Spatial and Temporal Trends in Water Quality in a Mixed-Use Landscape: Agriculture vs. Urban Areas

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The eutrophication of aquatic ecosystems is a growing water quality concern as it can promote the proliferation of harmful algal blooms that have severe environmental, health, and economic impacts. In United States alone, it is estimated that the combined costs of the impact of cultural eutrophication is $2.2 billion. Phosphorus (P) is considered the primary limiting nutrient for algae in freshwater systems, and agriculture is generally recognized as the dominant source of P from the landscape. However, much less is known about the role of urban nonpoint source (NPS) P losses, in part due to the variety of land uses within these areas (residential, industrial, commercial, etc.). Therefore, considering that there is a projected increase in urbanization and a global recognition to reduce nutrient enrichment, a greater understanding of the role of urban areas in P transport is required.

Here, water quality changes were investigated in an urbanized portion of the Grand River watershed at two different spatial scales: along the mainstem of the 7th order Grand River and the headwater reaches of Laurel Creek. The Weighted Regression on Time, Discharge, and Season (WRTDS) method was used to quantify how much total phosphorus (TP) and total suspended solids (TSS, as fine sediment is the primary vector for the transport of P) was transported to each reach. The variability in mass loads and yields due to random fluctuations in discharge were removed through flow-normalization so that water quality trends due to landscape changes could be evaluated. Key source areas were then identified by comparing temporal and spatial trends in water quality to trends in landcover using aerial imagery and GIS landcover data.

There were similar findings at the two scales considered; urban areas have the potential to exceed the TP and TSS yields observed in agricultural areas as substantial deterioration of

water quality was observed during the initial phases of construction (i.e., land clearing). However, once construction was completed, the water quality impacts declined. Although elevated TSS and TP yields after urbanization eventually improve, stream flows may remain elevated and more variable than those observed in reference catchments. At the smaller scale, while there was a 40% increase in stream flow in the reference catchment over the study period, the streamflow in the urbanized catchment increased by over 700%. The observed increases in stream flow were likely attributable to increased runoff from impervious groundcover and resuspension of river sediment (originating from urban sources) at higher stream flows. Therefore, urban areas have the potential to convey large mass loads of TSS and TP, even after their concentrations decrease. Accordingly, BMPs that focus on reducing runoff may be beneficial in developed areas. This study also emphasized that land use must be viewed as dynamic when assessing its impact on water quality, as the changes in land use themselves can drive changes in water quality. This was especially important in an area like the studied region where land that was historically agricultural, which may have legacy stores of P, is disturbed and converted to urban land. Lastly, multiple spatial scales should be used to investigate the effects of land use on water quality. At smaller spatial scales, potentially confounding factors such as differences in geology, soils, slope/aspect, vegetation type, and hydroclimatic variability can be effectively controlled to identify the effects of land use on water quality. The observations that are made at smaller spatial scales can then be validated at larger spatial scales to ensure that observed trends and processes do not represent only localized phenomena, but rather larger watershed-scale effects that can inform water management controls and priorities.

Lastly, this investigation underscores the need for a coordinated monitoring effort to maximize the utility of monitoring data in decision-making. It is critical that various jurisdictional levels of government and other stakeholders communicate objectives and coordinate monitoring efforts to take advantage of economies of scale, reduce redundancies, and collect data that can be integrated meaningfully to address monitoring objectives.

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Lastly, I am most grateful for the support of my friends and family throughout the ups and downs of academia. I have had the privilege of always knowing that I had their support throughout my endeavours.

Dedication

I dedicate this thesis to my father, Subramaniam Chandrakumaran. Although he could not pursue his own passion for engineering due to socio-political circumstances, he never failed to instill the hard work, ethics, and discipline that it took for me to thrive in engineering by leading by example. Words cannot express how grateful I am to have been provided the opportunities he was not and for his support along the way.

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List of Abbreviations

BMPs – best management practices

CCU – Clair Creek at University Ave (water quality monitoring station)

COW – City of Waterloo

DP – dissolved phosphorus

FN – flow-normalized (in reference to loads/yields)

FP – Freeport (water quality monitoring station)

GRCA – Grand River Conservation Authority

ha – hectare

IFN – incremental flow-normalized (in reference to loads/yields)

KDSF – Kitchener Downstream Far (water quality monitoring station)

kg - kilogram

KUS – Kitchener Upstrream (water quality monitoring station)

LCE – Laurel Creek at Erbsville Rd. (water quality monitoring station)

NPS – non-point source

NSE – Nash-Sutcliffe Efficiency

P – phosphorus

PP – particulate phosphorus

PS – point source

ROW – Region of Waterloo

SOLRIS – Southern Ontario Land Resource Information System

SRP – soluble reactive phosphorus

TDP – total dissolved phosphorus

TP – total phosphorus

TSS – total suspended solids

WDSF – Waterloo Downstream Far (water quality monitoring station)

WRTDS – Weighted regression on time, discharge, and season

WUS – Waterloo Upstream (water quality monitoring station)

WWTP – wastewater treatment plant

yr – year

Chapter 1

Introduction

1.1 Problem Statement

The cultural eutrophication of aquatic ecosystems can stimulate the growth of plants as well as harmful algal blooms that have substantial economic, environmental, and health impacts (Anderson, Glibert, & Burkholder, 2002). The decomposition of nuisance plants can cause fish kills (Carpenter et al., 1998), the degraded ecosystem may cause a loss of aquatic biodiversity (Seehausen et al., 2007), and the increased dissolved organic carbon may cause the formation of trihalomethanes, a carcinogen, during the chlorination and ozonation of drinking water treatment (Palmstrom, Carlson, & Cooke, 1988; Zamyadi et al., 2015). Of course, these issues also have an economic impact; in the United States alone, it is estimated that the combined costs of the impact of cultural eutrophication on drinking water, endangered species, and recreational purposes is $2.2 billion (Dodds et al., 2009).

In freshwater systems, phosphorus (P) is considered to be the primary limiting nutrient for algae (Schindler, 1977), and it is recognized that eutrophication may be controlled by restricting the nutrient loads entering these water bodies (Smith, 1998). Agriculture is recognized as a considerable source of P through fertilizer and manure application that build-up in soil reserves (Heathwaite & Dils, 2000), and is transported through a change in land management practices or climatic activity like intense rainfall (Bennett, Reed-Andersen, Houser, Gabriel, & Carpenter, 1999). However, less is known about other land uses, such as urban areas. While urban point sources, like municipal wastewater treatment plants are a known source of P, they are localized and more easily controlled (Smith, Tilman, & Nekola, 1999), and accordingly, are already typically intensively managed (Carpenter et al., 1998).

Urban nonpoint sources (NPS) of P include construction activities, stormwater runoff, lawn and garden maintenance, leaves from deciduous trees, and pet waste. Due to the variety of P sources and diverse land use types (residential, industrial, commercial, institutional) in urban areas, the role of these areas is less clear. For example, Bannerman, Owens, Dodds, & Hornewer (1993) found that residential lawns had an order of magnitude greater TP concentrations than industrial parking lots, and in some instances, urban areas have been cited to have greater P losses than agricultural areas, as, King, Balough, Hughs, & Harmel (2007) found that the soluble reactive P (SRP) released from golf courses are comparable to those of agricultural areas. Conversely, other studies have attributed declines in TP concentrations to the conversion of agricultural land to impervious urban land (Raney & Eimers, 2014). However, urban areas have been related to increased P mobility, as impervious areas do not allow or the same biotic uptake and retention in soils as agricultural and natural landscapes (Hobbie et al., 2017). Furthermore, while best management practices, such as swales, bioretention cells (rain gardens), stormwater management ponds, and constructed wetlands are implemented to capture nutrients, contaminants, and sediment, conflicting evidence exists as to how much, if any, P these systems can remove (O' Shea, Borst, & Nietch, 2004; Pennino, McDonald, & Jaffe, 2016). Moreover, the complex biogeochemistry of these best management practices may cause the captured particulate P (PP) to be released dissolved P (DP), a more bioavailable form of P (Song, Xenopoulos, Marsalek, & Frost, 2015). Considering that there is a projected increase in urbanization (United Nations, 2018), and a global recognition to reduce nutrient enrichment (Chesapeake Bay Watershed Agreement, 2008; Great Lakes Water Quality Agreement, 2012; HELCOM

Baltic Sea Action Plan, 2007; etc.), a greater understanding of the role of urban areas in P transport is required.

The transport of P is usually episodic in nature, as the primary vector of transport of P is fine sediment (Bennett, Carpenter, & Caraco, 2001). Thus, climate factors that promote erosional losses, like precipitation and the associated increase in stream discharge are an important driver of P transport (Carpenter et al., 1998; Outram, Cooper, Sünnenberg, Hiscock, & Lovett, 2016; Yoon, Chung, Oh, & Lee, 2010). However, while extremes in precipitation cannot be easily controlled, strategies that focus on land and watershed management can be implemented to improve water quality.

1.2 Research Objectives

Given that there is a need to assess the role of urban areas in the transport of nutrients, the goal of this study is to evaluate the changes in water quality (TP and TSS) in urban systems and compare them to those in agricultural areas to inform management priorities and strategies, by focusing on two spatial scales (along the main stem of the 7th order Grand River and in headwater reaches of Laurel Creek) to determine the most pertinent P reduction management priorities. The specific objectives of this study to achieve this goal were to:

1. Select a suitable mass load estimation method to (1) estimate daily concentrations of TP/TSS at both spatial scales and (2) calculate TP/TSS loads and yields along the mainstem of the Grand River, by using the existing water quality monitoring data from the Region of Waterloo, Grand River Conservation Authority as well as existing hydrometric data.

2. Determine the relationship between discharge and estimated TP/TSS loads to evaluate the role of one climate-related factor in the transport of TP/TSS in the headwater reaches of Laurel Creek and the main stem of the Grand River;

3. Consult existing orthoimagery, Google Earth™ imagery, and publicly available reports to assess the spatial and temporal relationships between land use change and water quality along the mainstem of the Grand River and in Laurel Creek;

4. Compare critical source areas of TP and TSS at the two studied spatial scales to determine the most pertinent P reduction management priorities;

5. Provide recommendations for improved monitoring programs.

1.3 Thesis Approach

To achieve our study goal, we integrated existing water quality data at two spatial scales to evaluate the impacts of land use on stream water quality. The first study phase examines land use and sediment and P relationships in a relatively larger drainage area (22,000 ha) along a highly urbanized reach of the Grand River, a 7th order river. Water quality monitoring data from 2007 to 2009 was used to analyse the role of discharge and land use on TP and TSS mass loads and yields at five sites located longitudinally along the Grand River. The second study phase was conducted at a smaller scale (3,100 ha) using higher spatial and temporal resolution data collected from 1998 to 2015. In this study, the effects of urbanization in a headwater reach of Laurel Creek, a tributary to the Grand River, could be compared to another dominantly agricultural undeveloped headwater reach. Although monitoring data for this phase was collected only for the months of May to August, high sampling frequency (~28 samples per season) provides greater temporal resolution than the first study phase.

Hence, while data could only be interpreted for the summer months, it allowed for the comparison of temporal trends in a headwater basin with active development and subsequent rehabilitation to a similarly sized agricultural reference basin with minimal land disturbances. Therefore, by utilizing these two complementary studies, key source areas at two different scales were compared to determine the most pertinent management priorities.

1.4 Thesis Structure

This thesis contains five chapters, with Chapter 1 (Introduction), Chapter 3 (Methods), and Chapter 4 (Results and Discussion) to be compiled and used in a future publication. Chapters 2 (Literature Review) and Chapter 5 (Conclusions, Implications, and Recommendations) are included for completeness.

Chapter 2

Literature Review

2.1 Urban Areas

The hydrology of streams is profoundly different in pre-urban and post-urban conditions. For one, the increases in impervious area associated with urbanization change the rates and magnitudes of hydrological flow paths in watersheds and the storm hydrograph; specifically, the peak of the hydrograph increases and the lag times typically decrease in urban watersheds (Driscoll, Clinton, Jefferson, Manda, & Mcmillan, 2010). Moreover, stream flow in urban areas typically have a higher frequency of extreme flow events and an increase in runoff which may be due to a decrease in vegetative cover which reduces interception and evapotranspiration as well as an increase in impervious area which reduces groundwater infiltration (Driscoll et al., 2010; Leopold, 1968; Wang, Endreny, & Nowak, 2008). Further, the urban heat island effect, or the modified movement of air masses and presence of aerosols that can act as condensation nuclei in urban areas, may cause a relative increase in precipitation in large urban areas (Bornstein & Lin, 2000; Karl, Diaz, & Kukla, 1988; Zhou et al., 2004). These increases in high intensity runoff events with greater runoff volumes may increase the losses of NPS nutrients and sediment as they are strongly dependent on hydrological events (Edwards & Withers, 2008).

Due to the variety of P sources and diverse land use types (residential, industrial, commercial, institutional) in urban areas, the role of these areas in water quality is complicated (Booth et al., 2004). For example, residential lawns have been found to have an order of magnitude greater TP concentrations than industrial parking lots (Bannerman, Owens, Dodds, & Hornewer, 1993). In some instances, urban areas have been cited to have greater P losses than agricultural areas, as, King, Balough, Hughs, & Harmel (2007) found that the soluble reactive P (SRP) released from golf courses are comparable to those of agricultural areas. Conversely, other studies have attributed declines in TP concentrations to the conversion of agricultural land to impervious urban land (Raney & Eimers, 2014). However, urban areas have been related to increased P mobility, as the hydrologic connectivity of impervious areas and stormwater drainage networks in urban areas enable the efficient transport of these pollutants directly to receiving waters (O'Driscoll et al., 2010), and impervious areas do not allow for the same biotic uptake and retention in soils as agricultural and natural landscapes (Hobbie et al., 2017). Furthermore, while best management practices, such as swales, bioretention cells (rain gardens), stormwater management ponds, and constructed wetlands are implemented to capture nutrients, contaminants, and sediment, conflicting evidence exists as to how much, if any, P these systems can remove(O' Shea et al., 2004; Pennino et al., 2016). Moreover, the complex biogeochemistry of these best management practices may cause the captured particulate P (PP) to be released dissolved P (DP), a more bioavailable form of P (Song, Xenopoulos, Marsalek, & Frost, 2015). Thus, it is critical that a better understanding of the impact of urban areas on P transport is obtained to effectively implement strategies that focus on land and watershed management to improve water quality.

In addition to the direct changes in surface was quality, land use and land use change also impacts channel geomorphology which also impacts surface water quality. For example, with urbanization, as bare surfaces are exposed, there is an increase in in-channel sediment storage, referred to as the aggradation phase. Once the impervious cover is completed however, an increase in discharge and a reduction in sediment supply cause sediment remobilization and channel scouring during the erosional phase (Wolman, 1967), and as sediment is remobilized, it may act as a vector for the transport of other contaminants and nutrients (Bilotta & Brazier, 2008). Therefore, the direct and indirect impacts of urban areas on water quality that must be considered when establishing P reduction management priorities.

2.2 Total Phosphorus (TP)

Phosphorus (P) is the primary limiting nutrient in freshwater aquatic systems (Schindler, 1977). While the effect of agricultural land use on P source, transport and fate has been well documented, much less is known about the role of urban landscapes in its fate and transport. The forms of P found in aquatic environments are operationally defined by the method of analysis (House, 2003). Total dissolved P (TDP) is the total amount of P that can pass through a 0.45µm membrane (Denison, Haygarth, House, & Bristow, 1998). The difference between TP and TDP is referred to as the particulate P (PP). The portion of TP that is biologically available is referred to as soluble reactive P (SRP) and constitutes a portion of the TDP and PP (Sharpley, Troeger, & Smith, 1991).

Pollution in aquatic systems originates from either point sources (PS) or NPS. PS pollution originates from a specific point on the landscape (e.g., effluent from wastewater treatment plants (WWTP) and is typically independent of hydrology (Withers & Jarvie, 2008). Conversely, NPS pollution is diffuse and originates from a larger area on a landscape. The transport of NPS pollutants is usually hydrologically driven and episodic in nature (Edwards & Withers, 2008).

Urban sources of P include fertilizer application to lawns and gardens, septic systems, leaking sewer lines, atmospheric deposition, spills from commercial or industrial areas, and wastes from domestic animals (Ator, Brakebill, & Blomquist, 2011), as well as non-domestic animals, such as waterfowl (Scherer, Gibbons, Stoops, & Muller, 2017). The event mean concentration of P is highly variable due to the combination of contributing P sources, and the differences in flow routing caused by the types of and cover and their slopes (Withers & Jarvie, 2008). The characteristics of several anthropogenic PS and NPS of P are summarized in Table 2.1.

Table 2.1 Characteristics of various anthropogenic sources of phosphorus (Withers & Jarvie, 2008)

Source		Discharge	Rainfall Dependency	Chemical Composition
Wastewater	**Sewage Treatment Works/industry**	Continuous	Low	Concentrated
	Combined Sewer Overflows	Episodic	High	Concentrated
	Septic Tanks	Episodic to semi-continuous	Low	Variable
Impervious Surfaces	**Road runoff**	Episodic	High	Variable (high suspended solids)
	Impervious farmyard surfaces	Episodic to semi-continuous	Low-High	Variable
Pervious Surfaces	**Field surface runoff**	Episodic	High	Variable (high suspended solids)
	Field tile drains	Episodic to semi-continuous	Low-High	Variable
	Field sub-surface runoff	Episodic	High	Dilute

Sources of P in watersheds include surface and subsurface runoff as well as in-stream P retention and cycling processes. House (2003) summarized instream components of the P cycle as being dominated by either physical, chemical-biological, or physico-chemical processes. Physical processes include the transfer of sediment-associated P from floodplains, the storage of sediment-associated P in floodplains, the re-suspension of sediment-associated P and its subsequent release from pore water in main channels, and deposition of sediment-associated P (Bowes & House, 2001). Bio-chemical processes include the sorption of SRP and TDP to sediments, the desorption of P from sediments, the decomposition of biomass, and uptake by macrophytes, phytoplankton and benthic algae (House, 2003). Physico-chemical processes include the erosion of P-deficit materials and the subsequent sorption/desorption of SRP, as well as the infiltration of water through the floodplain and the retention of SRP in the sediment (House, 2003).

TP yields can vary considerably across landscapes depending upon factors such as geology, soil type, percent imperviousness, land use and precipitation type, frequency and magnitude. The variation in TP yields reported in the literature for predominantly natural, agricultural, and urban land use types are summarized in Tables 2.2 through 2.4 and Figure 2.1.

Table 2.2 Total phosphorus yields from predominantly natural catchments.

Dominant Land Use	Location	Yield (kg/ha/yr)	Source
Natural	Vilarinho das Furnas, Portugal	1.5	(Santos et al., 2015)
Natural	Paradela, Portugal	0.5	(Santos et al., 2015)
Natural	Alto Cavado, Portugal	0.2	(Santos et al., 2015)
Natural	Arda, Portugal	0.4	(Santos et al., 2015)
Natural	Precambrian Shield, District of Muskoka, Canada	0.06	(Winter & Dillon, 2006)
Natural	Geum River, South Korea	1.3	(Yoon, Chung, Oh, & Lee, 2010)
Natural (geological)	Northern Mojave, USA	0.13	(Domagalski & Saleh, 2015)
Natural (geological)	Southern Mojave, USA	0.13	(Domagalski & Saleh, 2015)
Natural (geological)	Truckee, California, USA	0.43	(Domagalski & Saleh, 2015)
Natural (geological)	Crowley, Mono Owens Lake, USA	0.17	(Domagalski & Saleh, 2015)
Forest	Pond Branch[1]	0.028	(Duan et al., 2012)
Forest	Bay of Quinte, Ontario, Canada	~0.08	(Kim, Kaluskar, Mugalingam, & Arhonditsis, 2016)

[1] Watersheds or sections of watersheds that drain into Chesapeake Bay

Table 2.3 Total phosphorus yields from predominantly agricultural catchments.

Dominant Land Use	Location	Yield (kg/ha/yr)	Source
Agriculture	Xitiaoxi catchment, China	1.63-4.92	(Zhao et al., 2012)
Animal agriculture	Toenepi Stream, Waikato region, New Zealand	1.16	(Wilcock et al., 1999)
Agriculture	Okana Catchment, New Zealand	0.91	(Waters & Webster-Brown, 2016)
Agriculture	Okuti Catchment, New Zealand	0.68	(Waters & Webster-Brown, 2016)
Agriculture	Grindstone Creek, Southern Ontario, Canada	0.8	(Long et al., 2015)
Agriculture	Desjardins Canal, Southern Ontario, Canada	0.56	(Long et al., 2015)
Agriculture + WWTP PS	Sacramento River,	0.15	(Domagalski & Saleh, 2015)
Agriculture	Los Angeles-Ventura	0.52	(Domagalski & Saleh, 2015)
General agriculture	Genesee River	0.1-1.1	(Pollution from Land Use Activities Research Group, 1976)
General agriculture	Grand River/ Saugeen River	0.1-2.3	(Pollution from Land Use Activities Research Group, 1976)
General agriculture	Maumee River	1.4-9.1	(Pollution from Land Use Activities Research Group, 1976)
General agriculture	Menomonee River	0.3-0.6	(Pollution from Land Use Activities Research Group, 1976)
Pasture	Bay of Quinte, Ontario, Canada	~0.02	(Kim et al., 2016)
Cropland	Bay of Quinte, Ontario, Canada	~0.09	(Kim et al., 2016)

Table 2.4 Total phosphorus yields from predominantly urban catchments.

Dominant Land Use	Location	Yield (kg/ha/yr)	Source
Urban	Red Hill Creek, Southern Ontario, Canada	1.1	(Long, et al., 2015)
Urban	Indian Creek, Southern Ontario, Canada	1.0	(Long, et al., 2015)
Urban	Chesapeake Bay Watershed, USA	0.304-0.677	(Ator, Brakebill, & Blomquist, 2011)
Urban Point Sources	San Jaoquin River, USA	0.64	(Domagalski & Saleh, 2015)
Low-density Residential	Baisman Run[1]	0.031	(Duan, Kaushal, Groffman, Band, & Belt, 2012)
Urban	Carroll Park[1]	0.837	(Duan et al., 2012)
Suburban	Glyndon[1]	0.484	(Duan et al., 2012)
Urban	Dead Run[1]	0.245	(Duan et al., 2012)
Suburban/urban	Villa Nova[1]	0.336	(Duan et al., 2012)
Urban	Gwynnbrook[1]	0.145	(Duan et al., 2012)
General urban	Grand River/ Saugeen River	0.7-2.1	(Pollution from Land Use Activities Research Group, 1976)
General urban	Menomonee River	0.3-0.9	(Pollution from Land Use Activities Research Group, 1976)
Developing urban	Menomonee River	23	(Pollution from Land Use Activities Research Group, 1976)
Urban	Bay of Quinte, Ontario, Canada	~0.001	(Kim et al., 2016)

[1] Watersheds or sections of watersheds that drain into Chesapeake Bay

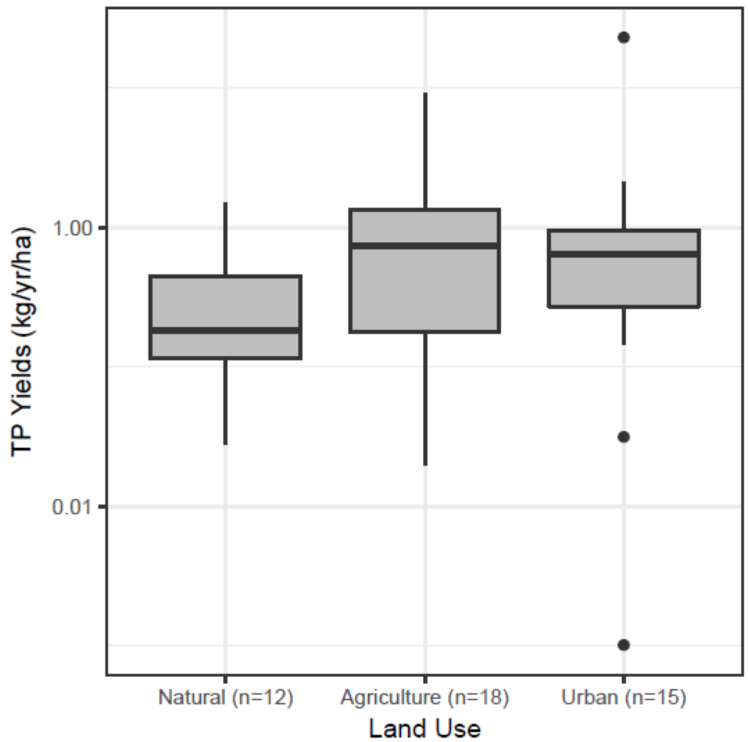

Figure 2.1 Total phosphorus yields reported in literature for various land use types

In urban areas, TP yields can vary considerably depending on the density and type of urban development. For example, TP yields ranging from 0.031 kg/yr/ha in a low density residential watershed within Chesapeake Bay (Duan, Kaushal, Groffman, Band, & Belt, 2012) to 23 kg/yr/ha in a watershed with urban development (Pollution from Land Use Activities Research Group, 1978) have been reported. Carle et al. (2005) have shown that increasing development density (i.e. total impervious area) is correlated to deteriorate d water quality. Accordingly, relatively low P loads are observed in low-density residential areas. Conversely, periods of urban development may have high P and sediment losses, as the exposed soil surfaces enable greater sediment and associated P export during construction (Carpenter et al., 1998; Novotny and Olem, 1994). In predominantly agricultural lands, TP yields can range from 0.15 kg/yr/ha in Sacramento, USA (Domagalski & Saleh, 2015), to 4.92 kg/yr/ha in Xitiaoxi catchment, China (Zhao, et al., 2012). Interestingly, the relatively small TP yield from the Sacramento River also includes TP loading from WWTPs. Natural yields vary from 0.028 kg/yr/ha in Pond Branch, a subwatershed of Chesapeake Bay (Duan et al., 2012), to 1.5 kg/yr/ha in a watershed in Portugal (Santos et al., 2015). In general, the literature demonstrates that although TP loading can vary greatly due to factors such as land use, geology, soil type, land management and hydro-climatic setting, TP loads from agricultural and urban areas are quite comparable, while the lowest loadings are generated from natural basins.

2.3 Total Suspended Solids (TSS)

The export of sediment from terrestrial to aquatic systems can have a significant impact on the suspended sediment concentrations in rivers, which in turn may have significant impacts on ecosystem services (Bilotta & Brazier, 2008). For example, suspended sediment concentrations can decrease light penetration and change the ability of periphyton and macrophytes to obtain energy through photosynthesis (Lloyd, Koenings, & Laperriere, 1987; Nieuwenhuyse & LaPerriere, 1986). In addition, high sediment loads can smother the eggs and larvae of salmonids and clog the feeding structure of benthic organisms and salmonid gills (Gray & Ward, 1982; Greig, Sear, & Carling, 2005). Moreover, fine cohesive sediment, i.e organic and inorganic particulate matter <63μm (McDonald, Stone, & Collins, 2011), acts as a vector for sediment-associated contaminant (e.g., P, heavy metals, persistant organic pollutant) transport (Dawson & Macklin, 1998; Handlin, Molina, James, Mcconville, & Dunnivant, 2014; Haygarth et al., 2006). In a study of sediment yields from urban areas in Montgomery County, MD, yields from urban areas were greater than from natural areas, but similar to rural areas (Allmendinger et al., 2007), thereby demonstrating that urban sources of TSS and deteriorated water quality can be as significant as agricultural sources.

Sediment yields can vary considerably as a function of land use and land use change (Wolman, 1967). For example, sediment yields can increase in both urban and agricultural landscapes because as vegetation is removed and bare soils are exposed (Roberts & Pierce, 1974). A summary of sediment yields reported in the literature for several land covers are presented in Tables 2.5 through 2.7 and Figure 2.2. The literature suggests that although sediment yields can vary significantly depending upon factors such as geology, soil type, slope, land use and precipitation, there is general agreement that urban and agricultural sediment yields are comparable. However, the literature review conducted for this study indicates that reported TSS yields from developing urban areas have been greater than those for any other land use type (e.g Pollution from Land Use Activities Research Group, 1978), likely due to the exposure of bare soils and their increased availability for erosion and transport during periods of runoff. Thus, urban areas should be considered as significant potential sources of TSS yields relative to agricultural and natural areas.

Table 2.5 Total suspended solids yields from predominantly natural catchments.

Dominant Land Use	Location	Yield (kg/ha/yr)	Source
Forested	Corbeira catchment, Spain	2	(Rodríguez-Blanco et al., 2016)
Forest	Smith Creek, North Carolina	291	(Lenat & Crawford, 1994)
80% forested, 10% agriculture	Cross River, Prince Edward Island	186	(Alberto, St-Hilaire, Courtenay, & Van Den Heuvel, 2016)
Mixed urban, agriculture, forest; more forest and agriculture	Hinkson Creek Watershed, Central Missouri	1009	(Zeiger & Hubbart, 2016)
Mixed urban, agriculture, forest; more forest and agriculture	Hinkson Creek Watershed, Central Missouri	1034	(Zeiger & Hubbart, 2016)
Forest	Xingu River, Brazil	15	(Riskin et al., 2017)

Table 2.6 Total suspended solids yields from predominantly agricultural catchments.

Dominant Land Use	Location	Yield (kg/ha/yr)	Source
Pasture	Corbeira catchment, Spain	5	(Rodríguez-Blanco et al., 2016)
30% agriculture	Souris River, Prince Edward Island	1642	(Alberto et al., 2016)
69% agriculture	Wheatley River, Prince Edward Island	405	(Alberto et al., 2016)
Agricultural	Devil's Cradle Creek, North Carolina	695	(Lenat & Crawford, 1994)
Cropped (winter cereal)	Corbeira catchment, Spain	2780	(Rodríguez-Blanco et al., 2016)
Cropped (corn)	Corbeira catchment, Spain	3090	(Rodríguez-Blanco et al., 2016)
General agriculture	Grand River/ Saugeen River	2-2200	(Pollution from Land Use Activities Research Group, 1978)
General agriculture	Menomonee River	230-410	(Pollution from Land Use Activities Research Group, 1978)
General agriculture	Genesee River	30-900	(Pollution from Land Use Activities Research Group, 1978)
General agriculture	Maumee River	500-5600	(Pollution from Land Use Activities Research Group, 1978)
Crop production	Landazuria watershed, Spain	360	(Merchán et al., 2018)
Soybean production	Xingu River, Brazil	67.1	(Riskin et al., 2017)

Table 2.7 Total suspended solids yields from predominantly urban catchments.

Dominant Land Use	Location	Yield (kg/ha/yr)	Source
Mixed urban, agriculture, forest; more urban	Hinkson Creek Watershed, Central Missouri	750	(Zeiger & Hubbart, 2016)
Mixed urban, agriculture, forest; more urban	Hinkson Creek Watershed, Central Missouri	1075	(Zeiger & Hubbart, 2016)
Mixed urban, agriculture, forest; more urban	Hinkson Creek Watershed, Central Missouri	1188	(Zeiger & Hubbart, 2016)
Urban	Marsh Creek, North Carolina	1320	(Lenat & Crawford, 1994)
Developing Urban	Menomonee River	27500	(Pollution from Land Use Activities Research Group, 1978)
Urban	Kelang River, Malaysia	1650-22830	(Balamurugan, 1991)
General urban	Menomonee River	210-280	(Pollution from Land Use Activities Research Group, 1978)
General urban	Grand River/Saugeen River	400-1750	(Pollution from Land Use Activities Research Group, 1978)

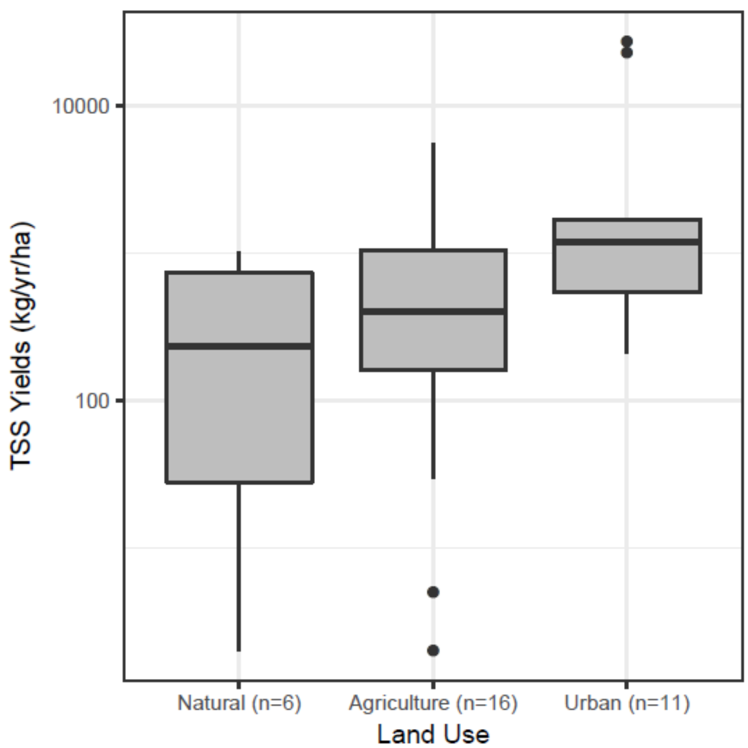

Figure 2.2 Total suspended solids yields reported in literature for various land use types.

Chapter 3

Methods

3.1 Site Description

The Grand River drains an area of 6800 km^2 and is Canada's largest tributary to Lake Erie (Figure 3.1) (Chomicki, Howell, Defield, Dumas, & Taylor, 2016). The watershed is dominated by agricultural activities, which comprise about 70% of the watershed. During the 19th century most of the forests in the watershed were removed and wetlands were drained for agriculture; only 5% of forest-cover remained in the watershed at one point (GRCA, 2016). However, through natural regeneration and tree planting, 19% of the watershed is now forested (GRCA, 2016). Urban areas, including the cities of Kitchener, Waterloo, Guelph, and Cambridge, are located in the middle portion of the watershed, and cover about 7% of the total basin area (Grand River Watershed Water Management Plan, 2014). Runoff from urban areas is routed directly into watercourses primarily through storm sewers or stormwater management ponds (Grand River Watershed Water Management Plan, 2014).

This study looked at the urban area located in in the central portion of the Grand River watershed to focus on two different study scales (Figure 3.1). The first phase of the study was conducted to examine discharge and sediment/P relationships at a relatively larger drainage area (22,000 ha) along a highly urbanized reach of the Grand River. Monitoring data collected from 2007 to 2015 enabled an analysis of the role of discharge and land use on TP and TSS at five sites located longitudinally along an urbanizing 7^{th} order river system to isolate the cumulative effects of land disturbances on water quality. The City of Kitchener is located along this reach, residing primarily on the west side of the Grand River, with a small portion on the east side. The west side of the Grand River is characterized by high imperviousness and channelized stream reaches of watercourses tributary to the Grand (Ministriy of Natural Resources and Forestry, 2011; Aquafor Beech Inc., 2015). The east side of the Grand is dominated by tilled agriculture (Ministry of Natural Resources and Forestry, 2011).

The second phase was conducted at a smaller scale (3,100 ha total) using 18 years (1998 to 2015) of monitoring data from Laurel Creek, a tributary to the Grand River, which permitted and evaluation of the effects of urbanization on water quality to be compared to a reference undeveloped sub-watershed. During this phase, monitoring data were only available for the months of May to August; however, they were collected with high frequency (~28 samples per season). The first water quality monitoring station was located on Clair Creek at University Ave. (CCU), a 3rd order stream that joins Laurel Creek just downstream of the station. This site was selected from the Laurel Creek Water Quality Monitoring Project because the headwater reaches of Clair Creek were subjected to urban development in the late 1990s (Ecosystem Recovery Inc., 2015). The second water quality station is situated on Laurel Creek at Erbsville Rd. (LCE), and drains a 4th order stream; although this basin is dominated by agriculture, this station acts as a "reference" catchment for this portion of the study, as very little land in the Grand River watershed remains unimpacted by anthropogenic activities (Grand River Watershed Water Management Plan, 2014), and this catchment has undergone minimal land use changes throughout the study period. However, although this basin is dominated by agriculture, it should be noted that portions of Laurel Creek were surrounded by wetlands in this catchment. Although the data from this monitoring program could only be interpreted for the summer months, it allowed for the comparison of temporal trends in a basin with active development to a similarly sized agricultural reference basin with minimal land disturbances throughout the monitoring period.

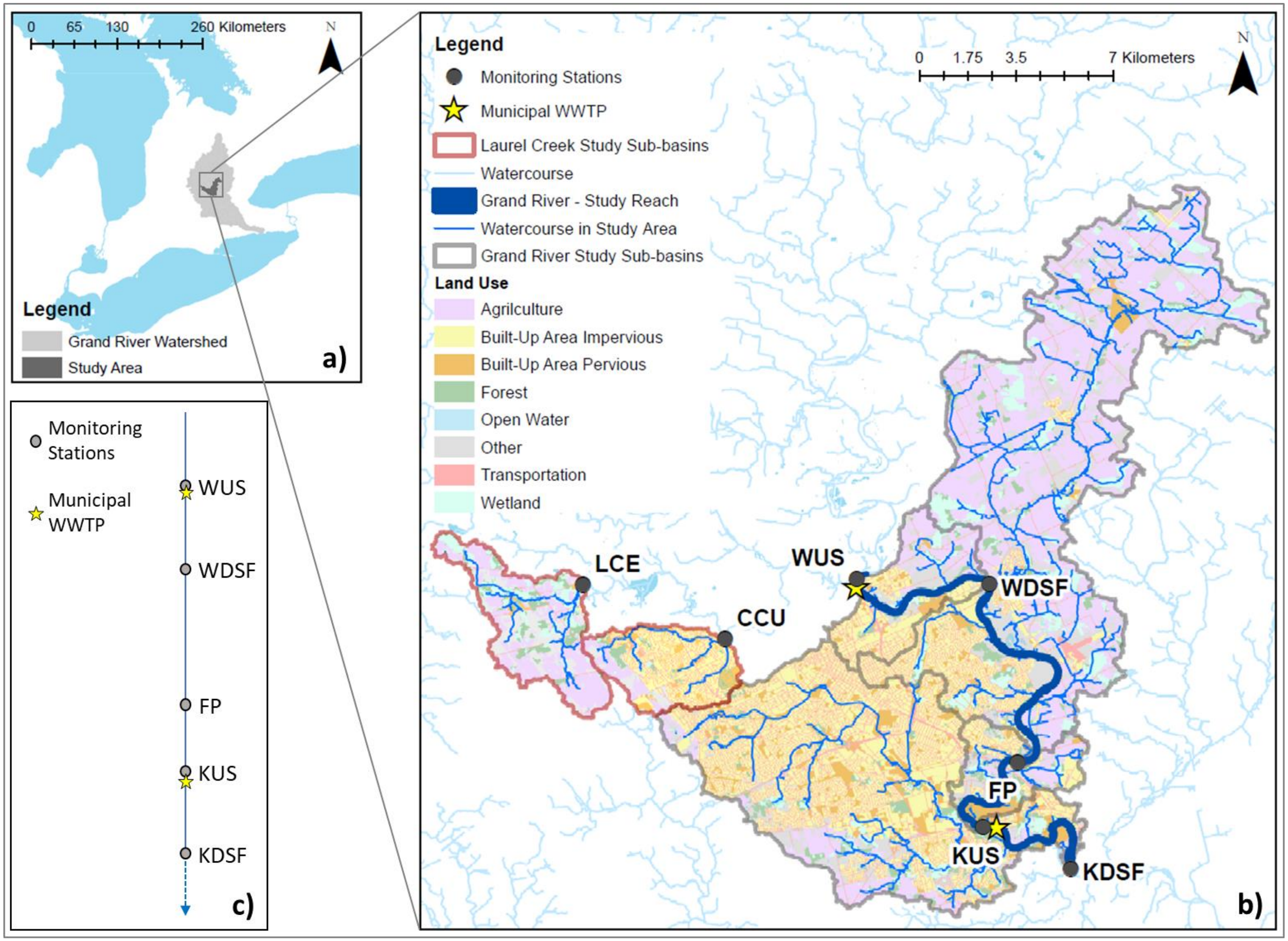

Figure 3.1 a) Location of the Grand River basin relative to Lake Erie (The NOAA Great Lakes Environmental Research Laboratory, n.d., GRCA, 2017a). b) Land use along the studied reach of the middle Grand River as per the 2011 Southern Ontario Land Resource Information System (SOLRIS) landcover data (GRCA, 2017b; GRCA, 2018a; GRCA, 2018b; 2014; Ministry of Natural Resources and Forestry, 2011). c) Simplified schematic of the main stem of the middle Grand River.

3.2 Data Sources

Total phosphorus (TP) and total suspended solids (TSS) water quality data for the main stem of the Grand River from 2007 to 2015 were obtained from the Region of Waterloo and the Grand River Conservation Authority (GRCA). Continuous discharge measurements were available for the Grand River at Bridgeport and the Grand River at Doon from the GRCA. Continuous discharge measurements at ungauged sites along the main stem were estimated by summing the additional discharge from tributaries to the Grand between the upstream gauged station and the water quality monitoring station. Missing discharge data for the Grand River at Bridgeport was estimated by establishing a linear regression relationship between the Bridgeport and Doon flow gauges (r^2=0.93).

Water quality data in the Laurel Creek watershed were collected for the months of May to August from 1998 to 2015 by the City of Waterloo. Continuous flow data for the study period at the monitoring locations of interest were obtained through the Water Survey of Canada and the Grand River Conservation Authority. Table 3.1 provides the details of the gathered datasets.

Table 3.1 Summary of water quality monitoring sampling data

Waterbody	Site	Source	Name	Years of Data	Sampling Method	n, TP samples	n, TSS samples
Grand River	Upstream of Freeport Creek	GRCA[1]	Grand Upstream of Freeport Creek (FP)	2007-2015	Grab	133	133
Grand River	Upstream of Waterloo WWTP	ROW[2]	Waterloo Upstream (WUS)	2007-2015	Grab	278	278
Grand River	Waterloo WWTP	ROW[2]	Waterloo WWTP	2007-2015	Composite	461	632
Grand River	Downstream of Waterloo WWTP (far)	ROW[2]	Waterloo Downstream Far (WDSF)	2009-2015	Grab	120	120
Grand River	Upstream of Kitchener WWTP	ROW[2]	Kitchener Upstream (KUS)	2007-2015	Grab	189	189
Grand River	Kitchener WWTP	ROW[2]	Kitchener WWTP	2007-2015	Composite	469	779
Grand River	Downstream of Kitchener WWTP (far)	ROW[2]	Kitchener Downstream Far (KDSF)	2007-2015	Grab	224	224
Laurel Creek	At Erbsville Rd.	COW[3]	Laurel Creek at Erbsville Rd. (LCE)	1998-2015, May-Aug only	Grab	576	576
Clair Creek	At University Ave.	COW[3]	Clair Creek at University Ave. (CCU)	1998-2015, May-Aug only	Grab	583	589

[1] Grand River Conservation Authority
[2] Region of Waterloo
[3] City of Waterloo

The Southern Ontario Land Resource Information System was used to identify land use types in the study area for 2011 and Google Earth™ aerial imagery was used to analyse land use changes over time. Topographic and virtual drainage network GIS data was obtained from the GRCA.

3.3 Load Estimation

The weighted regression on time, discharge, and season (WRTDS) method was used to estimate the mass loads of TP and TSS at each site. The WRTDS method was developed by Hirsch et al. (2010) and has previously been used to estimate mass loads of P and other constituents within the Chesapeake Bay (Hirsch, Moyer, & Archfield, 2010; Zhang, Moyer, & Ball, 2016), Lake Champlain (Medalie, Hirsch, & Archfield, 2012), and Mississipi River (Kreiling & Houser, 2016) basins. Although a variety of load estimation methods are available, WRTDS was selected for this study because of its flexibility and few assumptions required. In short, daily concentrations are estimated using records of daily stream flows, using Equation 1, below

$$\ln(c) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon \qquad (1)$$

where c is the concentration, Q is discharge, t is time in years, $\beta_0$through β_4 are fitted parameters, and ε is the unexplained variation (Hirsch et al., 2010). A more detailed description of the WRTDS method may be obtained from Hirsch et al. (2010). However, it should be noted that this method varies from typical load estimation methods because the β parameters are fitted for each concentration estimate. The relevance of each observation point is determined by its distance from the estimation point in time, discharge, and season, with greater weights assigned to smaller distances. The mass loads (or fluxes) at each station were then estimated using Equation 2

$$\hat{f} = 86.34\,\hat{c}\,Q \qquad (2)$$

where $\hat{f}$ is the expected value of the mass load in kg/d, 86.34 is a unit conversion factor, $\hat{c}$ is the expected value of concentration in mg/L, and Q is the daily discharge in m^3/s (Hirsch et al., 2010).

Moreover, WRTDS allows for removal of the variability in loads due to random fluctuations in discharge which makes comparing the influence of landscape factors on water quality easier; this approach is further discussed in Section 3.4.1.

However, it is recommended that the WRTDS method be utilized for datasets that span more than 20 years, and since the data sets from the main stem only span 9 years, the temporal component of the WRTDS method was muted by setting the window width to a very large number (100, in this case). The temporal component of the Laurel Creek dataset was not muted, as 18 years of monitoring data was available. All flux bias estimates for this study were less than 15% and the Nash Sutcliffe Efficiencies (NSE) varied between 0.04 and 0.77 with a median of 0.50. The details of these model evaluation parameters are provided in Table 3.2.

Table 3. 2 Summary of model fit including Nash Sutcliffe Efficiency (NSE) and estimation biases

Sites	TP Load NSE	TSS Load NSE	TP Bias	TSS Bias
WUS	0.46	0.22	-0.02	-0.08
WDSF	0.60	0.48	-0.02	0.01
FP	0.49	0.04	-0.04	0.11
KUS	0.62	0.52	-0.15	-0.07
KDSF	0.69	0.39	-0.09	-0.05
Erbsville	0.77	0.58	0.0	0.06
Clair	0.62	0.48	0.02	0.01

3.4 Spatial and Temporal Trend Analyses

3.4.1 Larger Scale - Mainstem of the Grand River

To isolate the cumulative effects of land use on water quality to each reach between monitoring stations, a high-level mass balance was conducted. In other words, the incremental mass load of TP/TSS entering a given reach was assumed to be the difference between the mass loads at the downstream station and the mass loads at the upstream station. For example, for the KUS-KDSF reach, the estimated annual mass load from KDSF was subtracted from the estimated annual mass load at KUS. Since the goal of this study is to address non-point sources of TP, mass loads from municipal wastewater treatment plants were also removed where required. A simplified schematic of the main stem study reach

(Figure 3.1) further illustrates the high-level mass balance approach. However, to confirm that the mass load distribution at each monitoring station was significantly different from those upstream and downstream of it, the non-parametric Kolmogorov-Smirnov test was used to test with a significance level of 5%. Reaches defined by monitoring stations with mass load distributions that are not significantly different should be interpreted with caution, as the mass loads estimated to be entering these reaches may be an estimate of random noise, although it is also possible that TP and TSS entering the reach (or that which is retained/remobilized) is negligible. Once mass load estimates for each reach were estimated, they were then normalized by the area draining into each reach to obtain incremental yields (units of kg/ha/year).

Moreover, since concentrations, loads, and yields are a function of streamflow (Hirsch & De Cicco, 2015), trends in water quality may be due to random fluctuations in streamflow as opposed to changes on the landscape. Therefore, since the goal of this study was to evaluate the relative role of two land use types, agriculture, and urban areas, on water quality, these random fluctuations in streamflow were removed using the flow-normalization method created by Hirsch et al. (2010). The equation used for flow normalization is provided below in Equation 3,

$$E\left[C_{fn}(T)\right] = \int_0^\infty w(Q,T) \cdot f_{Ts}(Q)dQ \qquad (3)$$

where $E\left[C_{fn}(T)\right]$ is the flow-normalized (FN) concentration for T, a specific day of a specific year, $w(Q,T)$ is WRTDS estimated concentration for a given time (T) and discharge (Q), and $f_{Ts}(Q)$ is the probability density function of discharge, specific to a particular time of year, at T_s (Hirsch & De Cicco, 2015). Thus, the unit of measurement analysed for this portion of the study is the incremental flow-normalized (IFN) yield.

3.4.2 Smaller Scale – Headwaters of Laurel Creek

Since the two catchments analysed at the smaller scale only considered monitoring stations that drain catchments without monitoring stations upstream, a mass-balance approach was not necessary here. However, flow-normalized mass loads were normalized by area to obtain flow-normalized (FN) yields.

Chapter 4

Results and Discussion

4.1 Streamflow and TP/TSS Mass Loads

It is recognized that climate drivers like antecedent conditions (Bieroza & Heathwaite, 2015; Zhang & Ball, 2017), intense precipitation events (Carpenter et al., 1998; Yoon et al., 2010), temperature (Jeppesen et al., 2009), and discharge (Outram et al., 2016) play an important role in the transport of P. Although we were not able to extensively investigate climate due to data limitations, it likely played a substantial role in the transport of P in the studied area, as there was a strong relationship between discharge, one climate factor, and the mass loads of TP/TSS at the monitoring stations at both spatial scales (Figures 4.1 and 4.2). However, while the climate cannot be readily controlled, integrated land and watershed management strategies focused on water quality improvement can be developed and implemented, and to inform the development of such strategies, this study focused on the role of land use in the in the transport of nutrients. Thus, we compared the relative impact of urban and agricultural land use on stream water quality in a mixed-use basin.

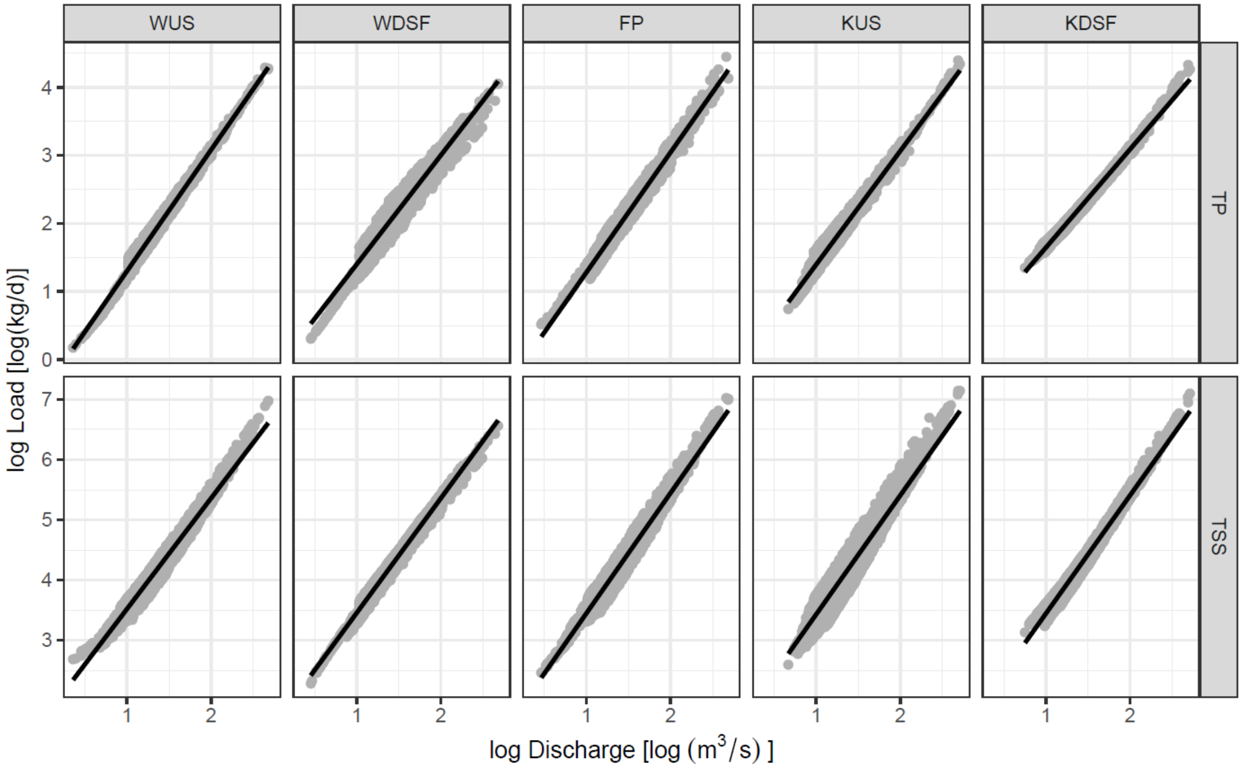

Figure 4.1 TP and TSS loads vs discharge for sites along the main stem of the middle Grand River. The strong linear relationship between discharge and load suggests that discharge plays a substantial role in the transport of TP and TSS mass loads.

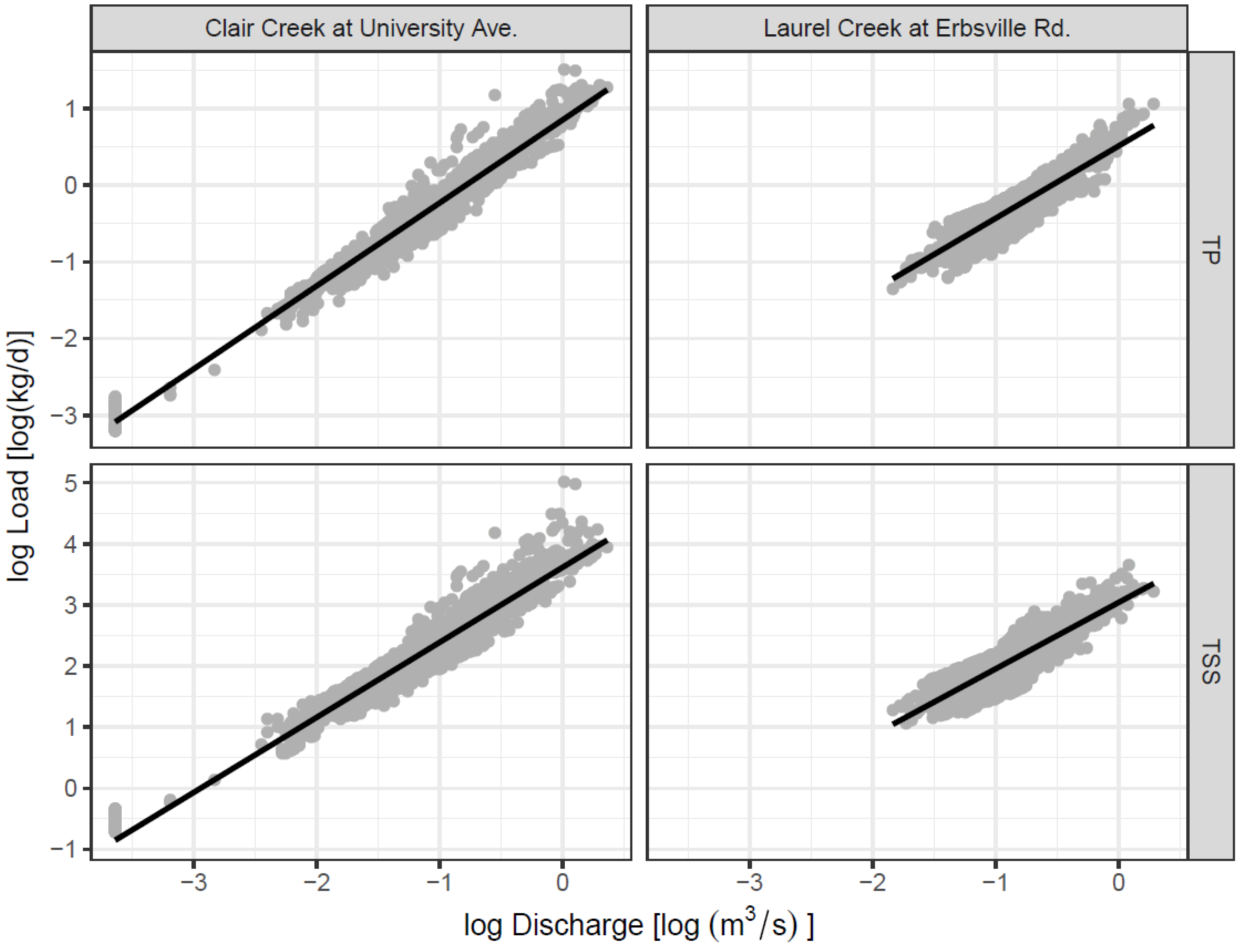

Figure 4.2 TP and TSS loads vs discharge for Laurel Creek sites. The linear relationship between discharge and load suggests that discharge plays a substantial role in the transport of TP and TSS mass loads.

4.2 TP and TSS Trends along the Mainstem of a 7th Order River

Agricultural land has been generally shown to have larger NPS nutrient and sediment yields than urban areas (Kim et al., 2016; Lenat & Crawford, 1994; Lotter, Sturm, & Ammann, 1998), and this is seen in Reach 1 and 3 along the mainstem of the Grand River; as we proceed downstream from the most upstream site, as agricultural areas increase, TP and TSS IFN yields do too. However, this relationship falls apart at Reach 4, where an increase in urban areas and a decline in agricultural areas (Figures 4.3c and 4.4c) does not correspond to a decline in TP/TSS IFN yields (Figures 4.3a and 4.4a).

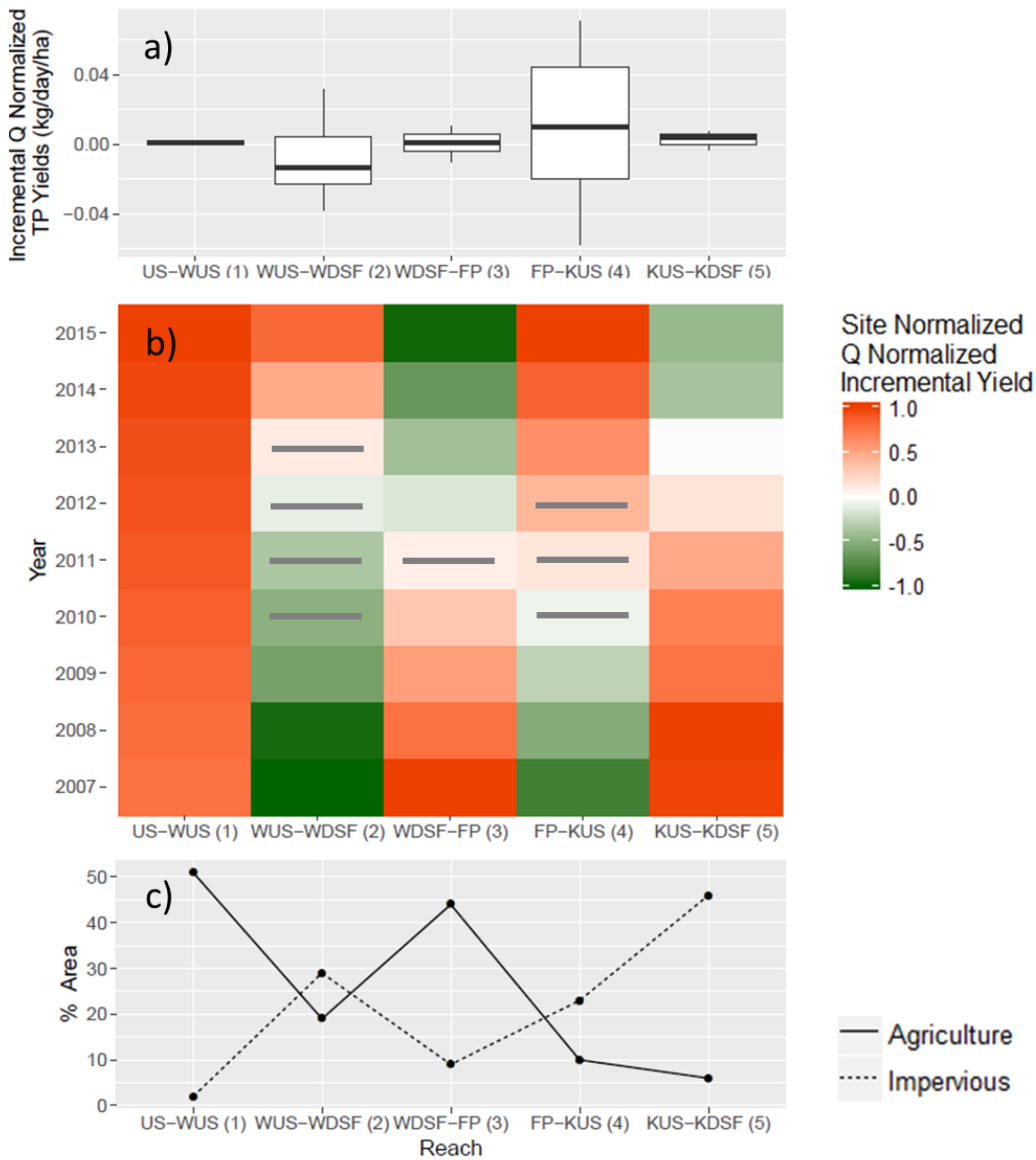

Figure 4.3 a) Incremental flow-normalized total phosphorus (TP) yields along study reach from upstream (left) to downstream (right). Reaches draining smaller areas correspond to greater variability, as these reaches may not have had as much time to buffer the fluctuations in water quality. b) Reach-normalized, incremental flow-normalized TP yields at each reach along the main stem of the middle Grand River. Each reach is normalized by its absolute maximum/minimum yield such that the year with the largest/smallest incremental flow-normalized yield is assigned a value of ±1; note that comparisons between sites cannot be made in b) due to reach-normalization. Orange squares indicates drainage areas that were sources for a given year, green indicates drainage areas that were sinks. Grey lines specify reaches that did not have significantly different distributions per the Kolmogorov-Smirnov test (α=0.05). The WUS-WDSF and FP-KUS reaches exhibit sink-to-source behaviour, while WDSF-FP and KUS-KDSF exhibit source-to-sink behaviour; these patterns may be related to the timing of the development of impervious areas in the area draining into these reaches. c) Percent of land draining into each reach that is agricultural and impervious, per 2011 SOLRIS landcover data.

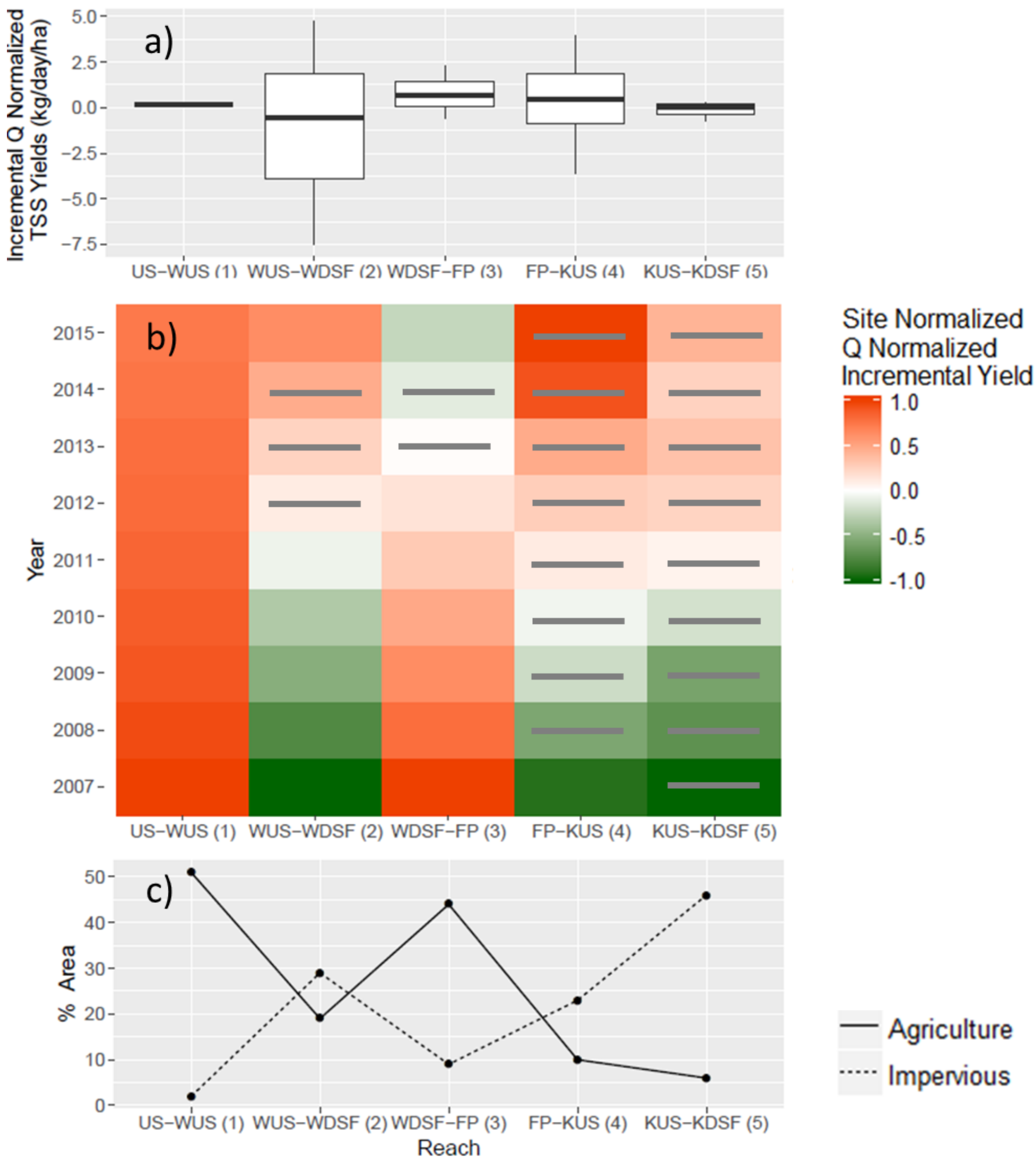

Figure 4.4 a) Incremental flow-normalized total phosphorus (TSS) yields along study reach from upstream (left) to downstream (right). Reaches draining smaller areas correspond to greater variability, as these reaches may not have had as much time to buffer the fluctuations in water quality. b) Reach-normalized, incremental flow-normalized TSS yields at each reach along the main stem of the middle Grand River. Each reach is normalized by its absolute maximum/minimum yield such that the year with the largest/smallest incremental flow-normalized yield is assigned a value of ±1; note that comparisons between sites cannot be made in b) due to reach-normalization. Orange squares indicates drainage areas that were sources for a given year, green indicates drainage areas that were sinks. Grey lines specify reaches that did not have significantly different distributions per the Kolmogorov-Smirnov test (α=0.05). The WUS-WDSF and FP-KUS reaches exhibit sink-to-source behaviour, while WDSF-FP and KUS-KDSF exhibit source-to-sink behaviour; these patterns may be related to the timing of the development of impervious areas in the area draining into these reaches. c) Percent of land draining into each reach that is agricultural and impervious, per 2011 SOLRIS landcover data.

However, after consulting historical aerial imagery, it was apparent that a single temporal land use snapshot, like that of SOLRIS 2011, was not enough to explain the water quality trends along this reach, as the changes in land use themselves likely drove changes in water quality. For example, Reaches 2 and 4 exhibited a sink-to-source behaviour from 2007 to 2009, as they transitioned from negative IFN yields to positive IFN yields. Using aerial imagery taken over several years, it was evident that at some point between 2006 and 2009, the construction of urban (impervious) areas commenced and bare surfaces with higher erosional potential were exposed (Figure 4.5). As would be expected, there was a corresponding increase in TP/TSS IFN yields along these reaches (Figures 4.3b, 4.4b). Conversely, Reach 3 exhibited a source-to-sink behaviour; at this reach there were bare surfaces already exposed at the start of the study period (Figure 4.5), and throughout the monitoring period, these bare surfaces with higher erosional potential were replaced by impervious cover. Thus, it appears that areas of construction are a P reduction management priority, as large quantities of TP and TSS were lost while bare surfaces are exposed, although water quality does appear to improve once the construction of impervious areas are completed.

Figure 4.5 Aerial imagery of urban development in the (a) WDSF-FP reach and (b) FP-KUS reach from 2006 to 2015. In WDSF-FP, exposed surfaces are apparent prior to the start of the study period in 2007. Over time, this area becomes increasingly impervious and corresponds to a decline in incremental flow-normalized TP yields. In the heatplots (Figures 4.3 and 4.4), the reach appears to switch form acting as a source to a sink of TP and TSS. Conversely, along the FP-KUS reach, there did not appear to be urban development prior to the start of the monitoring period, but it commences sometime between 2006 and 2009, and there was an associated increase in incremental flow-normalized TP yields along this reach, as indicated by the switch from sink to source in the TP and TSS heatplots (Figures 4.3 and 4.4). Images courtesy of Google Earth^{TM}.

While the water quality trends in Reaches 2, 3, and 4 may be attributed to construction activities, the trends in Reach 5 are not as easily explained. For one, the TSS mass load distributions along this reach are not significantly different from Reach 4 ($p>0.05$), so the reach may not truly go from a TSS sink to source. Moreover, the TP and TSS IFN yields do not show the same trend, as the TP IFN yields exhibited source-to-sink behaviour, while the TSS IFN yields exhibited sink-to-source behaviour. In this reach catchment, there were numerous construction sites that were at different stages of completion throughout the monitoring period. Thus, it is more difficult to distinguish the impacts of each individual construction project on water quality. Moreover, this reach contains a wastewater treatment plant and although the mass loads of TP and TSS from wastewater treatment plants were removed for this study, it is possible that it may still impact the speciation of TP and TSS along this reach. Accordingly, the cumulative effects of land use make it more difficult to interpret the relationship between land use and water quality along this reach.

The TP/TSS IFN yield trends in Reach 1 were not investigated extensively in this study, as this reach drains the Grand River upstream of the first monitoring station; thus, this catchment is much larger than the other catchments in this portion of the study (231,200 ha vs. 5,400 on average, respectively), so 1) there may have been scaling issues in comparing water quality trends in this reach to the four downstream reaches and 2) it was not feasible to assess land use change in such a large area.

4.3 TP and TSS Trends in Two Headwater Streams

In the two headwater basins that had increased spatial and temporal resolution in water quality data, similar trends were exhibited to those of the main stem of the Grand River for TP yields (Figure 4.6) and TSS yields (Figure 4.7).

The water quality trends along the main stem of the Grand River were also reflected in the smaller scale monitoring program with increased spatial and temporal water quality data. In CCU, the headwater catchment with construction from 1998-1999 (Ecosystem Recovery Inc., 2015), there was a corresponding increase in TP/TSS FN yields. Conversely, there was not as drastic a change in TP/TSS FN yields at LCE, a predominantly agricultural basin that does not appear to have undergone substantial land use change throughout the study period. Interestingly, further subdivision development in CCU in 2012 and 2013, did not result in a marked increase in TP/TSS yields during this period, likely because this construction seems to have coincided with rehabilitative activities downstream. Therefore, it is possible that the impacts of construction were buffered by these activities which included dredging, the installation of rock beds, and increased vegetation (Waterloo Region Record, 2012).

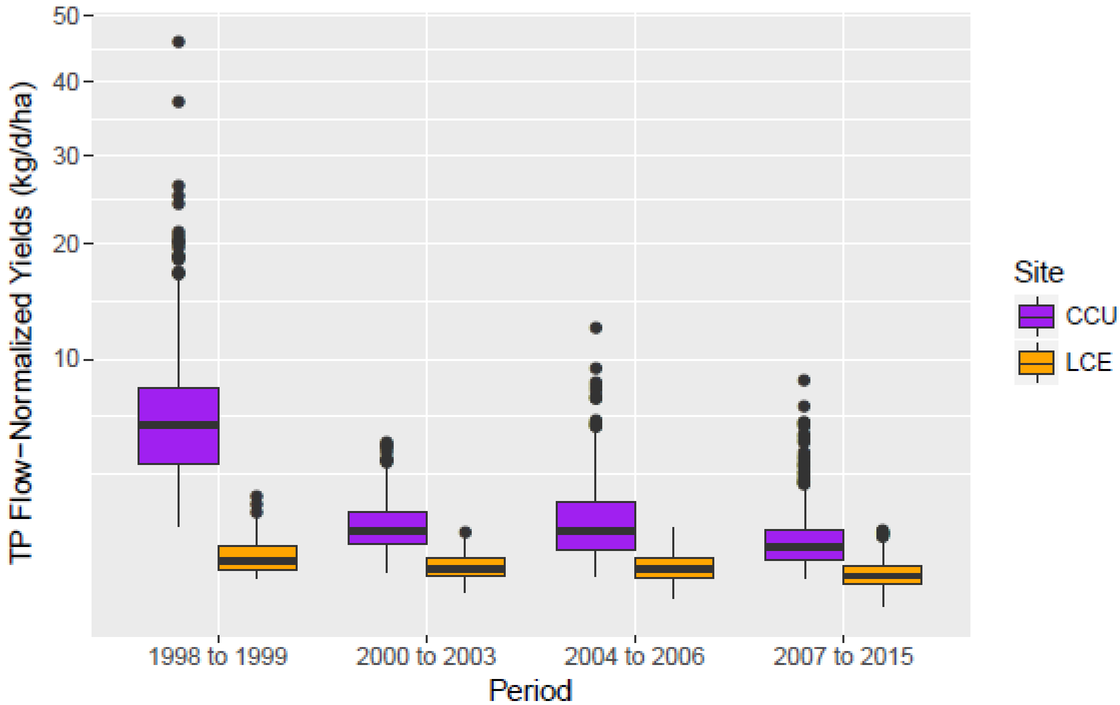

Figure 4.6 TP flow-normalized yields in Clair Creek at University Ave and Laurel Creek at Erbsville Rd catchments. During the 1998 to 1999 period, there was development in the headwater reaches of Clair Creek and relatively high TP FN yields. Once development was completed, there is a decline in TP flow-normalized yields. Conversely, there are no substantial changes in TP FN yields in the agricultural reference basin that has not undergone land use change over the study period.

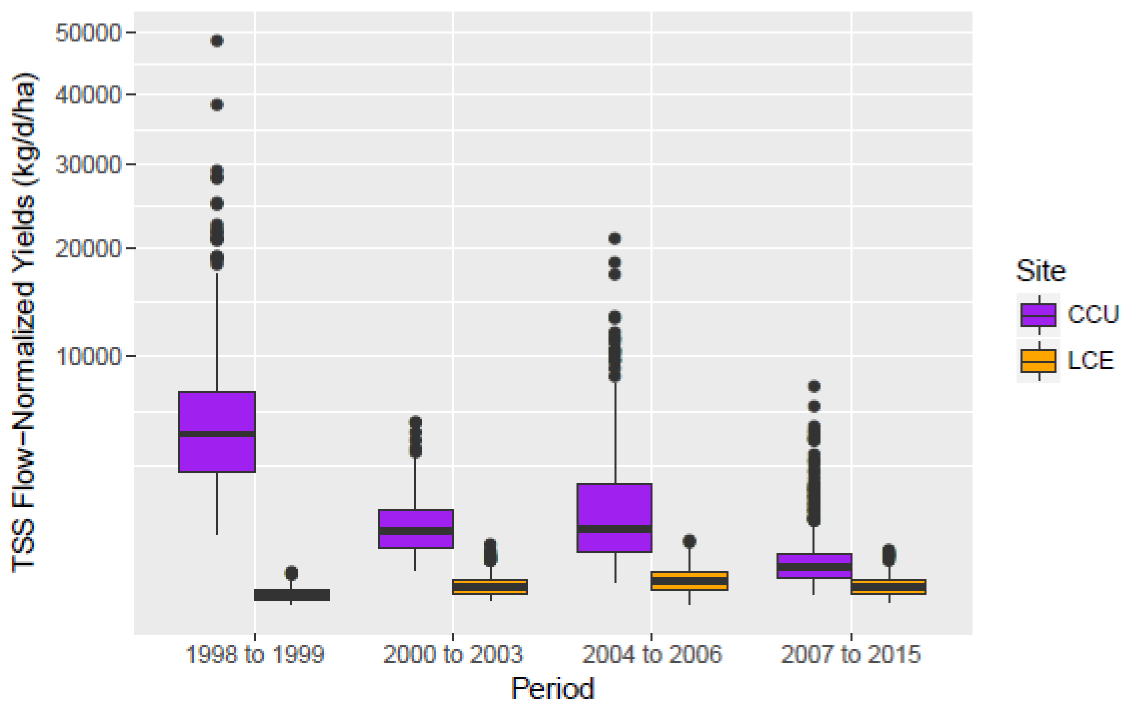

Figure 4.7 TSS flow-normalized yields in Clair Creek at University Ave and Laurel Creek at Erbsville Rd catchments. During the 1998 to 1999 period, there was development in the headwater reaches of Clair Creek and relatively high TSS FN yields. Once development was completed, there is a decline in TSS flow-normalized yields. Conversely, there are no substantial changes in TSS FN yields in the agricultural reference basin that has not undergone land use change over the study period.

Moreover, since finer scale temporal data was available for this study, the concentration-discharge (CQ) relationships were plotted to analyse the nuances of the impact of land use change on water quality (Figures 4.8 and 4.9). The CQ relationships reflect the same general patterns observed in Figures 4.6 and 4.7, however, they provided additional information on changes in discharge over time. Although the impacts on TP and TSS losses appeared to be temporary, the impacts on discharge may not be. Although both catchments saw an increase in discharge over time, the increase at CCU was an order of magnitude greater than that of LCE (~700% vs. ~40% respectively) and may be due to the increase in impervious area, as the hydrology of streams is profoundly different for pre-urban compared to post-urban conditions. With urbanization, the increases in impervious area change the rates and magnitudes of hydrological flow paths in watersheds and the storm hydrograph; specifically, the peak of the hydrograph increases and the lag time typically decreases in urban watersheds (e.g. Poff, Bledsoe, & Cuhaciyan, 2006; Rose & Peters, 2001). Moreover, stream flow in urban areas is characterized by a higher frequency of extreme flow events and an increased runoff ratio (O'Driscoll et al., 2010), and a decrease in vegetative cover typically reduces interception and evapotranspiration, which can increase flood frequency (Wang et al., 2008). Thus, the increase in discharge associated with urbanization indicates that these areas may have the potential to convey larger mass loads of nutrients even if their concentrations decline, and the implementation of BMPs that reduce urban runoff may be beneficial to decrease P losses.

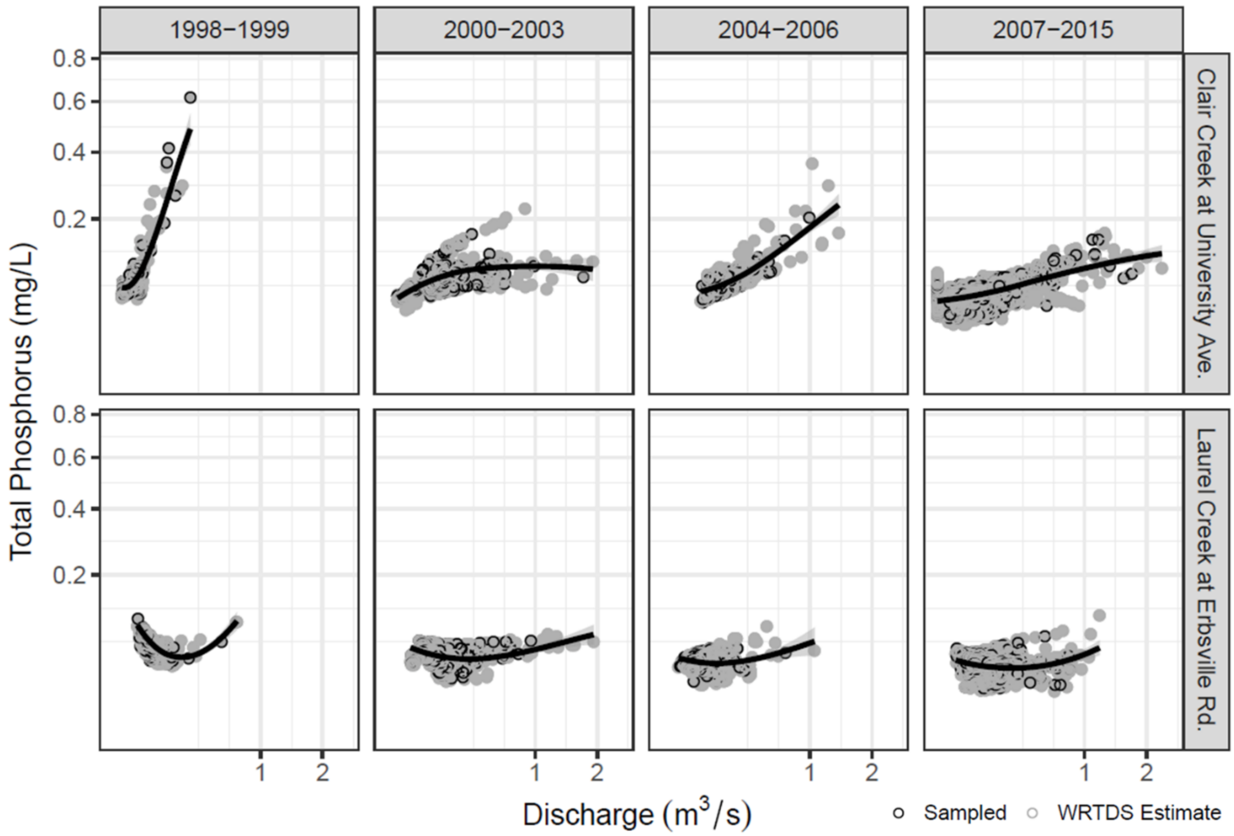

Figure 4.8 TP concentration-discharge (CQ) plots at Clair Creek at University Avenue (CCU) and Laurel Creek at Erbsville Rd. (LCE) from 1998-1999, 2000-2003, 2004-2006, and 2007-2015. The increase in CQ slope during the 1998-1999 period in CCU may be attributed to construction in its headwater reaches. Upon completion of construction, the CQ slope declined. Interestingly, even during construction in 2012 and 2013 in the headwater reaches of CCU, there is not a steep an increase in the CQ relationship as there was during the 1998-1999 period, likely due to the rehabilitative activities occurring downstream of the construction area. Conversely, the CQ patterns at LCE, the agricultural reference basin, does not show as prominent changes in CQ patterns overtime, likely because it did not undergo substantial land use change throughout the study period. Moreover, an increase in discharge at CCU is observed overtime but is not observed at the LCE site; this is likely due to an increase in impervious area in the CCU basin.

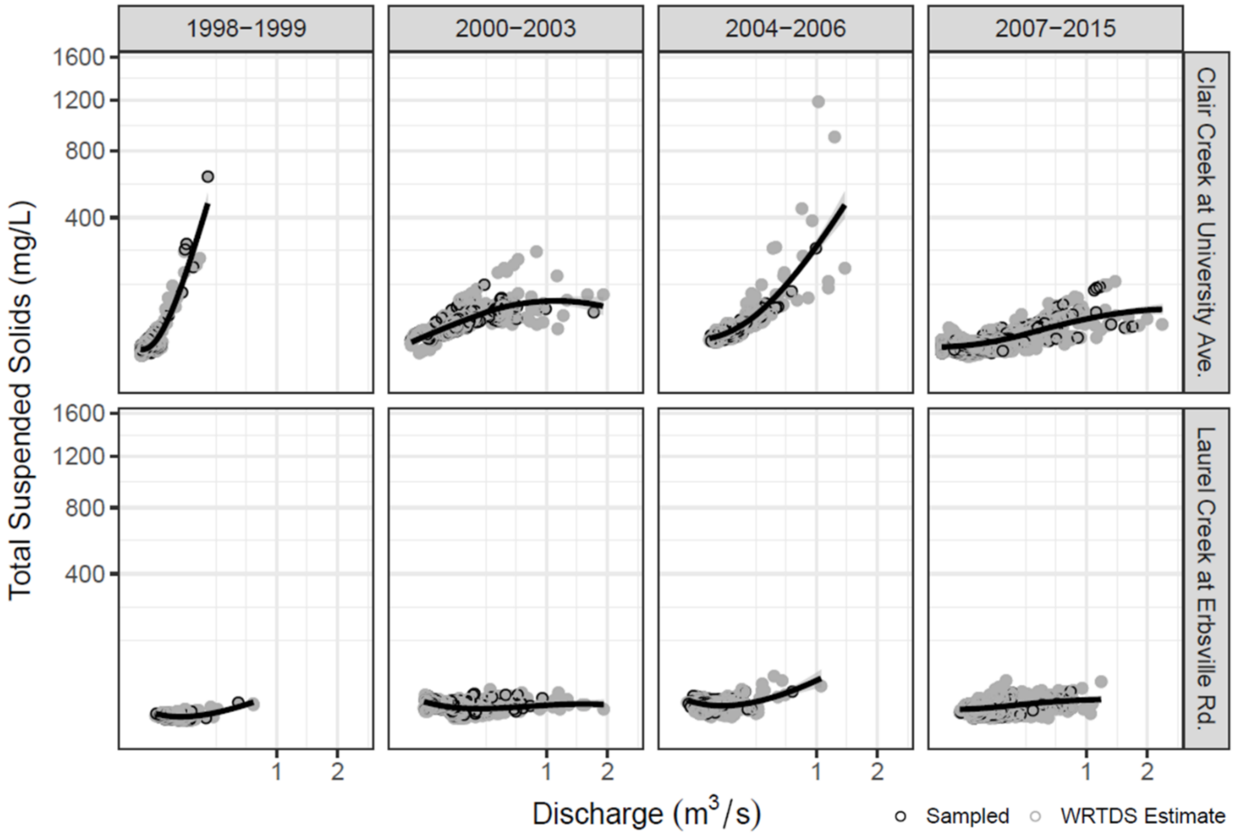

Figure 4.9 TSS concentration-discharge (CQ) plots at Clair Creek at University Avenue and Laurel Creek at Erbsville Rd. Clair Creek from 1998-1999, 2000-2003, 2004-2006, and 2007-2015. Similar to the patterns exhibited by the TP CQ relationships, the increase in the TSS CQ slope during the 1998-1999 period in CCU may be attributed to construction in its headwater reaches. Upon completion of construction, the CQ slope declined. Interestingly, even during construction in 2012 and 2013 in the headwater reaches of CCU, there is not a steep an increase in the CQ relationship as there was during the 1998-1999 period, likely due to the rehabilitative activities occurring downstream of the construction area. Conversely, the CQ patterns at LCE, the agricultural reference basin, does not show as prominent changes in CQ patterns overtime, likely because it did not undergo substantial land use change throughout the study period. Moreover, an increase in discharge at CCU is observed overtime but is not observed at the LCE site; this is likely due to an increase in impervious area in the CCU basin.

4.4 Management Priorities and Study Limitations

While this study has implications for water managers that wish to reduce nutrient losses from mixed-use landscapes, its limitations must also be recognized. For one, this study cannot distinguish between internal and external sources of TP/TSS with the existing datasets that were used. Here, we look at how land use impacts surface water quality, but land use also impacts geomorphology of rivers which in turn impacts the timing and quantity of sediment and nutrients propagated downstream. For example, with urbanization, as bare surfaces are exposed, there is an increase in in-channel sediment storage, referred to as the aggradation phase. Once the impervious cover is completed however, an increase in discharge and a reduction in sediment supply cause sediment remobilization and channel scouring during the erosional phase (Wolman, 1967). However, since managing TP/TSS once it is in-stream may be more difficult than managing it at its source (the land), there is great value in understanding their sources on land.

Moreover, there were a limited number of sites that were suitable for this study, as not all sites had continuous flow data, and the monitoring protocols between organizations varied, which meant that sampling at some sites did not reflect the full range of stream flows and also varied in monitoring duration. Thus, numerous sites with water quality data were excluded from this study, and consequently, the kinds of analyses that could be completed were limited because of a lack of statistical power. The issue of varied monitoring protocols among various jurisdictions working in the same area is common, as there are obstacles to implementing a concerted monitoring program, but this study emphasizes that if such a monitoring program can be created among these organizations, a greater understanding of P sources in mixed-use landscapes can be obtained. For example, if all the jurisdictions operating in the middle Grand River had a coordinated monitoring program, statistical analyses could have been employed to assess how various land uses within urban areas, such as residential, commercial, industrial, and institutional, contribute to P losses, as such an understanding can help refine urban NPS P loss reduction management priorities.

Despite these limitations however, this study still parsed out relevant information for water resources managers in determining nutrient reduction management priorities. For one, land use must be viewed as dynamic, as the transition from one land use type to another may yield large quantities of TP, TSS, as well as other sediment-bound contaminants. In the case of urbanization in areas that were historically agricultural, legacy stores of P that have accumulated in the soil have the potential to be released and propagate downstream (Bennett et al., 1999). Moreover, in agreement with literature, it was found that although construction constitutes a relatively small portion of the landscape, it has the potential to have greater erosional losses than those of agricultural areas (Carpenter et al., 1998; Novotny & Olem, 1996). Therefore, the construction of impervious surfaces constitutes a "hot moment" in nutrient and sediment transport, and strategies to reduce their losses must be implemented.

Chapter 5

Conclusions, Implications, and Recommendations

5.1 Conclusions and Implications

Phosphorus (P) is considered the primary limiting nutrient for primary productivity in freshwater systems, where it can contribute to the proliferation of harmful algal blooms that have the potential to disrupt the provision of safe drinking water. For example, in 2014, the City of Toledo, Ohio issued a Do Not Drink/Do Not Boil water order that impacted almost 500,000 people due to unsafe levels of algal toxins in their drinking water (American Water Works Association, 2016). Although agriculture is recognized as the predominant source of P to receiving streams, much less is known about P from other key landscape sources such as urban NPS, which include construction activities, stormwater runoff, lawn and garden maintenance, leaves from deciduous trees, and pet waste. Despite several decades of implementing a wide range of BMPs to mitigate sediment-associated P losses from the landscape to receiving water bodies, targeted water quality improvements have been largely unrealized (Strecker et al., 2001). These failures can be attributed to not only a lack of widespread implementation of BMPs, but also to large stores of previously-released, sediment-associated "legacy P" in soils and water bodies (Sharpley et al., 2013). As a result, there is a globally-recognized, ongoing need to reduce P transfer to receiving water bodies—this need has been articulated in many policy frameworks (Chesapeake Bay Watershed Agreement, 2016; Great Lakes Water Quality Agreement, 2012; HELCOM Baltic Sea Action Plan, 2007; etc.), including the International Joint Commission's call to reduce the TP entering Lake Erie by 40% by 2025 compared to 2008 levels (International Joint Commission, 2018). Because fine sediment is often the primary vector for P transport in river systems (Bennett et al., 2001), erosion-inducing precipitation and associated higher stream flows (i.e., discharge) are key drivers of P delivery to and transport in rivers (Edwards & Withers, 2008). Thus, climate change-associated extremes in precipitation can exacerbate P transport to receiving streams and downstream environments (Eilola et al., 2012; Jeppesen et al., 2009). While extremes in precipitation cannot be readily controlled, integrated land and watershed management strategies focused on water quality improvement can be developed and implemented. To inform the development of such strategies, there is a critical need to assess the role of urban areas in the transport of nutrients. Therefore, the goal of this investigation was to evaluate changes in water quality (TP and TSS) in urban systems and compare them to those in agricultural areas to inform management priorities and strategies.

Here, the impacts of land use on stream water quality were evaluated using a pre-existing, long-term monitoring dataset collected at two spatial scales. The first phase of the study was conducted to examine discharge and sediment/P relationships at a relatively larger drainage area (22,000 ha) along a highly urbanized reach of the Grand River. Monitoring data collected from 2007 to 2015 enabled an analysis of the role of discharge and land use on TP and TSS at five sites located longitudinally along an urbanizing river system. The second phase was conducted at a smaller scale (3,100 ha total) using 18 years (1998 to 2015) of monitoring data, which permitted and evaluation of the effects of urbanization on water quality to be compared to a reference undeveloped sub-watershed. During this phase, monitoring data were only available for the months of May to August; however, they were collected with high frequency (~28 samples per season). Although the data from this program could only be interpreted for the summer months, it allowed for the comparison of temporal trends in a basin with active development and rehabilitation to a similarly sized agricultural reference basin with minimal land disturbances throughout the monitoring period. By focusing on these two datasets, key source areas at different scales were compared and the most pertinent P reduction management priorities were determined.

To quantify how much TP and TSS was lost by the area draining into each monitoring station, the Weighted Regression on Time, Discharge, and Season method was used. Since this study focused on the impacts of land use on water quality, the variability in mass loads and yields due to random fluctuations in discharge were removed through flow-normalization so that water quality trends due to landscape changes could be evaluated. Key source areas were then identified by comparing temporal and spatial trends in water quality to trends in landcover using aerial imagery and GIS landcover data; the following conclusions were drawn:

1. Sediment and associated P yields produced during and immediately following development in catchments undergoing urban development are generally understood to increase relative to those produced prior to development. Notably, this work demonstrated that they also may exceed those frequently observed in agricultural areas (known to be significant sources of TSS and TP) for several years. Here, at the relatively larger (22,000 ha) catchment scale, increases in TSS and TP IFN yields coincided with the construction of impervious lands; however, they declined once construction of the impervious surfaces was complete. The same observations were made at the smaller (3,100 ha) catchment scale, where the TP/TSS FN yields declined upon completion of subdivision development (from a median TP FN yield of 8.4 kg/yr/ha during construction to 1.4 kg/yr/ha post development in the urbanizing catchment while the reference catchment only declined from 0.8 kg/yr/ha to 0.4

kg/yr/ha over the same period). Interestingly, at this site, during further development around 2012/2013 a marked increase in TP/TSS FN yields was not apparent, likely due to the implementation of post-development erosion control strategies for reducing sediment availability. Although the study of BMPs was out of the scope of this project, this underscores the importance of BMPs in mitigating the propagation of large pulses of sediment and associated nutrients to downstream bodies of water.

2. Although elevated TSS and TP yields after urbanization eventually improve, stream flows may remain elevated and more variable than those observed in reference catchments. Here, while there was a 40% increase in stream flow in the reference catchment over the study period, the streamflow in the developing catchment increased by over 700%. The observed increases in stream flow were likely attributable to increased runoff from impervious groundcover. Therefore, urban areas have the potential to convey large mass loads of TSS and P even after their concentrations decline. Accordingly, best management practices that focus on reducing runoff may be beneficial in these developed areas.
3. A single temporal snapshot of land use may not be adequate to assess the relationship between land use and water quality in longer term datasets. Here, the conversion of agricultural land to urban land corresponded to an increase in TP/TSS yields at both study scales. Moreover, as construction was completed, and bare surfaces became impervious, there was a subsequent decline in these yields. Thus, land use is not static and should not be treated as such when evaluating the impacts on water quality, especially in monitoring datasets that span several years.

4. By utilizing two scales of analysis, this investigation was able to (1) parse out the specific water quality effects of land use at the smaller scale while controlling for transport factors such as geology and climatic variability, as well as (2) confirm that these trends were not localized and were reflected at the larger scale and are therefore, relevant management priorities for the reduction of P. This emphasizes the need for coordinated long-term monitoring programs at various scales to understand the dominant controls on water quality.

5.2 Recommendations for Future Monitoring Programs

Given the projected increase in urbanization and uncertainty due to a changing climate, there is a critical need to evaluate the impacts of land use on water quality to foster urban resiliency through adaptation and mitigation; the work presented herein emphasizes the importance of water quality programs in aiding such an evaluation. However, in gathering water quality monitoring data, is not uncommon for jurisdictions to work independently of one another and implement varying monitoring protocols, as was the case with the data employed in this study. Consequently, the suitability of the hydrometric and water quality data varied between datasets, and the utility of these monitoring programs were not maximized. This underscores a need for a concerted effort in implementing monitoring programs to ensure that the maximum value of these programs is obtained, although this is often difficult in practice. Accordingly, the following recommendations have been made to assist in creating a monitoring program to effectively gather the data necessary to adapt to the stresses of climate and urbanization.

1. Various jurisdictional levels must communicate among one another and share resources to implement a coordinated monitoring program. These programs must

utilize a consistent time frame across all sites and a consistent sampling strategy so that spatial and temporal trends at various scales (i.e individual BMPs, residential/commercial/industrial areas, entire basins) may be evaluated.

2. Baseline monitoring must be conducted prior to planned land disturbances so that there is a reference point upon which management decisions can be based.
3. Adequate high flow sampling is required in future monitoring programs, as 1) the majority of NPS TP and TSS losses are believed to occur during these events, 2) it is when the system response is most variable, 3) high flows are frequently missed in monitoring programs and 4) there is an expected increase in high flow events with climate change. This does not imply that low and medium flow sampling are not required, as a representative suite of samples are required for mass loading estimates. Although issues with safety are usually why adequate high flow sampling is not conducted, strategies must be implemented to gather these samples since high flow events play a disproportionately large and less predictable role in NPS TP and TSS transport.
4. Sampling should span each season so that intra-annual trends in TP and TSS losses influenced by hydrological regimes, biological activity, seasonal agricultural activities etc. can be identified.
5. Sampling programs should span several years so that inter-annual trends in TP and TSS losses influenced by land use change and climatic variability may be assessed.
6. As land use is dynamic, data discussing land use activities throughout the monitoring period must be more accessible. Here, limited reports, maps, and land use studies were available to draw conclusions on the relationship between water quality and

land use. However, moving forward, improving data availability among study participants may allow for a greater understanding of the impacts of land use on water quality.

References

Alberto, A., St-Hilaire, A., Courtenay, S. C., & Van Den Heuvel, M. R. (2016). Monitoring stream sediment loads in response to agriculture in Prince Edward Island, Canada. *Environmental Monitoring and Assessment*, *188*(7), 415. https://doi.org/10.1007/s10661-016-5411-3

American Water Works Association. (2016). *Cyanotoxins in US Drinking Water: Occurrence, CAse Studies and State Approaches to Regulation.* American Water Works Association. Retrieved from https://www.awwa.org/Portals/0/files/resources/water%20knowledge/rc%20cyanotoxins/201609_Cyanotoxin_Occurrence_States_Approach.pdf

Anderson, D. M., Glibert, P. M., & Burkholder, J. M. (2002). Harmful Algal Blooms and Eutrophication Nutrient Sources, Composition, and Consequences, *25*(4b), 704–726. Retrieved from https://journals-scholarsportal-info.proxy.lib.uwaterloo.ca/pdf/01608347/v25i0004/704_habaenscac.xml

Aquafor Beech Inc. (2015). *City of Kitchener Integrated Stormwater Management Master Plan Public Open House.* Kitchener, ON. Retrieved 6 1, 2018, from https://www.kitchener.ca/en/resourcesGeneral/Documents/DSD_ENG_StormwaterMasterPlan_EA-Appendix-L-Record-of-Consultation_part2.pdf

Ator, S. W., Brakebill, J. W., & Blomquist, J. D. (2011). *Sources, fate, and transport of nitrogen and phosphorus in the Chesapeake Bay watershed: An empirical model: U.S. Geological Survey Scientific Investigations Report.* Reston, Virgina, USA: US Geological Survey.

Balamurugan, G. (1991). Sediment balance and delivery in a humid tropical urban river basin: The Kelang River, Malaysia. *Catena*, *18*(3–4), 271–287. https://doi.org/10.1016/0341-8162(91)90026-T

Bannerman, R. T., Owens, D. W., Dodds, R. B., & Hornewer, N. J. (1993). SOURCES OF POLLUTANTS IN WISCONSIN STORMWATER. *Water Science & Technology*, *28*(3–5), 241–259. Retrieved from https://www.fws.gov/southwest/es/Documents/R2ES/LitCited/4TX_Sal/Bannerman_1993_Pollutants_in_stormwater.pdf

Bennett, E. M., Carpenter, S. R., & Caraco, N. F. (2001). Human Impact on Erodable Phosphorus and Eutrophication: A Global Perspective. *BioScience*, *51*(3), 227. https://doi.org/10.1641/0006-3568(2001)051[0227:HIOEPA]2.0.CO;2

Bennett, E. M., Reed-Andersen, T., Houser, J. N., Gabriel, J. R., & Carpenter, S. R. (1999). A Phosphorus Budget for the Lake Mendota Watershed. *Ecosystems*, *2*(1), 69–75. Retrieved from https://link-springer-com.proxy.lib.uwaterloo.ca/content/pdf/10.1007%2Fs100219900059.pdf

Bieroza, M. Z., & Heathwaite, A. L. (2015). Seasonal variation in phosphorus concentration–discharge hysteresis inferred from high-frequency in situ monitoring. *Journal of Hydrology*, *524*, 333–347. https://doi.org/10.1016/j.jhydrol.2015.02.036

Bilotta, G. S., & Brazier, R. E. (2008). Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research*, *42*(12), 2849–2861. https://doi.org/10.1016/j.watres.2008.03.018

Booth, D. B., Karr, J. R., Schauman, S., Konrad, C. P., Morley, S. A., Larson, M. G., &

Burges, S. J. (2004). *Reviving Urban Streams: Land Use, Hydrology, Biology, and Human Behavior*. *Journal of the American Water Resources Association* (Vol. 40). Retrieved from https://journals-scholarsportal-info.proxy.lib.uwaterloo.ca/pdf/1093474x/v40i0005/1351_rusluhbahb.xml

Bornstein, R., & Lin, Q. (2000). Urban heat islands and summertime convective thunderstorms in Atlanta: three case studies. *Atmospheric Environment* (Vol. 34). Retrieved from https://journals-scholarsportal-info.proxy.lib.uwaterloo.ca/pdf/13522310/v34i0003/507_uhiasctiatcs.xml

Bowes, M. J., & House, W. A. (2001). Phosphorus and dissolved silicon dynamics in the River Swale catchment, UK: a mass-balance approach. *Hydrological Processes*, *15*(2), 261–280. Retrieved from https://journals-scholarsportal-info.proxy.lib.uwaterloo.ca/pdf/08856087/v15i0002/261_padsdiscuama.xml

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). NONPOINT POLLUTION OF SURFACE WATERS WITH PHOSPHORUS AND NITROGEN. *Ecological Applications Ecology*, *8*(3), 559–568. Retrieved from https://esajournals-onlinelibrary-wiley-com.proxy.lib.uwaterloo.ca/doi/pdf/10.1890/1051-0761%281998%29008%5B0559%3ANPOSWW%5D2.0.CO%3B2%4010.1002/%28ISSN%291939-5582%28CAT%29SpecialCollection%28VI%29VirtualIssue

Chesapeake Bay Program. (2008). *Chesapeake Bay Health & Restoration Assessment.* Annapolis, MD: Chesapeake Bay Program. Retrieved from https://www.chesapeakebay.net/documents/cbp_26038.pdf

Chomicki, K. M., Howell, E. T., Defield, E., Dumas, A., & Taylor, W. D. (2016). Factors influencing the phosphorus distribution near the mouth of the Grand River, Ontario, Lake Erie. *Journal of Great Lakes Research*, *42*(3), 549–564. https://doi.org/10.1016/j.jglr.2016.03.014

Dawson, E. J., & Macklin, M. G. (1998). Speciation of heavy metals on suspended sediment under high ¯ow conditions in the River Aire, West Yorkshire, UK. *Hydrological Processes*, *12*(9), 1483–1494. Retrieved from https://journals-scholarsportal-info.proxy.lib.uwaterloo.ca/pdf/08856087/v12i0009/1483_sohmostrawyu.xml

Denison, F. H., Haygarth, P. M., House, W. a., & Bristow, A. W. (1998). The Measurement of Dissolved Phosphorus Compounds: Evidence for Hydrolysis During Storage and Implications for Analytical Definitions in Environmental Analysis. *International Journal of Environmental Analytical Chemistry*, *69*(2), 111–123. https://doi.org/10.1080/03067319808032579

Dodds, W. K., Bouska, W. W., Eitzmann, J. L., Pilger, T. J., Pitts, K. L., Riley, A. J., … Thornbrugh, D. J. (2009). Eutrophication of U. S. freshwaters: Analysis of potential economic damages. *Environmental Science and Technology*, *43*(1), 12–19. https://doi.org/10.1021/es801217q

Domagalski, J., & Saleh, D. (2015). Sources and Transport of Phosphorus to Rivers in California and Adjacent States, U.S., as Determined by SPARROW Modeling. *Journal of the American Water Resources Association*, *51*(6), 1463–1486. https://doi.org/10.1111/1752-1688.12326

Driscoll, M. O., Clinton, S., Jefferson, A., Manda, A., & Mcmillan, S. (2010). Urbanization Effects on Watershed Hydrology and In-Stream Processes in the Southern United States. *Water*, *2*(3), 605–648. https://doi.org/10.3390/w2030605

Duan, S., Kaushal, S. S., Groffman, P. M., Band, L. E., & Belt, K. T. (2012). Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed. *Journal of Geophysical Research: Biogeosciences*, *117*(1), 1–12. https://doi.org/10.1029/2011JG001782

Ecosystems Recovery Inc. (2015). *City of Waterloo Clair Creek South Branch Schedule 'B' Environemtal Assessment.*

Edwards, A. C., & Withers, P. J. A. (2008). Transport and delivery of suspended solids, nitrogen and phosphorus from various sources to freshwaters in the UK. *Journal of Hydrology*, *350*(3–4), 144–153. https://doi.org/10.1016/j.jhydrol.2007.10.053

Eilola, K., Rosell, E. A., Dieterich, C., Fransner, F., Höglund, A., & Meier, H. E. M. (2012). Modeling Nutrient Transports and Exchanges of Nutrients Between Shallow Regions and the Open Baltic Sea in Present and Future Climate. *Ambio*, *41*(6), 586–599. Retrieved from www.kva.se/en

Grand River Conservation Authority (GRCA). *(2001). Grand River Watershed Virtual Drainage Network GIS Layer*. Cambridge, ON: Grand River Conservation Authority, 2001. Available https://maps.grandriver.ca/data-gis.html

Grand River Conservation Authority (GRCA). (2016). *Trees and Forest*. Retrieved from Grand River: https://www.grandriver.ca/en/our-watershed/Trees-and-forests.aspx

GRCA. (2017a). *Subcatchment Basins GIS Layer*. Cambridge, ON: Grand River Conservation Authority. Available https://maps.grandriver.ca/data-gis.htm

GRCA. (2017b). *Sewage Treatment Plants GIS Layer*. Cambridge, ON: Grand River Conservation Authority. Available https://maps.grandriver.ca/data-gis.html

GRCA. (2018a). *Watercourse GIS Layer*. Cambridge, ON: Grand River Conservation Authority. Available https://maps.grandriver.ca/data-gis.html

GRCA. (2018b). *Waterbody GIS Layer*. Cambridge, ON: Grand River Conservation Authority. Available https://maps.grandriver.ca/data-gis.html

Grand River Watershed Water Management Plan. 2014. Prepared by the Project Team, Water Management Plan. Grand River Conservation Authority, Cambridge, ON. 137p. + appendices

Gray, L. J., & Ward, J. V. (1982). *Effects of Releases of Sediment from Reservoirs on Stream Biota by*. Washington D.C.

Great Lakes Water Quality Agreement. (2012). *Great Lakes Water Quality Agreement.* Retrieved from https://binational.net//wp-content/uploads/2014/05/1094_Canada-USA-GLWQA-_e.pdf

Greig, S. M., Sear, D. A., & Carling, P. A. (2005). The impact of fine sediment accumulation on the survival of incubating salmon progeny: Implications for sediment management. *Science of the Total Environment*, *344*(1–3), 241–258. https://doi.org/10.1016/j.scitotenv.2005.02.010

Handlin, M., Molina, A., James, N., Mcconville, M., & Dunnivant, F. (2014). EFFECT OF

SUSPENDED UNCONTAMINATED SEDIMENT ON PERSISTENT ORGANIC POLLUTANT RELEASE SETAC. *Environmental Toxicology and Chemistry*, *33*(2), 375–381. https://doi.org/10.1002/etc.2430

Haygarth, P. M., Bilotta, G. S., Bol, R., Brazier, R. E., Butler, P. J., Freer, J., … Worsfold, P. (2006). Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: an overview of key issues. *Hydrological Processes*, *20*, 4407–4413. https://doi.org/10.1002/hyp.6598

Heathwaite, A. L., & Dils, R. M. (2000). Characterising phosphorus loss in surface and subsurface hydrological pathways. *The Science of the Total Environment*, *251*, 523–538. Retrieved from https://journals-scholarsportal-info.proxy.lib.uwaterloo.ca/pdf/00489697/v251-252inone/523_cplisashp.xml

HELCOM Baltic Sea Action Plan. (2007). *HELCOM Ministerial Meeting, Krakow, Poland, 15 November 2007.* Krakow, Poland. Retrieved from http://www.helcom.fi/documents/baltic%20sea%20action%20plan/bsap_final.pdf

Hirsch, R. M., & De Cicco, L. A. (2015). *User Guide to Exploration and Graphics for RivEr Trends (EGRET) and dataRetrieval: R Packages for Hydrologic Data Book 4, Hydrologic Analysis and Interpretation Techniques and Methods 4–A10*. Retrieved from https://pubs.usgs.gov/tm/04/a10/pdf/tm4A10.pdf

Hirsch, R. M., Moyer, D. L., & Archfield, S. A. (2010). Weighted regressions on time, discharge, and season (WRTDS), with an application to chesapeake bay river inputs. *Journal of the American Water Resources Association*, *46*(5), 857–880. https://doi.org/10.1111/j.1752-1688.2010.00482.x

Hobbie, S. E., Finlay, J. C., Janke, B. D., Nidzgorski, D. A., Millet, D. B., & Baker, L. A. (2017). Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution," by. *Proc Natl Acad Sci*, *16*(20), 4177–4182. https://doi.org/10.1073/pnas

House, W. A. (2003). Geochemical cycling of phosphorus in rivers §. *Applied Geochemistry*, *18*(5), 739–748.

International Joint Commission. (2018). *Binational Plans Call for 40 Percent Reduction to Algal-Fueling Nutrients*. Retrieved from IJC Great Lakes Connection: http://ijc.org/greatlakesconnection/en/2018/04/binational-plans-call-for-40-percent-reduction-to-algal-fueling-nutrients/

Jeppesen, E., Kronvang, B., Meerhoff, M., Søndergaard, M., Hansen, K. M., Andersen, H. E., … Olesen, J. E. (2009). Climate Change Effects on Runoff, Catchment Phosphorus Loading and Lake Ecological State, and Potential Adaptations. *Journal of Environmental Quality*, *38*(5), 1930–1941. https://doi.org/10.2134/jeq2008.0113

Karl, T. R., Diaz, H. F., & Kukla, G. (1988). Urbanization: Its Detection and Effect in the United States Climate Record. *Journal of Climate*, *1*(11), 1099–1123. https://doi.org/10.1175/1520-0442(1988)001<1099:UIDAEI>2.0.CO;2

Kim, D.-K., Kaluskar, S., Mugalingam, S., & Arhonditsis, G. B. (2016). Evaluating the relationships between watershed physiography, land use patterns, and phosphorus loading in the bay of Quinte basin, Ontario, Canada. *Journal of Great Lakes Research*, *42*(5), 972–984. https://doi.org/10.1016/j.jglr.2016.07.008

King, K. W., Balogh, J. C., Hughes, K. L., & Harmel, R. D. (2007). Nutrient Load

Generated by Storm Event Runoff from a Golf Course Watershed. *Journal of Environment Quality*, *36*(4), 1021–1030. https://doi.org/10.2134/jeq2006.0387

Kreiling, R. M., & Houser, J. N. (2016). Long-term decreases in phosphorus and suspended solids, but not nitrogen, in six upper Mississippi River tributaries, 1991–2014. *Environmental Monitoring and Assessment*, *188*(8), 454. https://doi.org/10.1007/s10661-016-5464-3

Lenat, D. R., & Crawford, J. K. (1994). Effects of land use on water quality and aquatic biota of three North Carolina Piedmont streams. *Hydrobiologia*, *294*(3), 185–199. https://doi.org/10.1007/BF00021291

Leopold, L. B. (1968). *Hydrology for Urban land Planning-A Guidebook on the Hydrologic Effects of Urban Land Use*. Washington. Retrieved from https://pubs.usgs.gov/circ/1968/0554/report.pdf

Lloyd, D. S., Koenings, J. P., & Laperriere, J. D. (1987). Effects of Turbidity in Fresh Waters of Alaska. *North American Journal of Fisheries Management*, *7*(1), 18–33. https://doi.org/10.1577/1548-8659(1987)7<18:EOTIFW>2.0.CO;2org/10.1577/1548-8659(1987)7<18:EOTIFW>2.0.CO;2

Long, T., Wellen, C., Arhonditsis, G., Boyd, D., Mohamed, M., & Connor, K. O. (2015). Estimation of tributary total phosphorus loads to Hamilton Harbour , Ontario , Canada , using a series of regression equations. *Journal of Great Lakes Research*, *41*(3), 780–793. https://doi.org/10.1016/j.jglr.2015.04.001

Lotter, A. F., Sturm, M., & Ammann, A. (1998). Influence of catchment quality and altitude on the water and sediment composition of 68 small lakes in Central Europe.

Aquatic Sciences, *60*(4), 316–367. Retrieved from https://link-springer-com.proxy.lib.uwaterloo.ca/content/pdf/10.1007%2Fs000270050044.pdf

McDonald, D., Stone, M. & Collins, A. (2011). *A review of literature on cohesive sediment transport processes, methodological frameworks and management strategies in relation the North Saskatchewan River.* Retrieved from the Alberta Government; https://open.alberta.ca/dataset/53713bfe-d056-4a9c-87ac-58c17dd12929/resource/4cba5de5-a348-48f5-913b-a7a4ddf370e8/download/2011-SedimentTransportManagementNSask-2011.pdf

Medalie, L., Hirsch, R. M., & Archfield, S. A. (2012). Use of flow-normalization to evaluate nutrient concentration and flux changes in Lake Champlain tributaries, 1990–2009. *Journal of Great Lakes Research*, *38*(4), 58–67. https://doi.org/10.1016/j.jglr.2011.10.002

Merchán, D., Casalí, J., Del Valle De Lersundi, J., Campo-Bescós, M. A., Giménez, R., Preciado, B., & Lafarga, A. (2018). Runoff, nutrients, sediment and salt yields in an irrigated watershed in southern Navarre (Spain). *Agricultural Water Management*, *195*, 120–132. https://doi.org/10.1016/j.agwat.2017.10.004

Ministry of Natural Resources and Forestry. (2011). Southern Ontario Land Resource Information System Version 2.0. Sault St. Marie, ON. Available: https://www.ontario.ca/data/southern-ontario-land-resource-information-system-solris-20

Nieuwenhuyse, E. E. Van, & LaPerriere, J. (1986). Nieuwenhuyse, LaPerriere - 1986 - Effects of placer gold mining on primary production in subarctic streams of

Alaska.pdf. *Journal of the American Water Resources Association*, *22*(1), 91–99.

The NOAA Great Lakes Environmental Research Laboratory. (n.d.). *Great Lakes Shorelines GIS Layer.* Ann Arbor, MI: The NOAA. Available https://www.glerl.noaa.gov/data/bathy/bathy.html

Novotny, V., & Olem, H. (1996). Water quality: prevention, identification and management of diffuse pollution. *Source: The Geographical Journal*, *162*(1), 109. Retrieved from http://www.jstor.org.proxy.lib.uwaterloo.ca/stable/pdf/3060267.pdf?refreqid=excelsior%3A7bc70e246ffbee9db7b6160072b70fd6

O'Shea, M., Borst, M., & Nietch C. (2012). THE ROLE OF STORMWATER BMPS IN MITIGATING THE EFFECTS OF NUTRIENT OVERENRICHMENT IN THE URBAN WATERSHED. Presented at Ninth Triennial International Conference on Urban Storm Drainage, Portland, OR, 9/8-13/2002.

Outram, F. N., Cooper, R. J., Sünnenberg, G., Hiscock, K. M., & Lovett, A. A. (2016). Antecedent conditions, hydrological connectivity and anthropogenic inputs: Factors affecting nitrate and phosphorus transfers to agricultural headwater streams. *Science of the Total Environment, The*, *545–546*, 184–199. https://doi.org/10.1016/j.scitotenv.2015.12.025

Palmstrom, N. S., Carlson, R. E., & Cooke, G. (1988). Potential links between eutrophication and the formation of carcinogens in drinking water. *Lake and Reservoir Management*, *4*(2), 1–15. https://doi.org/10.1080/07438148809354809

Pennino, M. J., McDonald, R. I., & Jaffe, P. R. (2016). Watershed-scale impacts of stormwater green infrastructure on hydrology, nutrient fluxes, and combined sewer overflows in the mid-Atlantic region. *Science of The Total Environment*, *565*, 1044–1053. https://doi.org/10.1016/j.scitotenv.2016.05.101

Poff, N. L., Bledsoe, B. P., & Cuhaciyan, C. O. (2006). Hydrologic variation with land use across the contiguous United States: Geomorphic and ecological consequences for stream ecosystems. *Geomorphology*, *79*(3–4), 264–285. https://doi.org/10.1016/j.geomorph.2006.06.032

Pollution from Land Use Activities Research Group. (1978). *Environmental management strategy from the Great Lakes system.* Windsor, ON: International Joint Commission. Retrieved from http://agrienvarchive.ca/download/PLUARG_env_man_strat.pdf

Raney, S. M., & Eimers, M. C. (2014). Unexpected declines in stream phosphorus concentrations across southern Ontario. *Canadian Journal of Fisheries and Aquatic Sciences*, *71*(3), 337–342. https://doi.org/10.1139/cjfas-2013-0300

Riskin, S. H., Neill, C., Jankowski, K., Krusche, A. V., McHorney, R., Elsenbeer, H., … Porder, S. (2017). Solute and sediment export from Amazon forest and soybean headwater streams: *Ecological Applications*, *27*(1), 193–207. https://doi.org/10.1002/eap.1428

Rodríguez-Blanco, M. L., Arias, R., Taboada-Castro, M. M., Nunes, J. P., Keizer, J. J., & Taboada-Castro, M. T. (2016). Sediment Yield at Catchment Scale Using the SWAT (Soil and Water Assessment Tool) Model. *Soil Science*, *181*(7), 326–334. https://doi.org/10.1097/SS.0000000000000158

Rose, S., & Peters, N. E. (2001). Effects of urbanization on streamflow in the Atlanta area (Georgia, USA): a comparative hydrological approach. *Hydrological Processes*, *15*(8), 1441–1457. https://doi.org/10.1002/hyp.218

Scherer, N. M., Gibbons, H. L., Stoops, K. B., & Muller, M. M. (2017). Lake and Reservoir Management. *Lake and Reservoir Management*, *11*(4), 317–327. https://doi.org/10.1080/07438149509354213

Schindler, D. W. (1977). Evolution of phosphorus limitation in lakes. *Science (New York, N.Y.)*, *195*(4275), 260–262. https://doi.org/10.1126/science.195.4275.260

Seehausen, O., van Alphen J. J. A., & Witte, F. 1997. Cichlid fish diversity threatened by eutrophication that curbs sexual selection. *Science*, *277*, 1808–1811

Sharpley, A., Jarvie, H. P., Buda, A., May, L., Spears, B., & Kleinman, P. (2013). Phosphorus Legacy: Overcoming the Effects of Past Management Practices to Mitigate Future Water Quality Impairment. *Journal of Environment Quality*, *42*(5), 1308–1326. https://doi.org/10.2134/jeq2013.03.0098

Sharpley, A. N., Troeger, W. W., & Smith, S. J. (1991). The measurement of bioavailable phosphorus in agriculture runoff. *Journal of Environmental Quality, 20*, 235-238.

Smith, V. H., Tilman, G. D., & Nekola, J. C. (1999). Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution*, *100*(1–3), 179–196. Retrieved from https://journals-scholarsportal-info.proxy.lib.uwaterloo.ca/pdf/02697491/v100i1-3/179_eioeniofmate.xml

Song, K., Xenopoulos, M. A., Marsalek, J., & Frost, P. C. (2015). The fingerprints of urban nutrients: dynamics of phosphorus speciation in water flowing through developed landscapes. *Biogeochemistry*, *125*(1), 1–10. https://doi.org/10.1007/s10533-015-0114-3

Strecker, E. W., Quigley, M. M., Member, A., Urbonas, B. R., Jones, J. E., & Clary, J. K. (2001). DETERMINING URBAN STORM WATER BMP EFFECTIVENESS. *Journal of Water Resources Planning and Management*, *127*(3), 144–149. Retrieved from www.bmpdatabase.

Wang, J., Endreny, T. A., & Nowak, D. J. (2008). Mechanistic simulation of tree effects in an urban water balance model. *Journal of the American Water Resources Association*, *44*(1), 75–85. https://doi.org/10.1111/j.1752-1688.2007.00139.x

Waterloo Region Record. (2012, Sept 6). *Clair Lake rehabilitation moving forward.* Retrieved from The Record: https://www.therecord.com/news-story/2615848-clair-lake-rehabilitation-moving-forward/

Waters, S., & Webster-Brown, J. G. (2016). The use of a mass balance phosphorus budget for informing nutrient management in shallow coastal lakes. *Journal of Hydro-Environment Research*, *10*, 32–49. https://doi.org/10.1016/j.jher.2015.11.002

Wilcock, R. J., Nagels, J. W., Rodda, H. J. E., O'Connor, M. B., Thorrold, B. S., & Barnett, J. W. (1999). Water quality of a lowland stream in a New Zealand dairy farming catchment. *New Zealand Journal of Marine and Freshwater Research*, *33*(4), 683–696. https://doi.org/10.1080/00288330.1999.9516911

Withers, P. J. A., & Jarvie, H. P. (2008). Delivery and cycling of phosphorus in rivers: A review. *Science of The Total Environment*, *400*(1–3), 379–395.

https://doi.org/10.1016/j.scitotenv.2008.08.002

Wolman, M. G. (1967). A Cycle of Sedimentation and Erosion in Urban River Channels. *Geografiska Annaler. Series A, Physical Geography*, *49*(2/4), 385–395. https://doi.org/10.2307/520904

Yoon, S. W., Chung, S. W., Oh, D. G., & Lee, J. W. (2010). Monitoring of non-point source pollutants load from a mixed forest land use. *Journal of Environmental Sciences*, *22*(6), 801–805. https://doi.org/10.1016/S1001-0742(09)60180-7

Zamyadi, A., Coral, L. A., Barbeau, B., Dorner, S., avio Lapolli, F. R., & ele Pr evost, M. (2015). Fate of toxic cyanobacterial genera from natural bloom events during ozonation. *Water Research*, *73*, 204–215. https://doi.org/10.1016/j.watres.2015.01.029

Zeiger, S., & Hubbart, J. A. (2016). Quantifying suspended sediment flux in a mixed-land-use urbanizing watershed using a nested-scale study design. *Science of the Total Environment*, *542*, 315–323. https://doi.org/10.1016/j.scitotenv.2015.10.096

Zhang, Q., & Ball, W. P. (2017). Improving riverine constituent concentration and flux estimation by accounting for antecedent discharge conditions. *Journal of Hydrology*, *54*, 387–402. https://doi.org/10.1016/j.jhydrol.2016.12.052

Zhang, Q., Moyer, D., & Ball, W. (2016). Decadal-scale export of nitrogen , phosphorus , and sediment from the Susquehanna River basin , USA : Analysis and synthesis of temporal and spatial patterns. *Science of the Total Environment, The*, *563–564*(May), 1016–1029. https://doi.org/10.1016/j.scitotenv.2016.03.104

Zhao, G., Hormann, G., Fohrer, N., Kiesel, J., Gao, J., & Li, H. (2012). Application of a nutrient model for sediment yield and phosphorus load estimation in an agricultural catchment in south China. *Fresenius Environmental Bulletin*, *21*(7A), 1894–1904.

Zhou, L., Dickinson, R. E., Tian, Y., Fang, J., Li, Q., Kaufmann, R. K., … Myneni, R. B. (2004). Evidence for a significant urbanization effect on climate in China. *PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA*, *101*(26), 9540–9544. Retrieved from www.pnas.orgcgidoi10.1073pnas.0400357101