, more Ca may have been available for P removal at higher flow rates. The cumulative volume of flow could be a driver of filter performance as well. Once the filter at LON passed 100 mm of surface runoff its performance declined while the material at ILD never passed 50 mm of total runoff and saw small reductions in P each event. A threshold volume of 100 mm of runoff may be the maximum amount of runoff the filter is able to treat before it is no longer effective. Wastewater P removal structures show the need to replenish the supply of materials when they are no longer able to remove P after reaching a threshold of water treated (Herrmann et al., 2014). The importance of flow rate and volume were evident in this study, high flow rates and overwhelming volumes would have decreased the ability of the filter to remove P.

Initial P concentration is another contributing factor to the filter's performance. A large amount of work with P removal material in agricultural drainage water is done in the lab setting with P standards ranging from 1-50 mg/L (Johansson Westholm, 2006; Barca et al., 2012). The real-world samples used in this study were often below 1 mg/L and thus may have made it more difficult for the filter to reduce the already low concentrations. Other studies have shown that the efficiency of a P removal material depends on the concentration of soluble P in the water being treated (Szabo et al., 2008; Barca et al., 2012). A large majority of field-based studies used real world samples with similar concentrations to those in this study and the results were in the same range as this study (Abu-Zreig et al., 2003, Boyer at al., 2011, Bryant et al., 2012, Zak et al., 2018). Several studies using PSM set up at field sites that specifically had a large amount legacy P built up in soils in order to ensure runoff had sufficient P concentrations for removal with mixed results (Bryant et al., 2012; Penn et al., 2017; Penn et al., 2020). Runoff with lower amounts of P provide less opportunity for that P to connect with metal ions in a filter product and begin chemical reactions (Zhang et al., 2016). Ideally, for strong P removal, a ratio of 5:3 of gypsum to phosphate is needed (Zhang et al., 2016). In order for good P removal, a sufficient amount of Ca and P need to present in the system and a reduction in either can cause reduced Ca- P formation (Chen et al., 2016). Typical wastewater that hasn't been treated has a P concentration of 12 mg/L, which provides plenty of opportunity for phosphate molecules to meet with metal ions in treatment filters (Herrmann et al., 2014). Additionally, better performance is achieved at much higher P concentrations, as in Ádám et al., (2005) which showed that by increasing initial P concentration from 2 to 15 mg/L a filter product was able to remove 8 times more P from solution. Low initial

concentrations of P in runoff, due to the other CPs on the fields in this study, may have prevented the filter material from performing better by inhibiting chemical reactions between metal ions and P.

3.4.3 Filter performance issues and potential for use

One of the major issues with the filter was the decrease in its performance over time. The P removal was strong in the first couple of events but after a few months the rate of removal slowed at ILD and LON began to release P. To combat the issues of performance over time, other P removal setups have added long residence times, mixing, and high concentrations. Waste water treatment plants and wetland filters can have residence times of hours or even days, which increases the contact between the P and metal ions (Barca et al., 2012). Mixing water with the P removal materials can cause an increase in instantaneous removal of P and reduce the frequency of new material being added into the system (Szabo et al., 2008). In gypsum field-based studies, the rate of gypsum needed for excellent removal of DRP over wider areas is several tones/ha or multiple truckloads in single filter systems (Bryant et al., 2012; He et al., 2018). These studies used dramatically more gypsum than the amount available in the Filtrexx® material. Filters for P in wastewater treatment plants can regularly be changed or adjusted in order to prevent a decrease in P removal (Barca et al., 2012). A release of DRP from CPs installed to reduce losses has been documented in grassed waterways and certain fields under no- till management (Hoffmann et al., 2009; Smith et al., 2015). To get the best performing P removal product need a controlled environment with abundant Ca, appropriate pH range, mixing and others (Szabo et al., 2008; Herrmann et al., 2014). Adding some of these changes to this system would have likely increased the amount of P removed but caused problems in other areas. Longer residence times would have left water on the fields potentially damaging crops and reducing yields. More material and increased mixing would have increased costs and labour required, neither of which is desirable in commercial agriculture. This may be the best we can get in real world conditions on fields already using lots of more conventional CPs.

In addition to a decreased performance over time there were clearly differences in how the materials performed at each site. The LON material never performed as well as ILD material, failing to reduce a high percentage of P during initial events. As both materials began to slow in removal rates, the LON site consistently saw increases in DRP after runoff had passed through the filter while ILD continued to reduce DRP, though at a lower rate. This is possibly due to the large amount of runoff produced at the LON site, 3 times more runoff moved through LON as it did ILD during the study period. After examining the material in Feb 2018 visual degradation of the filter material was observed at LON while the material at ILD remained fresh. It is possible a decomposition process of the woodchips had started and this was the cause of or a contributor to the DRP release in later events (Klimeski et al., 2014). Another possibility is that a change in pH or concentrations of ions and P in the runoff could have caused the dissolution of Ca-P precipitates or release of DRP from being adsorbed to Al or Fe oxides (Klimeski et al., 2012). The LON runoff also had to travel through a pipe where potential sediments from previous events could have been scoured off and this also could have increased P totals after the filter. In addition, a tile blockage

from September- November 2017 increased the volume of water travelling through the surface runoff pathway. This caused runoff events to last longer than normal and resulted in the filter sitting in water for days, instead of the typical few hours. Some surface runoff events were large rain and snowmelt events in January 2018, which led to an overwhelmed filter where runoff was simply flowing over top of the filter not passing through it thus resulting in no P removal. This is consistent with other work where the filter was overtopped by a large storm event that happened to be a major P loss event (Pionke et al., 2000; Koerner and Koerner, 2015). One of the hallmarks of a well-designed P removal structure is that it is able to handle all the flow from potential large events and variable source areas that expand under large storm events (Rao et al., 2012; Koerner and Koerner, 2015). Clearly more layers of the filter material needed to be stacked higher at LON in order to prevent the overtopping. Other possible contributors to poor performance may be the presence of other ions such as Mg which can inhibit the Ca-P reaction (Cao et al., 2007; Manimel Wadu et al., 2013). If the LON site had higher concentrations of Mg in its runoff water, it may explain some of the performance issues with the filter. Further investigation of the material inside the filter may lead to more concrete answers about the difference in performance of the two sites.

3.5 Conclusion

As with other research into agricultural CPs, the Filtrexx® filter used in this study seems to be best used as a site-specific product and may not be applicable in all conditions. The filter showed an ability to remove DRP and TP and greatly reduce TSS concentrations in surface runoff. After two seasons of use the filter was able to remove 0.02 kg/ha DRP, 0.04 kg/ha TP and 8.75 kg/ ha TSS at ILD representing 16, 18 and 57 % of total values respectively. At LON, after initial periods of reductions, samples after the filter saw an increase of 0.25 kg/ha of DRP, 0.12 kg/ha of TP but removed 37 kg/ha of TSS representing an increase of 21, 6 % and a decrease of 42%, respectfully. Results on an event-by-event basis show that the filter has an ability to remove DRP as well as PP+DUP and the removal of TSS is uncoupled from the removal of either form of P. Investigating a number of potential factors that could have influenced performance including time, season, flow, and P concentration left time as the most likely dominant force. The removal ability of the filter was strongest during the first few months of use and then began to perform poorly and caused P release at LON after 8 months of use. The filter material performed the strongest at the ILD site while decreasing over time, while at LON the material never resulted in major reductions of P after the first 4 events. The strong reductions in TSS suggest the physical filtration process of the filter worked well but this did not always translate into lower TP values and the chemical removal of DRP, though strong in some events, was not consistent. The P removal ability and inconsistent results of this filter are similar to other P removal products tested in field settings. This is a product that can target P leaving fields in surface runoff during the critical NGS and reduce dissolved forms of P, but not under all conditions nor over a long period of time. In order to be effective, the filter would need to be frequently replaced to reduce failures and samples would need to be taken to ensure the filter was still functioning which would make it prohibitively expensive for a typical farm operation. Further investigation into the filter material itself and other water chemistry parameters may help explain the performance issues and reveal more about the removal process and where the P goes when it is removed are needed. Though not enough reductions were

experienced to be a silver bullet solution to edge of field P losses, this product may be able to be used in combination with other strategies in controlled settings.

Chapter 4

Evaluating phosphorus storage and removal mechanisms in a commercially available filter in an agricultural setting

4.1 Introduction

Phosphorus (P) has been demonstrated to be a key factor in the development algal blooms in water bodies across the world. The primary source of P to the Great Lakes region of North America is runoff from agricultural fields (Great Lakes Commission, 2012). Although surface runoff and tile drains are both contributors of P to water bodies, recent research suggests that surface runoff is a larger source in undulating landscapes across Ontario, Canada (Van Esbroeck et al., 2016; Plach et al., 2019; Macrae et al., 2021). Although attempts have been made to reduce P losses at the edge of the field through conservation tillage and agronomic practices, such measures have not yet resulted in significant decreases in P loads from tributaries into Lake Erie (Maccoux et al., 2016; Stammler et al., 2017). In order to reach binational reduction targets for P entering Lake Erie, a push for technologies and Conservation Practices (CPs) that can reduce or remove P from runoff has been put in place. Examples of such measures may be vegetation buffer strips, bioreactors or filters containing phosphorus sorbing materials (PSM). Such treatment systems can build onto agronomic CPs on fields to improve overall P losses from fields.

In field applications of PSM for agricultural runoff include the use of filter socks, beds, and cartridges (Penn et al., 2017). The benefits of PSM in the field are that it can take up a relatively small footprint in agricultural fields and is useful in settings with very high soil test P (Penn et al., 2017). Phosphorus sorbing materials include a number of different products such as gypsum ($CaSO_4 . 2H_2O$), iron rich sand, steel slag and limestone (Buda et al., 2012). The metal rich materials provide ions that combine with phosphate to remove dissolved reactive P (DRP) from solution (Klimchouk, 1996). Calcium can precipitate with phosphate as hydroxyapatite, while Fe and Al combine with phosphate in a ligand exchange reaction (Penn et al., 2017). In laboratory studies, these materials are generally able to remove large amounts of DRP in both flow through and batch tests (Herrmann et al., 2014). However, when these materials are tested in the field, they are often not able to perform to the high removal levels seen in lab experiments (Klimeski et al., 2012; Penn et al., 2017). Differences between lab and field results can likely be explained by a number of factors including pH, residence time, flow rate and P concentrations (Szabo et al., 2008; Klimeski et al., 2012). The poor P removal performance in a field setting has limited the installation and implementation of such materials on a larger scale, especially in agricultural settings.

Many field studies of PSM performance have largely focussed on their overall performance, and less attention has been given to the mechanisms controlling P retention. In the laboratory, sorption isotherms are commonly used to determine the ability of PSM to sorb P, whereas analyses of P fractionation are much less common (Xu et al., 2006). Most previous studies have analyzed the P stored in materials using X-Ray Diffraction (XRD) to determine the crystalline structure of various P precipitates. However, such analyses require specialized equipment

(Bowden et al., 2009) that may be cost-prohibitive and therefore not possible to analyze on a large number of samples collected over a longer time period over a range of hydrological conditions. Phosphorus sorption capacity (Graetz and Nair, 2009) and P fractionation experiments (Zhang and Kovar, 2009) provide important information regarding the nature of P availability and retention in agricultural soils. Such methods can also be employed with filter materials, such that these tests, in conjunction with water chemistry, can be used to infer the predominant mechanisms driving P retention in the PSM, and if and how these may vary in space and time.

Numerous studies have used and tested PSM in lab settings, but few have combined lab experiments with field-based performance, especially in Canada. In this study, a commercially available filter product containing both gypsum and clay particles was placed on two agricultural fields in an effort to remove P from surface runoff. Each site experienced 10-12 runoff events over a two-year period with water samples collected during all events. Chapter 3 of this thesis demonstrated that although the filters were able to retain DRP, total P (TP) and total suspended sediments (TSS), these results varied temporally. The PSM was employed because dissolved reactive P is difficult to remove from runoff using current CPs. However, the PSM removed very little DRP from the runoff. Indeed, the majority of P removed by the filter in the field appeared to be TP which could have occurred through a physical removal mechanism. This chapter builds on Chapter 3, by exploring possible mechanisms driving the variable filter performance. This is done by analyzing the filter material itself for DRP concentration and removal efficacy (both new material and material left in the field), and by analyzing water samples from both lab and field studies for water chemistry parameters (i.e., selected ions) to infer retention mechanisms. The objectives of this study are: (1) quantify the amount of P stored in filter material after it had been in a field setting for 16 months, and determine the form that the P was retained in (specifically looking at metal oxide adsorption and Ca-P precipitation reactions); (2) compare the sorption potential of DRP in unused filter material with filter material that had been used at two sites over a 16-month period (3) characterize ion concentrations (Ca, SO_4, CO_3, Mg) in runoff samples and filter extracts to infer DRP removal mechanisms in the lab and field.

4.2 Methods

The commercially available filter material (Filtrexx®) used in this study was composed of large woodchips, small gypsum pellets and even smaller clay particles mixed together as shown in panel A of Figure 4.1. This material was all contained within a mesh fabric sock of about 16 inches wide. In the fall of 2016, material from the filters at ILD and LON was taken from the filter sock and stored before they had experienced any runoff events and labelled as "unused". One pallet of material was about 200kg and at installation was equally split between the two sites. It was placed in semi circles around surface runoff exit points from the fields and further described in Chapter 3. In February 2018, after a year and a half of use, roughly 500 grams of material from the filters at both sites was collected and brought back to the lab. This material was taken from the center of the innermost layer of the filter at each site to ensure it had interacted with all runoff over the filter's lifetime and labelled as "used". Figure 4.1 shows the used material from ILD (panel C) and LON (panel D) right after collection. All material was dried at 30°C for 24 hours, ground in batches

and subsequently sieved to < 2mm and homogenized prior to analysis, as shown in panel B of Figure 4.1. The grinding process broke up the large woodchip pieces which ranged in width from roughly 2-5 cm while the particles of gypsum and clay were already small and became blended into the mixture.

Figure 4.1 The Filtrexx® material before use (A), after being ground to <2mm (B), after use at ILD and after use at LON (D).

4.2.1 Solid-Phase P fractionation

The solid-phase P partitioning was determined for both used and unused materials from LON and ILD using the fractionation experiments following the procedure for calcareous soils presented in Zhang and Kovar (2009). This procedure was also used for P partitioning analysis of the soils at LON and ILD as described in Plach et al., (2018). Starting with 1g of the sieved (< 2mm) material, a series of steps were completed to extract various forms of DRP. The four fractions exacted from the material are described in Table 4.1.

After each of the four steps, the material and solutions were centrifuged at 10 000 RPM for 5 min (11,180 xg) and washed with saturated NaCl. This extract and wash from each step were combined into clean polypropylene tubes and stored at 4C until analysis. All of the samples from each step were analyzed for P within 24 hours of extraction in the Biogeochemistry Lab at the University of Waterloo using the ammonium-molybdate ascorbic-acid method on a Bran Luebbe AA3 (Seal Analytical, Seattle, USA). Samples from step 2 were corrected for interferences between the extract and acid-molybdate reagent by oxidizing excess dithionite as a result of allowing the samples to be exposed to air and the addition of ammonium molybdate to each sample to improve colour development (Weaver, 1974). Extracts for step 1 and 3 were neutralized with HCl and NaOH respectively before they were analyzed. The sum of the four fractions equaled "Total-P" retained within the filter material. For the entire procedure 10% duplicates were conducted and the relative percent difference between the duplicates were ≤6%. The fractionation analysis categorizes P into 4 operationally-defined categories based on how tightly held the P is in the material. The 4 categories are; 1) a Sol-P which is likely loosely adsorbed P on oxide surfaces (Al and Fe) and P compounds soluble in bases that is likely bound to clay 2) CBD-P reductant soluble P which are redox sensitive 3) HCl- P which is likely Ca bound P and 4) the residual bound Res-P which is released by a $K_2S_2O_8$ extraction. The sum of all four categories indicates the total amount of P held in the filter material. The total P values from the fractionation tests were calculated by multiply the weight/kg of the sum of all four fractions of DRP by an estimated value of 100 kg of material located at each site.

4.2.2 P sorption tests

Phosphorus sorption tests were conducted on used and unused material from both sites following the procedure outlined in Graetz and Nair (2009). Where 1g of the dried ground (< 2mm) filter material was combined with 25 mL of a 0.01M KCl solution with 0, 25 and 75 mg P/L as KH_2PO_4 dissolved in DI water in 50 mL conical polypropylene tubes and agitated for 18 hours on a mechanical shaker. As a result of low concentrations of P in runoff water seen in Chapter 3, concentrations beyond 75 mg P/L were not deem essential. The three target concentrations of mg P/L were chosen to get an idea of how much P the Filtrexx® material could sorb, not to reach its potential maximum sorption point. The highest concentration applied (75 mg P /L) was selected to match the concentration of P used to estimate the phosphorus sorption capacity for agricultural soils using the phosphorus sorption index (PSI) test (Graetz and Nair, 2009). Triplicate samples of the used and unused material from both sites were combined with each of the three P concentrations. The tubes were centrifuged at 5000 RPM for 5 mins (2,795 xg), filtered through a

< 0.45 um cellulose acetate filter (Delta Scientific) and stored at 4°C. The DRP concentrations of the filtrate from each sample were determined colorimetrically (described above). The detection limit for this DRP analysis was 1 µg/L with the analytical precision determined on 10% duplicates and the relative percent difference between these duplicates found to be ≤6%. To calculate the mg/kg of DRP sorbed the following method was used. The DRP value for a specific sample was subtracted from the initial DRP concentration in solution to determine the mg/L of P sorbed, this value was then divided by the amount of material used (0.001kg).

4.2.3 Ion analysis

Surface runoff samples collected over a 16-month period in the field were filtered (<0.45 mm cellulose acetate) and analyzed for DRP (described in Chapter 3), as well as major ions (Dionex ICS3000, IonPac AS18 and CS16 analytical columns). A subset of samples from the laboratory extractions of filter material was also analyzed for ions. Relevant cations measured included Ca^{2+} and Mg^{2+}, and anions included SO_4^{-2} and CO_3^-. Approximately 5% of samples were analyzed in replicate.

4.2.4 Data analysis

The ions (Ca^{2+}, SO_4^{-2}, Mg^{2+}, CO_3^-) loading for each of the overland flow events was calculated by multiplying the concentration of a discrete or composite sample by the average flow rate for the sample interval, multiplied by the length of time the sample represented:

$$\text{Event Load} = \sum_{i=1}^{n} Ci \, Qp \, Ti \qquad [1]$$

Where Ci is the concentration (mg/L) of a discrete or composite sample. $\overline{Q}p$ is the mean discharge (l/s) for the interval between samples and Ti is the time interval (s) represented by the sample. Following the determination of event loading, the Flow-Weighted Mean Concentrations for events were calculated as:

$$FWMC = Event\ Load / \text{Event Discharge} \qquad [2]$$

The differences in the before FWMCs and after filter FWMCs of each of the four ions were compared using a series of paired T Tests. The results of all individual runoff events were used with an n of 10 for ILD and 12 for LON. These were deemed significant at $p < 0.05$.

Differences in ion event loads were calculated as the event load after the filter subtract the event load before the filter. Positive results indicate the filter released ions while negative values demonstrate a removal of ions by the material.

4.3 Results

4.3.1 P fractionation in used and unused filter material

The unused filter material held approximately 60 mg/kg of P, primarily in the Sol- P form (Table 4.1). Following installation in the field and 1.5 years of use, the used material at both sites held large amounts of extractable P (200 – 325 mg/kg), the vast majority was stored in the least tightly held Sol-P form (Table 4.1). However, the other three fractions also increased over the time of use, suggesting that a small portion of the P removed from the runoff was converted into these more tightly held forms, e.g., occluded within metal oxides such as iron, and bound tightly with calcium (Table 4.1). The distribution of retained P across the different fractions differed slightly between the two sites. At the LON site, a greater proportion of the retained P was in the more tightly held fractions (i.e., CBD-P, HCl-P and Res-P) with an average 8 times increase than the ILD material which only doubled each of those fractions. Although it was exposed to less runoff over the study period (43 mm at ILD, 366 mm at LON), the material at ILD retained about 50 mg/kg more P overall than the LON material.

Table 4.1 The average amount of DRP held in the four fractions within the filter material as well as the total value in mg/kg of P. In brackets, +- 1 standard deviation for each fraction is shown. The unused material was collected in September 2016 and the used material was collected in February 2018. The likely form of P released during each step and the reagents used to release the P are also included (Zhang and Kovar, 2009).

Type of DRP	ILD Unused	ILD Used	LON Unused	LON Used	Reagents	Likely P Released
Sol-P	51.20 (1)	260.93 (36)	60.27 (0.2)	170.1 (15)	0.1 M NaOH 1M NaCl	Loosely bound P associated with metal oxides (Fe-P) or clay minerals
CBD-P	4.90 (0.9)	11.18 (3)	4.45 (0.8)	27.4 (4)	0.3M $Na_3C_6H_5O_7$ 1g $Na_2S_2O_4$ 1M $NaHCO_3$	Reductant soluble P (redox sensitive metal oxides)
HCl-P	4.87 (2)	8.47 (2)	2.40 (0.2)	17 (8)	0.5M HCl	Acid Soluble P (Ca-P)
Res-P	5.10 (1)	9.21 (1)	2.23 (0.1)	24.9 (3)	10% $K_2S_2O_8$	Refractory organic and mineral associated P
Total DRP	66.07 (0.5)	289.79 (42)	69.35 (0.6)	239.3 (30)		

4.3.2 Laboratory P sorption tests on used and unused filter material

Sorption tests conducted on both unused and used material from the two sites (Figure 4.3) demonstrates that the unused material from both sites and the used material from ILD were able to sorb similar amounts of P at all concentration levels. In contrast, the used material from LON had a reduced capacity to remove P from solution (Figure 4.2). At the highest concentration (75 mg/L), the used material at LON sorbed less than half the DRP of the other materials. At the lowest concentration of DRP at 0 mg/L there was a small release of DRP by the used material from the LON site, and this release was not observed in the unused samples or in the ILD used sample. Although a plateau is traditionally sought in laboratory sorption studies to determine a theoretical maximum in P sorption, the material in the current study did not reach a theoretical maximum in P sorption, even at the highest P concentration employed (75 mg/L) (Figure 4.2), indicating that the filter material had a strong potential to sorb considerable quantities of P in the idealized lab setting. In the field setting in the current study, DRP concentrations in surface runoff were most often <0.150 mg /L, and rarely exceeded 1.5 mg/L in discrete water samples, which is considerably smaller than the 75 mg/L used in the laboratory study. The sorption of ~1300 mg/kg at 75 mg/L (Figure 4.2) translates to approximately 0.13 kg of DRP sorption potential in the 100 kg of filter material installed at each site. Given that the theoretical maximum was not reached, the true sorption potential of the material is greater than the 0.13 kg estimate.
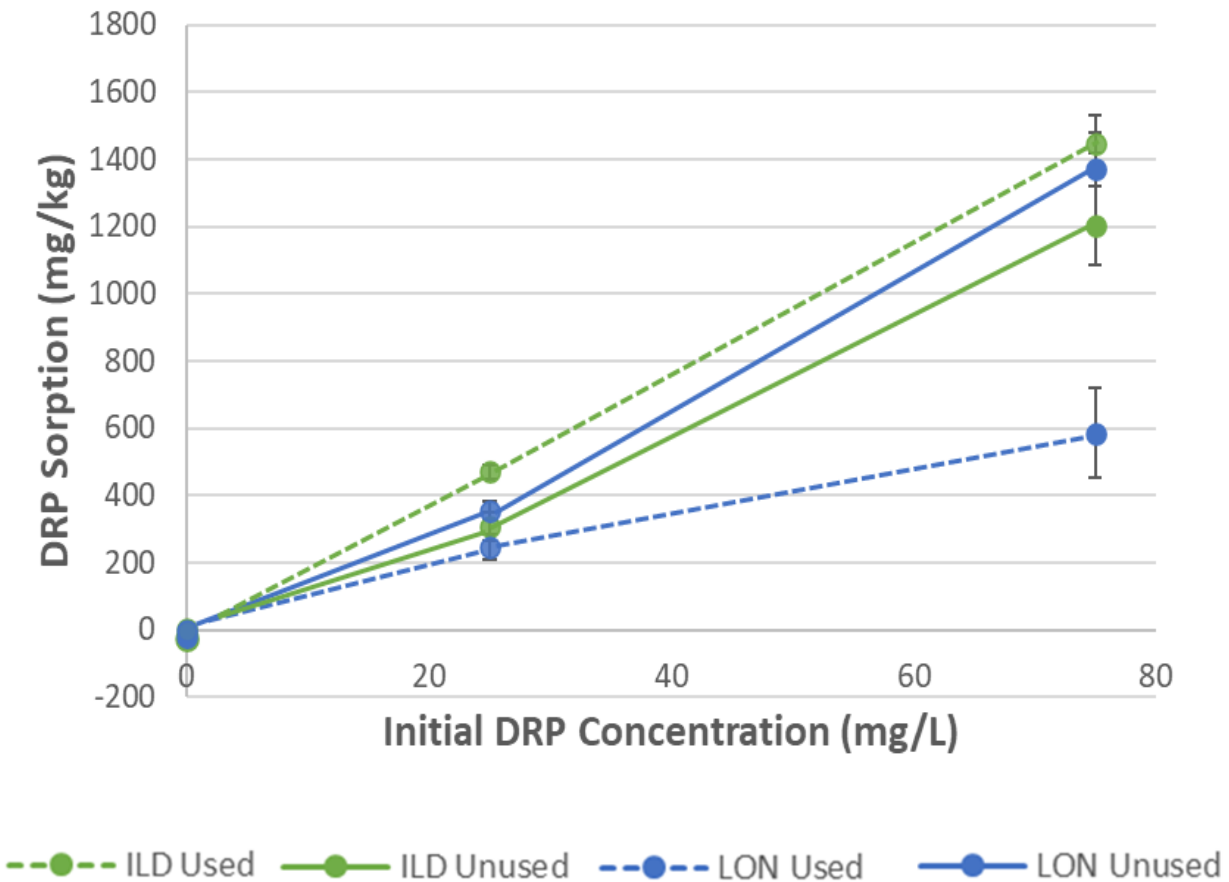
Figure 4.2 Average DRP sorbed by the filter material versus the amount of DRP in the initial solution for ILD and LON material both Used and Unused. A positive value indicates P sorption while a negative value indicated P release. Error bars represent +- 1 standard deviation.

4.3.3 Ion release during sorption tests on filter materials

To investigate possible mechanisms of DRP removal by the filter material, and determine if they varied between sites, samples from the first sorption experiments (Figure 4.3) were also analyzed for major ion concentrations. Unused material from both sites consistently released large amounts of Ca^{2+} and SO_4^{-2}, and small amounts of Mg. The used material from ILD released much less Ca and SO_4^{-2} than the fresh materials but slightly more than from the used LON material. Notably, CO_3 was released from the LON used material, but was not released from the used ILD material or any of the unused material. Across all parameters, there is little change in the moles of ions released, irrespective of the initial concentrations of P added to the material as part of the sorption tests.
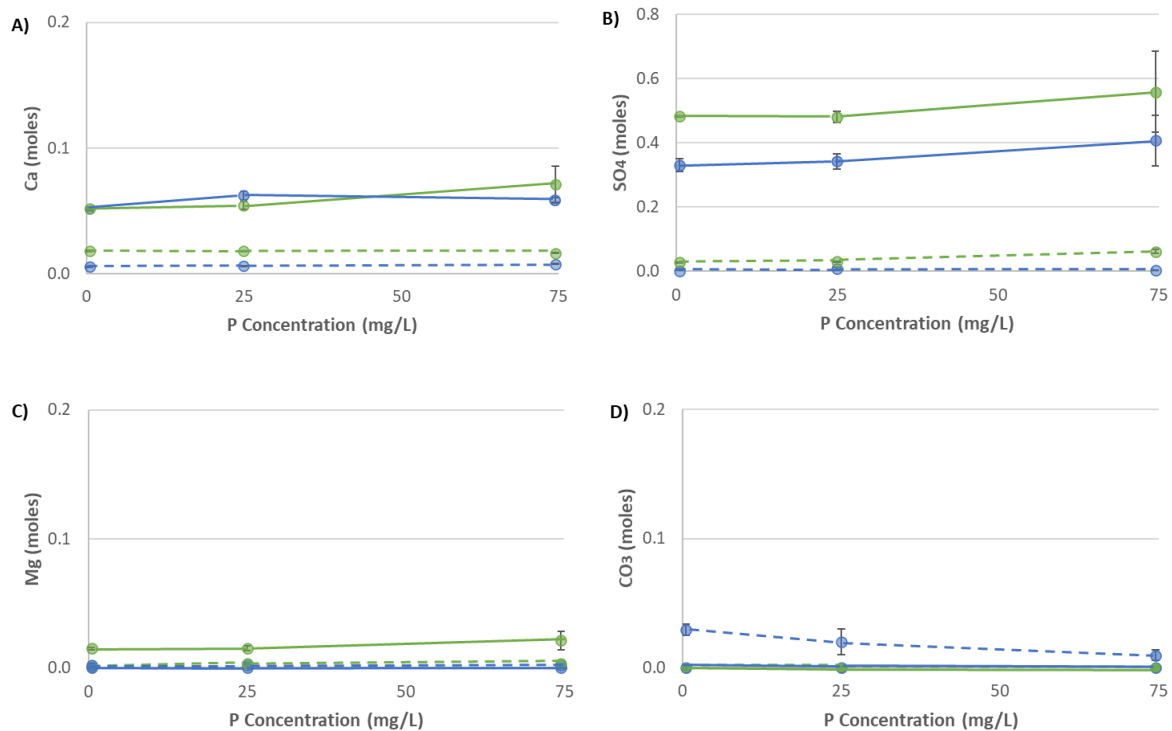
Figure 4.3 The average moles of A) Ca^{2+}, B) SO_4^{-2}, C) CO_3^-, D) Mg^{2+} released during the sorption tests on the filter material from before (Unused) and after (Used) the field experiment after 18 hours of shaking. The scale of graph B) is larger to accommodate the large amounts of SO_4 released. The green lines represent ILD and blue lines represent LON with dotted lines for used material and solid lines for unused material. Error bars represent +- 1 standard deviation for each value. Figure 4.3 shows the amount of DRP removed by the material in the same samples.

4.3.4 Ion concentrations in surface runoff before and after exposure to filter in the field

Ion concentrations in surface runoff samples before and after the filter provide insight into potential P removal mechanisms (Table 4.3). There were differences in ion concentrations in runoff between the two sites. At ILD, FWMC of Ca^{2+}, Mg^{2+} and SO_4^{-2} in surface runoff before the filter across all events were lower than those experienced at LON, whereas SO_4^{-2} concentrations were similar between the two sites.

There were also differences between the two sites in how ion concentrations in surface runoff changed after it had passed through the filter, and, how these changes varied in time. For example, concentrations of all four ions increased at the ILD site during the first five events. However, these increases were smaller or inconsistent during the subsequent 5 events, and this coincides with smaller removal of DRP in surface runoff by the filter (Table 4.2). In contrast, at

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the LON site, changes in ion concentrations were very inconsistent among samples collected above and below the filter. Although DRP was retained by the filter at the LON site during events 1-4, no clear relationships with ion FWMCs were observed.

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Table 4.2 Flow weighted mean concentrations (FWMC) of major ions and DRP in surface runoff before and after it passed through the filters for events occurring over the study period. Changes in concentration are expressed as a percentage of the concentration in runoff before it passed through the filter material in (brackets) beside the After concentration. A negative percent difference demonstrates a decrease in concentration after exposure to the filter.

| Site	Event	Date	Flow (mm)	FWMC DRP (mg/L)†,‡ Before	After (%)	FWMC Ca (mg/L)† Before	After (%)	FWMC SO$_4$ (mg/L)† Before	After (%)	FWMC Mg (mg/L)† Before	After (%)	FWMC CO$_3$ (mg/L)‡ Before	After (%)
ILD	1	Jan 12-13 2017	1.48	0.08	0.01 (-91)	8.80	29.84 (240)	1.66	32.43 (1820)	1.54	5.22 (300)	71.67	77.14 (7)
	2	Jan 17-18	0.08	0.03	0.00 (-98)	61.98	105.21 (80)	15.98	93.99 (500)	0.82	6.71 (900)	15.09	49.90 (300)
	3	Feb 28-March 1	2.58	0.30	0.04 (-88)	22.75	58.37 (156)	10.47	49.55 (374)	1.25	7.56 (566)	52.41	73.70 (41)
	4	March 30-31	1.27	0.10	0.00 (-99)	14.37	43.16 (206)	2.55	44.11 (1603)	0.87	6.68 (800)	52.14	70.32 (27)
	5	April 20-21	1.68	0.08	0.01 (-88)	18.34	25.15 (35)	7.28	25.29 (248)	1.44	4.86 (200)	18.46	39.63 (53)
	6	Jan 11-12 2018	12.92	0.26	0.26 (0)	27.41	28.39 (3)	22.49	23.57 (5)	2.32	2.19 (-7)	40.59	39.89 (-2)
	7	Jan 22-23	1.54	0.42	0.16 (-63)	32.31	34.93 (8)	9.42	20.01 (112)	2.50	2.26 (-10)	105.19	34.51 (-67)
	8	Feb 19-23	15.17	0.28	0.26 (-5)	13.20	14.06 (6)	1.07	1.37 (28)	3.20	3.17 (-2)	47.99	46.74 (-3)
	9	April3-4	1.12	0.19	0.13 (-30)	14.57	37.22 (162)	8.29	9.74 (17)	0.83	4.28 (400)	41.13	54.90 (34)
	10	April 15-17	5.49	0.27	0.26 (-5)	31.06	46.99 (51)	2.69	3.07 (14)	3.12	7.00 (129)	46.26	48.03 (4)
LON	1	Jan 11-12 2017	22.36	0.07	0.07 (-0.3)	16.67	16.63 (-0.2)	0.25	0.23 (-11)	4.81	4.76 (-1)	32.64	35.99 (10)
	2	Jan 17-18	5.94	0.03	0.30 (-12)	11.66	7.21 (-38)	4.12	1.46 (-65)	3.13	3.29 (5)	32.52	31.68 (-3)
	3	March 1-2	15.92	0.16	0.15 (-8)	32.83	38.13 (16)	0.68	2.14 (215)	7.79	7.79 (0)	59.40	56.26 (-5)
	4	May 5-6	60.67	0.01	0.01 (-32)	51.25	54.28 (6)	3.41	3.74 (10)	13.56	13.35 (-2)	60.09	58.77 (-2)
	5	Sept 5-10	41.22	0.36	0.60 (66)	66.73	60.53 (-10)	8.01	4.58 (-43)	19.34	17.68 (-9)	113.91	109.10 (-4)
	6	Oct 15-17	28.63	0.30	0.34 (15)	46.30	57.51 (24)	7.48	12.38 (65)	19.20	18.94 (-1)	137.10	128.63 (-6)
	7	Nov 2-3	19.94	0.13	0.51 (280)	20.54	20.69 (1)	2.75	2.61 (-5)	20.07	14.58 (-28)	48.87	35.34 (-28)
	8	Nov 4-7	39.52	0.16	0.23 (47)	22.88	27.89 (22)	6.12	5.22 (-15)	17.19	13.20 (-23)	81.01	72.61 (-10)
	9	Nov 16-19	15.60	1.62	1.70 (5)	34.36	36.57 (6)	7.24	7.44 (3)	13.67	10.44 (-23)	96.43	101.87 (6)
	10	Jan 11-12 2018	41.11	0.53	0.56 (6)	15.54	29.54 (90)	7.81	8.29 (6)	2.32	7.31 (214)	31.47	26.42 (-16)
	11	Jan 22-23	34.88	0.54	0.55 (2)	23.47	23.58 (0.5)	4.80	5.11 (6)	5.77	5.64 (-2)	23.46	20.36 (-13)
	12	Feb 19-21	40.73	0.33	0.34 (5)	20.43	17.60 (-14)	15.77	12.69 (12)	4.35	3.85 (-11)	27.32	17.31 (-37)

†Significantly different (<0.05) between the FWMC before and after the filter at ILD

‡ Significantly different (<0.05) between the FWMC before and after the filter at LON
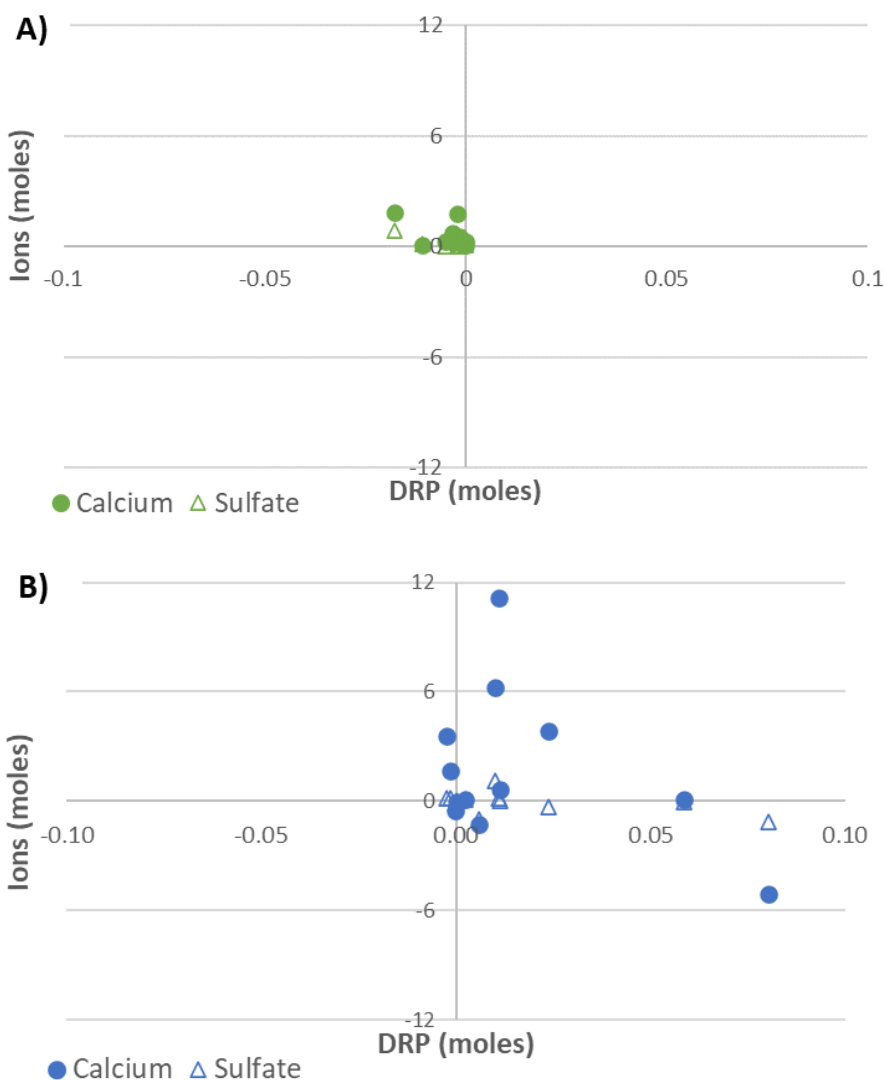
Figure 4.4 The change in moles of DRP versus the change in moles of ions (Ca^{2+} and SO_4^{-2}) before and after the filter. A) shows ILD events and B) shows LON events. Positive values indicate more DRP/ions in the samples collected after the filter compared to before and thus a release occurred.

A comparison of moles of ions released and the observed reductions in DRP (Figure 4.4) reveals no strong patterns at either ILD or LON. The event with the largest DRP removal rate coincided with the largest release of the ions by the filter at ILD but across all events at ILD, the moles of Ca^{2+} and SO_4^{-2} released by the filter were very similar. At the LON site, there was no clear trend between DRP reduction and ion release. The majority of events resulted in little change of either ion. However, a few events resulted in large release of Ca^{2+} with little change in SO_4^{-2}. The

event with the largest release of DRP from the filter was also one of the few to result in the filter retaining Ca^{2+} and SO_4^{-2}.

4.4 Discussion

4.4.1 How P is removed by the filter?

The results of the fractionation analysis demonstrate that adsorption onto metal oxides and clays is likely the dominant pathway for P removal in the filter material (Filtrexx®). The material from both sites was rich in Sol-P after being in the field, with an increase of nearly 4 times. Adsorption onto metal oxides and clay most often occurs through the rapid exothermic reaction of ligand exchange (Penn et al., 2017). In ligand exchange, a phosphate ion replaces a hydroxyl group on an Fe/Al oxide or clay compound and becomes incorporated into the structure (Liu et al., 2018). Additionally, Fe and Al metal ions have the ability to form metal-P hydroxides which sorb or entrap P and precipitate out of solution or link together through an oxygen atom (Szabo et al., 2008; Devlin et al., 2017). A study by Jiang et al., (2013) found that a sponge iron material rich in Fe_2O_3 was able to remove nearly 100% of the DRP added into solution using the ligand exchange process. The ligand exchange reaction for P removal requires less contact time with water and material than precipitation reactions (Penn et al., 2020). P removal efficiency using this method is highly dependent upon the ions in solution, specific metal and clay species, and pH (Wang et al., 2021). P adsorption onto metal oxides occurs most often at low pH (from 3-5) while adsorption onto clays occurs most often at neutral pH. A review from Gerard (2016) showed that clay particles increased DRP adsorption at pH 7 compared to pH 5 while metal oxides saw a decrease in P adsorption changing from pH 5 to 7. A study using lanthanum enriched clay also found its most effective P removal at pH between 5-7 and decreased once the pH was over 9. In the current study, field measurements of runoff pH showed consistent results of pH 7.5-9.0 which suggests that adsorption of P to the clay particles inside the filter may be the most dominate mechanism for P removal.

The results of the ion analysis suggest that a less used second mechanism for P removal in the Filtrexx® material is precipitation of P with Ca^{2+} which would be held in the HCl-P fraction. Phosphate from the runoff was binding with the newly available Ca^{2+} released from the gypsum through a precipitation reaction by combining calcium phosphate and water into Ca_5PO_43OH with a release of H+ (Zhang et al., 2016). This process requires a first step of gypsum dissolving into Ca^{2+} and $SO4^{-2}$ in the runoff followed by the second step of Ca^{2+} combing with P. Efficient removal of phosphate with this method has been recorded at 40-120 mg/L of Ca^{2+} and 3-10 mg/L of P with a pH above 8 (Kim et al., 2006; Barca et al., 2012; Klimeski et al., 2012). The field pH results around the filter ranging from 7.5-9.0 should allow the process to proceed however the recommended values for Ca^{2+} and P are all far higher than any concentrations seen in the field experiments of this study. This immediately suggests that the low levels of Ca^{2+} and P may have prevented this reaction from fully occurring despite the filter being in part filled with gypsum particles. Evidence of the first step, the dissolution of gypsum, is shown by the elevated FWMC's

of both components after the filter material especially at ILD. During the first few events with large P removal the amount of Ca^{2+} and SO_4^{-2} after the filter is often hundreds of times more than before indicating a large amount of gypsum is dissolving. However, at LON the FWMC's of Ca^{2+} and SO_4^{-2} show little change before and after the filter indicating that gypsum is not consistently dissolving during runoff events. The gypsum could be dissolving and releasing ions without the further step of Ca-P precipitation occurring because the conditions may not be correct. Studies maintaining constant P:Ca ratios (Kim et al., 2006) or very high P concentrations of 15 mg/L (Adam et al., 2004) demonstrated increased P removal from the Ca-P mechanism. Several studies have also documented poor performance from PSM as a result of low levels of P binding ions, such as Ca^{2+}, being released and thus limiting reactions (Johansson and Gustafsson, 2000; Barca et al., 2012; Penn et al., 2017). Since at LON gypsum was not consistently dissolving, there may not have been enough Ca^{2+} in the runoff to begin the P removal reactions. This could be a potential reason for such poor performance overall in P reduction by the filter in the field, there was simply not enough Ca^{2+} and P in the runoff. The second step of combining Ca with P to form highly stable Ca-P minerals likely didn't often occur either. This is most evident in the low levels of HCl-P found inside both filter materials. Additionally, when converted to moles (Figure 4.5), the change in Ca^{2+} are often similar to those of SO_4^{-2}. If the Ca-P reaction was consistently occurring, the free Ca ions would have been combined with P and the ion data would show low levels of Ca^{2+} but high levels of SO_4^{-2}. This difference is observed in the lab sorption tests (Figure 4.4) where the moles of SO_4^{-2} remaining are a few times larger than the moles of Ca^{2+} after the experiment. This suggests that at least in the controlled environment of the sorption tests, the Ca-P removal mechanism was likely occurring.

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In Chapter 3, time since installation was thought to be one of the most important factors in determining the performance of the filter. The reduced performance can also likely be explained by decreased availability in surface adsorption sites on the oxides and clays over time in the filter. After discovering the trend of ions being released during events with strong P reductions, time could also be a proxy for the supply of gypsum. As more gypsum is dissolved in subsequent surface runoff events the filter loses its ability to remove P via the Ca-P mechanism. The stark difference in the Ca^{2+} and SO_4^{-2} released from unused Filtrexx® material compared to the used material suggests that the used material had nearly exhausted its supply of gypsum and thus was degraded in its ability to remove P through Ca-P precipitation. The inconsistent release of Ca^{2+} from decreasing amounts of gypsum in the filter and overall low P concentrations were one of the potential causes of the decreased performance in P removal by the Filtrexx® material. A reduction in performance due to the exhaustion of P removal materials and release of P sorbing ions out of the system was seen in a number of studies (Postila et al., 2017; Penn et al., 2017). Using limestone, a column experiment saw decreased P reduction over time and the near completed exhausted the supply of Ca after a few weeks (Postila et al., 2017). A review of other PSM also found that their efficiency decreases over time as a result of saturation of P sorption sites, especially those using the ligand exchange mechanism (Mendes, 2020). For sufficient removal of P via chemical precipitation, frequent additions of new ions that remove P are required as well as regular supervision of levels to ensure proper chemical ratios (Herrmann et al., 2014). Other studies using

gypsum or lime for P removal saw increased results from using many tonnes/ha of it as a soil amendment (King et al., 2016; He, Li and Dong, 2018) or in a filter bed (Bryant et al., 2012; Kirkkala et al., 2012) and on sites with high soil test P. One of the possible causes for this discrepancy is the large initial concentrations of ions in the runoff at LON which may be caused by the longer and larger runoff events seen at the site which interacted with the Ca^{2+} rich soils preventing the gypsum from dissolving. Klimchouk (1996) details that if there is a disequilibrium of the gypsum dissolution reaction, as in high levels of Ca^{2+} and SO_4^{2-}, then gypsum is more likely to precipitate than dissolve. A diminishing supply of gypsum over time to provide Ca^{2+} could be the most likely cause for the decreased performance in P removal via the Ca-P mechanism with an ever-decreasing number of binding sites on the metal oxides and clays for the Fe-P mechanism.

4.4.2 Filter performance in the lab versus the field

The filter material showed a large ability to remove P from lab created solutions and runoff water used in the sorption tests. In the field experiments of Chapter 3, only one or two events at ILD reached the percentage of P removal observed in the lab experiments, demonstrating the better performance of the material in a lab setting. The sorption tests also detail that the filter material has a large ability to sorb P from solution, in much higher amounts than the P naturally occurring in runoff at both field sites, but these removal abilities varied depending on site. The used ILD material was able to remove as much P as the unused material and all three of these samples had much larger removal capacities compared to the used material from LON. The used material from LON was clearly degraded in its performance and this became worse with the higher concentrations of P used in the sorption tests. Sorption isotherms were previously conducted on soils at various depths from both LON and ILD and found a capacity to sorb P at about 200-300 mg/kg (Plach et al., 2018). A study conducted by Grubb et al., (2012) showed a sorption isotherm of pure gypsum levelling off in P removal at an initial concentration of 2400 mg/L where it adsorbed 24 700 mg/kg of P. Other PSM such as steel slag show an ability to sorb 5,300 mg/kg of P (Xiong et al., 2008), 27 300 mg/kg for rust and 1 426 mg/kg for sand with incorporated rust (James et al., 1992), 21 000 mg/kg for Fly Ash and 45 000 mg/kg for Flue Gas Desulfurization gypsum (Stoner et al., 2012). It appears that the maximum sorption capacity for high metal content products alone is much higher than other materials mixed with metals and other compounds. Based on these values it is likely that the max sorption capacity for the Filtrexx® material lies somewhere between 1300 to 5000 mg/kg which would put it on the lower end of other commonly used PSM. A few studies have shown that the lower the initial concentration of P in runoff the larger the discrepancies between maximum P retention in sorption isotherm studies compared to field scale studies (Klimeski et al., 2012; Penn et al., 2014). This would leave the material with plenty of ability to remove the smaller concentrations of P seen in runoff in the field experiments, but this did not happen.

There are many possible reasons for the difference in P removal rates from the sorption tests compared to the field results. Research by Klimeski et al., (2012) and Herrmann et al., (2014) show that P removal of PSM usually shows better results in laboratory tests compared to field studies and are not determinative of real-world results. Further, agitation batch tests, like the

sorption tests conducted in this experiment, have been proven to show a material has a longer period of use in the field than it actually does (Sovick and Klove, 2005; Herrmann et al., 2014). This is because the sorption experiments test the materials under ideal conditions; large surface areas, a controlled environment, long contact time, and well mixed on the shaker table. All of these conditions have been shown to influence P removal in other materials (Cucarella and Renman, 2009). In terms of surface area, a nano gypsum soil amendment was found to have better P removal ability than the conventional size because it had higher surface area and solubility (Chen et al., 2016). Klimochouk (1996) showed that increasing the grain size of gypsum by breaking it into small particles makes the gypsum more soluble and able to better sorb P. Additionally, a smaller grain size of gypsum resulted in 3 times more P sorption when applied to soils compared to gypsum of a larger grain size (Kordlaghari and Rowell, 2012). One possible reason for lower P removal for the Filtrexx® in the field is a result of the gypsum and clay pellets being large and mixed among even larger woodchips in comparison to ground and mixed material used in the sorption experiments. Additionally, longer contact times between PSM and water such as those filters used in wastewater treatment plants or flow through experiments show better results compared to those field materials with lower contact time (Penn et al., 2017; Postila., 2017). Szabo et al., (2008), demonstrated that most of the P that was removed from their experiment was done in the first 10 mins, but in the field the Filtrexx® material had interactions with runoff lasting seconds. The most effective filters in terms of P removal in a review by Penn et al., (2017) were those with residence times from hours to days, especially those using a Ca based removal mechanism, because it is a slower reaction. A review from Mendes (2020) found that a common trait among PSM with constantly changing flow volume is an inconsistent removal of P and over time which can potentially shift the PSM from P sinks to P sources which may also explain a potential P release from LON. Stoner et al., (2012) detail that gypsum can be a good source of Ca for P removal, but as a result of being poorly pH buffered it needs a longer retention time when used in a filter. If the contact time is short, its important to ensure a high probability of P ions meeting metal ions by mixing the solution and material (Szabo et al., 2008). With no mixing and shorter contact time, the amount of P removal could have been greatly reduced and relied upon chance interactions.

In the field, factors that can't easily be controlled and tend to change over space and time such as pH, P concentration and other ions in solution tend to decrease the performance of PSM (Postila., 2017; Penn et al., 2017). In order to see strong P removal from the Ca-P removal mechanisms the pH must be maintained at a high value, something that is difficult to keep consistent in an outdoor field environment (Klimeski et al., 2012). Grab samples of overland flow during 5 events in this study showed the runoff pH ranged between 7.5 and 9.0, and thus favourable pH conditions for both ligand exchange and Ca-P precipitation reactions to occur. However, any changes in pH and P or Ca concentrations can also dissolve Ca-P precipitates and release any phosphorus that was previously captured (Klimeski et al., 2012). Large scale steel slag filters failed to meet the removal levels predicted in lab studies as a result of carbonates in the runoff interfering with the Ca-P precipitation reaction and reducing P removal (Penn et al., 2020). Carbonates are also known to decrease Ca-P formation by combining with Ca to form $CaCO_3$ precipitations and blocking phosphate nucleation sites (Cao et al., 2007; Barca et al., 2012). As shown in the ion analysis from both the event samples and sorption test samples the LON material had larger amounts of CO_3 compared to the ILD material which may explain the differences in P removal

between the two. Mg can also reduce the number of Ca-P precipitates and higher concentrations of Mg in soils lead to more water-soluble P in soils (Manimel Wadu et al., 2013). Mg^{2+} can precipitate with Ca-P itself and eventually prevents the final HAP formation by causing more soluble forms to be created (Baker et al., 1998; Cao et al., 2007). The results of the ion analysis for event samples showed that more Mg was trapped in the filter material at LON compared to ILD presenting another possible reason for lower P removal levels at LON. Research from Xu et al., (2006) showed that organic matter can also inhibit P removal by competing for binding sites and even releasing P that was previously sorbed to removal material. One signal of potential DOC in the LON filter material is how much more degraded it appeared compared to ILD. Figure 4.1 showed nearly half of all woodchips extracted from the LON material being black and breaking down while a much small portion of the ILD material appeared to be actively degrading. The degradation of material could have been a cause of the DRP release that was seen in Chapter 3 results during large runoff events in the fall of 2017. As a result of many dynamic factors in real world environments, the filter material performed better in the controlled environment of the sorption tests. The maximum amount of DRP the Filtrexx® filter material can sorb is well beyond any concentration it would see in an agricultural setting but a number of factors including grain size of the material, contact time and a lack of a consistent environment may have impacted its performance in the field.

4.4.3 Risk of P re-mobilization from the filter

The results of the P fractionation experiment show that both sites increased the amount of DRP in the material by roughly 4 times over the study period. A majority of the DRP held in the material was in the least tightly held (Sol-P) form, but each site also saw an increase in each of the other three more tightly held fractions. Individually, the LON material saw larger increases in all three of these more tightly held categories (i.e., CBD-P, HCl-P, Res-P), potentially as a result of experiencing much larger runoff volumes. These results demonstrate that a large amount of DRP was deposited and remained inside the filter material over its time in the field. One large difference between the sites was that the ILD material contained more total DRP than the LON material, despite having much less runoff pass through and lower concentrations of DRP over all events. This may be explained by the multiple large runoff events at LON in the fall of 2017 which showed a large release of DRP from the filter material. Since a majority of the P held in the material was in the loosely bound Sol-P pool it could have been more easily re-mobilized and released downstream. The Sol-P portion could contain metal oxide bound P that has the potential to be released under anoxic conditions or could be clay bound P which is less likely to be released if oxygen levels change (Chorus and Mur, 1999; Antelo et al., 2005; Liu et al., 2012). Penn and Warren (2009), found that P adsorbed through ligand exchange reactions, like with clays, were more slowly released during repeated flushes with water and ammonium oxalate. This was demonstrated in Figure 4.3 as no DRP was released from the used materials when shaken with the 0 mg P/L water in the sorption tests showing the P held in the filter was not water soluble. Work done by Liu (2012) were able to see 75%-90% P desorption from metal oxides with NaOH ranging from 0.01M-0.1M. The desorption process works because OH- can be exchanged for phosphate

on metal oxides when solution pH is high (Ross et al., 2008; Liu et al., 2012). In the field, this suggests that if the filter material was encountering runoff water with high pH, there is a potential for the release of some of the sorbed P. The fractionation experiment showed that the though the Filtrexx® material gained DRP over the study period, a relatively small portion ($< 25\%$) of that DRP was in tightly held forms, leading to the risk for potential release in the future.

There was a discrepancy in how much P was trapped in the filter and how much was removed through the analysis of water samples collected before and after the filter. DRP amounts retained by the filters based on the extractions (0.022 kg at ILD, 0.017 kg at LON) were considerably smaller than the observed reductions in DRP loads by the filters in a field setting (0.148 kg at ILD, 0.041 kg at LON). Less than 50% of the DRP removal predicted by the water sample analysis was accounted for inside the filter material. This demonstrates that the P stored inside the filter does not account for all edge of field P losses, and suggests that caution should be used when estimating edge-of-field losses using retention by a filter. This pattern is similar to that seen in Hermann et al., (2014) where there was roughly the same amount of P trapped in the filter as escaped and transported downstream during its lifetime. The portion that did not remain inside the filter likely either continued to move down stream or were quickly deposited on the ground just beyond the filter, both of which could lead to more environmental problems. There are some possible reasons why not all of the P removed by the filter was captured inside of it. It is possible that some portion of P was able to combine with the Ca^{2+} and be transported out of the filter with the runoff. The Ca-P precipitation reaction process takes time and is a much slower reaction that can be reversed if pH or Ca^{2+} concentrations changes which could explain why it occurred downstream and not immediately inside the filter material (Klimeski et al., 2012). Additionally, there is evidence, especially at LON, that the filter was releasing DRP during large volume runoff events. P previously held in the Sol-P fraction could have been released with changes in oxygen and pH conditions which would have decreased the amount of P retained in the material (Kunaschk et al., 2015). Extracting the material after 1 and a half years of use showed degradation of the material, most specifically at LON, and this is another potential source for P release from the filter.

Work by Plach et al., (2018) on soils from ILD and LON underwent the same P fractionation analysis. The surface soils at ILD contained 700 mg/kg of DRP with 900 mg/kg at LON. The majority of the DRP held in the soils were in the CBD-P and HCl-P extractable portions with much smaller amounts in the Sol-P pool. This shows that P is held more tightly in the soils at these sites than in the filter material at the edge of field. However, since the filter material's fractionation results differ widely from the surface soils, it is likely that the filter was not simply trapping suspended soil particles, but rather was also removing P from runoff on its own and thus retaining it by a different mechanism. A study of other PSM found that several Ca rich materials such as steel slag, lime and opoka rock held the majority of sorbed P in the HCl extractable form with very little held in more soluble forms (Fe-P and Al-P) (Hylander and Siman, 2006; Drizo et al., 2008). This confirms that other Ca rich materials tend to have a substantial amount of extractable DRP in the HCl fraction and are more tightly held in these other materials than it was in the Filtrexx® material. A product like Filtrexx® containing a lot of gypsum should likely contain more Ca-P after use, thus the conditions were likely not met frequently enough in the field

for consistent Ca-P precipitation reactions. As a result of the Sol-P fractionation containing both P associated with metal oxides and P associated with clay particles the ligand exchange mechanism likely became the dominate form of P removal. In other PSM studies, X-Ray diffraction (XRD) is used to differentiate the type of crystalline minerals or P removal compounds, specifically those containing P or Ca^{2+}, is contained within the filter (Penn and McGrath, 2011). Other studies have examined the amounts of Ca-P precipitates in a filter material after use in an P removing experiment, looking for everything from dicalcium phosphate one of the more soluble forms to hydroxyapatite which is the most stable (Kim et al., 2006; Barca et al., 2012). Transmission electron microscopy is another process that can be used to help identify what type of metal oxide -P compound has formed in a material (Antelo et al., 2005). Recent work from Barrow et al., (2021) cautions from making major claims about Ca-P bound or metal-oxide/clay-P from fractionation methods as a result of uncertainty of exactly how much each is released with each extraction step. Thusly P fractionations, especially on this type of media, act as a guide to what may have occurred and like all operationally defined methods, there are limits with how much this method can exactly determine. However, the P fractionations results presented in this chapter provide a valuable indicator of the relative solubility of DRP that was retained by the filter. Further analysis on the specific minerals and P binding mechanisms that occurred within the Filtrexx® material is needed.

4.4.4 Economics and overall rating

The total cost of the Filtrexx® material used was approximately $400 for each site. As a result of P release from event 5 onwards, only the first 4 events where P removal occurred at the LON site were used in this calculation while all events from the study period were used at ILD because of consistent P removal. The material at ILD was able to remove 0.148 Kg of DRP (based on changes in DRP concentrations at the edge of the field) while the LON material was able to remove 0.041 Kg of DRP. Thus, the cost of removing 1 kg of DRP at ILD was $ 2 700 and at LON $ 9 760. These values are comparable to those determined in steel slag filters in Penn et al., (2020) which ranged from $500/Kg of P in a subsurface filter bed set up to roughly $6000 dollars/kg for a ditch filter system. However, are not as low as some other P removal methods such as a constructed wetland described in Gachango et al., (2015) which was able to remove P at a cost of 55-1148 €/Kg. On the price per kg of P removal alone the Filtrexx® material is not cost-effective. Possibilities of increasing the materials usefulness such as using it as a fertilizer are also not likely as studies have shown that spent gypsum does not release P back into soils because it does not contain enough P to act as a source (Grubb et al., 2012). Additionally, there is less P stored inside the filter then was removed through the course of the study lowering its reuse value even more. To extend a filter's life, the ability to rejuvenate a material is always a more cost-effective method than replacement outright (Penn et al., 2017). The results of this study determine that the likely cause of the filter failure was an exhaustion of the clay and metal oxide sorption sites coupled with improper conditions for Ca-P precipitations and a decreasing gypsum supply. Adding additional clay and gypsum particles to the filter after a period of a few months could be a potential solution. This may increase the lifespan of the filter, but at its current rate of removal would not be beneficial compared to other options currently available.

The key principles of effective PSM as detailed in Buda et al., (2012) are; low cost, high availability, low toxicity to soil and water, and potential for reuse of the material as a fertilizer/soil amendment. Of these conditions, the Filtrexx® material is initially low cost, available and showed no signs of any toxicity. The potential for reuse of the material is low and with the poor performance in terms of P removal the cost would increase with having to replace the material every few months. Penn et al., (2020) provided more specific guidelines on a wild designed PSM suggesting there must be an effective material in large amount, there must be enough contact time and flow rate through the material, and there needs an ability to rejuvenate or replace the material when needed. The main downfall of the Filtrexx® material with these criteria is there was likely not a large enough quantity of clay and gypsum inside for P removal after a few months. Other filters, such as the steel slag installations used in Penn et al., (2020) were recommended to be replaced every 4-6 months, which is about as long as the strong performance of the Filtrexx® lasted. Though meeting some criteria of effective filter type the Filtrexx® material failed in the most important factor of a PSM, the ability to remove sufficient amounts of P. Overall, because of minimal P capture, poor field performance especially over time and a low potential for reuse this filter product is unlikely to be an effective choice for P removal strategies in agricultural landscapes.

4.5 Conclusions

This study has answered numerous questions left after the field-based studies in Chapter 3 using lab experiments. Sorption tests showed the weak performance of the used LON material compared to ILD and unused material, suggesting its reduced ability to remove P, even in controlled lab experiments. Ion data (Ca^{2+} and SO_4^{-2}) showed that the release of sulfate and calcium during P removal events are likely caused by gypsum particles in the filter dissolving which provides the runoff with a source of Ca needed for Ca-P precipitation. The decrease in Ca^{2+} and SO_4^{-2} released overtime is coupled with a decrease in P removal ability, specially at ILD, suggesting the filter became depleted in the materials needed for P reduction by the Ca-P reaction. Finally, a P fractionation experiment showed that the filter at both sites were able to store a large amount of DRP over their time in the field and this P was not water soluble, but the majority of P was held in a loosely bound form, likely adsorbed onto the metal oxides or clay material within the filter. The amount of DRP stored in the filter is estimated to be 0.017 kg at LON and 0.022 kg at ILD which is less than the 0.041 Kg and 0.148 Kg DRP reductions calculated from the water samples. This shows that a large amount of DRP being removed by the filter is not remaining trapped inside, allowing the possibility of release downstream. Like many other P removal products, the Filtrexx® material showed a great ability to remove P in controlled lab experiments but was unable to repeat this success in the field. The decrease in metal-oxide binding sites and gypsum availability over time most likely contributed to its decreased performance over time after initial successes. Since most of the P held in the material was likely associated with metal oxides and clays, the runoff pH may not have been high enough for consistent P removal through the Ca-P precipitation reaction. If being used to remove P from fields, this filter will need to be changed frequently or rejuvenated with additional material to ensure an adequate supply of P removing compounds. The leftover material does not contain large amounts of P so reuse as a fertilizer is unlikely. Its potential use in

agricultural settings is thus limited because of the amount of material and cost needed in order to be effective is high and there are numerous other BMP's that can provide more benefit and have the potential to remove more P currently in wide use.

Chapter 5

Major conclusions of the thesis

This thesis has demonstrated that a commercially available geotextile filter is able to remove P from surface runoff in two agricultural fields. In Chapter 3, the filter was shown to have, over the study period, removed 16 and 18% of DRP and TP at ILD and caused a release of 21 and 6% of DRP and TP at LON. In terms of suspended sediments, the filter at ILD was able to remove 57% while the LON material removed 42%. Other PSM including steel slag and iron rich sand have shown similar levels (10-50%) of P removal in a wide variety of structures (Ayaz et al., 2012; Bryant et al., 2012: Sanford and Larson, 2016; Penn et al., 2017). Few studies have resulted in a PSM releasing P as was the case at LON (Penn et al., 2017). In Chapter 4, laboratory tests showed that the filter material has a large ability to remove P in its fresh form but material that had been exposed to runoff was degraded physically and in its P removal ability especially from LON. In the laboratory sorption tests, P removal of fresh material was 80% or higher at all P concentrations. Over the course of 18 months of runoff, the material at both LON and ILD was able to trap about 200 mg/kg of DRP inside. This is less than half of the DRP determined to be removed by each filter through the water samples suggest a majority of the removed P did not remain inside the filter. These results show that the material did not perform as well in the field as it did in the lab which is consistent with many PSM studies (Renman and Renman 2010; Klimeski et al., 2012; Postila et al., 2017).

The results of this thesis suggest that multiple mechanisms for nutrient and sediment removal were occurring within the filter material. Firstly, sediments were likely settled out through a physical removal process of getting trapped within the large pieces of woodchips in the filter (Choudhury et al., 2016). This process can only trap the heaviest sediments as the filter did not remove all TSS and most events had similar levels of removal. It is also possible that some portion of PP was trapped in the filter material this way resulting in lower TP values. The second mechanism of removal is chemical removal of DRP. This likely occurred mostly through a ligand exchange reaction between phosphate and metal oxides/clay particles inside the filter (Liu et al., 2018). After being in the field for 18 months the filter material the majority of all DRP held in the filter was associated with metal oxides/clays leaving it more exposed to release. Even though the filter is filled with Ca rich gypsum and the runoff samples showed evidence of this gypsum dissolving, only small amounts of P bound with Ca was found in the material. This is very different than other Ca rich materials such as steel slag and opoka rock which have shown the majority of P removed is held in some form of Ca precipitate (Hylander and Siman, 2006). The laboratory sorption tests did demonstrate P removal via Ca precipitation, especially with the unused material, once again highlighting differences between performance in controlled and uncontrolled environments.

Numerous factors could have impacted the ability of the materials to remove P in the field. The likely most important factor is the time after installation. Chapter 3 detailed how both sites saw the best P removal during events that occurred in the first 8 months of the study. After a few months, the gypsum contained in the filter was greatly reduced and the binding sites on metal oxides and clays were also likely nearly full, and thus additional P removal was unlikely. This is

consistent with other studies which involved PSM where materials were either replaced or started to experience decline after a few months of use (Hemmann et al., 2014; Penn et al., 2020). Flow rate through the material also likely played a role but this study did not isolate flow rate enough to determine its exact impact. Other studies have shown that lower flow rates allow for more contact time between runoff and material and thus result in larger P removal rates (Buda et al., 2012). Finally, P and metal ion concentration are also key to the effective use of PSM as the larger amount of P and ions available in water the easier it is to have removal (Johanssan and Gustafsson, 2000; Klimeski et al., 2012; Zhang et al., 2016). A number of lab studies of PSM use high levels of P that are much higher than what would be experienced in field settings (Szabo et al., 2008; Penn et al., 2017). As a result of multiple CPs already being in use on both field sites the concentrations of DRP in surface runoff was often very low ($\leq$0.5 mg/L) compared to other sites using PSM. Other factors including pH and filter material grain size also likely contributed to the difference in the materials performance in the lab and the field (Szabo et al., 2008).

This thesis also provides information on what would make this filter product economically viable in a typical agricultural operation. The first difficulty with this filter is that it is located at the edge-of-field and unlike other CPs, cannot provide the farm with secondary benefits of lower input costs or improved soil structure in addition to removing P. As shown in Chapter 4 the cost of removing 1 kg of TP with the filter was around $3000 at ILD and $10 000 at LON. In comparison to other PSM these values are on the high end (Gachango et al., 2015; Penn et al., 2017; Penn et al., 2020). Buda et al., (2012) suggest that P rich material from PSM can be used a fertilizer to provide an agronomic benefit after P removal had occurred. However, Chapter 4 demonstrated that less than half of the DRP removed by the filter was actually stored inside the material, reducing the usefulness of the saturated filter material as a fertilizer. Withers et al., (2015) confirm that the amount of P available to be recovered from a typical field is very small and likely not economically viable to capture. For all of these reasons, the Filtrexx® filter material is unlikely to be an economically sound investment for P removal at the field level in its current form.

This work has demonstrated how a geotextile full of PSM can be implemented on a field scale in the Great Lakes region. The stacking of multiple CPs on a single field was also explored, demonstrating a potential suite of practices that could be implemented at other fields. The results showed that that already low levels of P in runoff at the study sites can be reduced further but this is difficult and not consistent. Thus, although PSM have the potential to reduce P at the edge of the field, they may not be as effective as other CPs such as no-till or nutrient management. Additional research on the use of PSM in agricultural settings should focus on cost effective materials that can be replenished or recharged frequently, and also on P retention from fields that are less carefully managed. Further study should also take place at fields with legacy P to ensure adequate supply of P for removal. In order to reach P reduction targets in the next few years more conventional CPs such as reduced tillage and cover cropping are the most likely to help landowners lower P in runoff while providing additional agronomic benefits.

Bibliogrpahy

Abu-Zreig, M., Rudra, R. P., Whiteley, H. R., Lalonde, M. N., & Kaushik, N. K. (2003). Phosphorus Removal in Vegetated Filter Strips. *Journal of Environmental Quality*, *32*(2), 613–619. https://doi.org/10.2134/jeq2003.6130

Al-Kaisi, M., & Kwaw-Mensah, D. (2007). Effect of Tillage and Nitrogen Rate on Corn Yield and Nitrogen and Phosphorus Uptake in a Corn-Soybean Rotation. *Agronomy Journal*, *99*(6), 1548–1558. https://doi.org/10.2134/agronj2007.0012

Andrews, D. M., Lin, H., Zhu, Q., Jin, L., & Brantley, S. L. (2011). Hot Spots and Hot Moments of Dissolved Organic Carbon Export and Soil Organic Carbon Storage in the Shale Hills Catchment. *Vadose Zone Journal*, *10*(3), 943–954. https://doi.org/10.2136/vzj2010.0149

Antelo, J., Avena, M., Fiol, S., López, R., & Arce, F. (2005). Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface. *Journal of Colloid and Interface Science*, *285*(2), 476–486. https://doi.org/10.1016/j.jcis.2004.12.032

Ayaz, S. C., Aktaş, Ö., Findik, N., & Akça, L. (2012). Phosphorus removal and effect of adsorbent type in a constructed wetland system. *Desalination and Water Treatment*, *37*(1–3), 152–159. https://doi.org/10.1080/19443994.2012.661267

Baker, M. J., Blowes, D. W., & Ptacek, C. J. (1998). Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite wastewater disposal systems. *Environmental Science and Technology*, *32*(15), 2308–2316. https://doi.org/10.1021/es970934w.

Barca, C., Gérente, C., Meyer, D., Chazarenc, F., & Andrès, Y. (2012). Phosphate removal from synthetic and real wastewater using steel slags produced in Europe. *Water Research*, *46*(7), 2376–2384. https://doi.org/10.1016/j.watres.2012.02.012

Barrow, N. J., Sen, A., Roy, N., & Debnath, A. (2021). The soil phosphate fractionation fallacy. *Plant and Soil*, *459*(1–2), 1–11. https://doi.org/10.1007/s11104-020-04476-6

Bauwe, A., Kahle, P., & Lennartz, B. (2019). Impact of filters to reduce phosphorus losses: Field observations and modelling tests in tile-drained lowland catchments. *Water (Switzerland)*, *11*(12). https://doi.org/10.3390/W11122638

Bengtson, R.L., Carter, C.E., Morris, H.F., & Bartkiewicz, S.A. (1988). The inlfuence of subsurface drainage practices on nitrogen and phosphorus losses in a warm, humid climate. *Transactions of the ASAE*, *31*(3), 729–733.

Braskerud, B. C. (2002). Factors affecting phosphorus retention in small constructed wetlands treating agricultural non-point source pollution. *Ecological Engineering*, *19*(1), 41–61. https://doi.org/10.1016/S0925-8574(02)00014-9

Bryant, R. B., Buda, A. R., Kleinman, P. J. A., Church, C. D., Saporito, L. S., Folmar, G. J., Bose, S., & Allen, A. L. (2012). Using Flue Gas Desulfurization Gypsum to Remove Dissolved Phosphorus from Agricultural Drainage Waters. *Journal of Environmental Quality*, *41*(3), 664–671. https://doi.org/10.2134/jeq2011.0294

Bosch, N. S., Allan, J. D., Selegean, J. P., & Scavia, D. (2013). Scenario-testing of agricultural

best management practices in Lake Erie watersheds. *Journal of Great Lakes Research*, *39*(3), 429–436. https://doi.org/10.1016/j.jglr.2013.06.004

Bowden, L. I., Jarvis, A. P., Younger, P. L., & Johnson, K. L. (2009). Phosphorus removal from waste waters using basic oxygen steel slag. *Environmental Science and Technology*, *43*(7), 2476–2481. https://doi.org/10.1021/es801626d

Boyer, T. H., Persaud, A., Banerjee, P., & Palomino, P. (2011). Comparison of low-cost and engineered materials for phosphorus removal from organic-rich surface water. *Water Research*, *45(4)*, 803-814.

Buda, A. R., Koopmans, G. F., Bryant, R. B., & Chardon, W. J. (2012). Emerging Technologies for Removing Nonpoint Phosphorus from Surface Water and Groundwater: Introduction. *Journal of Environmental Quality*, *41*(3), 621–627. https://doi.org/10.2134/jeq2012.0080

Calvert, D. V.(1975).Nitrate, Phosphate, and Potassium movement into drainage lines under three soil management systems. *Journal of Environmental Quality*, *4(2)*, 183–186.

Canga, E., Kjaergaard, C., Iversen, B. V., & Heckrath, G. J. (2016). Agricultural Drainage Filters. I. Filter Hydro-Physical Properties and Tracer Transport. *Water, Air, and Soil Pollution*, *227*(8). https://doi.org/10.1007/s11270-016-2987-8

Cao, X., Harris, W.G., Josan, M. S., & Nair, V. D. (2007). Inhibition of calcium phosphate precipitation under environmentally-relevant conditions. *Science of the Total Environment.* 383, 205-215.

Carpenter, S.R., Caraco, N.F., Correll, D. L., Howarth, R.W., Sharpley, A.N., & Smith, V. H. (1998). Nonpoint pollution of sourface waters with phosphorus and nitrogen. *Ecological Applications.* 8(3), 559-568.

Chen, D., Szostak, P., Wei, Z., & Xiao, R. (2016). Reduction of orthophosphates loss in agricultural soil by nano calcium sulfate. *Science of the Total Environment*, *539*, 381–387. https://doi.org/10.1016/j.scitotenv.2015.09.028

Chorus, I., & Mur, L. R.(1999). Preventative Measures. *Toxic cyanobacteria in water: A guide to their public health consequences, monitoring and managementl*. 235-273.

Choudhury, T., Robertson, W. D., & Finnigan, D. S. (2016). Suspended Sediment and Phosphorus Removal in a Woodchip Filter System Treating Agricultural Wash Water. *Journal of Environmental Quality*, *45*(3), 796–802. https://doi.org/10.2134/jeq2015.07.0380

Cordell, D., Drangert, J. O., & White, S. (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change*, *19*(2), 292–305. https://doi.org/10.1016/j.gloenvcha.2008.10.009

Costa, D., Liu, J., Roste, J., & Elliott, J. (2019). Temporal Dynamics of Snowmelt Nutrient Release from Snow–Plant Residue Mixtures: An Experimental Analysis and Mathematical Model Development. *Journal of Environmental Quality*, *48*(4), 869–879. https://doi.org/10.2134/jeq2018.12.0440

Cucarella, V., & Renman, G. (2009). Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments-a comparative study. *J

Environ Qual, *38*(2), 381–392. https://doi.org/10.2134/jeq2008.0192

Dabney, S.M., Moore, M. T., & Locke, M. A. (2006). Integrated Management of in-Field Edge of Field and After Field Buffers. *Journal of the American Water Resources Association. 42(1)*, 15–24.

Dagnew, A., Scavia, D., Wang, Y., Muenich, R., & Kalcic, M. (2019). Modeling phosphorus reduction strategies from the international St.Clair-Detroit River system watershed. *Journal of Great Lakes Research. 45,* 742–751.

Darch, T., Carswell, A., Blackwell, M. S. A., Hawkins, J. M. B., Haygarth, P. M., & Chadwick, D. (2015). Dissolved Phosphorus Retention in Buffer Strips: Influence of Slope and Soil Type. *Journal of Environmental Quality*, *44*(4), 1216–1224. https://doi.org/10.2134/jeq2014.10.0440

Devlin, T. R., Di Biase, A., Wei, V., Elektorowicz, M., & Oleszkiewicz, J. A. (2017). Removal of Soluble Phosphorus from Surface Water Using Iron (Fe-Fe) and Aluminum (Al-Al) Electrodes. *Environmental Science and Technology*, *51*(23), 13825–13833. https://doi.org/10.1021/acs.est.7b02353

Diaz, O. A., Reddy, K. R., & Moore, P. A. (1994). Solubility of inorganic phosphorus in stream water as influenced by pH and calcium concentration. *Water Research*, *28*(8), 1755–1763. https://doi.org/10.1016/0043-1354(94)90248-8

Dils, J. L., & Heathwaite, H. M. (1999). The controversal role of tile drainage in phosphorus export from agricultural lands. *Water Science & Technology*, *39*(12), 55-61.

Dodd, R. J., & Sharpley, A. N. (2015). Recognizing the role of soil organic phosphorus in soil fertility and water quality. *Resources, Conservation and Recycling*, *105*, 282–293. https://doi.org/10.1016/j.resconrec.2015.10.001

Domagalski, J. L., & Johnson, H. M. (2011). Subsurface transport of orthophosphate in five agricultural watersheds, USA. *Journal of Hydrology*, *409*(1–2), 157–171. https://doi.org/10.1016/j.jhydrol.2011.08.014

Drizo, A., Cummings, J., Weber, D., Twohig, E., Druschel, G., & Bourke, B. (2008). New evidence for rejuvenation of phosphorus retention capacity in EAF steel slag. *Environmental Science and Technology*, *42*(16), 6191–6197. https://doi.org/10.1021/es800232r

Duncan, E. W., King, K. W., Williams, M. R., LaBarge, G., Pease, L. A., Smith, D. R., & Fausey, N. R. (2017). Linking Soil Phosphorus to Dissolved Phosphorus Losses in the Midwest. *Agricultural & Environmental Letters*, *2*(1), 170004. https://doi.org/10.2134/ael2017.02.0004

Elrashidi, M. A., Mays, M. D., Fares, A., Seybold, C. A., Harder, J. L., Peaslee, S. D., & VanNeste, P. (2005). Loss of nitrate-nitrogen by runoff and leaching for agricultural watersheds. *Soil Science*, *170*(12), 969–984. https://doi.org/10.1097/01.ss.0000187353.24364.a8

Espinosa, D., Sale, P., & Tang, C. (2017). Effect of soil phosphorus availability and residue quality on phosphorus transfer from crop residues to the following wheat. *Plant and Soil*, *416*(1–2), 361–375. https://doi.org/10.1007/s11104-017-3222-0

Favaretto, N., Norton, L. D., Johnston, C. T., Bigham, J., & Sperrin, M. (2012). Nitrogen and phosphorus leaching as affected by gypsum amendment and exchangeable calcium and magnesium. *Soil Science Society of American Journal*. 76, 575-585.

Foyjunnessa, McNeill, A., Doolette, A., Mason, S., & McLaughlin, M. J. (2016). Use of 33P to trace in situ the fate of canola below-ground phosphorus, including wheat uptake in two contrasting soils. *Crop and Pasture Science*, *67*(7), 726–738. https://doi.org/10.1071/CP15311

Gachango, F. G., Pedersen, S. M., & Kjaergaard, C. (2015). Cost-Effectiveness Analysis of Surface Flow Constructed Wetlands (SFCW) for Nutrient Reduction in Drainage Discharge from Agricultural Fields in Denmark. *Environmental Management*, *56*(6), 1478–1486. https://doi.org/10.1007/s00267-015-0585-y

Gagnon, B., Ziadi, N., Bélanger, G., & Parent, G. (2020). Validation and use of critical phosphorus concentration in maize. *European Journal of Agronomy*, *120*(May), 1–9. https://doi.org/10.1016/j.eja.2020.126147

Gaynor, J. D., & Findlay, W. I. (1995). Soil and phosphorus loss from conservation and concentional tillage in corn production. *Journal of Environmental Quality*, *24*(4), 734-741.

Gburek, W. J., & Sharpley, A. N. (1998). Hydrologic Controls on Phosphorus Loss from Upland Agricultural Watersheds. *Journal of Environmental Quality*, *27*(2), 267–277. https://doi.org/10.2134/jeq1998.00472425002700020005x

Gérard, F. (2016). Clay minerals, iron/aluminum oxides, and their contribution to phosphate sorption in soils - A myth revisited. *Geoderma*, *262*, 213–226. https://doi.org/10.1016/j.geoderma.2015.08.036

Glaister, B. J., Fletcher, T. D., Cook, P. L. M., & Hatt, B. E. (2014). Co-optimisation of phosphorus and nitrogen removal in stormwater biofilters: The role of filter media, vegetation and saturated zone. *Water Science and Technology*, *69*(9), 1961–1969. https://doi.org/10.2166/wst.2014.117

Gorazda, K., Wizarek, Z., Tarko, B., Nowak, A. K., Kulczycka, J., & Henclik, A. (2013). Phosphorus Cycle-possibilties for its rebuilding. *ACTA Biochimica Polonica*, *60(4)*, 725-730.

Gottschall, N., Edwards, M., Craiovan, E., Frey, S. K., Sunohara, M., Ball, B., Zoski, E., Topp, E., Khan, I., Clark, I. D., & Lapen, D. R. (2016). Amending woodchip bioreactors with water treatment plant residuals to treat nitrogen, phosphorus, and veterinary antibiotic compounds in tile drainage. *Ecological Engineering*, *95*, 852–864. https://doi.org/10.1016/j.ecoleng.2016.06.011

Graetz, D.A, & Nair, V.D. (2009). Phosphorus sorption isotherm detemination. In: Kovar, J.L., & Pierzynski, G.M. (Eds.), *Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Waters,* 2nd ed Virignia Tech University, 33-37.

Grant, K. N., Macrae, M. L., Rezanezhad, F., & Lam, W. V. (2019). Nutrient Leaching in Soil Affected by Fertilizer Application and Frozen Ground. *Vadose Zone Journal*, *18*(1), 1–13. https://doi.org/10.2136/vzj2018.08.0150

Grubb, K. L., McGrath, J. M., Penn, C. J., & Bryant, R. B. (2012). Effect of land application of phosphorus-saturated gypsum on soil phosphorus in a laboratory incubation. *Applied and Environmental Soil Science*, *2012*, 9–12. https://doi.org/10.1155/2012/506951

Hagerty, T.P., & Kingston, M.S. (1992). The Soils of Middlesex County. *Ontario Ministry of Agriculture and Food.*

Hanief, A., & Laursen, A. E. (2019). Meeting updated phosphorus reduction goals by applying best management practices in the Grand River watershed, southern Ontario. *Ecological Engineering*, *130*, 169–175. https://doi.org/10.1016/j.ecoleng.2019.02.007

Haygarth, P. M., Hepworth, L., & Jarvis, S. C. (1998). Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland. *European Journal of Soil Science*, *49*(1), 65–72. https://doi.org/10.1046/j.1365-2389.1998.00131.x

Haygarth, P. M., & Jarvis, S. C. (1997). Soil derived phosphorus in surface runoff from grazed grassland lysimeters. In *Water Research* (Vol. 31, Issue 1, pp. 140–148). https://doi.org/10.1016/S0043-1354(99)80002-5

Herrmann, I., Jourak, A., Hedstrom, A., Lundstrom, S., & Viklander, M. (2014). Enhancing the reliability of laboratory phosphorus filter tests:Effect of influent propertieis and interpretation of effluent parameters. *Water, Air and Soil Pollution*, *225:1766*, 1–11.

He, K., Li, X., & Dong, L. (2018). The effects of flue gas desulfurization gypsum (FGD gypsum) on P fractions in a coastal plain soil. *Journal of Soils and Sediments*, *18*(3), 804–815. https://doi.org/10.1007/s11368-017-1821-2

Hill, C.M., Duxbury, J., Geohring, L., & Peck, T. (2000). Designing constructed wetlands to remove phosphorus from barnyard runoff: A comparison of four alternative substrates. *Journal of Environmental Science and Health*. 35(8), 1357-1375.

Hinsinger, P. (2001). Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant and Soil*. 237(2), 173-195.

Hoffman, A. R., Polebitski, A. S., Penn, M. R., & Busch, D. L. (2019). Long-term Variation in Agricultural Edge-of-Field Phosphorus Transport during Snowmelt, Rain, and Mixed Runoff Events. *Journal of Environmental Quality*, *48*(4), 931–940. https://doi.org/10.2134/jeq2018.11.0420

Hoffmann, C. C., Kjaergaard, C., Uusi-Kämppä, J., Hansen, H. C. B., & Kronvang, B. (2009). Phosphorus Retention in Riparian Buffers: Review of Their Efficiency. *Journal of Environmental Quality*, *38*(5), 1942–1955. https://doi.org/10.2134/jeq2008.0087

Hoffman, D.W., Richards, N.R., & Morwick, F.F., (1952). " Soil survey of Huron county (No.13)." Experimental Farms Service, Canada Department of Agriculture and the Ontario Agricultural College.

Hylander, L. D., Kietlińska, A., Renman, G., & Simán, G. (2006). Phosphorus retention in filter

materials for wastewater treatment and its subsequent suitability for plant production. *Bioresource Technology*, *97*(7), 914–921. https://doi.org/10.1016/j.biortech.2005.04.026

Hylander, L. D., & Simán, G. (2006). Phosphorus fractionation in soils and wastewater sorbent materials as an indicator of material specific and storage-dependant availability. *Communications in Soil Science and Plant Analysis*, *37*(7–8), 1013–1030. https://doi.org/10.1080/00103620600584362

International Joint Commission (IJC), 2014. A balanced diet for Lake Erie: reducing phosphorus loadings and harmful algal blooms. *Report of the Lake Erie Ecosystem Priority* http://www.ijc.org/files/publications/2014%20IJC%20LEEP%20REPORT.pdf.

James, B. R., Rabenhorst, M. C., & Frigon, G. A. (1992). Phosphorus sorption by peat and sand amended with iron oxides or steel wool. *Water Environment Research*, *64*(5), 699–705. https://doi.org/10.2175/wer.64.5.6

Jarvie, H. P., Withers, J. A., & Neal, C. (2002). Review of robust measurement of phosphorus in river water: Sampling, storage, fractionation and sensitivity. *Hydrology and Earth System Sciences*, *6*(1), 113–132. https://doi.org/10.5194/hess-6-113-2002

Jenssen, P., & Krogstad,T. (2003).Design of constructed wetlands using phosphorus sorbing lightweight aggregate (LWA).*Consturcted Wetlands for Wastewater Treatment in Cold Climates*, *11*, 259–272.

Jiang, C., Jia, L., He, Y., Zhang, B., Kirumba, G., & Xie, J. (2013). Adsorptive removal of phosphorus from aqueous solution using sponge iron and zeolite. *Journal of Colloid and Interface Science*, *402*, 246–252. https://doi.org/10.1016/j.jcis.2013.03.057

Johansson, L., & Gustafsson, J. P. (2000). Phosphate removal using blast furnace slags and opoka-mechanisms. *Water Research*, *34*(1), 259–265. https://doi.org/10.1016/S0043-1354(99)00135-9

Johansson Westholm, L. (2006). Substrates for phosphorus removal - Potential benefits for on-site wastewater treatment? *Water Research*, *40*(1), 23–36. https://doi.org/10.1016/j.watres.2005.11.006

Karageorgiou, K., Paschalis, M., & Anastassakis, G. N. (2007). Removal of phosphate species from solution by Adsorption onto calcite used as natural adsorbent. *Journal of Hazardous Materials*. A139, 447–452.

Kholoma, E., Renman, G., & Renman, A. (2016). Phosphorus removal from wastewater by field-scale fortified filter beds during a one-year study. *Environmental Technology (United Kingdom)*, *37*(23), 2953–2963. https://doi.org/10.1080/09593330.2016.1170888

Kieta, K. A., Owens, P. N., Lobb, D. A., Vanrobaeys, J. A., & Flaten, D. N. (2018). Phosphorus dynamics in vegetated buffer strips in cold climates: A review. *Environmental Reviews*, *26*(3), 255–272. https://doi.org/10.1139/er-2017-0077

Kim, E. H., Yim, S. Bin, Jung, H. C., & Lee, E. J. (2006). Hydroxyapatite crystallization from a highly concentrated phosphate solution using powdered converter slag as a seed material. *Journal of Hazardous Materials*, *136*(3), 690–697. https://doi.org/10.1016/j.jhazmat.2005.12.051

King, K. W., Williams, M. R., Dick, W. A., & LaBarge, G. A. (2016). Decreasing Phosphorus Loss in Tile-Drained Landscapes Using Flue Gas Desulfurization Gypsum. *Journal of Environmental Quality*, *45*(5), 1722–1730. https://doi.org/10.2134/jeq2016.04.0132

King, Kevin W., Williams, M. R., Macrae, M. L., Fausey, N. R., Frankenberger, J., Smith, D. R., Kleinman, P. J. A., & Brown, L. C. (2015). Phosphorus Transport in Agricultural Subsurface Drainage: A Review. *Journal of Environmental Quality*, *44*(2), 467–485. https://doi.org/10.2134/jeq2014.04.0163

Kirkkala, T., Ventelä, A.-M., & Tarvainen, M. (2012). Long-Term Field-Scale Experiment on Using Lime Filters in an Agricultural Catchment. *Journal of Environmental Quality*, *41*(2), 410–419. https://doi.org/10.2134/jeq2010.0429

Klimchouk, A. (1996). The dissolution and conversion of gypsum and anhydrite. *International Journal of Speleology*, *25*(3/4), 21–36. https://doi.org/10.5038/1827-806x.25.3.2

Klimeski, A., Chardon, W. J., Turtola, E., & Uusitalo, R. (2012). Potential and limitations of phosphate retention media in water protection: A process-based review of laboratory and field-scale tests. *Agricultural and Food Science*, *21*(3), 206–223. https://doi.org/10.23986/afsci.4806

Klimeski, A., Uusitalo, R., & Turtola, E. (2014). Screening of Ca- and Fe-rich materials for their applicability as phosphate-retaining filters. *Ecological Engineering*, *68*, 143–154. https://doi.org/10.1016/j.ecoleng.2014.03.054

Koerner, R. M., & Koerner, G. R. (2015). Lessons learned from geotextile filter failures under challenging field conditions. *Geotextiles and Geomembranes*, *43*(3), 272–281. https://doi.org/10.1016/j.geotexmem.2015.01.004

Kordlaghari, M. P., & Rowell, D. L. (2006). The role of gypsum in the reactions of phosphate with soils. *Geoderma*, *132*(1–2), 105–115. https://doi.org/10.1016/j.geoderma.2005.04.022

Kunaschk, M., Schmalz, V., Dietrich, N., Dittmar, T., & Worch, E. (2015). Novel regeneration method for phosphate loaded granular ferric (hydr)oxide - A contribution to phosphorus recycling. *Water Research*, *71*, 219–226. https://doi.org/10.1016/j.watres.2015.01.001

Lake Erie LaMP. (2011). Lake Erie Binational Nutrient Management Strategy: Protecting Lake Erie by Managing Phosphorus. Prepared by the Lake Erie LaMP Work Group Nutrient Management Task Group. https://www.epa.gov/sites/default/files/2015-09/documents/binational_nutrient_management.pdf

Lam, W. V., Macrae, M. L., English, M. C., O'Halloran, I. P., & Wang, Y. T. (2016). Effects of tillage practices on phosphorus transport in tile drain effluent under sandy loam agricultural soils in Ontario, Canada. *Journal of Great Lakes Research*, *42*(6), 1260–1270. https://doi.org/10.1016/j.jglr.2015.12.015

Lee, K. H., Isenhart, T. M., & Schultz, R. C. (2003). Sediment and nutrient removal in an established multi-species riparian buffer. *Journal of Soil and Water Conservation*, *58*(1), 1–8.

Lemke, A. M., Kirkham, K. G., Lindenbaum, T. T., Herbert, M. E., Tear, T. H., Perry, W. L., & Herkert, J. R. (2011). Evaluating agricultural best management practices in tile-drained

subwatersheds of the Mackinaw River, Illinois. *Journal of Environmental Quality*, *40*(4), 1215–1228. https://doi.org/10.2134/jeq2010.0119

Lemunyon, J.L., & Gilbert, R. G. (1993). The concept and need for a phosphorus assessment tool. *Journal of Production Agriculture*, *6(4)*, 483–486.

Li, B., & Brett, M. T. (2013). The influence of dissolved phosphorus molecular form on recalcitrance and bioavailability. *Environmental Pollution*, *182*, 37–44. https://doi.org/10.1016/j.envpol.2013.06.024

Liu, R.T., Chi, L.N., Wang, X.Z., Sui, Y.M., Wang, Y., Arandiyan, H., (2018). Review of metal (hydr)oxide and other adsorptive materials for phosphate removal from water. *J. Environ. Chem. Eng.*, *6*, 5269-5286.

Liu, T., Wu, K., & Zeng, L. (2012). Removal of phosphorus by a composite metal oxide adsorbent derived from manganese ore tailings. *Journal of Hazardous Materials*, *217–218*, 29–35. https://doi.org/10.1016/j.jhazmat.2012.01.019

Lozier, T. M., Macrae, M. L., Brunke, R., & Van Eerd, L. L. (2017). Release of phosphorus from crop residue and cover crops over the non-growing season in a cool temperate region. *Agricultural Water Management*, *189*, 39–51. https://doi.org/10.1016/j.agwat.2017.04.015

Lozier, Tatianna M., & Macrae, M. L. (2017). Potential phosphorus mobilization from above-soil winter vegetation assessed from laboratory water extractions following freeze–thaw cycles. *Canadian Water Resources Journal*, *42*(3), 276–288. https://doi.org/10.1080/07011784.2017.1331140

Lu, C., & Tian, H. (2017). Global nitrogen and phosphorus fertilizer use for agriculture production in the past half century: shifted hot spots and nutrient imbalance. Earth System Science Data. 9 (1), 181-192.

Lu, S. Y., Wu, F. C., Lu, Y. F., Xiang, C. S., Zhang, P. Y., & Jin, C. X. (2009). Phosphorus removal from agricultural runoff by constructed wetland. *Ecological Engineering*, *35*(3), 402–409. https://doi.org/10.1016/j.ecoleng.2008.10.002

Lyngsie, G., Penn, C. J., Hansen, H. C. B., & Borggaard, O. K. (2014). Phosphate sorption by three potential filter materials as assessed byisothermal titration calorimetry. *Journal of Environmental Management*, *143*, 26–33. https://doi.org/10.1016/j.jenvman.2014.04.010

Maccoux, M. J., Dove, A., Backus, S. M., & Dolan, D. M. (2016). Total and soluble reactive phosphorus loadings to Lake Erie: A detailed accounting by year, basin, country, and tributary. *Journal of Great Lakes Research*, *42*(6), 1151–1165. https://doi.org/10.1016/j.jglr.2016.08.005

Macrae, M., Jarvie, H., Brouwer, R., Gunn, G., Reid, K., Joosse, P., King, K., Kleinman, P., Smith, D., Williams, M., & Zwonitzer, M. (2021). One size does not fit all: Toward regional conservation practice guidance to reduce phosphorus loss risk in the Lake Erie watershed. *Journal of Environmental Quality*, *50*(3), 529–546. https://doi.org/10.1002/jeq2.20218

Macrae, M. L., English, M. C., Schiff, S. L., & Stone, M. (2007). Intra-annual variability in the contribution of tile drains to basin discharge and phosphorus export in a first-order

agricultural catchment. *Agricultural Water Management*, *92*(3), 171–182. https://doi.org/10.1016/j.agwat.2007.05.015

Manimel Wadu, M. C. W., Michaelis, V. K., Kroeker, S., & Akinremi, O. O. (2013). Exchangeable Calcium/Magnesium Ratio Affects Phosphorus Behavior in Calcareous Soils. *Soil Science Society of America Journal*, *77*(6), 2004–2013. https://doi.org/10.2136/sssaj2012.0102

McDowell, R. W., & Nash, D. (2012). A Review of the Cost-Effectiveness and Suitability of Mitigation Strategies to Prevent Phosphorus Loss from Dairy Farms in New Zealand and Australia. *Journal of Environmental Quality*, *41*(3), 680–693. https://doi.org/10.2134/jeq2011.0041

Meinikmann, K., Lewandowski, J., & Hupfer, M. (2015). Phosphorus in groundwater discharge - A potential source for lake eutrophication. *Journal of Hydrology*, *524*, 214–226. https://doi.org/10.1016/j.jhydrol.2015.02.031

Mendes, L. R. D. (2020). Edge-of-Field technologies for phosphorus retention from agricultural drainage discharge. *Applied Sciences (Switzerland)*, *10*(2). https://doi.org/10.3390/app10020634

Mendes, L. R. D., Tonderski, K., Iversen, B. V., & Kjaergaard, C. (2018). Phosphorus retention in surface-flow constructed wetlands targeting agricultural drainage water. *Ecological Engineering*, *120*(May), 94–103. https://doi.org/10.1016/j.ecoleng.2018.05.022

Mittelstet, A. R., Heeren, D. M., Fox, G. A., Storm, D. E., White, M. J., & Miller, R. B. (2011). Comparison of subsurface and surface runoff phosphorus transport rates in alluvial floodplains. *Agriculture, Ecosystems and Environment*, *141*(3–4), 417–425. https://doi.org/10.1016/j.agee.2011.04.006

Murphy, J., & Riley, J. P. (1962). DETERMrNATION SINGLE SOLUTION METHOD FOR THE IN NATURAL. *Analytica Chimica Acta*, *27*, 31–36.

Noack, S. R., McBeath, T. M., McLaughlin, M. J., Smernik, R. J., & Armstrong, R. D. (2014). Management of crop residues affects the transfer of phosphorus to plant and soil pools: Results from a dual-labelling experiment. *Soil Biology and Biochemistry*, *71*, 31–39. https://doi.org/10.1016/j.soilbio.2013.12.022

Noack, S. R., McLaughlin, M. J., Smernik, R. J., McBeath, T. M., & Armstrong, R. D. (2012). Crop residue phosphorus: Speciation and potential bio-availability. *Plant and Soil*, *359*(1–2), 375–385. https://doi.org/10.1007/s11104-012-1216-5

Øgaard, A. F. (2015). Freezing and thawing effects on phosphorus release from grass and cover crop species. *Acta Agriculturae Scandinavica Section B: Soil and Plant Science*, *65*(6), 529–536. https://doi.org/10.1080/09064710.2015.1030444

Owens, P. N., Duzant, J. H., Deeks, L. K., Wood, G. A., Morgan, R. P. C., & Collins, A. J. (2007). Evaluation of contrasting buffer features within an agricultural landscape for reducing sediment and sediment-associated phosphorus delivery to surface waters. *Soil Use and Management*, *23*(SUPPL. 1), 165–175. https://doi.org/10.1111/j.1475-2743.2007.00121.x

Parfitt, R.L. (1979). The availability of P from Phophate-Goethite bridging complexes. Desorption and uptake by ryegrass. *Plant and Soil*, *53*, 55–65.

Pease, L. A., King, K. W., Williams, M. R., LaBarge, G. A., Duncan, E. W., & Fausey, N. R. (2018). Phosphorus export from artificially drained fields across the Eastern Corn Belt. *Journal of Great Lakes Research*, *44*(1), 43–53. https://doi.org/10.1016/j.jglr.2017.11.009

Penn, C., Bowen, J., McGrath, J., Nairn, R., Fox, G., Brown, G., Wilson, S., & Gill, C. (2016). Evaluation of a universal flow-through model for predicting and designing phosphorus removal structures. *Chemosphere*, *151*, 345–355. https://doi.org/10.1016/j.chemosphere.2016.02.105

Penn, C., Chagas, I., Klimeski, A., & Lyngsie, G. (2017). A review of phosphorus removal structures: How to assess and compare their performance. *Water (Switzerland)*, *9*(8), 1–22. https://doi.org/10.3390/w9080583

Penn, C. J., Bryant, R. B., Needelman, B., & Kleinman, P. (2007). Spatial distribution of soil phosphorus across selected New York dairy farm pastures and hay fields. *Soil Science*, *172*(10), 797–810. https://doi.org/10.1097/SS.0b013e3180d0a3c0

Penn, C. J., & McGrath, J. M. (2011). Predicting Phosphorus Sorption onto Steel Slag Using a Flow-through approach with Application to a Pilot Scale System. *Journal of Water Resource and Protection*, *03*(04), 235–244. https://doi.org/10.4236/jwarp.2011.34030

Penn, C. J., & Warren, J. G. (2009). Investigating Phosphorus Sorption onto Kaolinite Using Isothermal Titration Calorimetry. *Soil Science Society of America Journal*, *73*(2), 560–568. https://doi.org/10.2136/sssaj2008.0198

Penn, C., Livingston, S., Shedekar, V., King, K., & Williams, M. (2020). Performance of field-scale phosphorus removal structures utilizing steel slag for treatment of subsurface drainage. *Water (Switzerland)*, *12*(2). https://doi.org/10.3390/w12020443

Penn, C., McGrath, J., Bowen, J., & Wilson, J. (2014). Phosphorus removal structures: A management option for legacy phosphorus. *Journal of Soil and Water Conservation 69*(2), 51-56.

Pionke, H. B., Gburek, W. J., & Sharpley, A. N. (2000). Critical source area controls on water quality in an agricultural watershed located in the Chesapeake Basin. *Ecological Engineering*, *14*(4), 325–335. https://doi.org/10.1016/S0925-8574(99)00059-2

Plach, J. M., Macrae, M. L., Williams, M. R., Lee, B. D., & King, K. W. (2018). Dominant glacial landforms of the lower Great Lakes region exhibit different soil phosphorus chemistry and potential risk for phosphorus loss. *Journal of Great Lakes Research*, *44*(5), 1057–1067. https://doi.org/10.1016/j.jglr.2018.07.005

Plach, J., Pluer, W., Macrae, M., Kompanizare, M., McKague, K., Carlow, R., & Brunke, R. (2019). Agricultural Edge-of-Field Phosphorus Losses in Ontario, Canada: Importance of the Nongrowing Season in Cold Regions. *Journal of Environmental Quality*, *48*(4), 813–821. https://doi.org/10.2134/jeq2018.11.0418

Postila, H., Karjalainen, S. M., & Kløve, B. (2017). Can limestone, steel slag or man-made sorption materials be used to enhance phosphate-phosphorus retention in treatment wetland

for peat extraction runoff with low phosphorous concentration? *Ecological Engineering*, *98*, 403–409. https://doi.org/10.1016/j.ecoleng.2016.05.042

Powers, S. M., Chowdhury, R. B., MacDonald, G. K., Metson, G. S., Beusen, A. H. W., Bouwman, A. F., Hampton, S. E., Mayer, B. K., McCrackin, M. L., & Vaccari, D. A. (2019). Global Opportunities to Increase Agricultural Independence Through Phosphorus Recycling. *Earth's Future*, *7*(4), 370–383. https://doi.org/10.1029/2018EF001097

Rao, N. S., Easton, Z. M., Lee, D. R., & Steenhuis, T. S. (2012). Economic Analysis of Best Management Practices to Reduce Watershed Phosphorus Losses. *Journal of Environmental Quality*, *41*(3), 855–864. https://doi.org/10.2134/jeq2011.0165

Reddy, K. R., Diaz, O. A., Scinto, L. J., & Agami, M. (1995). Phosphorus dynamics in selected wetlands and streams of the lake Okeechobee Basin. *Ecological Engineering*, *5*(2–3), 183–207. https://doi.org/10.1016/0925-8574(95)00024-0

Renman, A., & Renman, G. (2010). Long-term phosphate removal by the calcium-silicate material Polonite in wastewater filtration systems. *Chemosphere*, *79*(6), 659–664. https://doi.org/10.1016/j.chemosphere.2010.02.035

Ribey, M. A., & O'Halloran, I. P. (2016). Consequences of Ontario P index recommendations for reduced manure and fertilizer phosphorus applications on corn yields and soil phosphorus. *Canadian Journal of Soil Science*, *96*(2), 191–198. https://doi.org/10.1139/cjss-2015-0072

Richardson, C., & Craft, C. B. (1993). Peat Accretion and N, P, and Organic C Accumulation in Nutrient-Enriched and Unenriched Everglades Peatlands on JSTOR. *Ecological Applications*, *3*(3), 446–458. http://www.jstor.org/stable/1941914?seq=1#page_scan_tab_contents

Richardson, C.J., & Marshll, P.E. (1986). Process controlling movement, sotrage and export of phosphorus in a fen peatland. *Ecological Monographs*, *56(4)*, 279–302.

Roberson, T., Bundy, L. G., & Andraski, T. W. (2007). Freezing and Drying Effects on Potential Plant Contributions to Phosphorus in Runoff. *Journal of Environmental Quality*, *36*(2), 532–539. https://doi.org/10.2134/jeq2006.0169

Rollin, A. L., & Lombard, G. (1988). Mechanisms affecting long-term filtration behavior of geotextiles. *Geotextiles and Geomembranes*, *7*(1–2), 119–145. https://doi.org/10.1016/0266-1144(88)90021-0

Ronkanen, A. K., Marttila, H., Celebi, A., & Kløve, B. (2016). The role of aluminium and iron in phosphorus removal by treatment peatlands. *Ecological Engineering*, *86*, 190–201. https://doi.org/10.1016/j.ecoleng.2015.11.011

Ross, G., Haghseresht, F., & Cloete, T. E. (2008). The effect of pH and anoxia on the performance of Phoslock®, a phosphorus binding clay. *Harmful Algae*, *7*(4), 545–550. https://doi.org/10.1016/j.hal.2007.12.007

Ryden, J.C., J.K. Syers, and R.F. Harris. (1973). Phosphorus in runoff and streams. In: N.C. Brady, editor, Advances in agronomy. Vol. 25. Academic Press, New York

Saadat, S., Bowling, L., Frankenberger, J., & Kladivko, E. (2018). Nitrate and phosphorus transport through subsurface drains under free and controlled drainage. *Water Research*, *142*, 196–207. https://doi.org/10.1016/j.watres.2018.05.040

Samreen, S., & Kausar, S. (2019). Phosphorus Fertilizer: The Original and Commerical Sources. Provisional Chapter. https://doi.org/10.5772/intechopen.82240

Sanford, J. R., & Larson, R. A. (2015). Evaluation of phosphorus filter media for an in-line tile drainage treatment system. *American Society of Agricultural and Biological Engineers Annual International Meeting 2015*, *3*, 2323–2328. https://doi.org/10.13031/aim.20152188727

Sarazen, J. C., Faulkner, J. W., & Hurley, S. E. (2020). Evaluation of nitrogen and phosphorus removal from a denitrifyingwoodchip bioreactor treatment system receiving silage bunker runoff. *Applied Sciences (Switzerland)*, *10*(14), 1–16. https://doi.org/10.3390/app10144789

Satchithanantham, S., English, B., & Wilson, H. (2019). Seasonality of Phosphorus and Nitrate Retention in Riparian Buffers. *Journal of Environmental Quality*, *48*(4), 915–921. https://doi.org/10.2134/jeq2018.07.0280

Scavia, D., Bocaniov, S., Dagnew, A., Hu, Y., Kerkez, B., Long, C., Muenich R., Read, J., Vaccaro, L., & Wang, Y. (2019). Watershed Assesment of Detorit River Phosphorus Loads to Lake Erie. Final project report produced by the University of Michigan Water Center. Available at: myumi.ch/detroit-river.

Schipanski, M. E., & Bennett, E. M. (2012). The Influence of Agricultural Trade and Livestock Production on the Global Phosphorus Cycle. *Ecosystems*, *15*(2), 256–268. https://doi.org/10.1007/s10021-011-9507-x

Schneider, K. D., McConkey, B. G., Thiagarajan, A., Elliott, J. A., & Reid, D. K. (2019). Nutrient Loss in Snowmelt Runoff: Results from a Long-term Study in a Dryland Cropping System. *Journal of Environmental Quality*, *48*(4), 831–840. https://doi.org/10.2134/jeq2018.12.0448

Schoumans, O. F. (2014). Description of the phosphorus sorption and desorption processes in coarse calcareous sandy soils. *Soil Science*, *179*(5), 221–229. https://doi.org/10.1097/SS.0000000000000065

Schreiber, J. D. (1999). Nutrient Leaching from Corn Residues under Simulated Rainfall. *Journal of Environmental Quality*, *28*(6), 1864–1870. https://doi.org/10.2134/jeq1999.00472425002800060024x

Schwer, C. B., & Clausen, J. C. (1989). Vegetative filter treatment of dairy milkhouse wastewater. *Journal of Environmental Quality*, *18*(4), 446–451.

Sharpley, A. (2016). Managing agricultural phosphorus to minimize water quality impacts. *Scientia Agricola*, *73*(1), 1–8. https://doi.org/10.1590/0103-9016-2015-0107

Sharpley, A., Jarvie, H. P., Buda, A., May, L., Spears, B., & Kleinman, P. (2013). Phosphorus Legacy: Overcoming the Effects of Past Management Practices to Mitigate Future Water

Quality Impairment. *Journal of Environmental Quality*, *42*(5), 1308–1326. https://doi.org/10.2134/jeq2013.03.0098

Sharpley, A. N. (1980). The enrichment of soil phosphorus in runoff sediments [Erosion]. *Journal of Environmental Quality*, *9*(3), 521-526.

Sharpley, A. N. (1981). The contribution of Pgospgorus Leached from Crop Canopy to Losses in Surface Runoff. *Journal of Environmental Quality*, *10*(2), 160-165.

Sharpley, A. N., Chapra, S.C., Wedepohl, R., Sims, J.t., Daniel, T.C., & Reddy, K.R. (1994). Managing agricultural phosphorus for protection of surface waters:issues and options. *Journal of Environmental Quality*, *23*(3), 437-451.

Sharpley, A. N., Kleinman, P. J. A., Flaten, D. N., & Buda, A. R. (2011). Critical source area management of agricultural phosphorus: Experiences, challenges and opportunities. *Water Science and Technology*, *64*(4), 945–952. https://doi.org/10.2166/wst.2011.712

Sharpley, A. N., McDowell, R. W., & Kleinman, P. J. A. (2004). Amounts, Forms, and Solubility of Phosphorus in Soils Receiving Manure. *Soil Science Society of America Journal*, *68*(6), 2048–2057. https://doi.org/10.2136/sssaj2004.2048

Sharpley, A. N., & Smith, S. J. (1995). Nitrogen and phosphorus forms in soils receiving manure. In *Soil Science*. 159(4), 253–258. https://doi.org/10.1097/00010694-199504000-00004

Sharpley, A. N., & Smith, S. J., Jones, O.R., Berg, W.A., & Coleman, G.A. (1992). The transport of bioavailable phosphorus in agricultural runoff. Journal of Environmental Quality. 21(1), 30-35.

Sharpley, A. N., Weld, J.L., Beegle, D.B., Kleinman, P.J.A., Gbuerk, W.J., Moore, P.A., & Mullins, G. (2003). Development of phosphorus indices for nutrient management planning strategies in the United States. *Journal of Soil and Water Conservation*. 58(3), 137-152.

Sims, J. T., Simard, R. R., & Joern, B. C. (1998). Phosphorus Loss in Agricultural Drainage: Historical Perspective and Current Research. *Journal of Environmental Quality*, *27*(2), 277–293. https://doi.org/10.2134/jeq1998.00472425002700020006x

Smith, D. R., Francesconi, W., Livingston, S. J., & Huang, C. hua. (2015a). Phosphorus losses from monitored fields with conservation practices in the Lake Erie Basin, USA. *Ambio*, *44*(2), 319–331. https://doi.org/10.1007/s13280-014-0624-6

Smith, D. R., King, K. W., Johnson, L., Francesconi, W., Richards, P., Baker, D., & Sharpley, A. N. (2015b). Surface Runoff and Tile Drainage Transport of Phosphorus in the Midwestern United States. *Journal of Environmental Quality*, *44*(2), 495–502. https://doi.org/10.2134/jeq2014.04.0176

Smith, D. R., Livingston, S. J., Suercher, B.W., Larose, M., Heathman, G.C., & Huang, C. (2008). Nutrient lossed from row crop agriculture in Indiana. *Journal of Soil and Water Conservation*, *63*, 396–409. https:// doi:10.2489/jswc.63.6.396

Søvik, A. K., & Kløve, B. (2005). Phosphorus retention processes in shell sand filter systems treating municipal wastewater. *Ecological Engineering*, *25*(2), 168–182.

https://doi.org/10.1016/j.ecoleng.2005.04.007

Sparks, D. L. (2003). Environmental soil chemistry. 2nd ed. *Academic Press, San Diego*.

Stammler, K. L., Taylor, W. D., & Mohamed, M. N. (2017). Long-term decline in stream total phosphorus concentrations: A pervasive pattern in all watershed types in Ontario. *Journal of Great Lakes Research*, *43*(5), 930–937. https://doi.org/10.1016/j.jglr.2017.07.005

Statistics Canada. (2016). 2016 Census of Agriculture. *Statistics Canada*. http://www.statcan.gc.ca

Stock, M. N., Arriaga, F. J., Vadas, P. A., Good, L. W., Casler, M. D., Karthikeyan, K. G., & Zopp, Z. (2019). Fall Tillage Reduced Nutrient Loads from Liquid Manure Application during the Freezing Season. *Journal of Environmental Quality*, *48*(4), 889–898. https://doi.org/10.2134/jeq2018.11.0417

Stoner, D., Penn, C., McGrath, J., & Warren, J. (2012). Phosphorus Removal with By-Products in a Flow-Through Setting. *Journal of Environmental Quality*, *41*(3), 654–663. https://doi.org/10.2134/jeq2011.0049

Su, J. J., van Bochove, E., Thériault, G., Novotna, B., Khaldoune, J., Denault, J. T., Zhou, J., Nolin, M. C., Hu, C. X., Bernier, M., Benoy, G., Xing, Z. S., & Chow, L. (2011). Effects of snowmelt on phosphorus and sediment losses from agricultural watersheds in Eastern Canada. *Agricultural Water Management*, *98*(5), 867–876. https://doi.org/10.1016/j.agwat.2010.12.013

Szabó, A., Takács, I., Murthy, S., Daigger, G. T., Licskó, I., & Smith, S. (2008). Significance of Design and Operational Variables in Chemical Phosphorus Removal. *Water Environment Research*, *80*(5), 407–416. https://doi.org/10.2175/106143008x268498

Tan, C. S., & Zhang, T. Q. (2011). Surface runoff and sub-surface drainage phosphorus losses under regular free drainage and controlled drainage with sub-irrigation systems in southern Ontario. *Canadian Journal of Soil Science*, *91*(3), 349–359. https://doi.org/10.4141/cjss09086

Tauro, F., Cornelini, P., Grimaldi, S., & Petroselli, A. (2018). Field studies on the soil loss reduction effectiveness of three biodegradable geotextiles. *Journal of Agricultural Engineering*, *49*(2), 117–123. https://doi.org/10.4081/jae.2018.799

Ulén, B., Aronsson, H., Bechmann, M., Krogstad, T., Øygarden, L., & Stenberg, M. (2010). Soil tillage methods to control phosphorus loss and potential side-effects: A Scandinavian review. *Soil Use and Management*, *26*(2), 94–107. https://doi.org/10.1111/j.1475-2743.2010.00266.x

Uusheimo, S., Tulonen, T., Huotari, J., & Arvola, L. (2020). Long-term (2001–2020) nutrient transport from a small boreal agricultural watershed: Hydrological control and potential of retention ponds. *Water (Switzerland)*, *12*(10). https://doi.org/10.3390/w12102731

van der Grift, B., Osté, L., Schot, P., Kratz, A., van Popta, E., Wassen, M., & Griffioen, J. (2018). Forms of phosphorus in suspended particulate matter in agriculture-dominated lowland catchments: Iron as phosphorus carrier. *Science of the Total Environment*, *631–632*, 115–129. https://doi.org/10.1016/j.scitotenv.2018.02.266

van der Salm, C., van Middelkoop, J. C., & Ehlert, P. A. I. (2017). Changes in soil phosphorus pools of grasslands following 17 yrs of balanced application of manure and fertilizer. *Soil Use and Management*, *33*(1), 2–12. https://doi.org/10.1111/sum.12333

Van Esbroeck, C. J., Macrae, M. L., Brunke, R. I., & McKague, K. (2016). Annual and seasonal phosphorus export in surface runoff and tile drainage from agricultural fields with cold temperate climates. *Journal of Great Lakes Research*, *42*(6), 1271–1280. https://doi.org/10.1016/j.jglr.2015.12.014

Van Esbroeck, C., Macrae, M. L., Brunke, R. R., & McKague, K. (2017). Surface and subsurface phosphorus export from agricultural fields during peak flow events over the nongrowing season in regions with cool, temperate climates. *Journal of Soil and Water Conservation*, *72*(1), 65-76.

Verheyen, D., Van Gaelen, N., Ronchi, B., Batelaan, O., Struyf, E., Govers, G., Merckx, R., & Diels, J. (2015). Dissolved phosphorus transport from soil to surface water in catchments with different land use. *Ambio*, *44*(2), 228–240. https://doi.org/10.1007/s13280-014-0617-5

Vidon, P., Allan, C., Burns, D., Duval, T. P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., & Sebestyen, S. (2010). Hot spots and hot moments in riparian zones: Potential for improved water quality management. *Journal of the American Water Resources Association*, *46*(2), 278–298. https://doi.org/10.1111/j.1752-1688.2010.00420.x

Vitousek, P. M., Naylor, R., Crews, T., David, M. B., Drinkwater, L. E., Holland, E., Johnes, P. J., Katzenberger, J., Martinelli, L. A., Matson, P. A., Nziguheba, G., Ojima, D., Palm, C. A., Robertson, G. P., Sanchez, P. A., Townsend, A. R., & Zhang, F. S. (2009). Nutrient imbalances in agricultural development. *Science*, *324*(5934), 1519–1520. https://doi.org/10.1126/science.1170261

Wang, Q., Liao, Z., Yao, D., Yang, Z., Wu, Y., & Tang, C. (2021). Phosphorus immobilization in water and sediment using iron-based materials: A review. *Science of the Total Environment*, *767*. https://doi.org/10.1016/j.scitotenv.2020.144246

Wang, Y. T., Zhang, T. Q., O'Halloran, I. P., Hu, Q. C., Tan, C. S., Speranzini, D., Macdonald, I., & Patterson, G. (2015). Agronomic and environmental soil phosphorus tests for predicting potential phosphorus loss from Ontario soils. *Geoderma*, *241–242*, 51–58. https://doi.org/10.1016/j.geoderma.2014.11.001

Watson, P. D. J., & John, N. W. M. (1999). Geotextile Filter design and simulated bridge formation at the soil-geotextile interface. *Geotextiles and Geomembranes*, *17*, 265–280

Watts, D. B., & Dick, W. A. (2014). Sustainable Uses of FGD Gypsum in Agricultural Systems: Introduction. *Journal of Environmental Quality*, *43*(1), 246–252. https://doi.org/10.2134/jeq2013.09.0357

Weyers, S. L., Gesch, R. W., Forcella, F., Eberle, C. A., Thom, M. D., Matthees, H. L., Ott, M., Feyereisen, G. W., & Strock, J. S. (2021). Surface runoff and nutrient dynamics in cover crop–soybean systems in the Upper Midwest. *Journal of Environmental Quality*, *50*(1), 158–171. https://doi.org/10.1002/jeq2.20135

Williams, M. R., King, K. W., LaBarge, G. A., Confesor, R. B., & Fausey, N. R. (2017). Edge-

Of-Field Evaluation of the Ohio Phosphorus Risk Index. *Journal of Environmental Quality*, *46*(6), 1306–1313. https://doi.org/10.2134/jeq2016.05.0198

Withers, P. J. A., Elser, J. J., Hilton, J., Ohtake, H., Schipper, W. J., & Van Dijk, K. C. (2015). Greening the global phosphorus cycle: How green chemistry can help achieve planetary P sustainability. *Green Chemistry*, *17*(4), 2087–2099. https://doi.org/10.1039/c4gc02445a

Xiong, J., He, Z., Mahmood, Q., Liu, D., Yang, X., & Islam, E. (2008). Phosphate removal from solution using steel slag through magnetic separation. *Journal of Hazardous Materials*, *152*(1), 211–215. https://doi.org/10.1016/j.jhazmat.2007.06.103

Xu, D., Xu, J., Wu, J., & Muhammad, A. (2006). Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. *Chemosphere*, *63*(2), 344–352. https://doi.org/10.1016/j.chemosphere.2005.08.036

Ye, Z. L., Chen, S. H., Lu, M., Shi, J. W., Lin, L. F., & Wang, S. M. (2011). Recovering phosphorus as struvite from the digested swine wastewater with bittern as a magnesium source. *Water Science and Technology*, *64*(2), 334–340. https://doi.org/10.2166/wst.2011.720

Zak, D., Kronvang, B., Carstensen, M. V., Hoffmann, C. C., Kjeldgaard, A., Larsen, S. E., Audet, J., Egemose, S., Jorgensen, C. A., Feuerbach, P., Gertz, F., & Jensen, H. S. (2018). Nitrogen and Phosphorus Removal from Agricultural Runoff in Integrated Buffer Zones. *Environmental Science and Technology*, *52*(11), 6508–6517. https://doi.org/10.1021/acs.est.8b01036

Zhang, H., & Kovar, J.L., (2009). Fractionation of soil phosphorus. In: Kovar,JL., Pierzynski, G.M. (Eds.), Methods of Phosphorus Analysis for Soils, Sediments, Residuals, and Waters, 2nd ed. Virginia Tech University, pp. 50-54.

Zhang, H., Liu, R., & Lal, R. (2016). Optimal sequestration of carbon dioxide and phosphorus in soils by gypsum amendment. *Environmental Chemistry Letters*, *14*(4), 443–448. https://doi.org/10.1007/s10311-016-0564-4

Zhu, Q., Schmidt, J. P., & Bryant, R. B. (2012). Hot moments and hot spots of nutrient losses from a mixed land use watershed. *Journal of Hydrology*, *414–415*(3), 393–404. https://doi.org/10.1016/j.jhydrol.2011.11.011

Zopp, Z. P., Ruark, M. D., Thompson, A. M., Stuntebeck, T. D., Cooley, E., Radatz, A., & Radatz, T. (2019). Effects of Manure and Tillage on Edge-of-Field Phosphorus Loss in Seasonally Frozen Landscapes. *Journal of Environmental Quality*, *48*(4), 966–977. https://doi.org/10.2134/jeq2019.01.0011