Effects of Land Use and Hydrophysical Drivers on Temporal and Spatial Variability of Phosphorus and Nitrate Export in an Agricultural Subwatershed in Southern Ontario, Canada

by

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Author's Declaration

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

Abstract

The eutrophication of streams and lakes has been a long recognized problem in North America, particularly in Lake Erie where harmful and nuisance algal blooms have had many deleterious effects on aquatic ecosystems. Non-point source (NPS) pollution from agriculture has been identified as a key contributor of excess nutrients, namely phosphorus (P) and nitrogen (N), in the Great Lakes basin. There remains a need for increased understanding of the processes and drivers of nutrient losses from agricultural watersheds in order to better limit the negative influence of excess nutrients on receiving water bodies. Much of the existing research on agricultural nutrient export has focused on the growing season and there is a need to better characterize the seasonality of nutrient processes, as well as understand the important nutrient transport pathways. The objectives of this research were to identify key source areas ('hot spots') and peak periods ('hot moments') of nutrient export in an agricultural watershed and to draw inferences between the observed nutrient export and sub-catchment land use and practices. This research also characterizes the role of antecedent moisture conditions (AMC), event size, discharge, and flowpath contributions as potential drivers of the spatial and temporal variability in nutrient loads and concentrations. Streamflow and water chemistry were monitored over a 16-month period at four sites with differing land uses, in the Hopewell Creek watershed in Southern Ontario. The western lobe of the watershed was observed to be the 'hot spot' for P loads during all seasons, while temporally, the early spring snowmelt period was identified as the 'hot moment' throughout the watershed. The area of the watershed with the highest proportion of tile-drained land did not correspond to the P 'hot spot', and was instead an area with high peak flows and livestock operations. Flowpath contributions were shown to be an important driver of total phosphorus (TP) concentrations and nitrate (NO_3^-) loads through stepwise multiple linear regressions. This research emphasizes the importance of year-round event based monitoring programs for estimating nutrient export and further, that subwatershed scale studies can be used to identify nutrient hot spots in an agriculturally dominated catchment with spatially variable land use practices. Flowpath contributions were found to be important drivers of nutrient dynamics and this suggests that understanding flowpath contributions in agricultural subwaterheds can increase the predictive power for nutrient export models.

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Chapter 1 – Introduction and Literature Review

1.1 Introduction and Problem Statement

Freshwater resources are crucially important both biologically, environmentally and for humans as they are used for consumption, industry, irrigation, and recreation (Carpenter et al., 1998). Eutrophication of surface water bodies is a widely recognized problem worldwide that has been shown to have detrimental effects on aquatic ecosystems (Banner et al., 2009). These effects are due to increased growth of algae and cyanobacteria that decrease oxygen levels and accelerate algal production that can result in fish kills (Sharpley et al., 2001). Since phosphorus (P) is commonly attributed to limiting growth in aquatic ecosystems, it is widely believed that P inputs to freshwater are the main cause of eutrophication (Sharpley et al., 1999; Gao et al., 2012). Non-point sources of nutrients from agriculture, have been identified as the largest contributors of nutrient exports to receiving streams, namely export of high levels of both nitrogen (N) and P (Arbuckle and Downing, 2001; Whitehead et al., 2011). As such, research into the dynamics and physical processes contributing to agricultural nutrient losses has increased in the past few decades as a way to better identify the drivers of nutrient export and limit the negative influence on receiving streams. There remains a need for increased understanding of nutrient processes during the non-growing season in Southern Ontario (Van Esbroeck et al., 2017) and year round monitoring studies within the Lake Erie basin will provide insight into Lake Erie P loading objectives including a 40% decrease in TP loads to Lake Erie (IJC, 2014). Additional information is needed on the contribution of different land uses within rural watersheds, and if and how nutrient concentrations and loads may differ both spatially and temporally. If such variability is found, research is needed to identify the primary nutrient transport pathways. This thesis explores these needs through the following objectives:

1) Determine the critical times and critical locations of nutrient (N and P) export in a mixed land use subwatershed using a year-round intensive event-based sampling strategy;
2) Infer possible causes of water chemistry observations using land use, land management and physiographic information for the subwatershed;
3) Characterize the effect of antecedent moisture, event size and discharge as potential drivers of temporal variability in nutrient export from two agricultural locations within the same subwatershed; and
4) Determine if flowpath connectivity, estimated from end-member mixing analysis (EMMA), increases predictive power of relationships between hydrophysical drivers and nutrient concentration and loads.

Objectives 1 and 2 are addressed in “Seasonal nutrient export dynamics in a mixed land use subwatershed of the Grand River, Ontario, Canada” (Chapter 2 of this thesis), while, objectives 3 and 4 are addressed in “Linking antecedent moisture conditions and flowpath connectivity as drivers of nutrient export in an agricultural catchment in Southern Ontario, Canada”. (Chapter 3 of this thesis).

1.2 Literature Review

1.2.1 Agricultural Nutrients in the Environment

Nutrient use in agriculture serves an economic benefit by increasing crop yields through the application of organic and inorganic fertilizers rich in N and P. While these nutrients naturally exist in the environment, increased rates of fertilizer application can result in an alteration of the balance of nutrient cycling and budgets, and can have deleterious environmental effects when excess nutrients are introduced to the system. Both N and P are exported from agricultural fields but P is believed to be responsible for eutrophication in receiving lakes (USEPA, 1988; Schindler 1977). Conversely, N can be an important nutrient in coastal systems (Beckert et al., 2011) and high N concentrations in groundwater can have harmful impacts on humans (Soares, 2000).

1.2.1.1 The Role of Agricultural Phosphorus in Eutrophication

Research on phosphorus export in agricultural systems has been studied for over 40 years (PLUARG, 1978; Sharpley and Syers, 1979), but has received increasing attention because despite the implementation of best management practices, lake eutrophication continues and the incidence of harmful algal blooms has increased (Carpenter et al., 1998). Phosphorus is used in agriculture as fertilizer in the form of inorganic commercial fertilizers or animal manure (Algoazany et al., 2007). These materials are added to fields to increase crop growth and yields, but can become problematic when excess P is exported to streams (Daloglu et al., 2012). The export of P from agricultural fields can result from over fertilization of crops and excess P that is not utilized by the crop remains on the field and can sorb to soil particles. Sharpley et al. (1999) reported that over half of the fields in a Pennsylvania agricultural watershed contained soil P concentrations exceeding the levels for optimal plant growth, and over-enrichment of P in soils has also been documented in Europe (Némery et al., 2005). The excess P in the soil is then lost during large runoff generating rain and snowmelt events which occur in small areas over short time periods (Sharpley et al., 2001).

Phosphorus export in agricultural catchments can be very episodic and P loss is largely event based (Macrae et al., 2007a; Chen et al., 2015), which was demonstrated in a Kansas watershed where 88% of total phosphorus (TP) loss occurred during high discharge events covering only 10% of the study time (Banner et al., 2009). These findings point to the need for intensive, storm-based sampling procedures rather than regular-interval sampling methods when estimating P losses (Grant et al., 1996). In particular, seasonality tends to play a role in P loss in temperate North America where the largest P exports tend to occur in the spring months due to large rain events (Vidon and Cuadra, 2011) and snowmelt events (Algoazany et al., 2007), as well as on soils with high antecedent moisture contents (Macrae et al., 2010). Additionally, event sampling throughout the year is important as P export dynamics are not as frequently studied during winter months and the non-growing season in North America (Gombault et al., 2015; Van Esbroeck et al., 2017).

Phosphorus Speciation and Transit Pathways

Phosphorus is lost via surface runoff and subsurface pathways. Surface runoff is an important process in the transport of P to surface waters. Surface runoff from storm events contains large proportions of sediments caused by erosion and as such, tend to have higher levels of particulate phosphorus (PP) (Grant et al., 1996). The amount of P transported as PP can be largely attributed to the sorptive capacity of the soil. Soil properties that have been shown to be conducive to increased P sorption include high levels of organic matter (Kronvang et al., 2009; Kröger et al., 2013), and high clay content (Eastman et al., 2010). Clay soils in particular can also have a higher potential for large P export occurring immediately following P fertilizer application, known as incidental P loss (Chardon and Schoumans, 2007). Concentrations of TP tend to be higher in surface runoff compared to subsurface flow, which occurs primarily during storm events (Haygarth et al., 1998; Algoazany et al., 2007) where there is a correlation between TP export and sediment loss (Yuan et al., 2013). Further, while concentrations of P tend to be higher in surface runoff, this is generally a minor component of total outflow (Li et al., 2010), but can account for a large proportion of P loss on an annual basis (Haygarth et al., 1998; Sharpley et al., 2001).

Subsurface export of P can occur under two conditions. It can be exported via groundwater or tile drains, the latter being very common in agricultural fields in North America, and it can influence the speciation of P being transported to the streams (Eastman et al., 2010). Due to the high sorptive capacity of P to soils, subsurface transport of P is primarily in the dissolved form (DP) (Algoazany et al., 2007), which is generally immediately available for biological uptake (Vidon and Cuadra, 2011) and termed dissolved reactive phosphorus (DRP). However transport of PP can still occur (Walling et al., 2008), vertically via macropore flow (Chardon and Schoumans, 2007) and horizontally in tile drains (Dolezal et al., 2001). Subsurface runoff tends to have higher DRP:TP ratios since there is a lower concentration of particulates in subsurface flow compared to overland flow. Other situations in which significant P losses can occur in the subsurface, include high levels of organic matter in the soil, sandy soils that have poor sorptive capacity, and soils that have been over fertilized (Dils and Heathwaite, 1999). Another mechanism in the subsurface is for P stratification to occur under certain tillage practices, which can increase DRP export (Daloglu et al., 2012). This stratification can cause a build-up of P in the top soil and can result in the release of DRP via groundwater flow as soil saturation increases (Domagalski and Johnson, 2011).

The influence of tile drains on runoff and nutrient transport is somewhat uncertain as tiles can reduce the amount of surface runoff which typically have higher P concentrations (Haygarth et al., 1998; Algoazany et al., 2007). However, tiles also tend to have higher DRP concentrations and higher outflow volume compared to surface runoff (Eastman et al., 2010; Rozemeijer et al., 2010). Further, it has been suggested that tile drains may act to increase the contributing area of subsurface runoff, particularly during storm events and peak flow conditions (Dils and Heathwaite, 1999). Studies have shown that P concentrations near the receiving stream are better predictors of surface water quality as opposed to soils located further away in the watershed (Sharpley et al., 2001).

An additional source of uncertainty around the roles of tile drains arises from the observation that tiles can exhibit variable responses to storms of similar size and tend to only influence nutrient export when the system is wet enough for the tiles to be flowing (Lam et al., 2016a). During peak flow events when stream discharge is high, there is a general linear relationship between stream discharge and tile discharge. However, during moderate flow events, tile response can vary dramatically (Macrae et al., 2007b; Hoorman et al., 2008) and can depend on seasonality, antecedent soil moisture conditions (Macrae et al., 2010), as well as intensity, timing and duration of precipitation (Vidon and Cuadra, 2010; Kröger et al., 2013). A better understanding of the variability of P speciation, concentration and export from tile drainage is important for modelling P export under future climate scenarios as this is an area of uncertainty (Li et al., 2010; Gombault et al., 2015).

Paired field studies offer a design to quantify or test differences in P loss in agricultural fields under differing subsurface drainage types (tiles vs natural), although this is complicated due to the variability in other physical properties of the fields (*i.e.*, soil type, slope, crop type etc.). While few studies exist which directly compare naturally drained fields to tile drained fields, one such study by Eastman et al. (2010), compared fields with the same soil type but differing methods of subsurface drainage (tile vs. natural) and found the impact of subsurface drainage differs depending on soil type. The naturally drained site with sandy loam soil experienced significantly higher surface runoff than the field with tile drains which shows that under certain conditions, tile drains can decrease P loads by decreasing the quantity of surface runoff and erosion (Eastman et al., 2010).

1.2.1.2 The Role of Nitrogen in Agriculture

Nitrogen (N) is a major component of fertilizers because many crops are N limited. Accordingly, when N is not utilized by plant material it is prone to export to surface water bodies (Zhu et al., 2011). The transport mechanisms and cycling dynamics of N are much different than that of P. N, and nitrate (NO_3^-) in particular, tends to be more associated with groundwater due to its negative charge (same charge as soils) and its high mobility and solubility in water (Abell et al., 2011). Further, the presence of tile drains can increase N export to streams as NO_3^- can leach vertically entering tile drains via matrix flow (Li et al., 2010), while P reaches tile drains primarily via macropores (Perks et al., 2015). As such, nitrate loss from agricultural areas is a common concern around the world. In Britain, approximately 70% of NO_3^- in surface and groundwater originates from agricultural lands (Neal et al., 2006).

Nitrogen Speciation and Transport Pathways

One of the two species of nitrogen of concern in the context of water quality is NO_3^- which, as mentioned previously, is negatively charged, and very soluble and mobile in water, making NO_3^- prone to leaching, particularly in coarse grained soils (Gilliam et al., 1999). The other species of concern is ammonium (NH_4^+), which is more commonly bound to soil particles and subject to erosive forces and transport during storm-flow rather than leaching (Pärn et al., 2012).

Excess P from fertilization can accumulate in soils on agricultural fields, while excess N can leach and accumulate in the subsurface. NO_3^-, being the more soluble, mobile, and bioavailable form (Neal et al. 2006), is of particular interest as agricultural streams have been shown to have a trend of increasing NO_3^- concentrations due to the build-up in groundwater caused by excess fertilizer application (Neal et al., 2006). Further, N export from fields has been shown to occur during years when no N fertilizers were applied, suggesting that groundwater can store high concentrations of NO_3^- (Stenberg et al., 2012).

Drainage tiles are also a major contributor of NO_3^- export as it has been shown that up to 90% of annual nitrate export can originate from tiles in agricultural watersheds (Rozemeijer et al., 2010). Tile drains decrease the residence times of N in the subsurface, creating less opportunity for mineralization and adsorption/ desorption reactions to occur. More specifically, it has been shown that tile drain water is much less denitrified compared to groundwater (Panno et al., 2008). This, coupled with the higher discharge rates associated with tile drains (Dolezal et al., 2001), leads to a high potential of N loss from tile drained systems (Rozemeijer et al., 2010).

1.2.2 Quantifying Nutrient Fluxes in Agricultural Systems

The quantification of the nutrients of interest is project-specific and depends on the research objectives. Studies tend to either focus on nutrient concentrations (*e.g.*, Long et al. 2014) or total loads (*e.g.*, O'Connor et al., 2011). Examining differences in nutrient concentrations can be beneficial in small field-scale studies when nutrient processes are of interest (Macrae et al., 2011). At a larger scale, nutrient load estimates can contribute to increased understanding of the influence of stream nutrient dynamics on receiving lakes (Whitehead et al., 2011; Long et al., 2015).

Meso-scale subwatershed studies are useful in contributing to the understanding of linking the previously mentioned scales of studies. Relationships between macronutrients (TP and NO_3^-) have been shown to be scale-dependent (Buck et al., 2004), and scaling up field scale observations can provide better input data for watershed nutrient models (Sliva and Williams, 2001; Uriarte et al., 2011; Zhou et al., 2016).

Small-scale studies of nutrient dynamics in headwater streams and catchments, including agricultural landscapes, are typically undertaken in order to gain an increased understanding of processes that control nutrient export. The processes and drivers that are typically studied include seasonal variability (Macrae et al., 2007a; Gombault et al., 2015), surface and subsurface water interactions (Garrett et al., 2012; Van Esbroeck et al., 2017), antecedent moisture conditions (Macrae et al., 2010; Davis et al., 2014; Outram et al., 2016), influence of tile drains (Macrae et al., 2007b; Williams et al., 2015; Lam et al., 2016a) and hysteresis effects (O'Connor et al., 2011; Sherriff et al., 2016). There is a recognition that in order to better understand the influence of agricultural non-point sources (NPS) of nutrients on receiving lakes, studies looking at the up-scaling of these field scale processes are required (El-sadek, 2007; Jencso et al., 2009; Mineau et al., 2015).

The high frequency of intensive event-based sampling strategies that are typical of small scale studies (Lam et al., 2016a; Van Esbroeck et al., 2017) is generally not logistically feasible on long temporal scales or over entire watersheds, where empirical models can better estimate nutrient loads. Models can be used to provide nutrient load estimates to receiving water bodies, which is of particular interest in the Great Lakes Basin including Lake Erie. Some models that have been used in the past include the Soil and Water Assessment Tool (SWAT) (Johnson et al., 2015), modified SWAT models (Collick et al., 2015), The Representative Elementary Watershed (THREW) model (Liu et al., 2014), integrated catchment (INCA-P) model (Whitehead et al., 2011), and GIS-based agricultural non-point source pollution model (AGNPS) (Emili and Greene, 2013). These models all have varying degrees of uncertainty related to simplifying the small-scale processes that drive nutrient export from agricultural landscapes.

1.2.3 Drivers of Nutrient Export

1.2.3.1 Land Management

While the quantity and concentration of both N and P are important in understanding the response of a water body to nutrient loading, the ratio of the two is vitally important as well. A study by Arbuckle and Downing (2001) found that N:P ratios to be significantly higher in areas dominated by row-cropping compared to areas dominated by animal pastureland. The reason for this is increased level of N in fertilizers applied for row-crops, and this difference in nutrient stoichiometry can impact whether or not the receiving water is likely to experience eutrophication (Arbuckle and Downing, 2001). Conversely, TP export has been found to be higher in agricultural areas that have livestock operations, including cattle grazing dairy operations (Aarons and Gourley, 2012), and poultry production (Niño de Guzmán et al., 2012).

1.2.3.2 Hydrologic Connectivity and Flowpaths

The contributions of stormflow from different flowpaths can have an important impact on the species of nutrients entering streams. Surface runoff tends to have high levels of particulate phosphorus (PP) due to erosion of the soil at the surface (Grant et al., 1996) and the soils capability to sorb P, which is increased by organic content (Kronvang et al., 2009) and clay content (Eastman et al., 2010). N species, including NO_3^-, tend to be more associated with groundwater due to their negative charge (same charge as soils) and their high mobility and solubility in water (Abell et al., 2011). Understanding the dominant transport pathways of water during a range of conditions allows better predictive capabilities as flowpaths can be a major control on how the systems responds to a runoff-generating event. The flowpath contributions are largely dependent on the hydrologic connectivity during the event response (James and Roulet, 2007). Past studies that have examined the response of flowpath dynamics to runoff-generating events have focused on forested catchments (James and Roulet, 2009; Ali et al., 2010) and have found basin morphology to be an important control on storm response. However, fewer have studied flowpath connectivity in agricultural and mixed land use catchments.

The aim of nutrient management strategies has been to identify critical source areas (CSAs), which are areas in a watershed that have both high loading rates as well as being prone to runoff generation (Buchanan et al., 2013). Whether or not an area of a watershed is prone to runoff generation is largely controlled by the hydrologic connectivity during a storm event, which can vary depending on the storm and antecedent moisture characteristics (Sen et al., 2010) and this varying degree of hydrologic connectivity has a large influence of the size of the runoff contributing area (Buda et al., 2009). High hydrologic connectivity in agricultural landscapes can cause increased sediment loss as well as increased P loss and is largely controlled by soil type (Sherriff et al., 2016). Further, it has been shown that the observed threshold response of P and sediment loss in a natural headwater catchment can be attributed to the activation of usually disconnected flow pathways (Perks et al., 2015).

The relationship between hydrologic connectivity and event response can be non-linear, indicating a threshold response of the system, where after reaching a threshold of moisture conditions, the discharge response can increase at a much higher rate (Macrae et al., 2010). This has been observed both in forested catchments (James and Roulet, 2007), as well as agricultural catchments (Macrae et al., 2010). As relative saturation of the watershed increases, the runoff contributing area increases. These areas that have a high risk of generating storm runoff are termed hydrologically sensitive areas (HSA) (Cheng et al., 2014). Determining the location of HSAs in a watershed is crucial for land managers trying to reduce nutrient loss.

High rates of phosphorus export can occur when overland flow processes dominate storm flow (Banner et al., 2009; Collick et al., 2015), which has been observed in a highly sloped agricultural catchment where approximately 80% of storm runoff was attributed to overland flow (Buda et al., 2009). P concentrations are generally higher in surface runoff and tile drain effluent (Sharpley and Syers, 1979), but it has also been shown that total dissolved phosphorus (TDP) concentrations in groundwater and throughflow pathways can be sufficiently high to contribute to stream pollution (Burkart et al., 2004); one study found that groundwater losses of TDP can be as high as 50-60% of total losses (Mellander et al., 2016).

Subsurface flowpaths (groundwater and tile drains) tend to have higher concentrations of NO_3^- compared to overland flow due to the mobility and solubility of N, while dissolved phosphorus (DP) can also be present in high concentration in the subsurface under anaerobic saturated conditions causing phosphorus solubility to increase (Flores-López et al., 2011). This reinforces that notion that determining the hydrologic contribution of each flowpath to a given stream under differing conditions is important to be able to manage nutrient losses at the watershed scale, particularly in watersheds that are primarily groundwater-fed (Mellander et al., 2016).

1.2.4 Quantifying Flowpath Connectivity Using End-Member Mixing Analysis

Hydrologic connectivity is influenced by climate, slope, landscape position, delivery pathway, and lateral subsurface flowpaths (Bracken and Croke, 2007) and can influence stream response (Ali et al., 2010) and nutrient export (Fraterrigo and Downing, 2008). A commonly used method for quantifying flowpath connectivity is end-member mixing analysis (EMMA), which involves estimating the hydrologic contribution from different source areas, or end-members (Hooper et al., 1990; Burns et al., 2001).

Geographic source end-members represent water originating from distinct geographical areas in a catchment and are distinguished by a consistent chemical signature. The chemical constituents used to define end-members need to meet some assumptions, including conservative mixing, constant end-member composition, and distinct chemical composition (Hooper, 2003). Examples of chemical constituents that have been used to distinguish end-members in the past include anions such as chloride (Cl^-), sulphate (SO_4^{2-}), carbonate (CO_3^{2-}) and cations such as potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), as well as other water parameters such as dissolved organic carbon (DOC), specific conductance (SC), and alkalinity (Alk) (Burns et al., 2001; Hooper, 2003; Ali et al., 2010; Kronholm and Capel, 2015).

EMMA has been successful in identifying end-member contributions to stream water in past studies in natural landscapes including forested catchments (Ali et al., 2010), and peatlands (Gracz et al., 2015), but there have been considerably fewer examples of EMMA being applied in agricultural landscapes (Kronholm and Capel, 2015). The complicating factor in agricultural areas is that tile drains constitute an additional transport pathway (or end-member) that needs to be reflected in the mixing model. The study by Kronholm and Capel (2015) identified four geographic sources of water (natural groundwater, overland flow, tile drain flow, and groundwater from irrigation) but found that in terms of estimating stream water contributions, temporal end members (slowflow and fastflow) may be more appropriate.

Chapter 2 - Seasonal nutrient export dynamics in a mixed land use subwatershed of the Grand River, Ontario, Canada

2.1 Overview:

Algal blooms in surface water bodies resulting from excess nutrient loading from non-point sources have been a recognised problem in North America and worldwide for decades. There is currently uncertainty over the relative contributions of non-point sources under different types of land management in rural watersheds, particularly over an annual cycle. Flow and water quality were examined throughout a mixed land use watershed in Southern Ontario, Canada to identify peak periods (‘hot moments’) and source areas (‘hot spots’) in the watershed. Data were simultaneously collected at four monitoring sites that differed in stream order, dominant land use and land management practices. Seasonal patterns were similar throughout the watershed for dissolved reactive phosphorus (DRP) and total phosphorus (TP), as spring was the dominant season with regards to mass loads of DRP and TP. A local phosphorus ‘hotspot’ was identified in one sub-catchment which had the highest DRP and TP concentrations as well as export load coefficient, in kg/ha, during every season and in most of the individual events. Nitrate (NO_3^-) concentrations were highest in the sub-catchment with the highest density of tile drainage, but had a weaker seasonal pattern compared to P. The hydrologic regime and chemical signatures of the watershed outlet were intermediate of the two upstream agricultural sub-catchments, indicating that the agricultural areas in the watershed have a strong influence on nutrient export dynamics, which are highly related to the flow regime. The results of this study suggest that stream discharge is a strong control on the export dynamics of DRP and TP, and that land management practices, specifically the presence of tile drains, is likely a strong control on NO_3^-.

2.2 Introduction

The eutrophication of surface water bodies is a worldwide problem that has been shown to have detrimental effects on aquatic ecosystems (Carpenter et al., 1998; Banner et al., 2009). The increased growth of algae and cyanobacteria, caused by elevated nutrient loads from watersheds, lowers oxygen levels, can result in fish kills (Sharpley et al., 2001) and may also be associated with health risks to humans and animals. In the Great Lakes region of North America, Lake Erie is particularly vulnerable to these processes and experiences frequent algal blooms (IJC, 2012; Michalak et al., 2013; IJC, 2014). There is significant pressure to reduce the occurrences of nuisance algal blooms; however, the drivers of these blooms in large systems such as Lake Erie are complex and may vary in space and time. An improved understanding of spatial and temporal variability in nutrient loads and speciation and how these are tied to land use and management practices is needed to aid managers and modellers in managing the watersheds of vulnerable surface water bodies. This information will also provide insight into the potential to achieve the objectives of the Nutrients Annex (Annex 4) of the 2012 Great Lakes Water Quality Agreement, and the targets set in 2016 under this agreement.

Non-point sources of pollution, mainly agricultural inputs of nutrients, have been identified as one of the largest contributors of nutrients to receiving streams, exporting high levels of both nitrogen (N) and phosphorus (P) (Arbuckle and Downing, 2001; Whitehead et al., 2011). Elevated nutrient loads in the tributaries to Lake Erie have largely been attributed to agricultural sources (IJC, 2014). Fertilizers and manure containing N and P are applied to crops to increase yields; however, although beneficial to crops, fertilizers serve as a major contributor of nutrient export to freshwater bodies (Chen et al., 2015). It is widely believed that P inputs to freshwater are one of the main causes of eutrophication in large lakes (Sharpley et al., 1999; Gao et al., 2012) as P has been identified as the limiting nutrient in freshwater surface water bodies

(Schindler, 1977). Alternatively, N is the limiting nutrient for coastal marine systems (Howarth and Marino, 2006) and is also problematic in groundwater that is used for drinking water due to human health risks (Soares, 2000).

The magnitude and speciation of N and P loads are spatially and temporally variable, and can differ with runoff pathways. Phosphorus has a high tendency to sorb to soil particles (Munn et al., 1973), which makes particulate phosphorus (PP) susceptible to export via erosion (Grant et al., 1996) primarily during high flow events (Grant et al., 1996; Haygarth et al., 1998; Algoazany et al., 2007). Although concentrations of P tend to be higher in surface discharge, this is generally a minor component of total outflow (Li et al., 2010) and subsurface flow (tile drainage) contributes more total discharge on an annual basis, making both tile drains and surface runoff significant P sources (Van Esbroeck et al, 2017). Subsurface flow is thought to have higher concentrations of dissolved reactive phosphorus (DRP) relative to PP in some systems (Algoazany et al., 2007) but not all (Lam et al., 2016a; Van Esbroeck et al., 2017). While high TP concentrations are typically associated with erosion and surface runoff, transport can still occur vertically in the subsurface via macropore flow (Chardon and Schoumans, 2007; Lam, et al., 2016b) and horizontally via tile drains (Dolezal et al., 2001). The export of DRP via tile drainage is problematic as this bioavailable form of P is rapidly transported from tile drains into tributaries and subsequently into lakes (Vidon and Cuadra, 2011; King et al., 2015). Tile drains can also be problematic for N losses. Due to the solubility and mobility of NO_3^-, the presence of tile drains can increase N export as NO_3^- can leach vertically, entering the tile drains through matrix flow (Li et al., 2010) as well as macropores (Perks et al., 2015).

The magnitude and speciation of contaminants can vary with land use, slope, soil texture and tile drain density. Many studies in agricultural systems examine nutrient export at the field or plot scale (Rozemeijer et al., 2010; Macrae et al., 2011; Stenberg et al., 2012, Lam et al., 2016; Van Esbroeck et al., 2017), which provides insight into the mechanisms driving nutrient fluxes. More recently, there has been a need to examine mechanisms that are important at the watershed scale (Beckert et al., 2011; Evans et al., 2014; Mineau et al., 2015). Studies have investigated relationships between land use and nutrient concentrations or export in watersheds that have multiple land uses using a GIS approach (Agnew et al., 2006). For example, Evans et al. (2014) found a strong correlation between the amount of agricultural land use and the concentration of dissolved nutrients in Oregon, USA. A similar relationship was found by Beckert et al. (2011) in Maryland, particularly in areas with high density of animal feeding operations. The same study found that watersheds that had the highest proportion of row crop agriculture had a strong correlation with mean baseflow total nitrogen (TN) concentrations (Beckert et al., 2011). These studies that investigate correlations between land use type and nutrient export require many watersheds within the same physiographic area and datasets that are often pre-existing and can be temporally limited (Mehaffey et al., 2005) Indeed, land use within a watershed can have a strong influence on water quality and nutrient export. The strength of influence can be scale-dependent, where large, higher-order streams can be impacted by land use far upstream in the headwater reaches, while smaller first- and second-order streams are strongly impacted by land use that is directly adjacent (Buck et al., 2004).

At smaller scales, paired watershed studies that directly compare sub-catchments with similar physiographic characteristics can provide insight to local controls on water quality and nutrient export. For example, Coulter et al. (2004) found that a Kentucky watershed with primarily agricultural land use exported significantly higher NO_3^- and DRP concentrations compared to the mixed and urban watersheds, which had higher temperatures and turbidity. Pieterse et al. (2003) reported similar results in The Netherlands and Belgium, where many agricultural tributaries exceeded water quality standards for both TN and TP. Paired watershed studies such as these are rare, but provide important insight into how land use and climate drivers interact to generate elevated nutrient loads.

The magnitude and speciation of nutrient loads also varies temporally. Phosphorus export in agricultural catchments can be highly episodic and P loss is largely event-based (Macrae et al., 2007a; Chen et al., 2015). In a Kansas watershed, Banner et al. (2009) reported that 88% of TP loss occurred during high discharge events covering only 10% of the study time. NO_3^- losses are less episodic than P, although they tend to increase under higher discharge events, particularly following fertilizer application (Macrae et al., 2007a), and generally have a strong correlation with discharge (Liu et al., 2014). These findings point to the need to use intensive, storm-based sampling procedures as opposed to regular-interval sampling methods when estimating P losses (Grant et al., 1996; Williams et al., 2015). Sampling programs should also include the non-growing season, particularly the winter snowmelt period, as large nutrient exports tend to occur during snowmelt events (Van Esbroeck et al., 2017; Macrae et al., 2007a; Algoazany et al., 2007) and in the spring months due to large rain events (Vidon and Cuadra, 2011). Nutrient exports can also occur following rainfall on soils with high antecedent moisture contents (Macrae et al., 2010). At present, there is a paucity of field data collected during the winter period. To better understand the relative contributions of different land uses to nutrient loads and species, it is essential that data are collected throughout the non-growing season (November – March) given that this is when a large proportion of nutrient loading can potentially occur.

This study uses an intensive, event-based runoff sampling approach to investigate the scalability of small-scale agricultural nutrient export mechanisms in a mixed land use watershed in Southern Ontario, Canada. We addressed two key research questions: Are observed temporal patterns consistent in space, throughout the watershed? Are spatial patterns consistent in time, at both event-based and seasonal scales?

The specific objectives addressed were:

1) to determine critical times ('hot moments'), and critical locations ('hotspots') of DRP, TP and NO_3^- export within the mixed land use watershed and,

2) to infer possible causes for water chemistry observations using land use and physiographic subwatershed GIS data.

2.3 Study Site

The study was conducted in the Hopewell Creek watershed, a mixed land use watershed located ~15 km east of Kitchener-Waterloo, Ontario. Hopewell Creek is a third-order stream that drains into the Grand River, which subsequently drains into Lake Erie. The Hopewell Creek watershed is 72 km^2 in area, and has soils which are texturally classified as dominantly sandy loam but there are also loams, organic soils and till. Soil types in watershed include Gray Brown luvisols, Melanic Brunisols and Humic gleysols (Presant and Wicklund, 1971). The catchment is predominantly groundwater-fed but can receive overland flow contributions to the streams during high flow events from the ponding of water at the surface in microtopographic lows (Macrae et al., 2007a), as well as inputs from tile drains which are common throughout the watershed. The Hopewell Creek watershed experiences a cool, temperate climate, with 916.5 mm precipitation (17 % as snowfall) annually (Environment Canada, 2017). 30-year mean air temperatures are 20.0°C in July and -6.5°C in January, with air temperatures typically at or below freezing between December and March.

The primary land use in the catchment is 46% agriculture, of which 24% is tile-drained (Table 2.1). Other land uses in the watershed include 41% natural areas, including forested areas, hedgerows and riparian areas, and 9% residential lands. Row crops are the most common agricultural practice in the watershed, and consist of corn-soybean-cereal rotations. Other agricultural practices include pasture land and livestock (dairy and poultry).

Four monitoring sites were established within the Hopewell Creek watershed (Figure 2.1). Headwater (HW) is the furthest upstream site and is located at the headwaters of the watershed with its catchment area being predominantly forested and the only sub-catchment in the study with no tile drainage (Figure 2.1). The stream is an ephemeral first-order stream which flows primarily during the spring freshet and during heavy rain events, usually in the spring and fall seasons. HW was chosen to serve as an "undisturbed" reference site to act as a natural analog to give an idea of pre-development conditions before artificial subsurface drainage was introduced throughout the landscape. Strawberry Creek (ST) and Maryhill (MH) are two streams adjacent to agricultural, tile drained fields that drain primarily agricultural sub-catchments. ST is a first-order stream with a contributing area of approximately 3 km^2, while MH is a second-order stream with a contributing area of approximately 15 km^2. While these two monitoring sites both have predominantly agricultural land uses, the land management practices vary. ST has primarily cash crops including soybean, corn, winter wheat and strawberries and has the highest proportion of tile drained fields. MH has a considerable livestock and grazing pastures in its sub-catchment with a lower proportion of tile drains. Terminus (TE) is located at the outlet of the watershed, and represents the entire 72 km^2 Hopewell Creek watershed. While three of the four sub-catchments are dominated by agricultural land use with some residential and natural lands, the relative proportions of each differs across sites (Table 2.1). The fourth sub-catchment, HW, has only 37% agricultural land use and no tile drains (Table 2.1). One of the sub-catchments, Strawberry Creek, has been the site of previous agricultural nutrient studies (*e.g*. Harris et al., 1999; Mengis et al., 2009; Macrae et al., 2007a; Macrae et al., 2007b; Macrae et al., 2010).

Table 2.1: Land use characteristics of contributing areas of the four monitoring sites within the Hopewell Creek Watershed

Site	**Drainage Area (km^2)**	**Tiled Cropland (%)**	**Natural Cropland (%)**	**Total Cropland (%)**	**Dominant Soil Type**	**Stream Order**	**Average Slope (%)**	**Drainage Density (m/ha)**
Headwater	1.08	0	37	37	Sandy Loam	1	3.09	14.46
Strawberry	2.61	65	25	90	Sandy Loam	1	1.43	10.42
Maryhill	14.77	41	23	63	Sandy Loam	2	1.68	12.88
Terminus	72.20	24	22	46	Sandy Loam	3	2.21	13.08

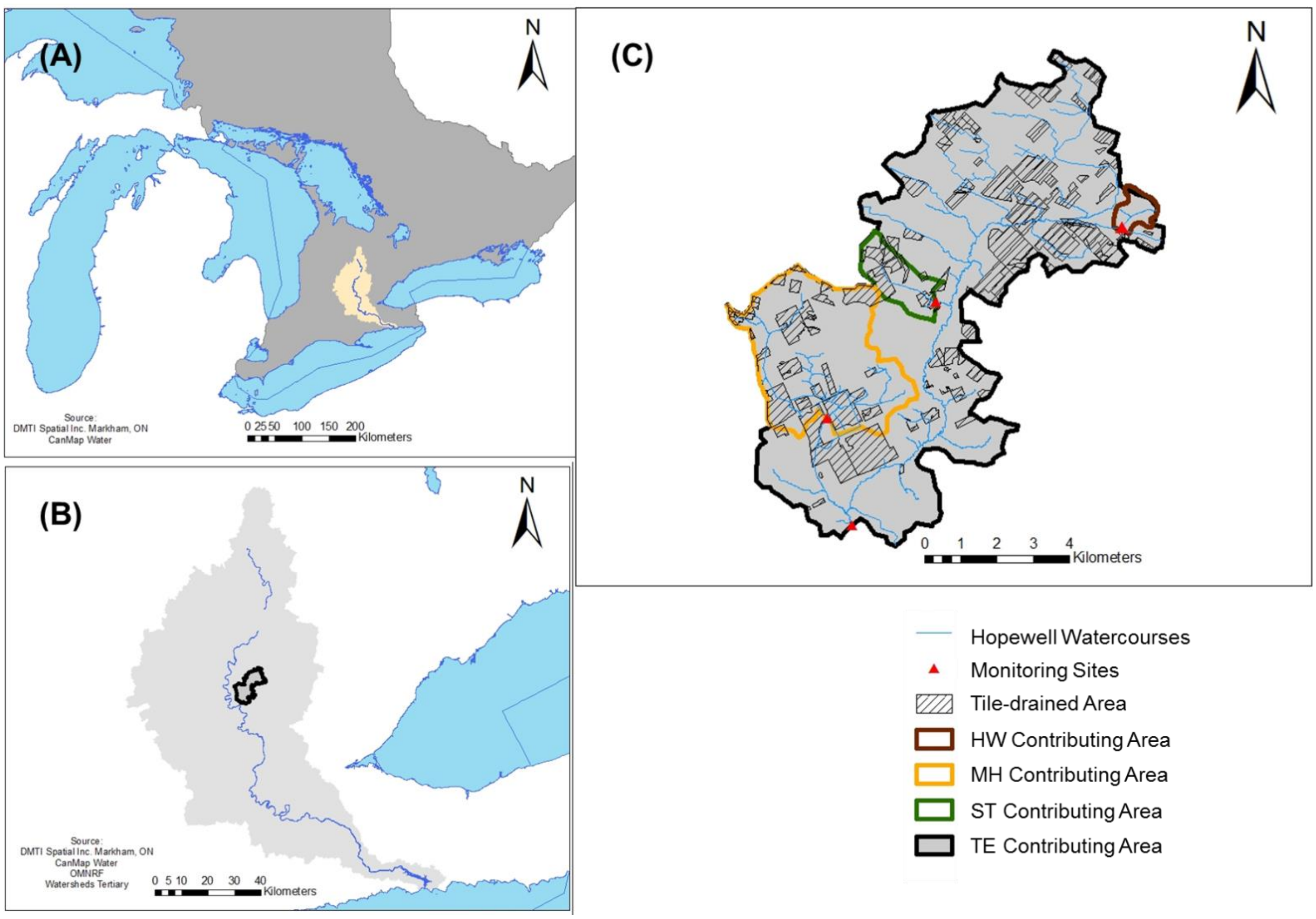

Figure 2.1: a) and b) Location of the Hopewell Creek watershed within the Grand River watershed in Southern Ontario, Canada. c) 4 monitoring sites and their associated sub-catchments in Hopewell Creek.

2.4 Methods

2.4.1 Research Design

Four monitoring sites were selected to monitor streamflow and hydrometric variables as well as water quality over a one-year study period (November 2014 – October 2015) to address the research objectives. Samples were collected year-round, during both baseflow and events (rain storms and thaws) to determine nutrient concentrations, loads and speciation, and, to relate differences to hydroclimatic drivers and/or management practices.

2.4.2 Field Methods

Hydrometric variables were measured continuously (30-minute intervals) at all four sites. Streamflow was recorded using Doppler Ultrasonic flow sensors (Starflow Model 6526, Unidata Ltd.) at the MH and TE sites, and using pressure transducers (HOBO U20, Onset Ltd.) at the HW and ST sites. Rating curves were developed for sites with pressure transducers, and flow rates estimated by the ultrasonic sensors were validated using manual gauging measurements (Swoffer Model 3000 Current Velocity Meter) under a wide range of flow conditions over the one-year study period. Any gaps in data (all short in duration) were filled using linear interpolation of established relationships between tributary streams and the basin outlet station (TE). Flow units (m^3/s) were normalized (mm) by the size of the sub-catchment for each of the monitoring sites in order to draw hydrologic comparisons.

Micrometeorological variables were recorded at 30 minute intervals (Sutron XLite 9210B data logger) using standard meteorological towers at each site. Towers were equipped with sensors for air temperature (Vaisala HMP155A), soil temperature (LiCor LI-7900-180) and soil moisture (LiCor LI-7900-175) at depths of 5, 10, and 15 cm. Precipitation was recorded at multiple locations throughout the watershed, including the use of a tipping bucket rain gauge at

MH. Temperature and precipitation data from the Environment Canada (EC) monitoring station at the Region of Waterloo International Airport, were used to as historic climate normals to compare to our meteorological dataset. The EC monitoring station is ~3 km south of the TE monitoring site. Snowfall was collected and recorded at ST, MH and TE using Belfort All Environment Universal Precipitation Gauge. Prior to spring snowmelt, snow surveys were conducted at all four sites in February 2015. The winter of 2014/ 2015 experienced no winter thaws, suggesting that the snow survey data was an accurate representation of snowmelt snow water equivalent (SWE).

During storm or thaw events, water samples were collected at all four sites between November 2014 and October 2015 using portable automated water samplers (Teledyne ISCO 6712) in acid-washed (10% H_2SO_4 acid), triple-rinsed, poly-ethylene sample bottles. A total of 16 runoff generating events were captured during the study period, along with periodic baseflow sample collection (approximately on a monthly basis). Water sample collection spanned the rising and falling limbs of each event hydrograph, and event-based sampling intervals ranged from 2-6 hours depending on storm characteristics and expected duration/ response. Over the course of the study period, 136 samples were collected from TE, 160 from MH, 110 from ST, and 96 from HW.

2.4.3 Sample Processing and Laboratory Analysis

Water samples were packed on ice in coolers and transported to the Biogeochemistry Lab at the University of Waterloo and processed immediately. Subsamples were filtered through 0.45 μm cellulose acetate filters (Flipmate, Delta Scientific) and stored in the dark at 4°C for the determination of dissolved nutrient species. An unfiltered subsample was preserved with acid (0.2% H_2SO_4 final concentration), and subsequently digested using acid (Kjeldahl) digestion

(Seal Analytical Hot Block Digestion System BD50) for the determination of TP. DRP and TP samples were analyzed using standard colorimetric methods in the Biogeochemistry Lab at the University of Waterloo using a Bran Luebbe AA3, detection limit 0.001 mg P L^{-1} (Seal Analytical). NO_3^- was analyzed using ion chromatography (DIONEX ICS 3000 with Ion Pac AS18 analytical column, detection limit 0.12 mg N L^{-1}). Approximately 5% of all samples were analyzed in replicate and found to be within 5% of reported values.

2.4.4 Data and Statistical Analysis

A total of 16 hydrologic events were observed during the study period. An event was determined from hydrograph analysis and was deemed to have commenced when a sharp increase in stream flow was observed, and deemed to have ended upon a return to seasonal baseflow conditions. Stream responses with multiple peaks were treated as separate events if the falling limb of the hydrograph was closer to baseflow conditions than to the peak flow of the event. In such cases, events were delineated using a synthetic recession curve. Events were sampled when autosamplers were triggered manually using the “delayed start” setting on the ISCO autosamplers. Consequently, 12 of the 16 events were captured by our autosamplers whereas four were missed when autosamplers failed to trigger or events were shorter than our chosen sampling interval. The missed events were all small events in terms of total discharge, and TP / flow regression estimates were used to estimate loads for them. Additionally, samples that were collected outside of the storm hydrographs were used in combination with seasonal grab samples for baseflow load calculations.

Event-specific flow-weighted mean concentrations (FWMC) of TP, DRP, and NO_3^- were calculated using the continuous streamflow data and the 6-24 samples collected throughout the event (method described by Williams et al., 2015). For each event, a nutrient load/export coefficient (kg/ha, referred to as ‘loads’ in this paper) was calculated using linear interpolation between samples within event hydrographs using equations from Williams et al. (2015). A seasonal baseflow load was also determined for each of the four seasons during which samples were collected. Baseflow loads were determined using linear interpolation of grab samples collected during baseflow conditions, and the streamflow which was determined to be baseflow. Total seasonal loads were then calculated as the sum of baseflow and event loads occurring in June - August (summer), March - May (spring), September - April (fall), or December - February (winter). Seasons were defined using the MAM, JJA, SON, DJF convention due to the March climatic conditions, where little precipitation was observed and a 2-week long spring freshet driven by radiation melt was observed.

The nutrient concentration data collected at all sites were not normally distributed as concentrations tended to be heavily skewed with considerably higher number of observations near the low end of the concentration distribution. Data could not be transformed to meet the assumption of normality, and consequently non-parametric statistics were used. Spatial comparisons of nutrient concentrations between the four sites were tested by the Friedman rank-sum test which does not assume normality and compares the median values of multiple groups. Correlations were estimated between flow and nutrient concentrations (both instantaneous and event-based) using Kendall’s tau correlation coefficient, which is also a non-parametric statistic that does not assume normal distributions of the samples, is monotonic, and is good at detecting non-linear relationships (Helsel and Hirsch, 2002). It is also a ranked-based test statistic, which means that low values of concentration data near the detection limit do not influence the results (Helsel and Hirsch, 2002).

2.5 Results

2.5.1 General Hydroclimatic Patterns During the Study Period

Annual precipitation during the study period was 694.6 mm (Figure 2.2), 24% below the 30-year average for the region. Air temperatures were typical of long-term averages throughout most of the year, with the exception of the winter period, which averaged -8.6°C between December and February, 3.1°C colder than the 30-year average. Streamflow was highly variable both spatially and temporally throughout the year, in response to precipitation and thaw events (Figure 2.2). On a seasonal basis, the highest flows occurred from early March to late April as a large snowmelt event of ~45 mm SWE was followed by three spring rain events (6.6- 13.0 mm in magnitude) within 7 days on saturated soils. June 2015 was considerably wetter than average with 124 mm of rainfall during the month (compared to the historical average of 82.4 mm for June), while the other growing season months from May- October (excluding June) were drier than average (298.5 mm, compared to the historical average of 420.0 mm). Overall, fall 2015 (September, October, November) was dry and atypical for Southern Ontario (200.6 mm of rainfall, which is 17% below average), causing low flow conditions as opposed to the usual fall wet up (Figure 2.2).

2.5.1.1 Spatial Variability in Stream Flow Responses

Three of the four sites (ST, MH, and TE) had similar baseflow conditions (1.92- 2.88 mm/ day). The four sites responded differently to rain and melt events throughout the year. HW (forested reference site) was ephemeral and exhibited no flow conditions during most of the growing season (May - October) although hydrograph responses were observed during the spring (March and April), and large rain events in June (Figure 2.2). MH (second-order agricultural stream) exhibited a flashy hydrograph and had the highest peak discharge during nearly every event, with only a few exceptions (Figure 2.2). Bank-full flow was frequently observed during site visits following large events. In contrast, ST (first-order agricultural stream) had considerably lower peak discharges, and although the duration of storm responses were similar to those of MH, streamflow rarely exceeded bank-full flow. The basin outlet site, TE, had a hydrograph that was intermediate between MH and ST in terms of peak discharge, but had total discharge values (in mm) that were similar to MH, suggesting that flow at the basin outlet was dominated by the second-order stream (MH) on the western lobe of the watershed (Figures 2.1, 2.2). Spatially, the MH site had the highest runoff ratios throughout the study period, with a mean runoff ratio of 0.56 for all monitored events. Yearly mean runoff ratios for the other sites were 0.13 at HW, 0.19 at ST, and 0.44 at TE. The spatial differences between the four sites in terms of runoff ratios and peak flows were consistent in time. The durations of event responses were similar throughout the watershed between MH, ST and TE, with HW being the only exception (with significantly shorter storm responses).

2.5.1.2 Temporal Variability in Streamflow Responses

Streamflow responses for individual events were highly variable throughout the year in terms of runoff volumes, runoff ratios and peak flows. Over the study period, a few peak flow events were dominant. For example, of the events that occurred throughout the year, snowmelt (event 5) had the largest total discharge at all sites (50-110 mm or 7-15% of the total annual flow), which was due to the long duration of the event (~15 days between March 11 – March 25). Although snowmelt represented the largest-magnitude event in terms of flow, peak flows during the snowmelt event (5.5×10^{-5}- 1.9×10^{-4} mm/s) were smaller than peak flows observed during some fall or spring rainfall events (*e.g.* event 1, November 2014 – 6.1×10^{-5}- 3.0×10^{-4} mm/s; event 7, April 2015 – 5.6×10^{-5}- 2.1×10^{-4} mm/s). The peak flow events were the same at three of the sites (ST, MH and TE), with the exception of HW, which had peak flows during spring rainfall but was ephemeral throughout most of the growing season. The temporal streamflow responses were consistent throughout the watershed with the exception of HW as the peak flow events were the peak events at the three other sites (Figure 2.2).

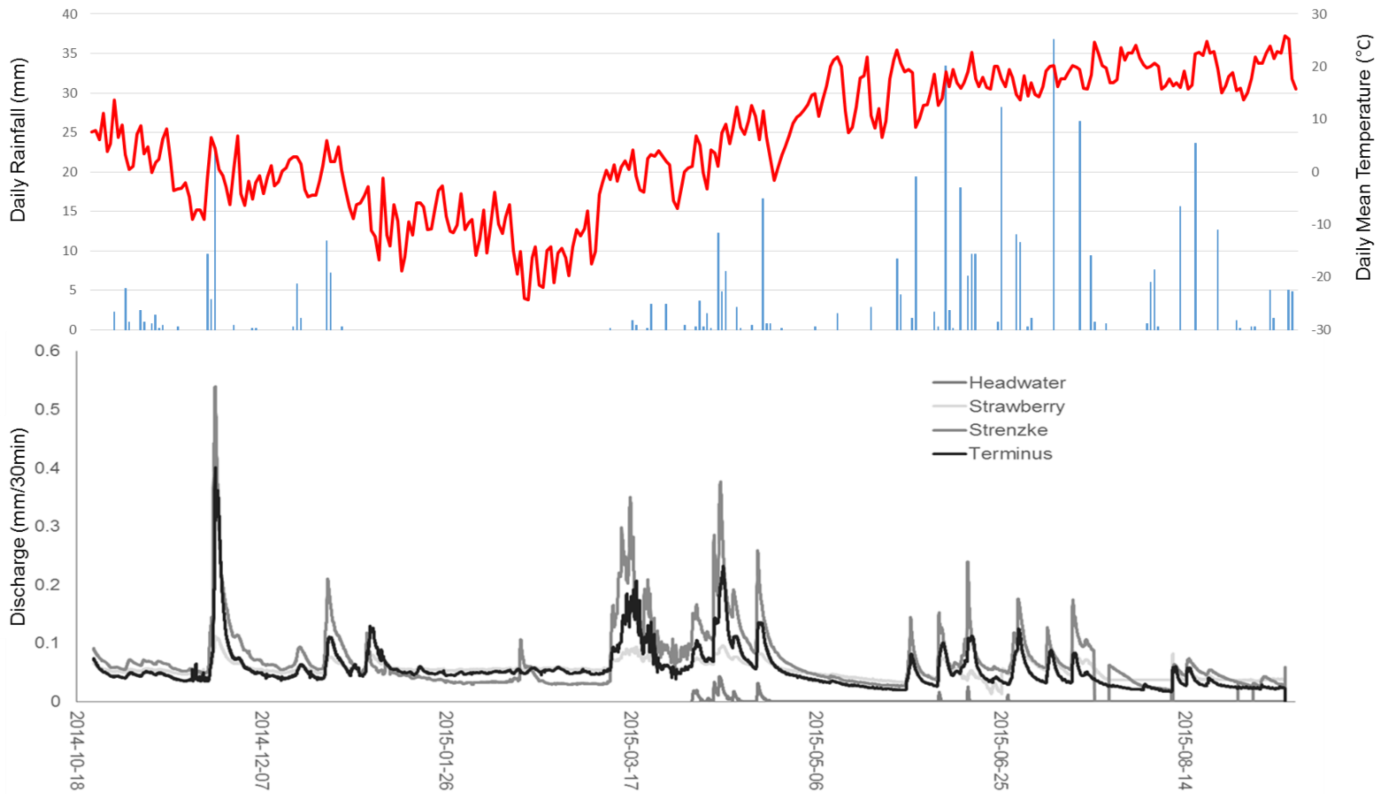

Figure 2.2: (a) Daily precipitation (mm) and mean air temperature (°C). (b) Discharge (mm/ 30 min) at the four monitoring sites in the Hopewell Creek watershed.

Nutrient export can be seasonally driven, as such the hydrologic seasonality was investigated to determine potential seasonal drivers on nutrient export (*i.e.* hydrology or land management). Strong seasonal patterns were observed with regards to streamflow. The spring season (March – May) had the greatest discharge, and this was consistent throughout the watershed at all four stations. This was due to a combination of snowmelt and rainfall on wet soils in spring. In contrast, flow was much lower throughout the summer season, despite the fact that it had the greatest rainfall (June – August). This was likely due to the higher temperatures and evapotranspiration rates during this period, which would have increased hydrologic storage potential. Summer storms were characterized as high-intensity precipitation with discharge that was short in duration as well as having short lag times. However, summer peak flows were lower than those occurring in spring 2015 and fall 2014 due to the drier antecedent conditions.

2.5.2 General Patterns in Nutrient Concentrations and Loads

DRP concentrations were higher during storm events compared to baseflow conditions, where concentrations were low and near detection limits during all seasons and at all sites. Flow-weighted mean concentrations (FWMC) of DRP exhibited little seasonal variation (Figure 2.3), although the snowmelt event (event 5) had the highest DRP FWMC of all events, and this was true for three sites with values of 0.051 mg/L at ST, 0.186 mg/L at MH, and 0.153 mg/L at TE (Figure 2.3). Water samples were not collected at HW for the snowmelt event as the site had not been fully instrumented in time for the snowmelt period. The ST, MH and TE sites had similar DRP concentrations during low flow periods. During event-related flow, ST showed the least temporal variability in DRP of all the sites, whereas MH and TE had higher DRP concentrations coinciding with large discharge events (Figure 2.3). During peak flow events, MH consistently had the greatest DRP concentrations, with TE as an intermediate between MH and ST. In contrast, HW was consistently low in DRP concentrations.

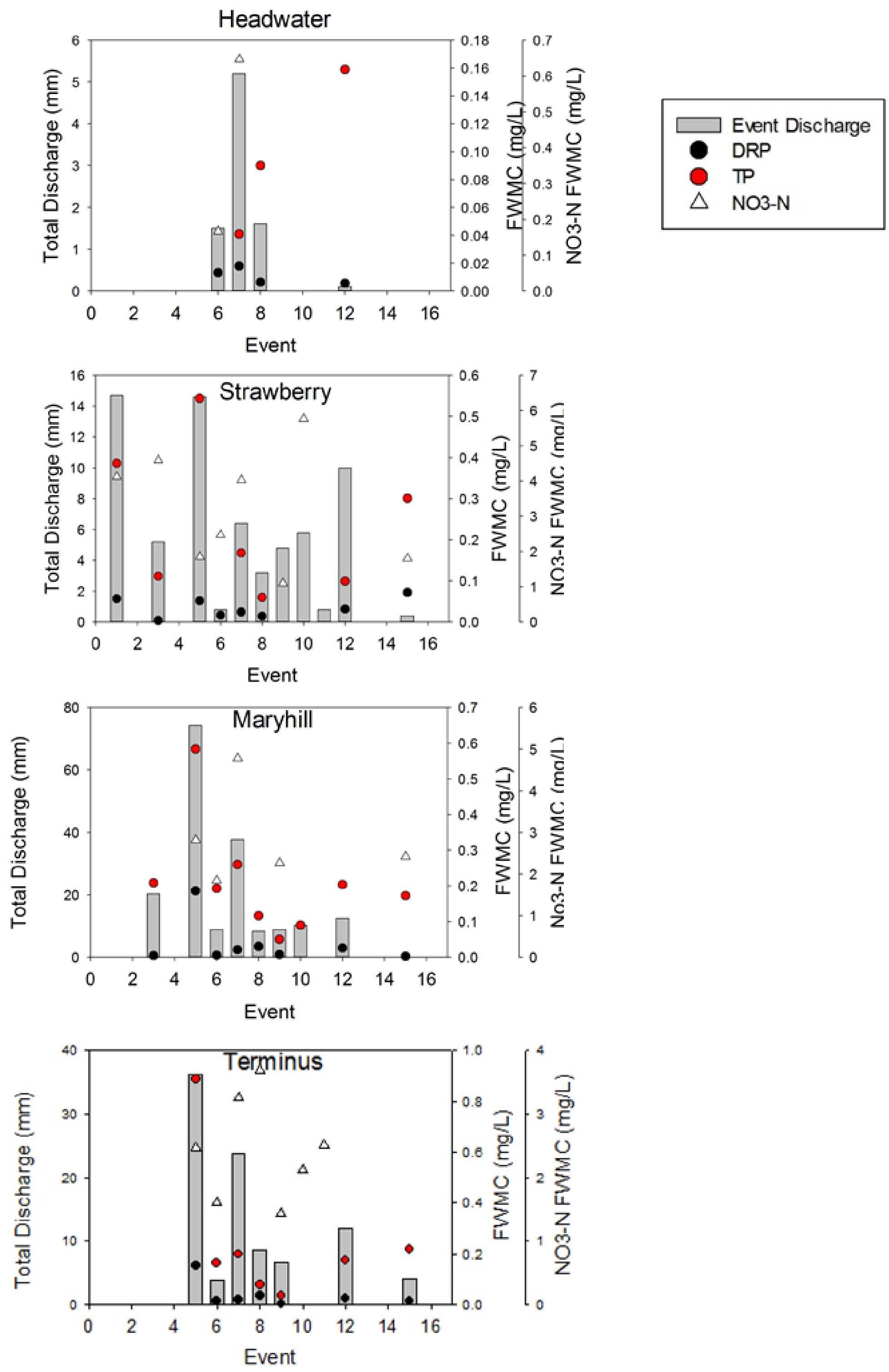

Figure 2.3: FWMC of DRP and TP (primary right y-axis) and NO_3^- (secondary right axis) in mg/L and total discharge (mm) for each event at (a) HW (b) ST (c) MH (d) TE.

TP concentrations were temporally and spatially variable and had a significant positive relationship ($p < 0.1$) with discharge at three of the four sites (ST: $\tau = 0.20$, $p = 0.001$; MH: $\tau = 0.07$, $p = 0.09$; TE: $\tau = 0.11$, $p = 0.03$). MH had the highest TP concentrations of all the sites during all seasons, suggesting a spatial 'hotspot' for TP. In addition to the seasonal pattern, MH was also the TP 'hotspot' during all sampled events, with the exception of event 15 which occurred during the summer (Figure 2.3). ST observed the highest amount of variability in event TP FWMC compared to the other three sites but had the strongest relationship with flow. Further, the DRP:TP ratio was generally the highest at ST throughout all seasons, which is typical of streams with high proportions of tile flow. TE had TP concentrations that were intermediate of MH and ST which was observed during all four seasons, further suggesting that the MH sub-catchment is the major contributor of TP in the watershed. Moreover, TE had the same temporal patterns as both ST and MH, during events as well as seasonally (Figure 2.3). The highest TP concentrations were observed during the March snowmelt (event 5) at all sites, which was synonymous with the 'hot moment' of DRP, indicating that snowmelt can be a key driver of P export for both DRP and TP in an agricultural system.

Seasonally, spring had the highest NO_3^- FWMC at all sites, and in particular, event 7 (April 8- April 16) had the highest NO_3^- concentrations of the year at HW, MH, and TE. Although event 7 had high NO_3^- concentration at ST as well (4.02 mg/L), this was lower than the concentrations of three other events at ST (events 1, 3 and 10). The 'hot moment' was not as apparent for NO_3^- as it was for DRP and TP. A seasonal pattern that was observed to be consistent throughout the watershed was that the highest NO_3^- FWMC occurred in the spring, following snowmelt, as well as in some fall rain events (Figure 2.3). Spatially, ST had the highest NO_3^- concentrations compared to the other sites, and this spatial pattern was observed throughout the year, on an event (Figure 2.3) and seasonal basis (Figure 2.4). Four of the five events with the highest NO_3^- concentrations occurred at ST, with one event during fall (November 23- November 28, 2014), one event during winter (December 24- December 28, 2014), one event during spring (April 8- April 16, 2015), and one event during summer (June 8- June 12, 2015). These observed high concentrations of NO_3^- at ST during all seasons suggests ST is a 'hotspot' for N.

2.5.2.1 Seasonal and Annual Nutrient Loads

Seasonal and annual DRP, TP and NO_3^- loads were calculated to determine the contribution of each monitored sub-catchment to annual nutrient export near the basin outlet. The total discharge at HW was essentially negligible at the yearly time scale. This, coupled with the relatively low FWMC of DRP, TP and NO_3^-, demonstrates that there is no significant nutrient export originating from the forested headwaters of the Hopewell Creek watershed. In contrast, nutrient loads at the agricultural and mixed land use sites were elevated relative to the natural (HW) site, and, exhibited both spatial and temporal variability.

Seasonal DRP loads at the other three sites were strongly influenced by discharge. As such, annual DRP loads predominantly occurred during the spring season throughout the watershed (Figure 2.4) when most runoff occurred. In contrast, the winter period had the lowest DRP loads due to the fact that most flow occurred as baseflow, and DRP concentrations were particularly low during baseflow conditions. Spatially, the same seasonal patterns were observed at all sites, but DRP loads were proportionally higher at MH and TE. These sites had substantially higher total discharge during the spring freshet (event 5, March 11- March 26, 2015), causing the DRP loads to be disproportionately higher during that event, compared to ST and HW. On an annual time-scale, MH contributed a much higher DRP load (0.3 kg/ha) compared to the other sites, ST (0.09 kg/ha), and TE (0.16 kg/ha). ST contributed lower seasonal loads relative the basin average (TE) during winter, spring and fall. However, summer loads at ST were higher than TE and similar to MH, largely a result of a summer rain event where ST had the highest event load (0.01 kg/ha) compared to MH (0.008 kg/ha) and TE (0.005 kg/ha).

Seasonal TP loads were greatest during the spring throughout the watershed due to the large discharge occurring during the spring freshet. The seasonal trend was similar to that of DRP although dampened, as spring did not contribute as high of a proportion of TP annual loads compared to spring DRP loads (Figure 2.4). While summer had low concentrations of TP, the high-intensity precipitation events on dry soils during the summer months were responsible for the export values seen across all sites, while DRP was relatively lower (low DRP:TP ratio at all sites), suggesting high PP export. Three rain events in the fall and early winter (November and December 2014) fell on wet, unfrozen soils, which also resulted in low DRP:TP ratios throughout the watershed, suggesting an additional condition for high PP export.

Spatial patterns of TP were consistent with those of DRP, in that MH contributed greater TP loads than both ST and TE during all seasons. This spatial pattern however, was not as pronounced as it was with DRP due to the higher variability in TP concentrations and the more complex nature of TP export with varying land use and transport pathways. Moreover, while ST exported lower annual TP loads than the watershed average (TE), this was seasonally variable. ST had greater TP loads than TE in the fall and summer, and lower TP loads in the winter and spring.

The relationship between TP export and total event discharge was examined to determine if a relationship existed at sites with varying land use. The relationship at HW was not significant ($p = 0.17$), although this could be attributed to the low number of events captured ($n = 4$). The remaining sites all had significant positive relationships ($p < 0.02$ for ST, MH, and TE), which is expected since discharge is used to calculate load. A spatial trend was observed as the strength of the positive relationship increased downstream with increasing stream size (ST: $\tau = 0.71$; MH: $\tau = 0.78$; TE: $\tau = 0.81$). The strength of this correlation suggests that land use / land management is a much less significant driver of nutrient export compared to total discharge, particularly as stream size increases

Seasonal patterns of NO_3^- export differed depending on location within the watershed (Figure 2.4c). ST had similar seasonal loads during all seasons with a range of 2.4 kg/ha (fall: 4.2 kg/ha; winter: 4.7 kg/ha; spring: 6.6 kg/ha; summer: 4.8 kg/ha), likely due to the consistently higher baseflow concentrations that were observed at the site. NO_3^- export at MH had a greater range of 9.7 kg/ha (1.9 kg/ha in winter to 11.6 kg/ha in spring) compared to the other agricultural site, ST, despite the similarity in annual loads (ST: 20.2 kg/ha; MH: 21.1 kg/ha). Spatially, the pattern that was apparent for NO_3^- loads was that the two agricultural sites exported greater NO_3^- loads than TE both annually, and during all four seasons. This differed from the spatial pattern of DRP and TP, where MH had considerably higher export values than ST, while TE had export coefficients that were intermediate of the two agricultural sites. The seasonal NO_3^- load data (Figure 2.4c) indicate that while a ‘hot moment’ was not observed, land use may have a strong influence on NO_3^- export as the annual loads were highest at the two agricultural sites.

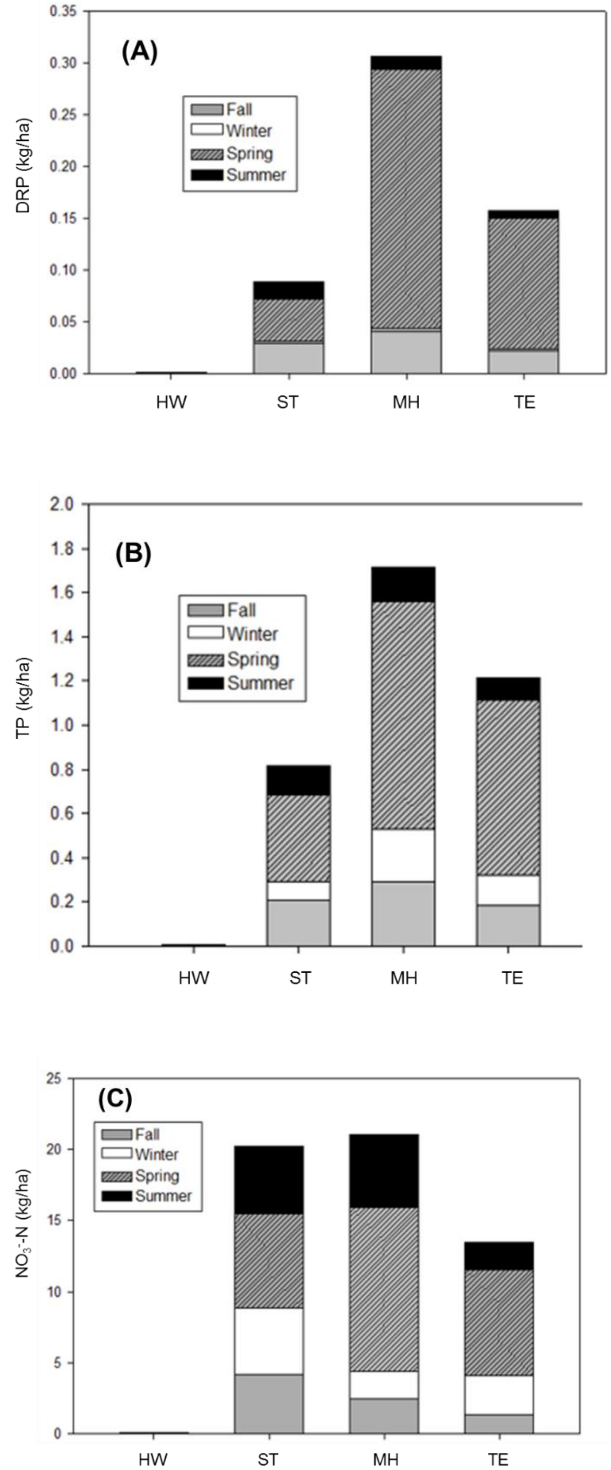

Figure 2.4: Seasonal and annual export coefficients at the four monitoring locations in the Hopewell watershed a) DRP b) TP and c) NO_3^-

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2.6 Discussion

This study has shown that agricultural land practices elevate nutrient concentrations in streamflow above background conditions for this region. HW was selected as a monitoring site to serve as an analogue of “background” or baseline conditions to get a sense of pre-settlement nutrient dynamics. The results from monitoring HW showed that it is not clear whether or not it is a true representation of background conditions as the hydrology of the stream was ephemeral. It is unclear whether this is site-specific, or, indicative of pre-development runoff conditions. The estimated loads from HW were negligible as a result of both the stream drying up during baseflow conditions and remaining dry during most of the summer months, but also due to the fact that nutrient concentrations were consistently low. These data suggest that land use, specifically agriculture, has an impact on N and P export. This has been shown in other studies in other regions including the United States Midwest (Arbuckle and Downing, 2001; Coulter et al., 2004), southeastern United States (Brion et al., 2011; Beckert et al., 2011; Niño de Guzmán et al., 2012), prairie landscapes (Dodds and Oakes, 2006), Europe (Peršić et al., 2013), tropical regions (Castillo, 2010), and New Zealand (Abell et al., 2011), as well as in other watersheds in Southern Ontario (Sliva and Williams, 2001), .

While there may not be a strong enough relationship between discharge and P or N concentrations to predict nutrient concentrations with great accuracy on an event scale, the data in Figure 2.3 suggest that event-based sampling regimes are important for load estimation in agricultural and mixed land use watersheds due to the amount of variability from site to site. Moreover, this is particularly true for P, as the events that had high discharge totals also had the highest TP FWMC, with the exception of HW (Figure 2.3). Additionally, the speciation of P differed spatially as MH generally had lower DRP:TP ratios, which indicates more P bound to particulates, while ST had higher DRP:TP ratios, indicating more P in the dissolved form (Figure 2.3). This spatial pattern was most prominent during event 12 (June 28- July 2, 2015), a large summer rain event in which the DRP:TP ratio was much higher for ST (0.31) compared to MH (0.13), TE (0.13) and HW (0.04); this suggests a considerable portion of P export via particulates at all sites except ST. TE had a ratio that was intermediate of the tributary sites and was similar to that of MH, further evidence that water quality at the basin outlet is strongly influenced by the MH sub-catchment.

Within the agricultural areas of the mixed land use watershed, this study has identified both 'hot spots' and 'hot moments' for nutrient loading. The MH site represents a 'hot spot' in the watershed, with consistently greater P concentrations and loads than the other sites. This spatial pattern was observed during all seasons and suggests that localized land management at the field scale is important. The two agricultural sites (ST and MH) were seemingly similar based on dominant land use (agriculture), soil type, sub-catchment scale topography (Table 2.1), but showed stark differences in the nutrient and flow dynamics. This suggests potential additional drivers, including land management. The MH monitoring site is located immediately downstream of livestock operations (dairy farm), which has been linked to high P concentrations in other studies (Niño de Guzmán et al., 2012), and is adjacent to pasture land, although cattle do not access the stream, which is fenced off. The floodplain of the stream is flat and receives runoff from adjacent sloped fields that are more prone to frequent surface inundation in comparison to the other sites. It is likely that much of the P losses at this site are generated by surface runoff as the high P concentrations and loads were observed during peak flow events during which surface overland flow was observed. The significance of overland flow in event-related P loss has been observed by others in the same region (*e.g.* Macrae et al., 2007a, 2010).

This study has also identified the occurrence of ‘hot moments’ within the mixed land use watershed. Seasonally, the dominant pattern was that spring had the highest nutrient loads than any other season, attributed to the large spring freshet that occurred from March 11- March 26, 2015. There were no mid-winter thaws during the winter of 2014/ 2015 that are typical in Southern Ontario (Environment Canada, 2017), which resulted in high flows in March during a two week period of radiation-melt with little rainfall. Further, discharge was a strong control on DRP and TP during both short temporal scales (events) and long temporal scales (seasons). However, this was more evident during events and seasons that had higher soil moisture (*i.e.*, excluding summer months). The large nutrient loads that were observed following snowmelt points to the importance of year-round stream sampling designs in order to capture these ‘hot moments’. The importance of monitoring the non-growing season for capturing large nutrient export has been shown in other studies and this is an area of increasing attention, particularly in cool temperate regions like the Great Lakes Basin (Van Esbroeck et al., 2017).

During the study period, the observed spatial pattern in the Hopewell Creek watershed differed between P and N. The MH sub-catchment was the major contributor of DRP and TP to the watershed outlet, while both agricultural sites, MH and ST, contributed proportionately higher NO_3^- loads. MH had the highest concentrations and load of both P species but the weakest relationship between P concentrations and flow. This suggests that most of the peak P occurs before peak flow, and that the P being exported is not in the dissolved form and may be caused by quickflow pathways. Moreover, the loads of NO_3^- were comparatively similar at both agricultural sites despite the larger annual discharge at MH, suggesting that there is more NO_3^- leaving the ST sub-ctchment compared to MH relative to flow. While both sites are agricultural, the land management practices differ within the two sub-catchments. MH has greater area of pasture land and more livestock, which has been shown to have lower N:P ratios compared to agricultural areas that are predominately row crops (Arbuckle and Downing, 2001; Niño de Guzmán et al., 2012). Additionally, ST has a higher proportion of tile-drained agricultural fields, 65% compared to 47% at MH, which has also been shown to be a significant transport mechanism for NO_3^- (Macrae et al., 2007b; Stenberg et al., 2012).

2.7 Conclusion

The results of this study show that multi-scale sub-watershed studies can identify local ‘hotspots’ for P export in mixed land use watersheds. Temporally, a considerable proportion of TP and NO_3^- were exported during the winter months, which did not include the large freshet in March. This points to the importance of year-round monitoring of nutrient export in order to better understand annual nutrient export dynamics and to more accurately inform watershed-scale nutrient models. Moreover, this is of particular importance in agricultural landscapes where land management activities include fertilizer application in the fall which can lead to large N and P exports during winter and spring thaw events. Further, drawing on the weight of evidence from sub-catchment land use (*i.e.*, presence of livestock operations) and statistical relationships between total discharge and TP loads, discharge and land management practices (*e.g.*, livestock and timing of fertilizer application) are likely stronger controls of P export than the presence of tile drainage. The local hydrologic regime should therefore be considered when land managers and farmers are determining site-specific best management practices.

Chapter 3 - Linking antecedent moisture conditions and flowpath connectivity as drivers of nutrient export in an agricultural catchment in Southern Ontario, Canada

3.1 Overview

Non-point source (NPS) pollution from agricultural catchments to receiving water bodies has been recognised as a serious problem in North America. In the Great Lakes Region, NPS pollution from surrounding agricultural lands has led to the eutrophication of streams and small lakes as well as the occurrence of harmful and nuisance algal blooms in Lake Erie. Although nutrient loads have been attributed to both surface runoff and tile drainage, the relative contributions of these pathways vary in time and space, challenging our ability to predict or model loads, set realistic targets, and make strategic land management decisions. An improved understanding of the drivers of NPS agricultural pollution is required to optimize land management practices that reduce excess nutrient runoff. Two agricultural sub-catchments in Southern Ontario, Canada that differed in land management practices were monitored over 16 months to characterize temporal patterns in discharge and total phosphorus (TP) and nitrate (NO_3^-) concentration and mass export, and, to relate these patterns to hydrologic flowpaths and antecedent moisture conditions. TP and NO_3^- loads at both sites increased with discharge, antecedent moisture conditions, and with precipitation magnitude, but predictive relationships were not found between TP and NO_3^- concentrations and these variables. The proportions of stream water samples originating from three geographical sources (overland flow, groundwater, and tile drain flow) were estimated using end-member mixing analysis (EMMA). The inclusion of flowpath proportions increased the predictive power of multiple linear regressions (MLR) for TP flow-weighted mean concentrations (FWMC) at one site and NO_3^- loads at the other site. The percentage of stream water that originated from overland flow was positively related to TP FWMC, while the percentage of stream water originating from groundwater was related to NO_3^-

loads. The results of this study suggest that EMMA can be used to estimate flowpath contributions in tile-drained agricultural landscapes, and that quantifying flowpath contributions can increase the predictive power of MLR models for nutrient concentrations and loads.

3.2 Introduction

Non-point source (NPS) pollution to water bodies has been identified as a major cause of water quality issues, including eutrophication (Banner et al., 2009). Agriculture has been identified as a large contributor of NPS pollution as a result of excess nutrient export (Arbuckle and Downing, 2001; Algoazany et al., 2007) of both phosphorus (P) (Sharpley and Syers, 1979; Sharpley et al., 1999) and nitrogen (N) (Correll et al., 1999; Evans et al., 2014) as well as sediment (Heathcote et al., 2013). Spatial variability in P loss has been related to soil texture, slope, and land management practices related to P application and tillage (Brion et al., 2011; Aarons and Gourley, 2012; Buchanan et al., 2013; Brand et al., 2014; Lam et al., 2016b). Significant temporal variability in hydrochemical export has also been observed (Sharpley et al., 1999; M L Macrae et al., 2007a; Macrae et al., 2010; van Bochove et al., 2011; Lam, et al., 2016a), although the specific drivers of this variability are poorly understood (Macrae et al., 2010). To improve our understanding of spatial and temporal variability in hydrochemical export, researchers have increasingly begun to investigate processes driving nutrient export. To better understand the source–mobilization–delivery–impact continuum (Bracken and Croke, 2007; Sherriff et al., 2016), numerous studies have focused on antecedent moisture conditions (James and Roulet, 2009; Vidon and Cuadra, 2010; Macrae et al., 2010) and their role on source activation (Ali et al., 2010) and on hydrologic connectivity from source to stream. In broad terms, hydrologic connectivity is defined as the unimpeded movement of water between two locations, either via natural flowpaths (*e.g.*, James and Roulet, 2007; Davis et al., 2014) or via man-made flowpaths such as tile drains (Kronholm and Capel, 2015; Lam et al., 2016a) in temperate zones in North America. While antecedent moisture conditions and flowpath connectivity have either been shown or presumed to have an influence on solute export in naturally drained landscapes, less is known about their co-dependence in artificially drained agricultural landscapes, thus paving the way for an emerging area of research (Outram et al., 2016).

In the context of agricultural landscapes, knowledge about antecedent moisture conditions and flowpath connectivity is required to better understand critical source areas (CSAs), which are areas that have the potential to contribute high nutrient export as a result of the combination of high supply and transport potential (McDowell and Srinivasan, 2009). Most landscapes are particularly vulnerable to P export during large storm events (Sharpley et al., 1999), when CSAs are activated. The relative contributions of tile drainage and overland flow to total runoff have recently been of interest to scientists and managers, as they influence both the mass and speciation of nutrient export to streams. Tile drainage may decrease overland flow by lowering the water table, thereby reducing nutrient export through this pathway. However, tile drainage can increase the contributing area to a stream during storm events and increase subsurface flowpath connectivity, thus leading to higher-magnitude hydrologic responses and biogeochemical fluxes (Dils and Heathwaite, 1999). Further, overland flow, groundwater and tile drain responses can vary depending on antecedent soil moisture conditions (Macrae et al., 2007b) as well as the timing, intensity and duration of precipitation (Vidon and Cuadra, 2010; Kröger et al., 2013).

Overland flow tends to have high levels of both dissolved reactive P (DRP) and particulate P (PP) due to erosion of the soil at the surface (Grant et al., 1996) and the capability of a soil to sorb P, which is affected by organic content (Kronvang et al., 2009), clay content (Eastman et al., 2010) and soil P content (Sharpley and Syers, 1979). The generation of overland flow, and the resulting large-magnitude events for P loss, tend to be associated with peak flow events, typically observed during the non-growing season or under wet antecedent moisture conditions (*e.g*. Van Esbroeck et al., 2017; Macrae et al., 2010). In contrast, N, particularly nitrate (NO_3^-), tends to be more associated with shallow groundwater due to its negative charge and its high mobility and solubility in water (Abell et al., 2011). Tile drains have the potential to enhance these losses due to the presence of macropores and preferential transport pathways, which rapidly flush nutrients from surface soil layers into tile drains; however, nutrient concentrations in tile drains can also be highly variable both during and among different events (Macrae et al., 2007b).

Understanding dominant water flowpaths and their controls during a range of conditions allows an improved ability to predict how a system responds to weather events (James and Roulet, 2007). Many past studies that have examined flowpath dynamics in response to snowmelt or rainfall events have focused on forested catchments (James and Roulet, 2009; Ali et al., 2010). Several of these studies used end-member mixing analysis (EMMA) as a tool to estimate the relative contributions of differing flowpaths, by identifying ionic or isotopic end-members which are quasi-conservative and assumed unique to each flowpath. EMMA has also been used as a way to infer source-to-stream flowpath connectivity: the presence and mixing of various end-members, as detected by this method, can be used as a surrogate measure for flow and solutes mobilized from various sources and effectively transported to streams (Ali et al., 2010). Other tools exist for determining flowpath contributions, including the use of water temperature as a proxy for groundwater contributions, as well as the comparison of N:P ratios during baseflow and storm events (Green et al., 2007). Recently, the application of EMMA has expanded to agricultural systems (Edwards et al., 2012; Mellander et al., 2012; Outram et al., 2016).

Previous studies on the drivers of solute export in a range of landscapes have either focused on a limited number of events (Soulsby et al., 2003; Mellander et al., 2012), or chosen to examine their dependence on antecedent moisture conditions (AMC) (Davis et al., 2014) or transport pathways (Buda et al., 2009; Mellander et al., 2016), in isolation. A few studies have investigated the development of predictive relationships between nutrient export and both AMC and precipitation at the field scale (Lam et al., 2016a) and the watershed scale (Macrae et al., 2010). However, with the exception of a recent study by Outram et al. (2016), most studies have not explored relationships between specific flowpaths, AMC and nutrient export in agricultural watersheds. Thus, the objectives of this study were to:

1) Characterize temporal variability in water flow and nutrient fluxes from two small agricultural watersheds over a one year period, and

2) Determine if the consideration of flowpath connectivity, estimated from EMMA, increases the predictive power of relationships between event dynamics (precipitation, and AMC) and nutrient export.

3.3 Study Area

The study was conducted in the Hopewell Creek watershed, a mixed land use watershed located ~15 km east of Kitchener-Waterloo, Ontario. Hopewell Creek is a third-order stream that drains into the Grand River, which subsequently drains into Lake Erie. The Hopewell Creek watershed is 72 km^2 in area, and has soils that are classified as dominantly sandy loam, with some loams, organic soils and till. Soil types in the watershed include Gray Brown luvisols, Melanic Brunisols and Humic gleysols (Presant and Wicklund, 1971). The catchment is predominantly groundwater-fed, but overland flow contributions to the streams can occur during high flow events from the ponding of water at the surface in microtopographic lows (Macrae et al., 2007a).

Two monitoring sites were established within the Hopewell Creek watershed, namely Strawberry Creek (ST) and Maryhill (MH), both of which are primarily agricultural in land use. Both streams flow adjacent to agricultural, tile-drained fields. Tile-drains at both monitoring sites can contribute significant flow to the stream when active. ST is a first-order stream with a contributing area of approximately 3 km^2, while MH is a second-order stream with a contributing area of approximately 15 km^2. Further, land use practices vary between the two sites. ST has crops that include corn, soybeans, winter wheat and strawberries. MH has cash crops of corn, soybeans, and winter wheat as well as livestock (cattle), grazing pastures and wetlands in its headwaters. Additionally, the ST sub-catchment has been the site of previous agricultural nutrient studies (Macrae et al., 2007a; Macrae et al., 2007b; Macrae et al., 2010).

3.4 Methods

The two agricultural sub-catchments associated with ST and MH were monitored for streamflow and hydrometric variables as well as water quality (both major nutrients and ions) to address the research objectives. Samples were collected during all seasons during both baseflow and events in order to capture a range of hydrologic conditions under which we would expect differing flowpaths, and hydrologic connectivity caused by variable source areas. Samples were identified using sample set numbers; these numbers indicate that the samples were collected during the same event, although do not provide information of the flow conditions during which the samples were collected.

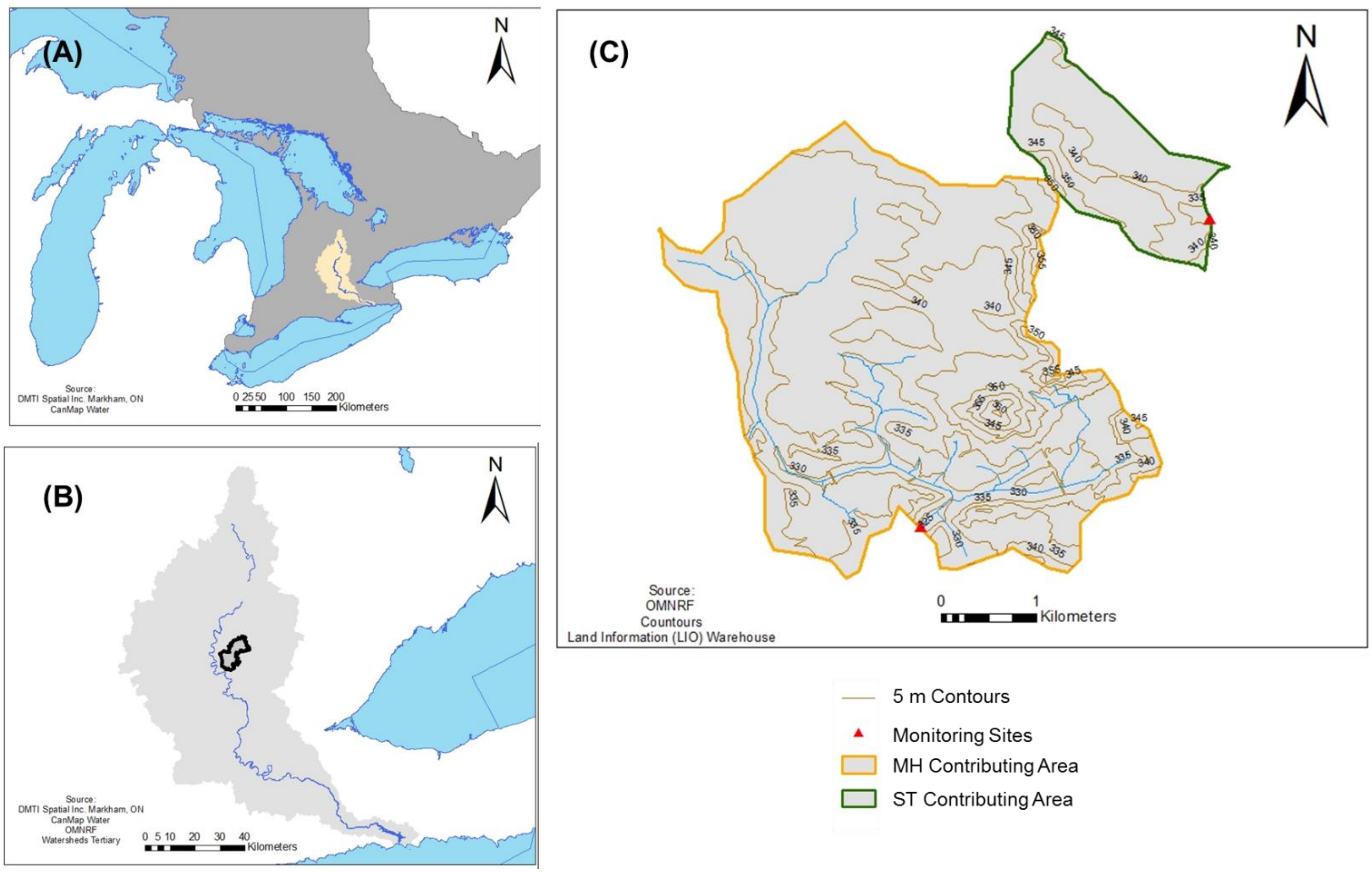


Figure 3.1: a) Location of Grand River watershed in Southern Ontario, Canada, b) Hopewell Creek watershed within the Grand River watershed, c) Two study sites and their sub-catchments. ST outlined in green and MH outlined in orange.

Hydrometric variables were measured continuously (30-minute intervals) at both sites. Continuous streamflow was recorded using Doppler Ultrasonic flow sensors (Starflow Model 6526, Unidata Ltd.) at MH and using a pressure transducer (HOBO U20, Onset Ltd.) at ST. A stage-discharge rating curve was developed at ST with manual flow gauging measurement (Swoffer Model 3000 Current Velocity Meter) under a wide range of flow conditions. At MH, a rating curve was developed using the same methods as ST to validate the estimated flow results from the ultrasonic flow sensor. Any gaps in data (all short in duration) were filled using linear interpolation of established relationships between tributary streams and a flow gauge located at the basin outlet.

Micrometeorological variables were recorded at 30 minute intervals (Sutron XLite 9210B data logger) using standard meteorological towers at each site. Towers were equipped with sensors for air temperature and relative humidity (Viasala HMP155A), soil temperature (LiCor LI-7900-180) and soil moisture (LiCor LI-7900-175) at depths of 5, 10, and 15 cm. Rainfall was recorded at MH using a tipping bucket rain gauge and total precipitation (including snowfall) was recorded at both sites using a heated bucket precipitation gauge (Belfort All Environment Universal Precipitation Gauge).

Stream water samples were collected at both sites using automated portable water samplers (Teledyne ISCO 6712) using pre-washed (10% H_2SO_4 acid) 1L poly-ethylene sample bottles. Samples were collected during event flow and baseflow and during all seasons over a 16 month period starting in November 2014 and ending in February 2016. In general, sampling frequency during events ranged from 2-hour to 6-hour intervals, and the number of samples collected during each event ranged from 6-24 to provide coverage of the entire storm hydrograph. Baseflow samples were collected approximately monthly.

Water samples were packed on ice in coolers and transported to the Biogeochemistry Lab at the University of Waterloo and processed immediately. Subsamples were filtered through 0.45 μm cellulose acetate filters (Flipmate, Delta Scientific) and stored in the dark at 4°C for the determination of dissolved nutrient species and ions. An unfiltered subsample was acidified (0.2% H_2SO_4 final concentration) and subsequently digested (Kjeldahl) for the determination of TP (Seal Analytical BD50, detection limit 0.001 mg P L^{-1}). Filtered samples were analyzed for nitrate, anions and cations using ion chromatography (DIONEX ICS 3000 with Ion Pac AS18 and CS18 analytical columns, detection limits: 0.12 NO_3^-; 10 mg CO_3^{2-} L^{-1}; 0.1 mg SO_4^{2-} L^{-1}; 0.67 mg Ca^{2+}). TP was analyzed using standard colorimetric techniques (Bran Luebbe AA3, Seal Analytical). Approximately 5% of all samples were analyzed in replicate and found to be within 5% of reported values.

Three end-members were considered for use in EMMA. Surface water (overland flow) grab samples were collected in observed surface water flowpaths adjacent to streams within the agricultural fields, as well as in microtopographic lows where storm water pooled. Tile water grab samples were collected from two tiles at MH and one tile at ST (3 tile drains total) while tile water was actively flowing and discharging into the streams. Overland flow and tile end-members were manually sampled during storm events at both sites (grab samples). One storm event per season was sampled to capture a range of flow and climatic conditions (6-12 samples for each end-member). Groundwater end-member samples (12 samples from each site) were collected during a two-week period of low flow in May and June 2015 when tile and overland flowpaths were not active and stream water samples were assumed to represent deep groundwater. End-member grab samples were processed and analyzed using the same methods as the stream water samples. Shallow groundwater samples were also collected from shallow groundwater piezometers or wells (~2 m depth) in the riparian areas adjacent to each of the monitored farm fields using a peristaltic pump. The baseflow stream water samples more accurately represented the groundwater end-member as the well and piezometer samples had a chemical signature similar to the tile end-member.

The selection of chemical constituents for the end-members was performed using the methods outlined by Hooper et al., (1990) and Hooper (2003). Ions were considered for analysis if they were quasi-conservative in nature and had random residuals, as described by Hooper (2003). Ions were then assessed based on differences between each of the three end-members with minimal variation between grab sample values from the same end-member. The remaining possible ions were then assessed based on stream water values, with the first criterion being that the mean stream water value had to fall within the range of the three mean end-member values (Table 3.1). The second criterion was that the standard deviation in the stream water samples had to be less than the mean (Hooper, 2003). The ions that satisfied all assumptions outlined by Hooper (2003) were then considered in subsequent EMMA computations (Table 3.1). Those ions for MH were CO_3^{2-} and Ca^{2+}, while at ST the ions were CO_3^{2-}, SO_4^{2-} and Ca^{2+}.

Table 3.1: Mean and (standard deviation) of ions selected for EMMA at MH and ST

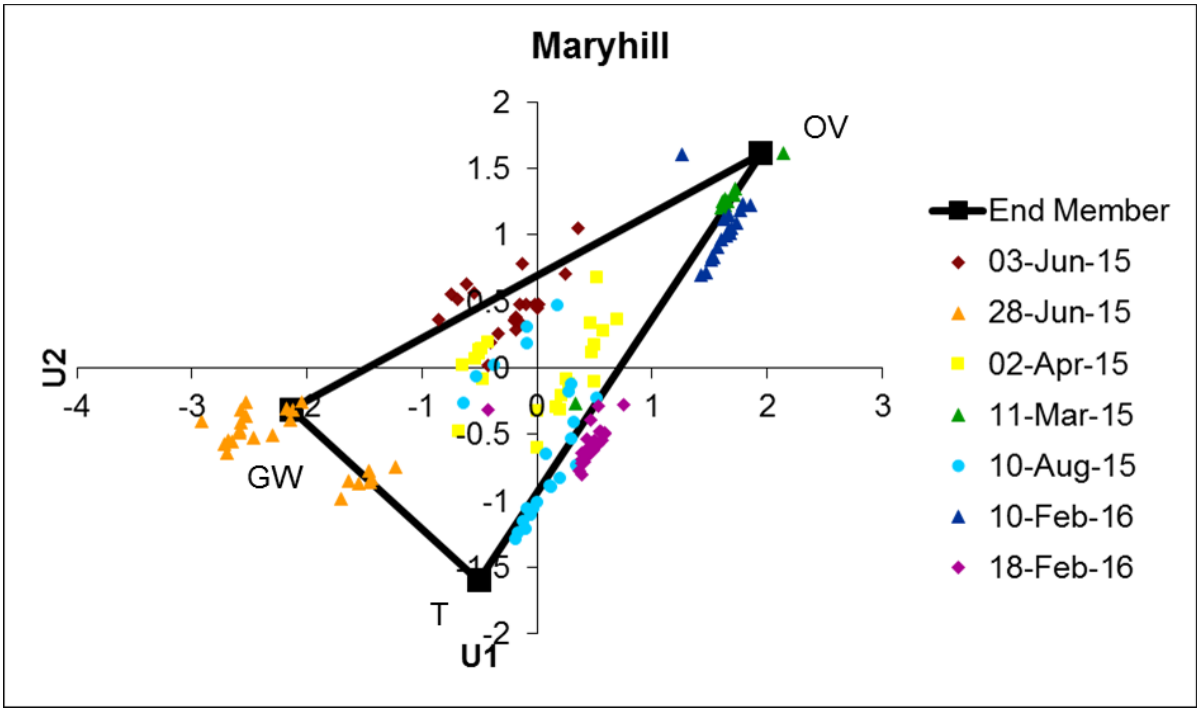
	Maryhill		**Strawberry Creek**		
Sample	**CO_3^{2-} (mg/L)**	**Ca^{2+} (mg/L)**	**CO_3^{2-} (mg/L)**	**SO_4^{2-} (mg/L)**	**Ca^{2+} (mg/L)**
Stream water	78.9 (43.6)	69.3(22.6)	65.7(36)	21.5(14.6)	72.6(22.9)
Overland Flow	27 (12.8)	19 (6.0)	23 (0.5)	0.3 (0.1)	12 (0.5)
Groundwater	126 (5.8)	103 (0.9)	88 (13.7)	30 (6.3)	93 (5.1)
Tile Effluent	84 (2.8)	107 (2.6)	99 (3.6)	12 (1.9)	104 (2.0)

The selected ions represented the unique chemical signatures associated with each end-member for each of the two sites. All ion concentration values were then fed into a principal component analysis (PCA) using R (R studio version 3.3.1). ST had three ions and therefore three principal components (PCs) with PC1 and PC2 representing 78.4 % of total variation. MH had two ions and therefore two principal components, PC1 and PC2. Matrix algebra was then used to project each of the stream water samples into U-space, bounded by the three end-members (*i.e.*, mixing triangle, Figure 3.2). The points that fall outside of the triangles are then projected onto the triangle using an algorithm that calculates the shortest distance to the nearest triangle edge (Burns et al., 2001; Garrett et al., 2012).

Further matrix algebra calculations were performed in Microsoft Excel to estimate the ion concentrations based on the relative flowpath proportions predicted by the EMMA model. Validation of the model was performed by plotting the observed ion concentrations against the predicted ion concentrations from the stream water samples. At both sites, Ca^{2+} represented the strongest variation in PC1, while CO_3^{2-} represented the strongest variation in PC2. Ca^{2+} and CO_3^{2-} were the two ions that were common to sites and additionally, both of these ions were predicted well by the EMMA models for both MH (R^2 values of 0.98 in both cases), and ST (R^2 values of 0.79 and 0.88 respectively). However, the model appears to be less accurate at predicting ion concentrations at high values, as seen in Figure 3.3.

Using the results of this model, the relative contribution from each source (end-member) was estimated for each stream water sample as the proportion of overland flow (% OV), groundwater (% GW) and tile flow (% T).

(A)



(B)

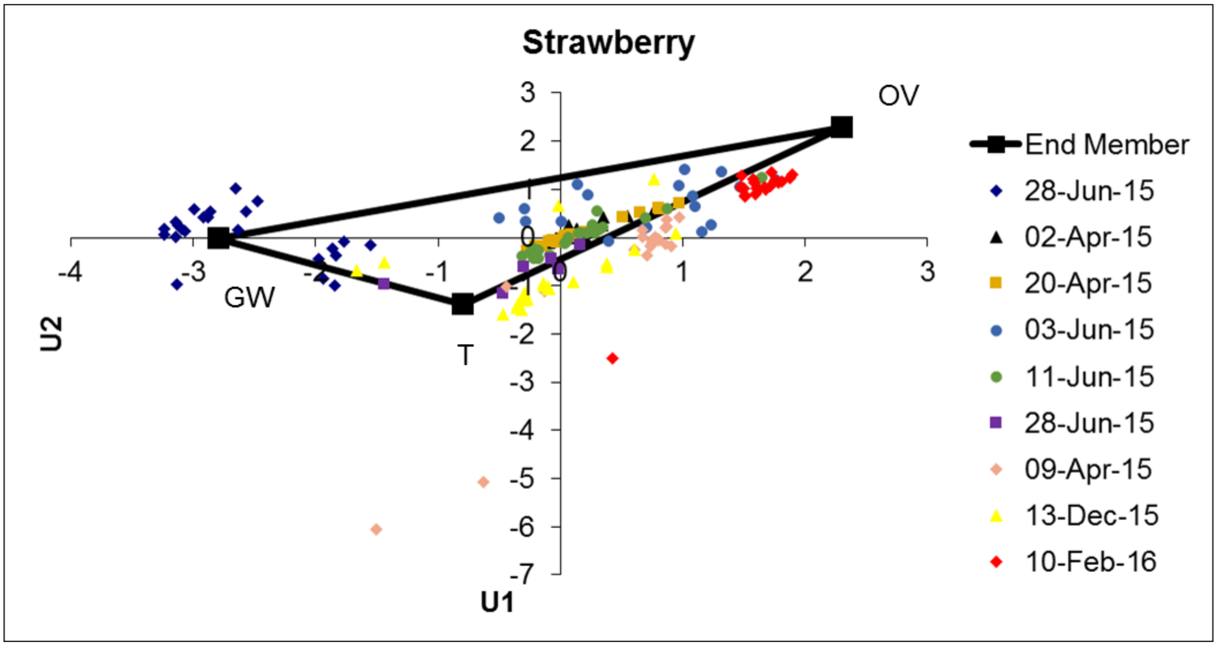


Figure 3.2: a) MH U-Space mixing diagram and b) ST U-Space mixing diagram

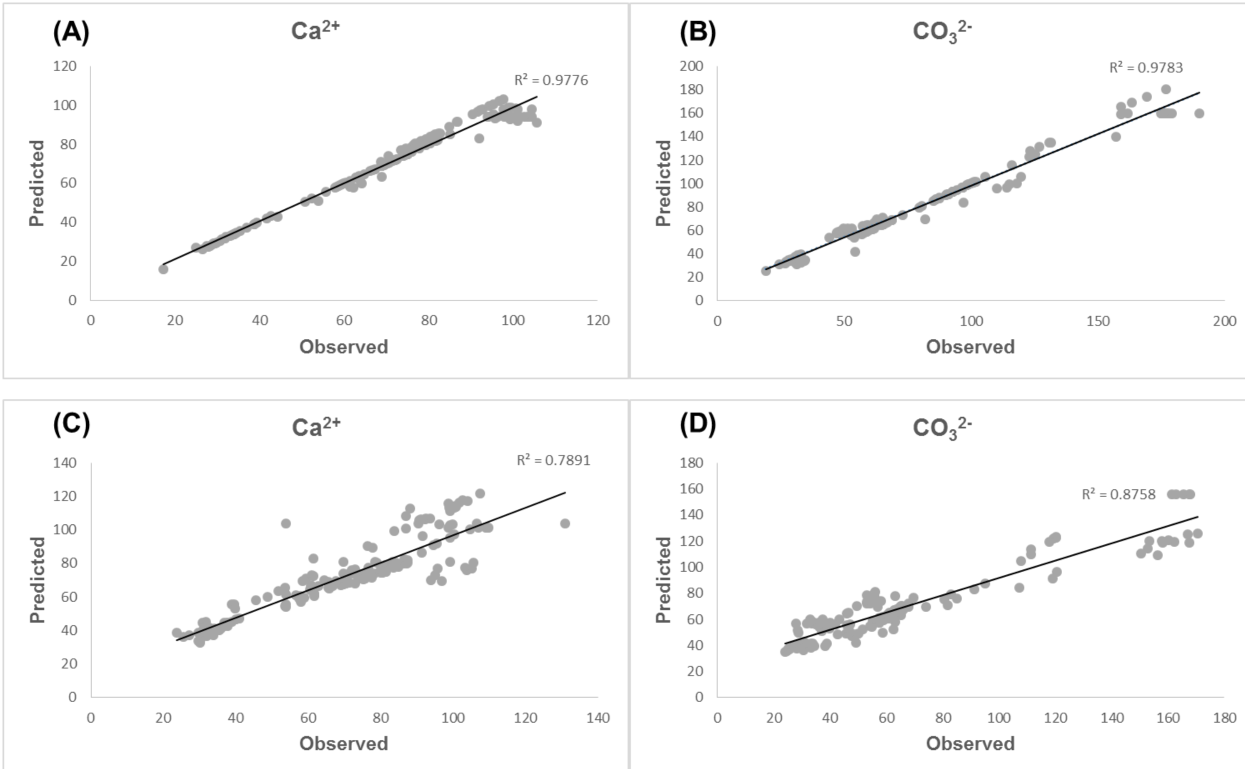


Figure 3.3: EMMA model-predicted versus observed values for a) MH Ca^{2+}, b) MH CO_3^{2-}, c) ST Ca^{2+}, and d) ST CO_3^{2-}

3.4.1 Statistical Analysis

Both single variable regressions and multiple linear regressions (MLR) were used to determine relationships between explanatory variables (discharge, event size, AMC, and flowpath connectivity) and response variables (flow-weighted mean TP and NO_3^- concentrations, event-based TP and NO_3^- loads). Discharge was the total flow occurring during the event calculated from the continuous flow records (m^3/s), event size was the measured total precipitation (mm), and AMC was the volumetric water content (VWC) at 5 cm depth the hour before the rise in the hydrograph. Following the results of the EMMA, flowpath contributions (%OV, %GW, %T) were also added to the MLR equations. In all cases, variables were tested for normality using the Shapiro-Wilk normality test to determine if variable distributions were significantly different from normal ($\alpha = 0.05$). All variables that failed the normality test ($p < 0.05$) were log-transformed to be used in the regressions.

Stepwise MLRs were carried out, a process whereby all different combinations of explanatory variables are assessed in order to determine the "best" model. Multicollinearity was assessed by computing the Variance Inflation Factor (VIF) in R. In cases where multiple models significantly predicted the response variables, the models were tested for performance using the *lm.select* function in the *asbio* package in R (R studio version 3.3.1). This function computes decision criteria including Bayesian Information Criterion (BIC), Mallow's Cp, adjusted R^2, and PRESS (Prediction Error Sum of Squares), which were all used to determine the most appropriate model.

3.5 Results

3.5.1 Monthly Discharge and Nutrient Concentrations

Total monthly discharge (in mm) was seasonally variable with the highest discharge months being March and April, and the lowest discharge months being August and September at both MH and ST (Figure 3.4). The two sites had similar temporal patterns, which was expected as they received similar precipitation with only minor variation during certain events. Further, the temporal trend exhibited by the two streams is fairly typical of monthly flow regimes in the region (GRCA, 2008). As is typical of the region, snowmelt (March 2015) was the largest single discharge event during the study period; however, the largest total monthly discharge was observed in spring (April 2015), particularly at MH, which was the result of substantial spring rainfall on saturated soils (Figure 3.4).

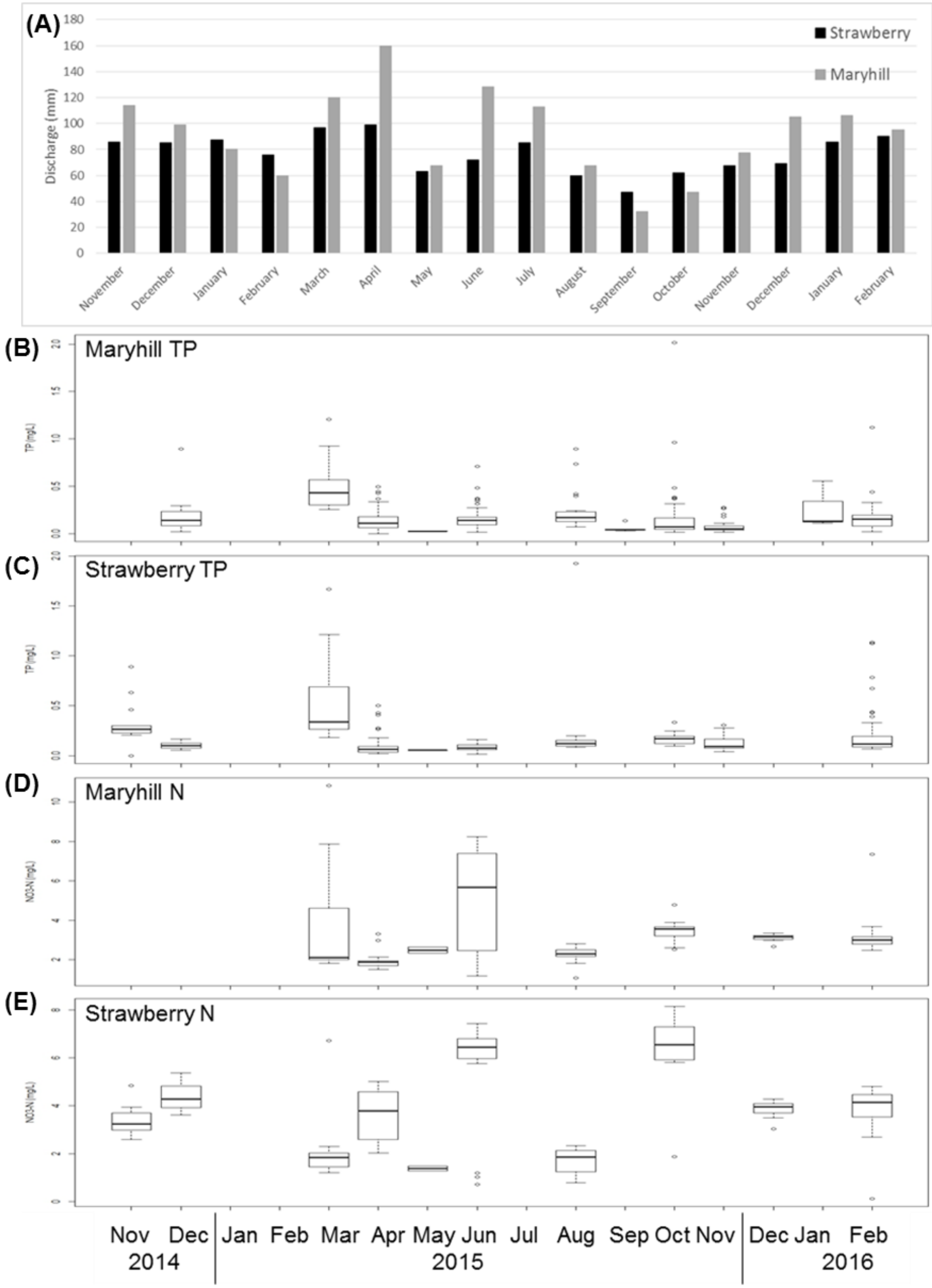


Figure 3.4: a) Monthly discharge b) Maryhill TP concentrations c) Strawberry TP concentrations d) Maryhill NO_3^- concentrations and e) Strawberry NO_3^- concentrations. In the boxplots, medians are indicated by the lines, the upper and lower limits of the boxes represent the 75th and 25th percentiles, the whiskers represent the 10th and 90th percentiles and the open circles are statistical outliers.

The spring months of March and April also had the highest median TP concentrations at MH, whereas ST had the highest TP concentrations in March and February. ST had the highest TP concentrations (indicated by outliers in the boxplots in Figure 3.4) in the months of February, March, April and November, and had relatively low TP concentrations during all other months of the study period. MH had generally higher TP concentrations than ST throughout the year (Figure 3.4): this was exaggerated during the months of June, August, October and December when concentrations were significantly higher. Both sites are adjacent to agricultural fields with similar general land use in the sub-catchments, but we observed elevated TP concentrations at MH throughout the majority of the year, and over a range of flow conditions. This likely suggests different drivers of TP concentrations between the two sites.

Nitrate concentrations were higher at ST compared to MH throughout most of the year, with the exception of August. The high discharge months of March and April resulted in higher median NO_3^- concentrations at ST than at MH, although MH had a greater number of large instantaneous NO_3^- concentrations (as seen by more outliers on the boxplots in Figure 3.4). Temporally, NO_3^- concentrations were most highly elevated in June (MH, ST) and October (ST). It should be noted, however, that MH had experienced consistently greater discharge than ST between March and August, whereas discharge at ST in September and October was greater than at MH. These temporal patterns may be indicative of a shift in flowpath connectivity and nutrient flushing.

3.5.2 Relationships between event discharge, antecedent moisture conditions and nutrient export

Multiple linear regressions (on log transformed variables when data were not normally distributed) were used to investigate relationships between nutrient export (loads and FWMC) and three explanatory variables, *i.e.*, discharge (mm), AMC (VWC prior to event), and event size (mm). Nitrate loads were significantly related to discharge (Figure 3.5) at both ST ($p = 0.02$) and MH ($p = <0.001$), but N loads were also significantly related to AMC ($p = 0.05$) and event size ($p = 0.05$) at the MH site. Nitrate FWMC were not significantly related to any of the explanatory variables in the multiple linear regressions (Figure 3.5), although FWMC of NO_3^- appear to increase with wetter VWC. At MH, this increase in NO_3^- FWMC appears to occur at VWC greater than 20%, which could indicate that greater soil moisture is required to activate tile flow at the MH site, since tiles are a major transport pathway (Macrae et al., 2007b).

TP load was also significantly related to discharge (Figure 3.6) at both ST ($p = 0.004$) and MH ($p = 0.027$) and the multiple linear regression with discharge, AMC and event size accounted for 82% of TP load variability at MH and 87% of TP load variability at ST. TP FWMC was not significantly related to any of the explanatory variables at MH in the multiple linear regression; however, a single linear regression with AMC showed a significant positive relationship ($p = 0.046$; Figure 3.6). In contrast, AMC had the opposite influence on TP FWMC at ST ($p = 0.02$; Figure 3.6), and a weakly positive relationship was instead found between FWMC and event size ($p = 0.097$).

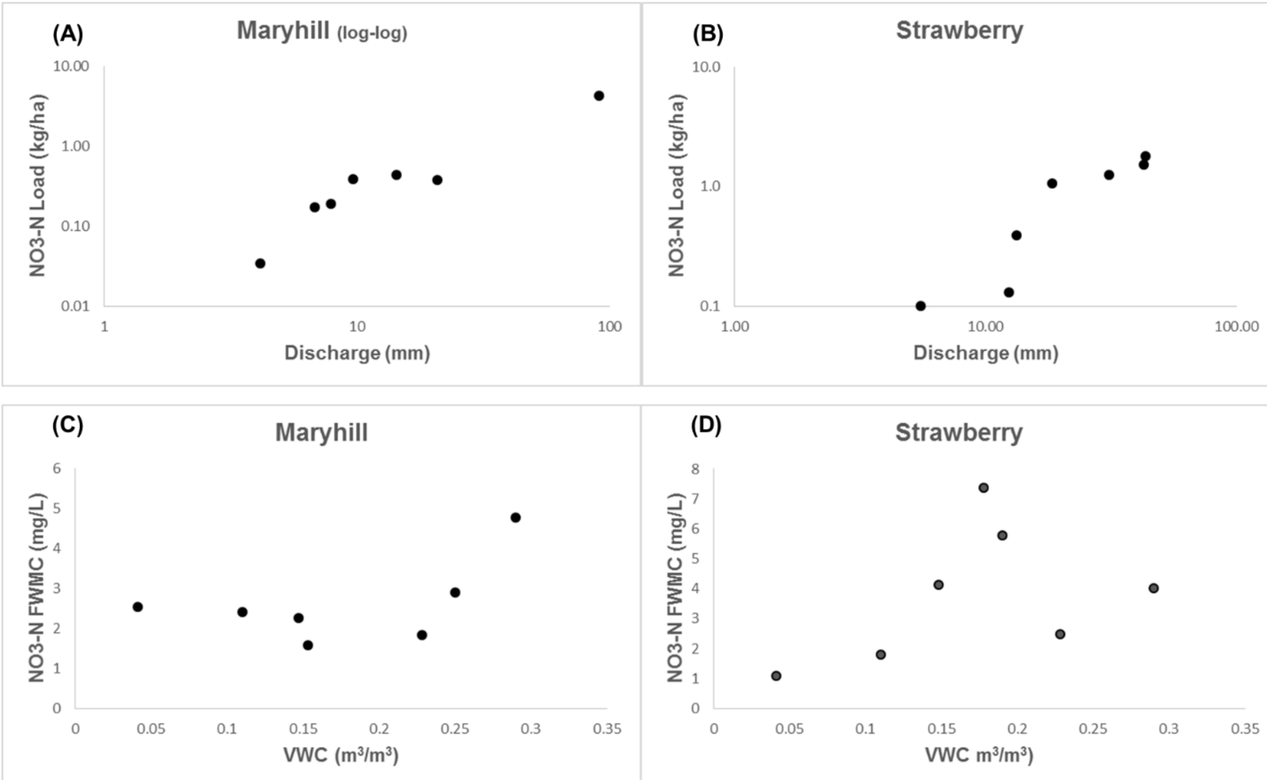


Figure 3.5: Nitrate event dynamics during the study period. A) Maryhill NO_3^- loads vs discharge B) Strawberry NO_3^- loads vs discharge C) Maryhill NO_3^- event FWMC vs antecedent VWC and D) Strawberry NO_3^- event FWMC vs antecedent VWC

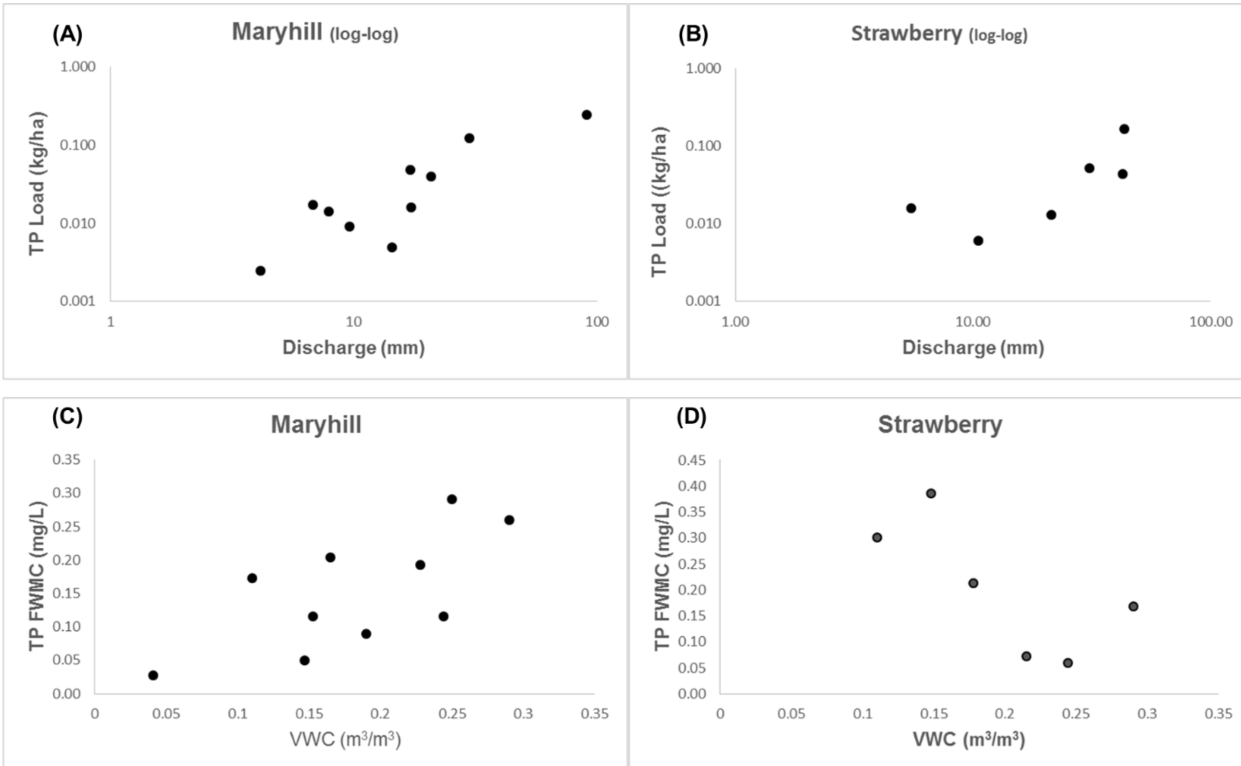


Figure 3.6: TP event dynamics during the study period. A) Maryhill TP loads vs discharge B) Strawberry TP loads vs discharge C) Maryhill TP event FWMC vs antecedent VWC and D) Strawberry TP event FWMC vs antecedent VWC.

3.5.3 End-Member Mixing Analysis, flowpaths and nutrients

The results from the end-member mixing models were used to infer variability in individual flowpath contributions from stream water samples that were analyzed for ions. The proportions of end-member contribution differed between the two sites as MH samples more frequently had a higher proportion of overland flow as indicated by the greater number of samples on the left side of the ternary diagrams (Figure 3.7). ST samples were commonly associated with a high proportion of tile drain flow as many of the samples in Figure 3.7b are located on the right side of the triangle.

At both sites, there was greater variability between events than within events, which is seen by the clustering of samples from the same sample set in the ternary diagrams (Figure 3.7). No clear trends emerged when the samples were grouped into three bins by natural *k*-means clustering for both TP (Figure 3.8) and NO_3^- (Figure 3.9). This lack of clustering could be explained by the tendency of individual samples to vary considerably in nutrient concentration depending on the timing of the hydrograph as well as hysteresis effects (James and Roulet, 2009), particularly associated with TP. This lack of visible patterns emerging from the ternary diagrams of TP (Figure 3.8) and NO_3^- (Figure 3.9), suggests that flowpath contributions may not be strongly related to nutrient concentrations of individual samples. This, coupled with the flowpath clustering by events suggests it may be more appropriate to investigate these relationships at the event-scale and led to investigation of the relationship between flowpath contributions and FWMC of TP and NO_3^- at both sites.

At MH, the contribution of overland flow (% OV) was added as an explanatory variable in the same multiple linear regression discussed in the previous results section "*event discharge, antecedent moisture and nutrient export*". The addition of % OV as an explanatory variable resulted in an increase in the adjusted R^2 value to 0.86 ($p = 0.032$) and a weakly significant relationship was found between TP FWMC and % OV ($p = 0.087$). Discharge was the weakest predictor of TP FWMC, and after removal, increased the adjusted R^2 from 0.86 to 0.88 and both explanatory variables, event size and % OV were significantly related to TP FWMC (event size $p = 0.007$; % OV $p = 0.02$). Nitrate analysis incorporated the other two end-members, % groundwater (% GW and % tile flow (% T)), given that groundwater and tile discharge are expected to be more closely linked to NO_3^- concentrations. The same iterative (stepwise) multiple linear regressions were performed with NO_3^- (both FWMC and load) as the response variables and no model was able to find a significant explanatory variable for either load or FWMC. Variance inflation factors (VIF) for all MLRs showed that multicollinearity between explanatory variables was not significant.

At ST, % OV was regressed using the same methods as the MH data, although no significant relationships were found between TP FWMC and any of the flowpath explanatory variables. % GW and %T were used as added explanatory variables in stepwise regressions with NO_3^- FWMC as the response variable and no combination of explanatory variables resulted in a significant relationship. The addition of the flowpath explanatory variables resulted in a significant MLR model for NO_3^- load where AMC, event size, % GW, and % T were the explanatory variables (Adjusted $R^2 = 0.90$; p-value = 0.02). This significant MLR increased the predictive power compared to the simple linear regression of NO_3^- load with discharge (Table 3.2). VIFs for all MLRs showed that multicollinearity between explanatory variables was not significant.

3.5.4 Antecedent Moisture and flowpaths

Linear regressions were performed between AMC and each of the three end member flow pathways (% OV, % GW, and % T) to determine if AMC was a significant driver of flowpath contribution. At both MH and ST, there were no significant relationships between AMC and any of the flowpaths ($p > 0.1$). Additionally, the MLRs that had AMC and one or more of the flowpaths as explanatory variables all had VIFs that were less than 10, suggesting there was no multicollinearity between AMC and any of the flowpaths.

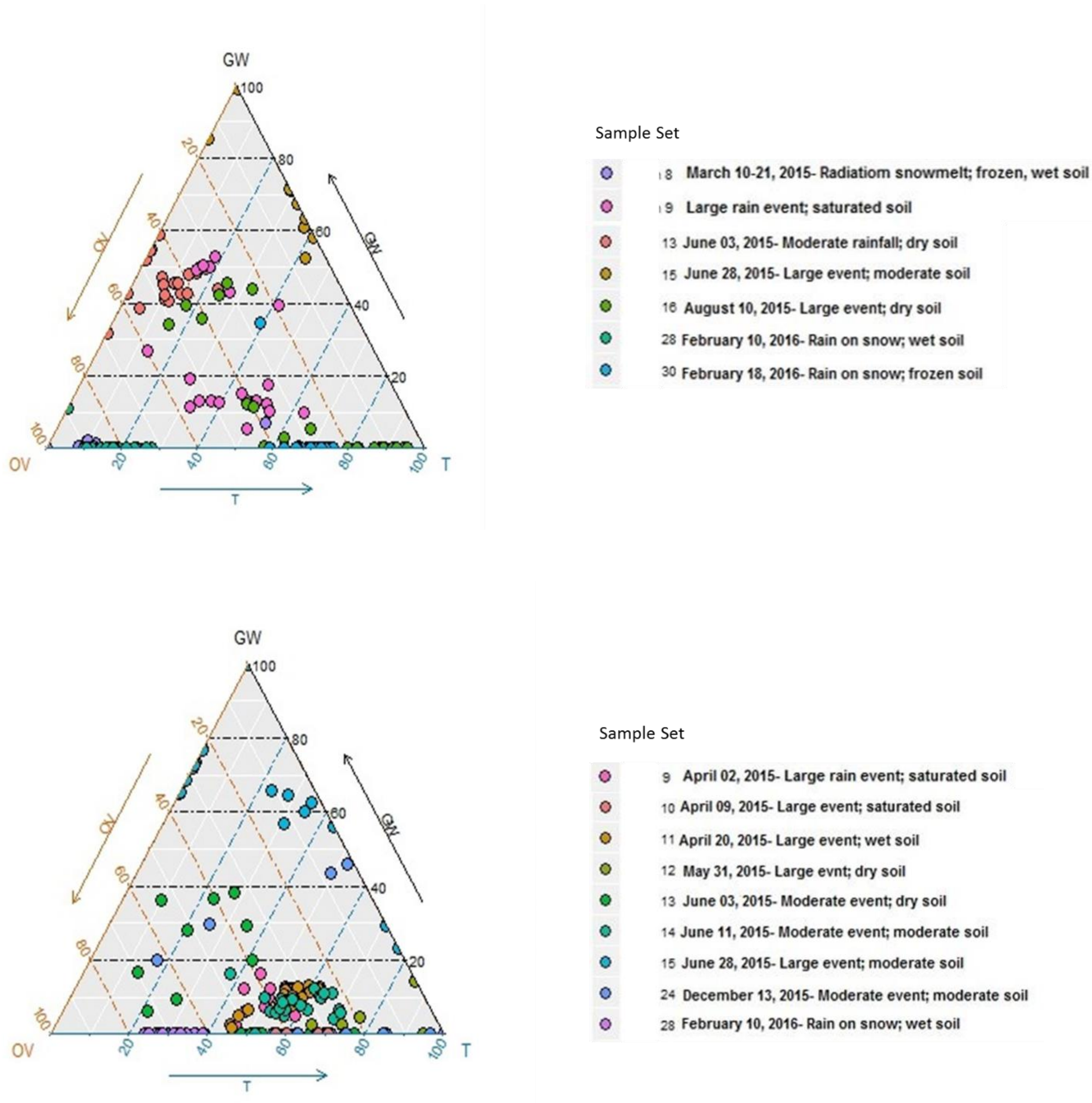


Figure 3.7: Ternary diagrams representing the estimated, relative contributions of three flowpaths, *i.e*., overland flow (OV), groundwater (GW) and tile drains (T), for each sample at A) Maryhill and B) Strawberry Creek for each sample set (event or suite of events)

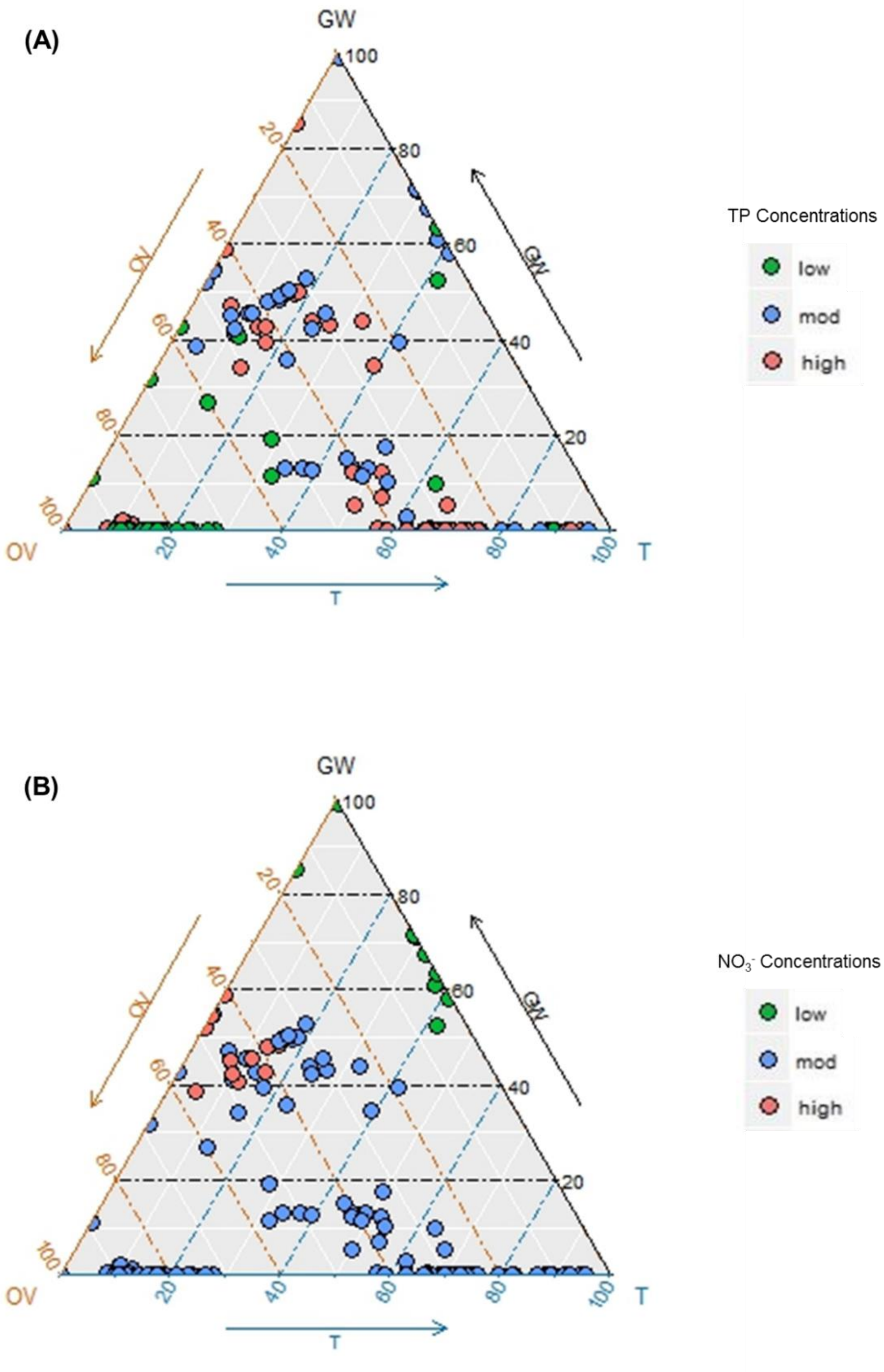


Figure 3.8: Maryhill ternary diagrams for A) TP concentrations divided by natural breaks binning. Low ≤0.1 mg/L; Mod = 0.1 – 0.3 mg/L; High ≥ 0.3 mg/L and B) NO_3^- concentrations divided by natural breaks binning. Low < 5 mg/L; Mod = 5 – 20 mg/L; High ≥20 mg/L

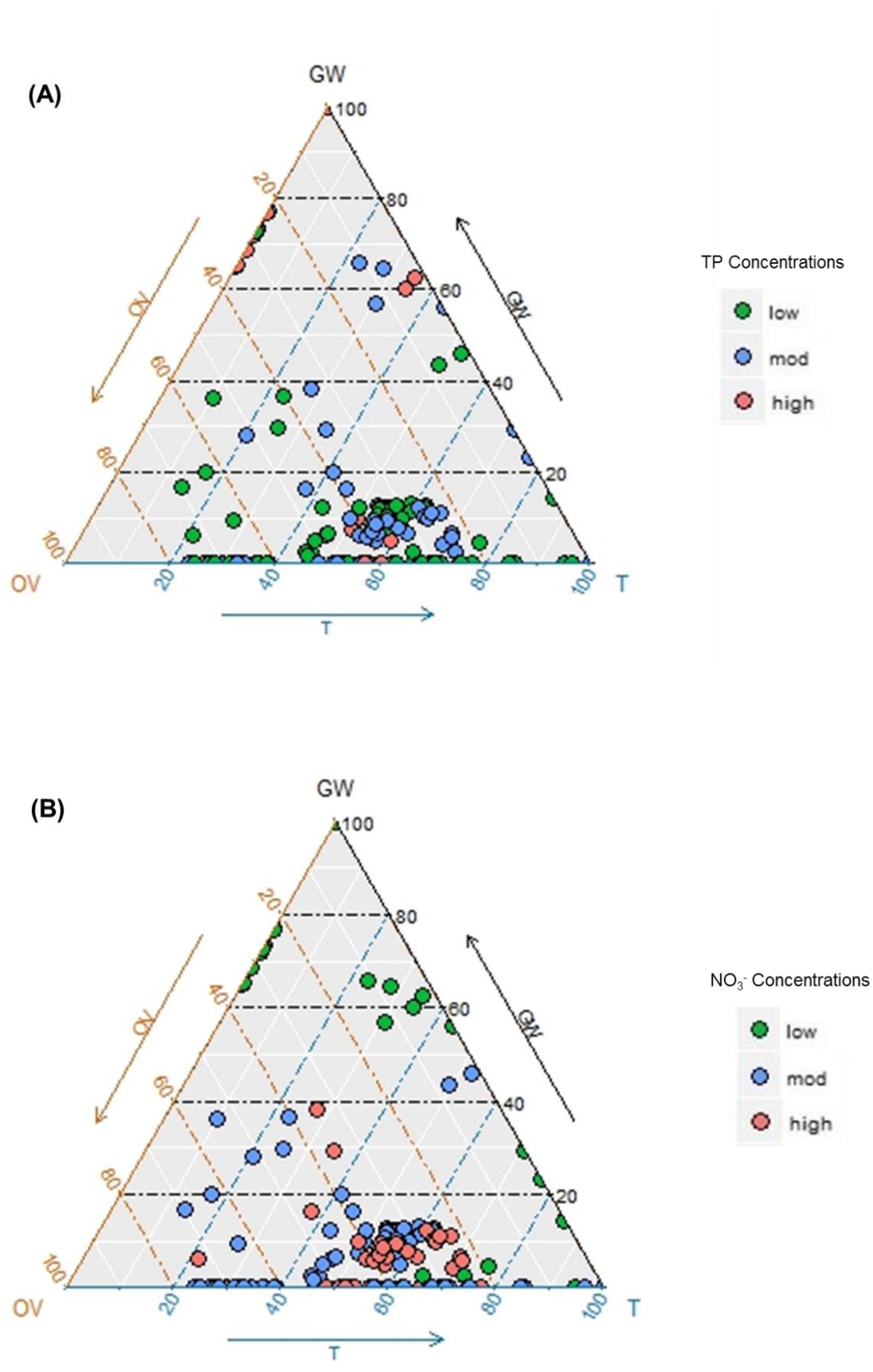


Figure 3.9: Strawberry ternary diagrams for A) TP concentrations divided by natural breaks binning. Low ≤0.1 mg/L; Mod = 0.1 – 0.2 mg/L; High ≥0.2 mg/L and B) NO_3^- concentrations divided by natural breaks binning. Low ≤10 mg/L; Mod = 10 – 20 mg/L; High ≥20 mg/L.

Table 3.2: Summary of multiple linear regression results. The * notation represents regression models using results from EMMA.

Site	Response Variable	Significant Explanatory Variable(s)	Adjusted R^2	p-value
MH	TP load	Discharge	0.81	0.013
MH	NO_3^- load	Discharge, AMC, event size	0.95	<0.001
MH	TP FWMC	AMC	0.31	0.05
MH	TP FWMC*	%OV, event size	0.89	0.004
MH	NO_3^- FWMC	N/A		>0.1
MH	NO_3^- FWMC*	N/A		>0.1
ST	TP load	Discharge	0.87	0.004
ST	NO_3^- load	Discharge	0.64	0.02
ST	NO_3^- load*	AMC, event size, %GW, %T	0.90	0.02
ST	TP FWMC	AMC (-)	0.20	0.02
ST	TP FWMC*	N/A		>0.1
ST	NO_3^- FWMC	N/A		>0.1

3.6 Discussion

The results of this study show that two agricultural sub-catchments within the same watershed can exhibit different export and concentration dynamics of TP and NO_3^- despite similar patterns in discharge. Loads of TP and NO_3^- were strongly related to discharge at both sites, which further supports results from numerous other studies in a variety of landscapes from agricultural (Macrae et al., 2007a; Lam et al., 2016a; Esbroeck et al., 2017) to natural (Castillo, 2010; Brion et al., 2011) and urban (Billen et al., 2007).

The high TP concentrations generally occurred during events with high discharge which resulted in elevated TP export at both sites. This points to the importance of sampling and monitoring stream nutrient and runoff dynamics during the non-growing season rainfall and snowmelt events. This was particularly evident at ST where the growing season months of May through September had the lowest TP concentrations while the non-growing seasons had the highest TP concentrations and discharge. At MH, the median monthly concentrations of TP during the growing season (May – September) were generally low as well, although a considerable number of samples had high concentrations in excess of 0.5 mg/L, which can be seen in the number of outlier samples during the growing season months (Figure 3.4).

Nitrate concentrations were higher at ST throughout the year and were highest during the months of June and October when crop fertilization typically occurs (Macrae, personal communication). Conversely, October nitrate concentrations were not as high at MH, although June exhibited the same pattern at both sites, likely caused by widespread N fertilization in the watershed. Moreover, this was compounded by the higher than average precipitation during the month of June throughout both sub-catchments, which was also reflected in the high discharge values (Figure 3.4). The high nitrate concentrations observed at ST in October were not seen at MH and could be the result of limited fall N fertilization, or decreased flowpath connectivity since October had relatively low total discharge.

It was hypothesized that the observed differences in nutrient concentration at the two sites were driven by different flowpath connectivity in the sub-catchments. Further, the stream responses from storm events resulted in differences in flowpath contributions between sites based on the comparison between ternary diagrams in Figure 3.7. The estimated flowpath contributions at both sites had greater variability between events than within events (Figure 3.7), suggesting that the flowpath signatures remained relatively consistent throughout an event. The differences in flowpath contributions between the two sites were frequently observed during sample collection, as active overland flowpaths were visibly hydrologically connected to the stream at MH but not at ST where overland flow was uncommon. The field observations were confirmed in the EMMA models as MH stream water samples generally had higher % OV compared to ST (Figure 3.7). The relative flowpath contribution results from the ST EMMA model indicated a higher contribution from tile drainage to total flow compared to MH as there was clustering observed in the bottom right corner of the ternary diagram (Figure 3.7). When the individual samples were grouped based on TP and NO_3^- concentrations, no obvious clustering was evident in the ternary diagrams (Figure 3.8 and 3.9). This suggests that flowpath contributions are not strongly related to nutrient concentration for an individual sample; this combined with the observation that flowpath contributions clustered on an event scale, led to the investigation of the role of flowpaths on nutrient FWMC and loads.

The strong positive relationships between TP load and discharge are expected as loads are the product of instantaneous concentrations multiplied by instantaneous flow from all event samples. However, discharge had a much weaker relationship with FWMC, suggesting an additional control, which was shown to be AMC at both sites, although, this relationship was positive at MH and negative at ST suggesting additional drivers.

TP FWMC was shown to increase with increasing AMC at MH (Figure 3.6c), while TP FWMC decreased with increasing AMC at ST (Figure 3.6d). The inverse relationship observed at ST has been shown in past studies (Sherriff et al., 2016) where tile drains contribute a significant proportion of flow in an agricultural stream, as well as following successive storm events (Mellander et al., 2012). The increasing trend between TP FWMC and AMC observed at MH was weakly significant with a simple linear regression and further, when TP FWMC was regressed with AMC, event size and discharge, there were no significant predictors. However, after implementing the EMMA model, and % OV added to the MLR of TP FWMC, the new

MLR with % OV and event size described 92 % of the variability in TP FWMC at MH. The adjusted R^2 for TP FWMC increased from 0.31 (without the % OV flowpath) to 0.89 (with % OV), suggesting that overland flow is an important driver in TP concentrations at MH. This relationship was not found at ST, which suggests that the drivers vary from site to site.

At ST, while there were no MLRs (with or without flowpath variables) that were able to significantly predict NO_3^- FWMC. NO_3^- loads were significantly predicted in the MLR using AMC, event size, % GW and % T. NO_3^- loads were also significantly related to discharge in a simple linear regression. The increase in adjusted R^2 from 0.64 to 0.90 when adding flowpath (% GW and % T) explanatory variables demonstrates that groundwater and tile drain runoff contribute to predictive power for NO_3^- loads. Moreover, there is a greater proportion of farm fields that are tile drained in the ST sub-catchment (65% of the sub-catchment area) compared to MH (41% of the sub-catchment area), which has been shown to be a large contributor of NO_3^-. Conversely, there were no significant predictor variables at MH for NO_3^- FWMC.

3.7 Conclusion

The development of models to estimate and predict nutrient export requires field and watershed-scale studies to inform the models of critical smaller-scale processes (Liu et al., 2014). While nutrient export models commonly use land use metrics to predict nutrient runoff based on modelled streamflow (Bennett, 2003; Coulter et al., 2004; Bennett et al., 2005), this study shows that great variability can exist within sub-catchments of similar land use. Utilizing EMMA in agricultural systems has not been done extensively and the results of this study provide evidence that estimating flowpath contributions can contribute to an increased understanding of the processes driving nutrient export in agricultural landscapes. Further, future studies can run EMMA models in other tile-drained agricultural landscapes to inform which flowpaths are driving nutrient export in a given watershed. Additionally, using overland flow, tile drain runoff, and groundwater as end-members in agricultural catchments can increase the predictive power of relationships between site-specific drivers and the export and FWMC of TP and NO_3^-.

Chapter 4 - Discussion and Major Conclusions of Thesis

Agricultural land use has been a known source of significant NPS P loading (Sharpley and Syers, 1979; Carpenter et al., 1998; and IJC, 2014). The timing of nutrient export from agricultural areas can be highly variable (Sharpley et al., 1999; Macrae et al., 2007a) and can be influenced by the presence of tile drains (Lam et al., 2016a; Van Esbroeck et al., 2017). This research explored the year-round spatial ('hot spots') and temporal ('hot moments') patterns of nutrient (N and P) export at multiple locations within a dominantly agricultural mixed land use subwatershed in Southern Ontario, Canada.

P losses were greatest in the early spring season following snowmelt and after rain events on saturated soils. This temporal pattern was observed throughout the watershed and highlights the importance of year-round stream monitoring to accurately estimate annual and seasonal P loads. Recognizing the spring freshet as a 'hot moment' in P export from agricultural lands is important for land managers and practitioners in order to develop best management practices that are effective during the non-growing season. The temporal pattern of NO_3^- export differed from that of P at ST, the site with the highest proportion of tile-drained fields. At ST, NO_3^- export was similar across all four seasons, however this temporal pattern was unique to the ST site. At MH and TE, spring was the season with the highest NO_3^- loads, however the seasonal load was proportionately less than that of DRP and TP.

Tile drains have been suggested as conduits for P export in agricultural landscapes (Dils and Heathwaite, 1999), and have been observed to be sources of increased P losses in edge-of-field studies in Ontario (Macrae et al., 2007a; Lam et al., 2016a; Van Esbroeck et al., 2017). At the subwatershed scale, the monitoring sites with higher proportions of tile-drained fields did not correspond to the P load 'hot spot'. Instead, the sub-catchment that consistently had the highest P concentrations and loads, MH, was the catchment that also had livestock operations which have been found in past studies to contribute high P loads to receiving water bodies (Aarons and Gourley, 2012; Nino de Guzman et al., 2012).

While land use and land management can influence the nutrient export dynamics in a watershed, Banner and colleagues (2009) found that no measure of land use metrics was able to predict TP loads during high discharge events. The results from *Chapter 2* of this thesis suggest that at the catchment scale, discharge is the primary driver of TP loads at all monitoring sites during all seasons.

P speciation was found to be related to the proportion of tile drains in a sub-catchment. The monitoring sites with higher proportion of tile-drained farm land had higher DRP:TP ratios, suggesting that tile drains increase the amount of P exported in the dissolved form. The influence of tile drains on the speciation of P has been observed at the field-scale in past studies (Eastman et al., 2010), which was also observed at the subwatershed scale in this study.

The results from *Chapter 2* suggest that MH is the 'hot spot' for TP within Hopewell and that the highest loads of TP occurred during the events with the highest discharge. However, NO_3^- loads (kg/ha) from ST were similar to that of MH despite lower discharge, suggesting that the drivers of nutrient export differ between the two agricultural monitoring sites.

Chapter 3 of this thesis explored the linkages between antecedent moisture, flowpath connectivity and nutrient export in tile-drained agricultural landscapes. Additionally, the efficacy of using EMMA as a tool to estimate flowpath contributions from tile-drained agricultural fields was examined.

EMMA has been used as an effective tool to estimate the relative contribution of flowpaths in natural forested catchments (*e.g*. Ali et al., 2010; Griffen et al., 2014), and more recently, has been applied to agricultural headwater streams in the United Kingdom (Outram et al., 2015). It was found that EMMA models could be utilized to estimate flowpath contributions of three geographic end-members, overland flow, groundwater, and tile flow. Separate models were generated at both sites using Ca^+, CO_3^{2-} chemical signatures at MH and Ca^+, CO_3^{2-}, and SO_4^- chemical signatures at ST.

Discharge was found to be the most significant driver (explanatory variable) of NO_3^- and TP loads at both sites (MH and ST). The addition of subsurface flowpath metrics (% groundwater, and % tile flow) increased the predictive power of NO_3^- loads at ST from an adjusted R^2 of 0.64 with discharge as the only explanatory variable, to an adjusted R^2 of 0.90 in a multiple linear regression that included AMC, event size, % GW, and % tile.

Antecedent moisture has been shown to be a driver of P export in some tile-drained agricultural landscapes (Macrae et al., 2010; Lam et al., 2016a), while overland flow has been found to be a driver in others (Grant et al., 1996). This study measured and quantified the relative contribution of different potential drivers through multiple linear regressions. Antecedent moisture conditions were found to have a significant relationship with TP FWMC at both MH and ST, although TP concentration increased with increasing AMC at MH, and decreased with increasing AMC at ST, suggesting additional drivers at the two sites. At MH, the addition of the % overland flow (estimated from EMMA) to a multiple linear regression where TP FWMC was the response variable, increased the adjusted R^2 of the regression from 0.31 with just AMC, to 0.89. These results suggest that the contribution of overland flow is significantly related to increased concentrations of TP at MH.

Chapter 3 demonstrated that TP FWMC were higher at MH when there were greater contributions from overland flow pathways and this result suggests that the TP ‘hot spot’ (MH) observed in the first manuscript is partly a result of a greater proportion of overland flow compared to the other sub-catchments in Hopewell Creek. Further, at ST variability in NO_3^- loads were explained partially by subsurface flow pathways (% GW and % T) which shows that results from the EMMA model align with past studies (Macrae et al., 2007b).

This study demonstrated that differing land use practices within an agricultural subwatershed can influence the timing (‘hot moments’) and location (‘hot spots’) of nutrient export. Moreover, the monitoring results highlighted the importance of year-round monitoring programs for capturing nutrient export dynamics due to the importance of the non-growing season. Moreover, by utilizing EMMA in a tile-drained agricultural landscape this thesis showed the importance of process-based studies to increase our understanding of field-scale processes in order to have more well-informed models. The results of this thesis can be used to better inform and improve nutrient modelling studies by demonstrating differences in drivers of TP and NO_3^- in two agricultural sub-catchments within the same subwatershed. Estimation of the dominant flow pathways in an agricultural sub-catchment can improve model accuracy and increases the overall understanding of the linkage between soil moisture conditions, event size, and flowpath contributions on nutrient export. Our results also show that EMMA can be used as an effective tool for estimating flowpath contributions in a tile-drained agricultural landscape, and that the flowpath estimates were able to increase the predictive power for modelling TP FWMC and NO_3^- loads. An increased understanding of nutrient flow pathways can be used to optimize land management strategies to reduce nutrient export.

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