EVALUATING THE RELATIONSHIPS BETWEEN LAND USE AND STREAM NUTRIENT AND CHLORIDE CONCENTRATIONS ACROSS SOUTHERN ONTARIO

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Abstract

Evaluating the Relationships Between Land Use and Stream Nutrient and Chloride Concentrations Across Southern Ontario

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Agricultural and urban land uses have been linked to the recent resurgence of eutrophication and salinization issues in the lower Great Lakes. This thesis examined the relationship between watershed land use and stream nitrate-nitrogen (NO_3-N), total phosphorus (TP), and chloride (Cl) concentrations across southern Ontario. Using a self-organizing map analysis, the watersheds were classified into eight distinct spatial clusters, representing four agricultural, two urban, and two natural clusters. Agricultural clusters under intensive row crop agriculture exhibited NO_3-N and TP concentrations up to twelve and five times higher, respectively, than the most natural-dominated cluster. Urban clusters had Cl concentrations up to nine times greater than the natural-dominated clusters. Three agricultural land use practices, namely continuous corn-soybean rotation, synthetic fertilizer application, and tile drainage, were positively correlated with stream NO_3-N concentrations, whereas Cl concentrations increased with urban area and human population density. This thesis also characterized sampling trends of the provincial stream water quality monitoring program and found that sampling frequency has declined since the mid-1990s, while current sites are monitored almost exclusively during the ice-free period. Sampling year-round is critical to capture seasonal variations in NO_3-N and Cl, while sampling across a full range of flow conditions is important for describing TP. Exclusion of sampling sites in close proximity of downstream municipal wastewater treatment plants and greenhouses can help isolate and better understand water quality impacts of non-point sources. Although intensive agricultural watersheds in southwestern Ontario draining into Lake Erie remain a priority for research and management, regions experiencing row crop expansion such as along the northern shore of Lake Ontario as well as rapidly urbanizing areas require further attention as these land use shifts will likely increase stream NO_3-N and Cl concentrations, placing further pressure on water resources in the lower Great Lakes.

Keywords: Water quality, southern Ontario, streams, phosphorus, nitrogen, chloride, self-organizing map

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Chapter 1: General Introduction

1.1 Nitrogen, phosphorus, and chloride in freshwater ecosystems

Nitrogen (N) and phosphorus (P) are essential elements for the growth and metabolism of plants and animals, but excessive quantities of these nutrients in freshwater can cause adverse health and ecological effects. Among the mineral nutrient elements, N is required by plants in the largest amounts (1 – 5% of plant dry weight) for the synthesis of cellular compounds including proteins, nucleic acids, chlorophyll, and phytohormones, all of which have crucial roles in plant growth and development (Hawkesford et al., 2012). Despite the abundance of N in the atmosphere (78% by volume), this gaseous form (N_2) is inaccessible to most organisms (Evert and Eichhorn, 2013). Certain plants such as legumes are able to form symbiotic relationships with N-fixing soil microorganisms to assimilate atmospheric N directly; however, most plants typically acquire N through reactive forms like ammonium (NH_4^+) and nitrate (NO_3^-) in soil to meet their N demands (Hawkesford et al., 2012). In terrestrial and aquatic ecosystems, reactive N is often in short supply and is thus considered to be a major limiting nutrient for primary productivity (Evert and Eichhorn, 2013). In the early twentieth century, the development of the Haber–Bosch process enabled the large-scale conversion of atmospheric N to ammonia, offering an unlimited supply of N that can be used for food production (Galloway et al., 2002). Since then, large quantities of inorganic N fertilizers manufactured via this process have been routinely applied to soils to maximize crop yields, circumventing limitations of biological N fixation (Galloway et al., 2002).

Alongside N, phosphorus is another important plant macronutrient. Phosphorus constitutes about 0.2% of plant dry weight, where it is a key component of energy-carrying molecules, nucleic acids, and phospholipids that are vital for energy transfer and cell function (Hawkesford et al., 2012). Unlike N, which can be fixed to bioavailable forms from an abundant atmospheric pool, the natural supply of P in soils relies on the weathering of P-bearing minerals (primarily apatite) in bedrock (Elser, 2012). The only form of P that can be assimilated by plants and microorganisms is inorganic phosphate, but it is naturally scarce in soils and often unavailable for uptake due to its low solubility and mobility as well as high sorption capacity to soil particles (Elser, 2012). As such, P deficiency in soils is widespread and limits primary productivity in natural systems. Historically, to supplement natural levels of P in soils, crop production relied on the addition of local organic matter (e.g., manure, crop residue) (Cordell et al., 2009). Since the mid-twentieth century, local sources of P have been largely replaced by fertilizer derived from mined phosphate rock in response to an increased demand for fertilizers to boost food production (Cordell et al., 2009). However, phosphate rock deposits are unevenly distributed globally, and the increasing demand for extraction is predicted to lead to the depletion of reserves within 30 to 300 years at current extraction rates (Cordell et al., 2021). This has raised concerns for the long-term sustainability of food systems relying on a finite resource for maintaining productivity.

Although the Haber–Bosch process played a vital role in sustaining a large proportion of the world's population, anthropogenic sources of reactive N now exceed contributions from natural biological fixation (Smil, 1999; Galloway et al., 2002). Likewise, anthropogenic activities have mobilized P from phosphate rock into the environment at rates vastly faster than the natural cycle (Cordell et al., 2009). Most of the reactive N and P used for food and energy production is eventually released to aquatic ecosystems with widespread impacts (Galloway et al., 2003; Elser et al., 2012). As N and P are common limiting factors for algal growth in freshwater, excessive additions of these nutrients can stimulate an increased growth of undesirable algae and aquatic plants, a process known as eutrophication (Carpenter et al., 1998). Oxygen consumption by decomposing algae can lead to hypoxic conditions, potentially triggering fish die-offs and shifts in species composition across trophic levels (Carpenter et al., 1998). Toxins produced by cyanobacteria and other noxious microorganisms can cause illness and mortality in livestock and humans (Carpenter et al., 1998). In heavily fertilized agricultural areas, nitrates can infiltrate groundwater and elevate concentrations in drinking water, increasing the risk of methemoglobinemia in infants ('blue baby syndrome') when levels of exposure are above 10 mg nitrate-N L^{-1} (Davidson et al., 2012). Chronic exposure to elevated nitrate concentrations has also been linked to certain cancers (Davidson et al., 2012).

In contrast to N and P, chloride (Cl) is widely distributed in nature, generally in the form of sodium (NaCl) and potassium (KCl) salts and is needed in small amounts for osmosis and ionic balance within cells and for photosynthetic reactions that produce oxygen (Evert and Eichhorn, 2013). Natural sources of Cl in freshwater systems include mineral salt deposits, atmospheric deposition, and weathering of soils and salt-bearing geological formations (Novotny et al., 2009). As Cl is a highly soluble and conservative ion that occurs naturally at low concentrations (<20 mg L^{-1}) in most surface waters (Hintz and Relyea, 2019), increases in concentrations above natural background levels are likely a result of anthropogenic influences (Dugan et al., 2017). Road salt application is the most pervasive anthropogenic source of Cl; concentrations of Cl in lakes and rivers contaminated with road salt can reach levels as high as 1,000 mg L^{-1} to 10,000 mg L^{-1} (Hintz and Relyea 2019). Contributions of Cl also originate from synthetic fertilizers, water softeners, wastewater, and industrial effluents (Dugan et al., 2017). Chronic exposure to elevated Cl levels can disrupt osmoregulation in aquatic organisms, leading to impairments in growth, reproduction, and survival (Nagpal et al., 2003). In drinking water, concentrations of Cl above 250 mg L^{-1} produce undesirable tastes and may cause corrosion in the distribution system (Health Canada, 1987). In addition, Cl can increase the transport of toxic heavy metals from soils to groundwater, where they may bioaccumulate in aquatic food webs and pose a risk to human health (Schuler and Relyea, 2018).

1.2 Nutrient enrichment and freshwater salinization in the lower Great Lakes

The Laurentian Great Lakes are an interconnected series of five major lakes (Superior, Michigan, Huron, Erie, and Ontario) that comprise the largest surface freshwater system on earth (Waples et al., 2008). Located along the border of Canada and the United States, these lakes cover a vast area of over 244,000 km^2 and contain approximately 23,000 km^3 of water, accounting for one-fifth of the world's surface freshwater (Waples et al., 2008). In addition to serving as a home and source of drinking water to 38 million people, the Great Lakes basin provides the backbone for a $4 trillion regional economy and supports a range of commercial, industrial, and recreational activities (Fergen et al., 2022; Campbell et al., 2015). The lakes are rich in biodiversity, hosting over 3,500 species of plants and animals, many of which are endemic to the region (Michalak, 2017). Over the last century, the Great Lakes have experienced a growing number of ecological disturbances related to the expansion of human activities in the basin. Activities such as urbanization, agriculture, and resource extraction have led to declines in water quality, with the most pressing challenges being eutrophication and harmful algal blooms (HABs), freshwater salinization, invasive species, and historical and emerging contaminants (Beeton, 2002). The most substantial impacts have occurred in the lower Great Lakes, as the highest concentration of urban areas, intensive agriculture, and industry are found in these basins. Given the immense ecological and economic importance of the Great Lakes, extensive research and management efforts have been undertaken to address these challenges.

1.2.1 Historical and current trends in nutrient enrichment

The occurrence of cultural eutrophication in the lower Great Lakes dates back to the nineteenth century, when P loading gradually increased from early European settlement and forest clearing for agriculture (Schelske et al., 1983). In the mid-twentieth century, P loading increased exponentially following the introduction of phosphate detergents, use of commercial fertilizers, and expansion of sewer systems (Small, 2018). By the late 1960s, Lake Erie was referred to as a "dead lake" due its severe eutrophication, evidenced by proliferations of HABs, extensive hypoxia, and shifts in benthic and fish fauna (Small, 2018). In response, a number of bi-national P abatement measures aimed largely at point source municipal and industrial inputs were implemented through the 1972 Great Lakes Water Quality Agreement between Canada and the United States (Small, 2018). These remedial measures, which primarily consisted of wastewater treatment upgrades and elimination of phosphates in commercial detergents, considerably reduced TP inputs into the lower lakes (Small, 2018). Between 1972 and 1985, annual P loading from municipal discharge to Lake Erie declined by 84% from 15,300 tons to 2,500 tons (Makarewicz and Bertram, 1991). Lake Erie responded quickly to these load reductions, with measurable decreases in offshore TP concentrations, phytoplankton biomass, and bottom-water hypoxia, while several ecologically and economically important fish species also made a recovery (Makarewicz and Bertram, 1991).

Despite initial success of these actions, HABs and hypoxia returned to the lower Great Lakes in the mid-1990s and have since been recurring with increased frequency and magnitude (McKindles et al., 2020). Compared to the algal blooms of the mid-1900s, current blooms are characterized by an increased presence of toxin-forming strains of cyanobacteria (e.g., *Microcystis*, *Dolichospermum*, *Planktothrix* spp.) and an excessive growth of nuisance macro-algae such as *Cladophora* spp. (Watson et al., 2016). Previous outbreaks of cyanobacteria HABs that peaked in mid-summer are now replaced by annual outbreaks of extensive blooms that persist throughout the summer and late fall (Watson et al., 2016). In the summer of 2011, Lake Erie experienced the largest *Microcystis* bloom in its recorded history, with an extent of over 5,000 km^2 and a peak intensity three times greater than any of its previously observed blooms (Michalak et al., 2013; see Stumpf et al. 2012 for measures of peak intensity). In Lake Ontario, cyanobacteria HABs have become common in regions such as Hamilton Harbour and the Bay of Quinte (Munawar and Fitzpatrick, 2018). With the growing prevalence of cyanobacteria HABs, the protection of water supplies is becoming increasingly challenging. In August 2014, the city of Toledo, Ohio detected hazardous concentrations (>1 $\mu g\ L^{-1}$) of microcystin in its municipal water supplies, resulting in a "do-not-drink" advisory that left over 450,000 residents without drinking water for three days (Stumpf et al., 2016). Exposure to cyanobacterial toxins via drinking water is linked to a variety of deleterious health effects from gastroenteritis to liver and kidney failure, and the removal of these toxins increases water treatment costs (He et al., 2016). In addition to cyanobacteria HABs, there has been a recurrence of nuisance algae blooms each summer in the eastern basin of Lake Erie; blooms along the northern and southern shores of Lake Ontario have also been reported (Watson et al., 2016; Munawar and Fitzpatrick, 2018). Expansive blooms of *Cladophora* spp. have fouled beaches and shorelines, clogged water intakes, and produced unpleasant odours, threatening socioeconomically important tourism and fishing industries (Watson et al., 2016; Howell et al., 2018).

There are a number of factors that may have led to the re-emergence of eutrophication-related issues in the Great Lakes over the past two decades. Following historical point source reductions of P, non-point source contributions from land use have become the largest source of nutrients entering the lakes (Watson et al., 2016). In recent years, changes in non-point source loads of N and P delivered by tributaries have been observed. While TP inputs have declined and remained relatively constant since the mid-1990s, the fraction of TP as soluble reactive phosphorus (SRP), a form of P highly bioavailable to cyanobacteria and nuisance algae, has increased in Lakes Erie and Ontario (Dove and Chapra, 2015), as well as in agricultural tributaries entering these lakes (Joosse and Baker, 2011; Michalak et al., 2013; Scavia et al., 2014). At the same time, stream NO_3-N concentrations in the basin have increased since the 1970s (e.g., Richard and Baker, 1993; Eimers and Watmough, 2016), corresponding to a simultaneous increase in offshore NO_3-N concentrations in the Great Lakes (Dove and Chapra, 2015). Growing evidence suggests that although P may control total phytoplankton biomass in freshwater, the supply and chemical speciation of N play a key role in phytoplankton community composition and toxin production

(Watson et al., 2016). Green algae and diatoms are abundant when both N and P are available; however, P-enriched systems with low levels of N provide cyanobacteria, particularly N_2-fixing species, a competitive advantage over other types of phytoplankton (Small, 2018). Moreover, specific chemical species of N, such as urea, have been found to be an energetically favorable nutrient source, potentially facilitating cyanobacteria HABs and influencing toxicity (Finlay et al., 2010). Increases in both SRP and NO_3-N concentrations have been predominantly attributed to changes in agricultural land use and associated land use practices.

Although external nutrient loading is considered the primary driver of recent re-eutrophication trends, factors internal to the lake can also influence algal productivity, such as the presence of invasive dreissenid mussels. During the late 1980s to early 1990s, widespread colonization of zebra (*Dreissena polymorpha*) and quagga (*Dreissena rostriformis bugensis*) mussels initially helped magnify water quality improvements from P abatement by acting as a sink for P (Auer et al., 2010; Dolan and Chapra, 2012). These improvements, however, were eventually offset by dreissenid-induced shifts in light regime and internal nutrient cycling in the lakes to conditions that favoured cyanobacteria HABs and the resurgence of *Cladophora* in nearshore regions (Auer et al., 2010). Selective feeding of zebra mussels likely promoted the dominance of *Microcystis*, as large colonies of *Microcystis* have been shown to be expelled as pseudofeces while other forms of phytoplankton are digested (Vanderploeg et al., 2001). Both zebra and quagga mussels can mobilize P from lake sediments and increase the availability of dissolved P which has been linked to increases in cyanobacteria HABs (Turner, 2010). Furthermore, improved water clarity and light penetration from dreissenid filtering, combined with the increased availability of substrate for attachment due to dreissenid expansions in the littoral zone, have facilitated the growth of *Cladophora* to greater depths and previously inhabitable areas (Kuczynski et al., 2016). Increases in internal P loading may have also stimulated cyanobacterial blooms. Anoxic events, for example, have been found to increase the release of P from sediments, whereas bioturbation and P remineralization from benthic invertebrates and fish are other mechanisms that can affect internal nutrient recycling (Conroy et al., 2005). However, quantification of the timing and amount of the release of legacy P from sediment is difficult, and generally, anthropogenic-derived external inputs of P to surface waters via overland flow is the primary determinant of downstream trophic status.

In conjunction with these external and internal factors, climate change has likely exacerbated the prevalence of cyanobacteria HABs through lake warming and increased nutrient delivery associated with extreme precipitation events. Warmer temperatures can extend the bloom season and accelerate the growth of multiple toxin-producing HABs (Wells et al., 2015). Higher temperatures also lead to prolonged periods of thermal stratification in the lakes, which tend to favor the development of surface blooms of buoyant cyanobacteria such as *Microcystis* and *Dolichospermum* (Wells et al., 2015). Since most P inputs are delivered during precipitation-driven high flow events, trends toward more intense and frequent storms in the late winter and early spring could lead to higher nutrient runoff, consequently increasing overall loads (Scavia et al., 2014). Modeling efforts by Daloğlu et al. (2012) demonstrated that recent increases in storm events have contributed to elevating SRP loads in the Sandusky watershed after the mid-1990s. Similarly, Michalak et al. (2013) attributed the massive *Microcystis* bloom in 2011 to record-breaking SRP loads produced by severe spring precipitation events coupled with trends in agricultural land use. Changes to climate oscillations and their atmospheric teleconnections (e.g., El Nino–Southern Oscillation, Pacific-North American teleconnection pattern) resulting from climate change can alter hydrometeorological conditions in the Great Lakes region (Tewari et al., 2022). Incorporation of large-scale climate indices alongside nutrient loading has been found to enhance the quality of HAB prediction in Lake Erie in a machine learning approach (Tewari et al., 2022), demonstrating the significance of meteorological factors in explaining the variability in the occurrence of HABs. Given the compounding influence of climate change, it is clear that cyanobacterial blooms and hypoxic events that have re-emerged in the lower Great Lakes will persist into the future unless management actions are taken (Michalak et al., 2013).

1.2.2 Salinization trends in the lower Great Lakes

Freshwater salinization is the process by which concentrations of dissolved salts increase in water and can often be identified from an increase in Cl, as it is an anion found in numerous salt compounds (Kaushal et al., 2005). Since the start of the 20th century, Cl concentrations in the Great Lakes, aside from Lake Superior, have steadily increased (Chapra et al., 2009). After reaching maximum levels in the late 1960s, concentrations in Lakes Huron, Erie, and Ontario substantially decreased, but then began to increase again beginning in the 1980s (Chapra et al., 2009). The declines in the 1960s were primarily a result of reductions in industrial discharge within the lake basins (Chapra et al., 2009). For instance, between 1965 and 1986, Cl loadings in Lake Erie decreased by 1,700 kilotonnes per annum (kta), a change that was attributed to the closure of industrial facilities along the Detroit River (Crucil et al., 1991). Similarly, Lake Ontario experienced a decline of 700 kta in Cl loading after the discontinuation of chlor-alkali production near Onondaga Lake in 1986 (Effler et al., 1990). The increases in Cl concentrations in recent years, however, appear to be linked to non-industrial sources, mostly notably the use of road salt (Chapra et al., 2009). Since the late 1970s, road salt usage for de-icing has been growing at an annual rate of 2 – 3% in the United States, with similar rates reported in Ontario (Chapra et al., 2009). Much of this usage occurs in the Great Lakes basin, particularly in the densely populated regions of southern Ontario (e.g., Greater Toronto Area) and cities in the northeastern states (Detroit, Cleveland). Correspondingly, road density, impervious surface coverage, and other urban metrics have been found to correlate with increased stream and lake Cl levels (e.g., Kaushal et al., 2005; Dugan et al., 2017; Mazumder et al., 2021). As parts of the Great Lakes basin continue to urbanize, elevated Cl concentrations may lead to widespread ecosystem impacts. Increases of Cl and other ions can foster the spread of halophilic organisms, altering the composition and function of aquatic communities (Stoermer, 1978). In extreme cases, rising salinity can intensify lake stratification and subsequently create anoxic conditions in the hypolimnion (Radosavljevic et al., 2022). This, in turn, enhances internal P loading to the water column (Radosavljevic et al., 2022), exacerbating eutrophication problems currently recurring in many parts of the lower Great lakes. Although recent increases have been mainly linked to road salt, other non-industrial sources (e.g., water softeners, KCl use in agricultural fertilizers), and new industrial inputs possibly have played a part as well, and it is difficult to definitively determine the underlying mechanisms (Chapra et al., 2009). Nevertheless, it appears that diffuse sources now have a greater impact compared to past influences and ongoing monitoring and management efforts must be supported to mitigate this issue.

1.3 Land use change in southern Ontario and water quality implications

Land use has been considered an important driver of changes in contaminant loading associated with recent nutrient enrichment and salinization trends in the Great Lakes. Within the lower Great Lakes basin, southern Ontario is a region that has experienced notable shifts in land use, specifically urban development and agricultural intensification (Eimers et al., 2020).

1.3.1 Urban development

Since 1971, the population of Ontario has doubled from 7.8 million to 14.6 million in 2019, with most of this growth occurring in urban areas in southern Ontario (Ministry of Finance, 2020). Urban areas in southern Ontario expanded alongside the growing population, increasing from 3,800 km^2 to 7,715 km^2 between 1971 and 2019. As the provincial population is projected to grow by an additional 35% over the next two decades (Ministry of Finance, 2020), further increases in urbanization will have significant implications for water quality. Road salt (mainly NaCl) is used as a de-icing agent on impervious surfaces to maintain public safety in the winter and has been applied at an increasing rate parallel to that of urban growth (Environment Canada, 2001). Urban areas in southern Ontario have one of the highest road salt usage rates on an area basis in Canada (Environment Canada, 2001). Most of the road salt in the winter and early spring is flushed directly to streams via stormwater drainage systems, while some are retained in groundwater and soil, serving as a source of Cl to surface waters via baseflow year-round (Rhodes et al., 2001). Mazumder et al. (2021) reported that increases in winter stream Cl concentrations across southern Ontario between the periods of 1965–1995 and 2002–2018 were largely explained by variance in urban growth. Likewise, a comprehensive analysis of Cl trends in surface and groundwaters of Ontario determined that Cl concentrations are highest and continuing to rise in urbanized and populated regions, notably throughout southern Ontario (Sorichetti et al., 2022).

Besides contributing to freshwater salinization, urban expansion can also impact nutrient delivery. With increasing coverage of impervious surfaces, urbanization can lead to flashier flows that are associated with greater erosion and transport of nutrient-laden runoff into streams, thereby increasing nutrient loading to lakes (Konrad and Booth, 2005). In urban streams draining into Hamilton Harbour, for example, over 50% of TP loads occurred during high flow, intense storm events (Long et al., 2015). Large areas within many municipalities across southern Ontario, such as Toronto, London, and Windsor, still rely on combined sewer systems, which can release a mixture of untreated, nutrient-rich sewage into waterways following heavy storm events and snowmelt. More efficient conveyance of runoff associated with increasing urbanization can exacerbate overflow events from these combined sewers. In addition, although point source pollution from municipal wastewater treatment plants (WWTPs) have largely declined since the 1970s, municipal and industrial wastewater effluent remains an important source of both N and P (Robertson et al., 2019). The conversion of natural or agricultural landscapes to urban areas often involves extensive land clearing and soil disturbance (Carpenter et al., 1998). Soil erosion can be particularly large from construction sites, carrying soil-bound nutrients to downstream water systems (Carpenter et al., 1998).

1.3.2 Agricultural intensification

Agricultural intensification, specifically the conversion from mixed crop and livestock farming to intensive row crop production (primarily corn and soybean), has been linked to increasing stream nutrient levels across southern Ontario (Liu et al., 2022). While the total farmland area in Ontario declined by 18% between 1976 and 2011, grain corn and soybean acreage expanded by 29% and 552%, respectively, mostly at the expense of pastureland (Smith, 2015). This shift in cropping system has been partly driven by urbanization, as growing populations are expanding into surrounding farmland, placing increased pressure on remaining agricultural areas to intensify production and maximize yields. Advancements in agricultural technology and increased market demand for row crops as sources of food, feed, fiber, and bioenergy have further increased the profitability of intensive crop-based agriculture (Smith, 2015).

The transition towards row crops has been associated with increases in nutrient inputs. Widespread use of inorganic N and P fertilizers has boosted crop yields, but the accumulation and runoff of these nutrients has also been a major contributor to increasing stream nutrient concentrations. Nutrient export from row crops is typically much higher than that from pasture-based agriculture. A three-year study in Missouri reported NO_3-N and TP losses from row cropped watersheds that were 20-times and four-times greater, respectively, than from pasture-dominated watersheds (Udawatta et al., 2011). Increased stream NO_3-N concentrations were observed after conversions of perennial grasses to row crops in Squaw Creek watershed, Iowa (Schilling and Spooner, 2006). The adoption of agricultural practices such as surface broadcasting of fertilizers, fertilizer application in proximity to storm events, and conservation tillage have been linked to higher SRP runoff (Daloğlu et al., 2012).

The extent of tile drainage has expanded rapidly alongside increases in row crop production and fertilizer usage in southern Ontario (Smith, 2015; Eimers et al., 2020). Tile drainage systems remove excess water from the soil profile during periods of high water input (e.g., large precipitation events, snowmelt) and have been fundamental in facilitating the expansion of row crops across poorly drained soils in southern Ontario. Although tile drainage can decrease erosion and subsequently the loss of particulate-associated nutrients, there is mounting evidence that tile drainage can expedite the transfer of dissolved N and P from the rooting zone to tributaries (see review by Skaggs et al., 1994). Tile-drained row crop area in watersheds has been positively correlated with both NO_3-N and SRP concentrations in streams of south-central Ontario (Liu et al., 2022). Tile drainage was determined to be the main mechanism of NO_3-N loss at an experimental site in southwestern Ontario, with the highest NO_3-N concentrations in tile drainage water observed under continuous corn rotation compared to other rotations over a three-year study period (Tan et al., 2002). Lam et al. (2016) reported the greatest annual P losses through drainage tiles during the non-growing season in southern Ontario, when tile drains were most active. Overall, pervasive shifts in southern Ontario towards intensive row crop agriculture, along with management practices such as increased fertilizer application and improved drainage, may have increased tributary NO_3-N and SRP concentrations, ultimately altering nutrient delivery to the lower Great Lakes.

1.4 Stream water quality monitoring in southern Ontario

With tributary loading now representing the largest input of nutrients to the lower lakes (e.g., Makarewicz et al., 2012), water quality monitoring in streams is a key component in efforts to manage non-point sources. In Ontario, long-term stream water quality monitoring has been conducted through the Provincial Water Quality Monitoring Network (PWQMN) since the 1960s (Sorichetti et al., 2022). The PWQMN currently includes over 400 stream locations that are sampled monthly by Conservation Authorities and analyzed for a range of water quality parameters, including nutrients and Cl (Sorichetti et al., 2022). Since the establishment of the network, the landscape across southern Ontario has experienced pervasive land use changes. Agricultural intensification and increased urbanization have modified hydrological patterns and increased pollutant availability and mobility to surface waters (Eimers et al., 2020). There may be a need to adjust monitoring locations to ensure that the spatial coverage of the network adequately captures the impact of these land use shifts. Another challenge to monitoring is that nutrient export fluctuates by season and hydrologic conditions. Phosphorus, for example, binds readily to soil particles and is thus transported in the greatest volumes via surface runoff and erosion during high flow events. Sampling at regular intervals may miss these important episodic events. In temperate climate areas such as southern Ontario, stream NO_3-N concentrations tend to vary seasonally, peaking during the non-growing season when plant uptake is minimal (Van Meter et al., 2020). Runoff of road salt typically cause higher Cl stream concentrations in the winter, although summer baseflow can also be elevated from groundwater contributions (Dugan et al., 2017). Monitoring year-round is hence essential to account for seasonal variability in concentrations and flows. Climate change further complicates monitoring as more frequent, intense rainfall and melt events could exacerbate nutrient runoff. Meanwhile, limited resources constrain how comprehensively monitoring can be conducted. Strategies are needed to ensure the sampling regime does not introduce seasonal, location, or hydrological biases that impact trends over time.

1.5 Study objectives and hypotheses

While point sources of nutrients and Cl to the lower Great Lakes have been largely mitigated, non-point sources originating from land use activities that are associated with recent recurrent eutrophication and salinization issues are still not well understood. In southern Ontario, two major land use shifts – urban development and agricultural intensification – have occurred concurrently with the re-emerging water issues. Potential links between land use practices from these shifts and changes in tributary loading have been suggested by a growing number of studies, however, existing research on land use change and water quality in southern Ontario has focused predominantly on the highly agricultural region of southwestern Ontario, leaving many areas across the region understudied. While relationships between stream nutrient concentrations and row crop production have been demonstrated within a number of small watersheds in Ontario (e.g., DeBues et al., 2019; Liu et al., 2022, Raney and Eimers, 2014a), it is unclear whether these relationships can still be detected across a broader geographic scale such as in southern Ontario, a larger, more heterogeneous region where there is a diversity of soil types, topography, climate gradients, and land uses that could potentially obscure the relationships previously identified at a small scale. Additionally, previous research has often focused on one nutrient (e.g., Long et al., 2014; Kim et al., 2016; Stammler et al., 2017), rather than both N and P despite growing evidence that both nutrients can co-limit aquatic primary production. A more comprehensive characterization of patterns in land use and stream chemistry across southern Ontario could help advance the understanding of landscape impacts and contribute to efforts to reduce tributary loading to the lower lakes. In addition, water quality information used to evaluate these relationships is often derived from long-term provincial monitoring programs. Although stream water quality monitoring in Ontario has been conducted for over five decades, it is uncertain whether existing sampling strategies are suited to capture impacts from recent land use shifts and climate change. Therefore, to address these knowledge gaps, the overall objectives of this thesis were to (a) identify relationships between land use patterns and stream NO_3-N, TP, and Cl across southern Ontario (Chapter 2); and (b) analyze existing long term stream monitoring data to identify potential limitations from the sampling program to focus future research and monitoring efforts (Chapter 3).

In Chapter 2, I explored the spatial variability in land use and landscape physiography across southern Ontario and potential relationships with stream water quality. Watersheds were first classified into clusters based on similarities in land use attributes/landscape features using a self-organizing map (SOM) analysis. The SOM was used for land use characterization as it is an unsupervised neural network algorithm that can extract prevalent patterns from high-dimensional data and is well suited to model complex, non-linear systems. Relationships were then determined between the clusters and stream decadal mean (2011 – 2020) concentrations of NO_3-N, TP, and Cl from the ice-free period (April – November). I hypothesized that elevated levels of NO_3-N in streams would be associated with row crop agriculture even when examined across a wide geographic range due to the high solubility and mobility of NO_3-N. In contrast, the linkage between land use and TP in streams was anticipated to exhibit more variability, as TP concentrations respond more to precipitation events that mobilize phosphorus from the landscape. Finally, since Cl delivery to waterways is primarily driven by road de-icing activities, pervasive stream enrichment of Cl was predicted across all cluster types as a result of the ubiquitous road network present throughout the study area; however, the highest stream Cl levels were expected within clusters containing greater urban development and human population densities due to the associated increase in roads and de-icing activities in these areas.

In Chapter 3, I characterized sampling trends of Ontario's Provincial Water Quality Monitoring Network (PWQMN) program to evaluate its capacity to detect water quality impacts from changes in climate and land use over time. Examining the full dataset also provided insight into how my data selection may have influenced findings of the previous chapter. Specifically, in Chapter 2, I only included water chemistry records from sites with minimal WWTP contamination that were collected during the ice-free period to isolate for the effects of non-point sources while addressing limitations around reduced winter sampling post-1990s. Thus, for Chapter 3, I first analyzed trends in sampling frequency and seasonality across the full period of record from 1964 to 2019. To explore the impacts of declining winter sampling, I compared stream NO_3-N, TP, and Cl concentrations in the ice-free (April – November) and ice-covered (December – March) periods over the past five decades. Finally, I assessed decadal mean (2010 – 2019) stream TP and NO_3-N concentrations at sites downstream of WWTPs and at sites without any known upstream point sources. I hypothesized that the highest concentrations of NO_3-N, TP, and Cl would occur in the ice-covered period, whereas WWTP and greenhouse discharge influenced streams would have elevated NO_3-N and TP concentrations.

Chapter 2: Land use and water quality in southern Ontario

2.1 Introduction

Eutrophication of surface waters and HABs resulting from excessive inputs of P and N threaten human health and aquatic ecosystems around the world (Smith and Schindler, 2009). In the North American Laurentian Great Lakes, early nutrient reduction efforts targeting point sources of P have improved water quality; however, the recent resurgence of HABs has shifted attention towards the management of non-point sources, especially from agriculture and urban areas (Watson et al., 2016). Despite the decline in TP loads in the Great Lakes (Dolan and Chapra, 2012), loadings of SRP, a highly bioavailable form of P conducive to algal growth, entering Lakes Erie and Ontario from agricultural tributaries have increased (Jarvie et al., 2017). Furthermore, although P is often the limiting nutrient in freshwater systems (Sharpley et al., 1994), there has been growing recognition that N limitation or the colimitation of both nutrients may be more significant than previously determined, prompting many to advocate for the simultaneous control of P and N (e.g., Elser et al., 2007; Conley et al., 2009; Lewis et al., 2011; Wurtsbaugh et al., 2019; Paerl et al., 2020). Rising NO_3-N concentrations in drinking water supply associated with N-enriched agricultural runoff have also caused alarm over potential health hazards to humans and wildlife (Camargo and Alonso, 2006). Another contaminant of concern is Cl, as marked increases in Cl concentrations in surface and groundwater within the Great Lakes region over the past decade due to winter road salt applications can alter aquatic community composition and corrode infrastructure (Chapra et al., 2009; Sorichetti et al., 2022). These trends have since led managers to focus greater attention on understanding and controlling non-point sources from land use in the Great Lakes basin.

Agricultural and urban land use have varying impacts on contaminant delivery to surface waters. In southern Ontario, shifting practices related to agricultural intensification include the increase in row crop (i.e., corn and soybean) production, expansion of subsurface tile drainage, and greater reliance on commercial fertilizers (Smith, 2015; Eimers et al., 2020). Southern Ontario generates the most significant proportion of soybean, corn, and winter wheat production in the country, accounting for 60%, 50%, and 57% of the national area of each crop in 2016, respectively (Statistics Canada, 2017). Substantial growth in soybean (+552%) and grain corn (+29%) acreage between 1976 and 2011 in Ontario has occurred alongside major declines in hay (-27%) and pasture (improved + unimproved; -102%) area over the same time period (Smith, 2015). Increases in row crops at the expense of pasture and livestock have been linked to elevated tributary NO_3-N and SRP concentrations (Schilling and Libra, 2000; Liu et al., 2022), which are speculated to have contributed to the similar nutrient trends in the lower Great Lakes (Dove and Chapra, 2015). Intensive row crop fields are often underlain by tile drainage to improve crop production; however, the consequent enhanced hydrological connectivity between fields and streams, along with the increased efficiency of runoff conveyance, can expedite nutrient transport (King et al., 2015). In addition, even though the adoption of conservation tillage has reduced sediment and particulate P loss, this practice may have inadvertently augmented SRP losses in tile drained landscapes, as it can favour the development of preferential flow pathways and the accumulation of labile P fractions at the soil surface that can be readily mobilized in runoff (Jarvie et al., 2017). While the application of N fertilizers has increased to support intensifying row crop agriculture, the dominant type of commercial N fertilizer used has shifted from ammonium nitrate to urea (Gilbert et al., 2014), a dissolved form of organic N that has been found to stimulate blooms of *Microcystis* and other cyanobacterial HABs as well as influence toxicity (Davis et al., 2010; Belisle et al., 2016; Paerl et al., 2016). Land use changes associated with urbanization also serve as non-point sources of pollution. Studies have reported correlations between higher development density and greater nutrient exports (Carle et al., 2005; Duan et al., 2012). Increases in impervious cover can lead to higher stream flashiness and more frequent peak flow events, which in turn, facilitate movement of pollutants to urban waterways (Konrad and Booth, 2005). The conversion of farmland to residential development involves construction activities that significantly disturb the soil and increase erosion and sediment transport, driving high stream P and N concentrations in urban catchments (Hopkins et al., 2017; Duval, 2018). However, newer urban developments with effective stormwater and erosion management measures, such as stormwater management ponds designed to slow runoff and capture pollutant-laden sediments, tend to have lower nutrient losses than older urban centers that drain directly into tributaries (Eimers et al., 2020). In addition to agricultural and urban land use changes, other factors including climate change, legacy nutrients, and invasive species further complicate nutrient dynamics and their impacts on water quality (Hecky et al., 2004; Joosse and Baker, 2011; Sharpley et al., 2013).

Although numerous studies have documented associations between watershed land use and nutrient loading to surface waters, considerable variation exists in the relationship between land use and water quality at the scale of entire watersheds (Omernik, 1977; Puckett, 1995; Jones et al., 2001; Allan, 2004). Part of this variability may be due to differences in land use types, practices, and intensities among watersheds (Eimers et al., 2020), but may also be attributed to inherent differences in watershed physiographic characteristics (e.g., hydrology, geology, soil type, and topography), which can affect watershed transport and subsequently the extent to which land use impacts water chemistry (Fraterrigo and Downing, 2008; Lintern et al., 2018). Despite extensive research in watershed science over the past decades, knowledge gaps remain in the understanding of the complex interplay between land use patterns, hydrological factors, and landscape physiographic features that control the export rates of nutrients within watersheds (Rode et al., 2010). Moreover, most previous studies examining the connections between land use and water quality rely on conventional statistical approaches (Giri and Qiu, 2016), such as Pearson's correlation analysis (Buck et al., 2004; Lee et al., 2009; Rodrigues et al., 2017), multiple linear regression (Ahearn et al., 2005; Dodds and Oakes, 2007; Nielsen et al., 2012), and principal component analysis (Carle et al., 2005; Tran et al., 2010). These approaches are commonly adopted because of their simplicity and speed, however, have assumptions of linearity between variables. Yet, hydrological systems are highly complex and dynamic, and a wide range of interrelated variables can affect water quality. Many statistically based tools may hence be inadequate when analyzing non-linear dependencies that are characteristic of such systems (Kim et al., 2018). To overcome this limitation, researchers have increasingly used non-linear methods, most notably artificial neural networks, for applications in water resources and hydrology (Maier and Dandy, 2000).

In particular, the SOM has been effectively employed to explain water quality patterns associated with land use and socio-environmental management (Kim et al., 2016; Neumann et al., 2017; Zhang et al., 2018; Gu et al., 2019). The SOM is an unsupervised artificial neural network that extracts information from large multi-dimensional datasets and maps it onto reduced dimensional space (Kohonen, 2013). Preserving topological relationships in the process, the algorithm produces a visualization of essential features that can be intuitively and meaningfully interpreted (Rauber et al., 2002). This method is appropriate for examining the relationship between land use and water quality across southern Ontario, a highly heterogenous region under growing pressures of urbanization and agricultural intensification. Although associations between agricultural land use, specifically row crop production, and increased N and P loss have been widely reported, previous studies in Ontario have been conducted on a small scale, such as at the field level (e.g., Tan et al., 2002; Lam et al., 2016), across a small number of watersheds (e.g., DeBues et al., 2019; Liu et al., 2022, Raney and Eimers, 2014a), or within a small geographic region (e.g., southwestern Ontario [Thomas et al., 2018; Nelligan et al., 2021]). In addition, most studies have primarily focused on one nutrient only (e.g., Long et al., 2014; Kim et al., 2016; Stammler et al., 2017). A more comprehensive characterization of patterns in stream water quality, using both nutrients, N and P, as well as Cl, an important contaminant in waterways, across a broader geographic scale in Ontario can provide better insight into landscape drivers of changes in the lower Great Lakes as well as inform land use planning and water resource management to address persistent eutrophication issues in the basin.

The overarching purpose of this study was to characterize the spatial variability in land use and landscape physiography across southern Ontario and test whether land use relationships with tributary water quality can be observed at a broader spatial scale amidst the wide range of soils, climate conditions, and land use within the study area. Specific objectives were to (a) classify watersheds in southern Ontario into clusters based on similarities in land use and landscape features using an SOM analysis, and (b) identify linkages between the clusters and tributary decadal mean (2011 – 2020) concentrations of NO_3-N, TP, and Cl; three water quality parameters that are frequently associated with agricultural and urban development. Relationships between stream NO_3-N with row crop agriculture and related land use practices (e.g., fertilizer and manure application, tile drainage) were expected even across a broad geographic scale due to the high solubility and mobility of NO_3-N and the strong influence of N inputs associated with row crop production. In contrast, the relationship between land use and stream TP was expected to be more variable than for NO_3-N, as TP is more sensitive to flow events. Lastly, as elevated Cl levels are most associated with de-icing activities, the enrichment of streams with Cl was predicted to be pervasive across all types of clusters due to the ubiquitous presence of roads throughout the landscape, but Cl concentrations will be highest in clusters with more urban areas and human population densities.

2.2 Methods

2.2.1 Study area

Southern Ontario encompasses an area of approximately 80,000 km^2, accounting for about 10% of the area in the province (Crins et al., 2009). Despite its small footprint, the region is home to over 12 million people, nearly one-third of the population of Canada, with the majority residing in large metropolitan centers located along the northern shoreline of Lake Ontario. The gentle topography, rich fertile soils, warm growing season, and abundant rainfall support extensive agriculture and woodlands across the region (Sharpe et al., 2014; Figure 2.1; Figure A1; Figure A4). Most soils in southern Ontario are tile drained, with over 40% (17,600 km^2) of croplands underlain by subsurface tile drainage networks (Figure A2). The bedrock in this region is primarily limestone, sandstone, and shale, overlain by surficial materials with till, glaciofluvial, and glaciolacustrine deposits predominating (Crins et al., 2009; Figure A3). All study watersheds are contained within the Ontario Mixedwood Plains ecozone which has a humid continental climate with warm summers and cold winters (Sharpe et al., 2014). To characterize regional climate conditions in the study area, long-term climate normals (1981 – 2010) from 27 meteorological stations across southern Ontario (shown in Figure 2.1) are presented in Table 2.1. Based on records from these stations, annual mean temperature and precipitation in the study area range from 5.8°C (Dalhousie Mills) to 9.9°C (Windsor), and 831 mm (Toronto) to 1247 mm (Blyth), respectively.

2.2.2 Watershed delineation

The study region was divided into watershed units in preparation for the SOM analysis. First, water quality monitoring stations were selected from the Ontario Provincial Water Quality Monitoring Network (PWQMN), a long-term stream monitoring program established in 1964 currently delivered by the Ontario Ministry of the Environment, Conservation and Parks (MECP) in collaboration with conservation authorities (MECP, 2020). The selection criteria of monitoring stations were based on the following conditions: (a) available NO_3-N, TP, and Cl concentration data in each year from 2011 to 2020; (b) within the Mixedwood Plains ecozone; (c) did not have any WWTP upstream; and (d) not located at a lake outlet (Table 2.2). Locations of WWTPs were identified with the assistance of conservation authorities and the MECP PWQMN lead scientist. Most sites do not have upstream WWTPs, and the few sites that did (9%)

were located at least 20 km downstream to minimize influence. Although the Salmon River and Napanee River PWQMN sites extend into the Canadian Shield, both were included in this study as they drain to the Bay of Quinte, which remains an Area of Concern in Lake Ontario (Arhonditsis et al., 2019). The upstream watersheds of these selected stations were then delineated using the sampling locations as drainage pour points in the Ontario Watershed Information Tool (OMNRF, 2022a). Watersheds in the remaining study area that were either ungauged or had stations that did not meet previous criteria were delineated using corresponding tributary mouths as pour points and the authoritative quaternary watershed boundaries of Ontario as reference (OMNRF, 2022b). Approximately 40% (31,969 km^2) of the study area is drained by streams with water quality records (meeting the criteria) over the study period (Figure 2.2).

Figure 2.1 Climate stations from Environment and Climate Change Canada (ECCC), general land use, and landform features in southern Ontario. Climate stations are labelled as follows: Barrie (BAR), Belleville (BEL), Blyth (BLY), Brockville (BRO), Chatham (CHA), Cobourg (COB), Cornwall (COR), Dalhousie Mills (DAL), Fort Erie (FTE), Godfrey (GOD), Hagersville (HAG), Hamilton (HAM), Hanover (HAN), Kingston (KIN), London (LON), New Glasgow (NGL), Orangeville (ORA), Oshawa (OSH), Ottawa (OTT), Peterborough (PET), Sarnia (SAR), South Mountain (SOU), St. Catharines (STC), Toronto (TOR), Waterloo (WAT), Wiarton (WIA), Windsor (WIN).

Table 2.1 Long-term average (1981–2010) annual temperature, annual precipitation, and agroclimatic indicators within southern Ontario, with Environment and Climate Change Canada climate stations ordered from west to east. Locations of climate stations are shown in Figure 2.1.

Station	Annual Temperature					Annual Precipitation				Agroclimatic Indicators	
	Average (°C)	Max (°C)	Min (°C)	T_{min} < -20°C (days)	T_{max} > 30°C (days)	Average (mm)	Rainfall (mm)	% Snowfall	Precip ≥ 10 mm (days)	Degree days > 5°C	Frost-free period (days)
Windsor	9.9	14.4	5.4	1	24	935	822	14	30.6	2688	195
Sarnia	8.3	13.0	3.7	2	15	878	770	13	27.0	2276	172
Chatham	9.8	14.1	5.4	1	17	882	803	9	28.4	2632	185
New Glasgow	8.7	13.0	4.4	2	6	952	871	9	32.7	2334	163
Blyth	7.2	11.5	2.8	5	11	1247	873	30	43.3	2120	143
London	7.9	12.7	3.0	4	10	1012	846	19	31.7	2211	164
Wiarton	6.6	11.2	1.9	7	4	1048	751	39	32.0	1881	148
Hanover	6.7	12.1	1.4	9	8	1087	820	25	34.5	1981	124
Waterloo	7.0	12.0	2.0	6	8	917	777	17	29.2	2033	147
Orangeville	6.3	11.3	1.3	9	6	902	750	17	29.4	1915	132
Hagersville	8.4	13.1	3.7	2	12	956	863	10	30.6	2311	158
Hamilton	7.9	12.7	3.1	3	11	930	792	17	30.6	2212	167
Barrie	6.9	12.0	1.9	12	10	933	710	24	28.9	2107	153
Toronto	9.4	12.9	5.9	1	12	831	714	15	27.0	2506	203
St. Catharines	9.0	13.6	4.4	1	14	880	754	16	28.2	2408	179
Fort Erie	8.6	13.2	4.0	3	5	1051	876	17	34.8	2304	160
Oshawa	8.1	12.1	4.1	3	4	872	766	12	28.6	2153	168
Peterborough	6.2	12.1	0.3	17	9	855	713	18	27.2	1916	132
Cobourg	7.5	11.8	3.1	5	1	890	794	11	30.7	2015	158
Belleville	8.1	12.6	3.6	8	8	912	772	15	29.9	2330	171
Godfrey	6.5	12.0	1.0	19	10	940	766	18	29.6	2059	132
Kingston	7.8	12.1	3.6	9	4	951	792	17	30.6	2272	169
Ottawa	6.6	11.4	1.9	17	12	920	756	19	28.7	2182	158
Brockville	7.5	11.9	3.1	9	5	987	807	18	30.7	2231	166
South Mountain	6.3	11.4	1.2	20	10	948	752	21	29.7	2097	139
Cornwall	7.6	12.1	3.1	9	12	1012	831	18	32.9	2337	164
Dalhousie Mills	5.8	11.3	0.2	25	9	1077	839	22	35.7	1989	128

Table 2.2 Number of PWQMN stations that remained after every stage of the selection process

Criteria	Number of stations
Original PWQMN dataset	2138
Available data from 2011 to 2020	415
Within Mixedwood Plains ecozone	359
Not lake outlets	354
Not influenced by WWTPs	230
NO3-N, TP, and Cl monitored concurrently	179

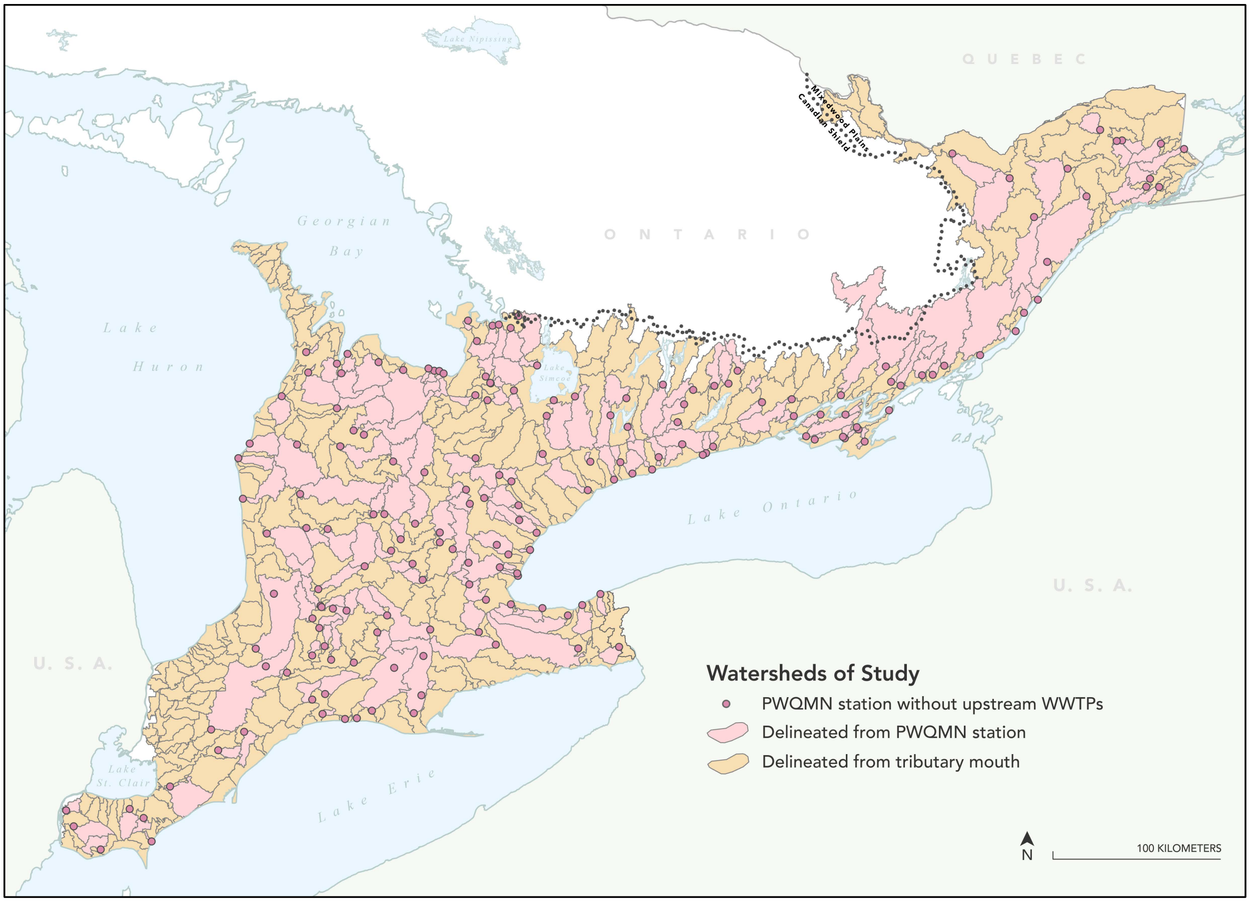

Figure 2.2 Delineated watershed units and Provincial Water Quality Monitoring Network (PWQMN) stations in southern Ontario without upstream municipal wastewater treatment plants (WWTPs)

2.2.3 Land use variables

All watersheds were characterized for 23 variables as summarized in Table 2.3. The average slope of the watershed terrain was extracted from the 30 m provincial digital elevation model from the Ontario Ministry of Natural Resources and Forestry (OMNRF, 2022c). Soil texture for the A horizon was collected from Agriculture and Agri-Food Canada's (AAFC) Detailed Soil Survey (AAFC, 2021), with the average percentage of total silt plus clay by weight for every watershed calculated based on area-weighted means.

Table 2.3 Land use variables used to characterize the study watersheds for the SOM analysis

Variable	Abbreviation	Unit	Definition	Data source
Slope	SLOPE	degree	Slope of watershed terrain	Provincial Digital Elevation Model
Soil texture (silt + clay)	SILTCLAY	%	Total clay plus total silt by soil weight	AAFC Detailed Soil Survey
Soybean + corn	SOYCORN	%	Land cultivated with soybean and com	AAFC Annual Crop Inventory
Wheat	WHEAT	%	Land cultivated with winter and spring wheat	AAFC Annual Crop Inventory
Pasture	PASTURE	%	Periodically cultivated land, including perennial crops and hay for forage	AAFC Annual Crop Inventory
Fruits and vegetables	FRUITVEG	%	Land cultivated with fruits and vegetables	AAFC Annual Crop Inventory
Field crops and other agriculture	FIELDAG	%	Land cultivated with cereals, oilseeds, pulses, and others	AAFC Annual Crop Inventory
Urban	URBAN	%	Built-up and developed land	AAFC Annual Crop Inventory
Exposed land/mining	EXPOSED	%	Non-vegetated and non-developed land	AAFC Annual Crop Inventory
Forest	FOREST	%	Coniferous, deciduous, and mixed forests	AAFC Annual Crop Inventory
Wetland	WETLAND	%	Land with water table near/at/above soil surface	AAFC Annual Crop Inventory
Water	WATER	%	Water bodies	AAFC Annual Crop Inventory
Other natural	OTHERNAT	%	Woody vegetation of low height and native grasses	AAFC Annual Crop Inventory
Continuous corn-soybean rotation	MONO	%	Area under a continuous corn-soybean rotation for at least 4 years	AAFC Annual Crop Inventory
Pasture to row crop	PTORC	%	Pastureland replaced by row crops (corn, soybean, or wheat)	AAFC Annual Crop Inventory
Urban development	TOURB	%	Agricultural/natural areas converted to urban uses	AAFC Annual Crop Inventory
Conversion to agriculture	TOAG	%	Natural areas converted to agricultural uses	AAFC Annual Crop Inventory
Tile drainage	TD	%	Area underlain with subsurface tile drainage	OMNRF Tile Drainage Area
Commercial fertilizer	FERT	%	Area on which commercial fertilizer was applied	Statistics Canada Census of Agriculture
Manure	MANURE	%	Area on which manure was applied	Statistics Canada Census of Agriculture
Livestock density	LIVDEN	animal units km^{-2}	Weighted livestock numbers divided by watershed area	Statistics Canada Census of Agriculture
Human population density	POPDEN	people ha^{-1}	Number of persons per hectare	Statistics Canada Census of Population
Shannon's Diversity Index	SHDI		Proportional abundance of each land cover class	AAFC Annual Crop Inventory

To quantify land use, the AAFC’s Annual Crop Inventory (ACI; 30 m resolution) datasets were obtained from 2011 to 2020 (ACI, 2022). Derived from satellite imagery acquired throughout the growing season, the ACI has over 60 land use categories, consisting of major annual and perennial crops, and urban and natural land uses. To simplify land use analysis, ACI data were aggregated into 11 categories based on similar land management activities (Appendix B), including: ‘Corn + soybean’, ‘Wheat’, ‘Pasture’, ‘Fruits + vegetables’, ‘Field crops and other agriculture’, ‘Urban’, ‘Exposed/barren land/mines’, ‘Forest’, ‘Wetland’, ‘Other natural’, and ‘Water’. Fruit and vegetable production was considered a separate category from other types of agriculture as orchards and vineyards are often managed more intensively, requiring higher rates of fertilization, whereas greenhouse effluent has been linked to higher stream NO_3-N and TP concentrations (e.g., Maguire et al., 2018). To account for the interannual variability of land use, a decadal average of percent cover for each land use category was calculated within the watersheds. Prior research has suggested that agricultural shifts, specifically conversions from agriculture of 'low intensity' (i.e., mixed livestock + cropland) to ‘high intensity’ (i.e., row crops), may be contributing to rising tributary NO_3-N concentrations (Eimers and Watmough, 2016; DeBues et al., 2019; Liu et al., 2022), whereas urbanization has been widely linked to increasing freshwater salinization (Kaushal et al., 2005). Therefore, several parameters of land use change over the study period were also determined from the ACI, including percent watershed area in which (a) crop rotations comprised of only corn and soybean for at least four consecutive years between 2011 and 2020; (b) pastureland (in 2011) was replaced by row crop (corn + soybean + winter wheat) agriculture (in 2020); (c) natural or agricultural land (in 2011) was converted to urban land (in 2020); and (d) natural land cover (in 2011) was converted to agricultural cropland (in 2020). To quantify landscape heterogeneity on a watershed scale, the Shannon Diversity Index (SHDI; Appendix C) was generated in FRAGSTATS (McGarigal and Ene, 2013) based on decadal mean ACI land use percent cover. Measures of landscape diversity provide insight into the spatial configuration of land use patterns, which has shown to correlate with stream water quality (Lee et al., 2009; Bu and Huang et al., 2016). Declines in SHDI have been attributed to rises in the relative dominance of corn and soybean production as well as cropland expansion (Medley et al., 1995), which are likely to have implications for nutrient delivery.

Extent of tile drainage was estimated as a proportion of total watershed area using tile drainage records from the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA, 2019). However, it is important to consider these records as an under-representation of the actual tile drainage network, given that many tiles were installed before modern record keeping and that site plan submission of private installations is not required by the province (Eimers et al., 2020). Land areas that received commercial fertilizer and/or manure application were extracted from Statistics Canada’s 2016 Census of Agriculture (Statistics Canada, 2016a). Originally collected at the census consolidated subdivision (CCS) scale, these data were converted to a watershed scale based on area-weighted means, then calculated as a percentage of total watershed area (see methods by DeBues et al., 2019). Also retrieved from the Census of Agriculture were animal livestock population numbers from each CCS. To account for the different sizes of animals, the populations of each livestock species were multiplied by equivalence factors shown in

Table 2.4, similar to those used by Jones et al. (2019), to obtain animal units (AU). Animal units provides a standardized metric for comparing different livestock species. Animal densities in each watershed were estimated by weighting the AUs by the proportion of areas of CCS within each watershed then dividing the sum of AUs by the total watershed area. Human population numbers were obtained from Statistics Canada's 2016 Census of Population (Statistics Canada, 2016b). Since human population data were compiled at the dissemination area (DA) level (i.e., geographic areas with 400 to 700 persons), population densities were calculated by first aggregating population numbers from census to watershed boundaries in proportion to areas of DA within each watershed, then dividing the population by the total area of each watershed (Neumann et al., 2017). All watershed analyses, with the exception of the SHDI calculation, were performed in ArcGIS Pro 2.9 (ESRI, 2021).

Table 2.4 Equivalence factors used to multiply with livestock population numbers

Animal species	Factor
Horse	0.50
Cattle	0.25
Pig	0.10
Goat	0.05
Sheep	0.05
Chicken	0.025
Turkey	0.025

2.2.4 Self-organizing map

An SOM analysis was performed to classify the watersheds using the 23 land use and landscape characteristics (Table 2.3) as input variables. After training the SOM with 459 data samples representing each watershed, the data were distributed onto a two-dimensional hexagonal lattice, whereby watersheds of similar features were mapped closer to each other. The number of nodes that the SOM lattice consisted of was set to 91 (7 × 13 matrix) to be close to the recommended $5\sqrt{\text{sample size}}$, of Vesanto and Alhoniemi (2000), while minimizing both quantization and topographical errors (Park et al., 2014). Similar to previous watershed analyses (Kim et al., 2016; Neumann et al., 2017), a Gaussian neighbourhood function was applied, while weight vectors were linearly initialized using the first two principal components of the dataset. Following the training process, a post-hoc hierarchical cluster analysis using Ward's method (Ward, 1963) was applied to quantitatively summarize major patterns (Clark et al., 2020).

The contribution of each input variable to the cluster structures of the trained SOM was visualized using component planes. Each plane shows the values of one variable in each node of the SOM using a grey scale representation from light (lowest values) to dark (highest values). Correlations between variables can be identified from similar patterns in matching positions of the component planes (Vesanto, 1999). To determine the most dominant features of each cluster, averages of each variable among the clusters were compared using a post-hoc Scheffe's multiple comparison test at a significance level of 0.05 (Kim et al., 2016). The SOM was implemented using R statistical software (R Core Team, 2021) and the R packages used for analyses and visualizations include 'SOMbrero' (Boelaert et al., 2014), 'NbClust' (Charrad et al., 2014), 'ggplot2' (Wickham, 2016), 'cowplot' (Wilke, 2020), and 'agricolae' (de Mendiburu, 2021). Detailed descriptions of the SOM algorithm can be found in Kohonen (2001).

2.2.5 Stream water quality

To link stream NO_3-N, TP, and Cl concentrations to the SOM clusters, watersheds that were delineated from the selection of PWQMN stations were first identified within each cluster. Water quality data from these watersheds were then screened to include only samples collected during the ice-free season (April to November) as sites were sampled most frequently during this period (Stammler et al., 2017). All selected sites were sampled at least six months out of the eight months during the ice-free period and at least nine years out of the ten years (2011 – 2020) to ensure sites had similar levels of data availability (i.e., total number of samples at each station ranged from approximately 70 to 95 samples). All PWQMN streams were sampled by local Conservation Authorities following a standardized protocol and samples were analyzed by the MECP using methods described in the Handbook of Analytical Methods for Environmental Samples (OMOE, 1983). Consistent methods of sampling and laboratory analysis ensured that results are comparable across the province (Raney and Eimers, 2014b). The NO_3-N, TP, and Cl records were visually inspected to identify outliers, resulting in the removal of less than 1% of the data. Individual concentration measurements were then averaged for each month from April to November, and then these monthly values were averaged to produce an annual growing season mean for each year (DeBues et al., 2019). To match land use data, these annual concentrations were averaged over the ten-year period to focus on decadal means (DeBues et al., 2019), which minimizes the influence of extreme high or low values as nutrient export can be sensitive to changes in hydrology and sampling effort across space and time (Stammler et al., 2017). These decadal mean concentrations were aggregated according to each cluster and a Scheffe's test was performed in R to compare the means between each cluster ($p < 0.05$). In addition, ordinary least squares regression was used to evaluate associations between land use variables and stream decadal concentrations across the PWQMN- delineated watersheds ($p < 0.05$). All data were log transformed prior to analysis to normalize their distribution.

2.2.6 Basin-wide streamflow and export

To estimate chemical export across the study domain, monthly records of streamflow (2011 – 2020) were retrieved from the archived hydrometric database of the National Hydrometric Program (ECCC, 2022). Hydrometric stations were selected based on data availability over the study period and absence of flow regulation. Monthly discharge volumes at the selected sites were summed for each year between 2011 and 2020 and then averaged to yield a decadal mean. The decadal mean discharge volumes (m^3 $year^{-1}$) were then divided by watershed area (m^2) to yield decadal mean annual runoff depth (mm $year^{-1}$) at each gauged watershed. Differences in decadal mean annual runoff were compared among the basins using a one-way ANOVA and Scheffe's test ($p < 0.05$). Because chemical export is mostly relevant to the recipient water body, annual areal export was estimated for each of the Lake Erie, Lake Ontario, Lake Huron, and St. Lawrence River drainage regions within the study area.

Two approaches to estimating areal export were explored. In the first method, mean (10^{th} – 90^{th} percentiles) annual mean runoff was first computed within each Great Lakes drainage basin. Then, within each basin, exports of NO_3-N, TP, and Cl from each cluster were calculated by multiplying mean (10^{th} – 90^{th} percentiles) basin runoff by both the areal coverage of each cluster within the basin and the mean stream NO_3-N, TP, and Cl cluster concentrations. Lastly, cluster exports were summed for each basin and were then divided by the basin area to generate total basin annual export per unit area (kg km^{-2} $year^{-1}$) within the study region. In the second method, watersheds with both decadal mean concentration and flow data were first identified. Areal normalized loadings per cluster were calculated using a bivariate normal distribution generated based on covariance between concentration and flow across all sites. For each watershed, drainage area of the watershed was then multiplied with the mean (10^{th} – 90^{th} percentiles) areal normalized loadings of the corresponding cluster that contains the watershed to yield annual mean (10^{th} –

90^{th} percentiles) loading. The individual loadings of watersheds were summed by basin and then divided by the total basin area within the study region to generate total basin annual export per unit area (kg km^{-2} year^{-1}).

2.3 Results

2.3.1 Self-organizing map analysis

The SOM classified the watersheds across southern Ontario into eight unique clusters (Figure 2.3). The characteristics of each cluster are summarized in Table 2.5, whereas the spatial distribution of each cluster across southern Ontario is shown in Figure 2.4. Relationships between variables can be visualized across component planes in Figure 2.3. The spatial distributions of each individual variable are also shown separately in Appendix D. The eight clusters fall into three primary groups based on land use: (i) agriculture-dominated clusters (1, 2, 3, and 4); (ii) urbanized clusters (5 and 6); and (iii) predominantly natural clusters (7 and 8). The first group of clusters (1 – 4) is comprised primarily of medium- to high-intensity agricultural landscapes of which 34-75% of total watershed area is row crop fields (i.e., corn and soybean in rotation with winter wheat), with some presence of pasture (6 – 24%) and other types of agriculture (2 – 5%). Most watersheds in clusters of this group are located in southwestern Ontario, while a small minority are in the eastern tip of the province (Figure 2.4). The most intensive cultivation of row crops occurs in clusters 1 and 2 (75% and 62%, respectively) and is associated with widespread tile drainage (61% and 49%) as a result of poorly drained soils in the region due to the flat topography (0.6° and 1.3°) and fine textured soils (average 68% and 64% silt plus clay, respectively). Extensive areas in both clusters 1 and 2 receive applications of commercial fertilizer (57% and 51%, respectively), however, intensive animal production in cluster 2 as reflected by the high livestock density (68 AU km^{-2}) has likely contributed to a greater proportion of areas fertilized by manure (21%) in this cluster. The relatively low pasture areal cover in cluster 2 (16%) further indicates the possible presence of concentrated animal feeding operations (CAFOs) in these catchments. Cluster 1 has the highest percentage area under continuous (at least four consecutive years) corn-soybean rotation (52%) and the most homogenous landscapes (SHDI = 1.2). By contrast, clusters 3 and 4 are more diverse (SHDI = 1.7) and are characterized by a greater proportion of area under mixed agriculture (crop and livestock). For instance, over one-third (34 – 43%) of watershed areas in clusters 3 and 4 are dedicated to row crop agriculture, while relatively more pastureland (18 – 24%) is available for livestock grazing and foraging (18 – 34 AU km^{-2}). The highest proportions of area with other field crops grown (i.e., oats, barley, beans, rye, tobacco, and ginseng) are also observed in clusters 3 and 4 (2% to 4%, respectively). Although clusters 2, 3, and 4 have smaller row crop areal production than cluster 1, important shifts from pasture to row crop over the past decade (7 – 9%) have occurred in clusters 2 to 4.

The second group of clusters (5 and 6) consists of urbanized watersheds located mainly in the Greater Toronto Area along the northwestern shore of Lake Ontario (Figure 2.4). High levels of urbanization in clusters 5 and 6 (59% and 30%, respectively) are accompanied by elevated population density (16.7 and 5.3 people ha^{-1}), with cluster 5 representing the most urbanized cores and cluster 6 reflecting peri-urban areas across southern Ontario. These populated regions continue to experience urban expansion, converting approximately 7% of agricultural or natural land into urban land over the study period (Table 2.5). Although cluster 5 is highly urbanized, it also has the most extensive area dedicated to fruit and vegetable production (6%), as it includes watersheds in the Niagara Peninsula, a region with warm, temperate climate conditions and fertile loam soils that provide a favourable environment for the cultivation of these crops. The remaining areas of the two clusters are dedicated to row crop agriculture (13 – 24%), pastureland (10 – 13%), and natural cover (10 – 29%). Similar to cluster 1, cluster 5 is characterized by low landscape fragmentation (SHDI = 1.2), which is influenced by the strongly homogeneous urban land use in the Toronto region.

The third group (clusters 7 and 8) is defined by large areal extents of natural land cover (43–60%), stretching from the Bruce Peninsula and southern Georgian Bay region towards south-central and eastern Ontario (Figure 2.4). Major natural land cover categories include forests (30 – 25%), wetlands (5 – 9%), water (1 – 4%), and others (e.g., grassland, shrubland; 8 – 12%). Both clusters have highly heterogenous landscapes (SHDI = 1.7). Slope is the highest (2.8°) in cluster 7, corresponding to the rolling terrain and steep topography of watersheds that lie within the Niagara Escarpment and Oak Ridges Moraine. A small portion of clusters 7 and 8 is allocated to less-intensive mixed agriculture, consisting of row cropping systems (12% and 18%, respectively) and low-density livestock operations (14 and 9 AU km^{-2}) supported by substantial pasture areas (30% and 18%), particularly in cluster 7. Cluster 8 is distinguished by having the highest percent natural cover as well as the greatest areal extent in which natural land use was replaced by agriculture (11%) over the study period.

Table 2.5 Self-organizing map classification of the watershed attributes in southern Ontario. White shaded variables represent land use characteristics ± standard error used for input for SOM training, gray shaded variables are decadal mean ± standard error of water quality parameters in the PWQMN-delineated watersheds corresponding to each SOM cluster. Bold numbers indicate the highest value for each variable among the clusters. Superscripts indicate statistically significant differences in each variable among the clusters based on Scheffe's multiple comparison test ($p < 0.05$). See Appendix D for proportional areal extent of PWQMN-delineated watersheds within each SOM cluster.

Variable	Unit	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7	Cluster 8
		n = 67	n = 89	n = 37	n = 24	n = 25	n = 39	n = 76	n = 102
SLOPE	degree	0.6 ± 0.05 ^{c}	1.3 ± 0.08 ^{b}	1.5 ± 0.10 ^{b}	1.5 ± 0.09 ^{b}	1.5 ± 0.13 ^{b}	1.6 ± 0.13 ^{b}	**2.8 ± 0.11** ^{a}	1.7 ± 0.08 ^{b}
SILTCLAY	%	**67.7 ± 2.3** ^{a}	63.7 ± 1.8 ^{a}	47.3 ± 2.8 ^{b}	44.9 ± 2.4 ^{bc}	43.5 ± 3.2 ^{bc}	43.7 ± 2.7 ^{bc}	38.6 ± 1.5 ^{bc}	33.8 ± 1.6 ^{c}
SOYCORN	%	**64.3 ± 1.1** ^{a}	51.3 ± 1.7 ^{b}	37.1 ± 1.6 ^{c}	29.0 ±1.5 ^{cd}	10.6 ± 2.0 ^{de}	20.4 ± 1.9 ^{de}	14.8 ± 0.8 ^{de}	10.3 ± 0.7 ^{e}
WHEAT	%	10.9 ± 0.6 ^{a}	**10.9 ± 0.6** ^{a}	5.7 ± 0.5 ^{b}	4.9 ± 0.7 ^{bc}	2.1 ± 0.4 ^{bc}	3.1 ± 0.4 ^{bc}	3.0 ± 0.2 ^{bc}	1.7 ± 0.2 ^{c}
PASTURE	%	6.1 ± 0.5 ^{d}	15.7 ± 1.2 ^{bc}	18.8 ± 1.6 ^{bc}	24.2 ± 1.9 ^{ab}	10.1 ± 1.5 ^{cd}	13.0 ± 0.9 ^{cd}	**30.0 ± 0.9** ^{a}	18.0 ± 0.7 ^{bc}
FRUITVEG	%	1.6 ± 0.3 ^{b}	0.4 ± 0.1 ^{b}	1.7 ± 0.3 ^{b}	0.6 ± 0.3 ^{b}	**5.6 ± 2.7** ^{a}	1.3 ± 0.3 ^{b}	0.6 ± 0.1 ^{b}	0.3 ± 0.1 ^{b}
FIELDAG	%	0.6 ± 0.0 ^{b}	1.5 ± 0.2 ^{b}	**3.7 ± 1.0** ^{a}	1.3 ± 0.2 ^{b}	0.5 ± 0.1 ^{b}	1.1 ± 0.3 ^{b}	1.0 ± 0.1 ^{b}	0.5 ± 0.0 ^{b}
URBAN	%	6.1 ± 0.5 ^{c}	4.7 ± 0.5 ^{c}	6.1 ± 0.8 ^{c}	4.2 ± 0.4 ^{c}	**58.9 ± 5.1** ^{a}	29.9 ± 2.8 ^{b}	6.3 ± 0.6 ^{c}	7.2 ± 0.7 ^{c}
EXPOSED	%	0.5 ± 0.0 ^{b}	0.7 ± 0.1 ^{b}	0.9 ± 0.1 ^{b}	0.9 ± 0.1 ^{b}	2.0 ± 0.2 ^{a}	2.1 ± 0.2 ^{a}	0.9 ± 0.1 ^{b}	**2.1 ± 0.2** ^{a}
FOREST	%	7.4 ± 0.7 ^{e}	12.1 ± 0.8 ^{de}	20.0 ± 1.2 ^{bcd}	25.3 ± 2.2 ^{abc}	7.5 ± 0.8 ^{de}	18.8 ± 1.5 ^{cd}	29.5 ± 1.2 ^{ab}	**35.2 ± 1.5** ^{a}
WETLAND	%	1.2 ± 0.2 ^{d}	1.2 ± 0.2 ^{d}	2.9 ± 0.5 ^{bcd}	3.7 ± 0.5 ^{bcd}	1.2 ± 0.1 ^{cd}	4.1 ± 0.6 ^{bc}	5.2 ± 0.3 ^{b}	**9.0 ± 0.5** ^{a}
WATER	%	0.6 ± 0.1 ^{b}	0.3 ± 0.1 ^{b}	0.8 ± 0.2 ^{b}	0.9 ± 0.5 ^{ab}	0.5 ± 0.1 ^{b}	2.7 ± 0.8 ^{ab}	0.8 ± 0.3 ^{b}	**3.9 ± 0.8** ^{a}
OTHERNAT	%	0.8 ± 0.1 ^{c}	1.2 ± 0.1 ^{c}	2.4 ± 0.2 ^{c}	4.9 ± 0.5 ^{bc}	1.1 ± 0.2 ^{c}	3.6 ± 0.4 ^{c}	7.9 ± 0.4 ^{b}	**11.9 ± 0.7** ^{a}
MONO	%	**52.2 ± 1.6** ^{a}	35.0 ± 2.1 ^{b}	27.0 ± 2.0 ^{bc}	20.2 ± 1.9 ^{cd}	7.3 ± 1.6 ^{d}	15.0 ± 1.7 ^{cd}	8.8 ± 0.7 ^{d}	6.4 ± 0.5 ^{d}
PTORC	%	2.4 ± 0.2 ^{c}	**9.4 ± 0.7** ^{a}	7.0 ± 0.8 ^{ab}	9.2 ± 0.6 ^{ab}	2.3 ± 0.6 ^{c}	3.0 ± 0.4 ^{c}	6.4 ± 0.3 ^{b}	3.2 ± 0.2 ^{c}
TOURB	%	3.4 ± 0.1 ^{b}	3.3 ± 0.1 ^{b}	3.8 ± 0.2 ^{b}	3.3 ± 0.2 ^{b}	6.6 ± 0.6 ^{a}	**7.4 ± 0.5** ^{a}	4.4 ± 0.2 ^{b}	4.3 ± 0.3 ^{b}
TOAG	%	3.6 ± 0.3 ^{cd}	3.7 ± 1.5 ^{cd}	6.3 ± 0.5 ^{bc}	6.9 ± 0.7 ^{bc}	1.6 ± 0.3 ^{d}	5.1 ± 0.5 ^{bcd}	7.0 ± 0.3 ^{b}	**10.8 ± 0.5** ^{a}
SHDI		1.2 ± 0.0 ^{c}	1.4 ± 0.0 ^{b}	1.7 ± 0.0 ^{ab}	1.7 ± 0.0 ^{ab}	1.2 ± 0.1 ^{c}	1.7 ± 0.0 ^{a}	1.7 ± 0.0 ^{a}	**1.7 ± 0.0** ^{a}
TD	%	**60.7 ± 2.3** ^{a}	48.6 ± 2.9 ^{a}	17.5 ± 1.6 ^{b}	15.1 ± 1.5 ^{b}	5.3 ± 1.7 ^{b}	10.7 ± 1.8 ^{b}	4.5 ± 0.4 ^{b}	4.0 ± 0.5 ^{b}
FERT	%	**56.5 ± 1.3** ^{a}	51.3 ± 1.8 ^{a}	38.0 ± 1.6 ^{b}	25.6 ± 1.6 ^{bcd}	13.4 ± 2.3 ^{cd}	26.2 ± 2.3 ^{bc}	20.0 ± 0.8 ^{cd}	13.4 ± 0.7 ^{d}
MANURE	%	4.4 ± 0.4 ^{c}	**21.4 ± 1.6** ^{a}	9.8 ± 0.7 ^{b}	7.6 ± 0.7 ^{bc}	2.6 ± 0.7 ^{c}	3.8 ± 0.4 ^{c}	4.9 ± 0.2 ^{c}	3.3 ± 0.4 ^{c}
LIVDEN	animal units km^{-2}	13.8 ± 1.5 ^{c}	**68.3 ± 6.2** ^{a}	34.2 ± 3.6 ^{b}	18.0 ± 1.3 ^{bc}	13.2 ± 4.0 ^{c}	12.7 ± 1.7 ^{c}	13.5 ± 0.8 ^{c}	9.3 ± 0.6 ^{c}
POPDEN	people ha^{-1}	0.5 ± 0.1 ^{c}	0.3 ± 0.1 ^{c}	0.6 ± 0.1 ^{c}	0.3 ± 0.1 ^{c}	**16.7 ± 2.2** ^{a}	5.3 ± 0.6 ^{b}	0.6 ± 0.1 ^{c}	0.7 ± 0.1 ^{c}
		n = 11	n = 37	n = 13	n = 12	n = 13	n = 11	n = 46	n = 36
NO_3-N concentration	mg L^{-1}	3.0 ± 0.49 ^{a}	**3.5 ± 0.18** ^{a}	1.7 ± 0.28 ^{b}	1.3 ± 0.17 ^{bc}	0.84 ± 0.12 ^{bcd}	0.77 ± 0.16 ^{bcd}	0.68 ± 0.06 ^{cd}	0.28 ± 0.04 ^{d}
TP concentration	mg L^{-1}	**0.15 ± 0.027** ^{a}	0.076 ± 0.008 ^{b}	0.052 ± 0.011 ^{b}	0.048 ± 0.011 ^{b}	0.076 ± 0.013 ^{b}	0.059 ± 0.013 ^{b}	0.030 ± 0.003 ^{b}	0.043 ± 0.005 ^{b}
Cl concentration	mg L^{-1}	64.6 ± 10.2 ^{bc}	33.4 ± 2.6 ^{c}	46.6 ± 14.3 ^{bc}	27.8 ± 5.9 ^{c}	**251.0 ± 34.0** ^{a}	109.6 ± 22.5 ^{b}	28.2 ± 3.3 ^{c}	31.8 ± 4.1 ^{c}

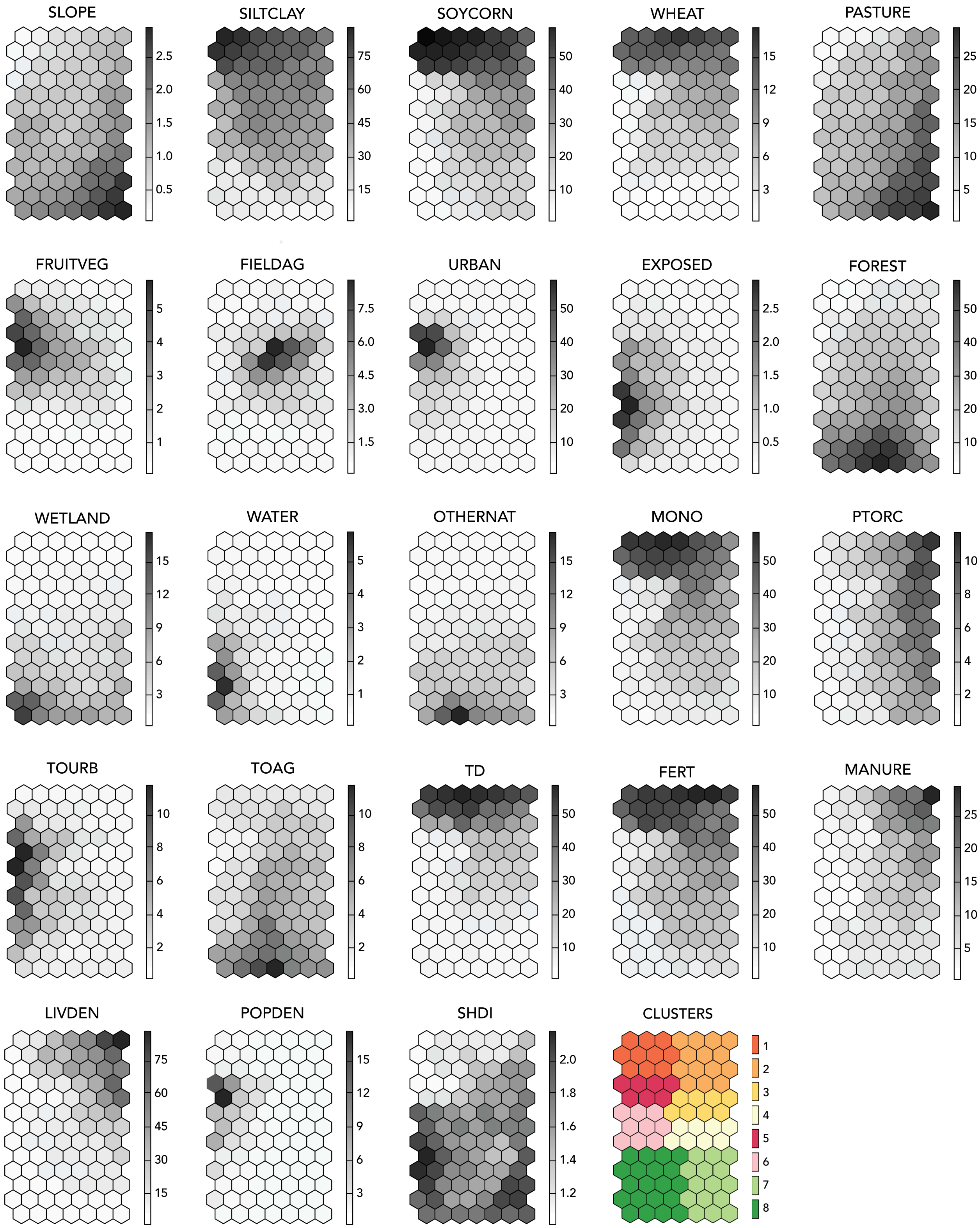

Figure 2.3 Self-organizing map component planes of watershed land use characteristics which visualizes relationships between variables. Bands on the right indicate the range of values of each variable. Units are the same as shown in Table 2.5. Second-level hierarchal SOM clustering is shown in colour at bottom right.

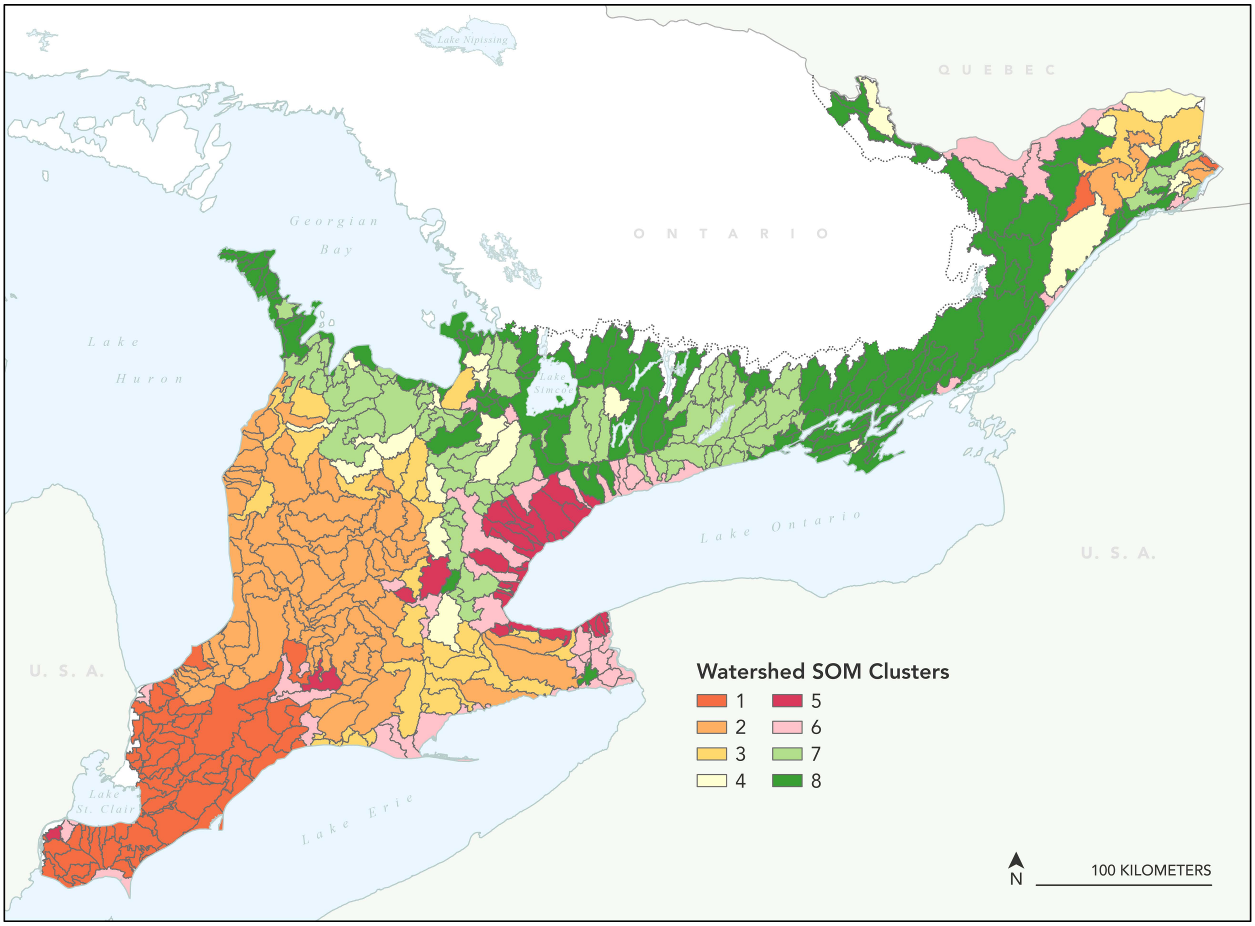

Figure 2.4 SOM classification of a total of 459 watersheds in southern Ontario. Clustering is based on Figure 2.3.

2.3.2 Water quality associations with land use

The PWQMN-delineated watersheds identified within each cluster represented a total area of 25% to 56% of each cluster except for cluster 6, where only 14% had water quality records that fit the criteria of this study (Appendix D). Stream decadal mean NO_3-N concentrations were highest in clusters 1 (3.0 mg L^{-1}) and 2 (3.5 mg L^{-1}), which are dominated by tile-drained row crop agriculture (62 – 75% row crop; 49 to 61% tile-drained: Table 2.5 and Figure 2.5a). Indeed, mean NO_3-N concentrations in these two highly agricultural clusters were five to twelve times higher than in the natural clusters (7 and 8) and approximately four times higher than in the urban clusters (5 and 6; Table 2.5). Mean concentrations of NO_3-N were higher in the mixed-agriculture dominated clusters 3 and 4 (1.68 and 1.34 mg L^{-1}) than those in the urbanized clusters 5 and 6 (0.84 and 0.77 mg L^{-1}), although no statistically significant differences were detected between these groups ($p > 0.05$). As expected, the lowest NO_3-N concentrations were observed in clusters 7 and 8 (0.68 and 0.28 mg L^{-1}), which had the greatest proportion of natural land use and a smaller presence of agriculture (~30% of watershed area). To evaluate the association between stream NO_3-N concentrations and row crop agriculture more clearly, ordinary least squares regression models were fitted to predict NO_3-N concentrations in response to the proportion of row cropped area, fertilized area, and tile-drained area relative to total watershed area. Positive linear relationships were found ($p < 0.001$) between NO_3-N concentrations and soybean plus corn cover (R^2 = 0.69; Figure 2.6a), fertilized area (R^2 = 0.65; Figure 2.6b), and tile-drained area (R^2 = 0.64; Figure 2.6c).

Similar to patterns in NO_3-N, cluster 1 had the highest decadal mean concentration of TP (0.15 mg L^{-1}; Table 2.5 and Figure 2.5b). Decadal mean TP concentrations in other clusters (2 – 8) were 50% to 80% lower from cluster 1, ranging from 0.030 to 0.076 mg L^{-1} and were not statistically different from one another ($p > 0.05$). All eight clusters contained watersheds with TP measurements above the Ontario Provincial Water Quality Objective of 0.03 mg L^{-1} intended to prevent excessive algal growth (CCME, 2004), with the highest exceedances occurring in cluster 5 (100% of all samples) followed by cluster 1 (91%) and cluster 2 (90%). In contrast to NO_3-N, TP concentrations did not demonstrate a clear pattern of association with any land use variables ($p > 0.05$). However, the significantly higher mean concentration observed in cluster 1 suggests a possible link between elevated TP and the combination of certain land use features found in this cluster, namely high proportions of row crop agriculture (75%), watershed area under continuous corn-soybean rotation (52%), fertilized area (57%), and tile drained area (61%) on fine textured soils (68% silt plus clay) and level topography (0.6°; Table 2.5). This also demonstrates that high intensity agricultural regions can contribute greater TP input than urban areas in the absence of influential point sources such as WWTPs.

Watersheds in the most urbanized and densely populated cluster 5 (59% urban cover and 16.7 people ha^{-1}) were the most enriched in Cl, with a decadal mean of 251 mg L^{-1} and a maximum of 491 mg L^{-1} in Sheridan Creek (Table 2.5 and Figure 2.5c). Representing peri-urban watersheds (30% urban) and a medium population density of 5.3 people ha^{-1}, cluster 6 had a decadal mean Cl concentration of 110 mg L^{-1}, half that of cluster 5. Approximately 23% and 10% of watersheds in clusters 5 and 6, respectively, exceeded the aesthetic objective of 250 mg L^{-1} for Cl in drinking water (Health Canada, 1987), potentially causing undesirable tastes to water and corrosion in the distribution systems of those regions. Agricultural clusters (1 – 4) and in particular, the least developed clusters (7 – 8) showed the lowest overall mean Cl concentrations (28 – 65 mg L^{-1}). Only clusters 2, 4, and 8 met the 120 mg L^{-1} long-term exposure Canadian Water Quality Guideline for Cl for the protection of aquatic life (CCME, 2011; Figure 2.5c). Overall, Cl records were strongly correlated ($p < 0.001$) with percent urban land cover of watersheds (R^2 = 0.61; Figure 7d), as well as watershed human population density (R^2 = 0.59; Figure 2.6e).

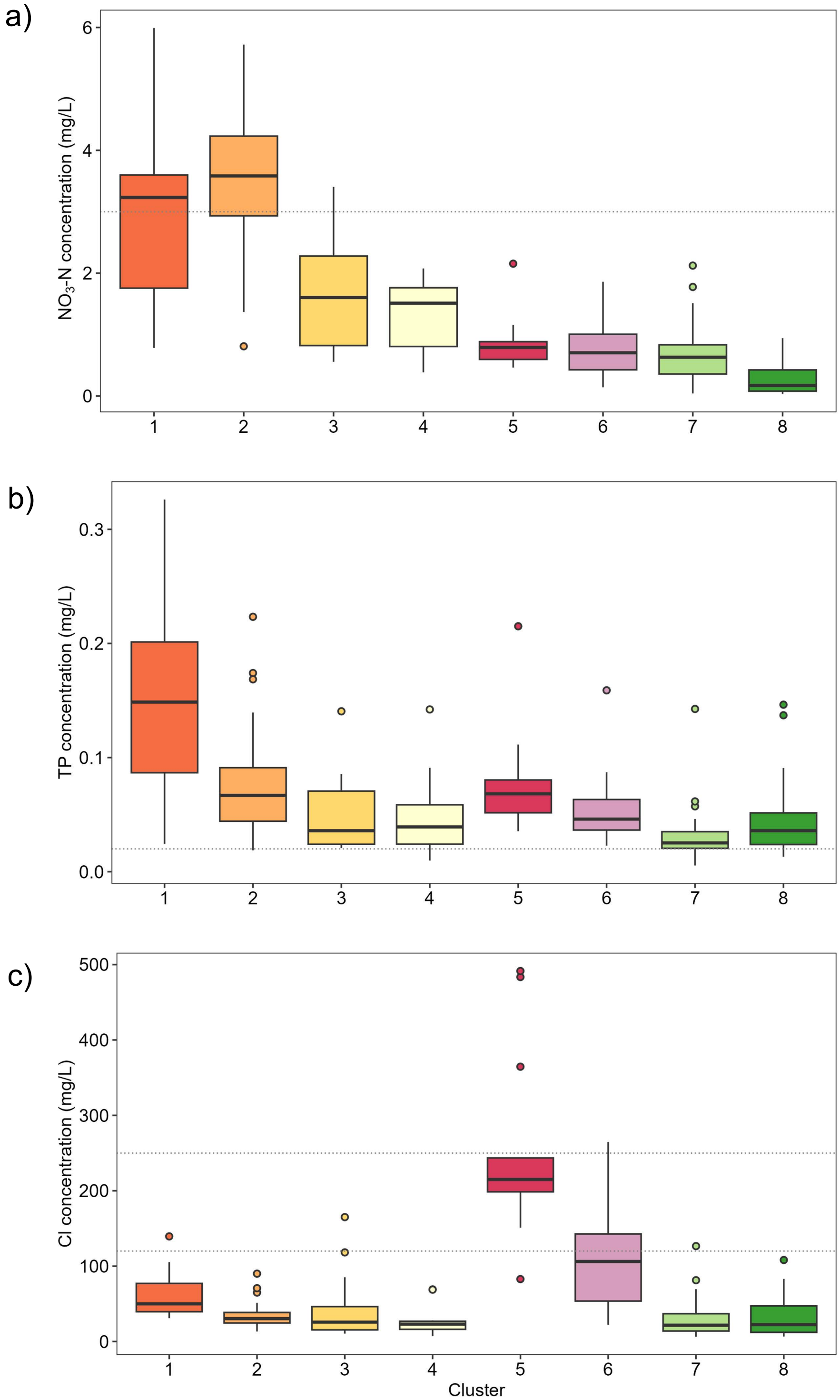

Figure 2.5 (a) Decadal mean NO_3-N concentrations (mg L^{-1}) of each SOM cluster. The dashed line indicates the Canadian Water Quality Guideline for the protection of aquatic life in freshwater (3 mg L^{-1}). (b) Decadal mean TP concentrations (mg L^{-1}) of each SOM cluster. Dashed line indicates the Provincial Water Quality Objective for TP (0.03 mg L^{-1}). (c) Decadal mean Cl concentrations (mg L^{-1}) of each SOM cluster. Lower dashed line indicates the chronic (120 mg L^{-1}) surface water guidelines for the protection of aquatic life, whereas the top dashed line represents the aesthetic drinking water objective (250 mg L^{-1}). The solid line within each box represents the median, while the lower and upper boundaries of the boxes are the 25th and 75th percentiles, respectively. Whiskers below and above each box mark the 10th and 90th percentiles; dots represent outliers.

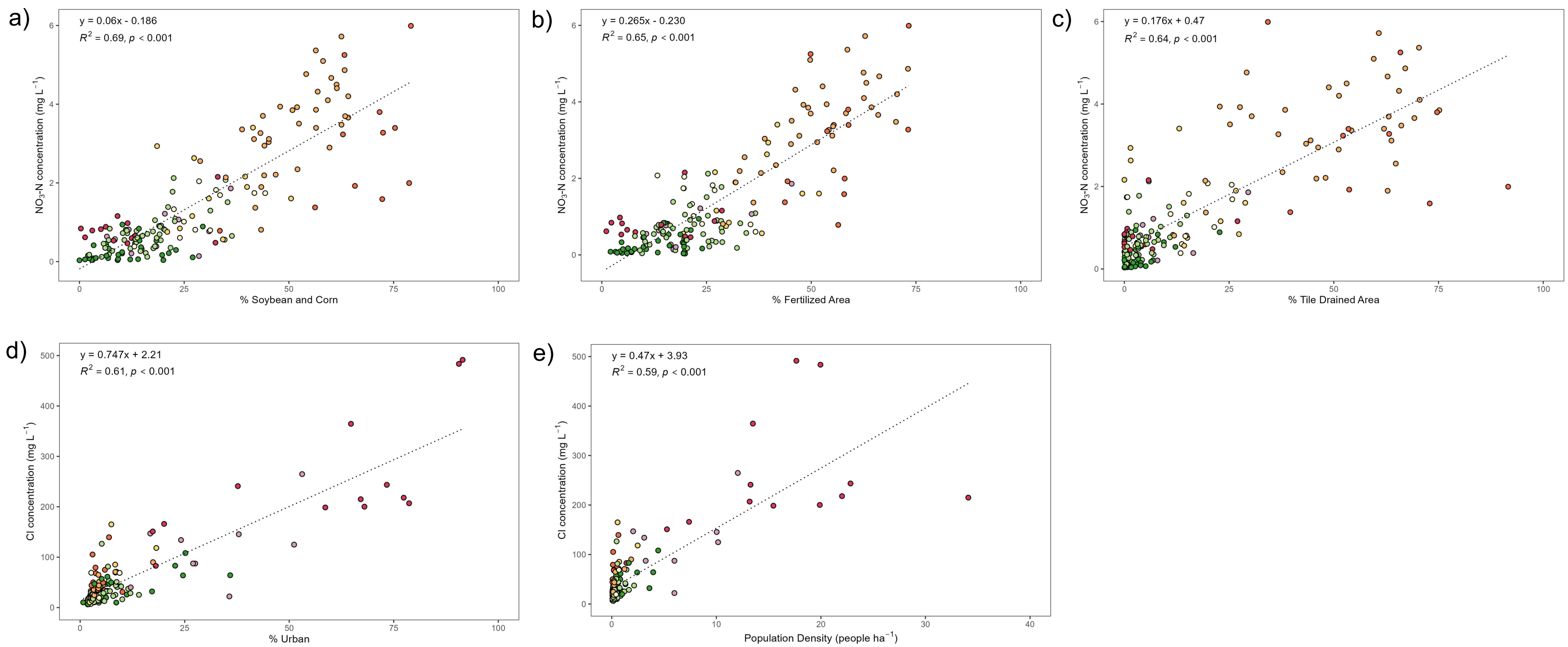

Figure 2.6 Relationship between decadal mean NO_3-N concentrations (mg L^{-1}) and (a) soybean and corn coverage (as a percentage of total watershed area), (b) fertilized area coverage, and (c) tile drained area coverage in PWQMN-delineated watersheds. Relationship between decadal mean Cl concentrations (mg L^{-1}) and (d) urban coverage (as a percentage of total watershed area) and (e) population density (people ha^{-1}) in PWQMN-delineated watersheds. Watersheds are symbolized according to the SOM cluster.

2.3.3 Basin-wide patterns in land use, climate, runoff, and export

To characterize land use across the major Great Lakes watersheds in southern Ontario, the areal proportions of each cluster were determined within each basin (Table 2.6; Figure 2.7). The Lake Erie basin was dominated by watersheds from agricultural clusters (1 – 4; 87%), primarily cluster 1 (35%) and cluster 2 (33%), while urban clusters (5, 6) comprised 10% of the basin area. In the Lake Huron basin, the lower half (51%) was distinctly composed of agricultural clusters (1 – 4), with cluster 2 (35%) predominating, and the upper half (48%) consisted of watersheds from natural clusters 7 and 8 in similar proportions. Notably, the Erie basin had the least number of watersheds from natural clusters 7 and 8 (1%), whereas the Huron basin had the least urban clusters (1%). In contrast, the greatest coverage of urban clusters was found within the Lake Ontario basin (12% and 14% for clusters 5 and 6, respectively) that were concentrated in the northwestern part of the basin and the remaining area is dominated by clusters 7 (24%) and 8 (42%). Approximately half of the St. Lawrence River basin was classified into cluster 8, one-third was classified into agricultural clusters (mainly cluster 4), and 14% consisted of cluster 6 watersheds.

Climate conditions (1981 – 2010) were relatively similar across the study region (Table 2.1). Among the major basins, Lake Erie experienced the warmest temperatures (annual mean 8.9°C; averaged from climate stations shown in Figure 2.1) and highest annual average rainfall (837 mm). Not surprisingly, the Lake Erie basin also accumulated the most growing degree days (GDD) above 5°C (2359 GDD) and had the longest average frost-free period (167 days). Within southern Ontario, the highest annual average precipitation was recorded in the Lake Huron basin (1039 mm; averaged from climate stations), where a larger proportion of precipitation occurred as snowfall (26%). Temperature and precipitation extremes varied more considerably across the basins. For example, Dalhousie Mills, in the easternmost region of the province (St. Lawrence River basin), had the greatest number of extreme cold days (T_{min} < -20°C), with 25 days per year exceeding this threshold on average (Table 2.1). In comparison, approximately only one extreme cold day per year occurred at locations such as Windsor (Lake Erie basin) and St. Catharines (Lake Ontario basin). Furthermore, the average number of days per year with precipitation greater than or equal to 10 mm ranged between 27 days (e.g., Sarnia, Toronto) and 43 days (Blyth).

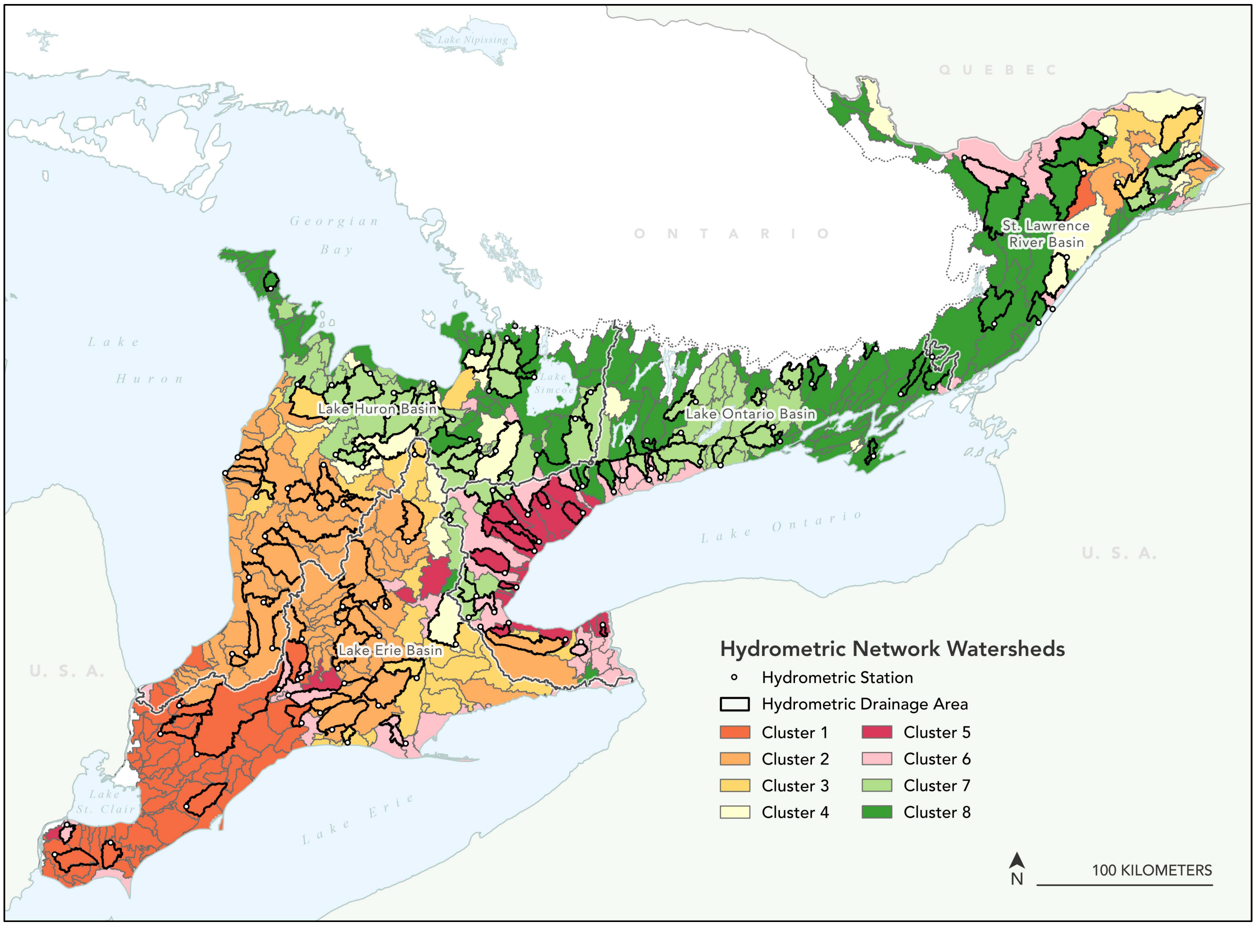

Figure 2.7 Hydrometric stations and hydrometric watersheds used for streamflow analysis across the Great Lakes basin in southern Ontario

Table 2.6 Areal proportion of each SOM cluster in the Great Lakes drainage basins within southern Ontario

Basin	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7	Cluster 8
Lake Erie	35	33	16	4	3	8	1	0
Lake Huron	2	35	8	7	0	1	25	23
Lake Ontario	0	5	1	1	12	14	24	42
St. Lawrence River	2	5	9	16	0	14	3	51

Differences in mean (2011 – 2020) annual runoff in watersheds across the Lake Erie, Lake Huron, Lake Ontario, and St. Lawrence River drainage basins were not substantial (Figure 2.8). The only significant difference in runoff was found between watersheds in the Lake Huron and Lake Ontario basins ($p < 0.05$), with higher average runoff depth in Huron (410 mm) as compared to Ontario (396 mm). The greatest variability in runoff was also found in the Huron (coefficient of variation [CV] = 23%) and Ontario (CV = 20%) basins, which may have been a result of several factors, including a more varied topography, higher land use diversity, as well as greater climate extremes in the Huron basin.

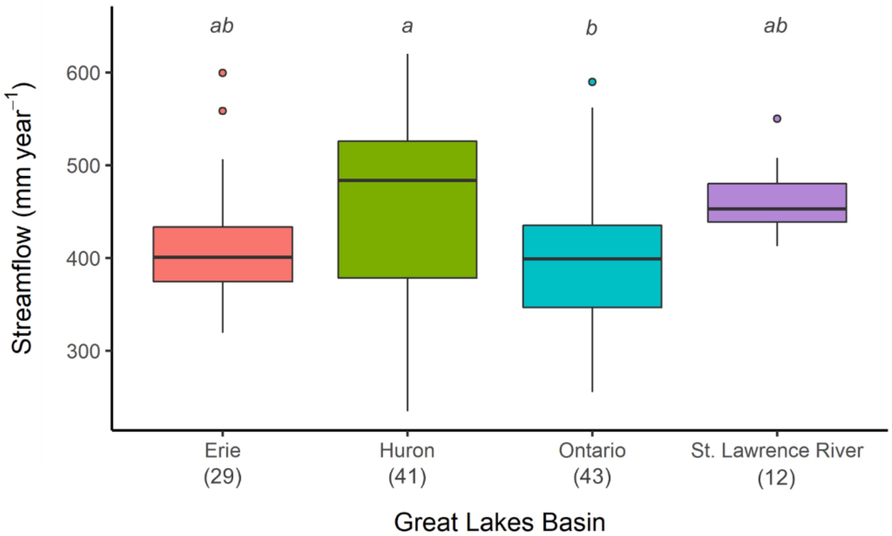

Figure 2.8 Decadal mean annual streamflow (*n*) in watersheds across the Great Lakes basins. Different letters denote significant differences according to Scheffe's test.

The two different methods used to calculate annual areal exports of NO_3-N, TP, and Cl across the four major drainage basins within the study domain yielded relatively comparable results (Table 2.7). Using the first method, annual NO_3-N and TP exports were predicted to be the highest at the Lake Erie basin, with an estimated mean of 1,110 kg NO_3-N km^{-2} and 36 kg P km^{-2} exported each year. Similarly, the second method also predicted that the greatest areal exports of NO_3-N (1,380 kg km^{-2} year^{-1}) and TP (54 kg km^{-2} year^{-1}) occurred within the Erie basin. The lowest areal NO_3-N (257 kg km^{-2} year^{-1}) and TP (16 kg km^{-2} year^{-1}) exports were reported to be within the Lake Ontario basin by the first method, but the second approach estimated the lowest TP and NO_3-N exports within the St. Lawrence River basin (246 kg NO_3-N km^{-2} year^{-1}, 18 kg P km^{-2} year^{-1}). Both methods identified Lake Ontario basin as having the highest Cl export (method #1: 23 metric tonnes [MT] km^{-2} year^{-1}; method #2: 36 MT km^{-2} year^{-1}) and Lake Huron basin the lowest (method #1: 12 MT Cl km^{-2} year^{-1}; method #2: 11 MT Cl km^{-2} year^{-1}). Although results were similar between methods, with differences generally less than 20%, the estimates generated from the second method were typically higher with greater variability than those of the first method (Table 2.7). Estimates for the Huron basin were most consistent (<10% difference) across methods, whereas the largest discrepancies (>40% difference) were observed for NO_3-N estimates for the Ontario and St. Lawrence River basins.

Table 2.7 Estimated annual mean ($10^{th} – 90^{th}$ percentiles) areal export of NO_3-N, TP, and Cl from major drainage basins within the study area

Basin	Method #1			Method #2		
	NO_3-N (kg km^{-2} year^{-1})	TP (kg km^{-2} year^{-1})	Cl (MT km^{-2} year^{-1})	NO_3-N (kg km^{-2} year^{-1})	TP (kg km^{-2} year^{-1})	Cl (MT km^{-2} year^{-1})
Erie	1110 (914–1414)	36 (30–46)	20 (16–25)	1380 (689–2248)	54 (34–79)	26 (22–45)
Huron	798 (535–1018)	21 (14–27)	12 (8–16)	858 (317–1574)	22 (10–36)	11 (10–20)
Ontario	257 (187–328)	16 (12–20)	23 (17–30)	447 (181–794)	22 (11–35)	36 (30–62)
St. Lawrence River	381 (289–451)	19 (14–22)	16 (12–19)	246 (47–526)	18 (9–28)	22 (17–42)

2.4 Discussion

2.4.1 Stream nitrate-N

Intensive row crop agriculture was clearly linked to increased decadal mean NO_3-N concentrations (Figure 2.6; Table 2.5), with stream NO_3-N levels at the most row crop dominated agricultural clusters (1 and 2) up to four times higher than at the urban clusters (5 and 6) and 12 times higher than at the predominantly natural clusters (7 and 8; Table 2.5). Although none of the clusters exhibited NO_3-N concentrations that approached the 10 mg L^{-1} drinking water quality guideline (Health Canada, 2013), concentrations in most watersheds of cluster 1 and 2 exceeded the 3 mg L^{-1} freshwater quality guideline for aquatic life (Figure 2.5; CCME, 2012). These elevated NO_3-N concentrations from agricultural watersheds in southwestern Ontario may have contributed to the rising NO_3-N concentrations observed in offshore waters of the Lake Erie, potentially stimulating aquatic productivity (Dove and Chapra, 2015). The strong association between watershed row crop intensity and NO_3-N concentrations in surface water found in this study has also been reported by other researchers in Ontario (e.g., DeBues et al., 2019; Nelligan et al., 2021; Liu et al., 2022) and in the midwestern United States (e.g., Schilling and Libra, 2000; Schilling and Spooner, 2006; Hatfield et al., 2009; Piske and Peterson, 2020). The slope of the regression analysis indicated a 0.7 mg L^{-1} rise in NO_3-N for every 10% increase in corn-soybean cover within watersheds (Figure 2.6a). Similarly, for the same rate of expansion in row crop area, Schilling and Libra (2000) suggested a 1.1 mg L^{-1} increase in NO_3-N based on measurements in Iowa watersheds that are intensively cropped with corn and soybean, whereas Liu et al. (2022) noted a 0.4 mg L^{-1} increase based on observations at seven small agricultural watersheds in east-central Ontario. These predictions indicate that continued growth in intensive agriculture is likely to be accompanied by increases in NO_3-N concentrations, particularly in watersheds within clusters 7 and 8 along the northern Lake Ontario shoreline, as these watersheds had the highest amounts of increase in agricultural area (7 – 11%) over the past decade (Table 2.5). Notably, all clusters experienced shifts from pasture toward row crop production, but the greatest transitions occurred in clusters 2 to 4 (7 – 9%), where higher proportions of mixed agriculture and livestock density were present in the watersheds (Table 2.5). Conversions of pasture and forage land to row crop farming found in this study are consistent with agricultural intensification trends across southern Ontario (Smith, 2015). This change has been largely driven by declining livestock production (mainly cattle and dairy cows; Smith, 2015), higher grain prices (Hume and Pearson, 2011), increased demand for corn-based ethanol production (Lark et al., 2015), introduction of cold-tolerant cultivars (Keddie and Wandel, 2001), as well as greater export demand to foreign markets (Camara, 2021). As longer growing seasons and increased crop yields in the future are projected for Ontario by climate change models (Cabas et al., 2010), areas under mixed agricultural land may continue to be replaced by row crop cover, potentially exacerbating NO_3-N losses.

The positive relationship between stream NO_3-N concentrations and row crop land use may be a product of several factors, including crop rotation, fertilization, and tile drainage. Watersheds in southwestern Ontario (cluster 1 and 2) which had the highest NO_3-N concentrations also had the greatest amount of land devoted to the continuous (at least four years) cultivation of corn and soybean (35 – 52%; Table 2.5), aligning with observations of corn-soybean being the most common crop rotation in the region (Macrae et al., 2021; Shirriff et al., 2022). By contrast, lower NO_3-N concentrations were found in clusters 3 to 8, which had fewer areas under corn-soybean only rotations (6 – 27%; Table 2.5) and also greater areas under other fields crops (e.g., rye, oats, barley) and pasture (e.g., perennial crops and hay), potentially indicating that crop rotations in these watersheds were more diverse and more likely to incorporate other crops, such as winter wheat or other cover crops (Shirriff et al., 2022). Streams draining landscapes with more diversified crop rotations and more pasture and perennial crops are likely to have lower NO_3-N concentrations. This is because cover crops can protect against soil erosion and absorb mineralized N and/or residual fertilizer N during active growth, which is subsequently released to the next crop upon decomposition of the cover crop residue, thereby reducing the potential for NO_3-N leaching (Millar and Robertson, 2015); whereas perennials have extended periods of water and nutrient uptake that optimize N cycling (Randall et al. 1997; Mitsch et al., 2001; Smith et al., 2013). Conversely, annual row crops, particularly corn, have lower N assimilation efficiency (~50% of applied N) than perennials, allowing the remaining available to be leached into waterways (Syswerda et al., 2012).

Annual cropping systems are intensively managed with high inputs of fertilizer and manure, which represent another important source of N. Nitrogen fertilizer applied in excess of crop requirements can increase the potential for NO_3-N accumulation and leaching in the soil profile (Malhi and Lemke, 2007). In this study, the proportion of watershed receiving commercial fertilizer was a strong predictor of mean stream NO_3-N concentrations across southern Ontario (R^2 = 0.65; Figure 2.6b), and similar correlations between fertilizer N and surface water NO_3-N have been reported in studies in the midwestern United States Corn Belt region (e.g., David et al., 2010; Li et al., 2013). As agriculture shifts to more intense forms with increasing regional concentration of livestock (e.g., concentrated animal feeding operations; Smith, 2015), manure becomes less available in many areas of annual crops, resulting in a greater reliance on commercial fertilizers to meet the high N demands of crops in areas of low livestock density. In Ontario, there has been a 43% decline in the volume of manure production between 1976 and 2011, whereas N fertilizer sales have increased (+824%) since the 1950s but the rate of increase has slowed down since the 1980s (Smith, 2015). Nitrogen application rates (fertilizer + manure) in Ontario vary by soil type and crop type; generally, they are estimated to range from 30 to 300 kg N ha^{-1} for corn and from 10 to 170 kg N ha^{-1} for wheat (Huffman et al., 2008). Much of the N fertilizer applied is utilized inefficiently, with only an estimated 30 to 40% of the N being absorbed by the crop, while the remainder is lost through various processes including leaching, denitrification, and soil erosion (Glass, 2003). There has also been a shift in the dominant type of commercial N fertilizer used from ammonium nitrate to urea (Paerl et al., 2016). One of the most abundant N fertilizers used for corn and soybean is urea, as it is often preferred over inorganic nitrogenous forms due to its low cost, high N content (46% by mass), stability in storage, and ease of application (Glibert et al., 2005). Urea rapidly converts into nitrate in soils but can also be exported to aquatic systems and then be assimilated as an N source by algae, potentially contributing to cyanobacterial blooms and toxin production (Belisle et al., 2016). Although overall manure production has declined due to decreases in cattle production, an enormous rise in chicken production in Ontario (+56% from 1976 to 2011; Smith, 2015) has likely increased the volume of poultry manure. High urea levels are found in poultry manure and most likely been heavily applied in cluster 2 watersheds where most chicken farms in the province are located. Using livestock manure as a fertilizer source can build soil organic matter and enhance soil health, yet applications of large amounts of manure can increase risks for NO_3-N leaching losses, and in some cases may even be higher than those of inorganic N fertilizers (Kirchmann et al., 2002). A recent study in western Iowa by Jones et al. (2019) showed that watersheds with higher livestock concentrations and generated manure N had stream NO_3-N that were two-fold higher than other watersheds despite little difference in commercial fertilizer N inputs.

This may explain why cluster 2, having the highest livestock density (68 AU km^{-1}) and manure-applied area (21%), had greater NO_3-N concentrations than cluster 1, even though similar proportions of fertilized area occupied both clusters (57% and 52% in clusters 1 and 2, respectively).

Subsurface tile drainage has enhanced crop production in the region but has also acted as a direct conduit for the movement of dissolved nutrients such as NO_3-N and SRP from fields to waterways (King et al., 2015). Most drainage networks discharge directly to ditches and streams, effectively bypassing riparian buffers and wetlands that trap nutrients and sediments in surface runoff (Helmers et al., 2007). As nitrate does not easily adsorb to particulate matter and is soluble in water, it is particularly susceptible to leaching through subsurface pathways such as tile drainage. Thus, unsurprisingly, higher stream NO_3-N concentrations were associated with an increased incidence of tile drainage in the watersheds (Figure 2.6c), although the slightly weaker relationship observed ($R^2 = 0.64$) relative to row crop and fertilized areas may be due to incomplete tile drainage records (Eimers et al., 2020). Currently, tile drainage underlies over 17,600 km^2 of southern Ontario, with the most intensively drained regions found in clusters 1 and 2 (49 – 61% of watershed area), where fine-textured soils with high clay and silt content (64 – 68%) predominate and combined with the level topography (0.6 – 1.3°) result in poor drainage conditions. Tile drainage has made cultivation possible on formerly waterlogged areas and has been critical in the expansion and economical production of row crops, as it can reduce crop loss from excess water stress and facilitate more consistent crop production amid increasing climate variability (King et al., 2015). Increasing profitability of row crop production from high commodity prices and improvement in crop yields has led to the rapid expansion of tile drainage since the 1960s. As producers adapt to uncertain climate conditions, continued increases in tile drainage extent are expected to accompany row crop expansions across east-central Ontario and even in northern Ontario with the support of government incentives, such as OMAFRA's Tile Loan Program in the south and the Regional Tile Drainage Initiative in the north.

2.4.2 Stream total phosphorus

Although no correlations were found between stream TP concentrations and any forms of land use, the highest mean TP levels were observed in cluster 1 (0.15 mg L^{-1}) which represented the most intensively tile-drained croplands in the region (Table 2.5). Agriculture can influence P loss in both particulate (PP) and dissolved forms: tile drainage and subsurface flow pathways contribute to dissolved P losses, whereas episodic P delivery is dominated by surface runoff and erosion of sediment-bound P (Schilling et al., 2020). Even though proportions of dissolved and particulate P concentrations were not measured in this study, it is possible that the high TP levels in cluster 1 were due to an increased contribution of dissolved P from intensive tile-drained row crop systems on fine-textured, glacially derived soils. Soils with higher clay content are more susceptible to the development of preferential flow paths (i.e., macropores, cracks, fissures) that bypass the buffering capacity of the soil matrix, directly conveying surface water with high SRP concentration to tiles (King et al., 2015). Preferential flows in soils, together with tile drainage, increase hydrological connectivity between fields and surface waters, thus promoting transport of dissolved P to the stream network (Jarvie et al., 2017). Furthermore, conservation tillage and surface broadcasting of fertilizer/manure without incorporation cause P to accumulate at the soil surface resulting in surface runoff with elevated concentrations of dissolved P (Jarvie et al., 2017). Direct runoff of surface-applied fertilizer and/or manure can also occur when they are applied shortly prior to runoff-inducing rainfall or when applied to frozen or snow-covered fields (Baker et al., 2014). While conservation tillage and tile drainage may have inadvertently enhanced the movement of SRP to streams, these agricultural practices can help reduce erosion and particulate P transport in croplands (Tiessen et al., 2010). In pasture areas, accelerated loss of sediment P via overland flow can result from livestock overgrazing and treading, whereas streambank erosion and PP export may be augmented when cattle have unrestricted access to watercourses (Cournane et al., 2011). In areas with high density of animal feeding operations, such as watersheds in cluster 2, manure application rates may exceed the capacity of nearby land to assimilate nutrients, leading to P buildup in soils and increased potential for PP to reach waterways through runoff (Kellogg et al., 2000). Compared to dissolved P, PP movement is more highly influenced by hydrologic conditions, as storm events and periods of high flow transport a disproportionately large amount of sediment-bound P (Dolph et al., 2019). More frequent and extreme precipitation events in the future arising from climate change (Kirchmeier-Young and Zhang, 2020) could increase nutrient losses by driving higher rates of erosion and export of PP, especially in areas dominated by fine-textured soils (e.g., southwestern Ontario) which are more vulnerable to erosion (Eimers et al., 2020).

Interestingly, mean decadal TP concentrations at urban-dominated clusters (4 and 5), ranging between 0.05 to 0.08 mg L^{-1}, were comparable to those at most agricultural clusters (2, 3, and 4; Figure 2.5). Prior studies have observed strong correlations of TP concentrations with impervious urban cover (e.g., Duan et al., 2012; Hobbie et al., 2017), with many reporting similar or even higher TP exports from urban areas than croplands (Winter and Duthie, 2000; Long et al., 2015; Kim et al., 2016; Thomas et al., 2018). Discharge from wastewater treatment facilities is often cited to be a large point source of P responsible for influencing regional concentrations under low flow conditions in particular (Thomas et al., 2018). However, as streams in this study had no known upstream municipal WWTPs (or had WWTPs that were over 20 km upstream), the impact of WWTPs on stream TP concentrations was negligible, which may explain why mean TP values in the urbanized clusters 4 and 5 were in the lower range of those reported in southern Ontario. Therefore, other factors such as altered hydrology caused by changes made to the watershed (e.g., impervious surface, stormwater drainage) and stream channel (e.g., channelization) are the more likely drivers of elevated TP concentrations in urban catchments of this study (Duan et al., 2012). For example, it is well known that urban drainage connections and imperviousness limit soil infiltration, increasing runoff volume and velocity as well as higher peak flows and stream flashiness in response to storm events (Hatt et al., 2004; Konrad and Booth, 2005). Brief periods of high flow events have been found to be responsible for over 50% to 90% of TP loads delivered to Hamilton Harbour from its streams (Long et al., 2015), and similarly, over 87% to 93% of exported TP occurred under high-flow conditions in urban and suburban watersheds in Maryland (Duan et al., 2012), which highlights the role of storm events in nutrient export with increasing urbanization. Besides the lack of P retention on impervious surfaces, high urban TP loading has also been attributed to storm water-induced bank erosion (Withers and Jarvie, 2008), temperature-induced SRP release from sediment and soils (Duan et al., 2012), in addition to fertilizer use on residential lawns (Pfeifer and Bennett, 2011). Notably, all clusters, even those dominated by natural cover, had TP measurements that exceeded the 0.03 mg L^{-1} provincial water quality objective, suggesting that continued P mitigations in both agricultural and urban landscapes are essential despite declines in stream TP concentrations across southern Ontario since the 1970s (Raney and Eimers, 2014b; Stammler et al., 2017).

2.4.3 Stream chloride

Surface water Cl concentrations are often reported to be the highest in urbanized and populated areas in seasonally snow-covered watersheds (Perera et al., 2009; Sorichetti et al., 2022), with streams draining urban landscapes having Cl concentrations up 10 times (Findlay and Kelly, 2011) to 100 times (Kaushal et al., 2005) greater than forested and agricultural streams. Numerous studies have observed positive associations between increasing Cl concentrations and measures of urban development including extent of impervious surface and road density (Rhodes et al., 2001; Kaushal et al., 2005; Winter et al., 2011), as well as human population (Todd and Kaltenecker, 2012). Consistent with this, Cl concentrations of the streams in this study increased as a function of urban coverage (R^2 = 0.61) and human population density (R^2 = 0.59) in the watersheds (Figures 2.6d, 2.6e). The highest mean Cl concentrations were 251 mg L^{-1} and 110 mg L^{-1} in urbanized clusters 5 and 6, respectively, which was up to nine times higher than concentrations in the least populated and natural dominated clusters (Table 2.5). The increasing salinization of surface and groundwaters across Ontario and northern United States has likely been the result of winter road salt applications (Kaushal et al., 2005; Sorichetti et al., 2022). Annually, over 5 million tonnes of road salt are spread on roadways in Canada, whereas another 10 to 15 million tonnes are applied in the United States (Brown and Yan, 2015), most of which enters streams primarily through surface runoff and groundwater discharge. Road salts can persist in watersheds beyond the time of application, leading to concerns about the accumulation of legacy Cl in soil and groundwater (Kelly et al., 2008; Perera et al., 2013; Mazumder et al., 2021). Notably, the lowest mean Cl concentration, 28 mg L^{-1}, observed at the most rural watersheds (e.g., cluster 4 and 7) in this study was higher than the average stream background Cl concentrations (17 mg L^{-1}) in mixed/treed catchments reported by Sorichetti et al. (2022), indicating the pervasive nature of road salt contamination across the study region. In rural watersheds with greater agricultural presence, effluent from septic systems and runoff of fertilizer (i.e., KCl) and livestock waste are other possible sources of Cl loading (Sherwood, 1989).

As the population of Ontario is expected to grow by one third over the next three decades, continued urban expansion in southern Ontario is likely to occur along with increases in winter road salting activities, thereby introducing new avenues of Cl exposure to surface water and groundwater (Sorichetti et al., 2022). This may further exacerbate Cl pollution in urbanizing regions and threaten aquatic biota in streams where Cl levels already regularly surpass the tolerance for freshwater life. For instance, the most frequent exceedances of the drinking water aesthetic objective (250 mg L^{-1}) and federal water quality guideline for chronic toxicity for the protection of aquatic life (120 mg L^{-1}) were in the highly urbanized (59% urban cover) cluster 5, followed by the peri-urban (30% urban) cluster 6 which had the greatest urban growth (7% total area) during the study period. Importantly, urban development in the region has occurred at the expense of highly productive agricultural land, prompting concerns of declining food security and agricultural sustainability (Francis et al., 2012). The greatest losses of prime agricultural land between 2000 and 2017 took place in southcentral Ontario, or the Greater Golden Horseshoe area, a region that experienced the highest population growth over the past two decades (Caldwell et al., 2022). Urban consumption of agricultural land decreases the amount of land available for specialty crops that have a narrow range of adaptation in Canada, affecting areas like the Niagara fruit belt where specialty crops significantly contribute to the local economy (Hoffman, 2001). Moreover, when farmland is converted to other uses, reduced production is replaced by either cultivating new land that is often more marginal and less fertile or by increasing productivity on remaining land (i.e., agricultural intensification), both of which require more intensive inputs, especially fertilizer. Major provincial interventions in land use regulation such as the Places to Grow Act and the Greenbelt Act have been successful in slowing rates of farmland loss since 2005 (Caldwell et al., 2022), providing some optimism for controlling urban sprawl and its associated costs.

2.4.4 Land use and export in major drainage basins

Although there exists a north to south gradient of increasing temperature as well as a general trend of increasing precipitation from northwest to southeast in Ontario (Baldwin et al., 2000), climate conditions and runoff across the major drainage basins (Lake Erie, Lake Huron, Lake Ontario, St. Lawrence River) within the study region were relatively similar. Hence, differences in NO_3-N, TP and Cl exports among the basins were likely mostly attributed to differences in concentrations associated with land use. The Lake Erie basin, which contains the largest proportion of watersheds from agriculturally dominated clusters 1 to 4 (87% of basin area; Table 2.6), was estimated to have the greatest annual areal exports of NO_3-N (method #1: 1,115 kg km^{-2}; method #2: 1,380 kg km^{-2}) and TP (method #1: 36 kg km^{-2}; method #2: 54 kg km^{-2}) by both methods (Table 2.7). As a prime agricultural region, the basin has highly productive soils, flat topography, and a long growing season (Hume and Pearson, 2011; OMAFRA, 2016). Most agricultural watersheds within the basin were classified into clusters 1 and 2 (Table 2.6), which were characterized by intensive tile-drained row crops as well as high-density livestock operations. These two clusters were also associated with the highest NO_3-N and TP concentrations out of all clusters (Table 2.5; Figure 2.6) and thus, catchments from these clusters have likely contributed to the high NO_3-N and TP export predictions for the Erie basin. A binational SPARROW (SPAtially Referenced Regression On Watershed attributes) study for the entire Great Lakes drainage basin suggests that the highest annual P (114 kg km^{-2}) and N yields (1,990 kg km^{-2}) occurred at the Erie basin, attributing this to the large agricultural extent within the basin (Robertson et al., 2019). Agricultural sources, especially fertilizers, were highlighted as a dominant land use source of P (54% of annual watershed P loading) and N (57% of annual watershed N loading) for Lake Erie (Robertson et al., 2019). Within the Lake Erie basin, agricultural catchments in southwestern Ontario were reported to have annual TP exports ranging from 31 kg km^{-2} to 263 kg km^{-2} and annual NO_3-N exports from 1,332 kg km^{-2} to 4,208 kg km^{-2} (Nelligan et al., 2021). The authors also found increased export at most of these watersheds between the 1970s to the mid 2010s, attributing this change to intensifying agricultural practices such as more extensive row cropping as well as increases in amount and density of tile drainage (Nelligan et al., 2019). High nutrient exports from the basin, coupled with the shallow lake depth, warm surface water temperatures, and short hydraulic residence time, make Lake Erie most susceptible to recurring large-scale HABs (Steffen et al., 2014). The NO_3-N and TP exports from the Erie basin estimated by both methods in this study were lower than those of other studies (e.g., Robertson et al., 2019; Nelligan et al., 2021). This was likely because the United States part of the basin was not considered and it is well recognized that the Erie basin in the United States is largely agricultural (i.e., Maumee River, Sandusky River) and contains the majority of the point sources (Robertson et al., 2019). For example, Robertson et al. (2019) estimated that contributions of total basin P and N loading from Canada were only 23% and 31% for Erie, as compared to Huron and Ontario where loading from the Canadian side is greater than 40%.

Among the major basins, Huron had the second highest annual yields of NO_3-N (method #1: 798 kg km^{-2}; method #2: 858 kg km^{-2}) and TP (method #1: 21 kg km^{-2}; method #2: 22 kg km^{-2}) and similar to the Erie basin, agricultural clusters comprised a major portion (51%) within Huron. The most prevalent agricultural watersheds in Huron were from livestock-dominated cluster 2, primarily located along the southeast shore of Lake Huron (Table 2.6). Due to a greater presence of livestock, manure has been identified as an equally important nutrient source in the Huron basin when compared to fertilizer (Robertson et al., 2019). Specifically, Robertson et al. (2019) estimated that manure represented 18% and 23% of total watershed P and N loadings, respectively, while fertilizer accounted for approximately 16% and 27% of P and N loadings, underscoring the need to consider manure management as a key aspect of nutrient management in the basin. The basin has the least urban development, with less than 1% of its area consisting of watersheds from peri-urban cluster 6. As a result, contribution of urban P and N sources were small, and the basin was also characterized by the lowest Cl export (method #1: 12 MT km^{-2}; method #2: 11 MT km^{-2}). Areal Cl export was greatest at the Lake Ontario basin (method #1: 23 MT km^{-2}; method #2: 36 MT km^{-2}), coinciding with it having the highest percentage of urban clusters (27% of basin study area). Urban watersheds within this basin contain the province's largest metropolitan centers primarily concentrated along the lake shoreline. Correspondingly, urban sources of P and N inputs to Lake Ontario were estimated to be more substantial when compared with agricultural and other sources (e.g., atmospheric, forest) with urban sources (Robertson et al., 2019). Urban WWTPs were estimated to contribute over 57% of total watershed P loading and 34% of total watershed N loading in the basin (Robertson et al., 2019). Mean areal NO_3-N exports from the Ontario basin were predicted to be 257 kg km^{-2} (method #1) and 447 kg km^{-2} (method #2), whereas TP exports were 16 kg km^{-2} (method #1) and 22 kg km^{-2} (method #2; Table 2.7).

Export predictions of NO_3-N and TP across the major basins from this study were lower than those from other studies (e.g., Robertson et al., 2019; Nelligan et al., 2021), likely due to the exclusion of concentrations that were influenced by WWTP effluent in this study. As WWTPs were estimated to contribute 41% of the total P loading and 27% of the total N loading in the Ontario basin (Robertson et al., 2019), this may explain the lower-than-expected export estimates for the highly urbanized basin. Urban areas are often associated with high areal P export (e.g., Winter and Duthie, 2000; Wellen et al., 2014; Kim et al., 2017). A SPARROW analysis of the Bay of Quinte watershed suggested a mean estimate of 120 kg TP km^{-2} yr^{-1}, whereas agricultural P export was found to vary considerably from 30 kg km^{-2} yr^{-1} to 127 kg km^{-2} yr^{-1} depending on the crop type (Kim et al., 2017). Urban catchments within the Lake Simcoe basin were also reported to export the most amount of TP within drainage waters, while forested catchments exported the least (Winter et al., 2007). For example, the most natural site (~22% agricultural area) exported only 2.3 kg km^{-2} $year^{-1}$, whereas areal export from more agriculturally dominated catchments (~77% agricultural area) was 32 kg km^{-2} $year^{-1}$ (Winter et al., 2007). Although NO_3-N export in the Lake Ontario basin was estimated to lower than from the Lake Erie and Huron basins, it is important to note there are some intensive agricultural catchments within the Ontario basin that export similarly high rates of NO_3-N. For instance, in south-central Ontario, agriculturally intensive tile-drained watersheds, Mystery and Brand Creeks, exhibited annual NO_3-N exports of 1,442 kg km^{-2} and 1,073 kg km^{-2}, respectively (Liu et al., 2022). Further, the area of focus of this study was only on southern Ontario, a region with the highest concentration of agriculture and urban development in the province, which was defined by the boundary of the Mixedwood Plains ecozone. Thus, areas in the major drainage basins that were within the Canadian Shield were not examined and exports from these regions were not accounted for, which may further explain the differences in estimated export from other studies. It should be noted, however, that areas on the Shield consisted mostly of natural land cover (e.g., forests, wetlands, and lakes), where less than 5% and 7% of the Canadian Shield region of the Lake Huron and Lake Ontario basins were collectively occupied by urban and agricultural land use, respectively.

This study compared two methods for calculating areal export of NO_3-N, TP, and Cl in the drainage basins within southern Ontario (Table 2.7). Major patterns in basin export derived from both methods were largely similar, however, estimates from the second method were consistently higher than from the first method. The greatest differences (40 – 55%) across methods were observed for NO_3-N exports for the Lake Ontario and St. Lawrence River basins. This discrepancy was likely because the second method accounted more rigorously for variability in both streamflow and concentration across the sites and also assigned greater uncertainty to clusters that had fewer gauged watersheds. Although the first method extrapolated variability of streamflow in each basin from a larger number of sites, flow data were not matched to concentration measurements at each watershed. In contrast, the second method only used sites with paired streamflow and concentration data within each cluster. This limited the number of sites that can be included in the second method, but it allowed for the calculation of total loading at each watershed, which provided the basis for deriving areal export in each basin. Overall, both methods provided insights into how land use patterns in each basin influence downstream export to the lower Great Lakes; however, the second method appears to be more consistent with the approach of the SOM land use analysis and better demonstrated the uncertainty associated with the estimates.

2.4.5 Land use practices

Aside from the need to protect water resources for healthy aquatic ecosystems and sustainable human use, recent geopolitical events and the finite nature of mineral phosphate reserves highlight the importance of limiting nutrient loss from land use. Modern agricultural production systems rely heavily on P fertilizers manufactured from phosphate rock to achieve high crop yields, yet deposits are concentrated in a small number of countries, many of which are located in 'politically unstable' areas, creating uncertainties regarding continuous supply and sustainable access (Blackwell et al., 2019). With fertilizer demand on the rise due to population growth, changes to dietary patterns, and development of biofuel production (Vermeulen et al., 2012), finite P resources will continue to diminish, potentially leading to fertilizer shortages that could threaten global food security. Moreover, recent spikes in global fertilizer prices have also resulted from supply disruptions caused by surging input costs and sanctions related to the Russia-Ukraine conflict (Hassen and Bilali, 2022). Increasing concerns around fertilizer availability and affordability, however, may encourage a rethinking of agricultural practices. For instance, farmers may become more reliant on using local manure sources and/or decide to cultivate more soybeans which require less N fertilizer, thereby lowering corn and wheat production (Legrand, 2022). Monitoring these types of changing agricultural practices over time will be important, as shifts could significantly impact future nutrient delivery.

Balancing agronomic productivity and conservation priorities is a key challenge. In landscapes like southern Ontario where snowmelt dominates nutrient export, many traditional practices for intercepting nutrients, such as erosion control using vegetation (e.g., grassed waterways, riparian buffers), are often ineffective under winter conditions (Macrae et al., 2021). Approaches to reducing N and P losses from intensive agriculture that are relevant to the study region include diversified crop rotations, improved fertilizer/manure management, and tile drainage water treatment. Since corn-soybean is the most practiced crop rotation in southwestern Ontario (Shirriff et al., 2022), addition of perennials and winter cover crops to cropping systems can lower the need for N fertilizer while enhancing total residue cover. For example, rotating fields to perennial hay or cover crops after a period of intensive annual cropping can help replenish soil nutrients and organic matter. Commonly adopted cover crops in the region are winter wheat, rye, oats, and red clover (Shirriff et al., 2022). It is also critical to avoid fertilizer or manure application in the late fall or winter given the elevated risk of direct nutrient transfer during snowmelt and rain-on-snow events (Baulch et al., 2019). Improved soil N testing methods (e.g., remote sensing based) to determine N credits from previous crops and manure applications can help optimize fertilization rates for meeting crop needs more precisely (Scharf et al., 2002). In areas of high livestock density, reducing the P content of manure by better matching dietary P to animal needs can be a cost-effective approach to minimizing P losses and can be accomplished through more precisely formulating animal diets, more accurate interpretation of published P requirements, and the addition of exogenous phytase or low-phytic acid grains into monogastric diets (Knowlton et al., 2004). Improved manure and wastewater handling and storage at animal production facilities can also minimize direct losses of nutrients to nearby surface waters (Sims et al., 2005). In pasture-based livestock systems, animal stocking rates need to be carefully managed to avoid overgrazing, whereas restricting livestock access to riparian areas can prevent streambank erosion and associated particulate P losses (Baulch et al., 2019). Rapid expansion of tile drainage has prompted development of methods promising for removing excess nutrient concentrations in tile discharge, such as controlled drainage, denitrification bioreactors, and constructed wetlands (Helmers et al., 2007). These methods require further investigation to determine feasibility of implementation on a larger scale. In urbanized areas, a substantial proportion of annual N and P export occur during high flows (e.g., Shields et al., 2008; Duan et al., 2012), and hence strategies have focused on controlling urban runoff, such as creating stormwater retention basins and implementing erosion measures at construction sites. Recent literature has also drawn attention to the contradictory effects of conservation practices

(Baulch et al., 2019; Jarvie et al., 2019; Osmond et al., 2019; Macrae et al., 2021; Kleinman et al., 2022), emphasizing the importance of understanding trade-offs (i.e., between dissolved vs. particulate nutrients, N vs. P, surface vs. ground waters, etc.) to avoid unintended consequences.

2.4.6 Research considerations

The SOM method provided a convenient means of watershed classification, identifying eight clusters with distinct land use characteristics across southern Ontario (Table 2.5). Such broadscale analysis was useful for simplifying heterogeneous landscape patterns, however, may have obscured smaller scale variability in land use in the process. For instance, although NO_3-N, TP and Cl concentrations were consistently lowest in clusters 7 and 8 where the largest extents of natural cover were found, land use in watersheds along the north shore of Lake Ontario has been linked to downstream eutrophication issues, such as toxic algal blooms in the Bay of Quinte, a Great Lakes Area of Concern (Kim et al., 2016). Within the Bay of Quinte watershed, Kim et al. (2016) conducted a similar SOM classification that yielded six distinct clusters (two agricultural, one pasture-dominated, one urban, one forested, and one transitional area), clearly illustrating that variability in land use exist within individual clusters identified in this study and should be explored further for regional management.

Changes in regional climatic conditions can further complicate nutrient management. Increases in winter streamflow in the Great Lakes region have occurred due to increasing winter temperatures and rainfall, reduced snowfall, as well as earlier snowmelt (Campbell et al., 2011; Vincent et al., 2018; Champagne et al., 2019). The consequence has been a seasonal shift in nutrient export to the non-growing season, during which greater losses in N and P may occur (Nelligan et al., 2021). However, as PWQMN sampling efforts have been based around the 'ice-free' season (April – November; Stammler et al., 2017), this study only examined tributary water quality data from this period and the extrapolated mean concentrations could hence be an underestimation of annual mean levels, as demonstrated by DeBues et al. (2019). Low-resolution sampling regimes are often unable to capture the full variability of nutrient concentrations, which is an important limitation given the sensitivity of stream TP concentrations to changes in hydrological conditions (Stammler et al., 2017). Year-round monitoring at greater intervals is needed to capture critical seasons (i.e., winter months) and time periods (i.e., spring runoff, storm events) to improve estimates of nutrient export.

Chapter 3: Stream water quality monitoring in southern Ontario: impacts of frequency, season, and location on nutrient concentrations

3.1 Introduction

Freshwater ecosystems constitute a small fraction of the Earth's surface (i.e., less than 1%), yet they support 10% of all animal species while also providing vital resources for humans (Dudgeon et al., 2006). At the same time, freshwaters are among the most threatened environments worldwide due to anthropogenic disturbances such as land use change, hydrological alterations, and the introduction of invasive species (Dudgeon et al., 2006). In the mid-1900s, water pollution legislation was introduced to address public health concerns in the United States (e.g., Federal Water Pollution Control Act of 1948), Canada (e.g., Canada Water Act of 1970), Europe (e.g., Surface Water Directive of 1975), Japan (e.g., Basic Law for Environmental Pollution Control of 1967), and many other countries. These pollution control measures drove the creation of water quality monitoring programs to help evaluate the effectiveness of policies based on water quality status and trends (Chapman et al., 2005). Long-term water quality monitoring has since been undertaken at regional, national, and even global scales (e.g., U.S. Geological Survey's National Water Quality Assessment Program [Hirsch et al., 1988], European Environment Agency's Eurowaternet [Lack, 2000], UNEP's Global Environment Monitoring System [Fraser et al., 2001]) and has been a valuable tool for understanding the complex dynamics of freshwater ecosystems and for guiding management actions (Myers and Ludtke, 2017).

Long-term monitoring programs operated by regulatory management agencies aim to describe water quality conditions over large areas and extended time periods. These programs traditionally consist of permanently established, fixed sites where periodic grab samples are collected (Strobl and Robillard, 2008). When early water quality management efforts were focused on controlling municipal and industrial point source discharges, sampling priorities were at locations above and below outfalls of point sources (Wiersma, 2004). However, as wastewater treatment and detergent phosphate bans in the early 1970s brought point source pollution under control, non-point sources from agricultural and urban landscapes have become the largest sources of water quality impairments (Watson et al., 2016). Current sampling networks must be adjusted so that spatial differences in water quality can be better characterized to allow for the identification of critical source areas, which may involve denser monitoring in regions that are highly populated, intensively cultivated, or rapidly changing in land use (Wiersma, 2004). Furthermore, low-frequency sampling (i.e., weekly or monthly) has historically been the standard practice of fixed-station water quality monitoring (Strobl and Robillard, 2008). These observations may not represent the full range of conditions occurring, particularly in streams where there are highly variable pollutant concentrations and/or discharge levels, or where streamflow responds rapidly to precipitation events (Khalil and Ouarda, 2009). Brief periods of high flow often transport the majority of pollutant loads (Lam et al., 2016), but these events are generally not well captured by ambient monitoring (Khalil and Ouarda, 2009). Routine monitoring programs that collect samples irrespective of streamflow conditions can result in a bias towards characterization of baseflow conditions (Long et al., 2014), which must be taken into consideration when estimates derived from these measurements are used to support management decision-making, such as for determining compliance with water quality standards.

In cold climate regions such as Canada, the seasonality of pollutant concentrations and transport as well as hydrological shifts associated with climate change are additional challenges that need to be addressed in water quality monitoring. For many monitoring programs across Canada, sampling has become based around the summer months (Miller et al., 2022) or ‘ice-free’ season (Stammler et al., 2017; Sorichetti et al., 2022) due to budgetary and logistical constraints. In seasonally snow-covered areas, however, the winter and spring months are a critical period when biological activity is low and nutrient exports can be particularly large (Liu et al., 2019). Nutrient delivery to streams during this period could hence be largely uncharacterized and lead to underestimations of annual loads. Current warming trends further complicate monitoring efforts, making it more difficult to assess impacts from land use (Miller et al., 2022). Adjustments in monitoring strategies may be required to better capture the impact of climatic changes.

Long-term monitoring of surface waters in southern Ontario, Canada, has been conducted since the 1960s by the Ontario Ministry of the Environment, Conservation and Parks (OMECP) in fulfillment of provincial and national water protection mandates (e.g., Ontario Water Resources Act, 1990; Clean Water Act, 2006) and binational agreement commitments (e.g., Great Lakes Water Quality Agreement of 1972). Protection of water supplies has been a primary agenda to ensure growing water demands can be met in this densely populated and agriculturally productive region. Urban and agricultural development have led to declines in stream water quality, contributing to nutrient enrichment, salinization, contamination by persistent chemicals, and other issues in the downstream Laurentian Great Lakes (Beeton, 2002). Drinking water contamination incidents, most notably the Walkerton *E. coli* outbreak in 2000, have further heightened the importance of monitoring to safeguard drinking water sources (Brown and Hussain, 2003). However, water quality monitoring can be challenging in a dynamic region like southern Ontario, where land use and management practices are shifting (Eimers et al., 2020). Over one-third of the Canadian population resides in southern Ontario, and continued population growth and urbanization are expected to occur, particularly within the Greater Toronto Area, where the population is projected to grow to over 10 million by 2046, representing a 42% increase from 2021 (Ministry of Finance, 2022). At the same time, urban growth and encroachment onto farmland may have contributed to trends of agricultural intensification. Conversions from less intensive pasture and mixed farming to more intensive row crop systems have become more widespread in southern Ontario over the past several decades (Smith, 2015). Row crop cultivation often requires greater fertilizer input and tile drainage intensity, while other agricultural land use practices, such as the use of reduced- or no tillage, have been adopted in response to soil conservation concerns (Eimers et al., 2020). These shifts in land use and agricultural practices combine to radically alter the landscape within southern Ontario, changing hydrological pathways and adding complexity to the understanding of pollutant transfer processes.

Water quality in rivers and streams across Ontario is monitored through the Provincial Water Quality Monitoring Network (PWQMN), which was established by the OMECP in 1964. Data from the program has been used to track long-term trends in water quality, identify critical areas with water quality problems, and assess the impacts of pollution control and watershed management activities. Over 400 stream locations throughout southern Ontario are currently sampled by Conservation Authorities and other partners on a monthly basis and measured for a range of physical, chemical, and biological parameters. Although the program has generated an extensive water quality database spanning over five decades, changes in government funding over time have resulted in inconsistencies in sampling frequency and a decline in the number of monitored sites. As sampling is managed by Conservation Authorities, monitoring activities can be adapted to respond to local concerns; however, systematic variations can also be introduced into the database due to differences in field sampling strategies and resources between authorities. Moreover, most samples are now being collected exclusively during the ice-free season (Stammler et al., 2017; Mazumder et al., 2021). Discrepancies in sampling seasonality may limit applications for seasonal-temporal analysis that is often necessary for examining agricultural watersheds, as these watersheds exhibit more pronounced inter-seasonal patterns in nutrient delivery (OMOE, 2012).

Understanding the characteristics and limitations of the PWQMN can help researchers better leverage the historical dataset to understand water quality changes in streams and the lower Great Lakes and identify drivers of change. Previous PWQMN-based studies have focused their analysis on the ice-free season to address sampling inconsistencies (e.g., Eimers and Watmough, 2016; Stammler et al., 2017; Mazumder et al., 2021), while other studies have excluded stream samples potentially impacted by point sources (e.g., WWTPs) to link stream nutrient concentrations to land use (e.g., Raney and Eimers, 2014b; DeBues et al., 2019; see Chapter 2). It is hence of interest to determine whether seasonal patterns in concentrations have been observed from long-term PWQMN data and the extent to which point sources (i.e., discharge from WWTPs and greenhouses) influence downstream concentrations, as these insights can assist with the interpretation of water quality conditions. The objectives of this study were to (a) characterize changes in PWQMN sampling frequency and seasonality between 1964 to 2019; (b) compare stream TP, NO_3-N, and Cl concentrations in the 'ice-free' (April – November) and 'ice-covered' (December – March) periods over the past five decades (1970 – 2019); and (c) assess decadal mean (2010 – 2019) stream TP and NO_3-N concentrations at sites downstream of point sources and at sites without any known point sources upstream. The highest concentrations of NO_3-N, TP, and Cl were expected to occur in the ice-covered period (e.g., Kaushal et al., 2005; Van Meter et al., 2020), whereas WWTP and greenhouse influenced streams were expected to exhibit elevated NO_3-N and TP concentrations (Maguire et al., 2018; Robertson et al., 2019).

3.2 Methods

3.2.1 Study area

Southern Ontario is the most densely populated and agriculturally productive region of Canada. The concentration of anthropogenic activities in tandem with the availability of long-term stream monitoring data provides an opportunity to examine the impacts of land use and point sources on water quality. To focus on this region and in alignment with the analysis conducted in Chapter 2, only PWQMN stations in southern Ontario were considered in this study. The Mixedwood Plains ecozone within the province was used to define the study area boundaries. Southern Ontario is bounded by the Canadian Shield to the north, Lake Huron to the west, and Lakes Erie and Ontario to the south. Topography varies across the region, ranging from flat terrain in the southwest and southeast to the rugged terrain of escarpments and moraines formed from glacial erosional and depositional processes at the northern boundary (Sharpe et al., 2014). Climate in southern Ontario is humid continental (Köppen Dfb/Dfa) and is modified by lake and topographic effects, resulting in moderated seasonal temperatures and elevated precipitation in areas east of Lake Huron and Georgian Bay (Baldwin et al., 2000). Long-term (1981–2010) climate records for the study region were taken from a selection of meteorological stations across the region (see Table 2.1). Average annual temperature ranges from 6.2°C (Peterborough) to 9.9°C (Windsor), with a regional average of 7.9°C. Average monthly temperatures are highest in July (21.1°C) and lowest in January (−6.3°C). Average annual precipitation also varies across the region, from 831 mm in Toronto to 1087 mm in Hanover, of which less than 25% on average falls as snow between December and April.

3.2.2 Characterization of sampling trends

Spatial and temporal sampling patterns of TP, NO_3-N, and Cl in the PWQMN program were characterized for the period between 1964 and 2019. The PWQMN database was retrieved from the Ontario Data Catalogue. Trends in sampling seasonality over time were determined by calculating the total number of stations that were sampled for each of the three parameters each month every year, which were then presented as a series of heatmaps. To estimate average sampling frequency, the total number of samples in each month, year, and decade were averaged across the stations. Locations of active stations in each decade were shown on maps along with the decadal number of samples, averaged across the three parameters, for visual assessment of spatial trends. The number of monitoring stations with an extended period of record and sufficient sampling frequency (herein referred to as 'long-term sites') were quantified in each decade for the three constituents. To qualify as a long-term site, locations must have been sampled for at least eight months each year for a minimum of seven years in each decade. The number of long-term sites was calculated within each conservation authority boundary to help determine spatial patterns in monitoring frequency across the study region.

3.2.3 Seasonal patterns of stream concentrations

Water quality analysis. Differences between stream TP, NO_3-N, and Cl concentrations in the 'ice-free' and 'ice-covered' periods were examined across the five decades (1970 – 2010). To address inconsistencies in sampling frequency across sites and between years, PWQMN data in each decade were screened to include only sites that had a minimum of seven years of data, where each year had to have at least six available out of the eight months during the ice-free season (April – November) and at least two available out of the four months during the ice-covered season (December – March). Any station with an upstream catchment that was nested within the catchment of another station was excluded in this analysis. As noted by Eimers and Watmough (2016), laboratory methods of NO_3-N analysis in the PWQMN program have changed over time, where stream samples prior to the early 1990s were first filtered and then analyzed for NO_3-N, while those subsequent to 1997 were analyzed unfiltered for 'total nitrates'. During the years when there was an overlap between methods, comparisons were made to confirm consistency in the NO_3-N values produced from both methods. When visually inspecting historical TP and NO_3-N measurements, some outliers were identified in the late 1970s and early 1980s (i.e., over 1000 mg TP L^{-1} and 100 mg NO_3-N L^{-1}). These abnormally high values could have been due to manual transcription errors as cautioned by the MECP (2023), influences of WWTP discharge, or use of a different unit of measurement that was incorrectly recorded (Raney and Eimers, 2014b). Due to the uncertainty surrounding these outliers, they were removed to prevent inflating subsequent calculations of mean values. Decadal ice-free and ice-covered seasonal averages were calculated by first averaging values for each month, then averaging monthly measurements to provide annual seasonal (ice-free vs. ice-covered) concentrations, and finally averaging seasonal concentrations into decadal seasonal means at each site. Decadal seasonal mean concentrations were compared across decades using the Wilcoxon signed-rank test ($p < 0.05$). In addition, a comparison of annual seasonal averages was conducted using the Wilcoxon signed-rank test ($p < 0.05$) at nine individual sites for each parameter. These sites were selected as they each had at least three decades of data, with a minimum of seven years each decade, and six or more months of sampling during the ice-free period or two or more months of sampling during the ice-covered period. As the number of parameters that was analyzed varied between sites and years, the set of sites differed for each parameter, although most sites were the same across the parameters.

Land cover characterization. As the number of stations available for analysis varied across decades and upstream land cover can also influence concentrations, it was important to consider land cover within the upstream catchments of the sampling sites to provide insight into differences in stream chemistry over time. Watersheds were delineated using the Ontario Watershed Information Tool, with pour points defined to be the location of each monitoring site (DeBues et al., 2019). Land cover data for each decade were obtained from multiple sources. Land cover for the 1970s was constructed based on the Canada Land Inventory (CLI) from 1966, supplemented with data from the Canada Land Use Monitoring Program (CLUMP) in 1971. This was because CLUMP land use data, although higher in resolution than CLI, was only compiled for the largest urbanized regions at the time, and therefore, spatial gaps in CLUMP coverage were filled by CLI (DeBues et al., 2019). It should be noted that since CLUMP data was not available for smaller metropolitan areas (e.g., Peterborough, Kingston, Barrie, Brantford), urban areas across the study area were likely underestimated for the 1970s. Land cover for the 1980s was approximated based on the 1983 Agricultural Resource Inventory, whereas data from the Agriculture and Agri-Food Canada's Semi-Decadal Land Use Time Series were used to represent land cover for the 1990s, 2000s, and 2010s. All land cover classes in the datasets were aggregated into three general land cover categories: urban, agriculture, and natural (Appendix F). Proportions of land cover were then calculated within each watershed in each decade using the corresponding historical land cover datasets. Stations were labelled according to the most dominant land cover in its upstream watershed: stations were 'agricultural' if agricultural land consisted of over 50% of total watershed area; 'urban' if urban coverage was at least 30%; 'natural' if natural land cover was over 50%; and 'mixed' if two land cover types shared similar areal proportions. Bar charts were created to show the dominant upstream land cover (i.e., agricultural, urban, natural, mixed) associated with the stations used for analysis in each decade.

3.2.4 Influence of point-sources on concentrations

To determine the degree of impact that point sources can have on stream concentrations, a selection of PWQMN sites with concurrent TP and NO_3-N records in the recent decade (2010 – 2019) were analyzed. As identified by previous studies (e.g., Stammler et al., 2017; Mazumder et al., 2021) and revealed in the characterization of the database, sampling has become based around the ice-free period, and therefore only concentrations in the ice-free months were considered. Stations that were sampled a minimum of six out of eight months each year of the decade were selected to ensure adequate nutrient variability was captured. In each year, monthly samples were aggregated into seasonal averages, which were then averaged over the decade to account for changes in hydroclimatic conditions. Stations were categorized according to the presence of upstream point sources, specifically WWTPs or greenhouses, within 20 km on the same stream branch. Locations of current WWTPs were provided by the OMECP through personal communication. The final subset used for analysis comprised of 79 sites with point source influence and 86 sites without any point sources upstream. As the TP and NO_3-N data were not normally distributed, a natural log transformation was applied prior to performing a one-way analysis of variance (ANOVA) to evaluate differences in mean concentrations between sites with and without upstream point sources.

3.3 Results

3.3.1 Sampling trends of the PWQMN

Sampling frequency varied throughout the history of the PWQMN. Although sites were typically sampled once per month (Appendix F), the average number of samples collected per year has declined over time (Figure 3.1). For example, from 1967 to 1994, an average of ten or more samples were analyzed annually for NO_3-N, TP, and Cl concentrations each year, reaching as high as 20 per year, whereas seven samples per year were more common post 1995 (Figure 3.1). Between 1964 and 2019, there was a general decrease in the number of stations in southern Ontario sampled for NO_3-N, TP, and Cl concentrations each month (Figure 3.2). The greatest number of stations were sampled in the late 1970s and early 1980s, when on average more than 400 stations were sampled monthly for NO_3-N and TP, and over 370 stations were sampled for Cl (Figure 3.2). The highest number of sites sampled for NO_3-N and TP was 502 and 501 stations in April 1977, respectively, while 473 stations were sampled for Cl in October 1977. A sharp decline in the number of monthly monitored sites has occurred since 1996; on average, fewer than 200 stations were analyzed for the three parameters from 1996 to 2002 (Figure 3.2). In some months (e.g., April 2002; February to April 2006), none of the constituents were measured at any station across the study region. The number of monitored sites was relatively consistent between months each year until approximately 1996, after which more stations were sampled between April and November ('ice-free' period) compared to December to March ('ice-covered' period; Figure 3.2). For example, the average monthly number of sites sampled for TP during the ice-free period between 1996 to 2019 was 248 stations, whereas the average number of monitored sites for the ice-covered period was 64 stations over the same period. This marked preference for sampling in the ice-free season was noted for NO_3-N and Cl as well (Figure 3.2).

The total number of sites analyzed for each constituent in each decade (excluding the 1960s) was contrasted with the number of sites that met the long-term criteria within individual decades (Figure 3.3). Specifically, a station was considered to be a 'long-term site' in a decade if it was sampled at least once a month for a minimum of eight months in a year and for a total of at least seven years. Declines in both the total number of monitored sites and in long-term sites were observed across the five decades (Figure 3.3). The highest number of sites monitored for all three parameters was during the 1970s (890 locations for NO_3-N and TP; 821 locations for Cl) and the lowest was in the 2010s (417 locations for all parameters). In contrast, the numbers of long-term sites were greatest in the 1980s for TP (379 sites) and Cl (348 sites), with increases of 44% and 41% compared to the number of long-term sites from the 1970s, respectively. The lowest number of long-term sites for NO_3-N, TP, and Cl was observed in the 2000s (54, 47, and 56 sites, respectively), which represented declines in numbers between 77% to 82% from the 1970s (Figure 3.3).

The PWQMN sampling network is well distributed across a range of land covers in southern Ontario (Figure 3.4). To describe changes in sampling locations over time, the total number of stations monitored and number of long-term sites in each decade were characterized within the administrative areas of 31 conservation authorities (CA) in the study region (Table 3.1; Figure 3.5), which vary in size from 453 km^2 (Hamilton) to 6,832 km^2 (Grand River). In most decades, CAs with larger administrative areas had a higher number of monitored sites than those with smaller jurisdictions. For example, Grand River, the largest conservation authority, had 39 active sites in the 2010s, whereas Kettle Creek and Catfish Creek, authorities with the smallest jurisdictions, only had four sites during the same decade (Table 3.1). Notably, Toronto, despite its smaller administrative area, sampled the most sites out of all CAs in the 1960s (33 sites) and 1990s (177 sites). Across all decades, the highest density of sites (number of sites per unit area) was found in the most populated and urbanized south-central region of Ontario (e.g., Credit Valley, Halton, Toronto, Central Lake Ontario), followed by the intensive agricultural southwestern Ontario (e.g., Essex, Lower Thames, Grand River, Niagara; Table 3.1; Figure 3.4). The total number of stations within most CAs declined by over 50% from the 1970s to the 2010s, although some CAs, such as Credit Valley, Halton, Toronto, Central Lake Ontario, and Kawartha, monitored the highest number of sites in the 1990s compared to other decades (Table 3.1).

The number of samples collected at each station within each decade differed by CA (Figure 3.4), however, certain CAs sampled more consistently than others, as evidenced by the larger number of long-term sites they maintained across the decades (Table 3.2) and greater total number of years in which samples were collected over at least eight months (Figure 3.9). Credit Valley, Grand River, Toronto, Niagara Peninsula, Ausable Bayfield, and Kawartha, were able to maintain long-term sites throughout the five decades from 1970 to 2010 (Table 3.2). Most of the remaining CAs had only two or three decades where there were any long-term sites (Table 3.2). Conservation authorities with the greatest number of sites that had a total of at least 40 years in which more than eight months were sampled include Grand River (7 sites), Credit Valley (5 sites) and Niagara Peninsula (4 sites). Most south-eastern CAs (e.g., Otonabee, Lower Trent, South Nation) did not have any long-term sites during the 2000s and 2010s (Table 3.2).

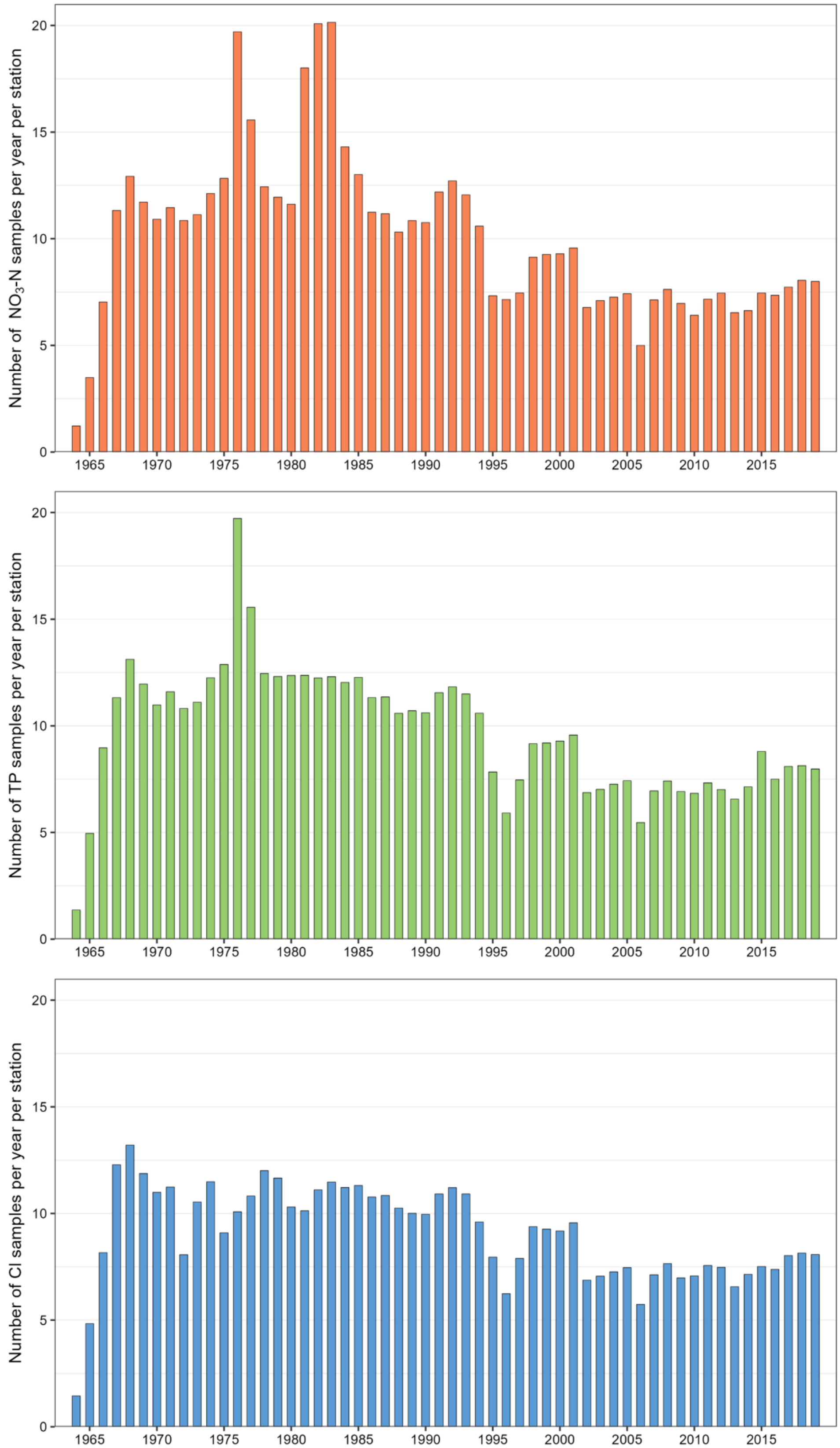

Figure 3.1 Annual number of samples analyzed for NO_3-N, TP, and Cl concentrations averaged across monitoring sites in southern Ontario between 1964 – 2019.

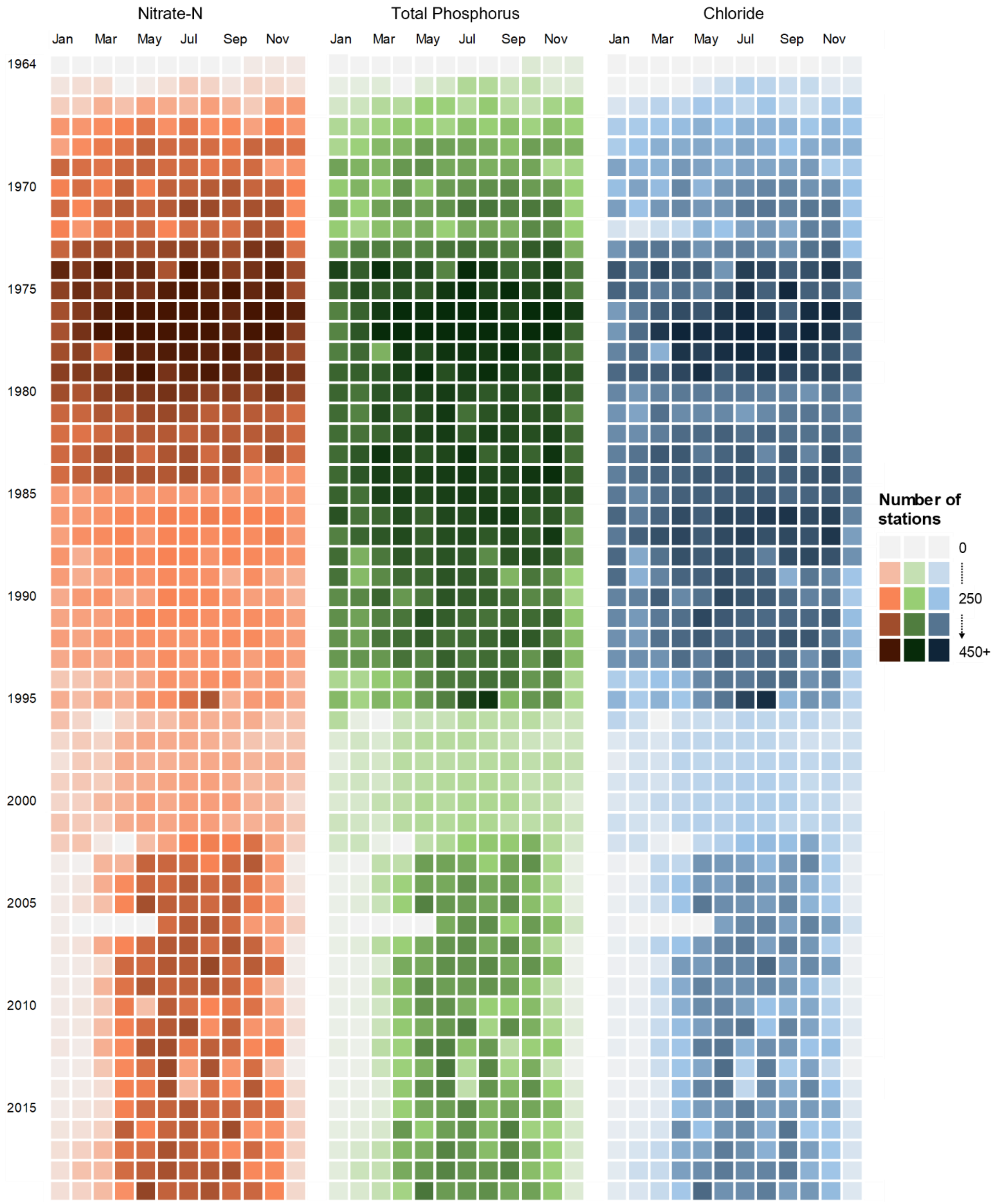

Figure 3.2 Total number of stations in southern Ontario sampled for NO_3-N, TP, and Cl concentrations each month from 1964 to 2019. Darker colours represent a greater number of stations monitored.

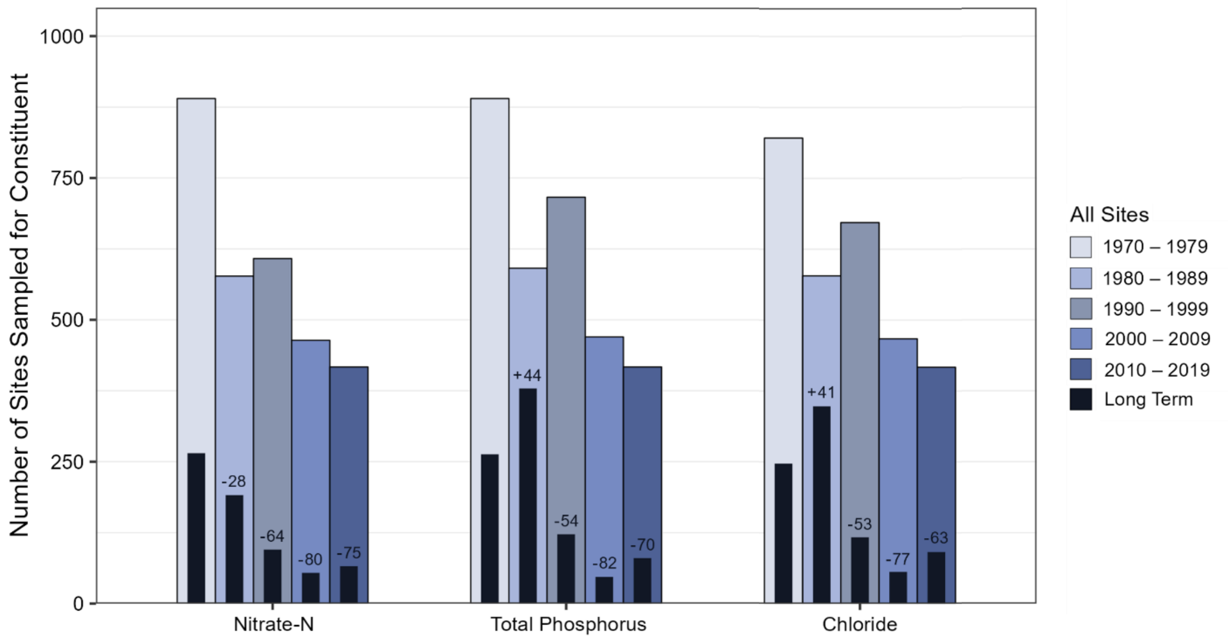

Figure 3.3 Total number of monitoring sites and long-term sites sampled by the PWQMN for concentrations of NO_3-N, TP, and Cl by decade, 1970 – 2019. The numbers above the bars of the long-term sites represent percentage change in the number of long-term sites of that decade relative to the number of long-term sites in the 1970s.

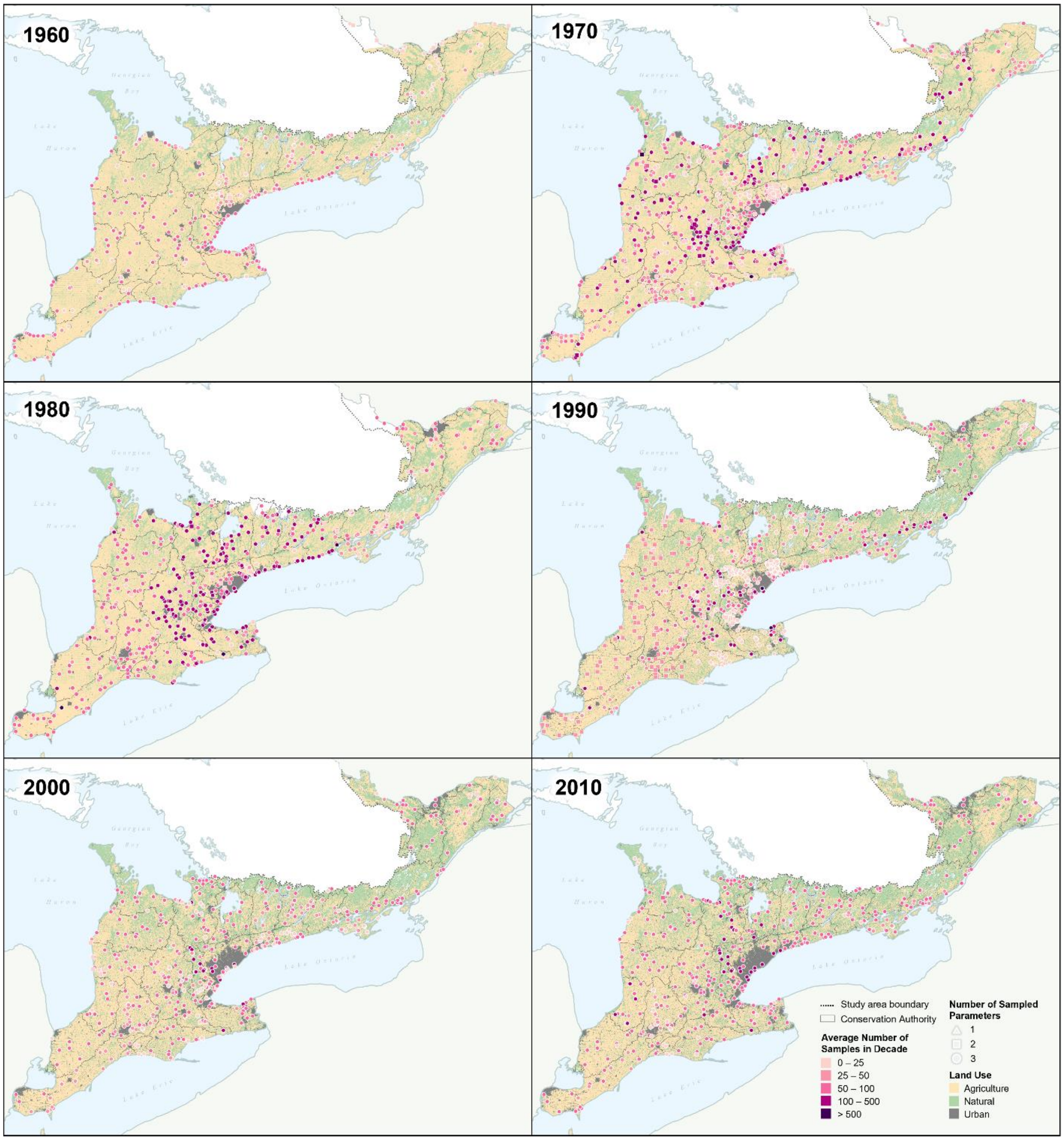

Figure 3.4 Locations of active sampling sites in each decade underlain by land use of that decade. Sampling stations with darker colours represent higher average number of samples collected at those locations, while shapes indicate the number of sampled parameters of study. Names of Conservation Authorities are presented in Figure 3.5.

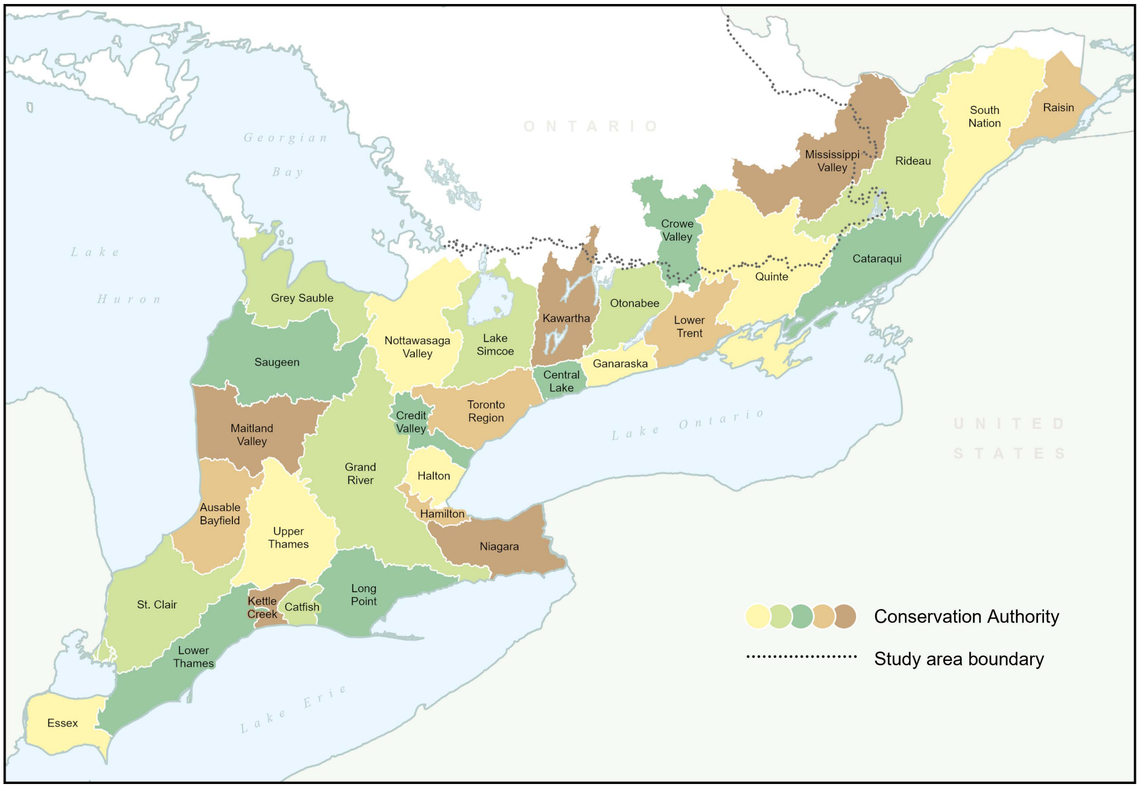

Figure 3.5 Location of Conservation Authorities across southern Ontario

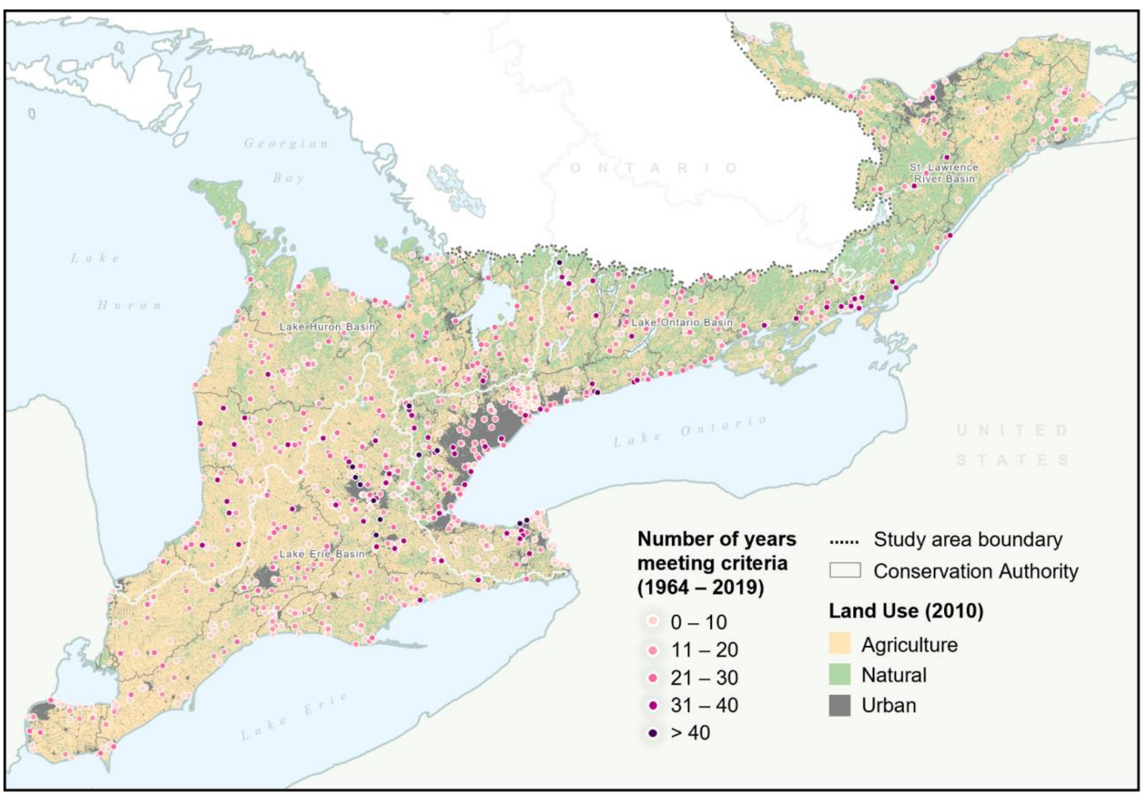

Figure 3.6 Number of years where at least eight months were sampled, averaged across the three constituents (NO_3-N, TP, and Cl) at PWQMN monitoring stations in southern Ontario. Names of Conservation Authorities can be found in Figure 3.5.

Table 3.1 Number of PWQMN stations sampled for concentrations of NO_3-N, TP, and Cl by decade within Conservation Authority (CA) jurisdictions, ordered from west to east. The number of stations reported for certain CAs (Crowe, Quinte, Mississippi Valley, Rideau Valley) does not represent all PWQMN stations within their jurisdiction, since this study only examined southern Ontario only. Locations of CAs are shown in Figure 3.5.

Conservation Authority	Administrative Area[a] (km^2)	Region[b]	Nitrate-N						Total Phosphorus						Chloride					
			1964 – 1969	1970 – 1979	1980 – 1989	1990 – 1999	2000 – 2009	2010 – 2019	1964 – 1969	1970 – 1979	1980 – 1989	1990 – 1999	2000 – 2009	2010 – 2019	1964 – 1969	1970 – 1979	1980 – 1989	1990 – 1999	2000 – 2009	2010 – 2019
Essex Region	1,691	SW	15	23	12	0	8	8	15	23	13	12	8	8	15	22	13	12	8	8
St. Clair Region	4,163	SW	11	20	14	1	10	9	11	20	14	10	10	9	11	19	14	10	10	9
Lower Thames Valley	3,283	SW	17	30	21	16	9	11	17	30	21	17	9	11	17	30	21	17	9	11
Ausable Bayfield	2,464	SW	15	28	14	1	11	11	15	28	15	13	11	11	15	26	14	13	11	11
Maitland Valley	3,279	SW	13	32	21	11	15	12	13	32	22	18	21	12	13	30	22	18	21	12
Kettle Creek	515	SW	4	15	9	0	4	4	4	15	9	7	4	4	4	15	9	7	4	4
Saugeen Valley	4,645	SW	9	49	22	2	18	19	9	49	24	24	18	19	9	42	24	24	18	19
Upper Thames River	3,444	SW	12	36	32	15	33	31	12	36	33	26	33	31	12	36	33	26	33	31
Grey Sauble	3,166	SW	11	27	14	0	10	10	11	27	14	14	10	10	11	27	14	14	10	10
Catfish Creek	491	SW	1	7	4	0	4	4	1	7	4	3	4	4	1	7	4	3	4	4
Long Point Region	2,861	SW	12	39	23	18	19	12	12	39	23	21	19	12	12	33	23	21	19	12
Grand River	6,832	SW	23	98	52	55	46	39	23	98	53	56	46	39	23	80	51	52	46	39
Hamilton Region	453	SW	7	9	4	3	6	6	7	9	4	3	6	6	7	9	4	3	6	6
Niagara Peninsula	2,433	SW	26	44	23	19	13	19	26	44	23	19	13	19	26	44	22	19	13	19
Nottawasaga Valley	3,571	SC	10	31	23	17	22	20	10	31	23	18	22	20	10	31	22	18	22	20
Credit Valley	949	SC	6	22	19	41	20	16	7	22	19	41	20	16	6	22	18	19	20	16
Halton Region	965	SC	7	22	16	45	21	11	7	22	17	45	21	11	7	22	16	27	21	11
Toronto and Region	2,488	SC	33	95	46	176	17	13	33	95	50	177	17	13	28	68	46	176	17	13
Lake Simcoe Region	3,334	SC	12	27	24	25	14	12	12	27	24	25	14	12	12	27	24	25	14	12
Central Lake Ontario	639	SC	9	13	12	10	15	10	9	13	12	10	15	10	9	13	12	10	15	10
Kawartha Region	2,352	SE	2	11	14	15	9	9	2	11	14	15	9	9	2	11	14	15	9	9
Ganaraska Region	930	SE	8	9	10	7	16	9	8	9	10	8	16	9	8	9	10	8	16	9
Otonabee Region	1,906	SE	17	26	19	19	19	14	17	26	19	19	19	14	17	26	19	19	19	14
Crowe Valley	215	SE	1	4	4	3	1	1	1	4	4	4	1	1	1	4	3	4	1	1
Lower Trent	2,055	SE	8	18	17	15	9	13	8	18	17	16	9	13	8	17	17	16	9	13
Quinte	3,084	SE	13	23	23	26	26	22	15	23	23	25	26	22	13	23	23	26	26	22
Mississippi Valley	1,254	SE	4	11	7	7	7	5	4	11	7	7	7	5	3	11	7	7	7	5
Cataraqui Region	3,363	SE	22	29	23	14	14	22	22	29	23	14	14	22	22	25	24	14	14	22
Rideau Valley	3,380	SE	21	29	19	9	9	9	21	29	19	9	9	9	21	29	19	9	9	9
South Nation River	4,144	SE	12	13	8	8	14	9	12	13	8	8	14	9	12	13	8	8	11	9
Raisin Region	1,670	SE	2	20	11	18	9	11	3	20	13	18	9	11	3	20	11	18	9	11
Others[c]			41	30	17	12	17	17	41	30	17	14	17	17	36	30	17	14	17	17

Notes:
[a] Administrative area within the study region
[b] SW = southwestern Ontario; SC = south-central Ontario; SE = southeastern Ontario
[c] 'Others' represent stations in southern Ontario that are not located within any CA administrative area

Table 3.2 Number of stations meeting long term criteria (i.e., sampled at least 8 months for at least 7 years in each decade) for concentrations of NO_3-N, TP, and Cl by Conservation Authority, ordered from west to east. Locations of CAs are presented in Figure 3.5. Non-zero numbers are shaded to improve readability. See Table 3.1 for administrative area and regional information.

Conservation Authority	Nitrate-N					Total Phosphorus					Chloride				
	1970 – 1979	1980 – 1989	1990 – 1999	2000 – 2009	2010 – 2019	1970 – 1979	1980 – 1989	1990 – 1999	2000 – 2009	2010 – 2019	1970 – 1979	1980 – 1989	1990 – 1999	2000 – 2009	2010 – 2019
Essex Region	3	0	0	0	0	3	11	0	0	1	2	9	0	0	2
St. Clair Region	7	1	1	0	0	7	9	1	0	0	6	9	1	0	0
Lower Thames Valley	2	1	1	0	2	2	14	1	0	5	2	14	1	0	5
Ausable Bayfield	5	1	1	6	9	5	13	1	5	9	5	13	1	6	9
Maitland Valley	12	0	0	0	0	12	14	5	0	0	11	14	6	0	0
Kettle Creek	3	0	0	0	0	3	7	0	0	0	3	7	0	0	0
Saugeen Valley	8	1	1	0	0	8	18	1	0	0	7	17	0	0	0
Upper Thames River	6	0	0	2	0	6	25	15	1	0	6	25	15	2	0
Grey Sauble	4	0	0	0	0	4	6	0	0	0	4	6	0	0	0
Catfish Creek	1	0	0	0	0	1	3	0	0	0	1	3	0	0	0
Long Point Region	9	12	0	0	8	9	12	0	0	8	6	13	0	0	8
Grand River	32	44	28	12	4	31	45	29	10	5	31	43	27	11	10
Hamilton Region	7	3	0	0	0	7	3	0	0	0	7	3	0	0	0
Niagara Peninsula	13	13	6	6	5	13	13	6	6	5	11	15	6	6	7
Nottawasaga Valley	12	12	6	0	0	12	15	6	0	0	11	14	5	0	0
Credit Valley	5	13	12	13	14	5	16	15	13	14	5	16	15	13	15
Halton Region	9	11	0	0	0	9	16	0	0	6	9	16	0	0	6
Toronto and Region	26	18	2	2	12	26	21	2	2	13	22	18	2	2	13
Lake Simcoe Region	16	18	0	0	0	16	21	0	0	0	16	21	0	0	0
Central Lake Ontario	7	7	0	0	0	7	8	0	0	0	7	8	0	0	0
Kawartha Region	4	11	0	3	3	4	14	3	3	5	4	14	3	6	7
Ganaraska Region	6	5	0	0	8	6	6	0	0	8	6	6	0	0	8
Otonabee Region	11	8	0	0	0	11	16	0	0	0	11	16	0	0	0
Crowe Valley	2	1	0	0	0	2	2	0	0	0	1	2	0	0	0
Lower Trent	8	8	0	0	0	8	10	0	0	0	8	9	0	0	0
Quinte	9	0	4	0	0	8	5	3	0	0	9	1	4	0	0
Mississippi Valley	0	0	4	0	0	0	0	4	0	0	0	0	2	0	0
Cataraqui Region	16	0	13	0	0	16	8	13	0	0	15	3	13	0	0
Rideau Valley	15	0	8	0	0	15	10	8	0	0	15	4	8	0	0
South Nation River	0	0	1	0	0	0	1	1	0	0	0	0	1	0	0
Raisin Region	0	0	5	9	0	0	9	5	6	0	0	1	5	9	0
Others	7	3	2	1	1	7	8	3	1	1	6	8	2	1	1

3.3.2 Seasonal patterns of stream concentrations

Decadal Stream Concentrations. The number of PWQMN stations that met the selection criteria for the analysis of decadal mean stream NO_3-N, TP, and Cl concentrations differed across decades (Figure 7), reflecting shifts in sampling frequency and locations of the sampling network over time. The 1970s and 1980s had the highest number of sites meeting the criteria (76–146 sites; Figure 3.8b; Figure 3.9b; Figure 3.10b), while the 2000s and 2010s had notably fewer sites (i.e., less than 10; Figure 3.8b; Figure 3.9b; Figure 3.10b). The upstream catchments of the majority (over 80%) of sampling sites in the 1970s and 1980s were dominated by agricultural land cover (Figure 3.7). Selected sites in the 1990s and 2000s encompassed a greater variety of upstream land cover, while the watersheds of sites in the 2010s were mainly urban (Figure 3.7). Due to the variations in sites used for analysis across the decades (Figure 3.7), temporal trends and comparisons in mean concentrations between decades cannot be determined.

Significant differences ($p < 0.05$) in decadal mean stream NO_3-N concentrations were observed between the ice-covered and ice-free seasons across all decades except the 2000s (Figure 3.8a). Median NO_3-N concentrations during the ice-covered period were almost twice as high as in the ice-free period in the 1970s (ice-covered: 1.5 mg L^{-1} [0.7–2.6 mg L^{-1}]; ice-free: 0.8 mg L^{-1} [0.3–1.8 mg L^{-1}]) and 1980s (ice-covered: 1.7 mg L^{-1} [1.1–2.5 mg L^{-1}]; ice-free: 0.9 mg L^{-1} [0.6–1.6 mg L^{-1}]). Concentrations in the ice-covered seasons of the 1990s, 2000s, and 2010s on average ranged from 0.3 mg L^{-1} to 0.6 mg L^{-1} higher than those in the ice-free seasons. None of the decadal mean NO_3-N concentrations in the five decades surpassed the maximum acceptable concentration of 10 mg L^{-1} for NO_3-N in drinking water (Figure 3.8a). However, in all decades, decadal mean NO_3-N concentrations regularly exceeded the freshwater guideline for the protection of aquatic life (3 mg L^{-1}). Most of these exceedances occurred during the ice-covered season (Figure 3.8a).

In contrast to NO_3-N, the only significant inter-seasonal differences in decadal mean TP concentrations were in the 1980s and 2010s (Figure 3.9a). In the 1980s, the median TP concentration of 147 sites was 0.08 mg L^{-1} (0.04–0.17 mg L^{-}1) in the ice-covered season and 0.07 mg L^{-1} (0.04–0.14 mg L^{-} 1) in the ice-free season. Median TP concentrations during the ice-covered and ice-free seasons in the 2010s were 0.10 mg L^{-1} (0.09–0.11 mg L^{-}1) and 0.08 mg L^{-1} (0.07–0.09 mg L^{-}1), respectively, across seven sites. Conversely, in the other decades (1970s, 1990s, and 2000s), mean TP concentrations in the ice-free season were higher than those observed during the ice-covered season, although statistically significant differences were not detected (Figure 3.9a). Decadal mean concentrations of TP regularly surpassed 0.03 mg L^{-1}, the provincial water quality objective (Ontario Ministry of the Environment, 1994) in all decades, with exceedances ranging from 71% (2000s) to 100% (2010s) of all samples. Furthermore, in all decades except the 2000s, at least one-third of the sites exhibited eutrophic stream conditions, with TP concentrations consistently exceeding 0.1 mg L^{-1}.

Decadal mean Cl concentrations were generally higher during the ice-covered months compared with the ice-free months, with significant inter-seasonal differences in the 1970s, 1980s, and 2010s (Figure 3.10a). Notably, Cl concentrations sampled during the ice-covered period in the 2010s were up to five times higher than in the ice-free period (Figure 3.10a). This is attributed to the exceptionally high Cl concentrations (>1000 mg L^{-1}) recorded at Etobicoke Creek, Mimico Creek, and the Don River during the ice-covered period in the 2010s; these levels also exceeded the short-term Cl exposure limit of 640 mg L^{-1} (Figure 3.10a). Differences in concentrations between the seasons during the 1970s (n = 76) and 1980s (n = 136) were smaller in magnitude, with medians of 23 mg L^{-1} (15–51 mg L^{-1}) and 26 mg L^{-1} (16–55 mg L^{-1}) for the ice-covered period and 22 mg L^{-1} (13–46 mg L^{-1}) and 24 mg L^{-1} (14–46 mg L^{-1}) in the ice-free period, respectively. Locations in all decades had concentrations above the long-term aquatic life guideline of 120 mg L^{-1} and the Canadian drinking water quality aesthetic objective of 250 mg L^{-1} (Figure 3.10a).

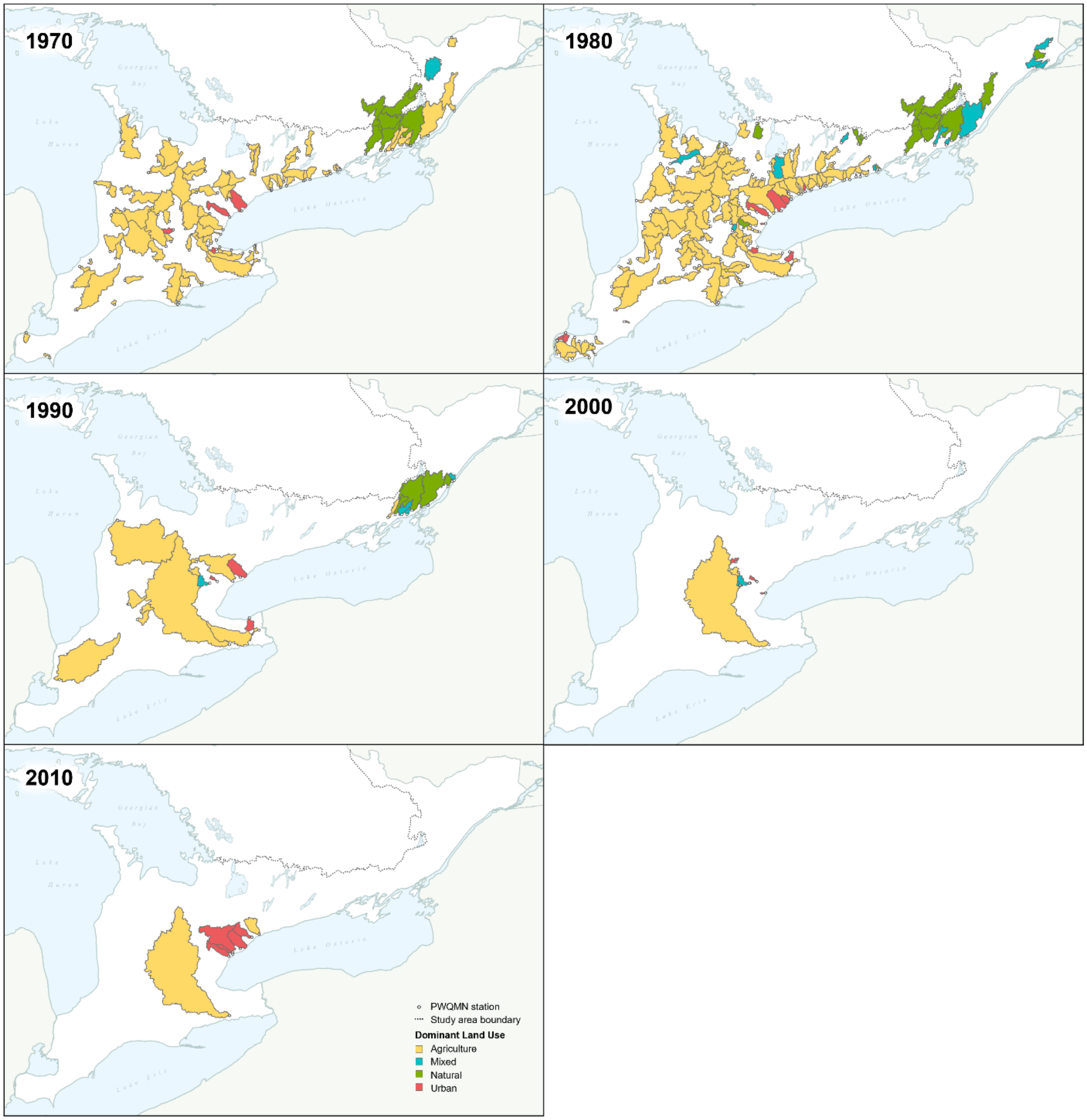

Figure 3.7 Locations of stations and watersheds available for seasonal analysis based on selection criteria. Colours of the watersheds represent the dominant land cover of the decade.

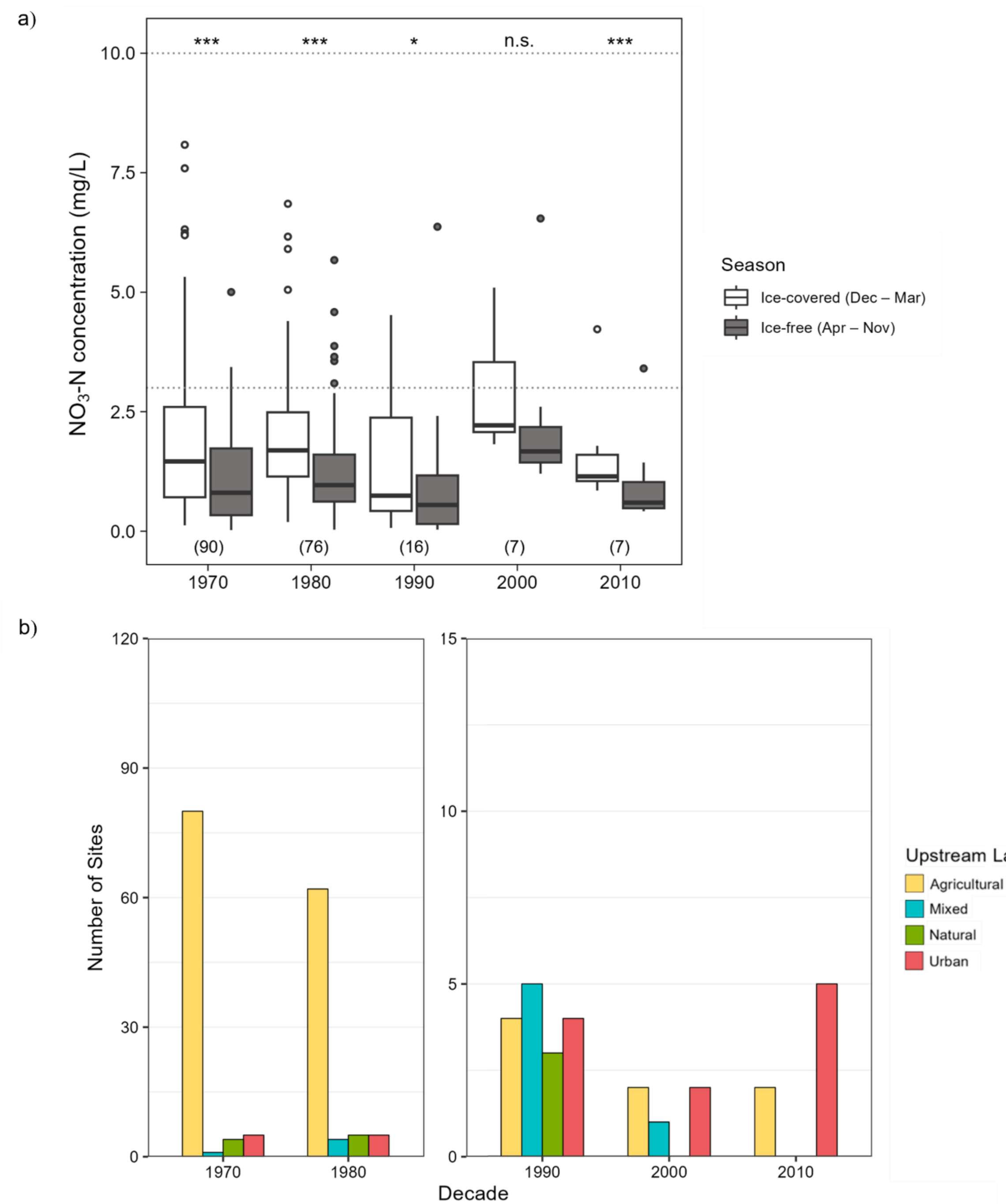

Figure.8 a) Decadal mean NO_3-N concentrations in ice-free (Apr–Nov) and ice-covered (Dec–Mar) seasons in each decade, 1970 – 2010. The number of sites available for analysis are indicated in brackets; these sites represent streams that were consistently sampled year-round in each decade. Asterisks denote significant differences between seasons: * ($p < 0.5$); ** ($p < 0.01$); *** ($p < 0.001$); n.s. (no significance). The upper dashed line indicates the maximum acceptable concentration for NO_3-N in drinking water (10 mg L^{-1}) and the lower dashed line indicates the freshwater guideline for the protection of aquatic life (3 mg L^{-1}). b) Number of sites in the decadal seasonal analysis that were characterized as agricultural, mixed, natural, or urban in each decade.

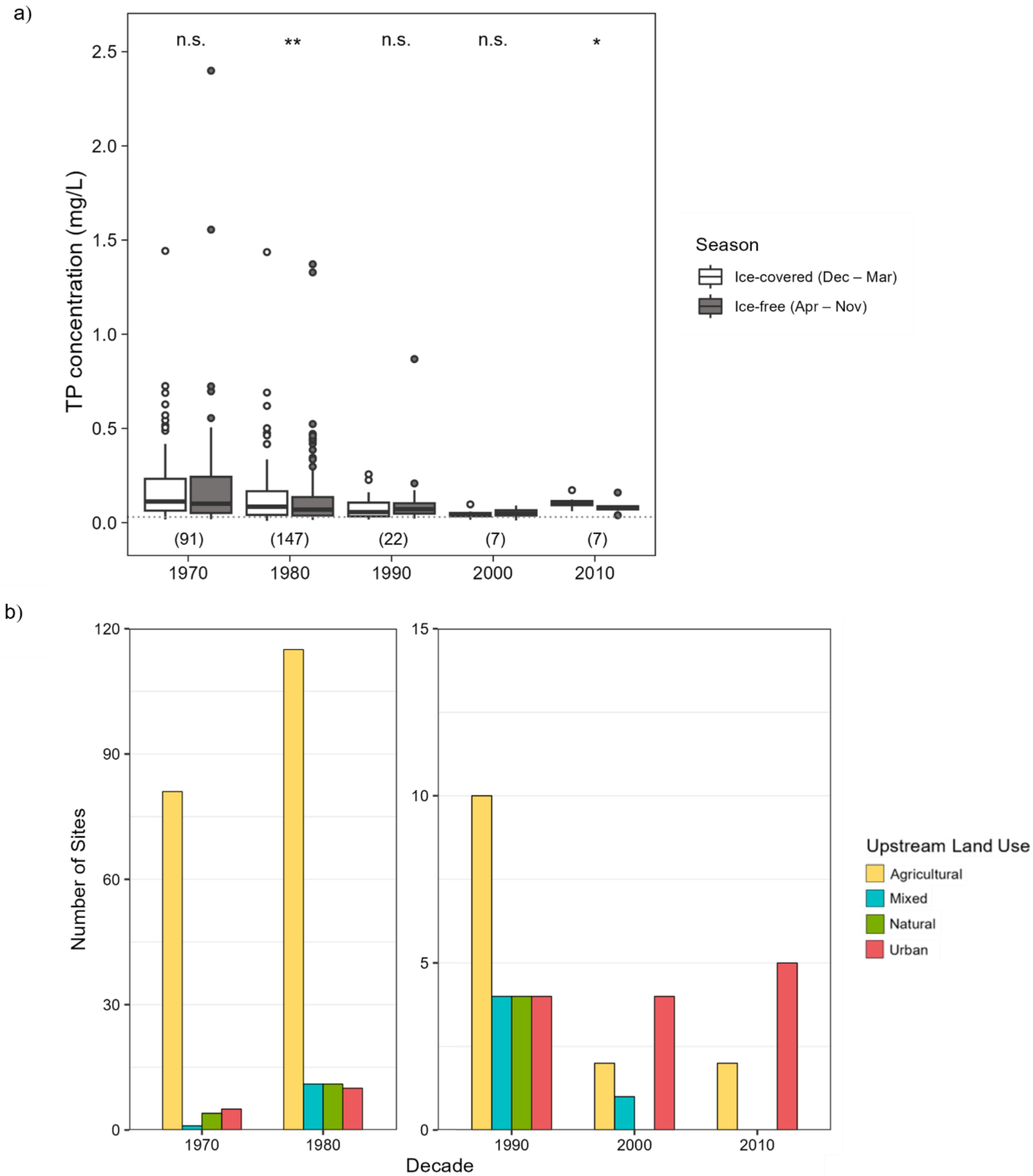

Figure 3.9 a) Decadal mean TP concentrations in ice-free (Apr–Nov) and ice-covered (Dec–Mar) seasons in each decade, 1970 – 2010. The number of sites available for analysis are indicated in brackets; these sites represent streams that were consistently sampled year-round in each decade. Asterisks denote significant differences between seasons: * ($p < 0.5$); ** ($p < 0.01$); *** ($p < 0.001$); n.s. (no significance). Dashed line indicates the provincial water quality objective for TP (0.03 mg L^{-1}). (b) Number of sites that were characterized as agricultural, natural, urban, or mixed land cover shown by decade.

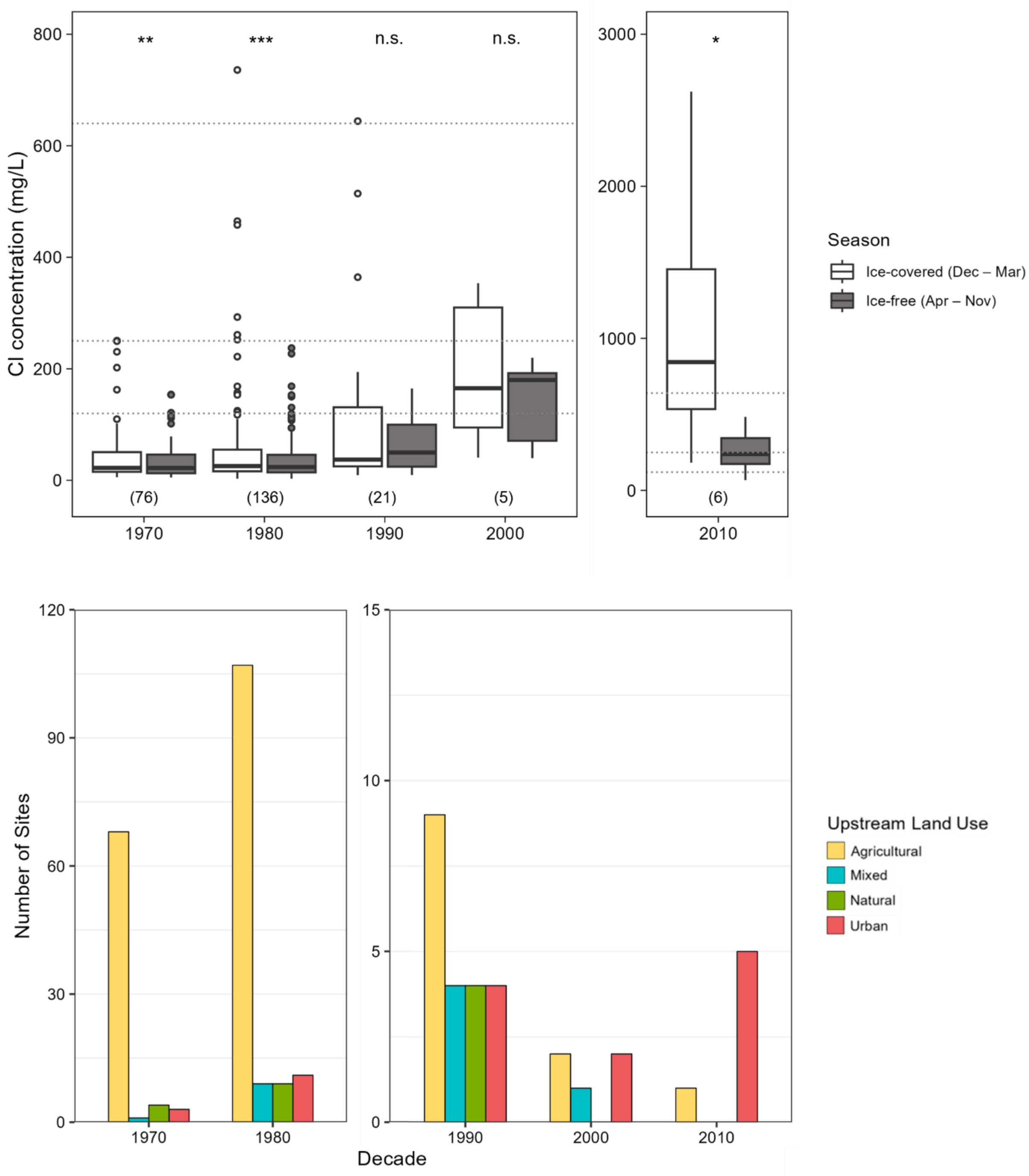

Figure 3.10 a) Decadal mean Cl concentrations in ice-free (Apr–Nov) and ice-covered (Dec–Mar) seasons in each decade, 1970 – 2010. The number of sites available for analysis are indicated in brackets (*n*); these sites represent streams that were consistently sampled year-round in each decade. Asterisks denote significant differences between seasons: * ($p < 0.5$); ** ($p < 0.01$); *** ($p < 0.001$); n.s. (no significance). Upper and lower dashed lines indicate the chronic (120 mg L^{-1}) and acute (640 mg L^{-1}) surface water guidelines for the protection of aquatic life. The middle-dashed line represents the aesthetic drinking water objective (250 mg L^{-1}). b) Number of sites that were characterized as agricultural, natural, urban, or mixed land cover shown by decade.

Annual Stream Concentrations. A number of land use changes have occurred in these watersheds between the 1970s and 2010s, including urban development, declines in farmland, and increases in natural areas. Urban areas expanded within all watersheds, with the most substantial increases observed in Fletchers Creek (+64% watershed area), Sheridan Creek (+37%) and Don River (+27%). These urban expansions occurred at the expense of agricultural land, as agricultural areas in all watersheds declined between 1970 to 2010 (Table 3.3). Most watersheds experienced an increase in natural land cover, with increases ranging 1% to 10% of total watershed area over the study period.

Annual mean NO_3-N concentrations recorded in the ice-covered season were significantly higher than those in the ice-free season in at least two decades at all sites, except for Silver Creek, where ice-free concentrations were found to be higher ($p < 0.05$; Figure 3.12). Inter-seasonal differences in NO_3-N concentrations could be up to three times higher in the ice-covered season compared with the ice-free season (e.g., Fletchers Creek in the 1990s). Across all sites, the urbanized Don River and Twelve Mile Creek, had smaller differences in concentrations (i.e., less than 0.3 mg L^{-1}) between the seasons (Figure 3.12). While concentrations between decades were relatively consistent at most sites, Silver Creek, Whitemans Creek, and Grand River appeared to exhibit upward trends (Figure 3.12). Agricultural watersheds, Whitemans Creek and Grand River, had some of the highest mean NO_3-N concentrations recorded in both seasons across the locations. Annual mean ice-covered concentrations at these two creeks ranged from 3.6 mg L^{-1} to 5.0 mg L^{-1}, whereas ice-free concentrations ranged from 1.9 mg L^{-1} to 4.0 mg L^{-1}. Conversely, urban Twelve Mile Creek had the lowest annual mean NO_3-N concentrations in both seasons across all decades; ice-covered concentrations varied between 0.27 mg L^{-1} (1970s) and 0.46 mg L^{-1} (2000s), while ice-free concentrations ranged from 0.14 mg L^{-1} (1970s) to 0.34 mg L^{-1} (1990s). Nitrate-N concentrations in Silver Creek, Whitemans Creek, and Grand River regularly exceeded the guideline of 3 mg L^{-1} for the protection of aquatic life during both the ice-covered and ice-free seasons. At Credit River, Don River, and Fletchers Creek, however, only concentrations collected during the ice-covered season exceeded this guideline. Although none of the nine sites exceeded the drinking water guideline (10 mg L^{-1}), continued monitoring is important as the Grand River is a source of drinking water, whereas other rivers discharge into important drinking water sources downstream, such as Lake Ontario.

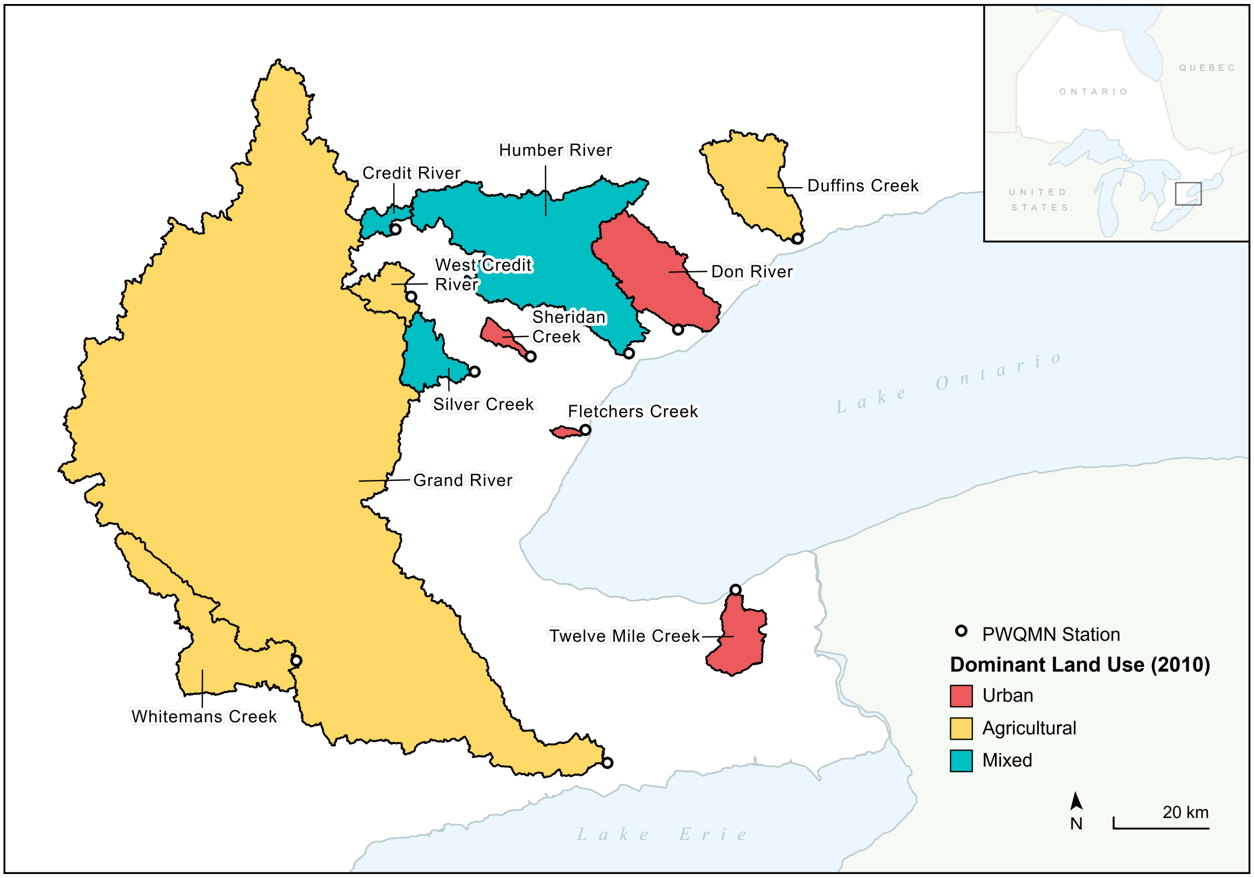

Figure 3.11 Watersheds selected for analysis of seasonal annual concentrations characterized by dominant land cover

Table 3.3 Percent land cover (of total watershed area) by decade within watersheds selected for analysis of seasonal annual concentrations. Watersheds are ordered by dominant land cover. Total change between 1970 and 2010 across land cover are also noted.

Watershed	Area (km^2)	Urban						Agriculture						Natural					
		1970	1980	1990	2000	2010	Δ	1970	1980	1990	2000	2010	Δ	1970	1980	1990	2000	2010	Δ
Don River	323	66	73	83	89	93	+27	30	21	12	7	3	-26	4	6	5	5	4	-1
Fletchers Creek	10	12	27	43	62	76	+64	84	69	53	34	21	-63	4	4	4	3	3	-1
Sheridan Creek	30	61	59	84	96	98	+37	35	12	12	3	1	-34	3	28	5	1	1	-2
Twelve Mile Creek	126	21	32	34	38	42	+21	62	42	41	36	33	-29	18	26	25	26	25	+8
Duffins Creek	278	6	6	16	19	23	+17	74	68	56	50	47	-26	21	27	28	31	30	+9
Grand River	6696	4	6	10	11	13	+10	79	75	71	67	66	-13	18	19	19	21	21	+3
West Credit River	97	2	4	9	11	14	+12	74	71	61	55	53	-21	24	25	31	34	33	+10
Whitemans Creek	394	1	2	6	7	8	+7	81	79	77	74	73	-8	18	19	17	19	19	+1
Credit River	43	11	21	26	32	37	+26	70	59	51	43	39	-31	19	20	23	25	24	+5
Humber River	894	18	22	28	34	40	+22	69	54	52	43	38	-32	13	24	21	24	23	+10
Silver Creek	127	6	10	16	19	21	+15	63	55	48	41	39	-24	31	36	37	40	40	+9

Annual mean TP concentrations remained largely consistent across the seasons (Figure 3.13). The only significant inter-seasonal differences were found in the 2000s at the predominantly agricultural Grand River and mixed urban/agricultural Humber River. At Grand River, concentrations were greater during the ice-free period than during the ice-covered period, while the opposite trend was observed at Humber River (Figure 3.13). Total P concentrations were also consistent across decades. The only exception was elevated TP concentrations in the 1970s at Credit River and Silver Creek. Across the sites, Don River, Humber River, Credit River exhibited the highest TP concentrations post 1970s. Consequently, the provincial water quality objective of 0.03 mg L^{-1} was most frequently exceeded at Don River, Humber River, Credit River, and Grand River over the five decades, although the majority of annual concentrations at all nine sites surpassed the objective.

Significant differences in annual mean Cl concentrations between seasons were found for Fletchers Creek, Sheridan Creek, Credit River, Twelve Mile Creek, and Duffins Creek, with greater Cl concentrations occurring during the ice-covered period than during the ice-free period (Figure 3.14). However, the most pronounced seasonal differences, as well as highest Cl concentrations, were observed during the 2000s and 2010s at the most urbanized Fletchers Creek (98% urban) and Sheridan Creek (76% urban). In contrast, agricultural and mixed land use sites generally exhibited consistent concentrations between seasons (Figure 3.14). Progressive increases in annual mean Cl concentrations in both seasons across the decades appear to have occurred at all sites except for Silver Creek (40 % natural), where concentrations have remained relatively stable over time. Only West Credit River, Whitemans Creek, and Twelve Mile Creek met exposure guidelines and drinking water objectives. All other sites exceeded the 120 mg L^{-1} chronic guideline. Furthermore, Credit River, Fletchers Creek, and Sheridan Creek surpassed the 250 mg L^{-1} aesthetic drinking water objectives, while Fletchers Creek and Sheridan Creek further exceeded the 640 mg L^{-1} acute exposure threshold.

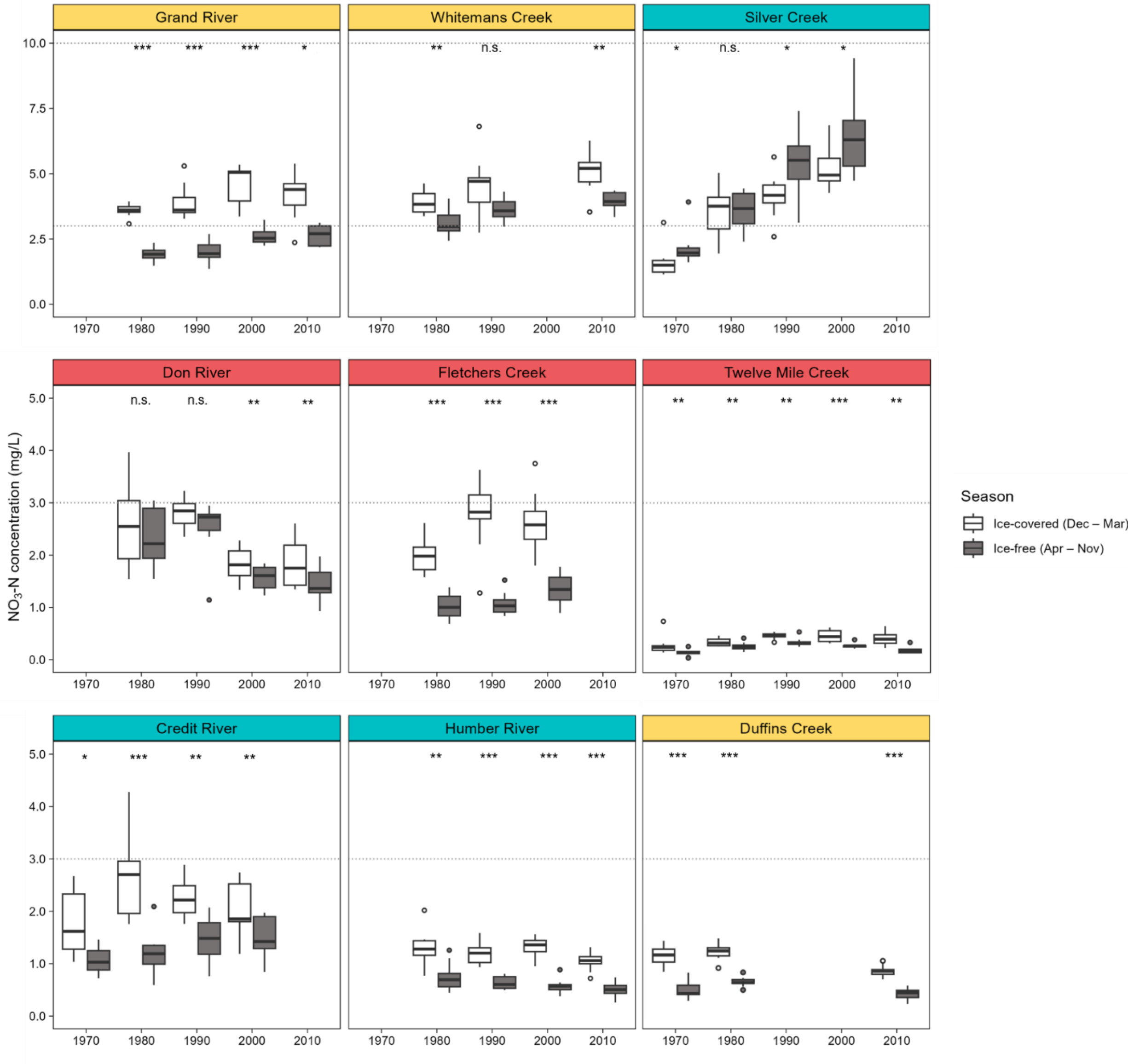

Figure 3.12 Annual mean NO_3-N concentrations in ice-free (Apr–Nov) and ice-covered (Dec–Mar) seasons at selected stations ranging in land cover. Red-coloured panels represent urban watersheds; yellow-coloured panels represent agricultural watersheds; and blue-coloured panels represent mixed land cover watersheds. Asterisks denote significant differences between seasons: * ($p < 0.5$); ** ($p < 0.01$); *** ($p < 0.001$); n.s. (no significance). Upper dashed line indicates the maximum acceptable concentration for NO_3-N in drinking water (10 mg L^{-1}) and the lower dashed line indicates the freshwater guideline for the protection of aquatic life (3 mg L^{-1}). Note the different y-axis for the first row of watersheds.

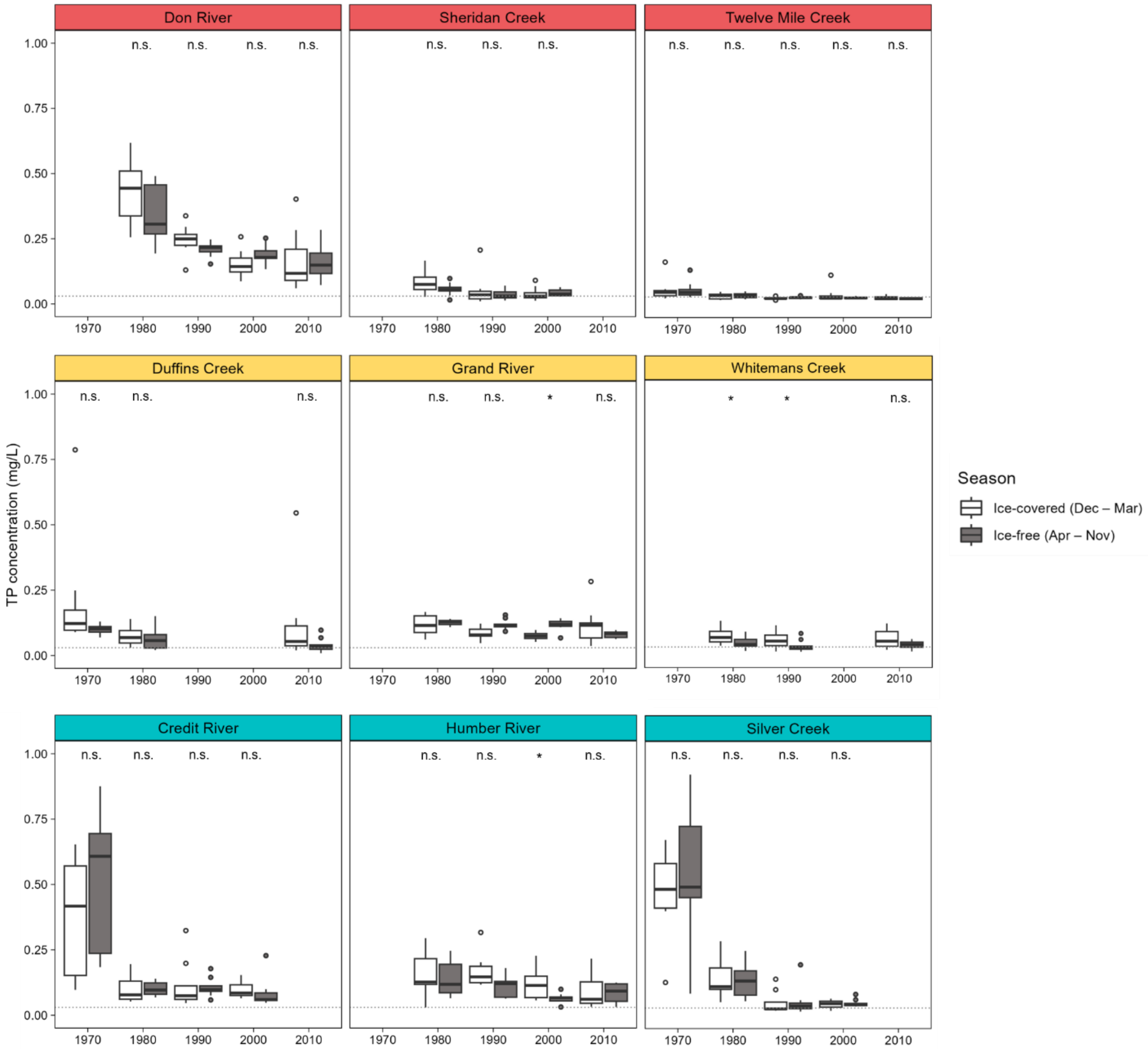

Figure 3.13 Annual mean TP concentrations in ice-free (Apr–Nov) and ice-covered (Dec–Mar) seasons in selected stations ranging in land cover. Red-coloured panels represent urban watersheds; yellow-coloured panels represent agricultural watersheds; and blue-coloured panels represent mixed land cover watersheds. Asterisks denote significant differences between seasons: * ($p < 0.5$); ** ($p < 0.01$); *** ($p < 0.001$); n.s. (no significance). Dashed line indicates the provincial water quality objective for TP (0.03 mg L^{-1}).

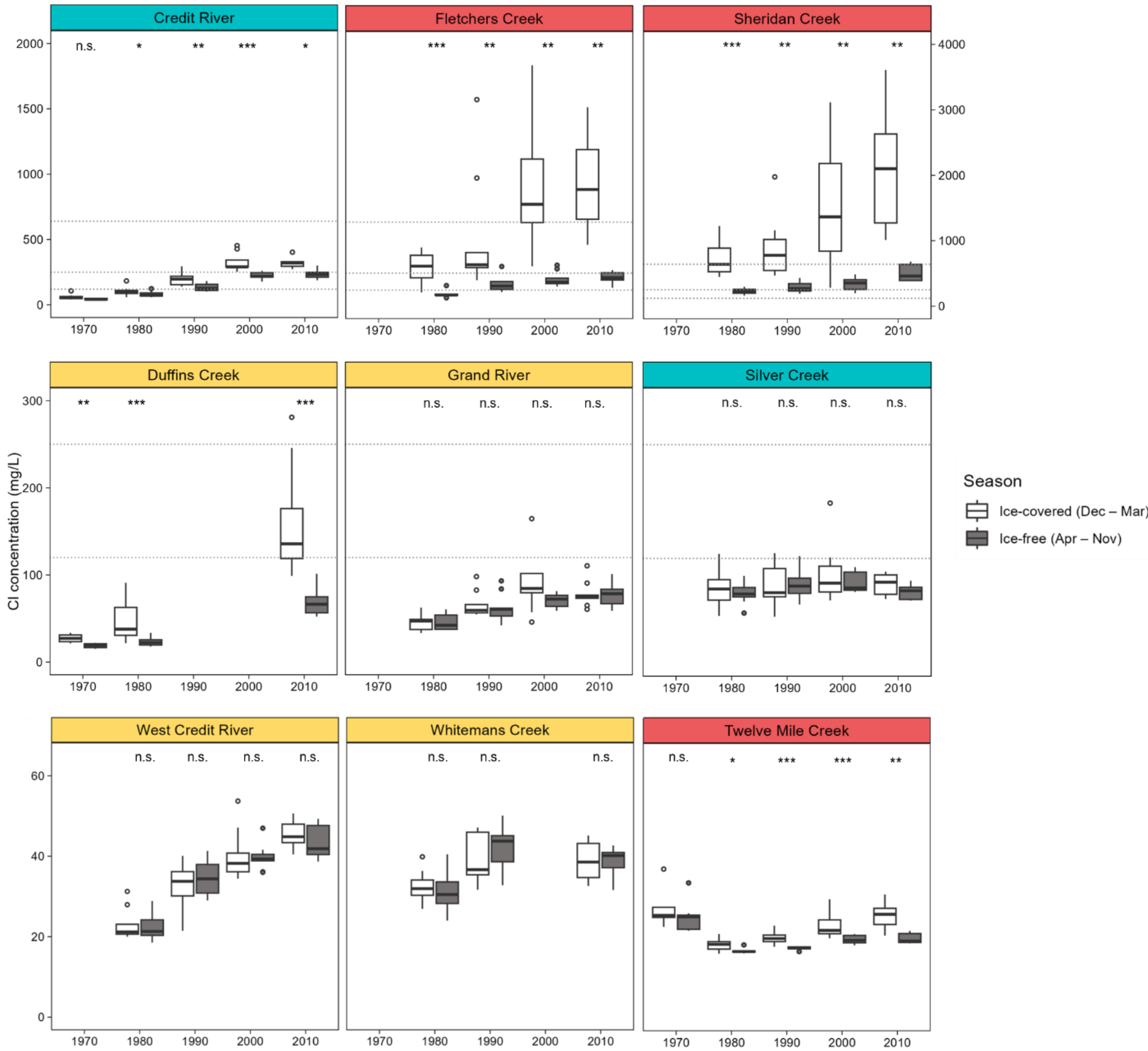

Figure 3.14 Annual mean Cl concentrations in ice-free (Apr – Nov) and ice-covered (Dec – Mar) seasons in selected stations ranging in land cover. Red-coloured panels represent urban watersheds; yellow-coloured panels represent agricultural watersheds; and blue-coloured panels represent mixed land cover watersheds. Asterisks denote significant differences between seasons: * ($p < 0.5$); ** ($p < 0.01$); *** ($p < 0.001$); n.s. (no significance). Upper and lower dashed lines indicate the chronic (120 mg L^{-1}) and acute (640 mg L^{-1}) surface water guidelines for the protection of aquatic life. The middle-dashed line represents the aesthetic drinking water objective (250 mg L^{-1}).

3.3.3 Influence of point-sources on water quality

In the study area, a total of 86 sites from the 2010s were classified as having no or minimal influence from point sources, while 79 sites were identified as being affected by upstream WWTPs or greenhouses located within a 20 km range (Figure 3.15; Figure 3.16). Among the major drainage basins, Lake Ontario had the highest number of sites unaffected by point sources (41; 80% of Ontario sites), whereas Lake Huron had the highest number of sites impacted by such sources (33; 62% of Huron sites). As hypothesized, streams influenced by upstream point sources exhibited significantly higher decadal mean (2010 – 2019) concentrations of both TP and NO_3-N compared to sites without any upstream point sources in the study region (see 'All'; $p < 0.05$; Figure 3.16). Decadal mean TP concentrations at sites without point sources ranged from 0.21 to 0.51 mg L^{-1} (interquartile range [IQR]), while sites influenced by point sources demonstrated higher TP concentrations (0.30 – 0.79 mg L^{-1}; IQR), reaching levels up to 1.5 times greater than those observed at sites without point sources. Similarly, decadal mean NO_3-N concentrations at influenced sites (IQR 0.96 mg L^{-1} – 3.65 mg L^{-1}) were up to twice as high as concentrations at uninfluenced sites (IQR 0.48 mg L^{-1} – 1.67 mg L^{-1}). Significant differences in TP and NO_3-N concentrations were found between the two types of sites in the Huron basin (Figure 3.15). Across the basins, sites within the Erie basin had the highest TP concentrations, and therefore, greatest exceedances of the 0.03 mg L^{-1} provincial water quality objective (Figure 3.15). The majority of exceedances of the freshwater guideline for NO_3-N (3 mg L^{-1}) were attributed to point source-influenced sites within the Erie and Huron basins (Figure 3.15). Notably, the highest decadal mean TP and NO_3-N concentrations were observed at streams influenced by greenhouse discharge, specifically, Muddy Creek and Sturgeon Creek located in the Leamington area along the northwestern shoreline of Lake Erie. Muddy Creek and Sturgeon Creek had mean TP concentrations of 1.4 mg L^{-1} and 4.7 mg L^{-1}, and mean NO_3-N concentrations of 0.30 mg L^{-1} and 0.26 mg L^{-1}, respectively.

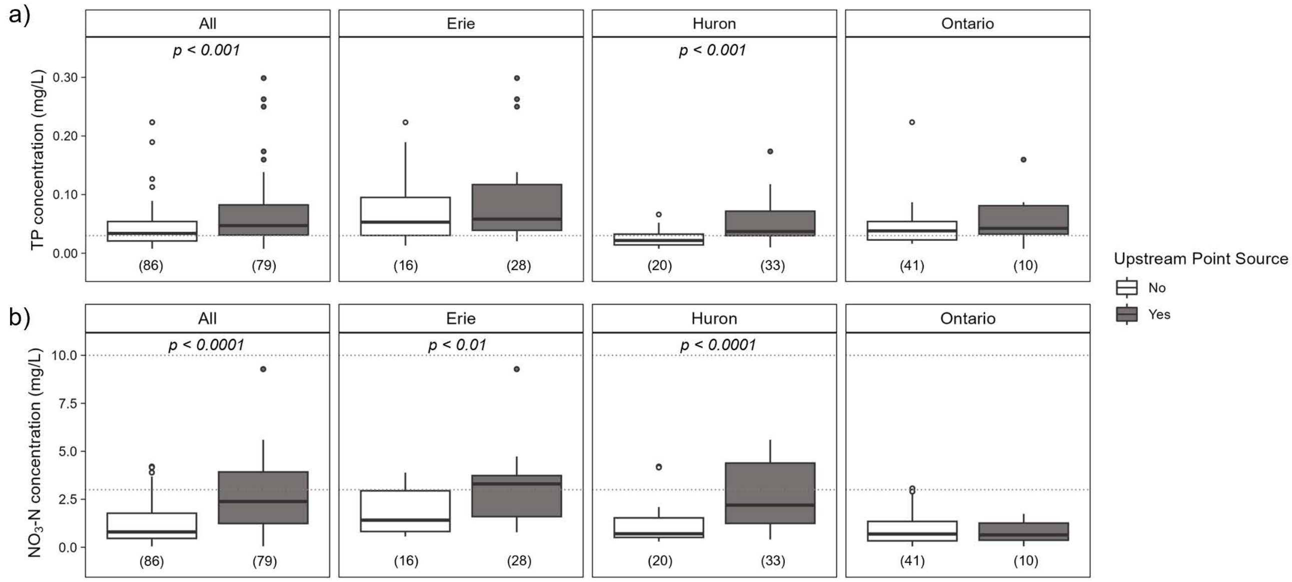

Figure 3.15 (a) Decadal mean (2010 – 2019) TP concentrations at stations with and without upstream point sources across major drainage basins within southern Ontario. The dashed line indicates the provincial water quality objective for TP (0.03 mg L^{-1}). (b) Decadal mean (2010 – 2019) NO_3-N concentrations at stations with and without upstream point sources across major drainage basins within southern Ontario. The upper dashed line indicates the maximum acceptable concentration for NO_3-N in drinking water (10 mg L^{-1}) and the lower dashed line indicates the freshwater guideline for the protection of aquatic life (3 mg L^{-1}).

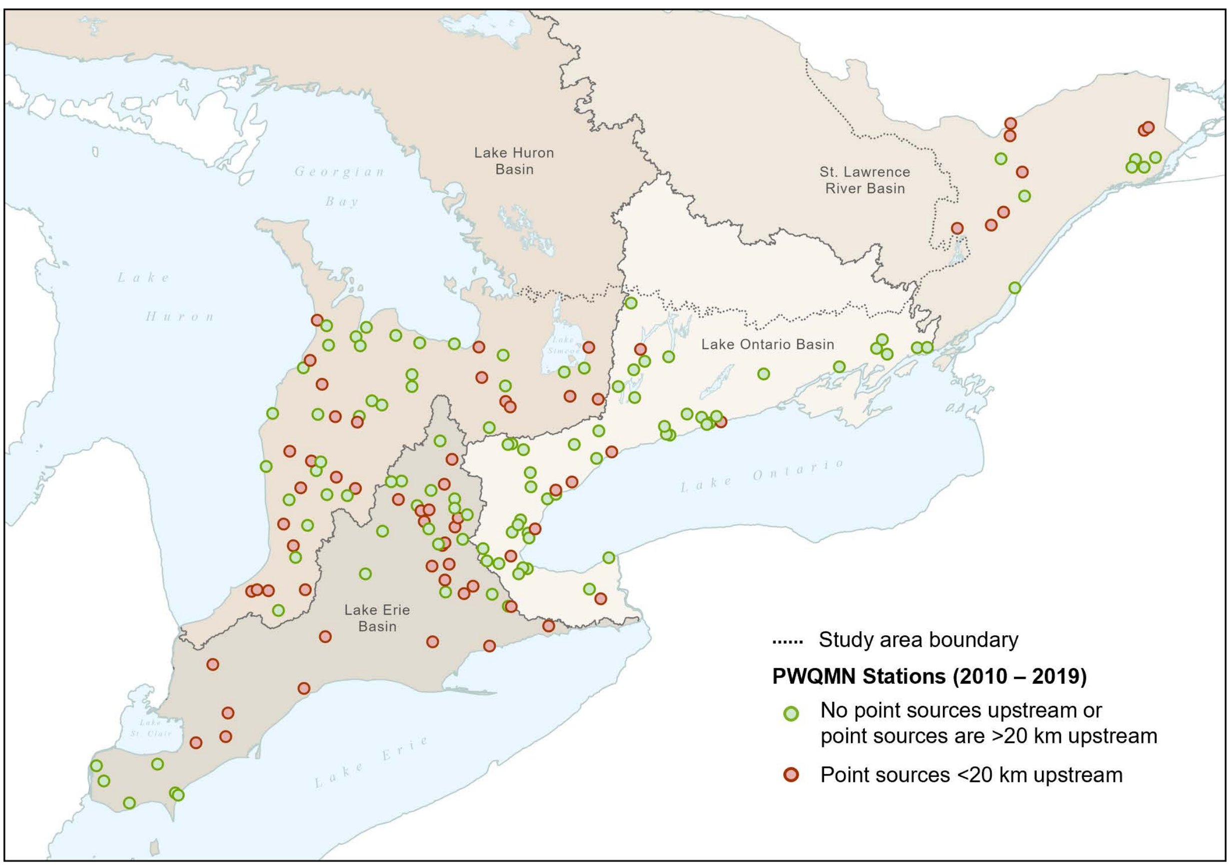

Figure 3.16 Active PWQMN stations between 2010 and 2019 characterized by presence of point sources upstream

3.4 Discussion

Historical PWQMN stream NO_3-N, TP, and Cl concentration data in southern Ontario were examined with respect to patterns in sampling frequency, seasonality, and location to determine how to better focus future monitoring efforts, particularly in light of changing climate conditions and land use shifts. Each of these patterns and potential impacts on water quality trends are discussed below.

3.4.1 Patterns in monitoring frequency

Although monthly sampling frequency (i.e., once per month) has remained consistent over the past 50 years, the average annual number of samples and the total number of stations sampled for NO_3-N, TP, and Cl concentrations in the 2000s and 2010s have declined by over 30% and 50%, respectively, compared to those in the 1970s (Figures 3.1 – 3.3). Even greater declines were observed for the number of 'long-term sites' (i.e., stations sampled more frequently and consistently over longer periods), with decreases ranging from 63% to 82% in the most recent 20 years compared with the 1970s (Figure 3.3). These trends indicate that the majority of PWQMN sites have been discontinued over time, and that many watersheds are now monitored more sparsely and irregularly. Drastic reductions in annual sampling frequency and the number of sampling sites beginning in 1995 (Figures 3.1-3.2) were the result of sharp budget cutbacks at the Ontario Ministry of Environment (now known as OMECP) by the government (Krajnc, 2000). Between 1991-92 and 1997-98, for example, the ministry's operating budget was cut by 68% in real 1998 dollars, while staffing was reduced by 40%, leaving fewer resources for carrying out mandates in scientific research, monitoring, and implementation (Krajnc, 2000). Although the ministry has gradually re-built the network since 2002, the current number of active sites remains below previous levels in the 1970s, with most stations now sampled a maximum of eight times per year (Figures 3.1-3.2). Similar declines have been reported for other long term monitoring programs. For instance, the total number of U.S. Geological Survey (USGS) sites monitored for NO_3–N, TP, and Cl as part of programs such as the National Stream Quality Accounting Network (NASQAN), Hydrologic Benchmark Network (HBN), and National Water Quality Assessment (NAWQA) has decreased over a range from 42% to 69% between 1975 and 2014 (Myers and Ludtke, 2017). At the same time, sampling frequency at some USGS sites has shifted from monthly to bi-monthly or quarterly (Myers and Ludtke, 2017). Similar to the PWQMN, these program scale-backs have been attributed to rising operational expenses over time, stagnant and declining budgets, and competition for resources with other monitoring activities (Myers and Ludtke, 2017).

Monthly stream sampling of the PWQMN primarily occurs during baseflow conditions, generating data that can be useful for assessing aquatic habitat quality and identifying spatial and long-term trends (Long et al., 2014). However, these samples tend to underestimate nutrient loading, as the majority of annual loads occur during brief, high flow events which are typically often missed by a monthly sampling program (Booty et al., 2014; Long et al., 2014). In southern Ontario, storm events can account for up to 90% of TP loads delivered from urban watersheds (Long et al., 2015), whereas snowmelt has been shown to contribute over half of annual TP export in agricultural watersheds (e.g., Macrae et al., 2007; Lam et al., 2016). Because TP concentrations tend to increase with flow, routine sampling at infrequent intervals tends to produce flux estimates biased towards periods of low flux (Booty et al., 2014). Thus, unsurprisingly, when compared to TP loads derived from a two-year event sampling dataset collected by the Toronto Region CA and the Ministry of Environment, PWQMN-based estimates showed substantially lower values (Booty et al., 2014). Thomas et al. (2018) found that a substantial fraction of TP was comprised of particulate P, which is transported from surface soil and the stream channel to streams during runoff events, and hence was largely uncharacterized by the monthly sampling of the PWQMN, leading to under-predictions of TP concentrations. Conversely, total N was found to be composed mostly of dissolved fractions, which are delivered continuously through subsurface pathways, and thus its characterization was relatively less impacted by sampling frequency and total N could be predicted by land use up to 85% of the time (Thomas et al., 2018; see also Liu et al., 2022). Therefore, while previous studies have demonstrated declines in the accuracy of nutrient load estimates with decreasing sampling frequency (e.g., Kronvang and Bruhn, 1996; Stelzer and Likens, 2006; Defew et al., 2013), this relationship is not uniform across all water quality parameters, with some more susceptible than others to greater uncertainties in load estimates as a result of low sampling frequency (Kerr et al., 2016).

To overcome limitations of monthly sampling, studies have recommended stratifying sampling frequencies to cover a range of hydrologic conditions (e.g., Makarewicz et al., 2012; Horowitz, 2013). Monthly sampling combined with more intense monitoring during high flow events have been shown to improve annual TP load predictions (Kronvang and Bruhn, 1996). However, not all sites require the same sampling frequencies. Event-based or flow-proportional sampling is more important in catchments that are more hydrologically responsive or have more substantial point source loading, such as watersheds with densely populated urban centres and intensively tile-drained fields, as Johnes (2007) observed higher uncertainty in load estimations for these areas when sampling infrequently. For baseflow-dominated systems, TP loads calculated from infrequent sampling programs were observed to be reasonably reliable indicators of loading, and thus sampling at lower frequencies may be adequate at sites that are less flashy (Johnes, 2007). Sampling strategies may also vary between seasons. While intensive storm events and preferential flow pathways lead to higher variability in summer nutrient concentrations as observed in tile-drained landscapes in Ohio and southwestern Ontario, only a small proportion of annual nutrient loading occurs during the summer (Williams et al., 2015). Frequent sampling during the winter and spring high flow periods are thus more critical than in the summer for more accurate quantification of annual fluxes in tile-drained agricultural watersheds (Williams et al., 2015).

3.4.2 Patterns in seasonal water quality

Sampling for NO_3-N, TP, and Cl concentrations at PWQMN sites has largely been conducted year-round until budget cuts in the mid-1990s; since then, the majority of sampling efforts have been concentrated on the ice-free period between April and November (Figure 3.2). Most sites are now only sampled eight times per year, representing the eight months of this period (Figure 3.1). To analyze potential impacts of this shift in sampling seasonality on observed trends in decadal mean concentrations, stations were selected based on data availability in both the ice-free and ice-covered seasons in each decade (Figure 3.7). The sharp decline in the number of stations available for analysis before and after the 1990s reflects a clear bias towards ice-free season sampling and less frequent winter sampling at most stations across southern Ontario in recent years (Figure 3.7). Declines in sampling during the ice-covered period have been associated with budgetary cutbacks and reduced monitoring capacity, in addition to logistical challenges in collecting samples in snow or through ice during the winter (Long et al., 2015). This sampling bias can lead to underestimations of annual nutrient export in cold temperate regions like southern Ontario, as most of the annual loads have been observed to occur in the winter and spring period (Makarewicz et al., 2012). Moreover, the lack of winter monitoring restricts the ability to fully capture and evaluate impacts of changing climate conditions, which is problematic as winters are becoming more hydrologically active. In eastern Canada, for instance, warmer winters have been associated with earlier spring snowmelt, increased winter precipitation as rainfall, and more freeze-thaw cycles and rain-on-snow events (Vincent et al., 2018), all of which could intensify nutrient export.

Because of this data gap, some PWQMN-based studies have opted to focus on data from the ice-free season only (e.g., Raney and Eimers, 2014b; Stammler et al., 2017; DeBues et al., 2019; Sorichetti et al., 2022; see Chapter 2). Thus, to assess the potential bias introduced when the ice-covered season is excluded from monitoring and/or analysis, seasonal differences in NO_3-N, TP, and Cl concentrations were analyzed across streams in southern Ontario. Decadal mean NO_3-N concentrations in the ice-covered season were typically up to twice as high as concentrations in the ice-free season (Figure 3.7a). This pattern was also observed for annual mean concentrations across watersheds of different land covers (Figure 3.12). Since all types of watersheds exhibited inter-seasonal patterns in NO_3-N, the seasonal variability in NO_3-N can be predominantly explained by seasonal climatic factors. High NO_3-N concentrations in the ice-covered period are associated with the increased transport of NO_3-N in runoff from snowmelt and rain-on-snow events that occur in the winter/early spring and intense rainfall events in the spring (Macrae et al., 2007; Long et al., 2015; Nelligan et al., 2021). During the growing season, less N is leached to streams due to an increase in microbial immobilization and plant uptake of N in the summer (Van Meter et al., 2020).

Notably, annual NO_3-N concentrations of agricultural streams in both seasons were substantially higher compared to seasonal concentrations in the urban and mixed land cover watersheds (Figure 3.12). Differences in annual mean concentrations were found to vary up to five-fold between the most agricultural watersheds (Grand River and Whitemans Creek) and an urban-dominated watershed (Twelve Mile Creek; Figure 3.12). These inflated NO_3-N concentrations at agricultural streams likely reflect long-term leaching and infiltration of excess fertilizer N inputs to groundwater (Long et al., 2014). Practices of spreading manure in the late fall and winter on snow or frozen ground can also increase risks of N leaching, contributing to higher concentrations in the ice-covered period (Lewis and Makarewicz, 2009). Furthermore, agricultural watersheds in southwestern Ontario are intensively tile-drained (see Chapter 2) and tile drains act as a direct conduit for dissolved nutrients into streams, bypassing riparian buffers. Tile drainage represents an important N transport pathway particularly during periods of high flow common in the winter and spring, although tiles can remain active year-round from infiltration via macropores and biopores, often found in fine-textured clayey soils characteristic of those in southwestern Ontario (Macrae et al., 2007). In addition, the majority of NO_3-N loss in row crop systems occurs during the corn phase, with most of this loss occurring in the winter after corn harvest (Syswerda et al., 2012), which is consistent with seasonal patterns in NO_3-N. As southern Ontario continues to experience agricultural intensification (i.e., shifts from mixed livestock/crops to annual row crops), monitoring in the ice-covered season will become more critical as these agricultural shifts may contribute to even further NO_3-N increases. Given that the PWQMN mainly captures baseflow conditions, frequent exceedances of 3 mg L^{-1} NO_3-N in streams may have potential implications for stream habitat quality particularly in agricultural areas.

Compared to the strong seasonal trends observed for NO_3-N, seasonal patterns in both the decadal and annual means of TP concentrations were not as evident (Figure 3.9a; Figure 3.13). The only inter-seasonal differences between decadal means were observed in the 1980s and 2010s, where ice-covered decadal mean TP concentrations were greater than ice-free concentrations by approximately 10% to 25% (Figure 3.9a). Annual mean TP concentrations at most selected sites were consistent between seasons (Figure 3.13). As the PWQMN captures variable hydrologic conditions only by chance, TP concentrations collected in the program were likely unable to reflect the inter-seasonal differences that may be present. Phosphorus transport occurs mainly through erosive events (e.g., snowmelt and high flow events) when prolonged surface runoff occurs, and P is predominantly lost in a particulate form, although flat, tile-drained areas with level clay soils (i.e., southwestern Ontario) are highly vulnerable to dissolved P losses as well (Macrae et al., 2021). Other studies have observed the highest TP loads in the spring and winter (Biagi et al., 2022), particularly in watersheds with higher levels of agricultural land use and tile drainage densities (Van Meter et al., 2020). In agricultural watersheds, erosion of soils containing elevated P from manure and fertilizer applications contributes to large TP fluxes during storms (Macrae et al., 2007). Indeed, inter-seasonal differences in annual mean TP concentrations were observed at agricultural streams in this study (Grand River and Whitemans Creek; Figure 3.13). In urban streams, the similar levels of concentrations observed across the seasons (Figure 3.13) might be attributed to urban point sources that contribute to higher concentrations during low-flow periods in the summer, which can homogenize seasonal concentration patterns across the year (Van Meter et al., 2020). At urban sites where proximal point sources such as upstream reservoirs or wastewater treatment plants exert greater influence than distal non-point sources, aseasonal patterns in concentrations are more likely to occur (Van Meter et al., 2020). With climate change forecasts, such as increasing frequency of precipitation falling as rain instead of snow, winter TP export may potentially become equivalent or even greater than those in other seasons (Long et al., 2015). Thus, a targeted water sampling strategy that better captures high flow events year-round is necessary to better elucidate patterns in the relationship between TP concentrations and land use.

Ice-covered decadal mean Cl concentrations were significantly greater than ice-free season concentrations in three out of the five decades ($p < 0.05$), with differences up to five-folds (Figure 3.10a). Chloride concentrations in streams often peak in the late winter and early spring due to de-icing salt runoff, and winter baseflow concentrations can be orders of magnitude higher than baseflow concentrations in the summer (Dugan and Arnott, 2023). The scarcity of regular monthly samples in the winter is thus concerning, as the highest concentrations of Cl are typically observed during this period but are not captured by the monitoring program. There also appears to be a clear land use pattern in annual inter-seasonal concentrations (Figure 3.14). Urban streams (Sheridan Creek, Fletchers Creek, Twelve Mile Creek) exhibited strong inter-seasonal trends, whereas differences between seasons were not observed in most agricultural and mixed-land use watersheds (Figure 3.14). In urban catchments, salinity peaks often occur in the winter and spring when salt-laden meltwater runs off impervious surfaces and flows through stormwater drains directly to tributaries (Oswald et al., 2019). In watersheds with more pervious land cover and lower road density, inter-seasonal differences may be less pronounced as more runoff is able to infiltrate into soils and enter groundwater, reducing the amount of road salt entering streams in the winter. During the summer, when Cl is transported along subsurface flow pathways, summer baseflow concentrations may be elevated, presumably reflecting groundwater Cl levels (Rhodes et al., 2001). In rural and suburban catchments, the highest Cl concentrations are often observed in the summer, when low flows concentrate surface and groundwater sources of Cl, and thus the summer period should not be overlooked as a time of risk to aquatic ecosystem integrity (Daley et al., 2009).

Urban streams exhibited the highest Cl concentrations (Figure 3.14), consistent with previous studies that have observed strong relationships between urbanization and stream salinization (e.g., Kaushal et al., 2005; Dugan et al., 2017; Oswald et al., 2019). Urbanization occurred across all nine watersheds of study between 1970 and 2010 (Table 3.3), with the highest increases in urban watershed area observed at Fletchers Creek (+64%). Under the combined influence of urban growth and climate change in the future, increases in impervious surfaces and salt application are expected to lead to more frequent exceedance of chronic toxicity thresholds, posing a threat to ecosystem function and the potability of surface waters (Daley et al., 2009). In the highly urbanized and populated Greater Toronto Area, high Cl concentrations persist into the growing season and may even surpass acute Cl exposure thresholds (Figure 3.14; Lawson and Jackson, 2021). Exposure to elevated Cl can cause physiological stress and disrupt osmoregulation in aquatic organisms, resulting in impaired reproduction, growth, and survival (Lawson and Jackson, 2021). Based on observations from 214 sampled sites across Toronto, Lawson and Jackson (2021) estimated that up to two-thirds of freshwater taxa can be impacted during the summer and an even higher proportion are likely impacted when Cl concentrations are orders of magnitude greater during the winter/spring.

Overall, the seasonal analysis indicates that year-round stream monitoring is essential for the detection of long-term trends. The inter-seasonal patterns of NO_3-N, TP, and Cl highlighted in this study demonstrate the importance of sampling across all seasons to capture variations in NO_3-N and Cl, whereas sampling across a full spectrum of flow conditions is more important for adequately describing TP. Elevated concentrations were not limited to the ice-free season, but rather, were found to be notably higher during the unmonitored ice-covered season. Shifts in the timing of nutrient export from the growing season to the non-growing season are anticipated under warmer and wetter climate conditions (Nelligan et al., 2021), while expansions in tile-drained row crop agriculture and continued urbanization may amplify the effects of climate change on nutrient export (Eimers et al., 2020). Monitoring across all critical seasons and time periods is thus required to generate accurate export estimates (Nelligan et al., 2021). However, limited resources and existing constraints can prevent the PWQMN from extending sampling efforts across seasons. To bridge the data gap, enhancing coordination efforts on data sharing among stakeholders can help address the potential bias caused by the exclusion of the non-growing season in sampling (Neumann et al., 2023). Collaborative approaches that incorporate locally collected historical data can provide a more comprehensive understanding of year-round water quality dynamics, which is important for informed decision-making and environmental management. An example of such an approach is a recent P export modelling framework by Neumann et al. (2023) that assembled water quality data from a multitude of agencies in addition to the PWQMN, including project-based initiatives by local conservation authorities, citizen science records from the Lake Partner Program, and academic research from Trent University. Citizen science can play an important role in expanding data collection year-round and has been shown to generate data comparable to those collected by trained professionals with adequate volunteer training and data validation (Jollymore et al., 2017).

3.4.3 Patterns in monitoring locations

Sampling disparities across CAs were evident in southern Ontario (Tables 3.2 and 3.3). Certain CAs sampled more consistently than the others, as shown by the higher number of long-term sites across the decades (Table 3.2) and the greater total number of years in which samples were collected over at least eight months (Figure 3.9). The Credit Valley, Grand River, Toronto Region, Niagara Peninsula, Ausable Bayfield, and Kawartha CAs were able to maintain at least one long-term site throughout the five decades from 1970 to 2010 (Table 3.2). These CAs are typically larger and supported by a greater municipal tax base, which provides more financial resources and personnel to carry out their monitoring activities. Although this chapter was focused on the PWQMN only, it should be noted the PWQMN is not representative of all sites monitored within each CA, as most CAs maintain additional sampling sites as part of shorter-term project-based initiatives. The spatial distribution of the PWQMN sampling network in each CA is influenced by a variety of factors, such as sampling convenience, land use, local water quality concerns, and catchment characteristics. Over time, declines in monitoring locations reflect difficult trade-offs that were made between data legacy, available resources, and changing ecological, socio-economic, and political priorities (Altenburger et al., 2015). Regions of the more populated and agricultural southwestern and southcentral Ontario have a higher density of sites and were also better sampled year-round compared to sites in southeastern Ontario. Expansion of monitoring across southeastern Ontario is important as this region is expected to experience shifts in agriculture (see Chapter 2), while large watersheds such as the Otonabee River and Lower Trent River ultimately drain to the Bay of Quinte, one of the last remaining Areas of Concern in the Canadian Great Lakes.

Streams influenced by upstream point sources (<20 km) exhibited higher decadal mean concentrations of both TP and NO_3-N compared to sites without any upstream point sources ($p < 0.05$; Figure 3.15). At point source influenced sites, TP can reach levels up to 1.5 times greater than uninfluenced sites, whereas NO_3-N concentrations at influenced sites can be twice as high (Figure 3.15). This indicates that when examining nutrient contributions of non-point sources from land use, researchers should consider sites under minimal influence from point sources to ensure that proximal point sources do not obscure impacts of non-point sources. The Lake Ontario basin has the highest number of sites unaffected by point sources, whereas Lake Huron has the highest number of sites impacted by point sources (Figure 3.16). Across southern Ontario, the northern shoreline of Lake Ontario may hence be a more ideal study region to examine land use impacts on water quality as this area is also experiencing increasing agricultural intensification and smaller degrees of urbanization (DeBues et al., 2019). In southwestern Ontario where a large number of sites are downstream of WWTPs, establishing or reactivating historical monitoring sites further away from WWTPs can help better elucidate impacts of intensive row crop agriculture in this region. Although not examined in this chapter, flow-regulation at some sites and sampling at lake outlets can further confound nutrient load results, and thus researchers should take into account potential implications and determine whether inclusion of these sites aligns with their research objectives. Future studies can also examine the extent to which flow monitored sites from the Water Survey of Canada align with water quality monitored sites from the PWQMN and other provincial water quality networks (e.g., Provincial Groundwater Monitoring Network, Ontario Benthos Biomonitoring Network) to determine if monitoring efforts can be better synchronized.

Interestingly, the highest decadal mean TP and NO_3-N concentrations were observed at streams influenced by greenhouse discharge, specifically Muddy Creek and Sturgeon Creek in the Leamington area along the northwestern shoreline of Lake Erie (see outliers in Figure 3.15). These results were similar to those reported by Maguire et al. (2018) and the Ministry of the Environment and Climate Change (MOECC; 2012). Maguire et al. (2018) compared bi-weekly water samples collected from greenhouse influenced and non-greenhouse influenced streams in southwestern Ontario over five years and found that greenhouses acted as point sources of effluent elevating the concentrations of nutrients. With increased flow from precipitation, dilution of nutrients in greenhouse influenced rivers was observed, which has implications for management (Maguire et al., 2018). Concerns of surface water quality standard exceedances from greenhouse inputs were also expressed by the MOECC (2012). Greenhouse agriculture is a growing sector that must be considered alongside typical urban point sources such as WWTPs in water quality planning.

To ensure the value and continuity of the PWQMN dataset, it is important to establish a response protocol that addresses policy, budget, and technical changes. This protocol should include a framework to guide the prioritization of sampling sites in the event of program modifications (i.e., reductions or expansions of sites) to maintain consistency in monitoring efforts. Monitoring activities should be targeted at regions undergoing significant land use changes, areas near pollution sources, and ecosystems susceptible to climate-related impacts. Recognizing that many monitoring programs including the PWQMN may not have the resources to address flow and seasonal biases, the uncertainties arising from sampling frequency should be acknowledged and effectively communicated when reporting results to enhance decision-making and stakeholder understanding (Williams et al., 2015).

Chapter 4: General Discussion and Conclusion

4.1 Major findings

With the decline in the proportion of nutrient loading from point sources, the role of tributaries in the Great Lakes basin has been recognized to be an important regulatory factor in influencing downstream trophic status. Although tributary nutrient concentrations and flow conditions differ across watersheds, common watershed characteristics such as land use and landscape features can help explain observed variations in nutrient loading. Establishing associations between non-point source concentrations with land use patterns in southern Ontario, one of the most densely populated and agriculturally intensive regions in the basin, can further our understanding of current re-eutrophication issues in the lower lakes. In this thesis, I quantified relationships between land use patterns and stream water quality across southern Ontario at a broad spatial scale. I further examined historical and current trends in provincial stream water quality sampling to provide a more holistic understanding of long-term monitoring in Ontario and additional context for interpreting water quality relationships with land use.

4.1.1 Chapter 2

In Chapter 2, I elucidated spatial patterns of land use and landscape features in watersheds across southern Ontario using an SOM analysis. I then identified relationships between these land use patterns and decadal mean stream NO_3-N, TP, and Cl concentrations from the ice-free season. Based on these relationships and decadal mean streamflow patterns, I further estimated chemical exports to each of the major drainage basins downstream. Watersheds were classified into eight clusters: four dominated by agriculture with varying intensities and crop types, two urban-dominated, and two predominantly natural. As predicted, even at a broad geographic scale, relationships between NO_3-N concentrations and row crop production prevailed. Clusters with the greatest proportion of tile-drained row crop agriculture had the highest NO_3-N concentrations, with levels up to 12 times higher than the most natural-dominated cluster. Strong positive linear relationships were observed between NO_3-N concentrations with three other land use variables, namely corn-soybean area (R^2 = 0.69), fertilized area (R^2 = 0.65), and tile-drained area (R^2 = 0.64). Compared to NO_3-N, land use relationships with TP were not as clear. The highest TP concentration occurred in the cluster with the greatest row crop cover, while the remaining agricultural clusters and urban clusters appeared to have similar TP concentrations. Also as hypothesized, urban clusters exhibited the highest Cl concentrations, up to nine times greater than the least urbanized clusters and Cl concentrations were found to increase with urban coverage and human population density. All clusters exhibited Cl levels that exceeded natural background concentrations (<10 mg/L; CCME, 2011), indicating the pervasiveness of Cl contamination across the study region. Based on the areal proportions of clusters and variation in streamflow in each basin, it was estimated that the most agricultural Erie basin exported the greatest quantities of NO_3-N and TP, whereas the most urbanized Ontario basin exported the most Cl.

A key finding from this chapter was that intensive row cropping and associated practices such as less diversified crop rotations, fertilizer application, and improved drainage are likely to be major contributors to elevated stream NO_3-N and TP levels. While current NO_3-N concentrations observed in southern Ontario remain below thresholds considered hazardous to human health, ongoing intensification of agricultural practices favoring row crop production may lead to further increases in NO_3-N export, potentially reaching levels that may pose risks to public health and freshwater life. The analysis from chapter two also highlighted that southwestern Ontario is a major hotspot for excessive nutrient loss due to the high concentration of row crop farming and livestock agriculture. As most watersheds in southwestern Ontario also drain into Lake Erie, where severe eutrophication issues have occurred, it is warranted that much of the research and management attention has focused on addressing water quality challenges in this region. An increased adoption of agricultural best management practices such as diversifying crop rotations, optimizing fertilizer inputs, improving tile drainage water quality, and manure management will play a profound role in reducing nutrient losses in this region.

Two types of watersheds were suggested to be studied more intensively. The first type comprises of watersheds experiencing greater shifts from pasture to row crop cultivation, predominantly located in clusters 2 to 4 (upper region of southwestern Ontario) and cluster 7 (north shore of Lake Ontario). With possible extension of the growing season from climate change alongside favourable economic conditions, more farmers may be motivated to switch from livestock to row crop farming in these regions. Although stream nutrient concentrations in these regions may not be as concerning as those from the intensively row cropped area in southwestern Ontario, minimizing nutrient losses should still be a priority in these transitional areas to reduce economic loss from excess fertilizer runoff and prevent exacerbation of downstream eutrophication issues. The second type involves watersheds experiencing higher rates of urban development. Even though Cl concentrations were highest in the most populated cluster 5, rapidly urbanizing adjacent watersheds (cluster 6) also require management attention as more roads and impervious cover will likely be accompanied by increases in stream salinity.

This chapter extended the application of the SOM exercise in the Bay of Quinte originally conducted by Kim et al. (2016) to the region of southern Ontario. Kim et al. (2016) successfully used the algorithm to detect land use patterns which formed the basis for characterizing spatial TP loading across the basin and identifying nutrient export hotspots. In this study, I followed a similar methodology to the previous work while introducing new elements. I incorporated N alongside P into the analysis because growing evidence suggests that both nutrients can co-limit algal productivity, while I also examined Cl as an indicator of urban pollution. I focused on non-point source impacts by excluding monitoring sites influenced by wastewater treatment plants. Furthermore, building upon previous research that has linked agricultural intensification with declining water quality, this study incorporated variables that would offer insights into this relationship, including agricultural type (e.g., corn + soybean, wheat, pasture), agricultural land use practices (e.g., tile drainage, crop rotation, fertilizer use), and changes in land use over time (e.g., pasture to row crop, urban development). These variables are not often considered collectively in existing studies. The approaches used to estimate chemical export in this chapter was relatively simplistic and provided an efficient means of generating a rough approximation of nutrient export from land use. Two methods of nutrient export estimation were explored, and although both yielded consistent results, the second method accounted for uncertainties more effectively. For applications requiring greater accuracy, more complex process-based modeling methods as used by other studies in the Great Lakes basin (see review by Arhonditsis et al., 2014) would be better able to dynamically represent physical and biogeochemical interactions over time and space.

4.1.2 Chapter 3

In Chapter 3, trends in sampling frequency, seasonality, and location of the PWQMN in southern Ontario were examined based on stream NO_3-N, TP, and Cl data. Due to financial cutbacks, there has been a decline in the number of monitoring sites (50% from 1970s to 2010s), and current sites are now monitored more sparsely and irregularly. As sampling is conducted once a month, the program mainly captures baseflow conditions, largely missing episodic, high flow events. Additionally, since the 1990s, the majority of sampling efforts have been focused on the ice-free period between April and November. Comparisons of inter-seasonal concentrations showed that both NO_3-N and Cl were typically higher in the ice-covered period, whereas the lack of patterns in TP may be a reflection of limitations in sampling frequency. Reliance on ice-free season data may lead to underestimations in annual loading. Regions with higher population density and agricultural activity, such as southwestern and southcentral Ontario, have a higher density of monitoring sites and more comprehensive year-round sampling compared to sites in southeastern Ontario. Concentrations of NO_3-N and TP at sites influenced by point sources can be up to twice as high than at uninfluenced sites.

These findings from Chapter 3 have implications for the conclusions drawn in Chapter 2. Since the water chemistry data used in Chapter 2 only covers the ice-free period, the cluster concentrations and basin areal export estimates presented may be lower than actual annual mean concentrations and export values. Total P concentrations were not found to have any clear relationships with land use in Chapter 2, but this could be attributed to limitations in the sampling frequency of the monitoring program. Future climate conditions, including increased precipitation frequency and intensity, as well as earlier spring freshets, can exacerbate nutrient export resulting from land use shifts. Because of the lack of year-round, storm-targeted data, solely relying on the PWQMN to capture impacts of climate change may not be sufficient. To better understand the relationship between TP and land use under a changing climate, researchers can supplement PWQMN dataset with data from flow-targeted monitoring, or short-term continuous monitoring. This approach is particularly needed in watersheds with flashy hydrology, which include extensively tile-drained or urbanized areas. Considering the limitations in resources for year-round monitoring, a multi-partner and collaborative approach is recommended to enhance monitoring efforts and facilitate data sharing to fill the gap in winter monitoring. Finally, the analysis from Chapter 3 suggested that the exclusion of WWTP-influenced sites in Chapter 2 helps focus on impacts from non-point sources. The Lake Ontario basin appears to be a more suitable area for examining land use impacts on water quality, as it has the least number of WWTP-influenced sites.

4.2 Research considerations and limitations

The SOM exercise from Chapter 2 was intended as an exploratory analysis to gain insights into land use patterns across the broad landscape of southern Ontario. While the SOM is commonly used for dimensionality reduction, small levels of redundancy likely existed between certain variables in this study. However, this overlap was not expected to severely impact the SOM classification results as the metrics were designed to measure different aspects of land use and their associated changes. For example, although manure application is likely associated with livestock density, manure is a valued commodity that is often exported beyond the local area of livestock production for use on row crop fields to supplement or replace synthetic fertilizer. Likewise, while areas with higher adoption of row crops may increase the potential for corn-soybean only rotations, this does not definitively indicate the presence of corn-soy rotation exclusively, as individual farming practices shape specific crop cycles. In addition, the although the SHDI incorporates data from all land use categories in each watershed, the index was a measure of landscape diversity that reflects both the number of land use categories and their relative abundances, which means even watersheds of the same type (i.e., agricultural) can have different SHDI values. Therefore, while acknowledging potential interdependencies between variables, the variables were designed to profile distinct aspects of land use that collectively offered descriptive insights through the SOM analysis. Nonetheless, follow-up validation accounting for input correlations could further strengthen the understanding of the observed patterns.

Several limitations associated with the datasets used in Chapter 2 restricted the scope and depth of the analysis. Most of the land use and agricultural crop information was derived from the AAFC Annual Crop Inventory. However, since the dataset was only available from 2011 onwards for Ontario, the overall analysis was confined to the most recent decade and historical long-term trends in land use were not examined. The crop inventory in Ontario had a spatial resolution of 30 m, with reported classification accuracies ranging from 76 – 92% for crop classes and 74 –76% for non-agriculture land cover between 2011 and 2020. Although classification errors during the construction of the dataset are inevitable, they may have caused certain land use categories to be overestimated or underestimated within the watershed. In addition, the Census of Agriculture was used to calculate fertilized area and livestock density within each watershed. The process of converting the census data to a watershed scale was bound to introduce some inaccuracies into watershed characterization. The conversions were based on area-weighted means, which assumes a uniform spatial distribution of data, but land use is heterogeneous and thus the values derived for each watershed from this conversion may not be entirely representative of actual conditions within the watershed. Limitations of the water chemistry data from the PWQMN have been discussed in detail in Chapter 3, including the decline in sampling frequency over time and the lack of storm-event and ice-covered season data. Criteria for site selection were used to address these limitations but resulted in a significant reduction in the number of stations and amount of water quality data that could be used for analysis. Alternative methods to minimize the impacts of these limitations can be explored to maximize the utilization of available data.

The selection of land use variables for watershed characterization in Chapter 2 could be further refined. For example, incorporating additional agricultural land use practices such as area under different types of tillage can contribute to a more comprehensive analysis of agricultural activities. While agricultural land use was relatively well characterized, urban land use was less descriptive due to data constraints of the AAFC crop inventory. Incorporating additional land use datasets to further distinguish urban areas into impervious vs. pervious surfaces or old vs. new urban may help to provide better insights into urban land use dynamics.

To correspond with Chapter 2, the analysis in Chapter 3 was limited to examining sampling patterns of NO_3-N, TP, and Cl from sites within the Mixedwood Plains ecozone. As a result, much of the broader water quality data available from the PWQMN dataset was not explored. Expanding the analysis to include additional parameters across the entire province could provide a more comprehensive understanding of long-term trends. Additionally, land use and its influence on water quality variability was not explicitly accounted for in the seasonal water quality analysis. Incorporating land use data into statistical models such as analysis of covariance or linear mixed effects models would allow testing for differences in decadal mean nutrient concentrations between seasons while controlling for the potential confounding effects of land use changes over time. This would help isolate the influence of seasonality from other factors. Lastly, monitoring sites can be better characterized based on their proximity to upstream point sources using increments (e.g., 5 or 10 km) in distance to provide more insight into the influence of point sources on water quality as a function of distance. Comparing the water chemistry of municipal treated wastewater effluent to receiving stream water quality may also help identify the optimal distance for monitoring stream water quality at sites located downstream of a WWTP.

4.3 Future research opportunities

This study identified agricultural activities, particularly in southwestern Ontario, as one of the main non-point sources of nutrients influencing stream water quality, and thus, highlights the importance of further targeted studies to improve our understanding of existing agricultural management practices on nutrient loss. In Chapter 2, the proportion of watershed area under a continuous corn-soybean rotation was found to correlate with increasing stream NO_3-N concentrations. Diversified crop rotations and cover cropping are practices that could help minimize N losses from agricultural fields, and field-scale studies that quantify impacts of these practices on soil health and nutrient cycling under local climatic and soil conditions over multiple growing seasons would be useful. Tile drainage was also found to correlate with stream NO_3-N concentrations in this study, however, the relationship was not as strong as for crop rotation likely due to incomplete records of tiled area across southern Ontario. Remote sensing methods for mapping tile drainage networks across agricultural regions could be explored to improve tile drainage records, whereas additional research is needed to better understand the scale and impact of tile drainage on nutrient transport dynamics under future climate scenarios. Fertilizer application was another factor that was linked to elevated stream NO_3-N levels. On-farm research evaluating fertilizer placement and application timing could help optimize fertilizer inputs while minimizing off-site nutrient losses. Lastly, the winter season is expected to become more hydrologically active under a changing climate and should hence be a period prioritized for water quality monitoring and nutrient loading modelling.

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Appendices

Appendix A: Supplementary land use maps

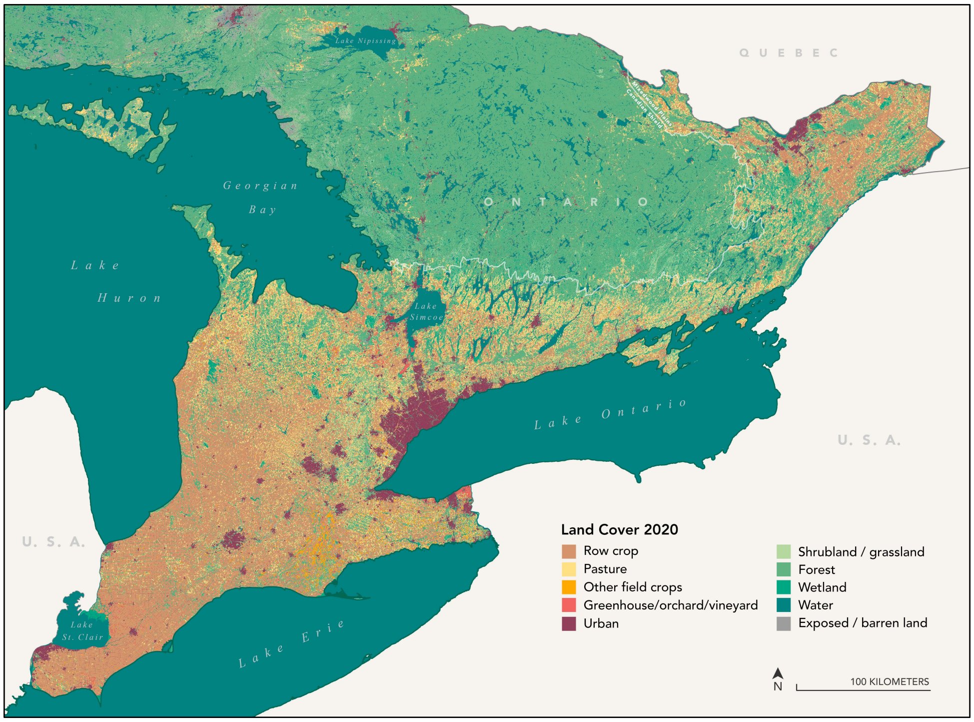

Figure A1. Land cover in southern Ontario from AAFC Annual Crop Inventory (2020)

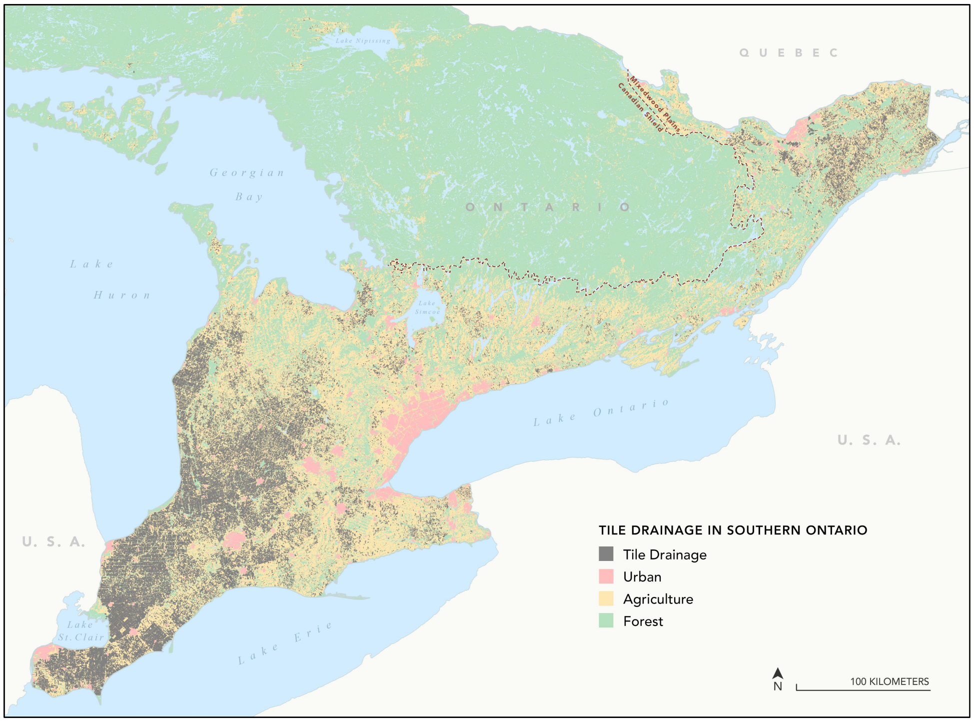

Figure A2. Tile drainage coverage (2021) and general land cover across southern Ontario

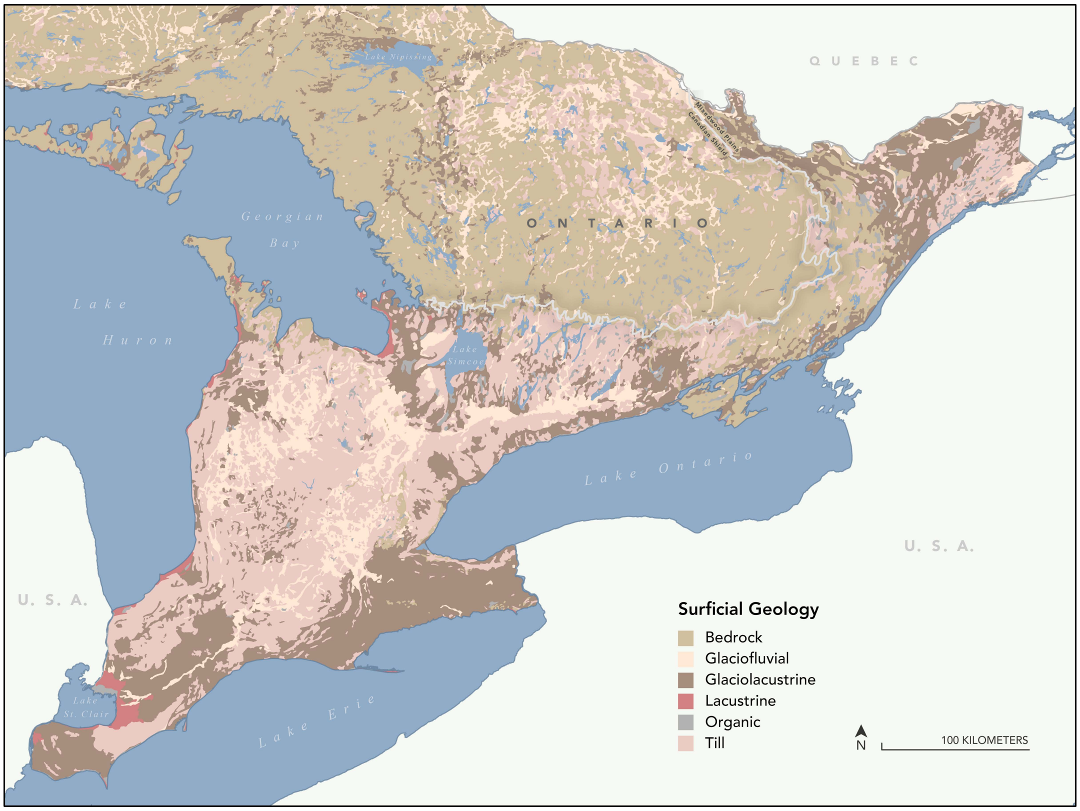

Figure A3. Surficial geology (quaternary geology) of southern Ontario

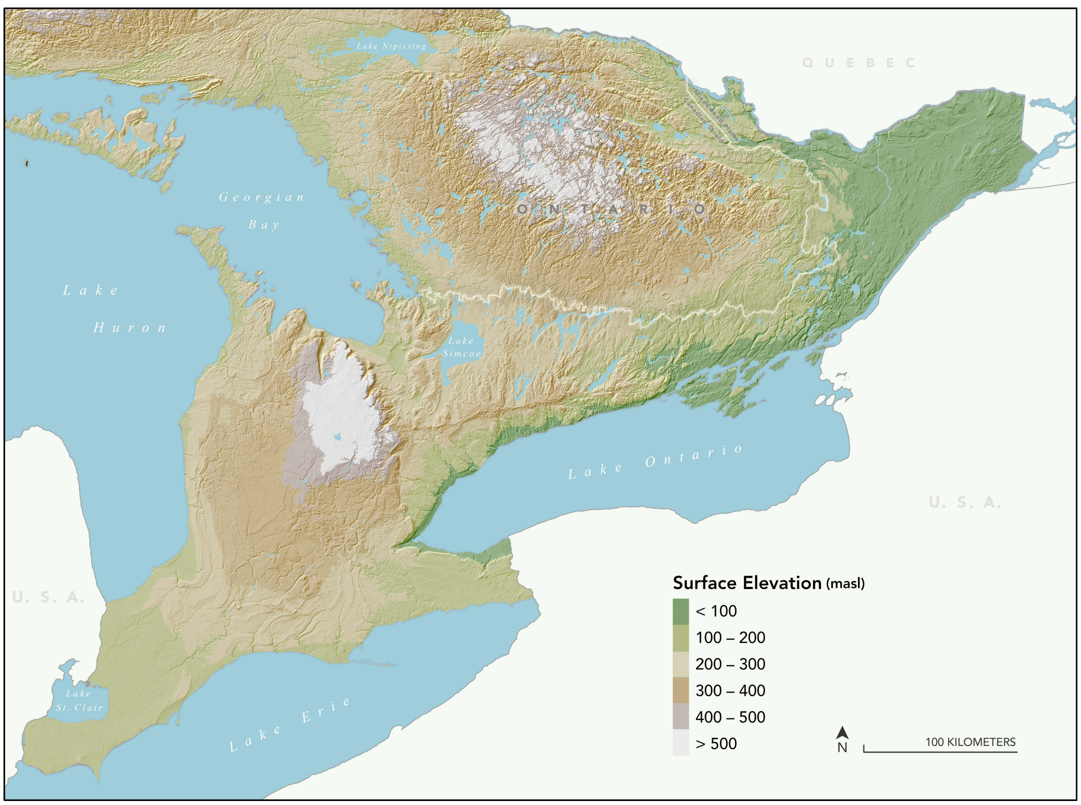

Figure A4. Surface topography of southern Ontario provides a gradient for surface runoff and groundwater flow

Appendix B: Annual Crop Inventory

Figure B. Categorization of AAFC Annual Crop Inventory classes with descriptions

Category	ACI Class	Description
Urban	Urban / Developed	Land that predominantly built-up or developed and vegetation associated with these land covers. This includes road surfaces, railway surfaces, buildings and paved surfaces, urban areas, industrial sites, mine structures, golf courses, etc.
Exposed Land/Mining	Exposed Land / Barren	Land that is predominately non-vegetated and non-developed. Includes: glacier, rock, sediments, burned areas, rubble, mines, other naturally occurring non-vegetated surfaces. Excludes fallow agriculture
Forest	Forest (undifferentiated)	Predominantly forested or treed areas. This class is mapped only if the distinction of sub-forest covers is not possible.
Forest	Coniferous	Predominantly coniferous forests or treed areas
Forest	Broadleaf	Predominantly broadleaf/deciduous forests or treed areas.
Forest	Mixedwood	Forest that is a combination of both the coniferous and broadleaf classes
Wetland	Wetland	Land with a water table near/at/above soil surface for enough time to promote wetland or aquatic processes (semi-permanent or permanent wetland vegetation, including fens, bogs, swamps, sloughs, marshes etc).
Wetland	Peatland	Wetlands that are commercially harvested for peat.
Water	Water	Water bodies (lakes, reservoirs, rivers, streams, salt water, etc).
Other Natural	Shrubland	Predominantly woody vegetation of relatively low height (generally +/-2 meters). May include grass or wetlands with woody vegetation, regenerating forest.
Other Natural	Grassland	Predominantly native grasses and other herbaceous vegetation, may include some shrubland cover.
Soybean + corn	Corn	
Soybean + corn	Soybeans	
Wheat	Wheat	This sub-cereal class is mapped only if the distinction of sub-wheat covers is not possible.
Wheat	Winter Wheat	
Wheat	Spring Wheat	
Pasture	Pasture / Forages	Periodically cultivated. Includes tame grasses and other perennial crops such as alfalfa and clover grown alone or as mixtures for hay, pasture or seed.
Fruits and vegetables	Hops	
Fruits and vegetables	Sod	
Fruits and vegetables	Herbs	
Fruits and vegetables	Nursery	
Fruits and vegetables	Buckwheat	
Fruits and vegetables	Canaryseed	
Fruits and vegetables	Hemp	
Fruits and vegetables	Vetch	
Fruits and vegetables	Other Crops	
Fruits and vegetables	Vegetables	This class is mapped only if the distinction of sub-vegetable covers is not possible.
Fruits and vegetables	Tomatoes	
Fruits and vegetables	Potatoes	
Fruits and vegetables	Sugarbeets	
Fruits and vegetables	Other Vegetables	
Fruits and vegetables	Fruits	This class is mapped only if the distinction of sub-fruit covers is not possible.
Fruits and vegetables	Berries	This sub-fruit class is mapped only if the distinction of sub-berry covers is not possible.
Fruits and vegetables	Blueberry	
Fruits and vegetables	Cranberry	
Fruits and vegetables	Other Berry	
Fruits and vegetables	Orchards	
Fruits and vegetables	Other Fruits	
Fruits and vegetables	Vineyards	
Field crops and other agriculture	Cereals	This class is mapped only if the distinction of sub-cereal covers is not possible.
Field crops and other agriculture	Barley	
Field crops and other agriculture	Other Grains	
Field crops and other agriculture	Millet	
Field crops and other agriculture	Oats	
Field crops and other agriculture	Rye	
Field crops and other agriculture	Spelt	
Field crops and other agriculture	Triticale	
Field crops and other agriculture	Switchgrass	
Field crops and other agriculture	Sorghum	
Field crops and other agriculture	Quinoa	
Field crops and other agriculture	Tobacco	
Field crops and other agriculture	Ginseng	

Figure B (cont). Categorization of AAFC Annual Crop Inventory classes with descriptions

Category	ACI Class	Description
Field crops and other agriculture	Oilseeds	This class is mapped only if the distinction of sub-oilseed covers is not possible.
Field crops and other agriculture	Borage	
Field crops and other agriculture	Camelina	
Field crops and other agriculture	Canola / Rapeseed	
Field crops and other agriculture	Flaxseed	
Field crops and other agriculture	Mustard	
Field crops and other agriculture	Safflower	
Field crops and other agriculture	Sunflower	
Field crops and other agriculture	Pulses	This class is mapped only if the distinction of sub-pulse covers is not possible.
Field crops and other agriculture	Other Pulses	
Field crops and other agriculture	Peas	
Field crops and other agriculture	Chickpeas	
Field crops and other agriculture	Beans	
Field crops and other agriculture	Fababeans	
Field crops and other agriculture	Lentils	
Field crops and other agriculture	Agriculture (undifferentiated)	Agricultural land, including annual and perennial crops; and would exclude grassland. This class is mapped only if the distinction of sub-agricultural covers is not possible.
Field crops and other agriculture	Too Wet to be Seeded	Agricultural fields that are normally seeded that remain unseeded due to excess spring moisture.
Field crops and other agriculture	Fallow	Plowed and harrowed fields that are left unsown for the growing season
Field crops and other agriculture	Greenhouses	Greenhouses have been visually identified from satellite imagery
Not included - masked out	Cloud	Areas unclassified due to cloud, shadow or other image quality factors.

Appendix C: Shannon Diversity Index

The Shannon Diversity Index is a unitless index that measures landscape diversity based on the variety and abundance of different land cover types within the watershed (McGarigal & Ene, 2013). The Shannon Diversity Index was calculated using the following equation:

$$SHDI = -\sum_{i=1}^{m} (P_i \cdot \ln P_i)$$

where m is the number of land cover classes and P_i is the proportion of watershed area covered by the land cover class. The value of the SHDI increases with a greater number of land cover types and/or a more equitable proportional distribution among land cover type.

Appendix D: Areal coverage of SOM clusters

Table D. Total number, total area, and proportional area coverage of PWQMN-delineated watersheds, tributary-delineated watersheds, and hydrometric watersheds (used for streamflow analysis) in each SOM cluster

Cluster	Area	Total Watersheds	PWQMN-delineated watersheds			Tributary-delineated watersheds			Hydrometric watersheds		
	(km^2)	#	Total Number	Total Area (km^2)	% Area	Total Number	Total Area (km^2)	% Area	Total Number	Total Area (km^2)	% Area
1	8661	67	11	2195	25	56	6465	75	7	2171	25
2	17416	89	38	8794	50	51	8623	50	28	5531	32
3	6888	37	13	2397	35	24	4491	65	7	1092	16
4	4983	24	12	2508	50	12	2475	50	6	1566	31
5	3111	25	13	1145	37	12	1966	63	9	828	27
6	6262	39	10	889	14	29	6073	97	14	1234	20
7	11156	76	46	6286	56	30	4841	43	34	5003	45
8	21163	102	36	7755	37	66	13408	63	20	3698	17

Appendix E: Spatial distribution of each variable across watersheds in southern Ontario

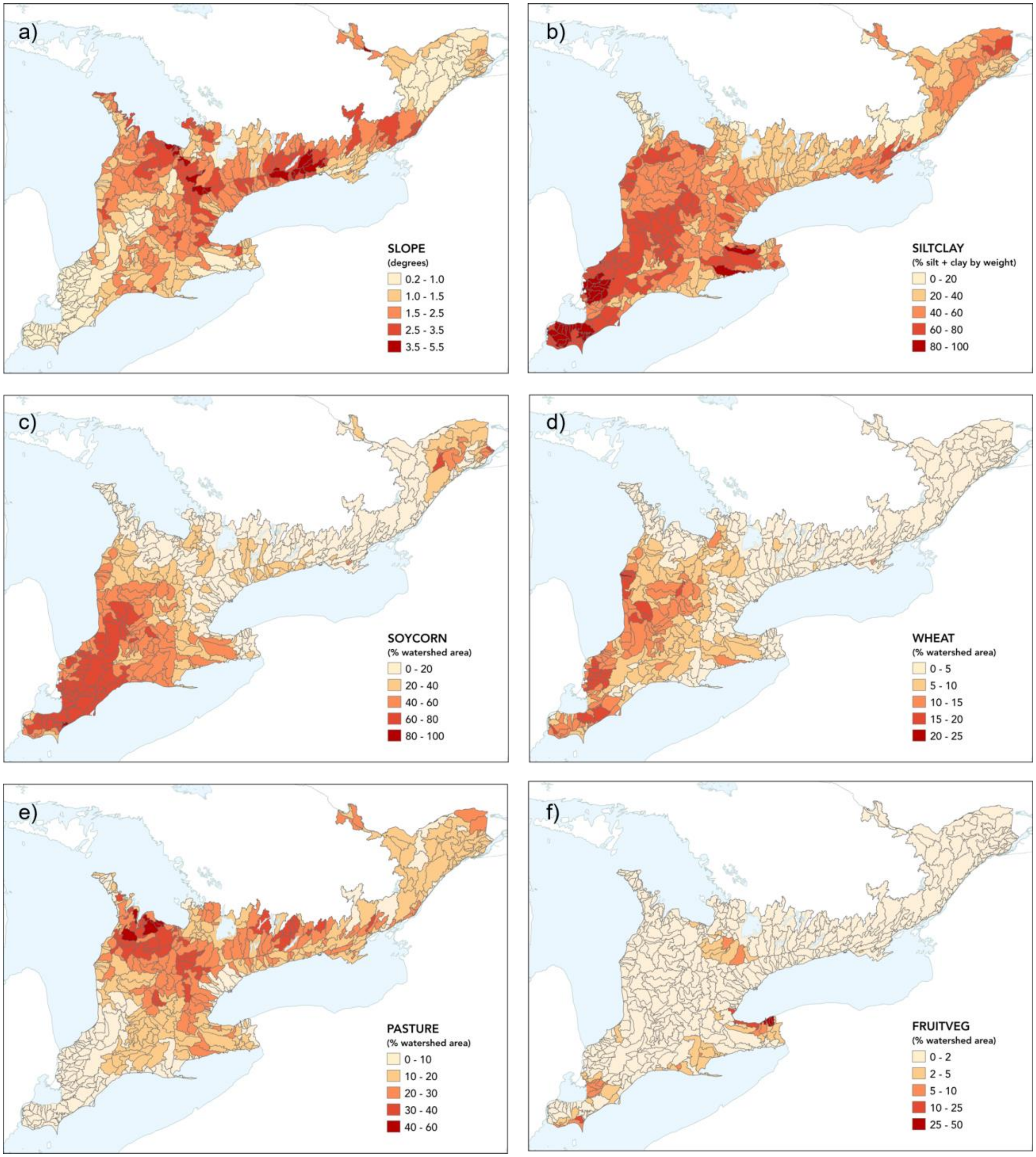

Figure E1. Average decadal mean of (a) slope, (b) soil silt plus clay, (c) soybean and corn areal coverage, (d) wheat areal coverage, (e) pasture areal coverage, and (f) fruit and vegetable areal coverage of watersheds across southern Ontario.

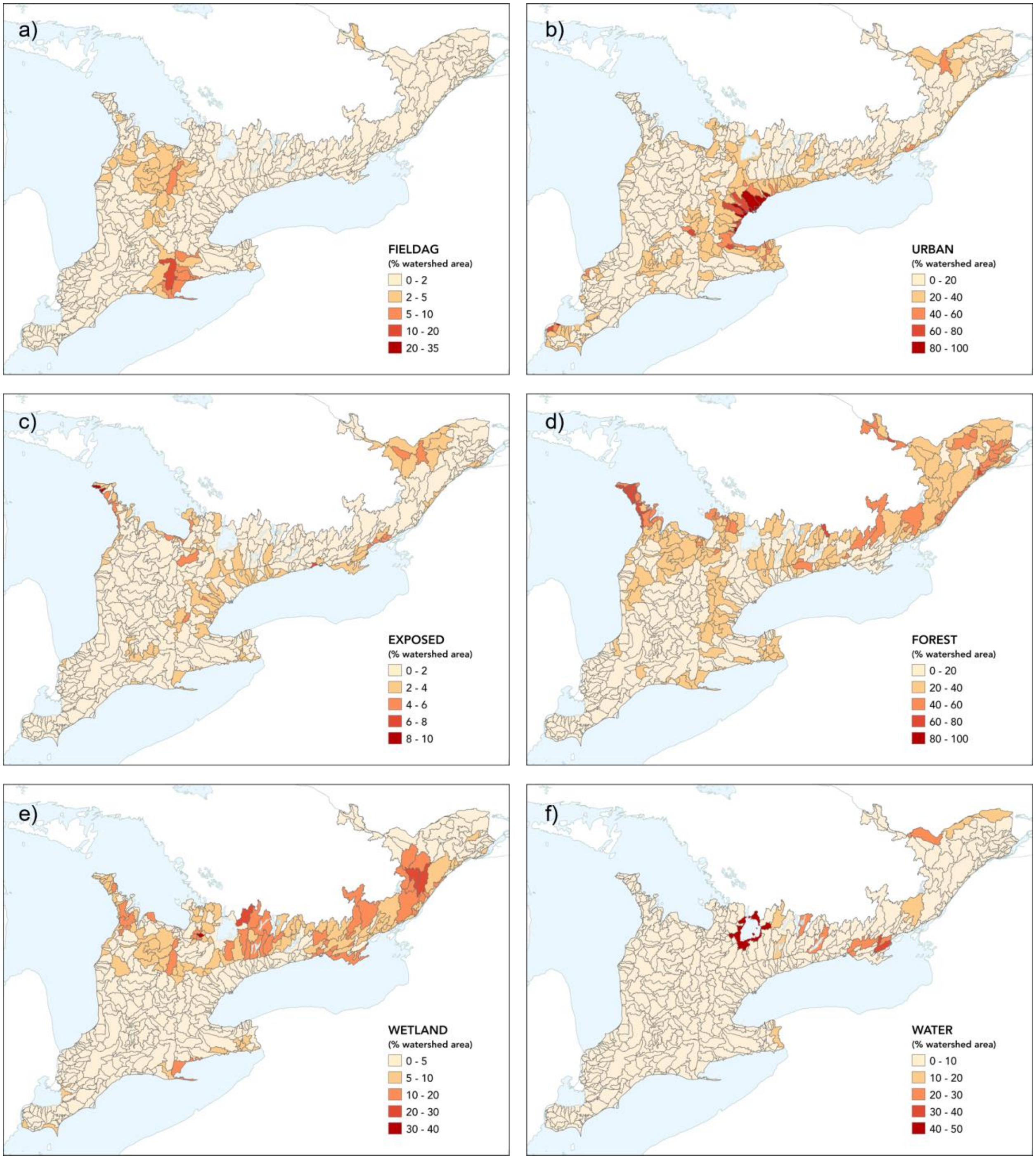

Figure E2. Average decadal mean of (a) other field crops agriculture areal coverage, (b) urban areal coverage, (c) exposed/bare l and areal coverage, (d) forest areal coverage, (e) wetland areal coverage, and (f) water areal coverage of watersheds across southern Ontario.

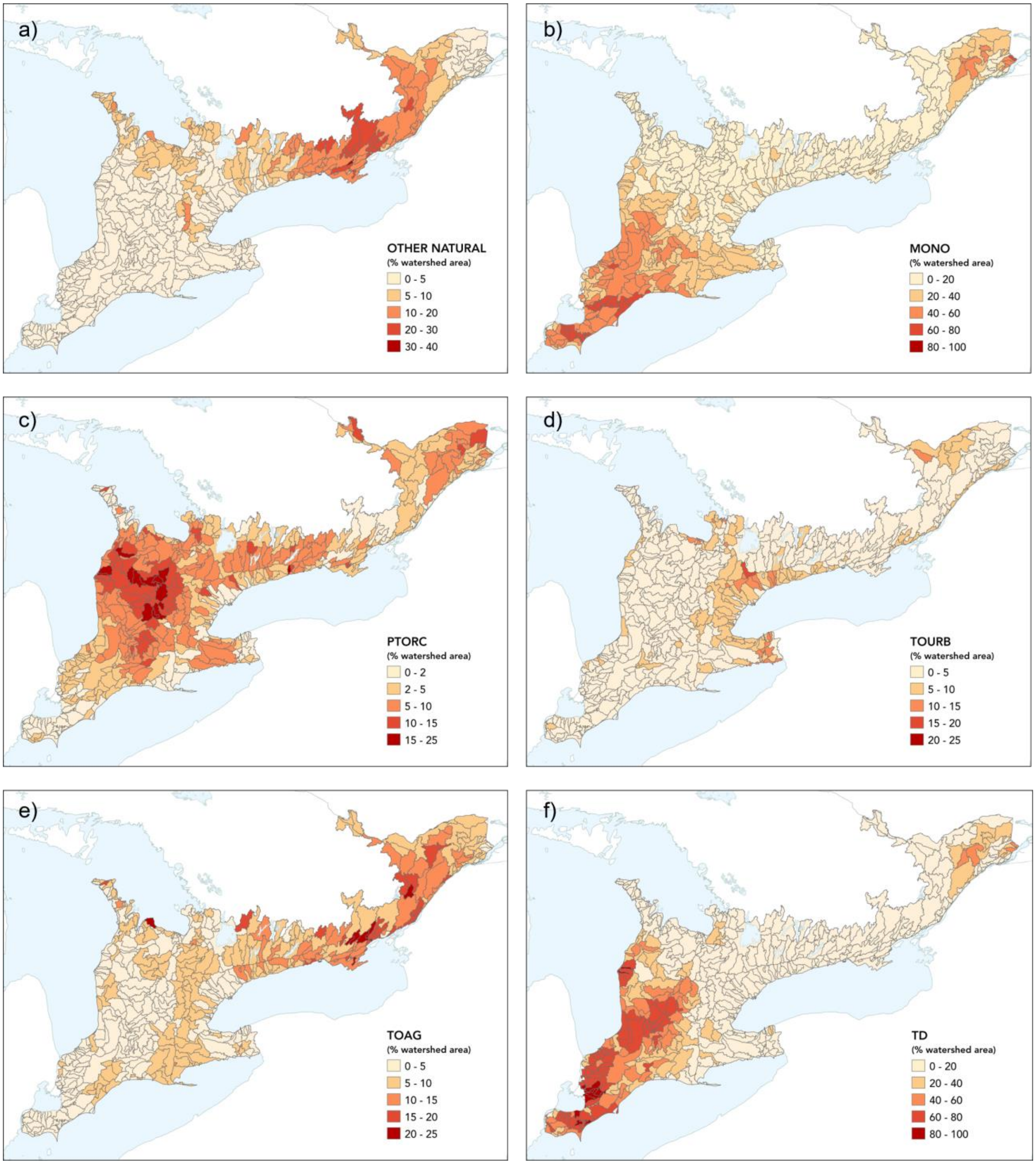

Figure E3. Average decadal mean of (a) other natural area areal coverage, (b) continuous corn-soybean areal coverage, (c) pasture converted to row crop areal coverage, (d) agriculture/natural land converted to urban land use areal coverage, (e) natural land converted to agricultural land use areal coverage, and (f) tile drainage areal coverage of watersheds across southern Ontario.

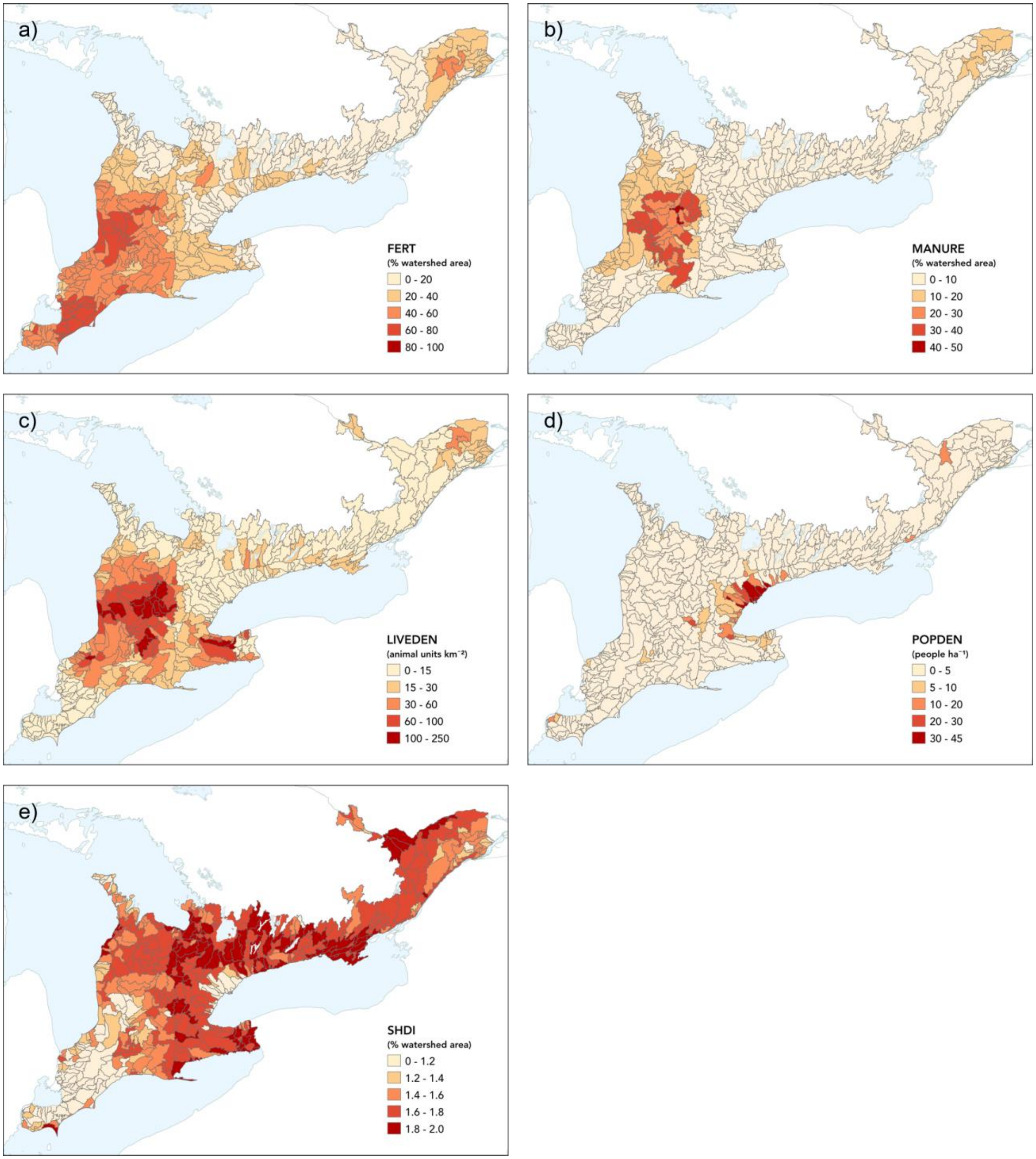

Figure E4. Average decadal mean of (a) fertilized area areal coverage, (b) manure applied area areal coverage, (c) livestock density, (d) population density, and (e) SHDI of watersheds across southern Ontario.

Appendix F: Supplementary information for Chapter 3

TP

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1964	0	0	0	0	0	0	0	0	1.0	1.0	1.0	1.0
1965	1.0	1.0	1.0	1.0	1.0	1.0	1.5	1.2	1.1	1.1	1.1	1.1
1966	1.4	1.2	1.2	1.1	1.4	1.1	1.2	1.5	1.1	1.2	1.4	1.2
1967	1.4	1.6	1.4	1.5	1.1	1.2	1.1	1.2	1.1	1.2	1.3	1.1
1968	1.3	1.2	1.5	1.5	1.3	1.3	1.5	1.4	1.3	1.6	1.2	1.1
1969	1.3	1.2	1.4	1.5	1.2	1.2	1.4	1.2	1.2	1.1	1.1	1.3
1970	1.1	1.2	1.3	1.5	1.1	1.2	1.1	1.1	1.2	1.2	1.1	1.1
1971	1.1	1.2	1.3	1.2	1.2	1.3	1.2	1.3	1.1	1.1	1.2	1.1
1972	1.3	1.2	1.3	1.7	1.7	1.2	1.2	1.0	1.1	1.0	1.1	1.0
1973	1.1	1.0	1.0	1.2	1.2	1.3	1.2	1.3	1.1	1.4	1.2	1.1
1974	1.2	1.1	1.1	1.3	1.6	1.5	1.4	1.3	1.0	1.1	1.1	1.0
1975	1.0	1.1	1.4	1.5	2.0	1.7	1.5	1.4	1.4	1.4	1.6	1.9
1976	1.7	2.1	2.6	2.0	2.3	2.4	2.2	2.0	1.9	1.8	1.8	1.7
1977	1.6	1.6	2.9	1.6	1.5	1.3	1.6	1.3	1.3	1.4	1.3	1.4
1978	1.3	1.2	1.5	1.3	1.2	1.2	1.3	1.4	1.4	1.6	1.4	1.2
1979	1.0	1.1	1.3	1.2	1.2	1.1	1.2	1.2	1.2	1.2	1.2	1.2
1980	1.1	1.1	1.3	1.4	1.2	1.1	1.5	1.1	1.1	1.1	1.1	1.1
1981	1.1	1.3	1.4	1.3	1.2	1.1	1.1	1.1	1.1	1.2	1.2	1.2
1982	1.1	1.1	1.4	1.5	1.2	1.1	1.0	1.1	1.1	1.1	1.1	1.2
1983	1.1	1.1	1.4	1.3	1.3	1.2	1.2	1.2	1.2	1.2	1.1	1.1
1984	1.1	1.3	1.3	1.3	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1985	1.1	1.1	1.3	1.4	1.2	1.1	1.1	1.1	1.1	1.2	1.2	1.1
1986	1.1	1.1	1.3	1.2	1.1	1.1	1.1	1.1	1.2	1.1	1.1	1.1
1987	1.1	1.1	1.3	1.3	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.1
1988	1.1	1.1	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1989	1.1	1.1	1.2	1.3	1.2	1.2	1.1	1.2	1.2	1.1	1.1	1.1
1990	1.1	1.1	1.2	1.2	1.2	1.2	1.1	1.2	1.1	1.2	1.1	1.1
1991	1.1	1.1	1.2	1.3	1.2	1.1	1.1	1.2	1.2	1.1	1.1	1.2
1992	1.1	1.1	1.2	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.2	1.1
1993	1.1	1.1	1.2	1.3	1.2	1.2	1.1	1.2	1.2	1.1	1.1	1.1
1994	1.0	1.2	1.2	1.4	1.2	1.2	1.2	1.2	1.2	1.3	1.2	1.2
1995	1.2	1.1	1.4	1.3	1.3	1.2	1.3	1.3	1.2	1.3	1.3	1.2
1996	1.2	1.1	3.0	1.2	1.7	1.7	1.2	1.1	1.1	1.1	1.1	1.1
1997	1.1	1.1	1.2	1.2	1.1	1.1	1.2	1.1	1.2	1.2	1.1	1.2
1998	1.2	1.1	1.3	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2	1.1
1999	1.1	1.1	1.4	1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.2	1.1
2000	1.2	1.4	1.1	1.0	1.2	1.1	1.1	1.2	1.1	1.1	1.1	1.1
2001	1.2	1.0	1.3	1.2	1.2	1.1	1.2	1.1	1.1	1.2	1.1	1.2
2002	1.3	1.1	1.2	0	1.2	1.2	1.1	1.1	1.0	1.2	1.1	1.1
2003	1.6	1.0	1.3	1.0	1.1	1.0	1.0	1.1	1.1	1.0	1.0	1.0
2004	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.1	1.1	1.0	1.1
2005	1.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.2	1.0	1.0	1.0
2006	1.0	0	0	0	2.0	1.1	1.0	1.1	1.0	1.0	1.0	1.0
2007	1.6	1.0	1.2	1.0	1.1	1.1	1.0	1.0	1.1	1.0	1.1	1.0
2008	1.9	1.0	1.0	1.1	1.0	1.1	1.1	1.1	1.0	1.1	1.0	1.1
2009	1.6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.0
2010	1.0	1.0	1.0	1.1	1.0	1.2	1.1	1.0	1.0	1.2	1.0	1.0
2011	1.0	1.0	1.1	1.1	1.0	1.2	1.2	1.0	1.2	1.1	1.0	1.2
2012	1.0	1.0	1.1	1.0	1.1	1.1	1.0	1.2	1.0	1.0	1.2	1.0
2013	1.0	1.8	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.1	1.0	1.2
2014	1.0	1.0	1.0	1.1	1.3	1.0	1.0	1.2	1.1	1.2	1.1	1.2
2015	1.0	1.0	1.0	1.2	1.1	1.1	1.2	1.4	1.4	1.6	1.4	1.6
2016	1.4	1.3	1.8	2.3	2.1	2.5	2.2	2.2	2.3	2.1	2.2	2.2
2017	2.0	2.0	2.0	2.1	2.5	3.3	3.1	3.2	3.3	3.3	3.1	2.8
2018	1.2	1.2	1.2	1.0	1.0	1.1	1.0	1.2	1.0	1.1	1.1	1.0
2019	1.1	1.1	1.3	1.0	1.2	1.0	1.0	1.1	1.1	1.2	1.1	1.0

NO_3-N

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1964	0	0	0	0	0	0	0	0	0	1.0	1.0	1.0
1965	1.0	1.0	1.1	1.8	1.0	1.0	1.3	1.3	1.2	1.2	1.1	1.2
1966	1.4	1.2	1.3	1.1	1.3	1.1	1.1	1.3	1.1	1.2	1.4	1.2
1967	1.4	1.6	1.4	1.5	1.1	1.2	1.1	1.2	1.1	1.2	1.3	1.1
1968	1.3	1.2	1.5	1.5	1.3	1.3	1.4	1.4	1.3	1.6	1.2	1.1
1969	1.3	1.3	1.4	1.6	1.2	1.2	1.4	1.2	1.2	1.1	1.1	1.3
1970	1.1	1.2	1.3	1.5	1.1	1.2	1.1	1.1	1.2	1.2	1.1	1.1
1971	1.1	1.2	1.3	1.2	1.2	1.2	1.2	1.3	1.1	1.1	1.2	1.1
1972	1.3	1.2	1.3	1.7	1.7	1.3	1.2	1.0	1.1	1.0	1.1	1.0
1973	1.1	1.0	1.0	1.2	1.2	1.3	1.2	1.3	1.1	1.4	1.2	1.1
1974	1.2	1.1	1.1	1.2	1.6	1.5	1.4	1.3	1.0	1.1	1.1	1.0
1975	1.0	1.1	1.4	1.6	2.0	1.8	1.5	1.3	1.4	1.4	1.5	1.8
1976	1.8	2.1	2.6	2.0	2.2	2.4	2.2	2.0	1.9	1.8	1.8	1.7
1977	1.6	1.6	2.8	1.6	1.5	1.3	1.6	1.3	1.3	1.4	1.3	1.4
1978	1.3	1.2	1.5	1.3	1.2	1.2	1.3	1.4	1.4	1.6	1.4	1.2
1979	1.0	1.1	1.3	1.2	1.2	1.1	1.2	1.2	1.2	1.2	1.2	1.1
1980	1.1	1.0	1.2	1.2	1.1	1.1	1.5	1.0	1.1	1.1	1.0	1.1
1981	1.0	1.3	1.8	1.7	1.9	1.8	1.7	1.8	1.8	2.0	1.9	2.0
1982	1.8	1.9	2.6	2.6	2.0	1.8	1.7	1.8	1.8	1.8	1.9	2.1
1983	1.8	1.9	2.3	2.3	2.1	2.0	1.9	1.9	2.1	1.7	1.8	1.9
1984	1.7	2.2	2.1	2.3	1.6	1.2	1.1	1.1	1.1	1.2	1.2	1.2
1985	1.2	1.2	1.5	1.7	1.3	1.2	1.2	1.2	1.2	1.3	1.3	1.2
1986	1.1	1.1	1.4	1.3	1.1	1.1	1.2	1.1	1.3	1.2	1.1	1.1
1987	1.2	1.1	1.3	1.4	1.4	1.3	1.2	1.2	1.1	1.2	1.1	1.2
1988	1.1	1.2	1.3	1.2	1.1	1.1	1.1	1.1	1.2	1.1	1.2	1.1
1989	1.2	1.1	1.3	1.5	1.3	1.3	1.2	1.3	1.3	1.2	1.2	1.1
1990	1.1	1.1	1.3	1.4	1.4	1.2	1.2	1.3	1.2	1.3	1.2	1.2
1991	1.2	1.2	1.3	1.4	1.3	1.2	1.2	1.3	1.3	1.2	1.2	1.3
1992	1.1	1.2	1.4	1.4	1.3	1.3	1.3	1.3	1.2	1.2	1.4	1.2
1993	1.2	1.2	1.4	1.4	1.4	1.3	1.2	1.2	1.3	1.2	1.2	1.2
1994	1.1	1.4	1.4	1.7	1.4	1.3	1.3	1.3	1.3	1.4	1.4	1.3
1995	1.4	1.2	1.6	1.5	1.4	1.4	1.4	1.3	1.4	1.4	1.4	1.3
1996	1.4	1.5	4.5	1.3	1.8	1.7	1.2	1.1	1.1	1.1	1.1	1.1
1997	1.2	1.1	1.2	1.2	1.1	1.1	1.2	1.1	1.2	1.2	1.1	1.2
1998	1.2	1.1	1.3	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2	1.1
1999	1.1	1.1	1.4	1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.2	1.1
2000	1.2	1.4	1.1	1.0	1.2	1.1	1.1	1.2	1.1	1.1	1.1	1.1
2001	1.2	1.0	1.3	1.2	1.2	1.1	1.2	1.1	1.1	1.2	1.1	1.2
2002	1.3	1.1	1.2	0	1.2	1.2	1.1	1.1	1.0	1.2	1.1	1.1
2003	1.6	1.0	1.3	1.0	1.1	1.0	1.0	1.1	1.1	1.0	1.0	1.0
2004	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.1	1.1	1.0	1.1
2005	1.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.2	1.0	1.0	1.0
2006	1.0	0	0	0	0	1.1	1.0	1.1	1.0	1.0	1.0	1.0
2007	1.6	1.0	1.2	1.0	1.1	1.1	1.0	1.0	1.1	1.0	1.1	1.0
2008	1.9	1.0	1.0	1.1	1.0	1.1	1.1	1.1	1.0	1.1	1.0	1.1
2009	1.6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.0
2010	1.0	1.0	1.0	1.1	1.0	1.2	1.1	1.0	1.0	1.2	1.0	1.0
2011	1.0	1.0	1.0	1.1	1.0	1.2	1.1	1.0	1.2	1.1	1.0	1.2
2012	1.0	1.0	1.1	1.0	1.1	1.1	1.0	1.2	1.1	1.0	1.2	1.0
2013	1.0	1.8	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.1	1.0	1.2
2014	1.0	1.0	1.0	1.1	1.3	1.0	1.0	1.2	1.1	1.1	1.1	1.2
2015	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.0	1.0	1.2	1.1	1.0
2016	1.0	1.0	1.0	1.1	1.0	1.2	1.1	1.1	1.1	1.0	1.1	1.0
2017	1.0	1.1	1.0	1.1	1.1	1.2	1.1	1.1	1.2	1.1	1.1	1.0
2018	1.2	1.1	1.2	1.0	1.0	1.1	1.0	1.1	1.0	1.1	1.1	1.0
2019	1.1	1.1	1.3	1.0	1.2	1.0	1.0	1.1	1.1	1.2	1.1	1.0

Cl

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1964	0	0	0	0	0	0	0	0	0	2.0	1.3	1.1
1965	1.3	1.0	1.5	1.0	1.0	1.1	1.7	1.3	1.1	1.1	1.2	1.2
1966	1.2	1.1	1.2	1.1	1.4	1.1	1.1	1.4	1.1	1.2	1.5	1.3
1967	1.4	1.6	1.4	1.5	1.3	1.4	1.1	1.2	1.1	1.3	1.3	1.1
1968	1.2	1.2	1.5	1.5	1.2	1.3	1.5	1.4	1.3	1.6	1.2	1.1
1969	1.3	1.3	1.4	1.6	1.2	1.3	1.4	1.2	1.1	1.1	1.1	1.3
1970	1.1	1.2	1.3	1.5	1.1	1.2	1.1	1.1	1.2	1.2	1.1	1.1
1971	1.1	1.2	1.3	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.2	1.1
1972	1.1	1.0	1.0	1.3	1.5	1.2	1.2	1.0	1.1	1.0	1.1	1.0
1973	1.1	1.0	1.0	1.2	1.2	1.2	1.1	1.2	1.0	1.3	1.0	1.0
1974	1.1	1.0	1.0	1.2	1.5	1.4	1.3	1.2	1.0	1.1	1.1	1.0
1975	1.0	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.0	1.0	1.0
1976	1.0	1.0	1.0	1.0	1.1	1.0	1.1	1.0	1.0	1.1	1.0	1.1
1977	1.0	1.0	1.1	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1978	1.1	1.1	1.2	1.1	1.1	1.1	1.3	1.4	1.4	1.6	1.4	1.2
1979	1.0	1.1	1.3	1.1	1.2	1.1	1.2	1.1	1.1	1.1	1.1	1.0
1980	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1981	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1982	1.0	1.0	1.1	1.1	1.1	1.0	1.0	1.1	1.0	1.0	1.0	1.1
1983	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2	1.1	1.1	1.1
1984	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.0	1.1	1.1	1.1	1.1
1985	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1986	1.1	1.0	1.1	1.1	1.0	1.0	1.1	1.1	1.1	1.1	1.0	1.1
1987	1.1	1.1	1.1	1.2	1.2	1.1	1.1	1.1	1.0	1.1	1.0	1.1
1988	1.1	1.1	1.2	1.1	1.1	1.0	1.0	1.1	1.1	1.1	1.1	1.1
1989	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1990	1.0	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.0	1.1	1.1	1.1
1991	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1992	1.1	1.1	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1993	1.1	1.1	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1994	1.0	1.2	1.1	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
1995	1.1	1.1	1.4	1.3	1.3	1.2	1.6	1.2	1.2	1.3	1.3	1.2
1996	1.3	1.3	2.8	1.2	1.7	1.7	1.2	1.1	1.1	1.1	1.1	1.1
1997	1.2	1.1	1.2	1.2	1.1	1.1	1.2	1.1	1.2	1.2	1.1	1.2
1998	1.2	1.1	1.3	1.1	1.1	1.1	1.1	1.1	1.2	1.1	1.2	1.1
1999	1.1	1.1	1.4	1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.2	1.0
2000	1.1	1.4	1.1	1.0	1.2	1.1	1.1	1.2	1.1	1.1	1.1	1.1
2001	1.2	1.0	1.3	1.2	1.2	1.1	1.2	1.1	1.1	1.2	1.1	1.2
2002	1.3	1.1	1.2	0	1.2	1.2	1.1	1.1	1.0	1.2	1.1	1.1
2003	1.6	1.0	1.3	1.0	1.1	1.0	1.0	1.1	1.1	1.0	1.0	1.0
2004	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.1	1.1	1.0	1.1
2005	1.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.2	1.0	1.0	1.1
2006	1.0	0	0	0	0	1.1	1.0	1.1	1.0	1.1	1.1	1.0
2007	1.6	1.0	1.2	1.0	1.1	1.1	1.0	1.0	1.1	1.0	1.1	1.0
2008	1.8	1.0	1.0	1.1	1.0	1.1	1.1	1.1	1.0	1.1	1.0	1.1
2009	1.6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.0
2010	1.0	1.0	1.0	1.1	1.0	1.2	1.1	1.0	1.0	1.2	1.0	1.0
2011	1.0	1.0	1.0	1.1	1.0	1.3	1.1	1.0	1.2	1.1	1.0	1.2
2012	1.0	1.0	1.1	1.0	1.1	1.1	1.0	1.2	1.1	1.0	1.2	1.0
2013	1.0	1.8	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.1	1.0	1.0
2014	1.0	1.0	1.0	1.1	1.3	1.0	1.0	1.2	1.1	1.2	1.1	1.2
2015	1.0	1.0	1.0	1.2	1.1	1.1	1.1	1.0	1.0	1.2	1.1	1.0
2016	1.0	1.0	1.0	1.1	1.0	1.2	1.1	1.1	1.1	1.0	1.1	1.0
2017	1.0	1.1	1.0	1.1	1.1	1.2	1.1	1.1	1.1	1.1	1.1	1.0
2018	1.2	1.1	1.2	1.0	1.0	1.1	1.0	1.1	1.0	1.1	1.1	1.0
2019	1.1	1.1	1.3	1.0	1.2	1.0	1.0	1.1	1.1	1.2	1.1	1.0

Figure F1. Number of samples collected in each month by the PWQMN for TP, NO_3-N, and Cl averaged across stations in southern Ontario

Table F1. Land use classes from each land use dataset used in seasonal analysis classified into general land cover categories of urban, agriculture, and natural

Land Use Category	Urban	Agriculture	Natural
Canada Land Use Monitoring Program / Canada Land Inventory	Mines, quarries, sand and gravel pits	Cropland	Non-productive woodland
	Outdoor recreation	Horticulture	Productive woodland
	Urban built-up area	Improved pasture and forage crops	Swamp, marsh or bog
		Orchards and vineyards	Unproductive land – rock
		Unimproved pasture and range land	Unproductive land – sand
			Water areas
Agricultural Resource Inventory	Built Up	Corn System	Reforestation
	Extraction	Extensive field vegetables	Swamp, marsh, bog
	Recreation	Grain system (sod crops, grains)	Water
		Grazing	Woodland
		Hay	
		Idle Agricultural Land	
		Market gardens/truck farms	
		Mixed	
		Monoculture	
		Nursery	
		Orchards	
		Pasture	
		Pastured woodland	
		Sod farms	
		Tobacco system	
AAFC Semi-Decadal Land Use Time Series	High Reflectance Settlement	Cropland	Forest
	Roads	Land Converted to Cropland	Forest Regenerating after Harvest <20 years
	Settlement		Forest Wetland
	Vegetated Settlement		Forest Wetland Regenerating after Harvest <20 years
	Very High Reflectance Settlement		Grassland Unmanaged
			Other Land
			Water
			Wetland