THE EFFECTS OF AGRICULTURAL LAND USE CHANGE ON NITROGEN AND PHOSPHORUS IN NORTH SHORE LAKE ONTARIO TRIBUTARIES

A Thesis Submitted to the Committee on Graduate Studies in Partial
Fulfillment of the Requirements for the Degree of Master of Science in the
Faculty of Arts and Science

TRENT UNIVERSITY

Peterborough, Ontario, Canada

Environmental and Life Sciences M.Sc. Graduate Program

September 2022

ABSTRACT

The Effects of Agricultural Land Use Change on Nitrogen and Phosphorus
in North Shore Lake Ontario Tributaries

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Row crop agriculture and associated land use practices including tile drainage and conservation tillage have been cited as a probable cause of re-emerging eutrophication in the lower Great Lakes. In this thesis, I sought to quantify and evaluate the effect of agricultural land cover and land use changes on total phosphorus (TP) and nitrate-nitrogen (NO_3-N) concentrations and export in north shore Lake Ontario tributaries. This included (a) a long-term data analyses at 12 large watersheds (47 to 278 km^2) using historical land cover and water quality data (1971-2010), and (b) a space-for-time study examining 12 small sub-catchments (< 8 km^2) with majority (> 50%) row crop, pasture, or forest cover. Concentrations of TP were greatest in urbanized watersheds and declined particularly during the first decades of the study period, while NO_3-N concentrations were greatest and steadily increased in agricultural catchments with increasing row crop cover. The space-for-time approach revealed that TP concentrations were similar across agricultural land uses and that export was most dependent on runoff. Meanwhile, NO_3-N concentrations and export were greatest in row crop catchments and were positively related to row crop area. These results suggest that increases in row crop cover and associated agricultural practices including increased nutrient amendments and tile drainage may be responsible for increased NO_3-N concentrations and export in northern Lake Ontario tributaries.

Keywords: Water quality, Lake Ontario, streams, agriculture, nitrogen, phosphorus

Acknowledgements

Personal Acknowledgements

I must first acknowledge the generous patience and persistence of my supervisor, Dr. Catherine Eimers, whose steady encouragement helped me to the finish. I also thank her for nudging me towards her program in the first place back in July 2015. I would like to also thank the patience and input of my supervisory committee, Dr. Shaun Watmough, Dr. Mohamed, and Dr. Jessica Mueller for their probing questions and excellent ideas throughout the development and writing of my proposal and chapters. I am grateful as well to Dr. Eric Sager for sparking and nurturing my love of science, without which I would not have written this. Thanks also to Mike Smith and Pam Lancaster at Ganaraska Region and Conservation Authority for assisting with site selection.

I could not have completed the hands-on part of my thesis without the essential lab instruction of Kevin Adkinson and Liana Orlovskaya. I am also incredibly grateful for the assistance I received on each field sampling trip from Tanner Liang, Conor Gaffney, Freddy Liu, Patrick Levasseur as well as Cathy’s summer students, particularly during the early, cold, wet, and wintery storm-chasing adventures in the old truck and Geography van. Thanks again to Freddy Liu, who assisted with my GIS analysis, and to my R buddies Tanner Liang, Erin Hayward, and Abby Wynia for R-related inspiration. An honorable mention to James English for his supportive commiseration during ‘T-word’ struggles.

The writing in this thesis is dedicated to Lisa Miller-Pond, who always made my writing struggles seem more bearable and whom I wish could have been around to celebrate my last rough draft. I also thank Lisa, Bruce Pond, and my mother, Jennifer DeBues, for their thoughtful questions, opinions, ideas, and support throughout the entirety of my degree. Finally, I thank my partner Caileigh McKnight for her love and encouragement while enduring the brunt of ‘thesising’ especially during the pandemic. Thanks for helping me get that monkey off my back.

Funding and Partnership Acknowledgements

This research would not have been possible without the partnership, funding, and logistical support from:

- NSERC Discovery Grant
- Ontario Graduate Scholarship
- Ganaraska Region Conservation Authority
- Trent University

I also acknowledge the Ontario Ministry of Environment, Conservation, and Parks for providing data from their Provincial Water Quality Monitoring Program, as well as the Ontario Ministry of Natural Resources and Forestry, the Ontario Ministry of Agriculture, Food and Rural Affairs, and Agriculture and Agri-food Canada for providing spatial data.

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List of Abbreviations

AAFC	Agriculture and Agri-Food Canada
CCME	Canadian Council of Ministers of the Environment
CLI	Canada Land Inventory
CLOCA	Central Lake Ontario Conservation Authority
CLUMP	Canada Land Use Monitoring Program
GLWQA	Great Lakes Water Quality Agreement
GRCA	Ganaraska Region Conservation Authority
GTA	Greater Toronto Area
IJC	International Joint Commission
LC	Land Cover
LTER	Long-term Ecological Research Project
LU	Land Use
LULC	Land use and land cover
N	Nitrogen
N:P	Nitrogen to phosphorus ratio
NO_3^-	Nitrate
NO_3-N	Nitrate-nitrogen
OFAT	Ontario Flow Assessment Tool
OMECP	Ontario Ministry of the Environment Conservation and Parks
ORM	Oak Ridges Moraine
P	Phosphorus

PCBs	Polychlorinated biphenyls
PWQMN	Provincial Water Quality Monitoring Network
SOLRIS	Southern Ontario Land Resource Information System
SRP	Soluble reactive phosphorus
SWAMP	Stormwater Assessment Monitoring and Performance Program
TN	Total nitrogen
TP	Total phosphorus
TRCA	Toronto Region Conservation Authority
WSC	Water Survey of Canada
WWTP	Wastewater treatment plants

Chapter 1 - General Introduction

1.1 Background

There has been a long history of large-scale anthropogenic disturbance within the Laurentian Great Lakes, with widely-acknowledged effects on water quality throughout the region (IJC, 2009). These disturbances, which include agriculture and urban development, are the source of much of the total nutrient loads delivered to fresh and saltwater ecosystems both globally (Abell et al., 2011; Groffman et al., 2003; Le Moal et al., 2019; Schindler et al., 2006) and in the Great Lakes region (Higgins et al., 2012; Joosse and Baker, 2011; Kane et al., 2015; Munawar and Fitzpatrick, 2018). In the past, nutrients, specifically nitrogen (N) and phosphorus (P), were delivered from point sources to waterbodies directly, whereas non-point source loadings from agricultural and urban landscapes are now the largest sources of nutrients in many developed countries (Le Moal et al., 2019).

Nutrient enriched waterbodies experience eutrophication and an overall decline in ecosystem health (Freedman, 2010; Le Moal et al., 2019). The consequences of eutrophication for the Great Lakes are particularly concerning, as regional economic activities that are dependent on the lake’s health are estimated to total billions of dollars (Allan et al., 2013; Kehl, 2018), thus making the management of non-point nutrient sources a priority. However, resolving such a diffuse and complex issue with innumerable specific nutrient sources is particularly difficult (Kehl, 2018). This thesis examines the effect of one source of non-point nutrient pollution, agriculture, and how changes in agriculture since 1971 may have affected both instream concentrations of N and P, and their delivery from the landscape to one of the Great Lakes, Lake Ontario.

1.2 The importance of N and P in freshwater ecosystems

In all ecosystems, N and P are essential but often limiting nutrients and are consequently important drivers of ecosystem productivity. Nitrogen is a component of amino acids, proteins, as well as a constituent of chlorophyll and is therefore critical in a variety of biological processes including photosynthesis (Conley et al., 2009; Leghari et al., 2016). Although abundant in the atmosphere, nitrogen gas is not accessible to most organisms that instead require more reactive and water-soluble nitrogenous compounds like nitrate (NO_3^-) for growth. However, nitrogenous compounds, typically found in soil, water, or plant tissues are far less abundant than nitrogen gas and are therefore limiting factors of productivity in terrestrial and aquatic ecosystems (Evert et al., 2013). Regular fertilization of agricultural systems is often needed to ensure healthy and abundant harvests when N is limited.

Long-term elevated levels of NO_3-N in freshwater streams can negatively affect aquatic ecosystems and threaten drinking water sources. While an essential nutrient, excess N can be toxic to organisms, including humans, by limiting the oxygen-carrying capacity of blood, a condition named Methemoglobinemia (also known as 'blue baby syndrome') (Wolfe and Patz, 2002). For humans, the maximum allowable concentration of NO_3-N in drinking water is 10 mg/L (Ontario Ministry of the Environment, 2003), while for freshwater systems the maximum 7-day allowable concentration is 3 mg/L according to the Canadian water guidelines for the protection of aquatic life (CCME, 2012). Freshwater bodies experiencing prolonged NO_3-N concentrations above this threshold may see declines in health, reproduction, and survival of the most sensitive species in the ecosystem (CCME, 2012).

In contrast, P is needed by organisms in smaller quantities than N, although it is still a critical constituent of energy-carrying compounds (i.e. adenosine triphosphate), nucleic acids, and cell membranes (Evert et al., 2013). Phosphorus is also one of the most limiting factors in freshwater ecosystem productivity. This is mainly because of the general scarcity of P, its uneven distribution in ecosystems, and its immobility in soil (Evert et al., 2013). In southern Ontario's limestone-based soils and freshwater systems, P is plentiful relative to northern Ontario's Precambrian Shield-based soils. However, much of the P in southern Ontario is biologically unavailable as reactive forms of phosphorus often bind to cations like calcium, forming insoluble compounds that are inaccessible to plants and other organisms (Malhotra et al., 2018).

Although N and P are essential nutrients, their limited abundance means unusual increases may lead to harmful increases in productivity. When excess N, but particularly P, arrives in freshwater systems, algal growth increases along with rates of decomposition and biological oxygen demand, eventually resulting in fish die-offs and dead zones, threatening both ecosystem integrity and those communities dependent on the ecosystem's services (Conley et al., 2009; Freedman, 2010; Thornton et al., 2013). This process of excess nutrient enrichment, known as eutrophication, has been described by some as a 'wicked' problem due to its complex causes and compounding consequences (Thornton et al., 2013). Eutrophication presents an ongoing challenge for ecosystem managers in the Laurentian Great Lakes system. While historical attempts to mitigate eutrophication and limit nutrient inputs to the Great Lakes have met some success, the recent re-emergence of eutrophication symptoms in nearshore areas of several Great Lakes highlights the need for new, additional management approaches.

1.2 Nutrient enrichment in the lower Great Lakes

The Laurentian Great Lakes has been the scene of a decades-long water quality struggle. Throughout the 20th century, increasing quantities of nutrient-enriched water flowed from growing urban communities and intensifying agricultural landscapes to the Great Lakes. This influx of nutrients caused widespread eutrophication of both coastal and offshore freshwaters, threatening ecosystems, industries, and human health (International Joint Commission (IJC), 1972). The most notable case of eutrophication occurred in Lake Erie, which in 1965 was described as "in its death throes" by Alan Edmonds in an article published in MacLean's magazine (Edmonds, 1965). The deteriorating state of the Great Lakes, particularly Lake Erie, motivated research to mitigate the damage. Researchers in the Experimental Lakes Area in northwestern Ontario famously utilized whole-lake fertilization experiments to determine that N, but most importantly P concentrations were the most limiting factor in freshwater lake systems (Schindler, 1971, 1977).

Understanding the role of nutrients in freshwater eutrophication paved the way for effective nutrient control measures and water quality improvements. The 1972 Great Lakes Water Quality Agreement (GLWQA) signed by the United States and Canada aimed to "restore and enhance water quality in the Great Lakes" (International Joint Commission, 1972) and formed the basis for bi-national initiatives aimed at improving water quality in the region. These initiatives included measures designed to control eutrophication by reducing inputs of Total P (TP) and other nutrients into the Great Lakes (International Joint Commission, 1972). The measures were initially successful at curtailing point source nutrient loading from industrial and municipal wastewater discharges, as well as reducing the use of phosphate detergents (Dove and Chapra, 2015). This led to a dramatic decline in offshore TP concentrations throughout the Great Lakes during the 1970s and 80s, most notably in Lake Ontario, as illustrated in Figure 1.1 (Dove and Chapra, 2015). Declines in P inputs subsequently reduced phytoplankton abundance, relieving symptoms of eutrophication. Remedial action plans developed to restore the most polluted and damaged areas of the Great Lakes have led to the spending of nearly $23 billion (USD) resulting in some notable improvements in ecosystem conditions (Hartig et al., 2020). Yet despite initial success, eutrophication has returned to parts of the Great Lakes (Kane et al., 2014; Watson et al., 2016). Re-emerging symptoms of declining ecosystem health in the lower Great Lakes began to appear in the late 1990s with nearshore algal blooms and declining water quality (J. M. Kerr et al., 2016), including notable decreases in dissolved oxygen levels in deeper sections of Lake Erie (Joosse and Baker, 2011). However, many of the symptoms of this re-emerging eutrophication differed from those seen in the water quality crises of the 1960s and 70s.

The differences between the re-emergent eutrophication issues and the water quality crisis of the 1960s and 70s can be demonstrated by examining Lake Ontario. In certain areas of the lake, nearshore algal blooms continue to occur (Higgins et al., 2012; Munawar and Fitzpatrick, 2018) despite overall decreases in nearshore algae abundance (Winter et al., 2012). Lake Ontario (like Lake Erie) also faces problems with the re-emergence of toxic nearshore algal blooms. Benthic mats of *Cladophora* have been reported along the north and south shores of Lake Ontario (Munawar and Fitzpatrick, 2018; Perri et al., 2015; Winter et al., 2011), while harmful blue-green algal blooms of cyanophyta have become common in certain areas including Hamilton Harbour and the Bay of Quinte (Munawar and Fitzpatrick, 2018). However, the dominant blue-green algal (cyanophyta) species seen in the re-emerging harmful algal blooms is *Microcystis* rather than the *Anabaena* and *Aphanizomenon* observed in the 1960s and 1970s (Kelly et al., 2019). These differences between the historical eutrophication symptoms and the re-emerging present-day symptoms suggest alternate mechanisms may be responsible for the most recent changes in water quality in the lower Great Lakes (Joosse and Baker, 2011).

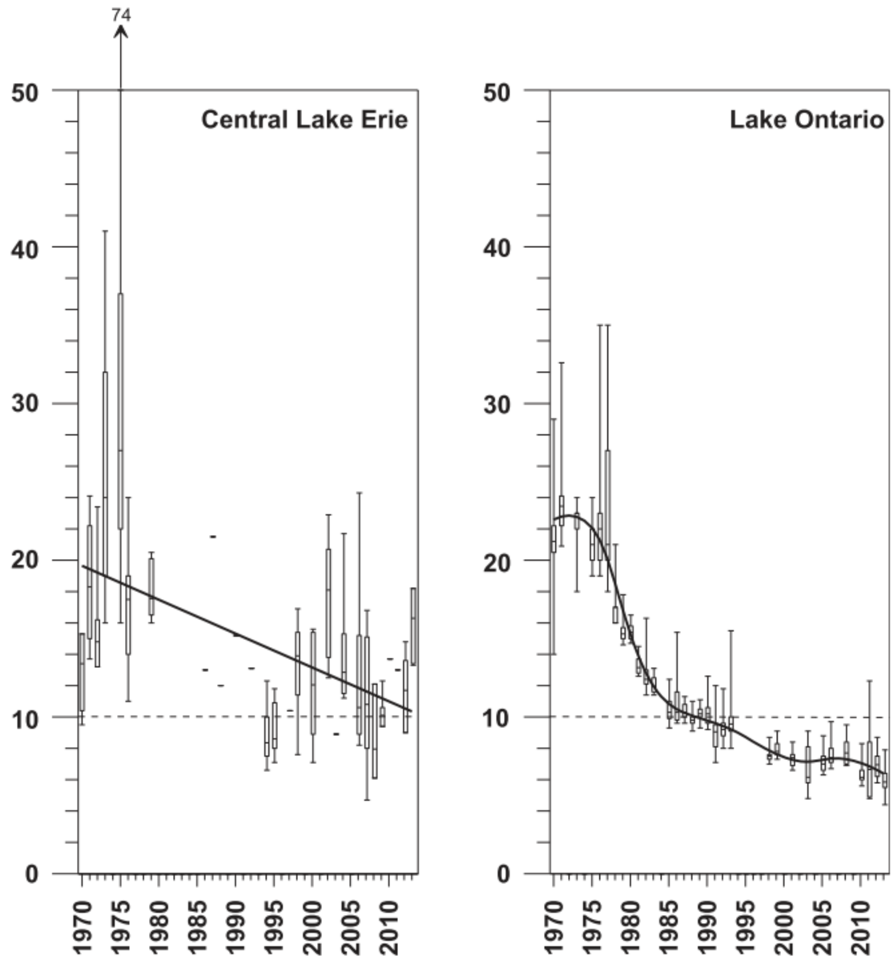

Figure 1.1 Trends of open lake TP concentrations (µg/L) in May to April for the lower Great Lakes. Dashed line identifies the GLWQA TP target concentration (Dove and Chapra, 2015).

Although emerging and unsolved water quality questions in Lake Ontario may be a cause for concern, Lake Erie has been the focus of much of the research on water quality in the Great Lakes (Dove and Chapra, 2015; Joosse and Baker, 2011; Kane et al., 2014; Scavia et al., 2014; Watson et al., 2016). This is understandable as Lake Erie's water quality concerns are widespread and severe (Watson et al., 2016), but this does not mean water quality concerns in Lake Ontario are unworthy of attention. Declining nearshore water quality increases pressure on the lake ecosystem and threatens those that benefit economically and socially from the lake's ecosystem services (Allan et al., 2013; Kehl, 2018; Makarewicz and Howell, 2012). Lake Ontario already sustains some of the greatest cumulative stress of all the Great Lakes, due in part to its location as the last in the Laurentian Great Lakes chain but also due to its rapidly changing drainage basin. Lake Ontario drains the rapidly urbanizing ‘Greater Golden Horseshoe’ region of Ontario, home to approximately 9 million people and forecast to grow to 14.8 million by 2051 (Ontario Ministry of Municipal Affairs and Housing, 2020). This urban growth is accompanied by evolving and intensifying agricultural land (Smith, 2015) combining to radically alter the landscape within the Lake Ontario basin. All the while, the lake also has to contest with the pressures of climate change, invasive species, shoreline development, and industrial contaminants such as mercury and PCBs (Allan et al., 2013; Kehl, 2018). Although re-emerging eutrophication in the nearshore of Lake Ontario is not the only stressor to the lake’s ecosystem, understanding the potential causes of this eutrophication may help direct action that alleviates the pressure on Lake Ontario.

1.4 Sources of re-emergent water quality concerns

As the most limiting factor of ecosystem productivity in freshwater lakes, P has been the focus of the investigation into nearshore eutrophication in Lake Ontario. Research into nearshore *Cladophora* blooms in Lake Ontario has found TP concentrations in the water column to be a good predictor of variability in *Cladophora* populations (Makarewicz and Howell, 2012). Similarly, cyanophyta blooms in the Bay of Quinte area have been associated with elevated TP concentrations (> 25 µg/L) (Kelly et al., 2019). This research adds to the decades of research establishing TP as the primary driver of algal productivity in Ontario’s freshwaters (Higgins et al., 2018), as well as the historical success of TP controls to limit algal blooms (Dove and

Chapra, 2015). Therefore, it is unsurprising that influential studies tout TP management as the best tool for mitigating symptoms of eutrophication (Dove and Chapra, 2015; Watson et al., 2016). However, nearshore TP concentrations have declined significantly in nearshore waters of Lake Ontario since 1976, stabilizing by 1996 (Winter et al., 2012) and mirroring tributary loading and offshore trends (Dolan and Chapra, 2012; Dove and Chapra, 2015). Likewise, TP concentrations in many Lake Ontario streams and rivers have either stabilized or continued to decline for reasons that cannot be explained by factors such as improved wastewater treatment (Raney and Eimers, 2014a; Stammler et al., 2017). Unexplained declines in TP concentrations in some Lake Ontario tributaries are at odds with re-emerging eutrophication in the lake.

Explanations other than tributary P loading as the cause of troublesome nearshore blooms have included internal P loading (Dove and Chapra, 2015; Watson et al., 2016), and changes in P cycling due to the presence of invasive dreissenids (a family of mussels), most notably *Dreissena polymorpha* (zebra mussels) (Watson et al., 2016). It has been hypothesized that the arrival of dreissenids in the 1990s to the Great Lakes has helped to concentrate P in the nearshore region of Lake Ontario, and fuelled increases in benthic algal growth (Dove and Chapra, 2015; Hecky et al., 2004). While dreissenid populations are abundant in nearshore areas, and help to improve conditions for *Cladophera* blooms, they are unlikely the cause of re-emerging symptoms of eutrophication in Lake Ontario. Higgins et al. (2012) found that while dreissenid mussels may at times increase P bioavailability for *Cladophera* blooms, the effect was not sufficient to produce the scale of blooms seen in nearshore regions of Lake Ontario. Indeed, the authors suggested that external P loading from tributaries was a more likely driver of benthic algal blooms (Higgins et al., 2012).

A potential answer to the question of declining TP concentrations in Lake Ontario tributaries despite re-emerging algal blooms may be found in the tributaries and nearshore regions of Lake Erie. There, a similar pattern has been observed where TP loads declined between 1981 and 2011 in two of the three major rivers draining from the US into Lake Ontario (Baker et al., 2014). While TP declined, concentrations of soluble reactive P (SRP), the bioavailable form of P, increased in two of the three large rivers (Baker, 2014). Increases in tributary SRP levels have also been linked to phytoplankton and cyanophyta abundance (Kane et al., 2014), despite stable offshore SRP concentrations and re-emerging offshore blooms in Lake Erie, combining to sow some doubt to the idea (Dove and Chapra, 2015). Increases in SRP, even with overall decreases in TP, have been attributed to agricultural land use changes, particularly increases in the use of P fertilizer on cropland (Michalak et al., 2013). Linear relationships between row crop area and SRP have been seen in Ontario, likely due to associated land use practices like the installation of subsurface drainage, increased fertilizer usage, or conservation tillage (Jarvie et al., 2017; Liu et al., 2022; Williams et al., 2016).

Other than changes in the delivery of SRP to the lower Great Lakes, another possible driver of re-emergent water quality concerns may be increasing supplies of N (Watson et al., 2016). Lake concentrations of NO_3-N increased by approximately 60% since 1970 (Dove and Chapra, 2015) and NO_3-N concentrations in tributaries simultaneously increased over the same time period (Eimers and Watmough, 2016). Interestingly, much of the increase in tributary NO_3-N concentrations was observed among predominantly agricultural watersheds rather than urban watersheds (Eimers and Watmough, 2016). There have been suggestions for other nutrients like N to be considered in water quality studies of the lower Great Lakes (Hellweger et al., 2022; Munawar and Fitzpatrick, 2018). Microcystis blooms have been observed in water with low N:P ratios (Watson et al., 2016), while microcystin abundance has been linked to N availability as well as SRP (Davis et al., 2015). Harmful algal blooms of cyanophyta in the Bay of Quinte have been found at times to be N limited, although the extent of this is debated (Kelly et al., 2019; Munawar and Fitzpatrick, 2018). In Lake Erie, research has found evidence of seasonal shifts in nutrient limitation of cyanophyta from P to N (Belisle et al., 2016). In fact both low continuous N loading and large fluxes of N have been found to increase the growth of cyanobacteria, especially under certain light conditions (Chaffin et al., 2018). Models of potential reductions in P loading to Lake Erie have projected possible decreases in Microcystis biomass, but increases in toxin production due to increased light availability (Hellweger et al., 2022). Overall, this research highlights the complex nature of nutrient limitation and importance of N limitation and loading when developing management strategies for eutrophication in the Great Lakes.

Changes in urban sources are also important to consider. At the peak of the water quality crisis during the 1960s and 1970s, many of the nutrients entering the lower Great Lakes were from point source polluters (i.e., factories, municipal wastewater treatment plants), particularly in developed urban and industrial centres (Dolan and Chapra, 2012). Since then dramatic decreases in point source pollution from these sources, as well as regulations on household goods like fertilizers and detergents, have contributed to subsequent declines in TP to Lake Erie and Ontario (Dolan and Chapra, 2012). Despite this, nutrient losses are associated with urban areas due to erosion, construction, and pollution; percent impervious cover in urban areas has been associated with greater stream TP concentrations (Nagy et al., 2012). However, modern suburban developments are somewhat different to urban and suburban development in the 1960s and 70s. Stormwater management, which may include ponds, ditches, and buffers, is now required at new developments in the province (Bradford and Gharabaghi, 2004). These are generally effective at reducing P runoff (Duan et al., 2016, 2012; Sønderup et al., 2016), which may explain decreases of TP (Raney and Eimers, 2014a; Stammler et al., 2017) and stable NO_3-N concentrations in urban streams despite increases of NO_3-N in agricultural ones (Eimers and Watmough, 2016).

1.5 The changing agricultural landscape of Ontario

The agricultural landscape of Ontario has evolved throughout the entire 20th century; however, the most notable change during this time has been the loss of approximately 4 million hectares of agricultural land (44% decline) between 1921 and 2011 (Smith, 2015). The area of agricultural land declined in part due to afforestation of poor and unproductive agricultural land, particularly on the rocky and infertile Shield region, but also because of the consumption of agricultural land for urban development (Hofmann, 2001; Smith, 2015). In addition to the large decline in agricultural land area there have been major shifts in the type of agriculture practiced in Ontario with substantial increases in row crop area (especially corn and soybean), primarily at the expense of smaller scale livestock and pastureland (Smith 2015).

Grain corn, which is N-intensive, and soybean, a N-fixer, currently dominate crop production in Ontario. Their widespread use in food, feed, manufactured goods, and biofuel have likely driven their popularity (Smith, 2015), while climate change lengthens the growing season, thus extending yields (Cabas et al., 2010). Technological developments have further enhanced crop-yields and made intensive crop-based agricultural increasingly profitable compared with pasture-based agriculture. In addition, the intensification and specialization of beef and dairy agriculture has favoured large producers, rendering smaller and less-intense operations less profitable (Thornton, 2010). A consequence of this change in profitability has been a steady decline in pastureland throughout the province (a decrease of more than 1 million hectares since

1945), and a considerable increase in the land dedicated to the production of soybeans, corn, and wheat (552%, 28%, and 127%, respectively, between 1976 and 2011; Smith, 2015; Figure 1.2).

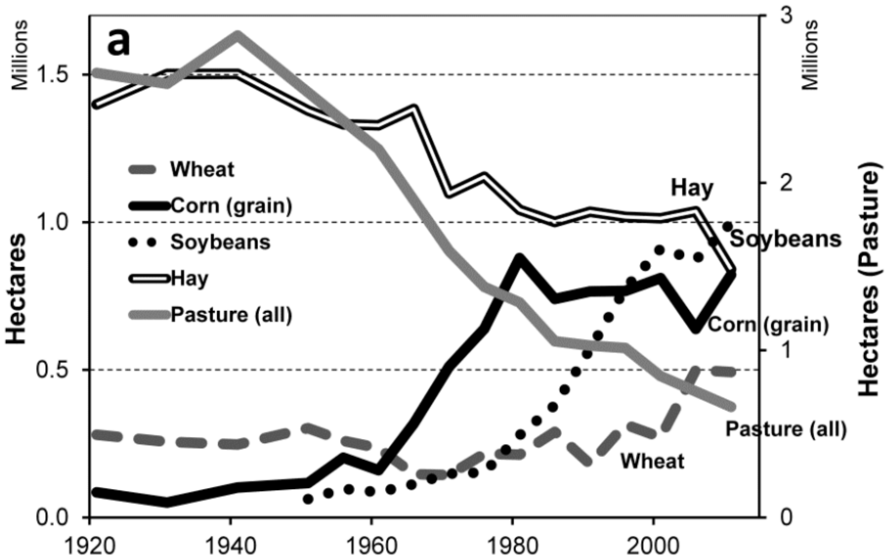

Figure 1.2 Changes in the area of agricultural land covers between 1921 and 2011 in Ontario (Smith, 2015).

Attendant with these changes have been major shifts in nutrient inputs associated with row crop production. For example, between 1954 and 1970 sales of P fertilizer increased by 133% and N fertilizer by 669% (Smith, 2015). While P fertilizer sales slowed and peaked in 1979, sales of N fertilizer continued to increase a further 71% by 2010 (Smith, 2015). Along with increases in fertilizer sales, there have been increases in tile drain installation (Veeman and Gray, 2010). While expensive to install, tile drainage increases the length of the growing season by drying and warming the fields sooner in the spring, and also stabilizes soil moisture regimes (Smith, 2015). Expansions in crop-based agriculture have led to an increase in tillage. However, there have been changes in tillage practices linked to soil preservation efforts; the use of conventional tillage dropped from 78% to 44% between 1991 and 2006 and was replaced by no tillage or conservation tillage practices. Conservation tillage is a form of tillage where more than 30% of crop residue is left on fields, as opposed to conventional tillage where almost all crop residue is integrated with the soil (Wade et al., 2015). No-till practices forgo tillage entirely (Wade et al., 2015) and were employed on approximately half of the total area in crops in Ontario by the late 2000s (Veeman and Gray, 2010). These changes in agricultural land use practices, triggered by the shift in Ontario toward crop-based agriculture, have fundamentally altered much of the province's remaining agricultural land and likely contributed to water quality changes as well.

1.6 Agricultural change and water quality

The possible implications of Ontario's changing agricultural land use and land cover (LULC) for water quality are complex. The degree of non-point source nutrient pollution from agricultural landscapes depends fundamentally on two key factors: the quantity of erodible or leachable nutrients in the landscape, and the transportation of these nutrients from the landscape to streams, rivers, and lakes via subsurface drainage and surface runoff. Agricultural LULC change can modify both factors thereby affecting the export of nutrients to waterbodies.

In pasture-based agriculture, nutrients are added to soil via manure. While much of the nutrients found in manure may originate from fields, some nutrients may enter this system from supplementary feed given to animals due to nutritional deficits (Castillo et al., 2000) and during winter months when grazing resources are limited (Beaulac and Reckhow, 1982). Livestock such as dairy cows are inefficient at utilizing N and P, particularly in feed, resulting in nutrient-rich manure deposited across pastureland (Castillo et al., 2000; Sharpley et al., 2001). While some of these nutrients are recycled within the pasture system, nutrients that are not bound by soils or consumed by vegetation may be eroded and transported to nearby streams and rivers via surface runoff (McDowell et al., 2011).

Most P losses from pastureland occur during large rain events or spring freshets (Kinley et al., 2007; Lam et al., 2016). Overall, P export during freshet and event flows may account for more than 99% of annual TP losses from pastureland to waterways (Lam et al., 2016). Livestock traffic results in soil compaction (especially when already saturated), which limits infiltration and generates more overland flow and soil erosion (Cournane et al., 2011). While a considerable source of P to watersheds, pasturelands are also a source of N. Pasture-based agriculture can increase N in downstream waterbodies compared to natural land covers. A New Zealand study found that NO_3-N concentrations were four times higher in pasture-draining streams compared with forested streams (Quinn and Stroud, 2002).

Crop-based agriculture requires regular nutrient inputs, particularly compared to pasture-based agriculture. Harvesting crops removes nutrients from an agricultural system necessitating further nutrient inputs, while inefficient nutrient uptake by some plants (particularly popular crops like corn) as well as losses via leaching and volatilization increase nutrient demand (Randall et al., 1997). A study of agricultural regions in Arkansas found N and P inputs in row crop dominated regions (>50% cover) to be five and three times higher, respectively, than inputs in pasture dominated regions (Slaton et al., 2004). Within the row crop-dominated regions, N inputs were at least six-times greater than P inputs (Slaton et al., 2004).

Nutrient losses from row crop-dominated systems are considerable, particularly for N, as has been shown in the agriculturally intensive US midwest. Row crop-dominated systems in Arkansas have been found to experience a net negative or neutral nutrient balance despite the high inputs, in contrast to pasture regions that may see net gain in nutrient balance (Slaton et al., 2004). In Iowa, stream NO_3-N concentrations have been positively correlated to the area of row crops in watersheds (Schilling & Libra, 2000), while lakes in row-crop dominated watersheds have higher N:P ratios (50:1 with >90% row crop cover) than lakes with greater pasture land cover in their watersheds (Arbuckle and Downing, 2001). Furthermore, the conversion of grassland to row crops in approximately 10% of a 4700-ha watershed increased NO_3-N export by 30% (Schilling & Spooner, 2006). In a study of the same region, P losses were not as strongly linked to row crop agriculture, with TP export most strongly correlated to field slopes and annual stormflow (Schilling et al., 2020a). Other studies in the Midwest have found approximately 20-times greater NO_3-N and four-times greater TP export from row crop-dominated watersheds than from pasture-dominated watersheds (Udawatta et al., 2011). Even without nutrient amendments, some crop-covered fields have been found to retain far less N than grass fields; an experiment that varied crop cover across multiple fields found that drainage water from fields of alfalfa and perennial grasses contained 35 times less N than drainage water from corn and corn-soybean fields (Randall et al., 1997). This result was attributed to the higher evapotranspiration rates of grasses and alfalfa (cover crops), reducing drainage, as well as higher N uptake and immobilization throughout the soil profile than for row crops (Randall et al., 1997). While the intensity of row crop agriculture is greater in the US Midwest than in Ontario, these studies still offer an insight into the relationship between land cover and nutrient export.

Much of the N export from row crops is facilitated by subsurface tile drainage. Tile drainage allows water in the soil to drain to a certain depth before being collected by a series of pipes and delivered to drainage ditches and streams downstream of the field. This enables nutrients, especially dissolved forms of N and P, to move directly through the soil to water bodies. Tile drainage is extremely effective at transporting nutrients from fields to waterways. A study of nutrient loading to Hardin Creek, Iowa found 98% of the stream's NO_3-N and 99.7% of orthophosphate (a highly soluble form of P) load were delivered via subsurface drainage (Schilling et al., 2020b). While tile drainage may reduce overland flow thereby decreasing TP loss via reduced soil erosion (Fraser and Fleming, 2001), tile drainage may still facilitate P export from fields in Ontario (King et al., 2015; Lam et al., 2016), especially during winter and spring months (Lam et al., 2016; Macrae et al., 2019). Overall, the change in agricultural land cover in Ontario from pasture to row crops, accompanied by the intensification of crop-based agriculture via increased nutrient inputs and improved drainage, may have led to increased nutrient export from agricultural land to water bodies like Lake Ontario.

1.7 Objectives, approach, and hypothesis

Much of the existing research on LULC change and water quality has focused on the highly agricultural area of southwestern Ontario that drains to Lake Erie (Bast et al., 2009; Joosse and Baker, 2011; Nelligan et al., 2021; van Bochove et al., 2011), and there has been relatively little research on the effects of similar changes in the Lake Ontario basin. Considering these knowledge gaps, the overarching objective of this thesis was to quantify long-term LULC and nutrient changes in Lake Ontario tributaries and evaluate associations between them. Quantifying and evaluating the effect of LULC changes on stream nutrient concentrations and export is particularly important in the Lake Ontario watershed due to the potential consequences of continued nutrient loading to the lake ecosystem. Two approaches were taken to address the research objective, including (a) long-term data analysis in large mixed-land use watersheds using existing landcover and water quality datasets (Chapter 2), and (b) a space-for-time approach that employed more frequent (new) measurements of water quality and quantity in smaller catchments with more homogeneous land cover (Chapter 3).

In Chapter 2, I capitalized on existing spatial and water quality data to quantify long-term (30-year) changes in agricultural land cover and associations between land cover change and stream TP and NO_3-N concentrations. Due to the availability and length of existing spatial and water quality data, the first objective was limited to the period of 1971 to 2011 at 12 quaternary watersheds along the north shore of Lake Ontario. For this analysis, only growing season data (May to September) were utilized as long-term water quality data are collected on an infrequent basis (post-1995). I hypothesized that row crop area and tile drainage area would increase over time at the expense of pasture and forage land, while conventional tillage area would decrease in agriculture-dominated watersheds. I hypothesized further that TP concentrations would decline and NO_3-N increase in agriculture-dominated watersheds, and that these changes would not be exhibited in urban-dominated watersheds.

In Chapter 3, I employed a space-for-time approach to overcome limitations in the frequency and range of data used in Chapter 2 and to better isolate the effect of specific LULC types on water quality throughout an entire year. Chapter 3 involved year-round and event-targeted measurements in 12 small (< 7.5 km^2) catchments, 10 of which were located within larger quaternary watersheds examined in Chapter 2 (Soper Brook, Wilmot Creek, Graham Creek, and the Ganaraska River). Water quality and discharge measurements were collected downstream of five crop-dominated, five pasture-dominated, and two forested catchments. I hypothesized that TP concentrations and export would be greatest in pasture catchments, while NO_3-N losses were expected to be highest in row crop catchments.

Chapter 2 - Stream nutrient and agricultural land-use trends from 1971 to 2010 in Lake Ontario tributaries

As published: DeBues, M.J., Eimers, M.C., Watmough, S.A., Mohamed, M.N., Mueller, J., 2019. Stream nutrient and agricultural land-use trends from 1971 to 2010 in Lake Ontario tributaries. J. Great Lakes Res. 45, 752–761. https://doi.org/10.1016/j.jglr.2019.05.002

2.1 Introduction

Southern Ontario is home to 36% of the population of Canada, most of whom live within urban areas (Ontario Ministry of Finance, 2017). Over the last fifty years, urban growth in southern Ontario has been rapid, fuelled by urbanization in the Greater Toronto Area (GTA) where urban land area doubled between 1974 and 2014 (Wang et al., 2015). However, southern Ontario is also home to the vast majority of the province's prime agricultural land (Statistics Canada, 2018), and is therefore responsible for most of the province's considerable agricultural output, accounting for approximately 15% of the nation's net farm income in 2017 (Statistics Canada, 2018). This intersection between high quality agricultural land and a growing urban population makes southern Ontario one of the most important, yet dynamic, regions in Canada.

Unsurprisingly, this same intersection creates challenges for water resource management in the province. Numerous studies have documented the often-deleterious effect of land use and land cover change (LULC) on water quality and quantity (Duan et al., 2012; Groffman et al., 2003; Nagy et al., 2012; Raney and Eimers, 2014b). Nutrient-rich water draining from the landscape can trigger algae blooms in the Great Lakes, reducing water quality and damaging fish and plant life. Two nutrients of concern are phosphorus (P), and nitrogen (N) (Carpenter et al., 1998). Both P and N are important in controlling eutrophication in surface waters (Conley et al., 2009; Lewis and Wurtsbaugh, 2008), although P is understood to be the most limiting in freshwater systems (Higgins et al., 2018), while NO_3-N in drinking water poses a considerable health risk to humans (Wolfe and Patz, 2002) and wildlife (Camargo et al., 2005; CCME, 2012). Total P (TP) concentrations in offshore Lake Ontario are now a third lower than in 1985 (Dove and Chapra, 2015). However, simultaneously, NO_3-N concentrations increased by nearly 60% between 1970 and 2010 (Dove and Chapra, 2015). Although the cause(s) of NO_3-N increases have sometimes been ascribed to internal lake factors (Dove, 2009; Finlay et al., 2007; Hecky et al., 2004) and atmospheric deposition (Dove and Chapra, 2015), agricultural runoff in lake tributaries is recognized as an important external source of nutrients to the Great Lakes (Joosse and Baker, 2011; Robertson and Saad, 2011).

While agriculture is acknowledged as an important non-point source of both N and P, various agricultural land uses can contribute differently to nutrient release. For example, croplands, particularly those with corn and soybean, are associated with much higher N export than grasslands (Schilling and Libra, 2000; Schilling and Spooner, 2006; Udawatta et al., 2011). Cropland is often accompanied by the installation of subsurface (tile) drainage, which can facilitate the subsurface export of TP (Kleinman et al., 2015; Macrae et al., 2007) and particularly NO_3-N to waterways by improving drainage beneath the rooting zone and expediting transfer to downstream surface waters (King et al., 2015; Kinley et al., 2007; Randall et al., 1997). Meanwhile, pastureland is associated with lower N:P surface water ratios than cropland (Arbuckle and Downing, 2001), with P losses from pastureland associated with soil erosion and untreated manure (Cournane et al., 2011; McDowell, 2006). Phosphorus losses from both cropland and pastureland can be variable (Beaulac and Reckhow, 1982); however, few studies have directly compared the influence of different forms of agricultural land use (i.e. row crops, pasture) on nutrient export (Beaulac and Reckhow, 1982; Udawatta et al., 2011).

Research on LULC and Great Lakes water quality has focused on the high-intensity agricultural region of southwestern Ontario that drains into Lake Erie. However, recent research in the Lake Ontario drainage basin has found decreases in tributary TP (Raney and Eimers, 2014a; Stammler et al., 2017) and increases in NO_3-N stream concentrations (Eimers and Watmough, 2016). Increases in urban land cover throughout southern Ontario have been primarily at the expense of surrounding agricultural land (Hofmann, 2001), and while agriculture remains an important landcover in Ontario, both the type of agriculture and management practices have been changing. Since 1976, on a provincial scale, Ontario has witnessed an increase in the growth of cash crops, where land dedicated to corn and soybean has increased by 28% and 552%, respectively (Smith, 2015). Due to the prior lack of high-intensity agriculture along the north shore of Lake Ontario, considerable shifts in agricultural practices in this region may have a more pronounced (and detectable) impact than in the southwest/Lake Erie drainage area of the province, where agriculture historically has been more intensive. Thus, the objectives of this study were firstly to quantify changes in LULC in 12 Lake Ontario tributaries between 1971 and 2010, and secondly to determine whether changes in LULC cooccurred with changes in growing season tributary TP and NO_3-N concentrations over the same period.

2.2 Methods

2.2.1 Site location and characteristics

All 12 watersheds selected for this study flow south into Lake Ontario (Figure 2.1; Table 2.1), and share similar physical characteristics, particularly in terms of slope, soil, and hydrology, each of which influence stream nutrient concentrations. The entire area falls within the Köppen Dfb climate zone, and average (1971–2000) precipitation was relatively consistent across the watersheds, ranging from 793 mm/year at the westernmost basin (Etobicoke; measured at Pearson Airport) to 872 mm/year at Gages Creek (measured at Cobourg), of which ~85% falls as rain. Average annual temperature over the 1971–2000 period was 7.5 °C at Pearson and 7.1 °C at Cobourg, with highest monthly average temperature occurring in July (19.6 °C at Cobourg; 20.8 °C at Pearson) and minimum in January (−6.0 °C at Cobourg; −6.3 °C at Pearson). Watersheds were chosen to represent a range of urban and agricultural locations (Figure 2.1; Table 2.1). Most watersheds in the study are free of upstream municipal wastewater treatment plants (WWTPs; Raney and Eimers, 2014b); and, for the most part, WWTP outlets are instead located downstream of water quality monitoring locations. However, there are a few exceptions. Etobicoke Creek had multiple small wastewater treatment plants (Owen and Johnson, 1966) that were phased out in the late 1960s and early 1970s (White, 2003). Duffins Creek and Rouge River also contained wastewater treatment plants that were phased out by 1980 (TRCA, 2007).

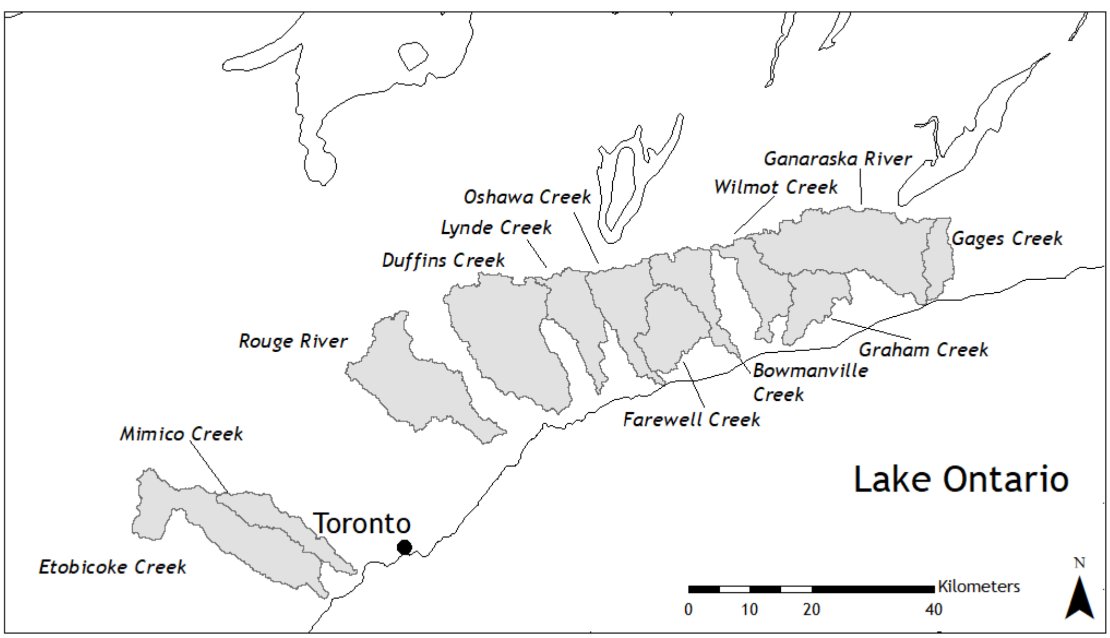

Figure 2.1 Map of watersheds in Chapter 2 study.

Table 2.1 Characteristics of the 12 study watersheds, ordered west to east. Watersheds were delineated and characterized using the OMNRF (Ontario Ministry of Natural Resources and Forestry) Ontario Flow Assessment Tool (OFAT) using a PWQMN sampling location as the pour point for each watershed. All variables were calculated by OFAT except tile drainage cover, which was estimated using the Ontario government's 2018 tile drainage layer.

Watershed Name	***Area (km^2)***	***Average Slope (%)***	***Tile Drainage Cover (%)***	***Modelled mean annual precipitation 1981-2010 (mm)***
Etobicoke	218.9	1.9	6.2	815
Mimico	72.6	2.0	0.0	819
Rouge	218.1	2.9	1.2	840
Duffins	278.6	4.3	0.8	861
Lynde	104.4	4.0	3.3	868
Oshawa	115.2	4.7	4.2	881
Farewell	107.1	3.5	6.6	888
Bowmanville	89.3	5.2	8.3	900
Wilmot	85.6	5.3	2.9	913
Graham	76.8	4.3	1.0	907
Ganaraska	277.9	6.0	3.5	923
Gages	46.6	5.7	15.3	930

2.2.2 Data sources

Water quality data (1970–2010) at each watershed outlet were obtained from the Ontario Provincial Water Quality Monitoring Network (PWQMN), which was established by the Ontario Ministry of Environment Conservation and Parks (OMECP) in 1964. The PWQMN currently includes over 400 locations throughout southern Ontario (Land Information Ontario, 2015), and streams are sampled by local Conservation Authorities and chemically analyzed by the OMECP, which provides consistent methods of laboratory analysis across all stations (Land Information Ontario, 2015).Watersheds considered in this study fall within the jurisdictions of three different Conservation Authorities, including the Toronto and Region Conservation Authority (TRCA;

Mimico, Etobicoke and Rouge), the Ganaraska Region Conservation Authority (GRCA; Wilmot, Graham, Ganaraska and Gage) and the Central Lake Ontario Conservation Authority (CLOCA; Lynde, Farewell, Bowmanville and Oshawa). As such, field sampling strategies to capture different hydrologic conditions may have varied across the three Conservation Authorities, and over time. Indeed, as a long-term government-funded monitoring network, the PWQMN has been affected by changes in policy and funding, creating gaps and inconsistencies in the dataset. Streams were typically sampled monthly, although sampling frequency varied extensively over the period of record. For example, Etobicoke Creek was sampled 20 times during 1978, but only twice during 1980. Furthermore, sampling has become based around the growing season: during the 1970s, 45% of sampling occurred between May and September; however, by the 2000s this had increased to 64%, with fewer than 5% of sampling events occurring in the winter. This means that many watersheds in more recent decades have few to no data between December and May. For this reason, this study focuses on data collected during the Ontario growing season (May–September), although dormant season data (October – April) are considered for comparison. The PWQMN monitors a suite of water quality parameters including physical conditions, nutrients, and metals (Land Information Ontario, 2015). This study utilizes TP and NO_3-N data collected between 1970 and 2010, with some exceptions noted below.

To account for the phasing out of wastewater treatment plants upstream of the sampling location on Etobicoke Creek, data prior to 1973 were removed from this analysis. Although the exact dates that wastewater treatment plants were phased out in the Etobicoke Creek watershed are unknown, exploratory data analysis suggested that plants were removed by 1973. For example, between 1971 and 1973 NO_3-N concentrations in Etobicoke Creek declined by approximately 75%, while TP concentrations declined 90%. Neighbouring Mimico Creek (see

Figure 2.1) did not have a wastewater treatment plant and showed no such dramatic change; NO_3-N and TP concentrations between 1964 and 1974 were comparable to the concentrations observed in Etobicoke Creek in 1973. Similarly, wastewater treatment plants in Duffins Creek and Rouge River watersheds were not removed until the start of the 1980s. Therefore, water quality data from prior to 1980 were omitted from the analysis of these two sites.

Land cover data between 1970 and 2010 were retrieved from several sources. Land cover for the 1970s was constructed using data from the Canada Land Use Monitoring Program (CLUMP) in 1971 (Natural Resources Canada, 1999a), and the Canada Land Use Inventory (CLI) from 1966 (Natural Resources Canada, 1999b). CLUMP land use data were of a higher resolution than CLI data, and exploratory comparisons between the two data sets suggested that CLI may overestimate agricultural land cover in urban watersheds due to poorer resolution. Therefore, when possible, CLUMP was used to construct 1970s land cover, although CLI was used to fill spatial gaps in CLUMP coverage. Land cover for the 1980s was constructed using the 1983 Agricultural Resource Inventory (Ontario Ministry of Agriculture Food and Rural Affairs, 1983)' whereas SOLRIS (Southern Ontario Land Resource Information System) 1.2, based on Landsat remote sensing data collected between 2000 and 2002 (Ontario Ministry of Natural Resources and Forestry, 2008), was used to construct 1990s land cover as other data sources had insufficient resolution. SOLRIS 2.0, based on data collected between 2009 and 2011 (Ontario Ministry of Natural Resources and Forestry, 2015), was used to construct 2000s land cover. SOLRIS 1.2 does not classify agricultural land; however, the 'undifferentiated' category in SOLRIS 1.2 was used as a substitute for agricultural land cover (Ontario Ministry of Natural Resources and Forestry, 2008). Natural land cover was defined as the combination of forest, wetland, shrubland, and other similar types of land classification that describe typical undeveloped natural land cover.

Agricultural land-use (as opposed to cover) data were obtained from Canadian Census of Agriculture records at a county scale, in census years 1971, 1981, 1991, and 2001. These data, collected by Statistics Canada on a county scale, record the area of crop cover, fertilizer area and tillage practices (conventional, conservation or no-till) for the year of each census. Row crop cover was defined as the sum of corn (grain and silage), soybean, and wheat (winter and spring). County-scale records were converted to watershed-scale as described below. As tile drainage records by year are not available in Ontario, the current (2018) extent of recorded tile drainage was estimated using data provided by the Ontario Ministry of Food and Rural Affairs (Land Information Ontario, 2012).

2.2.3 Data treatment

Watersheds were delineated using the Ontario Flow Assessment Tool (OFAT), with pour points for each catchment taken from the PWQMN database of sampling locations. It should be noted that OFAT defines basin boundaries based on topography, and thus may over or underestimate true drainage area in watersheds with substantial urban cover and/or agricultural tile drainage Nevertheless, Eimers and MacDonald (2014) found that total annual runoff (mm) was not significantly different across watersheds that were almost entirely urban (i.e. Mimico) versus watersheds dominated by rural/agricultural landcover (e.g. Wilmot) suggesting that watershed boundaries defined by OFAT are reasonably accurate for the study region. Proportions of land cover in each of these watersheds were calculated using ArcGIS 10.5 by clipping watershed polygons to the different historical land cover layers. Land cover (LC) data were left mostly untreated. In contrast, census based agricultural land use (LU) data had to be converted from a township scale to a watershed scale, and this was done based on area weighted means. LU data were categorized into ‘row crops’ (corn + wheat + soybean), ‘pasture’ (improved + unimproved pasture + hay fields), and ‘other agricultural’ covers (includes other grain + fruit + vegetable crops). Land use in each watershed was calculated as both a proportion of total watershed area and as a proportion of agricultural land.

Percent coverage of fertilized land and the areas of conventional, conservation and no-till tillage practices were also calculated. Fertilizer records from the Census of Agriculture do not specify type of fertilizer or the timing of fertilizer application, only the proportion of agricultural land fertilized. Proportions of land subjected to conventional till, no-till, or conservation till practices only began to be documented in 1991. As agricultural census data and historical land cover layers do not typically fall on the same year, each census dataset was paired with a land cover layer from the same decade. Thus, measurements of agricultural LU are coarse estimates, both temporally and spatially.

To account for differences in sampling frequency across decades and amongst PWQMN stations, Ontario growing season (May–September, inclusive) stream chemistry data were the focus of this study although non-growing season averages were also calculated for comparison. Previous hydrologic analyses in this region indicate that on average (1970–2000) ~30% of annual runoff occurs during the May–September period, but this can vary from as low as 21% to as high as 50% depending on year (Eimers and McDonald, 2015; Eimers and Watmough, 2016). The total number of measurements used to calculate a growing season average was generally consistent amongst watersheds, and median sample size (i.e., n) was 40, 48, 20 and 37 in the 1970s, 80s, 90s and 2000s, respectively. However, there were a few exceptions; specifically, only three samples were taken at Ganaraska in the 2000s, whereas 13 and five samples were taken at Lynde and Farewell, respectively, during the 1970s. Because flow data are not available at many of the basins over the period of interest and/or Water Survey of Canada flow gauges are located distant from the water quality monitoring stations, concentrations were not volume-weighted and only arithmetic means of concentrations are reported. Because nutrient export may be extremely sensitive to hydrologic conditions as well as to the flow path that runoff follows, changes in hydrology and sampling effort across sites or over time could affect mean nutrient concentrations. To avoid this issue and to account for differences in sampling effort across years, we focus on decadal averages and nutrient concentrations were averaged over ten-year periods, spanning 1970 to 2010. Additionally, decadal averages of nutrient concentrations are an appropriate scale to consider because they correspond to agricultural census data. To accomplish this, the 10 years of stream chemistry records following each agricultural census were grouped together and matched with the Census of Agriculture data.

Processed PWQMN data failed the assumptions of parametric tests, even when transformed. The non-parametric Kruskal-Wallis rank sum test and the Dunn post-hoc test were used to assess significant changes in NO_3-N and TP across decades in each watershed individually. All comparisons were run using the Dunn post-hoc tests. Trends in LULC and stream chemistry were compared by watershed. Mann-Whitney tests were used to compare growing season and non-growing season average nutrient concentrations amongst the three most urbanized and three most agricultural watersheds. Data analysis was performed using R statistical software.

2.3 Results

2.3.1 Land use and land cover

Urban land cover increased throughout the entire study area between 1971 and 2010, with the greatest increases occurring within watersheds in the Greater Toronto Area (Table 2.2). The Rouge River watershed underwent the largest increase in urban cover (7% of total watershed area in 1971 to 52% in 2009–11), whereas urban increases were smaller in the most agricultural watersheds (e.g., 1–5% between 1971 and 2009–11 at Graham Creek and Ganaraska River, respectively; Table 2.2). Increases in urban land cover came at the cost of agricultural land, which declined in each study watershed (Table 2.2). Unsurprisingly, the greatest declines in agriculture occurred in watersheds where urban area increased the most, including Rouge, Etobicoke, and Mimico (Table 2.2). Even watersheds that remained predominantly agricultural lost some agricultural area over the 40-year period. For example, Gages declined from 91% agriculture in 1971 to 71% in 2009–11, although part of this loss was due to an increase in natural land cover, which more than doubled between 1971 and 2010 (i.e., 7% to 20%; Table 2.2).

Although total agricultural land area declined across the region, the proportion of agriculture covered by row crops increased in all watersheds between the 1970s and 2000s. In addition, the absolute area of row crops increased in half of the watersheds over the same period. In the most agricultural watersheds, row crops accounted for 62% (Gages) to 76% (Oshawa) of farmed land in the 2000s, up from 41% and 50% in the 1970s (Figure 2.2). Even the most urbanized watersheds showed modest increases in row crop cover; the average area of agricultural land covered by row crops increased from 49% (Mimico) and 61% (Etobicoke) in the 1970s to 79% in the 2000s.

Table 2.2 Percent land cover (of total watershed area) between 1971 and 2011, as well as the percent of agricultural land covered by row crops, fertilized, and tilled conventionally between the 1970s and 2000s in each watershed. Differences between the earliest and latest values are noted. Sites are ordered by location from west (more urban) to east (more rural).

Watershed Name	Natural					Urban					Agriculture					Row Crops					Fertilizer					Conventional Tillage		
	1971	1982-1983	2000-2002	2009-2011	Δ	1971	1982-1983	2000-2002	2009-2011	Δ	1970s	1980s	1990s	2000s	Δ	1970s	1980s	1990s	2000s	Δ	1970s	1980s	1990s	2000s	Δ	1990s	2000s	Δ
Etobicoke	5	3	6	6	+1	18	50	59	62	+43	76	46	34	32	-44	61	68	73	79	+18	12	43	57	55	+43	61	50	-11
Mimico	1	0	3	3	+2	49	82	87	89	+40	49	17	10	8	-41	49	62	80	79	+30	8	39	61	53	+45	69	55	-14
Rouge	10	8	14	14	+4	7	29	47	52	+45	79	62	39	34	-45	72	76	66	78	+6	21	61	55	63	+42	53	53	0
Duffins	18	19	28	28	+10	4	6	13	14	+10	75	73	59	57	-18	56	68	63	71	+15	18	48	49	56	+38	54	32	-22
Lynde	13	14	23	23	+10	5	7	14	18	+13	80	78	63	59	-21	58	67	72	76	+18	28	56	59	62	+34	43	42	-1
Farewell	8	14	17	17	+9	24	25	30	33	+9	67	61	53	51	-17	50	61	66	68	+18	26	47	68	62	+36	45	28	-17
Bowmanville	22	28	30	30	+7	3	7	9	10	+7	74	65	61	60	-14	53	61	63	68	+15	21	46	61	58	+37	48	33	-15
Oshawa	11	11	17	17	+5	15	18	19	21	+6	73	70	64	62	-11	54	61	61	68	+15	22	46	56	56	+34	51	38	-13
Wilmot	20	23	28	28	+7	3	7	7	7	+4	76	70	65	64	-12	44	61	61	68	+24	15	46	56	56	+41	51	38	-13
Graham	25	27	35	35	+9	1	3	5	5	+4	74	70	60	61	-14	43	61	61	68	+25	15	46	56	56	+41	51	36	-15
Ganaraska	40	39	45	44	+4	1	3	5	5	+3	58	58	51	51	-8	43	61	61	68	+25	14	45	54	54	+40	52	26	-26
Gages	7	10	20	20	+13	2	8	9	9	+7	91	82	71	71	-20	42	54	58	61	+19	13	36	49	51	+38	47	25	-22

The area of land fertilized also increased between the 1970s and 2000s, consistent with the increase in row crop agriculture (Table 2.2). The area of fertilized land within the most agricultural watersheds (60% agriculture) at least doubled, although almost all that increase occurred during the 1970s. For example, data from the 1971 agricultural census indicate that between 8 and 28% of total row crop area in all watersheds was fertilized, but by the 1981 census 39–61% of land was fertilized (Table 2.2). Conversely, the proportion of row crop area under conventional tillage dropped from an average of 50% to 34% in the most agricultural watersheds, although tillage monitoring only began in 1991 (Table 2.2).

2.3.2 Stream total phosphorus

Growing season concentrations of TP were generally highest at the most urbanized watersheds (Mimico, Etobicoke) in all decades, (53–78 μg/L; Figure 2.3), and concentrations within some of the urban watersheds have remained within the eutrophic category (75 μg/L) (Dodds et al., 1998) over the entire monitoring period (1970–2009). In contrast, TP concentrations in the growing season were typically lower in the predominantly agricultural watersheds (17–33 μg/L; Figure 2.3). Significant declines in TP occurred in all three of the predominantly (50%) urban watersheds over the period of record, with the largest decreases occurring between the 1970s and 1980s (Figure 2.3). In contrast, there were less consistent changes in TP concentration in the most agricultural watersheds, with six of the nine predominantly agricultural watersheds (50% agriculture) showing significant declines, including Lynde, Bowmanville and Duffins watersheds (Figure 2.3) where the proportion of urban cover tripled between 1971 and 2009–11 (Table 2.2). Notably, TP did not increase at any of the study watersheds over the period of record. The range in mean TP concentrations during the 2000s at watersheds with 50% agricultural cover was 10 to 44 μg/L, putting these streams on the boundary between oligotrophic (25 μg/L) and mesotrophic (25–75 μg/L) conditions (Dodds et al., 1998). Mean TP was generally higher in the non-growing season than in the growing season across all decades in the most urban and agricultural watersheds (Figure 2.5). Differences between non-growing season and growing season TP were higher in the three most agricultural watersheds compared with the three most urban watersheds.

2.3.3 Stream nitrate-N

Concentrations of NO_3-N followed a distinctly different pattern from TP. During the 2000s, NO_3-N concentrations were highest in the most agricultural watersheds (0.62–1.48 mg/L; Figure 2.4) and lowest in the most urbanized watersheds (0.50–0.70 mg/L; Figure 2.4). Furthermore, the greatest and most consistent increases in NO_3-N occurred in the most agricultural watersheds, including Wilmot, Graham, and Gages Creeks (Figure 2.4). While less consistent, NO_3-N in both Oshawa and Ganaraska also increased. In contrast, NO_3-N patterns were less consistent in the most urbanized watersheds. Nitrate-N was relatively stable over time at Etobicoke and Mimico Creeks, whereas NO_3-N levels in the Rouge River, which underwent the greatest increase in urban cover over the 40-year period, declined significantly, most notably between the 1970s and the 1980s after which NO_3-N stabilized (Figures 2.2 and 2.4). Differences between non-growing season and growing season stream NO_3-N concentrations were significant at both the three most urbanized and the three most agricultural watersheds (Figure 2.6). However, in contrast to TP, these differences were consistent across the most rural watersheds.

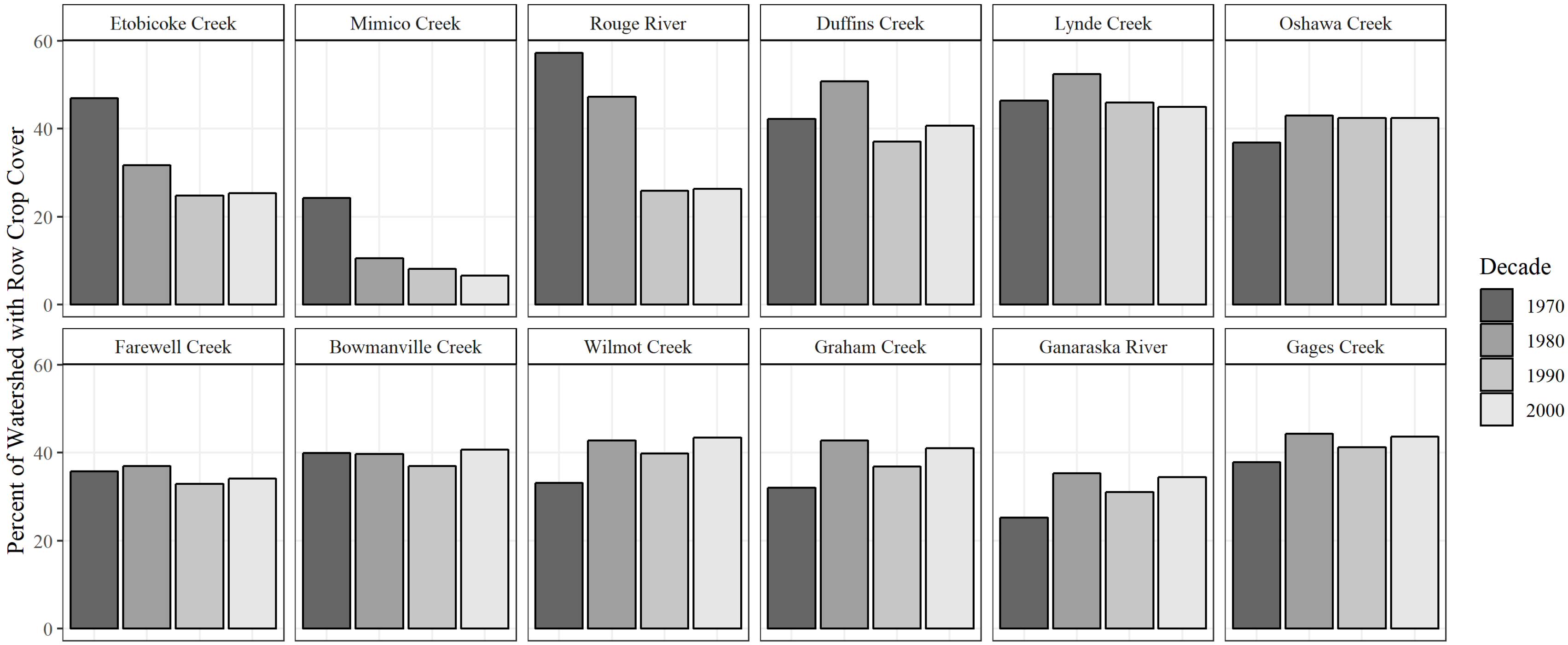

Figure 2.2 Percent cover of watershed with row crops between the 1970s and 2000s.

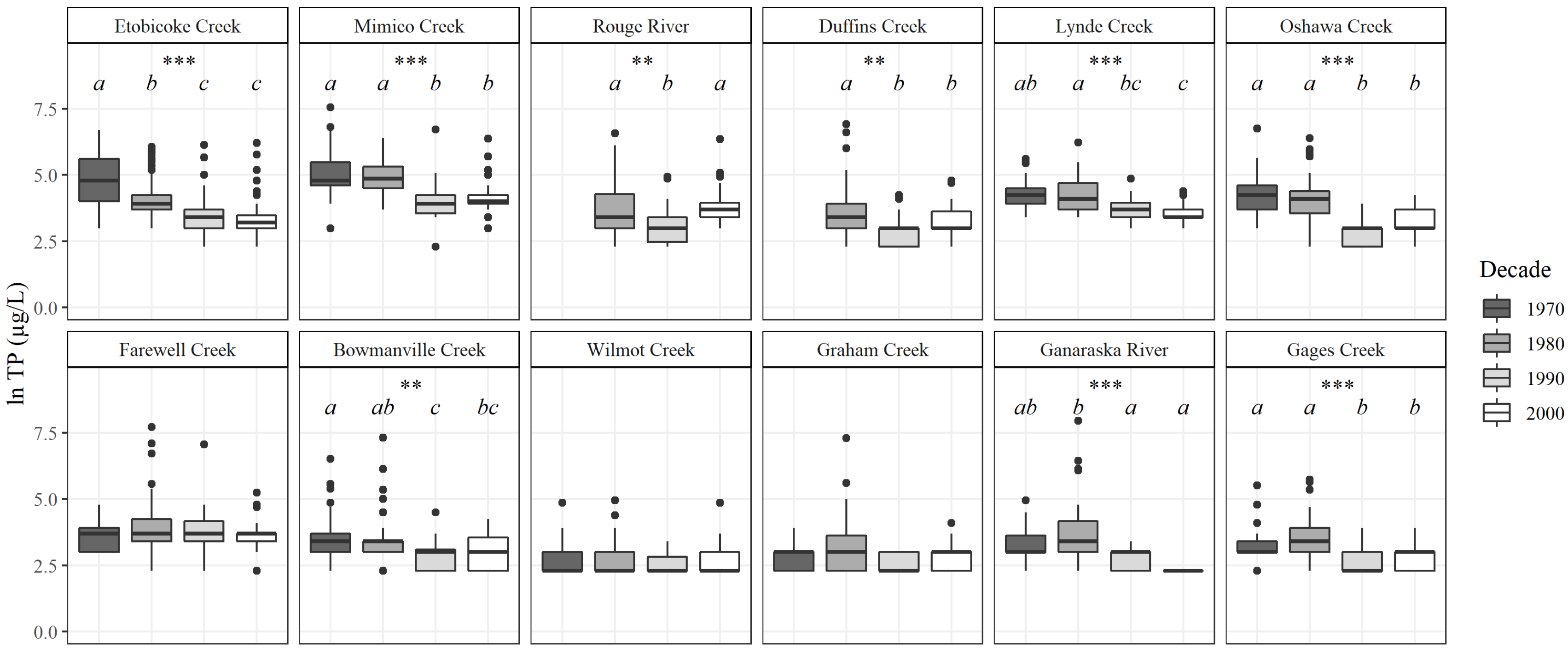

Figure 2.3 Ln TP concentrations (µg/L) during the growing season (May to September), in the 12 study watersheds between the 1970s and 2000s. Asterisks denote overall significant differences across all decades: * ($p < .5$); ** ($p < .01$); *** ($p < .001$). Letters denote significant ($p < .05$) differences between specific decades.

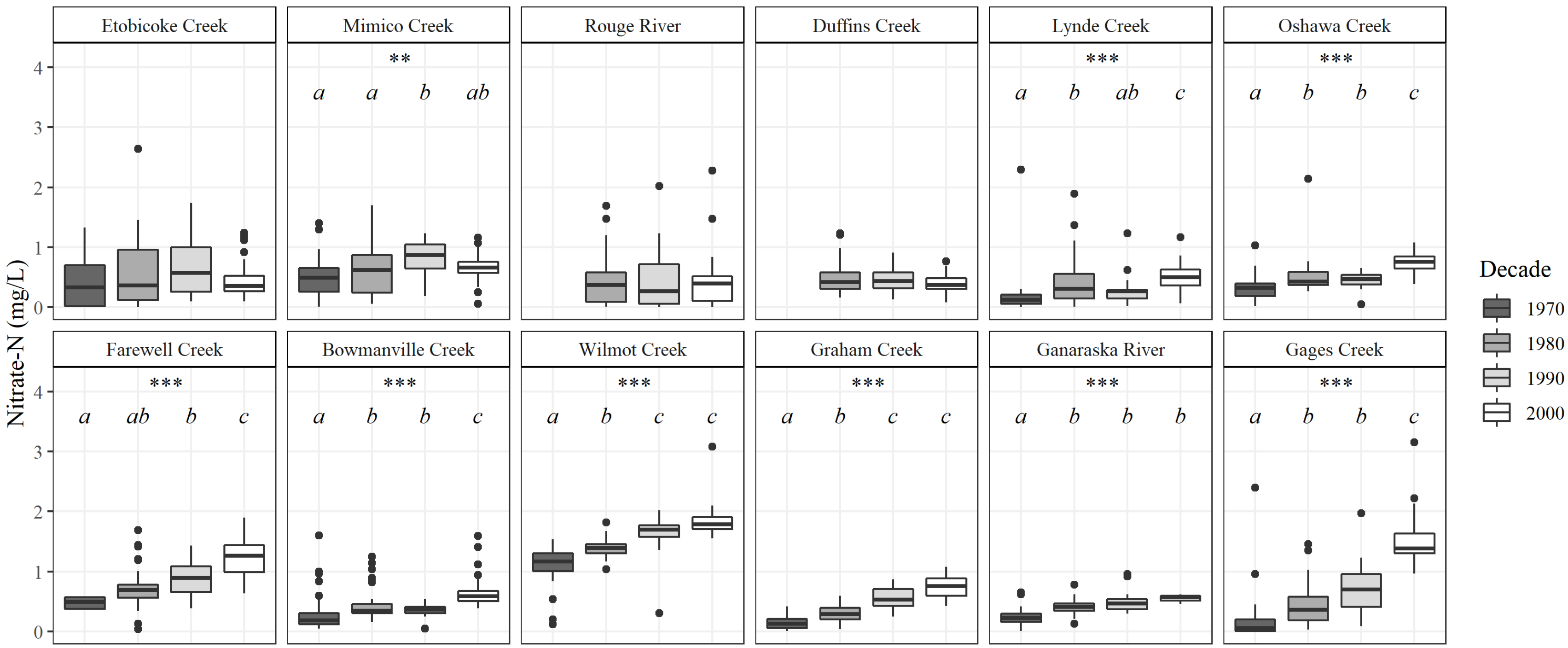

Figure 2.4 NO_3-N concentrations (mg/L) during the growing season (May to September), in the 12 study watersheds. Asterisks denote overall significant differences across all decades: * (p < .5); ** (p < .01); *** (p < .001). Letters denote significant (p < .05) differences between specific decades.

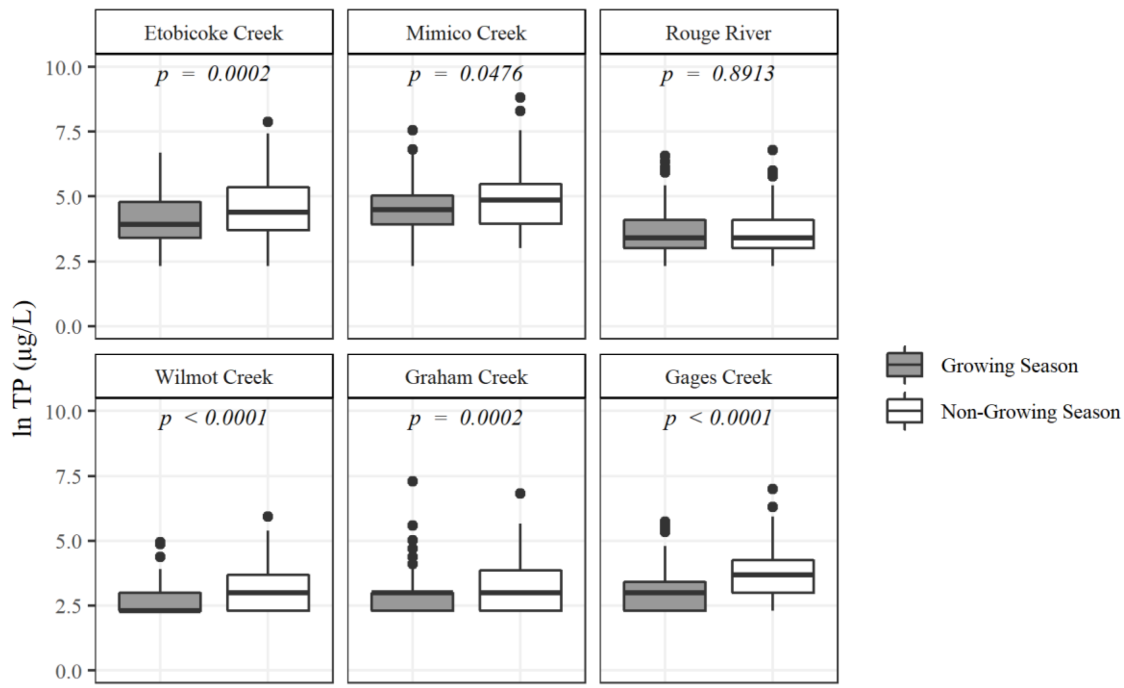

Figure 2.5 Ln TP concentrations (µg/L) during the growing (May to September), and non-growing season (October to April), in a selection of the most urban and agricultural watersheds.

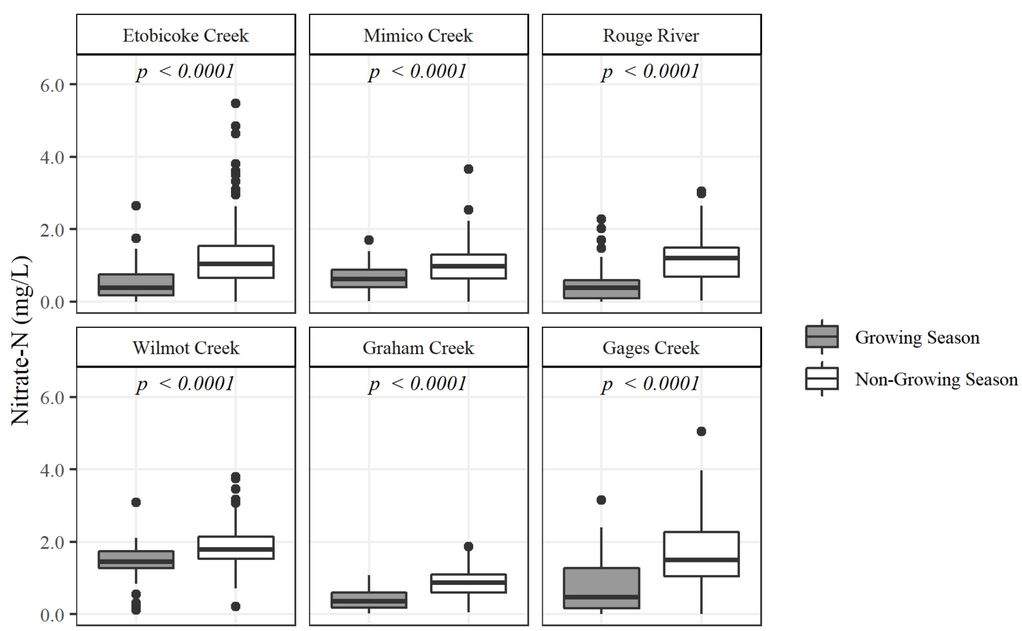

Figure 2.6 Nitrate-N (mg/L) during the growing (May to September), and non-growing season (October to April), in a selection of the most urban and agricultural watersheds.

2.4 Discussion

2.4.1 Land use and land cover change

Land cover in southern Ontario has changed dramatically over the past several decades, including increases in urban cover, declines in total agricultural area, and increases in the importance of row crops within agricultural landscapes (Hofmann, 2001; Smith, 2015). These changes are reflected within the 12 study watersheds described here: urban area expanded by up to 7-fold (Rouge), and this was largely at the expense of agricultural land, which underwent commensurate declines in the most urbanizing watersheds. Declines in productive agricultural area in southern Ontario are of concern, given the relatively small area of suitable soil and climate conditions for food production in Canada (Hofmann, 2001). Despite the loss of total agricultural area, there were large increases in proportional row crop coverage across all watersheds, including the most urbanized watersheds in Toronto (Mimico and Etobicoke). Row crops in Ontario are predominantly (grain) corn, soybean and (winter) wheat, and these three row crops account for an average of 67% of the total farmed area in the most agricultural watersheds in this study. Increases in area devoted to crop production observed in this study are consistent with trends across southern Ontario, where row crops are largely replacing pasture and forage land (Smith, 2015), although as noted earlier, the north shore of Lake Ontario is somewhat 'behind' in these shifts compared with the Lake Erie drainage area of southwestern Ontario. Shifts from livestock toward row crop farming could be a product of several factors, including higher grain prices and the use of corn for ethanol production (Wu et al., 2017), as well as advances in agricultural technology and cold-hardy cultivars (Smith, 2015; Rickard and Fox, 1999). The gradual intensification of the beef and dairy industries over the past five decades has also disadvantaged smallholder livestock producers (Thornton, 2010). In addition, periodic disease outbreaks in the meat industry (Smith, 2015) as well as a desire for more flexible work schedules may be contributing to the decline in livestock farming, particularly by younger, incoming farmers. In the future, the trend of increasing row crop cover may be influenced by climate change, which is projected to increase crop yields by extending the growing season in Ontario (Cabas et al., 2010). Clearly, it is possible for row crop agriculture to continue to expand in watersheds along the north shore of Lake Ontario, and such growth would amount to considerable further intensification of agricultural landscapes throughout the study area.

These patterns in LULC corresponded with two very divergent patterns of stream nutrient concentrations. Levels of TP were consistently highest in the most urbanized streams and lower in the more agricultural streams, and trends in TP were predominantly negative, particularly in urban streams. In contrast, NO_3-N concentrations were generally higher in agricultural than urban streams; and unlike TP, trends in NO_3-N were generally positive, particularly in the agricultural watersheds where increases in total row crop cover were the largest and most consistent. Notably, there have been no commensurate changes in stream flow over the period of record – either upward or downward – that could either counter or explain the observed trends in stream chemistry. Eimers and Watmough (2016) found that decadal-scale seasonal runoff averages at three of the twelve watersheds that have flow records were generally consistent between the 1970s and 2000s. Possible drivers of changes in TP and NO_3-N concentrations are discussed below.

2.4.2 Stream total phosphorus

Total P concentrations declined over time in seven out of twelve (67%) watersheds, which is consistent with recent research that has detected widespread TP declines at sites across Ontario (Raney and Eimers, 2014a; Stammler et al., 2017). Previous research on the north shore of Lake Ontario found 68% of streams (n = 113) underwent declines in TP concentrations between 1975 and 2010 (Raney and Eimers, 2014a). This proportion is similar to a broader southern Ontario study that found declines in 57% of streams (n = 56; Stammler et al., 2017). Both studies examined a range of land cover types. Raney and Eimers (2014b) speculated that urbanization at the expense of agricultural land might contribute to TP declines, due to an increase in impervious surfaces causing a reduction in soil erosion. However, our study found that TP concentrations were generally lower in agricultural watersheds than in the most urbanized watersheds, suggesting that simultaneous urbanization and decreases in stream TP concentrations may be coincidental. This is supported by Stammler et al. (2017) whose recent study of growing season TP concentrations throughout Ontario found TP declines occurred in rural watersheds with very low amounts of urbanization (Stammler et al., 2017). However, this study could not determine the mechanism(s) responsible for decreasing TP in watersheds throughout the study area (Stammler et al., 2017).

It is unclear what drove TP declines in the most heavily urbanized streams (Mimico and Etobicoke), where most urban development occurred prior to 1983 (Table 2.2). While dramatic decreases in offshore TP concentrations in the Great Lakes between 1970 and 1990 (Dove and Chapra, 2015) can be attributed to restrictions placed on point source TP polluters, particularly industry and municipal waste water treatment plants (Dolan and Chapra, 2012), this same explanation cannot apply to the study watersheds since we either omitted sites with upstream WWTPs or omitted data prior to the removal of upstream WWTPs. It should also be noted that although we report higher TP concentrations in urban compared with agricultural watersheds, a simple ‘space for time’ expectation of higher TP concentrations with an expansion in urban area is likely overly simplistic and potentially incorrect. Modern urbanization occurring at the edge of the GTA is likely considerably different than urbanization that occurred prior to the 1970s - a time when urban cover at Mimico Creek was already 50% of total watershed area. Starting in the late 1960s, increased attention to the quality of urban stormwater resulted in a shift from rapid stormwater conveyance offsite toward the retention of stormwater in dry and wet ponds (Chocat et al., 2001; Drake and Guo, 2008). Stormwater management has been required at new urban developments in Ontario since the early 1990s (Bradford and Gharabaghi, 2004) and stormwater ponds and retention basins that slow runoff and allow sedimentation generally reduce P losses in runoff (SWAMP, 2005). Stormwater ponds are more effective at retaining P than drainage ditches (Sønderup et al., 2016), which characterized older urban areas. In addition, urban cover is not uniform within watersheds of the scale considered in this study (46.6 to 279 km^2) and a range of land covers within urban areas exist, from older, high-density urban areas to more modern, lower-density suburban areas. Research at the Baltimore Long-Term Ecological Research project (LTER) found that TP export from ‘suburban’ watersheds was at most half of the TP export from a more established ‘urban’ watershed (Duan et al., 2012). Similarly, research in Florida found that TP concentrations were correlated with percent impervious cover in watersheds (Nagy et al., 2012) suggesting that older, denser urban areas with more impervious cover will have higher TP concentrations than newer, less dense, and more pervious suburban areas. Thus, recent (i.e., post 1990) urbanization that has occurred in watersheds like Rouge may be associated with lower TP concentrations compared with watersheds that have older, denser urbanized cover like Mimico. Indeed, differences in TP concentration in the 1990s and 2000s are smaller between agricultural streams and the more recently urbanized streams like Rouge compared with Mimico (Figure 2.3).

In contrast, modest declines in TP at agricultural streams may be the result of a complex array of agricultural practices, and inherent limitations of PWQMN data. Five of the nine watersheds with 50% agriculture showed significant declines in stream TP concentrations between the 1970s and 2000s. Declines in TP (from 1970s to 2000s) in the agricultural watersheds were generally smaller (average of 42%) compared with the heavily urbanized streams (Mimico: 67%, and Etobicoke: 75%). The relationship between agricultural land-use changes and P concentrations is complex, and a variety of factors could contribute to declines in TP that were observed for the agricultural streams. For example, the transition from pasture to row crops could reduce P losses associated with manure and animal-based soil erosion (Cournane et al., 2011), but could increase tillage-based soil erosion. The decline of conventional tillage at our study sites since the 1990s may reduce sediment loss but could increase overall P losses to surface waters if P fertilizer is not incorporated effectively into the soil layer (Tiessen et al., 2010). Increases in tile drainage across our study watersheds may also reduce P losses through surface runoff, but subsurface P export can account for half of total TP export in some watersheds (King et al., 2015; Macrae et al., 2007). Finally, declines in P fertilizer sales from 1981 to 2010 in Ontario (Smith, 2015) and within-stream TP retention (Jarvie et al., 2012) could also reduce overall TP losses to streams.

Aside from the complex relationships between agricultural land-use change and stream TP concentrations, PWQMN data have a limited ability to detect changes in TP concentrations. Data used in this study are from the growing season only, and storm events are not explicitly targeted in the program (Stammler et al., 2017). As well, the 12 basins considered in this study fall within the jurisdictions of three different Conservation Authorities, and sampling effort to target storm events versus baseflow likely varied both amongst agencies and over time. Total P losses are widely acknowledged to be greatest during the winter and spring as well as during large rain events (Lam et al., 2016); therefore, PWQMN growing season data, with their low sample frequency, cannot offer a complete insight into changes in year-round stream TP concentrations. Furthermore, TP concentrations across all decades in the most urban and agricultural watersheds indicate that mean nongrowing season TP is generally higher than growing season TP concentrations (Figure 2.5). Additionally, this analysis indicated a greater difference in TP concentrations between the non-growing and growing season concentrations in the three most agricultural watersheds compared with the three most urban watersheds (Figure 2.5). This suggests that average annual TP concentrations in agricultural areas may be higher than the growing season data suggest and that there may be an implicit LULC bias in the PWQMN TP record. Comprehensive non-growing season and storm event data would enhance the findings of this study and provide greater insight into the relationships between LULC change and stream TP trends. On-going research is focussed on better discriminating the effects of hydrology relative to land use change on TP export in this region.

2.4.3 Stream nitrate-N

In contrast with TP, patterns in NO_3-N concentrations were much more consistent, and NO_3-N increased significantly for eight of the nine predominantly agricultural streams. Increases in row crop cover and changing land use practices within agricultural watersheds appear to be the most probable cause of these increases. Numerous studies have documented a connection between increases in row crop cover and higher NO_3-N concentrations. A 1982 review found that mean total nitrogen (TN) export in row crop catchments was approximately double the TN export from urban or pasture-dominated catchments (Beaulac and Reckhow, 1982). More recently, an almost 50% decline in row crop area in southern Estonia between 1987 and 1997 resulted in a decrease of TN export from 26 to 5.1 kg ha^{-1} yr^{-1} (Mander et al., 2000). In Missouri, TN export from row crops was almost 7-times higher (29 kg ha^{-1} yr^{-1}) than from pastureland (4.3

kg ha^{-1} yr^{-1}) (Udawatta et al., 2011). In Iowa, the conversion of grasslands to row crops in approximately 10% of a 47 km^2 watershed increased NO_3-N export by 30% (Schilling and Spooner, 2006). Furthermore, Schilling and Libra (2000) found a significant linear correlation between percent row crop cover and mean NO_3-N stream concentrations within agricultural watersheds. While there was no correlation between row crop cover and mean stream NO_3-N concentration in any decade in this study (data not shown), this is likely due to the very low variability in row crop coverage across the study watersheds (see Figure 2.2). A study with a larger sample size and sufficient variation in row crop area would be needed to properly examine the relationship between row crop cover and NO_3-N concentrations in Ontario streams. Like TP, NO_3-N data considered in this study are from the growing season only, and similar to TP, NO_3-N levels were higher in the non-growing compared with growing season (Figure 2.6). However, this pattern in NO_3-N was consistent for both the most urban and most agricultural watersheds. Therefore, while it is possible this analysis of growing season NO_3-N concentrations may underestimate annual mean NO_3-N levels, there is little suggestion of a LULC bias in the PWQMN NO_3-N record. Similarly, while differences in event-based sampling across streams and over time could have a large impact on average TP concentrations, NO_3-N export is generally less hydrologically sensitive (Raney and Eimers, 2014b) and we infer that highly consistent decadal increases in NO_3-N across the most agricultural watersheds are more likely driven by LULC change.

Compared with TP, the mechanisms behind the relationship between row crop cover and NO_3-N concentrations are relatively well understood. Crops, particularly cash crops like corn, require large quantities of N fertilizer, whereas soybeans, which have undergone a meteoric rise in southern Ontario over the last several decades (Smith, 2015), are N-fixing legumes.

Expansions in either crop may be associated with greater NO_3-N export (Schilling and Spooner, 2006). A large amount of cropland is drained in Ontario, and it is well-understood that tile drainage facilitates the movement of NO_3-N below the rooting zone, allowing dissolved NO_3-N to drain from fields and also bypass riparian areas that might retain the nutrient (King et al., 2015; Kinley et al., 2007; Randall et al., 1997; Schilling et al., 2015a). Although it is not possible to quantify fertilizer application practices and tile drainage installation dates accurately, increased rates of N fertilizer application between 1970 and 1990 (Table 2.2) are clearly associated with expansions in row crop area over the same period. We assume that tile drainage installation has been proportional to increases in row crop area but note that research on the prevalence of tile drainage and its contribution to NO_3-N export in Ontario is lacking. Furthermore, there may be a potential lag-time, or legacy effect, between changes in fertilizer input and stream nutrient chemistry.

2.5 Conclusions

Although previous studies have reported declines in stream TP and increases in NO_3-N in this region (Eimers and Watmough, 2016; Raney and Eimers, 2014a; Stammler et al., 2017), the two nutrients have never previously been considered together, and the role of LULC change has not been explicitly considered. This study found that increases in row crop agriculture co-occurred with regional nutrient trends, on a watershed scale. Although decreases in TP appear to be widespread, they are stronger in urban watersheds than agricultural watersheds. Declines in TP in urban streams may be related to improved stormwater (and sediment) management in new urban developments. TP declines in agricultural watersheds are likely to be multifaceted, and the general low frequency, non-hydrologically focussed nature of the PWQM network may be ill equipped to offer much insight into the drivers of TP change. By comparison, the lower hydrologic sensitivity of NO_3-N losses compared with TP suggest that PWQMN data can provide insight into the drivers of rising NO_3-N. The greatest concentrations and most consistent increases in NO_3-N occurred within the most agricultural watersheds. These watersheds also experienced increases in the area of row crop cover, although increases in the proportion of row crop cover within agricultural areas were noted across all 12 watersheds. Although there was no explicit correlation between row crop cover and NO_3-N concentrations, a pervasive co-occurrence of increasing row crop cover and NO_3-N concentrations as well as examples from previous research suggest that the two are likely related. Research examining the mechanisms behind this relationship, especially the role of tile drainage in Ontario, is currently lacking. Agricultural land-use in Lake Ontario watersheds is dynamic, and there is significant scope for further increases in row crop area along the northern Lake Ontario shoreline if demand for cash crops like corn and soybean remains strong. Therefore, understanding the effects of further row crop growth on nutrient losses, as well as possible mitigation strategies, is important for the protection of surface and ground water quality in the Lake Ontario basin.

Chapter 3 - The effect of agricultural land use on nitrogen and phosphorus export in twelve small catchments along the north shore of Lake Ontario

3.1 Introduction

Nutrient enrichment of freshwater and estuarine ecosystems is a global water quality issue that threatens both ecosystem and human health. For decades, anthropogenic manipulation of the nitrogen (N) and phosphorus (P) cycles has increased the availability of N compounds in the atmosphere and hydrosphere, while P enrichment has caused eutrophication of freshwater systems that are normally P-limited (Schindler et al., 2006). Increases of NO_3-N can lead to lake acidification in base-poor watersheds (Schindler et al., 2006; Sullivan et al., 1997), or eutrophication of N-limited marine (Azevedo et al., 2015; Conley et al., 2009; Lewis and Wurtsbaugh, 2008) and freshwater systems (Watson et al., 2016). Elevated NO_3-N concentrations in drinking water can also pose a threat to human (Wolfe and Patz, 2002) and aquatic life (Camargo et al., 2005). High NO_3-N concentrations in freshwater streams have prompted concerns over water quality amongst public and scientific communities in Canada (CCME, 2016), New Zealand (Larned et al., 2016), Europe (Gustafsson et al., 2012; Karydis and Kitsiou, 2012; Yevenes and Mannaerts, 2011) and the United States (Beckert et al., 2011; Jones et al., 2018b; Schilling and Wolter, 2009). The European Union recently established directives that aim to control NO_3-N concentrations throughout the continent (De Girolamo et al., 2017).

While NO_3-N enrichment of freshwaters is considered a recent problem, excessive P levels have long been a water quality issue, and the Laurentian Great Lakes area of North America is a notable example. Excessive P loading led to the eutrophication of Lake Erie in the 1960s and expansions of nuisance macroalgae in Lake Ontario, prompting bi-national efforts to reduce point-source P loading (Dove and Chapra, 2015; Han et al., 2012). These efforts were largely successful, and total P (TP) levels declined by approximately 70% in Lake Ontario since 1970 (Dove, 2009), such that non-point sources are now the primary source of P delivery to the lakes (Dolan and Chapra, 2012; Han et al., 2012). While TP levels in the lower Great Lakes have declined over the past four decades, the fraction of P that is soluble and reactive (SRP) appears to have increased in Lake Erie and its major tributaries (e.g. Maumee, Sandusky), and these increases are speculated to be the cause of continued algal blooms in Lake Erie (Baker, 2010).

Over the same period of P decline, NO_3-N concentrations in offshore Lake Ontario increased by approximately 60% between 1970 and 2010, for reasons largely unexplained (Dove and Chapra, 2015). Like P, non-point sources of N are currently estimated to account for the majority of N loading to Lake Ontario, almost all of which is delivered via tributaries (Robertson and Saad, 2011). Recent observations suggest that concentrations of NO_3-N in tributaries draining into the north shore of Lake Ontario increased steadily over the same period that lake NO_3-N levels increased (DeBues et al., 2019; Eimers and Watmough, 2016). Increases in NO_3-N levels were highest and most consistent in farming-dominated watersheds, where agricultural land use has shifted from pasture/mixed livestock farming to intensive row crop farming over the last several decades (DeBues et al., 2019; Smith, 2015).

While there is evidence for a relationship between agricultural land use and stream nutrient concentrations in other agricultural regions, the relationship in Ontario remains largely unexplored. High NO_3-N river export in Italy (De Girolamo et al., 2017), and the United States (Beckert et al., 2011; Jordan et al., 1997; Schilling and Spooner, 2006) has been linked to the area of a watershed’s crop cover and agricultural land use/land cover (LULC) change. Nitrogen losses from crop-based agricultural regions, like the US ‘Corn Belt’ in Iowa, are much higher than N losses from pasture-based agriculture (Abell et al., 2011; Arbuckle and Downing, 2001; Ballantine and Davies-Colley, 2014) and natural systems (Schilling and Spooner, 2006; Udawatta et al., 2011). High NO_3-N losses from crop-based agriculture are facilitated by subsurface tile drainage that transports NO_3-N from below the rooting zone into nearby surface waters (Arenas Amado et al., 2017; King et al., 2015; Ruffatti et al., 2019).

Drivers of SRP increases in Lake Erie and its tributaries are under debate but are speculated to be a result of increases in no-till agriculture within the Corn Belt that dominates much of the American portion of the Lake Erie basin (Baker et al., 2014; Michalak et al., 2013). No-till and reduced tillage are best management practices that preserve organic matter in soils and improve overall soil health (Verbree et al., 2010) but may prevent the binding of P to soil organic matter, thereby increasing P losses triggered by rain and snow-melt events resulting in overland or near-surface flow (Tiessen et al., 2010; Verbree et al., 2010). These tillage practices may also exacerbate dissolved P losses if soil macropores or drainage systems allow surface applied fertilizer to by-pass the soil matrix (King et al., 2015; Macrae et al., 2019, 2007). Overall, these studies suggest substantial uncertainty over the effect of long-term agricultural shifts on nutrient delivery to surface waters in the Great Lakes basin.

In Ontario, much of the research on LULC change and water quality has focused on the highly agricultural Lake Erie basin (Bast et al., 2009; Joosse and Baker, 2011; van Bochove et al., 2011), leaving the historically less intense agricultural region along the north shore of Lake Ontario less studied. Furthermore, observations of rising NO_3-N (DeBues et al., 2019; Eimers and Watmough, 2016) and declining TP concentrations (Raney and Eimers, 2014a; Stammler et al., 2017) in tributaries draining the northern Lake Ontario watershed remain unexplained. An exploration of the relationship between LULC and water quality in Lake Ontario tributaries may shed light on drivers of nutrient shifts across the broader region. The results of Chapter 2 were limited by a lack of year-round and event-based sampling, potentially underestimating mean annual TP and NO_3-N concentrations. The results presented in Chapter 2 were also muddied by an insufficient variation in agricultural land cover types to fully examine the relationship between land cover and nutrient concentrations; a space-for-time approach would help to address the inadequacies of Chapter 2 while potentially reinforcing the findings. The objective of this study was to examine the effect of agricultural land use on stream NO_3-N and P concentrations and export at twelve small (< 10 km^2) catchments along the north shore of Lake Ontario where shifts in agriculture from pasture and mixed farming to intensive row-crop systems have been observed over the past four decades (see Chapter 2; DeBues et al., 2019). These smaller catchments enabled the isolation of specific agricultural land cover types. Water was sampled from streams draining rural catchments dominated by row crop, pasture, or forest cover over twelve months and across high- and low-flow conditions. It was hypothesized that NO_3-N concentrations and export would be greatest at catchments dominated by row-crops whereas TP concentrations were expected to be higher at sites with more pastureland.

3.2 Methods

3.2.1 Site description

Twelve small catchments (between 0.04 and 7.30 km^2), located between Bowmanville and Port Hope, Ontario, approximately 80 km east of Toronto (Figure 3.1; Table 3.1), were chosen for this study. Of these twelve catchments, ten are located within several of the larger quaternary watersheds that were considered in Chapter 2, including Soper (C01, C10, P02), Wilmot (P01, P04, N05), Graham (P12, C09) and Ganaraska (P08, N02). The two remaining catchments (C05, C06) are situated outside of a quaternary watershed, south of the Ganaraska River (Appendix A1). Water in the region flows from the Oak Ridges Moraine (ORM) in the north into Lake Ontario in the south. Soil throughout the ORM is composed of mostly sand and sandy loam, while bands of finer textured soil occur south below the glacial Lake Iroquois shoreline (Webber et al., 1946). Drainage is generally related to antecedent moisture conditions, soil texture, and slope. Soils in the study region are generally coarse-textured and well-drained along the steeper edge of the moraine while soils become progressively less well-drained toward the lakeshore where finer textured soils are more common and the landscape is less sloping (Webber et al., 1946). Agriculture is the dominant land use throughout the study region, accounting for 60-66 % of the land cover in Soper Brook, Graham Creek, and Wilmot Creek watersheds, and 51 % in the Ganaraska River Watershed (see Chapter 2; DeBues et al., 2019). The headwaters and valleys of the Ganaraska are largely protected from development with 44 % of the watershed covered by forest and wetlands (see Chapter 2; DeBues et al., 2019). Within the study region, small urban centres are situated mainly along the Lake Ontario shoreline (Fig. 1).

Climate across the study region is humid continental (Koppen Dfb), with four distinct seasons, hereafter defined as summer (June-August), fall (September-November), winter (December-February) and spring (March – May). Climate data for the study region were taken from the nearest Environment and Climate Change Canada weather monitoring station in Oshawa (43°55'22 N, 78°53'00 W), 15 km west of Bowmanville. Long-term (1981-2011), daily average temperature ranges from a low of -4.8 °C (January) to 20.6 °C (July), with a mean precipitation of 872 mm per year, of which 12% is snow, and an approximately even distribution of total precipitation across seasons (summer 25 %, fall 29 %, winter 22 %, spring 24 %).

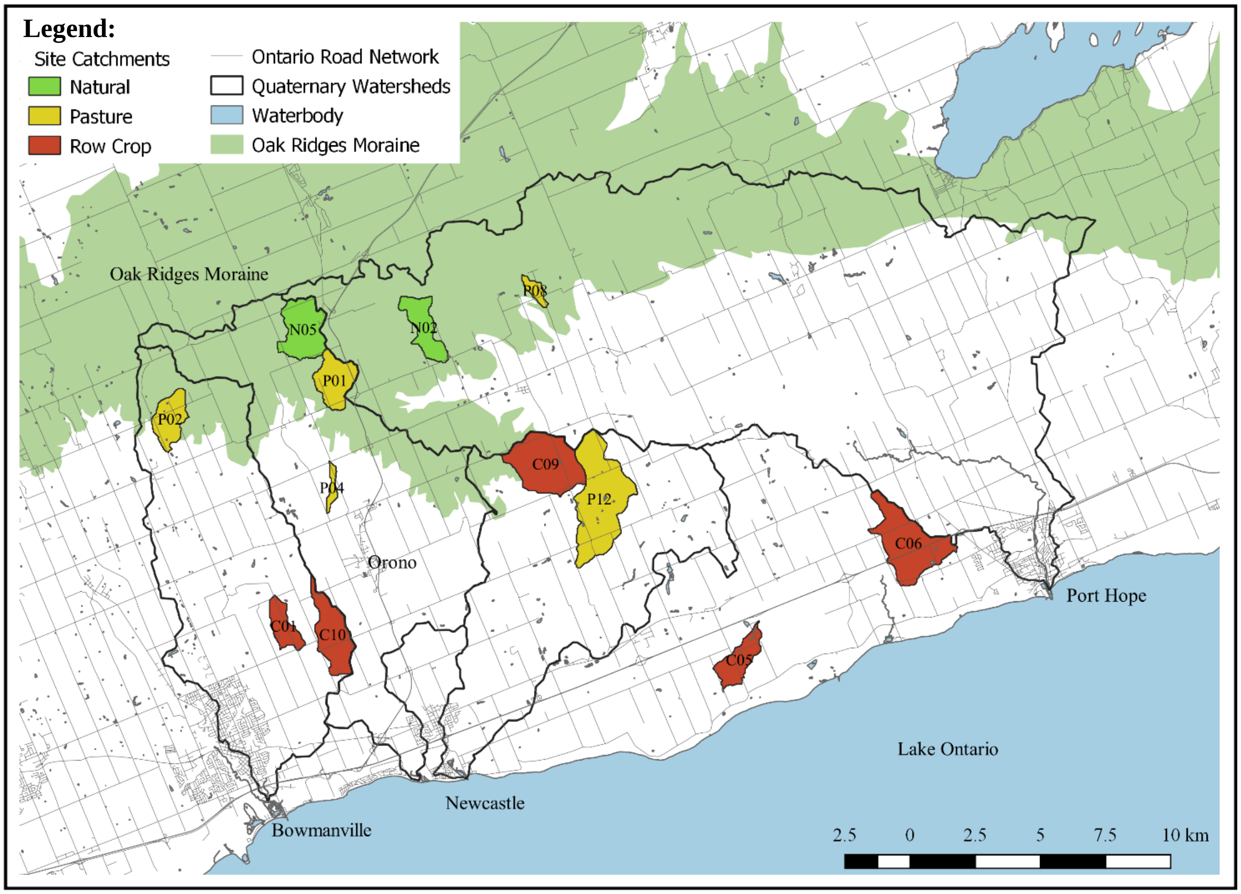

Figure 3.1 Study Area indicating the location and type of the sample sites and displaying land cover data from Agriculture and Agri-Food Canada (AAFC) 2016 annual crop inventory. Quaternary watersheds from left to right: Soper Brook, Wilmot Creek, Graham Creek, Ganaraska River.

3.2.2 Land cover data

Annual crop inventories (2014 to 2016; AAFC) and remotely sensed estimates of agricultural cover produced by AAFC (Fisette et al., 2013) were compared to examine crop rotation and changing agricultural land use immediately prior to the start of the study in June 2016. The self-reported accuracies of these layers range from 87.9% to 89.6% and the resolution of the layer is 30 m (AAFC, 2019). Observed errors in the annual crop inventories were corrected; for example, there were several instances in the 2014 crop inventory where wheat fields were misidentified as shrubland. These misidentifications could be confirmed using aerial imagery. Land cover was then calculated at every catchment (% of total catchment area, and % of agricultural area) for each of the three years. Land cover was classified into three main categories: row crops (predominantly corn, soybean, winter wheat), pasture (grazing and hay fields), and forest (predominantly forest, but included small areas of other ‘natural’ cover, i.e., wetlands).

3.2.3 Sampling sites

Sampling sites were selected to cover an agricultural land use gradient that included row crop, pasture, and forested sites. Candidate sites were identified using satellite imagery and annual crop inventories from AAFC. Preliminary site visits revealed that flow in most first-order streams was intermittent, and thus all study sites were selected to be least second-order streams. The number of selected sampling sites was a compromise between statistical replication and sampling effort; it was important that all sites could be sampled in a relatively brief period (four to six hours by car) to maintain consistency in flow conditions during a sampling campaign.

Sites with more than 50% row crop cover (as a percentage of agricultural area) were subsequently classified as ‘Row Crop’ (C01, C05, C06, C09, C10), whereas sites classified as ‘Pasture’ (P01, P02, P04, P08) or ‘Forest’ (N02, N05) had at least 50% pasture or forest landcover, respectively (Table 3.1). All row crop and pasture sites were agriculture-dominated catchments with 49% or more land cover dedicated to agriculture. Previous years’ (2014 to 2016) agricultural land cover in each catchment, obtained from AAFC annual crop inventories, can be found in the appendix (A2).

Table 3.1 Characteristics of study site catchments. Site ID corresponds to location in Figure 3.1. Land cover obtained from the 2016 annual crop inventory prepared by Agriculture and Agri-Food Canada (AAFC). Individual land cover percentages are with respect to total watershed area, while crop cover percentages are with respect to total crop area (sum of row crop and pasture). Natural land cover includes types of forest, wetland, and grassland. * Located entirely on ORM. † Located partly on ORM.

				Percentage of watershed area				Percentage of crop area			
	Site	Slope (%)	Area (km^2)	Natural (%)	Urban (%)	Pasture or Grass (%)	Crops (%)	Wheat (%)	Corn (%)	Soybean (%)	Other (%)
Row Crop	C01	2.2	1.5	28	5	16	52	0	35	65	0
	C05	3.1	2.0	27	5	18	50	17	50	18	15
	C06	3.0	5.3	16	5	23	56	10	38	52	0
	C09†	6.4	5.2	28	3	27	42	39	19	42	0
	C10	1.7	3.2	5	3	12	80	1	85	14	0
Forest	N02*	9.6	2.2	96	1	3	0	*No Crops*			
	N05*	6.5	3.3	86	3	8	4	0	80	5	15
Pasture	P01*	7.1	2.4	33	3	51	12	24	18	58	0
	P02†	6.6	2.1	33	5	50	12	6	70	18	6
	P04	3.1	0.51	4	8	64	25	15	74	11	0
	P08*	6.4	0.52	29	7	65	0	*No Crops*			
	P12	3.2	7.3	49	3	28	21	18	31	51	0

3.2.4 Sample collection and analysis

Sampling occurred across a full hydrologic year (June 1, 2016, to May 31, 2017) approximately monthly, with additional sampling during rain or anticipated high-flow (e.g., spring melt) events (n = 20). High-flow events are important as the greatest nutrient (particularly P) export occurs during storms and winter thaws (Kinley et al., 2007). Sampling frequency was restricted by weather and ice conditions during the winter (actual sampling frequency varied from 9 to 20 samples across sites). Anticipated high-flow events were sampled in all four seasons and were selected based on local weather forecasts (i.e., events anticipated to affect all sites based on local weather station reports), as well as subjective assessments of antecedent moisture conditions. As the categorization of stream flow was subjective, the effect of flow on nutrient concentration and export was not investigated in this study, but the attempted inclusion of both low- and high-flow conditions guarded against bias toward low- or high-flow sampling.

Stream velocity was measured at each site visit using a Marsh-McBirney flow meter, and instantaneous discharge was calculated using standard stream gauging methods. As the 12 catchments were not continuously gauged, instantaneous discharge from every catchment was correlated with instantaneous discharge at a nearby Water Survey of Canada (WSC) discharge monitoring station (Mackie Creek 02HD023; 14.7 km^2), which allowed daily stream discharge at each study catchment to be estimated by proration, assuming hydrologic responses were similar across catchments (Appendix A3). Mackie Creek is also a tributary of Soper Brook and drains site P02.

Water sampling was performed using grab samples, including both unfiltered and filtered (*in situ*; 0.45 µm) water samples (CCME, 2011). Conductivity, pH, and temperature were measured *in situ* using a handheld Oakton multimeter. Samples were transported to the laboratory in chilled containers for subsequent chemical analysis. Analytical methods followed those developed by the Ontario Ministry of the Environment, Conservation, and Parks (1983), although *in situ* coarse filtering of water samples did not occur and was potentially a source of error in water quality measurements. Filtered water samples were analyzed for NO_3-N whereas unfiltered samples were used to analyse total nitrogen (TN) and total P (TP). Nitrate-N and chloride (Cl^-) were determined by ion chromatography using a Dionex Ion Chromatograph. Total N, total organic carbon (TOC) and total inorganic carbon (TIC) were analyzed using gas-phase chemiluminescence of ozone and nitrogen monoxide (TOC 5000A, Shimadzu Corp, Tokyo, Japan). Water samples that were analyzed for TP were digested following a colourimetry method which included a persulphate autoclave procedure (U.S. Environmental Protection Agency, 1978). Nitrate-N and TN data were used to calculate the ratio of NO_3-N to TN for each sampling point. Supplementary stream chemistry parameters (Conductivity, pH, temperature, TOC, TIC, and Cl^-) were obtained to ensure catchment geochemistry and stream hydrology were otherwise comparable.

3.2.5 Data analysis

Annual and seasonal chemical exports were calculated for each of the 12 catchments using an interpolation method referred to as the ‘mid-point method’ (J. G. Kerr et al., 2016). This method has been widely used to estimate constituent loads and/or flow weighted mean concentrations in central Ontario streams (e.g. Casson et al., 2010; Kerr and Eimers, 2012) and is similar to the ‘period-weighted method’ used elsewhere (Dann et al., 1986; Likens, 2013). Preliminary tests were used to compare annual nutrient loads calculated using the mid-point method with seven load estimates (time-weighted flow [Q] and concentration [C], discharge-weighted C, mean discharge-weighted C, time-weighted C, time and discharge weighted, Linear interpolation of C, and the Beale Ratio estimation) using the RiverLoad R software package (Nava et al., 2019) and an estimate produced from the USGS LOADEST software (Runkel et al., 2004). These preliminary tests found no significant difference between the mid-point estimates and these other load estimates (Appendix A4 and A5); thus, only mid-point values were reported here as they can allow seasonal comparisons of load estimates among sites. Annual and seasonal volume-weighted mean concentrations were calculated by dividing the total chemical load by the total volume of flow over the same period.

Statistical analysis of nutrient concentrations was performed using R statistical software (R Core Team, 2018). Data were organized, analyzed, and graphed using base R software, ‘tidyverse’ (Wickham, 2017) and ‘ggrepel’ packages (Slowikowski, 2018). Volume-weighted means were transformed to meet the assumptions of parametric data. Differences in nutrient concentrations among land use types and seasons were analyzed using a linear mixed-model ANOVA with repeated measures and Tukey HSD post-hoc tests performed using ‘lme4’ (Bates et al., 2015), ‘car’ (Fox and Weisberg, 2018), and ‘multcomp’ (Hothorn et al., 2008) packages. Scatter plots were used to explore relationships between land use categories and volume-weighted nutrient concentrations, and linear regression tests were performed when parametric data assumptions were met.

3.3 Results

3.3.1 Hydroclimatic conditions

Conditions in the year of study (2016-2017) were vastly different from long-term means for the region (Table 3.2). Except for March and May, every month was warmer than the long-term average (0.5 °C [Dec] to 4 °C [Jan]), whereas precipitation was 27% lower during the first half of the study period. Between June and November, the region was in a state of severe drought (Agriculture and Agri-food Canada; AAFC Drought Monitor: http://www.agr.gc.ca/drought), which was punctuated by large rainfalls in July and August. In July, 70 % of the total rain fell in two events (17 and 25 mm), while 71 % of August’s rain fell in three events (28, 20 and 14 mm; Oshawa climate station; ID: 6155878), two of which (in August) were sampled (Figure 3.2). In contrast, the last six months (December – May) saw widespread flooding due to a 43% increase in rainfall and 26% decrease in snowfall over long-term means (Table 3.2). This limited snow accumulation and contributed to a wetting of the watersheds prior to spring.

As a result, stream discharge was extremely low during the summer and fall (i.e., Jun: -36%) and relatively high during the winter/spring (i.e., May: +105.9%) when several high-flow periods were sampled (Figure 3.2 and Table 3.3). Sampling attempts revealed that two streams (P04 & P08) dried up entirely (Jul-Jan & Jul-Sep respectively), while one stream (C05) had no measurable discharge during August field visits and two others (C01 & C06) experienced such a reduction in flow that stream flow was almost imperceptible during August and September. In contrast, spring and winter flows accounted for 71% of the total annual water discharge over the hydrologic year at Mackie Creek with discharge peaking on May 5th. Although runoff at Mackie Creek was highest in April and May (76 and 104 mm, respectively), mean January runoff (57 mm) was greater than either February (53 mm) or March (54 mm). The difference in summer/fall and winter/spring flows at sites more distant from the ORM might have been even greater due to a potentially reduced groundwater contribution. Higher than normal rainfall during the winter and spring resulted in record flooding and high-water levels throughout the study region (Carter and Steinschneider, 2018). Instantaneous discharge measurements from each site across the study period can be found in Appendix 11.

Table 3.2 Comparison of climate normals from 1981-2011 and weather during 2016-2017 at the Oshawa WPCP Environment and Climate Change Canada weather monitoring station (ID: 6155878).

	Daily Average Temperature (°C)		Total Precipitation (mm)		Rainfall (mm)		Snowfall (cm)	
Month	1981-2011	2016-2017	1981-2011	2016-2017	1981-2011	2016-2017	1981-2011	2016-2017
Jun	17.6	18.5	73.9	31.2	73.9	31.2	0	0
Jul	20.6	22.1	73.1	74.0	73.1	74.0	0	0
Aug	20.0	23.0	77.4	86.4	77.4	86.4	0	0
Sep	15.9	18.4	94.0	57.5	94.0	57.5	0	0
Oct	9.5	11.8	70.1	49.4	70.0	49.4	0.1	0
Nov	4.2	6.3	84.8	45.0	80.0	45.0	4.7	0
Dec	-1.2	-0.7	70.7	66.4	45.8	33.4	24.9	33.0
Jan	-4.8	-0.8	65.6	99.2	30.0	93.2	35.6	6.0
Feb	-3.6	-0.1	56.6	68.2	31.7	33.2	24.9	35.0
Mar	0.4	-0.1	54.2	55.7	40.7	54.7	13.5	1
Apr	6.6	8.8	72.7	113	70.6	113	2	0
May	12.3	11.7	78.9	167.1	78.9	167.1	0	0

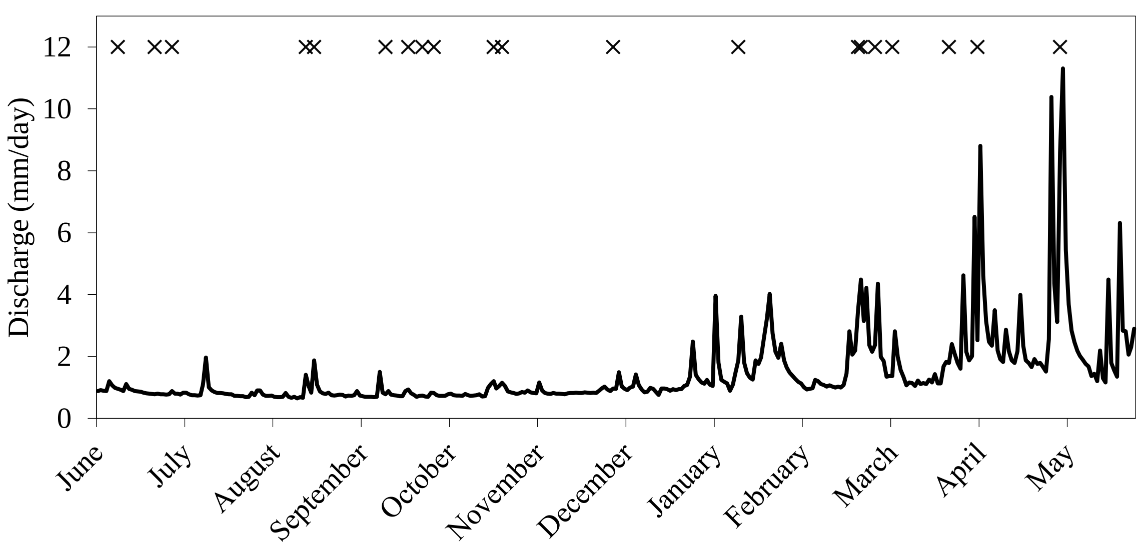

Figure 3.2 Daily discharge from Mackie Creek (WSC station 02HD023; 14.7 km^2) between June 2016 and May 2017. Dates of stream water sampling are indicated with an ‘x’.

Table 3.3 Comparison of monthly mean discharge (mm/day) (2006 to 2020) and monthly mean discharge from May 2016 to April 2017 at Mackie Creek (WSC station 02HD023).

	Monthly Mean Discharge (m^3/s)		
Month	2006-2020	2016-2017	% Dif.
Jun	41.4	26.4	-36.2%
Jul	35.5	25.9	-27.2%
Aug	32.8	25.5	-22.2%
Sep	30.0	23.5	-21.8%
Oct	36.3	26.2	-27.6%
Nov	39.7	25.7	-35.1%
Dec	48.1	33.5	-30.3%
Jan	54.1	59.0	9.1%
Feb	44.6	49.2	10.3%
Mar	78.2	56.1	-28.2%
Apr	84.6	76.3	-9.8%
May	52.1	107	105.9%

3.3.2 Stream nutrient concentrations

Total inorganic carbon and pH were similar across all sites, evidence of relatively uniform carbonate rich geology (Table 3.4). Stream N and P concentrations at sites of the same land use category were similar with a few exceptions (Table 3.4). Volume-weighted NO_3-N concentrations at site C10 were higher (17.0 mg/L) than any of the other row crop sites, which ranged between 1.47 mg/L (C09) and 5.65 mg/L (C01). While TN followed a similar pattern (C10; 14.2 mg/L), ratios of NO_3-N/TN were more consistent. On average, close to 100% of the TN was inorganic NO_3-N at row crop catchments (mean = 0.96) whereas the proportion was closer to 50% at pasture (0.53) and forested catchments (0.51). Notably, analysis found greater (although implausible) concentrations of NO_3-N than TN at site C10. Lastly, there was also variation in TP amongst sites within the pasture-dominated land use category, with site P04 routinely experiencing extremely high TP concentrations (Table 3.5), particularly during the spring (observable in Figure 3.4).

Differences in nutrient concentrations amongst land use categories were partially consistent with the study's hypotheses (Table 3.5). Nitrate-N concentrations differed considerably between the three categories ($F_{(3,2,6)} = 11.48$, $p = .0033$) and were significantly higher at row crop sites (mean of 6.3 mg/L) than either pasture (0.63 mg/L; $p < .0001$) or forested catchments (0.32 mg/L; $p = .0193$). In contrast, TP concentrations tended to be higher at row crop and pasture sites compared with streams dominated by forest cover, although these patterns in TP concentrations were not statistically significant ($F_{(3,2,6)} = 1.23$, $p = .3370$).

Table 3.4 Summary of stream chemistry at each study site. Nutrient values are volume-weighted means from across the entire twelve-month sampling period, while *in-situ* pH and cond. (conductivity) are arithmetic means. Temperature ranges can be found in Appendix A6.

	Site ID	*n*	TN (mg/L)	NO_3-N (mg/L)	NO_3-N/TN ratio	TP (µg/L)	TOC (mg/L)	TIC (mg/L)	Cl^- (mg/L)	pH	Cond. (µS/cm)
Row Crop	C01	20	5.92	5.65	0.95	181	8.42	41.25	31.4	8.14	544
	C05	13	4.67	3.76	0.81	114	12.6	37.69	33.1	7.95	560
	C06	20	3.76	3.49	0.93	170	7.91	41.81	147	8.15	889
	C09	20	1.69	1.47	0.87	205	6.89	41.03	26.7	8.32	486
	C10	20	14.2	17.3	1.22	145	7.01	45.37	48.0	8.08	702
Forest	N02	20	0.26	0.08	0.29	63.3	5.50	37.07	19.0	8.14	372
	N05	19	0.78	0.57	0.73	105	7.19	34.72	33.4	8.26	444
Pasture	P01	20	0.72	0.52	0.73	81.5	6.37	47.34	106	8.27	754
	P02	20	0.80	0.56	0.69	219	8.12	44.58	17.6	8.35	466
	P04	9	3.30	1.53	0.46	892	27.1	49.37	21.1	8.09	570
	P08	17	0.62	0.12	0.19	113	7.44	47.86	40.1	8.23	592
	P12	20	0.79	0.44	0.56	107	8.87	36.13	43.9	8.21	515

Mean NO_3-N and TP concentrations remained largely consistent across the seasons. The exception to this was at row crop sites where NO_3-N concentrations were significantly greater during the winter than during the summer or autumn (Table 3.5 and Figure 3.3). Nitrate-N concentrations were more consistent across seasons at forested and pasture-dominated catchments. Overall, differences in NO_3-N were greater across land use types than between seasons (Figure 3.3). In addition, concentrations of NO_3-N at row crop sites regularly surpassed 10 mg/L, the maximum acceptable concentration for NO_3-N in drinking water (Ontario Ministry of the Environment, 2003) and consistently exceeded 3 mg/L (57% of samples), which is the freshwater guideline for protection of aquatic life (CCME, 2012). Site C10 was responsible for all samples that exceeded the drinking water guidelines and recorded a minimum NO_3-N concentration of 11.3 mg/L. Total P was generally higher during the non-growing season compared with the summer and fall; however, inter-season differences were not significant (Table 3.5 and Figure 3.4). While there was no clear pattern in TP concentrations, stream conditions were regularly eutrophic at all sites with TP concentrations regularly surpassing 100 μg/L and consistently exceeding 30 μg/L, the provincial water quality objective (Ontario Ministry of the Environment, 1994).

Table 3.5 Volume-weighted TP and NO_3-N concentrations (µg/L) and export (kg ha^{-1} $season^{-1}$) by season and across land uses. Letters above mean concentrations denote significant (p <.05) differences between seasons.

		Total Phosphorus								Nitrate - N							
		Concentration (µg/L)				Export (kg ha^{-1} $season^{-1}$)				Concentration (mg/L)				Export (kg ha^{-1} $season^{-1}$)			
	Site	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring
Row Crop	C01	189	252	123	191	0.146	0.190	0.174	0.442	2.42	2.09	7.06	7.03	1.86	1.58	9.96	16.3
	C05	65.2	121	63.8	160	0.0502	0.0915	0.0900	0.370	4.28	4.83	4.36	2.89	3.29	3.65	6.15	6.67
	C06	188	182	205	141	0.145	0.138	0.289	0.325	2.84	2.52	5.44	2.85	2.19	1.90	7.67	6.58
	C09	78.8	90.0	341	204	0.0606	0.0679	0.481	0.472	1.11	0.94	2.35	1.23	0.853	0.709	3.33	2.83
	C10	89.9	90.0	167	169	0.0692	0.0680	0.235	0.391	12.6	17.1	22.2	15.9	9.72	12.9	31.4	36.8
	Mean	*122*	*147*	*180*	*173*	*0.0941*	*0.111*	*0.254*	*0.400*	*4.65*^{a}	*5.50*^{a}	*8.29*^{b}	*5.99*^{ab}	*3.58*	*4.15*	*11.7*	*13.84*
Forest	N02	123	37.5	76.7	43.7	0.0947	0.0283	0.108	0.101	0.164	0.0519	0.0396	0.0761	0.127	0.0392	0.0559	0.176
	N05	91.3	61.1	122	114	0.0702	0.0461	0.173	0.264	0.643	0.835	0.577	0.454	0.495	0.631	0.814	1.05
	Mean	*107*	*49.3*	*99.5*	*79.0*	*0.0825*	*0.0372*	*0.140*	*0.183*	*0.404*	*0.444*	*0.308*	*0.265*	*0.311*	*0.335*	*0.435*	*0.614*
Pasture	P01	104	69.7	86.6	74.8	0.0800	0.0525	0.122	0.173	0.652	0.708	0.482	0.441	0.502	0.534	0.679	1.02
	P02	247	87.2	346	178	0.190	0.0658	0.488	0.412	0.241	0.0721	0.865	0.635	0.185	0.054	1.22	1.47
	P04	634	634	674	1192	0.0405	0.0397	0.0788	0.228	0.251	0.625	0.768	2.70	0.0160	0.0391	0.0899	0.517
	P08	151	164	144	66.1	0.116	0.123	0.203	0.153	0.151	0.0832	0.0861	0.139	0.116	0.0629	0.122	0.322
	P12	103	89.2	137	97.5	0.0792	0.0673	0.193	0.225	0.456	0.283	0.598	0.384	0.351	0.214	0.844	0.887
	Mean	*248*	*209*	*278*	*321*	*0.101*	*0.0698*	*0.217*	*0.283*	*0.350*	*0.354*	*0.560*	*0.860*	*0.234*	*0.181*	*0.591*	*0.843*

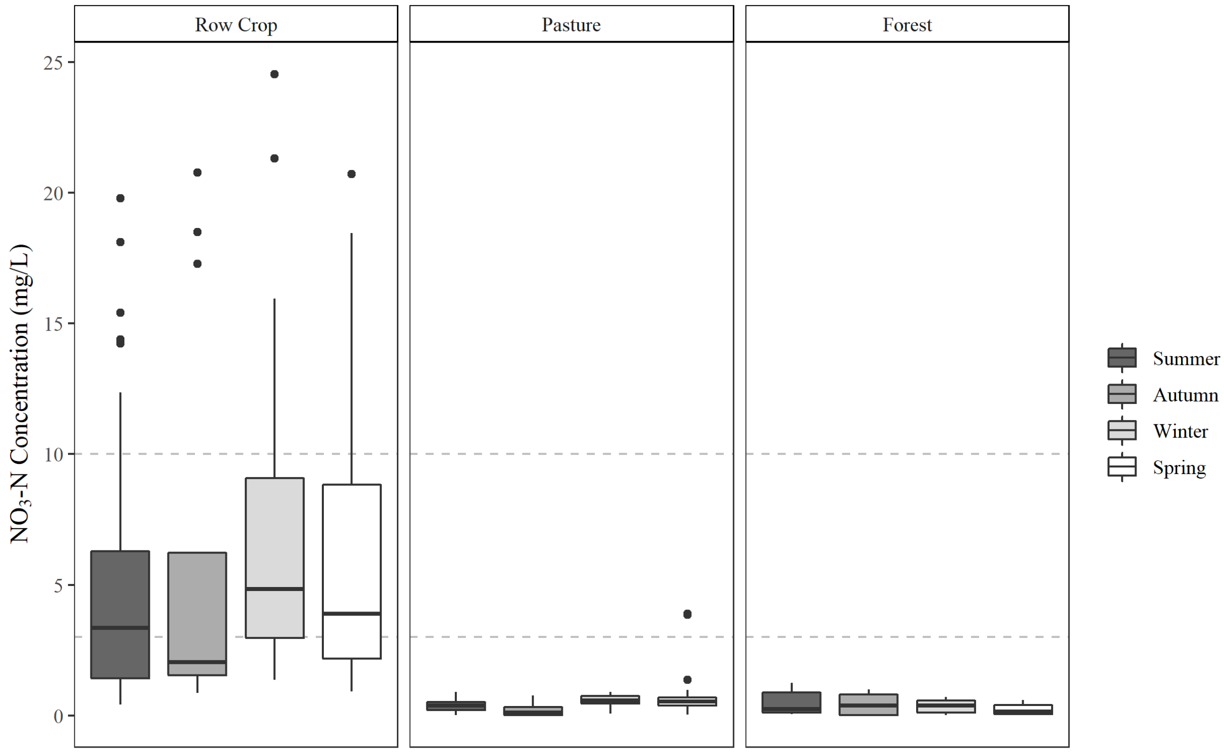

Figure 3.3 Box-whisker plots of NO_3-N concentrations (mg/L) by season and across land uses. The ends of the box are the first and third quartiles and the median is indicated by the horizontal line. Whiskers indicate 1.5 x IQR, and outliers are shown as dots. Upper dashed line indicates the maximum acceptable concentration for NO_3-N in drinking water (10 mg/L) and the lower dashed line indicates the freshwater guideline for the protection of aquatic life (3 mg/L).

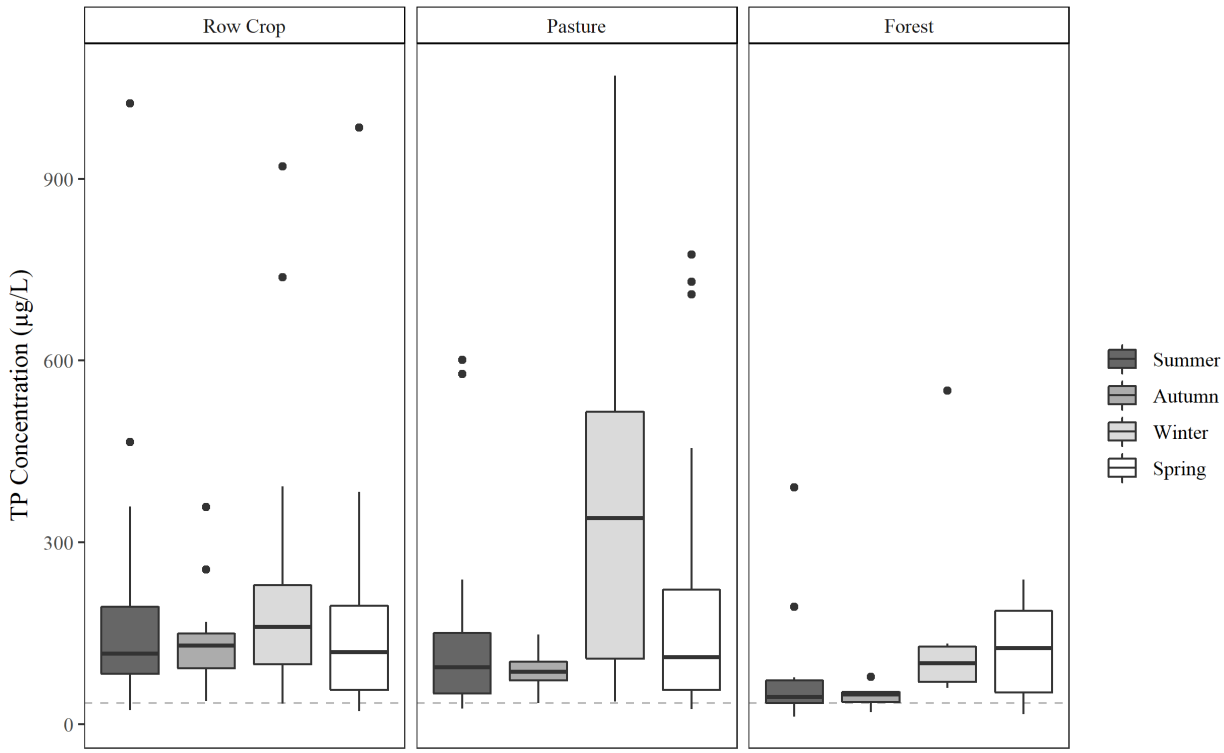

Figure 3.4 Box-whisker plots of TP concentrations (µg/L) by season and across land uses. Dashed line indicates the provincial water quality objective for TP (30 µg/L)(Ontario Ministry of the Environment, 1994).

The relationship between percent row crop cover and volume-weighted mean NO_3-N concentrations was positive but non-linear (Figure 3.5a). Catchments with higher row crop cover had greater NO_3-N concentrations than catchments with little row crop cover. However, C10, a site with more than 75% row crop cover, had much higher NO_3-N concentrations than any of the other row crop catchments (> 15 mg/L). The relationship between row crop cover and NO_3-N was linear when percent corn cover was considered alone (R^2 = .94, $p < .001$; Figure 3.5b). Corn accounted for between 0 and 60 % of total crop cover in 2016 at the 12 sites. In contrast, there was no relationship between pasture cover and TP concentrations; annual volume-weighted TP concentrations were between 60 and 220 µg/L at all sites apart from P04, which was far higher (890 µg/L; Figure 3.6).

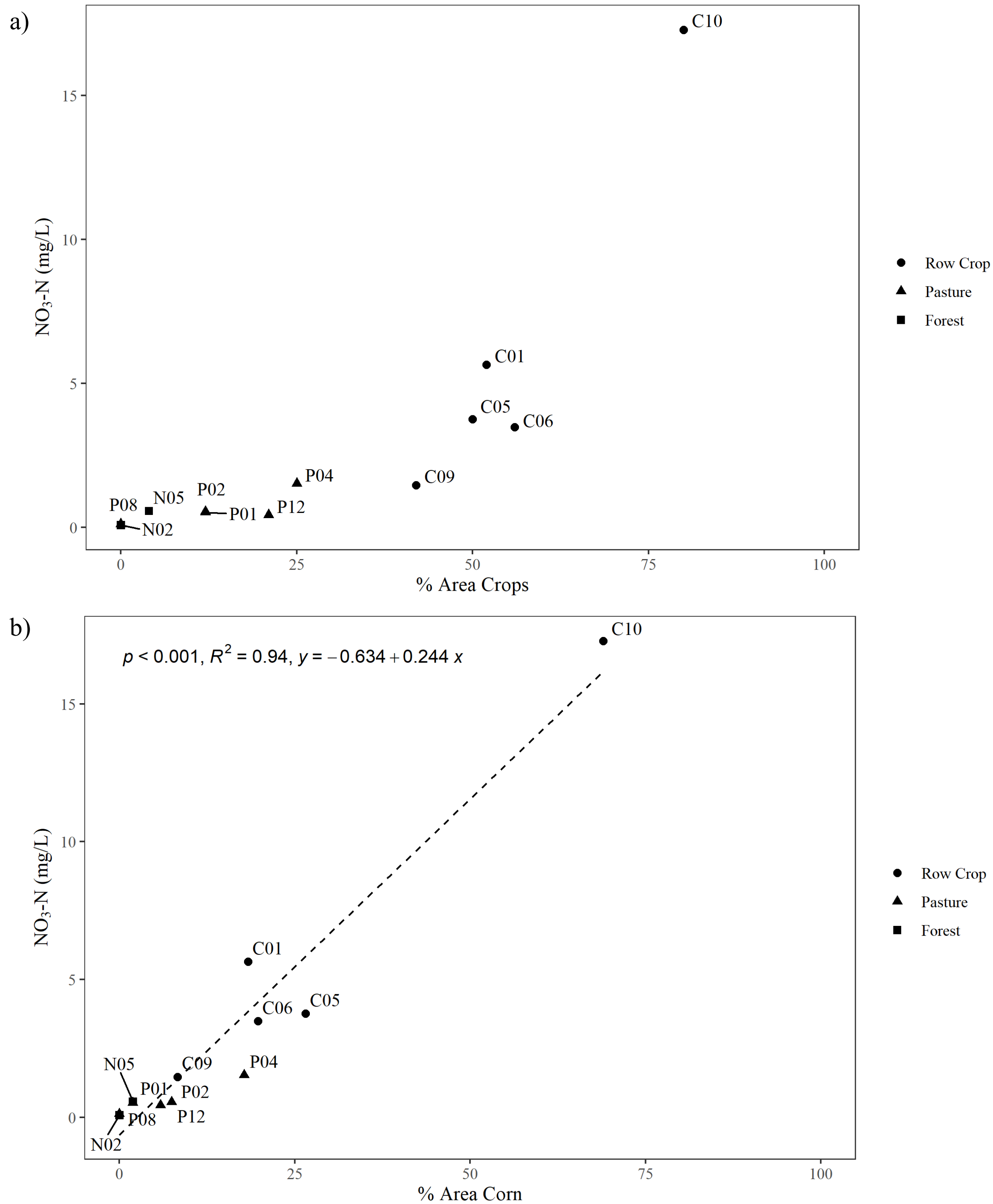

Figure 3.5 a) Annual volume-weighted mean NO_3-N concentration by percent row crop cover for each catchment. **b)** Annual volume-weighted mean NO_3-N concentration by percent corn cover for each catchment. Dashed line indicates a linear regression line of best fit. Land/crop cover is expressed relative to total catchment area.

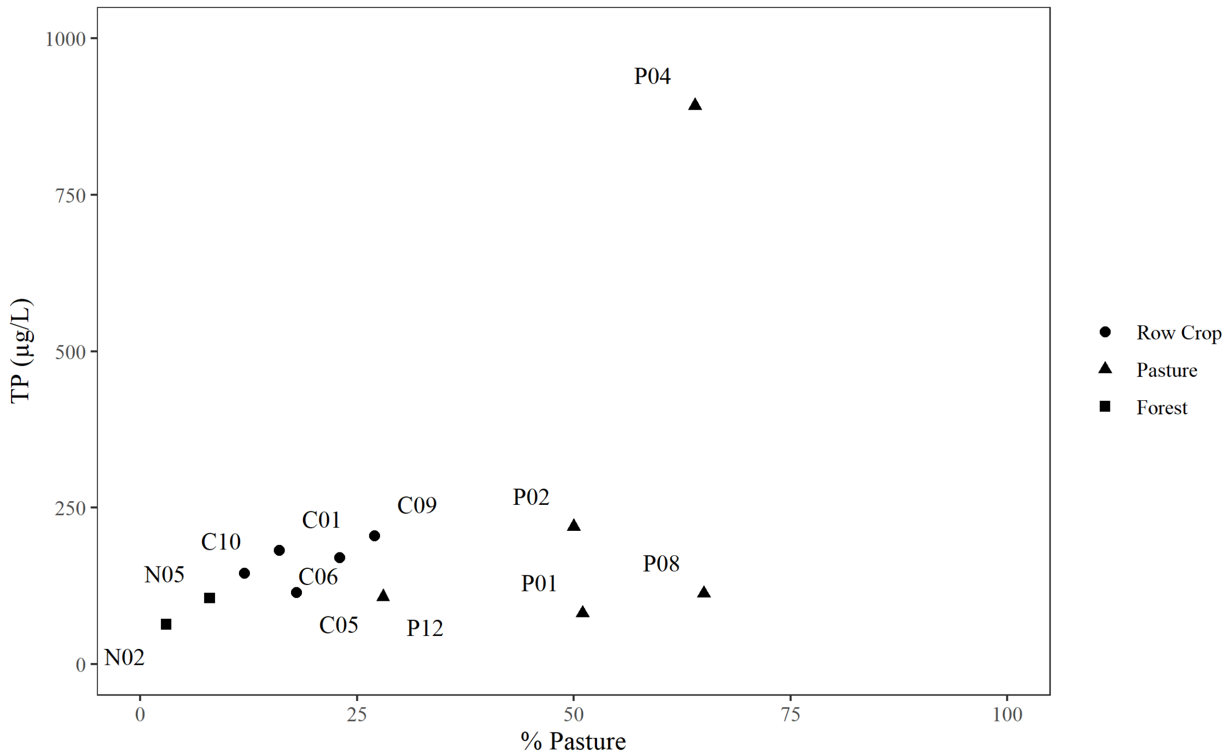

Figure 3.6 Percent pasture cover and annual volume-weighted mean TP concentration for each catchment. Pasture cover is expressed relative to total catchment area.

3.3.3 Stream nutrient export

Stream NO_3-N export followed a similar pattern to NO_3-N concentrations and was higher at row crop catchments compared with pasture or forest cover sites (Figure 3.7). Average annual NO_3-N export across all five row crop sites was 33 kg ha^{-1} yr^{-1} (Table 3.5) but declined to 19 kg ha^{-1} yr^{-1} when C10 was excluded. In contrast, average NO_3-N export at pasture and forested sites was an order of magnitude lower at 1.85 kg ha^{-1} yr^{-1} and 1.7 kg ha^{-1} yr^{-1}, respectively. Export of NO_3-N was greatest during the non-growing season, when exceptionally high flows and NO_3-N concentrations resulted in increased export across all land cover types (Appendix A8). The effect of increasing discharge on NO_3-N concentration was limited (Appendix 10) with half of all sites showing no relationship, while three experienced weak positive correlation (C01, C10, P02), and three weak negative correlation (C05, P01, N05). Like TP concentration, annual export did not vary greatly amongst land uses (row crop: 0.86 kg ha^{-1} yr^{-1}, pasture: 0.63 kg ha^{-1} yr^{-1}, forest: 0.44 kg ha^{-1} yr^{-1}) but could be quite different across individual catchments and seasons (i.e., P02 winter: 0.49 kg ha^{-1} yr^{-1}, P01 winter: 0.12 kg ha^{-1} yr^{-1}). Total P export was greatest at most sites during the winter and spring (Figure 3.8 and Appendix 7). Concentrations at only three sites (C09, C10, and P02) were positively related to discharge (Appendix 9), meaning heightened winter and spring export was largely due to increases in runoff as seasonal concentrations of TP were similar at most sites (Figure 3.4).

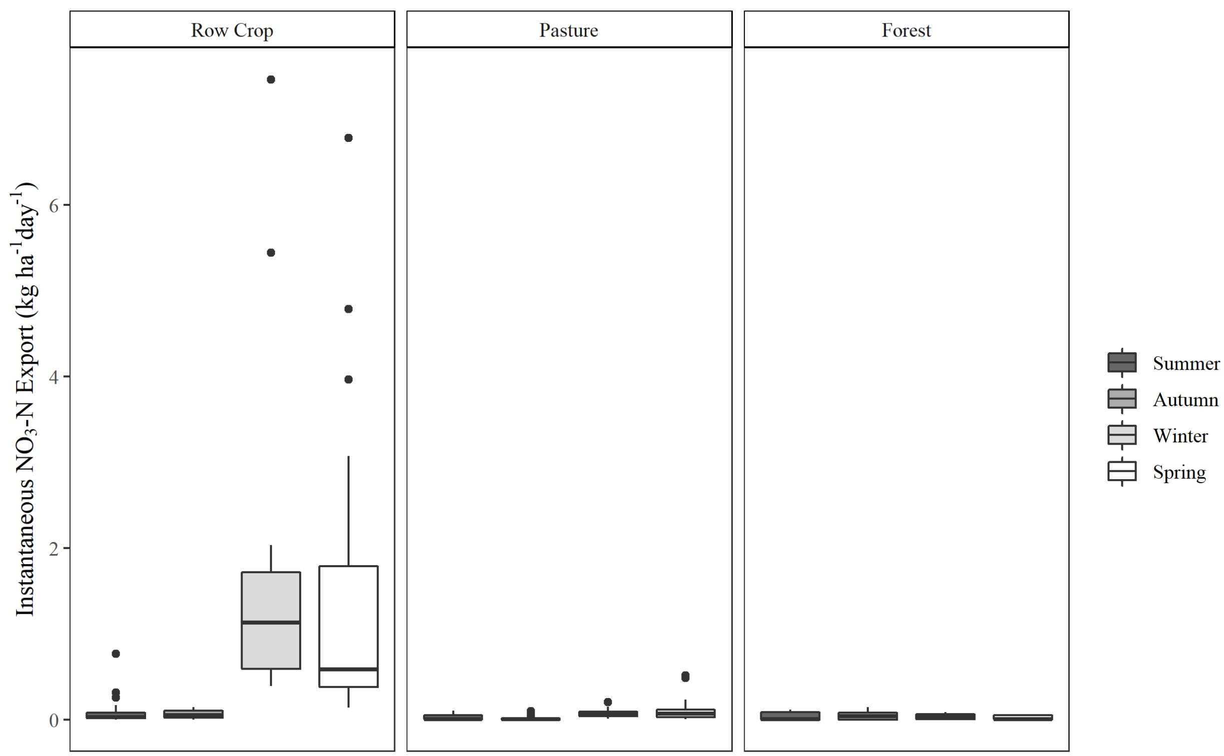

Figure 3.7 Box-whisker plots of instantaneous NO_3-N export (kg ha^{-1} day^{-1}) by season and across land uses.

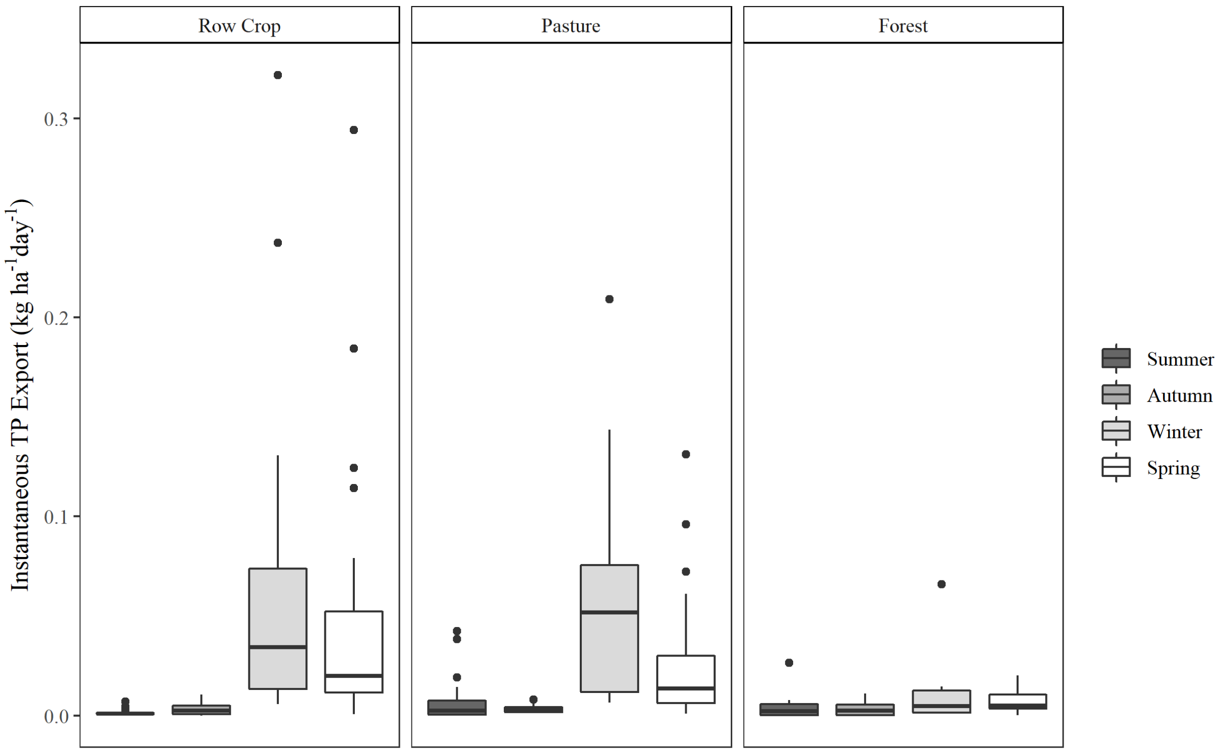

Figure 3.8 Box-whisker plots of instantaneous TP export (kg ha^{-1} day^{-1}) for each season and across land uses.

3.4 Discussion

3.4.4 Nitrate-N

Nitrate-N concentrations and export were greatest at row crop catchments, and the proportion of corn cover in each catchment was a good indicator of average NO_3-N concentrations across the study sites (Figure 3.5b). The NO_3-N to TN ratio was also highest at row crop sites and approached 100%. These observations are consistent with other studies that have found catchments with larger proportions of row crops to have higher NO_3-N concentrations (Lee et al., 2001; Raney and Eimers, 2014b). Volumetric mean NO_3-N concentrations at row crop streams in our study ranged from 1.28 and 16.5 mg/L, with a mean of around 5 mg/L. These values are similar to other studies of larger watersheds in the region (1 to 7 mg/L; Liu et al., 2022) and slightly greater than the 2.9 mg/L value reported by Raney and Eimers (2014b) in row crop catchments within the Kawartha Lakes region of Ontario. These values are also similar to total nitrate- and nitrite-N concentrations reported at the Multi-Watershed Nutrient Study agricultural watersheds (30.6 to 80.9 km^2) of southwestern Ontario (2.05 to 9.07 mg/L; Nelligan et al., 2021). Nitrate-N export estimates at row crop, pasture, and forested sites in this study (19 – 33, 3.2 and 1.7 kg ha^{-1} yr^{-1}, respectively) were also similar to previous reports. Again, another study in the Ganaraska region found annual NO_3-N export ranged from 8.0 to 16 kg ha^{-1} (Liu et al., 2022), while modelling for nearby Gages Creek estimated annual NO_3-N export between 2015 and 2019 to average around 5.0 kg ha^{-1} (Biagi et al., 2022). Similar annual export has been observed in sub-watersheds of the Grand River (9.2 to 12 kg ha^{-1}; Irvine et al., 2019) and elsewhere in southwestern Ontario (2.8 to 41 kg ha^{-1}; Nelligan et al., 2021). Notably, comparable values were observed in similar sized watersheds during an experiment in Missouri, which found row crop landscapes export 29 kg ha^{-1} yr^{-1} of TN compared with 4.3 kg ha^{-1} yr^{-1} and 2.0 kg ha^{-1} yr^{-1} at pasture and forested landscapes, respectively (Udawatta et al., 2011). Elsewhere in the US, Robertson and Saad (2011) estimated via modelling that fertilized cropland on the US side of the Great Lakes contributed an average of 22 kg ha^{-1} yr^{-1} of NO_3-N to the lakes themselves. Export of NO_3-N at row crop-dominated sites reported in this chapter were consistently similar to those from the literature despite the unusual hydroclimatological conditions during the study, emphasizing the influence of agricultural LULC on NO_3-N export.

While there were significant differences in NO_3-N concentrations and export between land use types, there were also considerable differences in NO_3-N losses amongst row crop sites themselves (Figure 3.3; Figure 3.7). Some of these differences can be seen by examining the row crop sites with the least (C09) and greatest NO_3-N concentrations (C10). Both catchments are similar in area (C09: 5.18 km^2, C10: 3.15 km^2), and are predominantly crop-dominated landscapes; however, NO_3-N concentrations were more than ten-times higher at C10 (Table 3.4). This may indicate that nutrient-intensive agriculture is not uniform at row crop sites throughout the study area. Instead, differences in land use practices within row crop agriculture are likely an important driver of NO_3-N concentrations. Stream NO_3-N concentrations may fluctuate due to differences in fertilizer application (related to crop type and rotation, soil conditions, or farming philosophies) (Liebig et al., 2002; McLellan et al., 2015), drainage characteristics (presence, age, or intensity of drainage) (Arenas Amado et al., 2017; Hanrahan et al., 2021; Ruffatti et al., 2019; Schilling et al., 2015b), as well as physical differences in geography (including topography, soil, riparian zone, stream morphology and productivity) (Jones et al., 2018a; McLellan et al., 2015). Notably, annual crop inventories performed by AAFC estimated that the catchment of C10 experienced relatively little crop rotation between 2014 and 2016 (2014: 67% corn, 2015: 76% corn, 2016: 75% corn), especially compared to C09 (Appendix A2). In particular the consistent planting of corn in C10, a crop high in N-demand, may exhaust the soil of nutrients requiring greater fertilizer input at C10 than C09; reducing the input of nutrients is an important factor in mitigating nutrient losses from agricultural fields, particularly via subsurface drainage (Hanrahan et al., 2021). The strong positive relationship between corn cover and NO_3-N concentrations (Figure 3.5b) emphasizes the effect that not only a lack of rotation, but particularly the planting of corn has on nutrient concentrations and export. The stream draining C10 also exhibited some of the smallest variation in temperature (Appendix A6) throughout the study period (C10 range: 15°C, compared to C09 range: 20.2°C) and was similar to catchments draining from the ORM (i.e., N05: 17.2°C, P01: 14.4°C) where potentially greater groundwater contributions to discharge have a moderating effect on stream temperature. The difference in temperature ranges between

C10 and C09 could therefore be an indicator of greater subsurface drainage at C10, which may in turn facilitate NO_3-N export (Goeller et al., 2019). These and the other factors discussed above may have contributed to the stark differences in NO_3-N concentrations and export between C09 and C10.

Another factor that may have affected NO_3-N concentrations were the unusual hydroclimatic conditions seen between June 2016 and May 2017. Large rain and snow-melt events that produce overland flow and flooding may result in increased stream NO_3-N concentrations (Pionke et al., 1996), particularly when following extended periods of dryness (Loecke et al., 2017). Although the scope of this study did permit some investigation into the relationship between flow and nutrient concentrations (Appendix 10) these relationships were varied and weak, while differences in NO_3-N concentrations across land use types were consistent throughout the entire study period, despite highly variable hydrologic conditions. The considerable differences in NO_3-N concentrations and export between land use types emphasizes the importance of land use when it comes to managing NO_3-N in surface waters.

Several of the streams in this study consistently exhibited NO_3-N concentrations higher than the Canadian water quality guidelines for the protection of aquatic life. These guidelines suggest a maximum long-term term exposure threshold of 3 mg/L of NO_3-N (CCME, 2012), although they note that lower concentrations may be needed to protect particularly sensitive organisms like Lake Trout (*Salvelinus namaycush*) (Camargo et al., 2005; CCME, 2012). Self-regulating freshwater systems in Canada, free from anthropogenic influence, contain less than 4 mg/L of NO_3-N, while in oligotrophic systems the concentrations are much lower (CCME, 2012). Although an essential nutrient, high levels of NO_3-N affect organisms by limiting the oxygen-carrying capacity of their blood (Camargo et al., 2005), an effect termed

Methemoglobinemia, or blue baby syndrome (Wolfe and Patz, 2002). It is important to note that continued high NO_3-N concentrations will affect the health of instream and downstream ecosystems.

3.4.5 Total P

Although average TP concentrations and export were higher at agricultural catchments than at forested catchments, there were no significant differences in TP concentrations between pasture and row crop dominated sites. This was in part due to the substantial variability in TP concentrations across pasture-dominated catchments. Nevertheless, TP concentrations measured in this study were similar to those reported previously for other sites in Ontario. For example, Raney and Eimers (2014b) reported volume-weighted TP concentrations of 50 µg/L at a row crop-dominated watershed in the Kawartha Lakes region. In small Ontario watersheds (< 75 km^2) a study of PWQMN data (1995-2005) found TP concentrations in most streams to range from 10 to 300 µg/L (Chambers et al., 2008). Stream TP concentrations measured at the very small (< 7.5 km^2) catchments in this study (volume-weighted mean 37.5 [N02] to 1192 µg/L [P04]) are higher than concentrations reported at the outlets of the larger (47 - 278 km^2) quaternary watersheds they drain into (average 17-33 µg/L during the growing season; see Chapter 2; DeBues et al., 2019), highlighting the important contribution of agricultural landscapes to overall TP export from these watersheds.

Meanwhile, estimates of annual TP export from row crop (0.6 – 1.1 kg ha^{-1} yr^{-1}) and pasture (0.4 – 1.2 kg ha^{-1} yr^{-1}) catchments in this study were similar to several other estimates of TP export in Ontario. In slightly larger (15 km^2) central Ontario row crop-dominated watersheds, TP export was estimated at 0.18 to 0.25 kg ha^{-1} yr^{-1} (Raney and Eimers, 2014b), which is lower than other estimates in row crop landscapes which can range from approximately 0.18 to 2.96 kg ha^{-1} yr^{-1} (Irvine et al., 2019; Mander et al., 2000; Nelligan et al., 2021; Plach et al., 2019; Robertson and Saad, 2011), but similar to other work in the Ganaraska area (0.15 to 0.35 kg ha^{-1} yr^{-1}; Liu et al., 2022). Higher export values shown in this study may again be a consequence of catchment size, and the importance of agricultural landscapes to TP export. However, larger agricultural catchments, including one Missouri-based study, found TP export in row crop sites to be as high as 3.82 kg ha^{-1} yr^{-1} (Udawatta et al., 2011). Total P export from row crop dominated watersheds in Iowa average 1.7 kg ha^{-1} yr^{-1} (Schilling et al., 2020), greater than the higher estimates of row crop TP export in this study.

The hydroclimatic conditions observed during the study period may also have influenced TP export. Total P concentrations and export are highly dependent on hydrology, with P concentrations and export often increasing during heavy storms (Sharpley et al., 2008), as well as during snowmelt and rain-on-snow events (Kinley et al., 2007; Lam et al., 2016; McDowell et al., 2001; Miles et al., 2013). For example, a study in Maryland measured TP concentrations of 40 µg/L during baseflow and 175 µg/L during storm events (Lee et al., 2001) and Raney and Eimers (2014b) similarly found that TP concentrations were up to three-times higher in high flow compared with delayed flow. Although there were only limited positive relationships between discharge and concentration at three sites (Appendix 9), the unusually wet conditions seen in the latter half of the study had a positive effect on TP export. A notable example was a high-flow storm and melt event on March 1st when more than half of the total spring export and 26% of the total annual export in P12 was lost in one day. At the same site, two late summer storms may have accounted for 44% of the total summer TP export. Total P export was greater during the winter and spring compared to the summer and fall at each catchment, despite concentrations being similar throughout the year. Although seasonal differences in TP concentrations were not observed during this study, it is possible that a targeted water sampling strategy, which better captured high flow events, might elucidate patterns in the relationship between land use and TP concentrations.

While there appeared to be no dramatic differences in TP concentration or export amongst land uses, TP varied considerably between sites (Figure 3.6). Total P losses appeared to be dependent on individual site characteristics during specific seasons, with high spring and winter TP concentrations at P04 being a notable example (634 to 1192 µg/L during the wet winter and spring). It is probable that differences in individual land use practices and site characteristics account for the high values at P04, as well as the diversity of TP concentrations across all sites. The P04 stream drains a small cow pasture-dominated catchment that also directly drains a barn, feeding area, and enclosed animal pen. The stream itself is poorly defined, with little baseflow, and on satellite imagery gives the appearance of a waterlogged, animal-trodden, wet strip that extends through the field towards the barn. There is no apparent riparian buffer. Confined animal enclosures and feedlots are known to be considerable sources of P to streams (McDowell et al., 2001), and while P04 is strictly neither of these, the proximity of the barn and enclosed animal pen to the stream resulted in similarly large P concentrations (Lee et al., 2001). Similarly, winter grazing or grazing on water-logged soil (Cournane et al., 2011), winter manure spreading (Miles et al., 2013) and the lack of riparian buffers (Sharpley et al., 2015) can all increase P losses from pasture-based fields.

3.5 Conclusions

The objective of this study was to examine the effect of agricultural land use on stream NO_3-N and P concentrations and export. As with larger-scale research on small north-shore Lake

Ontario tributaries (see Chapter 2; DeBues et al., 2019), NO_3-N concentrations and export were greatest in catchments dominated by row crops, while differences in TP concentrations and export did not appear to hinge on agricultural cover alone. Nutrient concentrations were highly variable within land cover types likely due to specific agricultural land use practices (i.e., riparian buffers or drainage characteristics). While a targeted long-term study may be able to better explore the mechanisms behind differences in nutrient chemistry, our study supports the theory that long-term increases in NO_3-N concentrations in Lake Ontario tributaries may be due to the conversion of low-intensity pasture and mixed-use agricultural land to high-intensity, tile-drained row crops.

Chapter 4 - General Discussion and Conclusion

4.1 Major Findings

The objective of this thesis was to quantify and evaluate associations between long-term changes in LULC and water quality in tributaries of Lake Ontario. I combined two approaches to achieve this objective. In Chapter 2, I examined and quantified changes in agricultural land cover within tributaries of Lake Ontario where declines in TP and increases in NO_3-N concentrations have been previously reported. I then evaluated associations between observed LULC and nutrient changes. I sought to reinforce my understanding of these associations in Chapter 3 while also overcoming limitations in the datasets utilized in Chapter 2. Here, I employed a space-for-time approach, isolating specific LULC types in small catchments and monitoring TP and NO_3-N losses throughout a hydrologic year. The combination of long-term data analysis in large basins

(Chapter 2) and frequent, year-round measurements at small sub-catchments within the larger basins, offered a more holistic evaluation of the effect of LULC change on water quality in Lake Ontario tributaries.

The first approach, described in Chapter 2, examined trends and patterns in agricultural land uses and stream TP and NO_3-N concentrations between 1971 and 2011 in 12 Lake Ontario tributaries. I hypothesized that row crop area and NO_3-N would increase while TP would decrease in agriculture-dominated watersheds. While the total area of agricultural land declined in all watersheds, the proportion of agricultural land dedicated to row crops increased. The results found total P concentrations were most associated with urbanized watersheds and declined over time. Nitrate-N concentrations were highest in agricultural watersheds and steadily increased between 1971 and 2010. The findings of the first approach broadly met the hypotheses, although TP concentrations did not decline across all agriculture-dominated watersheds, remaining stable in several.

The second approach, described in Chapter 3, tested the effect of land cover (row crop, pasture, and forest) on stream TP and NO_3-N concentrations and export in 12 small (< 7.5 km^2) watersheds along the north shore of Lake Ontario, 10 of which are nested within four of the larger quaternary watersheds considered in Chapter 2. I hypothesized that TP concentrations and export would be greatest in pasture catchments, while NO_3-N concentrations and export would be greatest in row crop catchments. Once again, the hypotheses were mostly supported by the results. Nitrate- N concentrations and export were highest in row crop catchments, although TP concentrations and export were not clearly affected by land covers and were more likely a condition of specific agricultural land use practices and local geography, as well as the unusual climate conditions observed during the study period. Nonetheless, the results improve on the findings of the first approach and suggest that long-term increases in NO_3-N concentrations in Lake Ontario tributaries may be a result of increasing row crop cover and related agricultural practices. These findings also imply value in the space-for-time approach used in Chapter 3 to better isolate the effect of LULC changes on water quality, but that the starkness of the differences between row crop and pasture on NO_3-N in particular may be reduced at broader scales.

4.2 Implications of agricultural intensification

These findings imply that continued increases in row crop cover, subsurface drainage, and the general intensification of agriculture in the region could result in further increases in NO_3-N export. A linear relationship between row crop cover and NO_3-N concentrations has been identified elsewhere in Canada (Liu et al., 2022) including in Europe and the US (Jordan et al., 1997; Chuman et al., 2013) at varying spatial scales (Schilling & Spooner, 2006; Sorrano et al., 2016). While observed in the second chapter, the relationship between row crop cover and NO_3-N concentrations was non-linear. This may be simply a consequence of a short one-year study period and small sample size. The high NO_3-N concentrations found in one catchment (C10) are not necessarily unusual (Schilling and Spooner, 2006); however, the row crop landscape in Ontario is not homogenous.

Differences between a high NO_3-N catchment (17.3 mg/L) like C10, and a low NO_3-N catchment like C09 (1.47 mg/L) illustrate the potential for further increases in NO_3-N concentrations and export in Ontario if agricultural intensification continues. Both catchments (C10 and C09) are similar in area (C09: 5.18 km^2, C10: 3.15 km^2), and are crop-dominated landscapes. However, there are many differences, the most important of which may be crop rotation. While the agricultural area of each catchment is crop-dominated, only 61% of agricultural land in C09 was given to row crops compared to 86% of C10. Of that land, 85% of C10 was corn covered, while C09 was dominated (81%) by less N-demanding crops, wheat, and soybean. In addition, only 5% of the total land cover in C10 was forest or wetland, compared to 28% of C09. An examination of land cover alone highlights the opportunities for agricultural intensification in the C09 catchment. Other differences in drainage and riparian cover would likely amplify the effects of land cover and crop selection on NO_3-N concentrations and export between the two sites (McLellan et al., 2015). The heterogeneity of agricultural landscapes in this study region means that row crop agriculture in this region is not uniform and highlights the possibility of further intensification in row crop agriculture.

4.3 Weather, Hydrology, and N export

The unusual weather and subsequent hydrologic conditions across the June 2016 to May 2017 study period examined in Chapter 3 underlines the important consequences of weather extremes and climate change on N export. The sampling period began during a prolonged and severe drought (1 in 10-20 year drought), which lasted until December 2016 (AAFC, 2021). This caused three streams to completely dry up, and for the flow in all others to become reduced. Local farmers complained of empty wells and commented on the unusual dryness of some local streams. What followed was a historically wet period, resulting in extensive flooding of several catchments and many coastal areas around Lake Ontario and the St. Lawrence River. The period from December to January was rainy, with unusually little snow fall and almost no regular snow cover, an increasingly common occurrence in southern Ontario. While February and March received some snowfall, regular rain events and warm temperatures kept the snowpack small, and the soil wet. Copious quantities of rain followed during April and May resulting in waterlogged fields and high streamflow at all catchments.

The abrupt change in weather from one extreme to another (as observed in Ontario between 2016-2017), has been popularly termed as “weather whiplash” (Loeke et al., 2017) and has consequences for NO_3-N export. As NO_3-N export is transport-limited (Jones et al., 2017; Sinha et al., 2017), dry periods lead to lower-than-normal levels of N export. While N export is limited in dry periods, lowered water tables may increase rates of nitrification due to the aerobic soil environment, and may lower rates of denitrification (Groffman et al., 2002), leading to increases in available N. Furthermore, droughts reduce crop yields, leading to lower N uptake by crops, and a larger pool of available N in agricultural soils (Loeke et al., 2017). When dry periods are followed by wet periods, the “whiplash” effect results in larger than normal N export (Loeke et al., 2017). All leachable N, made available by drought conditions, is readily flushed out of soils during wet periods (Jones et al., 2017; Sinha et al., 2017; Loeke et al., 2017).

Future climate change in Ontario is expected to result in more extreme climate variation and increases in winter and spring wetness (McDermid et al., 2015). This would potentially increase the frequency of “weather whiplash” (Loeke et al., 2017). Combined with “weather whiplash”, increases in wetness may lead to increases in N export (Sinha et al., 2017), while winter warming may shift the timing of that export (Casson et al., 2019, 2012). Continued increases in row crop cover may exacerbate the effect of climate change on NO_3-N export. Increases in row crop agriculture, accompanied by fertilizer amendments and subsurface drainage, may therefore amplify the effect of “weather whiplash” and climate change on NO_3-N export timing and quantities.

4.4 Weaknesses and opportunities

The limitations of external datasets, used extensively in the second chapter, restricted the depth and extent of insights that could be made into the relationship of changing agriculture and water quality in Lake Ontario tributaries. Firstly, there were limitations to the PWQMN dataset. The PWQMN water quality data used in Chapter 2 were collected by multiple agencies, over four decades, and included many different staff members. While this is expected of a long-term, large-scale dataset, this scope presents many opportunities for methodological errors and variation. Funding changes to the monitoring program within the four decades resulted in uneven and changing sampling frequency, with storm-event and non-growing season data severely lacking despite the importance of these periods to water quality research (Lam et al., 2016). Secondly, the design of the second chapter excluded the use of hydrologic data that may have been available and could have been used to estimate changes in export over time. While limitations in the PWQMN water quality dataset may have restricted the inferences that could be made with export data, such estimates may still have been useful when examining the effect of changing LULC on TP and NO_3-N entering Lake Ontario. Thirdly, limitations in agricultural census data, and good spatial data on agricultural land use practices like tillage (tracking began in the census only by 1991), nutrient application, and tile drainage (often unreported), restricted the scope of the second chapter. Changes in these land use practices between 1971 and 2010 were likely considerable (Smith, 2015); data characterizing these changes may have helped elucidate the specific effects of these practices in observed water quality changes.

Study design weaknesses of the third chapter hampered estimates of export and concentration data. Physical and logistical restraints meant that a maximum of 12 sites could be visited over a one-year period. A greater replication of sites and an extended study period would ensure the study could accurately characterize export from a heterogenous landscape. A longer and larger study may be able to account for changes in crop cover rotation and hydroclimatic conditions. The design of the third chapter could be improved methodologically. Only 20 data points were recorded over the course of the year, and although this was in part due to extremely dry conditions during the first half of the monitoring period, deployment of automated water samplers (i.e., ISCOs) would have improved the resolution of mean concentration and export measurements as well as inter-season comparisons. The lack of *in situ* coarse filtering of water samples may have led to inaccurate water quality measurements due to contamination by biological material and debris. Finally, improvements in stream gauging and gauging site selection would have improved the accuracy of the hydrologic prorating used in the third chapter to estimate daily discharge.

There remain opportunities for further research on agricultural LULC and water quality in the northern Lake Ontario shoreline region. One of the most interesting research opportunities would be to investigate the scale and impact of subsurface drainage on nutrient transport in Ontario. While there is a body of research internationally that has examined the effects of drainage on NO_3-N export (Ikenberry et al., 2014; Randall et al., 1997; Schilling et al., 2015b, 2012) and a growing body of research looking at the effect of drainage on P export in southwestern Ontario (Lam et al., 2016; Macrae et al., 2019, 2007), the scale and effect of increasing tile drainage in the Lake Ontario region has not been extensively characterized, largely due to incomplete records of tile area (Eimers et al., 2020). Increases in tile drainage throughout this region may have resulted, and continue to result, in considerable water quality changes. The extent to which the third chapter's results are affected by drainage are unclear. Lastly, the effects of climate variability on nutrient export in Ontario are not well-understood.

Understanding the effects of future climate scenarios on nutrient export, accounting for phenomena such as the “weather whiplash” effect (Loecke et al., 2017), would be useful for ecosystem managers when recommending land use management practices or setting nutrient loading targets.

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Appendices

Appendix A: Supplementary Information for Chapter 3

Table A1 Coordinates of study sites in Chapter 3.

	Site	Latitude	Longitude
Row Crop	C01	43.946601	-78.647706
	C05	43.923876	-78.452786
	C06	43.951957	-78.352740
	C09	43.991516	-78.523917
	C10	43.936731	-79.637746
Forest	N02	44.041292	-78.568090
	N05	44.045805	-78.635949
Pasture	P01	44.028138	-78.627860
	P02	44.017350	-78.706166
	P04	44.991487	-78.632468
	P08	44.056128	-78.519420
	P12	43.965931	-78.515527

Table A2 Agricultural land cover (as a percentage of active agricultural land) at each catchment between 2014 and 2016 as determined by AAFC's remotely sensed annual crop inventory.

		Pasture/Forage			Wheat			Corn			Soybean			Other Agriculture		
	Site	2014	2015	2016	2014	2015	2016	2014	2015	2016	2014	2015	2016	2014	2015	2016
Row Crop	C01	20	48	23	4	0	13	41	29	39	32	25	14	3	3	12
	C05	18	29	27	0	0	0	21	44	27	61	38	51	0	0	0
	C06	26	31	27	1	4	6	15	33	25	59	30	34	0	0	0
	C09	23	35	41	0	8	25	44	19	12	33	40	27	0	2	0
	C10	22	16	13	1	0	1	67	76	75	10	12	12	0	0	0
Forest	N02	94	76	78	0	0	0	0	5	0	6	0	7	0	0	0
	N05	86	47	37	3	0	0	0	10	16	10	0	1	0	0	3
Pasture	P01	83	79	69	2	1	4	5	8	3	11	4	10	0	0	0
	P02	86	66	72	1	3	1	7	4	12	6	18	3	0	0	1
	P04	74	82	70	0	0	4	26	0	20	0	23	3	0	0	0
	P08	100	82	97	0	7	0	0	0	0	0	0	0	0	0	0
	P12	55	55	51	3	0	7	11	18	12	31	21	20	0	0	0

Table A3 Correlation coefficients of the discharge relationship between study sites and Mackie Creek (WSC station 02HD023).

	Site	R^2	n
Row Crop	C01	.66	20
	C05	.81	10
	C06	.45	20
	C09	.71	20
	C10	.67	20
Forest	N02	.66	20
	N05	.26	20
Pasture	P01	.66	20
	P02	.38	20
	P04	.53	10
	P08	.58	15
	P12	.90	20

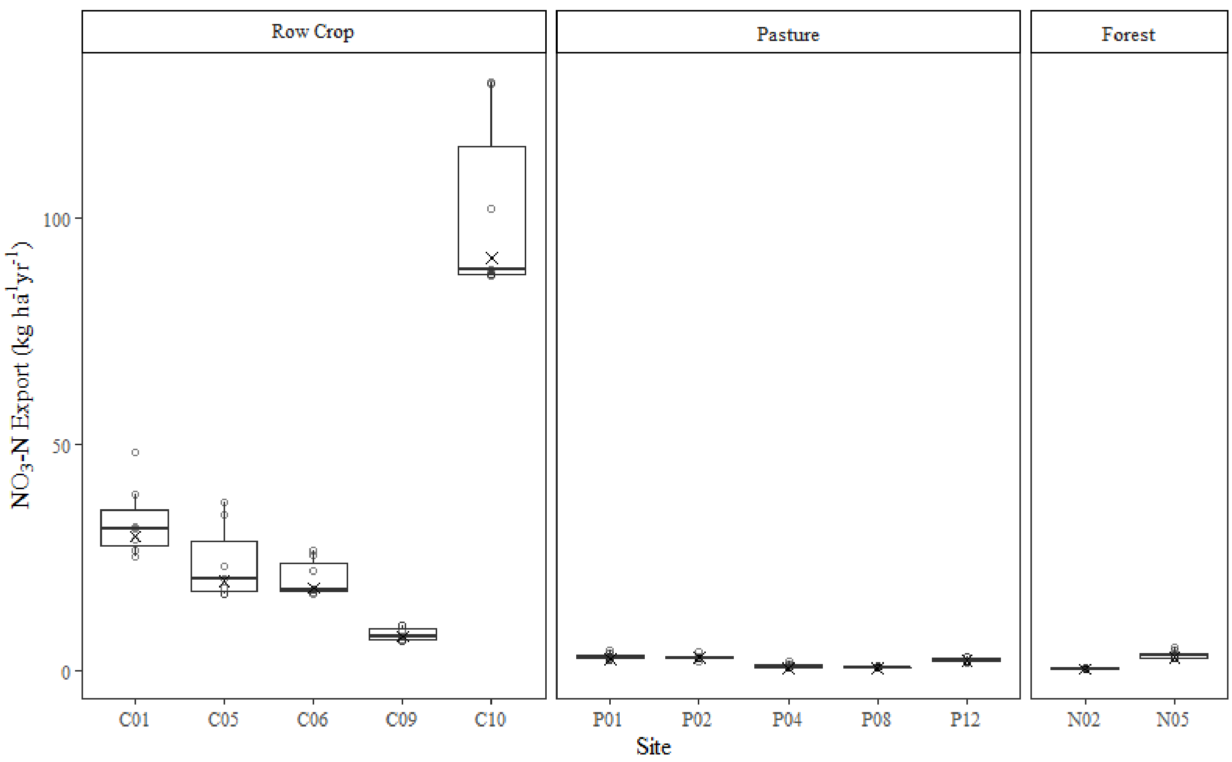

Figure A4 Box-whisker plots of NO_3-N export (kg ha^{-1} yr^{-1}) across sites as calculated using seven load-estimation methods from RiverLoad software and estimates from LOADEST. Points indicate specific values of estimates for each site. Crosses indicate estimates calculated using the midpoint method.

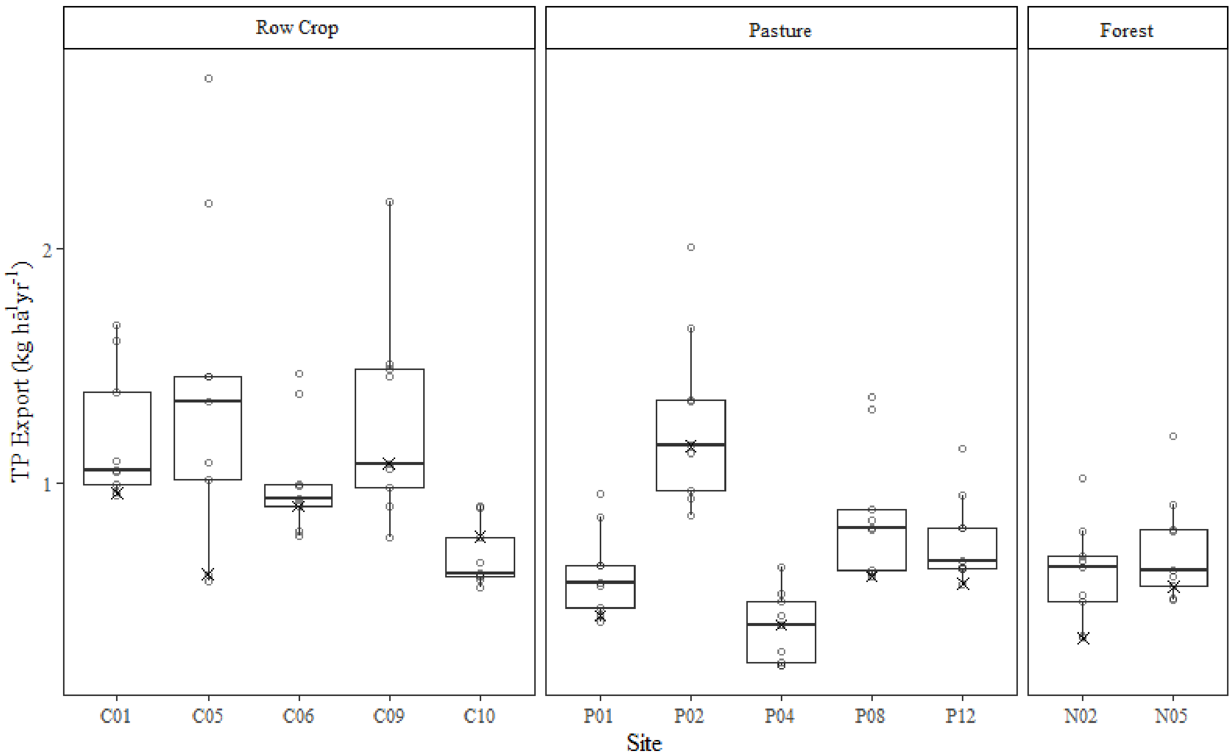

Figure A5 Box-whisker plots of TP export (kg ha^{-1} yr^{-1}) across sites as calculated using seven load-estimation methods from RiverLoad software and estimates from LOADEST. Points indicate specific values of estimates for each site. Crosses indicate estimates calculated using the midpoint method.

Table A6 Stream temperatures at catchments. * Note catchment P04 was dry between June and January due to low-water conditions.

	Site	Maximum Temperature (°C)	Minimum Temperature (°C)	Temperature Range (°C)
Row Crop	C01	22.6	1.6	21.0
	C05	24.0	2.4	21.6
	C06	23.7	2.7	21.0
	C09	22.6	2.4	20.2
	C10	19.0	4.0	15.0
Forest	N02	24.3	2.9	21.4
	N05	19.5	2.3	17.2
Pasture	P01	18.6	4.2	14.4
	P02	22.8	0.9	21.9
	P04	10.0	1.2	8.8*
	P08	22.3	1.2	21.1
	P12	27.4	1.0	26.4

Table A7 Instantaneous TP export (g ha^{-1} day^{-1}) across sites during the entire study period.

	Row Crops					Forest		Pasture				
Date	C01	C05	C06	C09	C10	N02	N05	P01	P02	P04	P08	P12
2016-06-08	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
2016-06-21	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*	*No data*
2016-06-27	1.47	0	0.771	1.44	0.969	0.149	5.73	6.79	3.05	0	0	0.0928
2016-08-13	3.52	0	7.03	1.213	0.965	2.21	26.6	38.5	42.3	0	9.93	2.00
2016-08-16	2.32	0	0.995	3.04	0.972	0.25	4.71	7.89	14.3	0	6.50	0.308
2016-09-10		0	0.371	1.64	0.737	0.179	7.66	11.0	2.96	0	0	0.833
2016-09-18	4.52	0	0.854	1.11	0.765	0.00682	3.38	19.0	2.22	0	0	0.832
2016-09-23	1.27	0	0.301	0.387	0.256	0.109	1.17	2.80	0.593	0	0	0.235
2016-09-27	2.59	0	0.736	0.926	0.485	*No data*	6.43	4.97	1.40	0	0	0.370
2016-10-18	1.67	0	5.707	3.23	0.698	0.159	4.57	7.40	3.95	0	2.28	1.39
2016-10-21	2.52	0	4.94	4.28	0.490	0.210	5.86	7.89	3.55	0	2.70	1.42
2016-11-29	1.23	0	8.09	10.6	0.236	0.162	11.1	4.56	4.09	0	1.34	1.93
2017-01-12	14.8	12.0	73.7	26.2	73.8	1.04	6.57	12.0	26.1	67.0	9.46	7.11
2017-02-23	5.69	7.07	29.7	238	6.80	0.843	14.6	6.45	64.7	29.7	144	11.9
2017-02-24	34.3	39.1	131	322	40.9	2.67	66.0	84.1	209	113	67.2	51.7
2017-03-01	124	12.6	184	114	69.3	3.31	20.2	61.2	72.3	131	25.2	54.2
2017-03-07	2.82	4.40	28.9	11.67	0.621	0.144	9.96	6.17	13.6	96.1	0.853	1.73
2017-03-27	12.0	27.7	24.5	9.27	6.77	0.316	17.8	9.63	10.4	6.11	10.7	4.54
2017-04-06	15.9	294	46.3	6.58	19.8	4.49	4.08	7.07	2.19	50.5	11.3	18.8
2017-05-05	52.3	12.9	15.2	79.0	27.6	5.48	10.6	14.3	19.6	5.15	28.6	30.0

Table A8 Instantaneous NO_3-N export (g ha^{-1} day^{-1}) across sites during the entire study period.

	Row Crops					Forest		Pasture				
Date	C01	C05	C06	C09	C10	N02	N05	P01	P02	P04	P08	P12
2016-06-08	35.5	124	93.7	31.4	766	0.572	97.5	97.6	10.5	4.44	3.35	10.0
2016-06-21	37.1	254	23.6	21.5	317	0.361	86.6	100	6.28	0	0	7.32
2016-06-27	45.9	0	23.5	23.5	166	0.551	77.3	88.7	6.14	0	0	0.664
2016-08-13	14.0	0	40.4	11.9	110	0.789	47.2	70.8	19.2	0	9.42	3.84
2016-08-16	16.9	0	2.66	45.0	123	2.36	7.36	57.6	14.9	0	24.2	5.46
2016-09-10	34.9	0	8.32	14.3	88.1	0.493	95.1	105	4.55	0	0	2.47
2016-09-18	26.7	0	14.9	20.3	78.7	0.0225	94.1	88	4.96	0	0	3.17
2016-09-23	17.1	0	20.3	15.7	71.6	0.160	117	71.3	0.457	0	0	3.32
2016-09-27	24.2	0	17.2	14.9	91.5	0.389	73.8	90.9	4.43	0	0	3.71
2016-10-18	21.4	0	32.5	30.0	104	0.0321	80.2	48.0	0.802	0	0.0205	3.04
2016-10-21	15.3	0	51.9	59.7	96.5	0.0132	82.0	79.6	0.206	0	0.342	2.93
2016-11-29	16.7	0	146	122	128	0.0605	143	101	2.97	0	4.39	0.255
2017-01-12	721	1690	2031	515	7463	0.114	62.8	93.5	68.4	79.6	9.41	38.6
2017-02-23	666	391	1131	502	1748	0.852	62.0	83.9	153	34.5	51.9	*No data*
2017-02-24	1398	691	1447	474	5443	5.11	83.9	94.9	204	81.5	31.7	62.0
2017-03-01	3962	773	2838	545	6782	1.16	51.0	109	165	231	9.42	151
2017-03-07	307	310	482	137	289	1.26	*No data*	69.1	46.6	513	8.36	24.6
2017-03-27	273	581	839	311	587	0.121	50.1	46.6	31.0	5.91	*No data*	14.8
2017-04-06	972	711	1912	378	3071	0.311	57.3	84.1	63.1	109	28.9	24.5
2017-05-05	1365	1790	537	447	4786	3.00	52.7	89.4	111	484	34.7	132

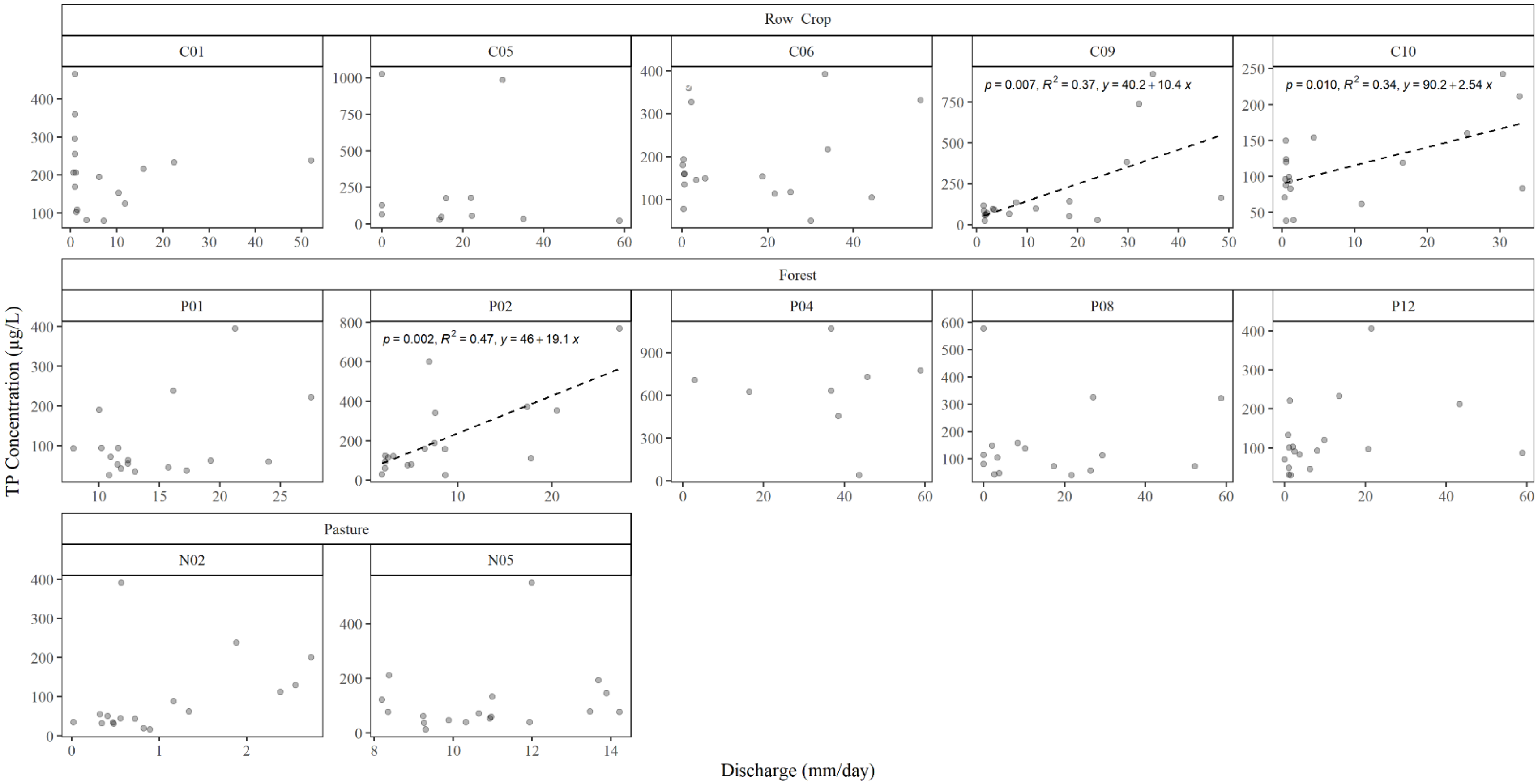

Figure A9 Concentrations of TP (µg/L) by instantaneous discharge (mm/day). P values, R-squared values, equations and linear trendlines reported for statistically significant correlations ($p < .05$).

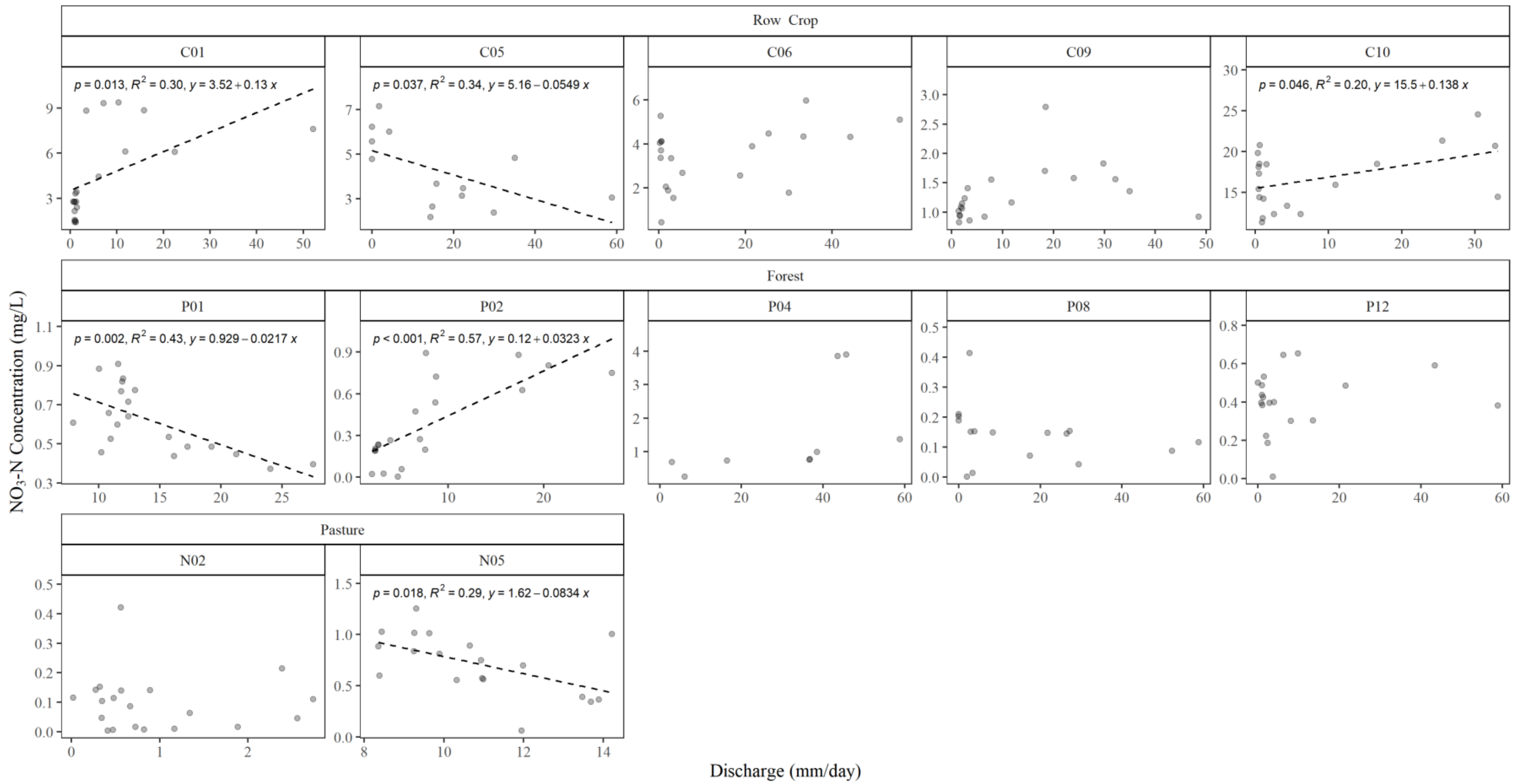

Figure A10 Concentrations of NO_3-N (µg/L) by instantaneous discharge (mm/day). P values, R-squared values, equations and linear trendlines reported for statistically significant correlations (p < .05).

Table A11 Instantaneous discharge (mm/day) across sites during the entire study period. Observed discharge from Mackie Creek (02HD023) was 535 mm between June 2016 and May 2017.

	Row Crops					Forest		Pasture				
Date	C01	C05	C06	C09	C10	N02	N05	P01	P02	P04	P08	P12
2016-06-08	1.48	1.74	2.80	2.55	6.20	0.665	9.64	11.9	3.96	1.76	2.21	2.50
2016-06-21	1.12	4.24	0.574	2.03	2.56	0.348	8.44	12.0	2.68	0	0	1.85
2016-06-27	1.34	0	0.571	2.06	1.17	0.481	9.24	12.4	2.68	0	0	0.132
2016-08-13	0.979	0	2.15	1.45	0.968	0.565	13.7	16.2	7.04	0	6.34	0.904
2016-08-16	1.13	0	0.622	3.20	1.04	0.559	11.9	11.0	7.58	0	16.5	1.02
2016-09-10	1.26	0	0.206	1.41	0.612	0.324	10.7	11.6	2.36	0	0	0.628
2016-09-18	0.969	0	0.441	1.87	0.511	0.0196	9.26	10.0	2.39	0	0	0.827
2016-09-23	0.617	0	0.385	1.65	0.362	0.343	9.31	10.8	2.03	0	0	0.761
2016-09-27	0.875	0	0.464	1.60	0.505	0.275	8.35	11.8	2.32	0	0	0.761
2016-10-18	0.991	0	1.59	3.51	0.564	0.471	9.89	7.90	3.23	0	1.54	1.37
2016-10-21	0.987	0	3.39	6.48	0.558	0.410	10.9	12.4	4.72	0	2.58	1.57
2016-11-29	1.20	0	5.42	7.82	0.614	0.824	14.2	13.0	5.12	0	2.89	2.32
2017-01-12	11.8	35.0	34.0	18.5	30.4	1.17	11.0	19.2	7.67	10.6	13.2	5.90
2017-02-23	7.15	14.7	25.3	32.2	11.0	1.34	11.0	17.3	17.4	4.75	44.6	12.3
2017-02-24	15.8	22.1	33.4	35.0	25.5	2.38	12.0	21.3	27.1	10.6	20.6	12.8
2017-03-01	52.1	22.3	55.6	29.8	32.8	2.56	13.9	27.5	20.5	16.9	22.3	25.6
2017-03-07	3.48	14.3	18.8	11.8	1.57	0.893	8.20	11.5	8.67	13.2	2.02	3.81
2017-03-27	6.14	15.8	21.6	18.3	4.39	0.726	8.38	10.2	6.56	0.862	7.81	4.89
2017-04-06	10.4	29.9	44.2	24.0	16.6	1.88	10.3	15.7	8.71	11.1	20.0	8.07
2017-05-05	22.4	58.8	30.0	48.5	33.1	2.74	13.5	24.0	17.8	12.6	39.7	34.7