Historical Trends in Water Quality in the Grand River, Ontario: Reconstruction of Phosphorus Loadings

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.

Saliy Shaker

Abstract

Phosphorus, a mineral nutrient, is an essential element in aquatic systems. It is only available for biological activity in the form of orthophosphate and soluble restrictive phosphate. Eutrophication, caused by nutrient enrichment, is a problem in many freshwater systems, which results in increased algal blooms, anoxic conditions, and consequently, biodiversity loss and ecosystem failure. Low dissolved oxygen levels trigger the release of sediment bound phosphorus, which reinforces eutrophication. Nutrients in aquatic systems are provided by point and non-point sources and these sources can be affected by several factors, including population, land-use, and climate change. There are many long-term historical phosphorus studies on rivers, but there are very few that are conducted on the Grand River watershed and none that look at factors that might be driving the phosphorus loadings.

The Grand River watershed, located in Ontario, Canada, is a highly agricultural watershed with a growing population of approximately one million. It has experienced eutrophication, which has led to excessive production of cyanobacteria and regions of hypoxia. In this study, historical phosphorus concentration data (Total Phosphorus, Soluble Reactive Phosphorus, and Particulate Phosphorus) in five sites along the Grand River were analyzed temporally and spatially from 1965 to 2010 in the upper, middle, and lower parts of the watershed. The Particulate Phosphorus was calculated by subtracting SRP from TP. Several other data such as climate, land-use, geology, and population were also explored and considered as possible factors that may have influenced the trends over time.

TP, SRP, and PP average flow weighted concentrations and fluxes were calculated in 2-6 year intervals. SRP load was higher prior to the early 1970’s, declined in the 1970’s, was more stable in the 1980’s and 1990’s, and increased in the 2000’s. The initial decrease in SRP in the early 1970’s was likely due to the phosphorus ban in detergents in 1973 that was implemented over several years. The constant SRP loadings in the 1980’s and 1990’s, despite population and urban development growth, may have been due to upgrades in waste water treatment plants during that time period. The recent increase in phosphorus in more recent years coincides with a large increase in the number of livestock in the 2000’s and population growth. SRP and PP loads increase from upstream to downstream regions are likely due to nutrient accumulation by the river. The higher loads and

concentrations of SRP in the CGR is expected because the region is highly urbanized and contains most of the tile drainage in the watershed.

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Dedication

I dedicate this thesis to my parents who have gone through many hardships to protect me and provide me with the best opportunities. Without their support and love, I would not be the person I am today. They taught me to be persistent and perseverant and to follow my dreams.

Table of Contents

List of Figures

List of Tables

Chapter 1
Introduction

Rivers are a major resource of drinking water, are ecologically and economically important, and a-re ecosystems where major biogeochemical cycling occurs (Conley et al, 2009; Fu et al., 2003; Peterson et al., 2001). In many parts of the world a supply of clean water is scarce and this is becoming the case in Canada as well. Among the issues is eutrophication, the increase in algal blooms caused by excess nutrient export, such as phosphorus in phosphorus-limited freshwater systems (Schindler, 1974). In lakes, when algal blooms die and settle down to the hypolimnetic zone, they are decomposed by aerobic bacteria that utilize and exhaust the dissolved oxygen levels in the water column which consequently leads to declines in fish populations (Vollenwieder, 1968; Beeton, 1965; Kemp and Boynton, 2000). Anoxia, or the absence of oxygen, causes changes to biogeochemical cycling by leading to hydrogen sulfide and inorganic phosphorus release from sediments (Cowan and Boynton, 1996; Fenchel and Blackburn, 1979). The addition of nutrients to the upper water column via upwelling reinforces further eutrophication (Hagy et al., 2004). Major eutrophication and changes to nutrient biogeochemical cycling has been observed in lakes and reservoirs caused by natural and anthropogenic disturbances such as land use changes, increases in agricultural activity, climate change, population increase (Vollenweider, 1968; Vitousek et al., 2009; Liu et al., 2012; Jeppesen et al., 2005).

Phosphorus, a dynamic and biologically active element, is usually quantified in aquatic systems by the particulate (Particulate Phosphorus, PP), dissolved (Soluble Reactive Phosphorus, SRP) and the sum of these fractions (Total Phosphorus, TP). Phosphate ($PO4^{3-}$), the dissolved ion, a fraction of SRP, can be sorbed to particles and during cycling can be released from the particulates into the water column. Phosphate is also formed by the enzymatic hydrolysis of dissolved and particulate organic phosphorus by the activity of microorganisms (Correll, 1998). The phosphate ion, dissolved and particulate, is the only form of phosphorus that is assimilated by biological activity such as bacteria, phytoplankton, and macrophytes (Correll, 1998). As it is in high demand in phosphorus-limited systems, the concentration of phosphate is usually low (Schindler, 1974). When deposited, particulate phosphorus may be utilized by filter feeders, bacteria, and fungi, ultimately releasing orthophosphate back into the water (Correll, 1998). Particulate phosphorus thus contributes to the total bioavailable phosphorus in rivers, which can then be assimilated by phytoplankton (Edmond et al., 1981; Correll, 1998; Correll et al., 1999; Bennett et al., 2001), therefore it was considered in this study. Extraction of inorganic phosphorus from rocks, which is commonly used in fertilizer, has increased since the 1950's (Tilman et al., 2002), but began to decrease in Canada after the 1980's (Korol, 2002). Globally, phosphorus export from fertilizer is 14.2 Tg of $P \cdot y^{-1}$ and manure is 9.6 Tg of $P \cdot y^{-1}$ and their application collectively exceeds the phosphorus uptake by crops (MacDonald et al., 2011). Human feces and urine accounted for 30-50% phosphorus and detergents accounted for 50-70% phosphorus, in wastewater discharge (EPA, 1976). More recently, an average person produces approximately between 0.750 and 0.9 kg P $person^{-1}$ yr^{-1} of which approximately 20% to 50% is captured by secondary treatment of sewage (CRC, 2005; Kristensen, 2002; Glennie et al., 2002).

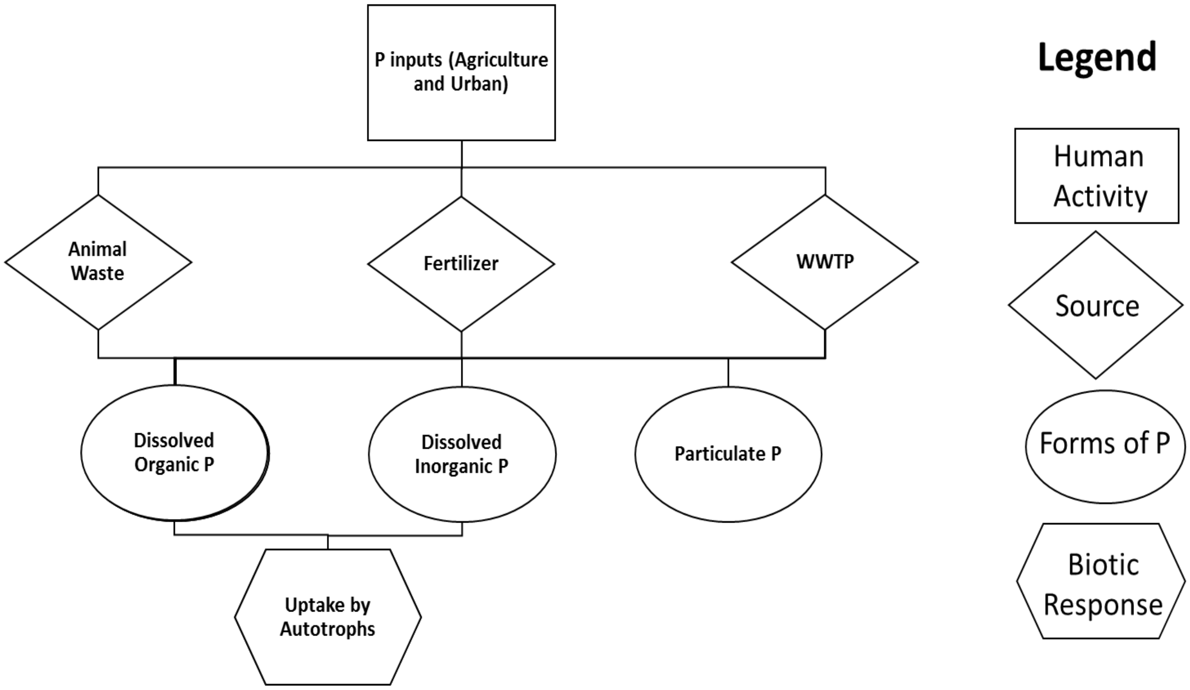

Figure 1. Simple conceptual model of phosphorus sources and sinks (Schofield, 2012).

In the 1960's phosphorus from laundry detergents contributed heavily to phosphorus inputs to rivers from WWTP discharge (Maki et al., 1984). In response to eutrophication caused by high phosphorus levels, heavy focus was directed towards reducing those inputs. The Great Lakes Water Quality Agreement of 1972 required all municipal WWTP with discharge of over 3800 m^3/L to limit the annual TP average in their effluent to 0.1 mg/L (Dolan, 1993). The Canadian government became committed towards reducing phosphorus in detergent to 8.7% in 1970 and reduced it further to 2.2% in 1972 (Maki et al., 1984; Schindler, 1974).

More recently, there has been a growing concern over the ecological health of the Grand River, located in southern Ontario, as population and urban development continues to increase (Cooke, 2011). This river is a paradigm for studying the effects of a number of elements, such as fertilizer runoff from agricultural lands and point source discharges from urban areas as population, urban development, animal farming, and extreme climate increases (Figure 4-6). Given that land-use, population, and climate patterns have changed over time, it is vital to examine the historical trends of phosphorus loads in the Grand River watershed and to connect these changes in anthropogenic activity to changes in phosphorus export. The Grand River is a culturally important river because of tourism and fisheries, with highly cultivated lands extending from the central to the lowest region of the catchment and with an increasing population in the central regions (Cooke, 2011). It is also Lake Erie's largest Canadian tributary, providing 40% of the phosphorus load within its eastern basin (Sandra Cooke, personal communication). The TP in eastern Lake Erie has been on the rise since 1995 (Charlton and Milne, 2004), and in 2002 it experienced the highest spring TP loadings since the 1970's (Rockwell et al, 2005). As a result of these critically high TP loadings in Eastern Lake Erie, it is crucial to gain a better understanding of the historical nutrient dynamics patterns and causes in the Grand River watershed.

Although there are many long term studies that have demonstrated how phosphorus is influenced by different factors temporally and spatially (Jeppesen et al., 2005; Billen et al., 2007; Parr and Mason; 2003; Duan et al., 2007; Li et al., 2006; Ovalle et al., 2013; Tao et al., 2010; Zhang et al., 2013) there are no long-term phosphorus studies on the Grand River watershed that examine phosphorus loadings as well as their drivers. A previous study by Hood (2012), investigated the long term phosphorus concentration trends in the Grand River, however, the study did not analyze loadings and used arithmetic instead of flow weighted concentrations. Using arithmetic concentrations can raise potential problems for instances where concentration in the river might have been overestimated during high flow events or underestimated during low flow conditions (Meal et al., 2011). It may be difficult to fit best management practices for large rivers within highly urban and agricultural watersheds such as the Grand River Watershed (Hood, 2012). This is due to best management practices being partial towards smaller less complicated watersheds that do not consider the temporal dynamics of nutrients or the difference in landscape throughout the watershed (Brannan et al., 2000; Gitau et al., 2006; Garen et al., 2005).

In this study information and data from several sources including the Provincial Water Quality Monitoring Network (PWQMN), the Canadian Water Survey, and Grand River Conservation Authority (GRCA), were analyzed in order to better understand the trends in nutrient concentrations and fluxes and potential contributing factors. The phosphorus data was collected for 28 sites, but only five sites were analyzed in this study due to their location, large sample number, and coverage over the years. Although the sampling dates back to 1965, this was not the case for all of the sites that were monitored including some of the sites analyzed here. Spatial and temporal trends of land-use, climate, agriculture, and development were examined in order to identify possible causes of the phosphorus patterns observed.

The objective of this study is to analyze the historical trends in phosphorus loadings in the Grand River basin and the impact of changing environmental and anthropogenic factors on the trends. Flow weighted concentrations and loads of different forms of phosphorus are examined over the past 46 years from 1965 to 2010 in 3 regions of the watershed. I hypothesized that the land-use, climate, and population changes and variability over the years and across the whole watershed would drive phosphorus loadings accordingly (Howarth et al., 1996); and that loads and concentrations would increase from upstream to downstream regions due to more urban land use but the load would also be higher due to the cumulative effect of rivers (Vannote et al., 1980). More specifically, the phosphorus ban in detergents in the early 1970’s should have lowered the SRP loadings from WWTP discharges in the Grand River watershed. After that drop in SRP load and concentration, it should have increased with population growth (point source) and intensified animal farming (non-point source). Fertilizer application accounts for a large portion of the PP load to rivers (Stadelmann et al., 2002), therefore we would expect PP trends in loadings and concentrations correlate with the trends in fertilizer use. Historically, PP loadings would have been expected to be high in the 1960’s and 1970’s and decrease in the 1980’s due to less fertilizer use. In addition, recent increases in temperature would have likely caused high runoff and consequently an increase in both SRP and PP.

Chapter 2
Materials and Methods

2.1 Study Area

The Grand River, a seventh order river, constitutes the largest tributary river flowing into the north side of Lake Erie and has one of the biggest watersheds in Southern Ontario. It comprises 10% of the total Lake Erie drainage area (Nelson et al., 2004) with an average annual discharge of 62 m^3 s^{-1}, draining an area of approximately 6800 km^2 and a length of 300 km (table 2 & 5). It is one of the two major tributaries draining into Lake Erie (Singer, 2003). The Grand River has a population of approximately 1 million people, half of which reside in the region of Waterloo (Table 3, Fig 4). The watershed is situated in a landscape that has been shaped by the last glacial period, resulting in highly variable soil and topography (Jyrkama & Sykes, 2007). Agricultural land constitutes 71% of the basin, followed by 12 % wetland, 7% forested, and 5% urban land (Table 4). There are 29 sewage treatment plants across the watershed, ranging mostly from traditional secondary treatment (degradation of biological content of sewage) to advanced tertiary treatment (nutrient removal and improvement of water quality) (Table 3). Approximately 80% of the population is serviced by conventional or advanced wastewater treatment while 20% is receives septic system treatment (Cooke, 2006). About 66% of the population serviced by WWTPs are serviced by secondary treatment and the remaining third by tertiary treatment (GRCA, 2008). The secondary and tertiary treatments may be adequate in sewage phosphorus removal and may not contribute to overall eutrophication as much but they may also not capture all of the phosphorus in sewage as population grows. The Grand River watershed has eight different tributaries and is divided into three distinct regions that are organized by geology and land use (Fig 8).

The catchment contains Paleozoic limestone and shale overlain by calcite rich glacial drift. The basin geology is mainly silt and clay tills on top of permeable limestone with outwash sand, kame, and gravel deposits (Rott et al., 1998). Landforms formed during the last ice retreat event, 12500 to 15000 years ago, and subsequent erosion produced the characteristics observed in the landscape within the Grand River watershed (Holysh et al., 2000; Nelson et al., 2004). The upper part of the watershed is characterized by till plains, providing the region with low permeability and varying elevation (Holysh et al., 2000). The soil is poorly drained, and as a result, the land requires tilling for agriculture (Nelson et al., 2004). The Quaternary geology combined with the extensive agricultural activity in this region heavily contributes to runoff. Two of the four major reservoirs, Conestoga and Belwood Lake, capture most of the runoff, and according to Cooke & Loomer (2011), the water in terms of phosphorus and dissolved oxygen is of better quality in the upper reaches than the lower reaches which will be verified in this study.

The central region of the Grand River is characterized by highly permeable sand and gravel kame and moraines with high variability in elevation, and large groundwater reserves used as a drinking water supply (Nelson et al., 2004). The western part of this region is very arable and has extensive tile drainages (Cooke, 2011) (Fig 10). Water quality in this region is considered fair at best, as it comprises the major urban cities, wastewater treatment plants, and intensive agriculture, which severely degrade the water quality in this region (Cooke & Loomer, 201l). Nutrient-rich sites are usually found to be downstream of urban development or intensive agriculture (Cooke, 2006). In those regions, high levels of phosphorus contribute to prolific aquatic plant growth and consequently to lower levels of dissolved oxygen.

The lower region of the Grand River (LGR) extends across lacustrine clay deposits and lower elevation variability (Holysh et al., 2000), supporting agriculture and generating significant runoff (Nelson et al., 2004). The surface water quality in terms of nutrients in this part of the watershed is generally not as poor as the central regions, however, quality still tends to be relatively marginal (Cooke & Loomer, 2011). In the LGR, the phoosphorus concentration always exceeded the provincial Water Quality Objective of 0.03 mg/L from 2003-2008, approaching 10 times the objective in the spring (Cooke, 2010). This appears to be due to the geology and land use practices. The geology sets boundaries of the type of water quality one would expect in a specific region while land use alteration contributes to the overall condition of the river (Cooke, 2011). For example, subbasins characterized by clay and till plains usually have the highest nutrient loads. The lower reaches of the Grand River tend to progressively deteriorate as it travels from upstream to downstream due to cumulative impact and river impoundments which make the lower reaches of the river have a lake-like behavior (Cooke, 2006).

2.2 Material

Nutrient data were obtained from the Provincial Water Quality Monitoring Network (PWQMN) (Aaron Todd, personal communication). The PWQMN a network of Ontario Conservation Authorities, the Ministry of Environment (MOE), Ontario parks, and local municipalities formed to monitor water quality parameters and make it available for free. The water quality monitoring in the Grand River began in 1965, covering 400 sites in Ontario, 28 of which are within the Grand River watershed. The 28 sites cover data between 23 and 48 years between 1965 and 2012. The Grand River Conservation Authority (GRCA) collects eight samples per year per site from March to November, while the samples are analyzed in the MOE. Prior to 1996, 12 samples were collected every year, one for each month. Some sites were sampled more frequently than others, with some sites consisting of several samples per month and others consisting of less than 1 sample per month. Site 16018403502 (3502) is collected more frequently by the MOE to get a better estimate of the loading to Lake Erie (Fig 8) (Cooke, 2006). Furthermore, there was less winter data and more summer data indicating a bias towards summer sampling. For all nutrients, the upper reaches have less data over the years than the middle and lower reaches. To increase accuracy, I increased the number of samples and years sampled by combining two sites in the upper and the central regions of the watershed. Each of the two sites were close to one another and did not have major water control infrastructure or tributaries in between. In the lower reaches, the site I chose had two different PWQMN identification numbers before and after 1980, therefore the two datasets were combined to give a longer time frame.

Lastly, there were several outliers in the dataset, which were likely typos or recording errors. Many values appeared to be enlarged by a factor of 1000 while others were either negative or were a much larger number than the surrounding values. The outliers were either excluded, corrected by dividing by a factor of 1000, or made a positive value in cases where it was most obvious. This study investigates data from 1965 to 2011 at 5 sites (Fig 8) within the Grand River, located in the upper, middle, and lower parts of the basin (Fig 7). The three regions were constructed based on their geographical location as well as the location of the sites chosen. The nutrients TP and SRP were selected based on their relevance to the health of aquatic ecosystems. Particulate Phosphorus (PP) was calculated by subtracting SRP from TP. Because the TP used in this data analysis was not filtered, the TP concentration refers to the total dissolved phosphorus and mostly an unknown part of particulate phosphorus (Meybeck, 1982). For the sake of simplicity, here we are assuming that TP is PP plus SRP.

The concentration data were then used as input to the Flux32 software, to calculate flux (concentration x discharge). Flux32 is a software designed for estimating loadings of water quality constituents at a site over a time period in a tributary or river (Walker, 1999). This model was obtained from the US Army Corps of Engineers (David Soballe, Personal communication). Grab-sample nutrient concentrations for at least one year, corresponding flow measurements (daily or instantaneous), and a complete flow record (mean daily flows) is required. Flux32 maps the flow over concentration relationship from the sample data and the entire flow data and uses the preferred algorithm to calculate a load for a single parameter at a site over a time period. This provides an estimate of total mass transport, flow, and associated errors for the whole period of study. Flux32 also has the ability to classify the data into groups based on flow, date, and/or season to reduce bias (Walker, 1999). Flux32 was used to calculate fluxes over two, five, or six years in the Grand River. The Flux32 calculated the load from the FWMC (Flow Weighted Mean Concentration) and flow for 2 to 6 year time spans. FWMC is the fraction of total load over total flow and it is more representative than arithmetic concentrations because concentrations are strongly influenced by stream flow (Meal et al., 2011). Therefore, normalizing concentrations for flow removes any variations that might indicate a trend in results when it is actually due to correlations with flow. This method was chosen specifically for the Grand River watershed because there was a weak positive relationship between concentration and discharge. The equation for calculating the FWMC is as follows:

□□□□=1□(□□∗□□)1□(□□)

Where q_i = flow in the i^{th} sample

c_i = concentration in the i^{th} sample

The FWMC represents the total load divided by the total discharge over a time period. The ratio of PP to SRP was calculated by dividing the PP flux by the SRP for a specific time period for the different regions.

Daily river discharge data was retrieved from the Water Survey of Canada's hydrometric archive, a publicly accessible online data (Environment Canada, 2012), and GRCA (Stephanie Shifflett, personal communication). The flow station closest to the sampling sites was used to calculate load. For the site located at the mouth of the Grand River, Dunville, flow data was available from 2009-2010 only. As a result, two stations upstream of the site, York and Mackenzie, were used to estimate the total flow for the LGR from 1974-2008. Combining the two upstream flows from 2009-2010 yielded higher flows than observed in 2009-2010 in site of the LGR. Using a proportional correction approach (estimated over actual multiplied by 100%), it was determined that the actual flow was approximately 86% of the estimated flow. Using the t-test, it was found that there was no significant difference between the estimated and corrected values and the actual values from 2009-2010, therefore, this method was used to extrapolate the flows for the years prior to 2009.

Climate data, obtained from the GRCA, were completed by filling in gaps at some stations using data from other nearby climate stations. Daily temperature (°C) and total precipitation (mm) data is available from 1950 to 2005 at 21 stations within the watershed. The averages of the minimum and maximum temperatures were calculated for each day.

A population census was obtained from Statistics Canada for the counties within the watershed. The population within the watershed boundaries was calculated by estimating the portion of the counties within the basin then multiplying the total population by the percentage within the watershed. If there was a city within the watershed with a known population, the population was subtracted before estimating the county population within the basin. This approach is fairly accurate considering the largest populations are within the largest cities in the center of the basin: Kitchener, Waterloo, Cambridge, and Brantford.

Table 1. Summary of Data used for this thesis project and their sources, contacts, and the year of the data.

Data	Source	Timeline
Phosphorus in UGR	Ontario Ministry of the Environment	1977, 1978-1993, 1995-2010
Phosphorus in CGR	Ontario Ministry of the Environment	1965-2009
Phosphorus in LGR	Ontario Ministry of the Environment	1974-2010
Discharge	Enviroonment Canada/GRCA	1964-2010
Precipitation	Environment Canada/GRCA	1950-2005
Temperature (interpolated)	Environment Canada/GRCA	1950-2005
Tile Drainage	GRCA	2003
Population	Statistics Canada	1966-2001 (Every 5 years)
Elevation	GRCA	2003
% Soil Erosion	GRCA	2011
Agriculutre	http://odesi1.scholarsportal.info.proxy.lib.uwaterloo.ca	1966-2006 (Every 5 years)
Landuse	Map Library	2007

2.3 Regions

The three areas chosen for this study were constructed based on the location of the sites chosen in each of the regions (Fig 7). This was implemented so each region could be better represented by the sites analyzed in this study. The three regions are named Upper Grand River (UGR), Central Grand River (CGR), and Lower Grand River (LGR). Using GIS layers and other data (Tables 2-5), characteristics were developed for each of the regions.

The UGR is characterized by 70% agriculture, 25% forest and wetland, and 5% urbanized land. Within this region, the Grand River flows for approximately 35 km, and has an average discharge of 5.5 m^3/s and an elevation of 530-475 m.a.s.l. The UGR has an area of 585 km^2, comprising 9% of the total Grand River watershed. The population density in the UGR is 113 people/km^2, with a population of approximately 66000. This region has smaller and fewer WWTP with a total capacity of 1726 m^3/day. Slope erosion, which is the % area of land that is undergoing erosion, accounts for 0.05% of the land in this region. The sites in the UGR have a PWQMN identification number of 16018409002 (9002) and 16018403902 (3902).

The CGR land cover is constituted of 69% agriculture, 19% forest and wetland, and 12% urban land. The length of the river spans over 110 km through an area of 3167 km^2 with an elevation of 547-310 m.a.s.l and a discharge of 41 m^3/s. The CGR population density (170 people/km^2) is the highest among the three regions, as it contains the three major cities, Kitchener, Waterloo, and Cambridge. This region has the largest WWTPs with a total capacity of 339 x 10^3 m3/day. The slope in this region is 110m with 0.63% slope erosion. The CGR sites have the PWQMN identification numbers 16018401002 (1002) and 16018401102 (1102).

Agriculture makes up 72% of the LGR land cover, whereas wetlands and forests make up 19% of the land cover, and urban land-use makes up 9%. The river in this region runs for 138 km and has an elevation of 310-170 m.a.s.l. The population density is 122 people/km^2 and a total WWTP capacity of 112 x 10^3. The area of this region is 3015 km^2 with 1.13% slope erosion. One location was chosen to be analyzed for this region which had two site number 16018403583 (3583) and 16018403502 (3502) over the years.

Due to the large number and variability in time and space in the dataset available for analysis, we looked at selected sites over the entire period of the data collection to gain better understanding of the nutrient trends over time. Five sites in the three regions in the watershed were analyzed in detail.

The UGR is represented by sites 9002 and 3902 located at 0 and 13 km from the headwaters respectively. Sites 1002 and 1102 at 127 and 131 km from the headwaters, respectively, are downstream of major treatment plants and represent the CGR. The major WWTP are in Kitchener, Waterloo, Cambridge, and Guelph (Fig 8; Table 3). The LGR is represented by sites 3502 and 3583, located at approximately 255 km form the headwaters (Fig 8; Table 2). There is also a large WWTP in the LGR located at Brantford. Comparisons between the different regions will give us an understanding of the changes in the nutrient trends and dynamics within the Grand River over time. Different anthropogenic and environmental factors will be examined to aid in determining the causes in the shifts in phosphorus patterns. The temporal patterns in fluxes of TP, SRP and PP were evaluated in the UGR, CGR, and LGR sites from the years 1977 to 2010 (missing 1978 and 1994), 1965 to 2009, and 1974 to 2010, respectively, to understand spatio-temporal patterns.

Chapter 3

Results

3.1 Temporal Trends

Total Phosphorus

TP, SRP, and PP loads were high prior to the 1970's, decreased in the 1970's, and increased in the 2000's (Fig. 2). For example, faster decreases can be seen during some period and there is an increasing trend in more recent periods. The CGR and LGR sites show an increasing trend in the period of 2005-2009. Of the three stations, the TP average flux was highest in the LGR until 2005-2009, when the CGR recorded the highest flux value (520 tons/year) among the 3 regions. The average TP flux decrease from 1975 to 2005 was greater in the LGR (278 tons/year) than the CGR (204 tons/year). In the UGR the decrease in the average flux from 1975-2009 was lower (0.53 tons/year) than the decrease in the downstream regions.

Upper Grand River Sites: In the years 1977 and 1979, the average TP flux and concentration values were 8.35 tons/year and 0.050 mg/l, respectively. The TP increased in 1980-1984 (average flux: 13 tons/year, average concentration: 0.076 mg/l). In 1985-1989, the average flux decreased to 6.78 tons/year and the average concentration to 0.0389 mg/l. There was another large decline, from 1990-1994 (average flux: 5.84 tons/year, average concentration: 0.034 mg/l) to 1995-1999 (flux: 3.77 tons/year, concentration: 0.023 mg/l). A spike in the trend appears in 2000-2004 (average flux: 10.6 tons/year, average concentration: 0.061 mg/l) followed by a decrease in the period 2005-2009 (average flux: 7.82 tons/year, average concentration: 0.040 mg/l).

Central Grand River Sites: In the CGR, there was an increase in average TP concentration and flux from 1965-1969 to 1970-1974. The average concentration increased from 0.226 mg/l to 0.362 mg/l, while average flux increased from 262 tons/year to 421 tons/year. This increase was followed by a sharp decline from 1970-1974 (average flux: 421 tons/year, average concentration: 0.362 mg/l) until 1985-1989 (flux: 169 tons/year, concentration: 0.126 mg/l). Another increase appeared in 1990-1994 (average flux: 302 tons/year, average concentration: 0.223 mg/l). In 1995-1999, TP values decreased (average flux: 110 tons/year, average concentration: 0.093). Between 2000 and 2009, TP average flux and concentration increased by 340 tons/year and 0.198 mg/l, respectively.

Lower Grand River Site: TP average flux in the LGR decreased from 1975-1979 (496 tons/year) to 2000-2004 (218 tons/year). The decrease in average flux slowed down between 1985-1989 (365 tons/year) and 1990-1994 (361 tons/year). TP average concentration increased 3 times over the 31 years, in 1980-1984 (0.284 mg/l), 1990-1994 (0.181 mg/l), and 2005-2010 (0.158 mg/l). Over the years, the overall average flux and concentration decreased by approximately 151 tons/year and 0.067 mg/l, respectively.

Soluble Reactive Phosphorus

The SRP declined over time until the more recent years (2005-2010). Unlike TP and PP, the SRP average flux and concentration increased in all of the 3 regions. The average flux was highest in the LGR until 2005-2009 where the CGR had the highest flux value (139 tons/year) among the 3 regions. The SRP flux decrease from 1975 to 2005 was higher in the LGR (35 tons/year) than the CGR (30 tons/year). On the contrary, the PP flux in the UGR increased from 1975 to 2005 (1.67 tons/year).

Upper Grand River Sites: In the UGR the TP average flux and concentration values in 1977 and 1979 were 5.816 tons/year and 0.035 mg/l, respectively. The UGR TP increased in 1980-1984 (average flux: 10.5 tons/year, average concentration: 0.062 mg/l). In 1985-1989, the average flux plummeted to 5.30 tons/year and the average concentration to 0.030 mg/l. Following the steep drop, the TP suddenly decreased again from 1990-1994 (average flux: 4.44 tons/year, average concentration: 0.026 mg/l) to 1995-1999 (average flux: 2.61 tons/year, average concentration: 0.016 mg/l). In 2000-2004 the SRP peaked again (average flux: 6.67 tons/year, average concentration: 0.037 mg/l) followed by a further smaller increase in 2005-2009 (average flux: 7.49 tons/year, average concentration: 0.38 mg/l).

Central Grand River Sites: In the CGR, there was an increase in SRP average concentration and average flux from 1965-1969 to 1970-1974. The average concentration increased from 0.133 mg/l to 0.154 mg/l, while average flux only increased from 177 tons/year to 178 tons/year. There was a sharp decrease in 1975-1979 (average flux: 79.7 tons/year, average concentration: 0.061 mg/l). The SRP increased gradually from 1980-1984 (average flux: 76.9 tons/kg, average concentration: 0.062 mg/l) to 1990-1994 (average flux: 88.8 tons/year, average concentration: 0.066 mg/l). Another dip appeared in 1995-1999 (average flux: 37.1 tons/year, average concentration: 0.031 mg/l). Between

2000 and 2009, TP average flux and concentration increased by 89.3 tons/year and 0.051 mg/l, respectively.

Lower Grand River Sites: SRP average flux and concentration patterns were not similar to those of TP and PP. SRP average flux in the LGR increased from 1975-1979 (93.9 tons/year) to 1985-1989 (124 tons/year). It then decreased gradually until 2000-2004 (58.5 tons/year). In contrast, the average concentration increased from 1975-1979 (0.043 mg/l) to 1980-1984 (0.064 mg/l). It dropped to 0.054 mg/l in 1985-1989 and gradually decreased to 0.05 mg/l. The average concentration dropped further to 0.032 mg/l in 2000-2004. Both the flux and concentration increased in 2005-2010 (average flux: 116 tons/year, average concentration: 0.053 mg/l).

Particulate Phosphorus

PP average concentration and flux trends were similar to the TP trends and showed a general decline over time and an increasing trend in more recent years in the CGR and LGR (Fig 2). PP average flux was highest in the LGR until 2000-2009 where the CGR average flux was highest (380 tons/year) among the 3 regions. The TP average flux decreased from 1975 to 2005 was higher in the LGR (243 tons/year) than the CGR (175 tons/year). In the UGR the PP average flux decrease from 1975 to 2010 was lower (2.210 tons/year) than the decrease in the downstream regions. Upper Grand River Sites: PP flux and concentration decreased slightly from 1977-1979 (average flux: 2.536 tons/year, average concentration: 0.0152 mg/l) to 1980-1984 (average flux: 2.519 tons/year, average concentration: 0.0147 mg/l). It dropped to a flux of 1.480 tons/year and a concentration of 0.0085 mg/l in 1985-1989. It steadily decreased until a rise (average flux: 3.913 tons/year, average concentration: 0.0231 mg/l) in 2000-2004. In 2005-2009, the average flux plummeted to 0.326 tons/year and the concentration to 0.002 mg/l.

Central Grand River Sites: In the CGR, there was an increase in TP average concentration and flux from 1965-1969 to 1975-1979. The average concentration increased from 0.093 mg/l to 0.233 mg/l, while average flux increased from 85 tons/year. This increase was followed by a sharp decline in 1980-1984 (average flux: 138 tons/year, average concentration: 0.362 mg/l) and decreased further in 1985-1989 (average flux: 169 tons/year, average concentration: 0.062 mg/l). In 1990-1995, the constant decrease was interrupted by an increased in PP (average flux: 213 tons/year, average concentration: 0.157 mg/l). PP values decreased again in 1995-1999 (average flux: 73 tons/year, average concentration: 0.062 mg/l). After 2000, PP average flux and concentration escalated, increasing from 2000-2004 to 2005-2009 by 250 tons/year and 0.147 mg/l, respectively.

Lower Grand River Sites: PP average flux in the LGR decreased from 1975-1979 (402 tons/year) to 2000-2004 (159 tons/year). The average flux increased from 1985-1989 (245 tons/year)

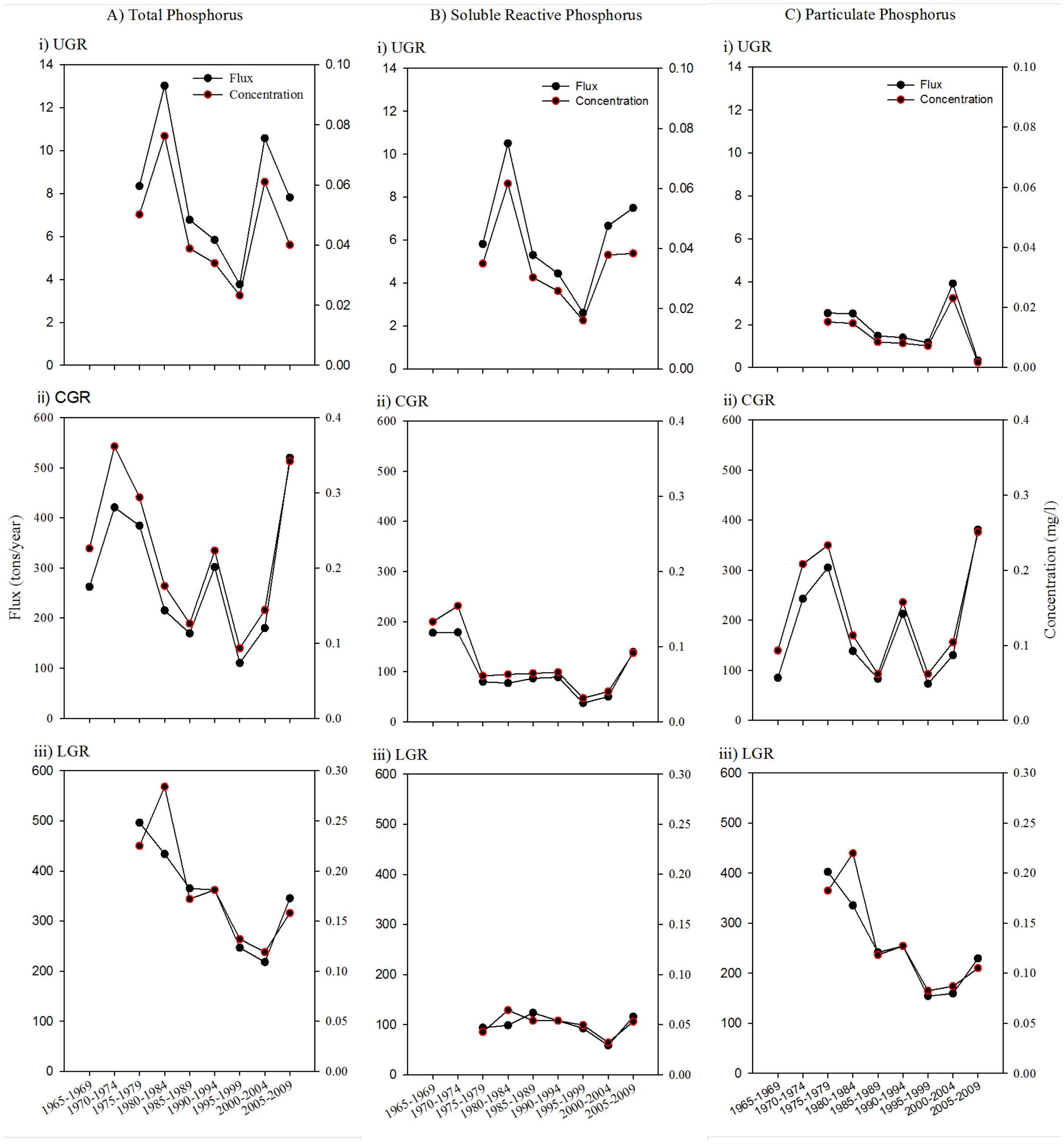

Figure 2. TP, SRP, and PP average FWMCs and average loads in the three regions of the Grand River; UGR (1977-2010), CGR (1965-2009), and LGR (1974-2010) displayed over time. Note: Missing years in UGR (1978, 1994).

to 1990-1994 (254 tons/year). PP average concentration showed an increase 3 times over the 35 years, in 1980-1984 (0.220 mg/l), 1990-1994 (0.127 mg/l), and 2005-2010 (0.105 mg/l). Over the years, the overall average flux and concentration decreased by approximately 173 tons/year and 0.077 mg/l, respectively.

Particulate Phosphorus:Soluble Reactive Phosphorus Flux Ratio

The PP:SRP increased from the 1960's then decreased in the 1980's (Fig 3). However, in the CGR the PP:SRP ratio increased from 1965-2010. In the UGR, PP:SRP average flux ratio decreased from 1977-1979 (0.44) to 1980-1984 (0.24). The ratio then increased to 0.59 in 2000-2004. It then dropped to 0.04 in 2005-2009. From 1977-1979 to 2005-2010, the PP:SRP ratio declined by 0.39 and from 1977-1979 to 2000-2004 it increased by 0.15.

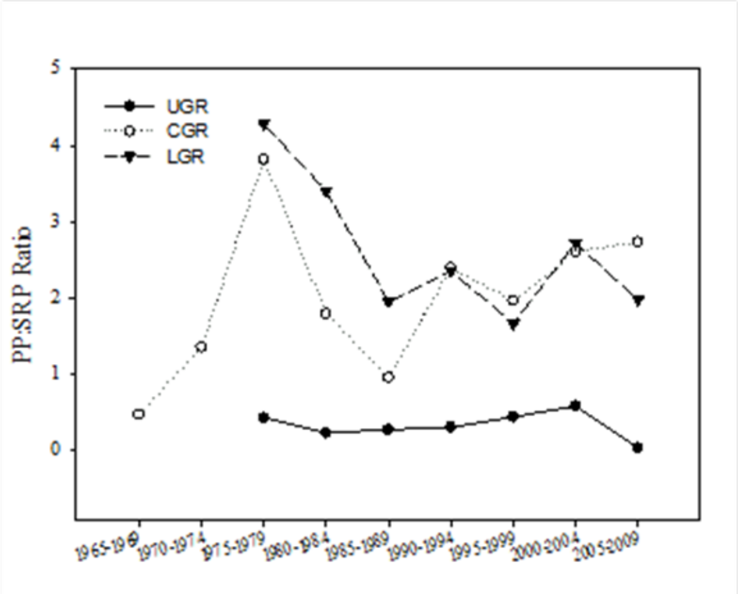

Figure 3. PP:SRP average flux ratio in the Grand River in the UGR, CGR, and LGR from 1977-2010, 1965-2009, and 1974-2010, respectively. Note: There are missing years in the flow corresponding concentrations for the UGR (1978, 1994).

PP:SRP average flux ratio in the CGR increased from 1965-1969 (0.48) to 1975-1979 (3.82). It proceeded to decrease until 1985-1989 (0.96), increased in 1990-1994 (2.39), decreased in 1995-1999 (1.97), and increased to 2005-2009 (1.98). In the CGR, the PP:SRP average flux ratio from 1965-1969 to 2005-2009 increased by 2.26 and from 1975-1979 to 2005-2009 decreased by 1.084.

From 1975-1979 to 1985-1989, the LGR flux PP:SRP ratio decreased from 4.28 to 1.95, respectively. Overall, the ratio decreased from 1975-1979 to 2005-2010 by a factor of 2.3. It increased in 1990-1994 (2.36) and 2000-2004 (2.72).

3.2 Spatial Trends

Between 1978 and 2010, TP load increased from the UGR to the LGR until 2005 (Fig 2). TP flow-weighted average concentration shows a different trend than the load trend where it is higher in the CGR than the LGR during more time periods. The concentration in the CGR (0.294 mg/l) is higher than the LGR (0.225 mg/l) in 1975-1979. This is reversed from 1980-1984 to 1984-1989, where the LGR average concentration is higher than the CGR. In 1990-1994, the CGR average concentration (0.223 mg/l) was higher than the LGR average concentration (0.181 mg/l). The average concentration in the LGR (0.132 mg/l) exceeded that of the CGR (0.093 mg/l) in 1995-1999. Between 2000-2004 and 2005-2009, the CGR average concentrations increased again and were higher than those of the LGR average concentrations, especially in 2005-2009.

Similar to TP load, SRP average flux increased from the UGR to the LGR until 2005-2009 where the CGR (139 kg/year) had a higher average concentration than the LGR (116 kg/year). When compared to TP average concentrations between CGR and LGR, SRP average concentration varies a lot more between the two regions. The SRP average concentration in the LGR was higher than the CGR in 1980-1984 and 1995-1999. Prior to 1980, the SRP average concentration was 0.061 mg/l in the CGR and 0.043 in the LGR. After 1980, the LGR average concentration was 0.064 mg/l while the CGR average concentration was slightly lower with a concentration of 0.063 mg/l. Initially, the average concentration in the CGR was higher than the LGR but became less obvious from 1985-1989 to 1990-1994. In 1995-1999, the LGR average concentration (0.05 mg/l) was higher than the CGR (0.031 mg/l). From 2000-2004 to 2005-2010, the CGR had higher average concentration values than the LGR but was more noticeable in the more recent years with value of 0.053 mg/l in the LGR and 0.091 mg/l in the CGR.

When comparing the PP average load and concentration values between the CGR and LGR, it followed the same trend as the TP load increase from the UGR to the LGR until 2005 (Fig 1). Similar to TP, PP average concentration had a different trend than the average load trend where it is higher in the CGR than the LGR during more time intervals. The average concentration in the CGR (0.233 mg/l) is higher than in the LGR (0.182 mg/l) in 1975-1979. From 1980-1984 to 1984-1989, the LGR average concentration becomes higher than the CGR average concentration. In 1990-1994, the CGR average concentration (0.157 mg/l) was higher than the LGR average concentration (0.127 mg/l). In 1995-1999 the average concentration in the LGR (0.083 mg/l) exceeded that of the CGR (0.062 mg/l). Between 2000-2004 and 2005-2009, the CGR average concentrations increased again and were higher than those of the LGR concentrations but the difference between the sites were higher in the later years.

PP:SRP average flux ratio was higher in the LGR than the CGR from 1975-1979 to 1985-1989 and in 2000-2004 (Fig 3). The difference in the ratios was highest in 1980-1984 with a ratio of 3.82 in the CGR and a ratio of 4.28 in the LGR. The ratio of PP:SRP flux was lowest in the 1990-1994 with the CGR and LGR have ratios of 2.40 and 2.36, respectively.

Chapter 4

Discussion

4.1 Past to Present

Generally, TP and SRP concentrations and fluxes were high prior to the 1970's, decreased during the 1970's, experienced less variation in the 1980's and 1990's, and started increasing after 2000 (Fig 2). The Grand River and tributaries experienced stress from rising phosphorous loading in the late 1960's and early 1970's from domestic and agricultural sources (Cooke, 2006; Fig 4&5). The decline in SRP in the 1970's likely resulted from the introduction of the ban in phosphate containing laundry detergents and the upgrades of WWTPs. Although the phosphate ban legislation was established in 1972, it was implemented over several years, hence the reason we are seeing a continued decline over the following years. Smaller SRP declines were observed in the 1980's and 1990's despite continued population growth (Fig 4). This may be due to increased awareness and use of best management practices by farmers, as well as WWTP upgrades in the 1980's and again in the 1990's. The latter occurred in the largest WWTP's in the basin, Waterloo, Kitchener, Cambridge, and Brantford, located in the central and lower reaches of the watershed (Fig 8). All WWTPs, except Cambridge, were built prior to the commencement of the PWQMQ program. The Waterloo, Kitchener, and Brantford plants are secondary treatment plants and were upgraded to improve dechlorination and aeration in 1987, 1989, and 2008, respectively (City of Kitchener, personal communication; Kelly Hagan, personal communication). The fairly large tertiary WWTP of Cambridge was built in 1978, however, this is not reflected in a noticeable decline in SRP around that time. This may be due to the steady increases in animal farming and population over the years. PP concentration and flux decreased after 1980 and continued to decrease in the 1990's which may have been caused by the decrease in chemical fertilizer application over time (Fig 5). A possible factor that might have influenced those trends could be the legacy effect of historical fertilizer application (Woltemade, 2000; van Bochove et al., 2011). Similarly, a preliminary analysis of phosphorus analyzed during the period of 1981 to 2001 by the GRCA identifies a decrease in TP concentrations. This was attributed to successful planning and upgrades of WWTP's and best management practices by farmers and residents of the watershed which have helped improve the water quality during that time period (Cooke, 2006).

In the more recent years (between 2000 and 2010), there appears to be an increase in both the PP and SRP concentrations and loadings in the Grand River watershed. Although use of phosphate based fertilizer has been decreasing over the years, animal farming has intensified (Fig 5) which can supply the river with more SRP from manure (Spires and Miller, 1978). Agricultural lands are prone to runoff and the soils may still contain fertilizer phosphorous that was applied years prior. Increased development and land-use changes may have promoted PP export from the soils (Woltemade, 2000; Howarth et al. 2002). The reason we may be seeing an increase in TP in more recent years may be because animal manure provides more TP than chemical fertilizers globally, making phosphorus from manure a major driver in the global nutrient cycling (Bouwman et al., 2009; Galloway et al., 2010). In a study by van Bochove et al. (2011), the central and upper parts of the Grand River were found to have higher phosphorus loadings in more recent years due to phosphorus desorption in soil. We speculate that the widespread historical fertilizer application in the Grand River enriched the soils to levels that are now at high risk of PP desorption, which may have caused the elevated phosphorus loads observed in the Grand River after 2000.

Furthermore, temperature increased over time and precipitation increased from the 1970's to the 1990's. This could have had a substantial impact on the nutrient dynamics. Freshwater systems are vulnerable to climate change, which can impact the water quality of aquatic ecosystems. Increased temperature and increased winter rainfall in some European rivers have increased the nutrient export from agricultural fields into rivers (Weyhenmeyer et al., 1999, 2005; George et al., 2004).

Other long-term studies on watersheds in the Lake Erie basin have found similar patterns of SRP loads decreasing in the 1970's and increasing in the 2000's. In the highly agricultural rivers of Ohio, the Sandusky and Maumee showed a decline in SRP in the 1970's and an increase in the 1990's and 2000's (Daloğlu et al., 2012). Using results from SWAT modeling, it was identified that the increased precipitation, changes in fertilizer application methods, and best management practices that increase phosphorus in stratified soil were contributing to the increased SRP from the mid 1990's until 2010. A smaller urbanized Lake Erie watershed, Cuyahoga River, also shows a similar trend of increasing TP and SRP in the 2000's, where the increase in TP was associated with storm events and the increase in SRP was associated with dry events (Yuan et al., 2013). It was also pointed out that TP and SRP loadings were extraordinarily high in the early 1980's. This is consistent with our results, which also show high PP levels in the 1980's. Another long-term study on the Yangtze River in

China has also shown an increasing trend in SRP in some of its tributaries in more recent years presumably due to urban and industrial development (Liu et al., 2003).

A study by Hood (2012) shows a decrease in TP and SRP concentrations in the Grand River from 1965-2009. This puzzling incongruence could be explained by the difference in the methods used to analyze the datasets. For example, in Hood (2012) arithmetic concentrations were used instead of flow weighted concentrations. This would have skewed results towards lower values due to a sampling bias towards higher flow events (Fig 7) because the concentrations were not normalized for flow. In this study, the outliers and typos were also not excluded and hence may have altered the TP and SRP concentration patterns.

The ratio of PP:SRP in all the regions decreased in the 1980's (Fig 3), which corresponds with the time when chemical fertilizer use began to decrease. Generally, the PP:SRP ratio decreased from the 1970's to the 2000's and is supported by a more aggressive decline in PP than SRP. This denotes that PP in runoff may have decreased over this time period accordingly with decreasing fertilizer use. The CGR and LGR PP:SRP ratio seem to have a slight increasing trend in the 2000's. This could have been caused by the shift in sampling methods that target higher precipitation events, which can lead to more particulate nutrients in runoff. Furthermore, considering the more intense increase in animal farming in the more recent years, there should be a decreasing rather than an increasing trend in more recent years. On the other hand, the increasing ratio could be an indication of phosphorus desorption in soil, resulting in increased phosphorus in runoff from the central region since it has extremely fertile soil and an extensive tile drainage network (Fig 10). It has been shown that tile drainages tend to increase SRP and PP transport in high flow events but the SRP export may continue to be high in successive flow events due to desorption from soil (Gentry et al., 2007; Gächter et al., 2004). Further work is required to pinpoint whether the PP:SRP ratio is indeed increasing. This can be done by looking at yearly ratios rather than 5 year intervals and running a statistical analysis on the data to see whether the increase is significant.

The effects of seasonality have been observed to be major in watersheds where climate, eutrophication, and land-use practices vary from season to season (Alberts et al., 1978). For many agricultural watersheds in the northeastern US, approximately half of the annual precipitation ends up in the river. The sources and impacts of the stream flow may vary among seasons. During the winters, subsurface discharge under fully recharged hydrological conditions may dominate stream flow. While during the summers, deeper subsurface discharge may control the stream flow (Pionke et al., 1999).

SRP concentrations were found to be twice as high in the summer than the winter in highly agricultural watersheds in Pennsylvania (Gburek and Heald, 1974). More than 60% of the exported SRP took place in the spring from February to April as a result of high flows due to ice melt. In another study on the mixed land-use Mahatango Creek in Pennsylvania, the maximum SRP loads were observed between September and December while PP concentration and flux values were highest during storm events. In a study by Richards et al., (2008), a 30 year trend analysis in seven Lake Erie tributaries identified that rivers experienced the greatest SRP decrease in the summer and fall seasons, while greatest SRP increases were associated with the spring season. Similarly, seasonal characteristics that can alter phosphorus concentration and load values may apply to the Grand River watershed, as it is in a similar geographical location and it is also a highly agricultural basin with a fair amount of urbanization. It has also been observed, the Grand River water quality deteriorates as it passes through the city of Waterloo located in the central reaches due to the impact of non-point agricultural sources in spring runoff (Cooke, 2011). Therefore, a seasonal analysis is required to further explore the causes of these trends.

4.2 Upstream to Downstream

TP and SRP increases from the higher reaches to the lower reaches. In the 1970's, after the ban of phosphorus in detergents, the most prominent decrease in SRP occurred in the CGR (Fig 2). This suggests that the WWTP effluents have a larger impact on the dissolved component of the riverine phosphorus. Riverine SRP is usually derived from urban effluents and agricultural land with tile drainages (Meybeck, 1982; Mason et al., 1990; Xue et al., 1998). This is consistent with our findings of highest concentration in the CGR, since the CGR has the highest population density and the largest WWTP capacity among the 3 regions (Table 3; Fig 4). This region also has most of the tile drainages in the watershed (Fig 10). In comparison, Cooke (2006) reports similar trends of arithmetic phosphorus concentrations from 2000 to 2004, where they are lower in the upper region and have higher dissolved oxygen concentrations, therefore having the best water quality in the watershed. Hood (2012) observed a similar trend of increasing phosphorus concentrations from upstream to downstream reaches in the Grand River basin. A long term study by Duan et al., (2007) also demonstrated increasing nutrient loads from a less urbanized region to a more urbanized one, which is associated with increasing urban and industrial development as well as the accumulation of nutrients as it flows downstream.

The phosphorus (TP & SRP) concentrations in the CGR and LGR were generally similar, but the CGR values were sometimes higher. This can be supported by the fact that the central region is more populated and urbanized than the other regions and is continuing to expand (Table 3). PP and SRP loads were generally higher in the LGR than the CGR. The general increase in loads with distance downstream suggest phosphorus loads are collected and accumulated from various sources in the upstream regions as seen in several other watersheds (Alexander et al., 2007, Duan et al., 2011). While PP usually constitutes 95% of the TP naturally carried by rivers (Meybeck, 1982), the Grand River PP constitutes between 63-81 % of the TP in the LGR. A study on two agricultural watersheds in Sweden identified that the percentage of PP in the Phosphorus load was 35-66 % (Kronvang, 1992). The PP:SRP ratio decreases farther upstream with the TP comprising 49-79% PP in the CGR (Fig 3). The increase in the percentage of PP in TP from CGR to LGR can be explained by several factors including higher soil erosion and clay and silt dominated geology in the lower region. Although the Grand River has an overall low erosion risk (van Bochove et al., 2011), soil erosion increases downstream (Table 5), most likely caused by the higher urbanization and land disturbances in the lower reaches. Erosion increases when there is land disturbance, high flow, and a lack of soil erosion management leading to higher sediment export to streams (Wolman, 1964; Clark & Woolcok, 2000). This likely makes the river in those regions more susceptible to phosphorus enrichment due to phosphorus mobilization in the soil (Sharpley et al., 1990), which ultimately increases nutrient delivery to streams. The CGR and the LGR, where PP:SRP ratio tends to be much higher have more slope erosion and the lower reaches are clay dominated, which may provide the river with suspended sediments when land is altered and erosion is enhanced (Gumbs & Lindsay, 1982).

The CGR also has the highest population density, largest WWTP capacity, and it is more urbanized than the UGR and LGR. This may explain why we notice more nutrient supply in the CGR. Groundwater recharge increases at the end of the central region and the beginning of the lower region, below the city of Cambridge (Sandra Cooke, personal communication; Holysh; 2000). This would play an important role as a dilution effect for the phosphorus concentrations in the LGR. In the more recent years, the CGR has had higher TP and SRP values than the LGR could be due to the intensification of animal agriculture in the central region in more recent years, but this needs to be confirmed by looking at cropland area change over the years. In Goolsby (2000), the highly agricultural Mississippi River basin also experienced an increase in downstream nutrients due to a cumulative effect. Thus, the high SRP and PP loads in the CGR and LGR may also be due to the cumulative effect of phosphorus loads from the upstream sources.

In 1982, a Basin Study was conducted, which recommended several steps to improve water quality in the Grand River (GRCA, 2014). The Guelph WWTP was upgraded, which improved water quality in the Speed tributary where the WWTP is located (CGR). There are also several WWTP upgrades and improvements in the Waterloo and Kitchener cities planned for the future. Lastly, the Rural Water Quality program was developed in 2001 to help farmers maintain the quality of the river water running through their farms (GRCA, 2014).

Since anthropogenic non-point inputs of phosphorus from croplands are associated with soil erosion and runoff, soil erosion may influence the PP:SRP ratio as well as the TP fluxes in streams (Liu et al., 2000). Many studies in the literature have identified that phosphorus flux is significantly impacted by extensive agriculture practices, which may leave soils vulnerable to erosion and exposes the soil phosphorus to runoff (Boomer et al., 2012; Powers et al., 2013; Coulter et al., 2004). However, it is still unclear whether agriculture has increased over the years since we are seeing an increase in animal agriculture but a decrease in fertilizer use over time. The PP decrease in UGR in the 2000's may not be significant since values are substantially lower than the values in the more downstream regions. The more or less stable loads and concentrations over the years in the UGR, suggest that population and land alterations are the major factors contributing to the changes in the phosphorus loads in the Grand River watershed.

As predicted, prior to the 1970's, the high SRP and PP fluxes and concentrations were correlated with high SRP from WWTP discharges and high fertilizer application, respectively. After the ban in detergent phosphates in the 1970's, the SRP load and concentration decreased. As expected, this decrease was more prevalent in the central part of the Grand River where most urbanization is found. The PP decreased in the 1980's, in correspondence with the decrease in fertilizer use which began after the year 1980. In the 2000's both SRP and PP increased. The increase in SRP correlated with a large increase in livestock numbers but the constant increase in population could also be a factor. Large population is also the reason we see higher loads and concentrations in the CGR where most of the urban development and large WWTPs are. PP increase in more recent years may be due to increased PP in runoff from phosphorus desorption in the soil due to increased land alteration and a legacy effect of fertilizer. Generally, SRP loads seem to have been controlled by point sources from WWTP's in the 1960's and 1970's while recently it seems to have shifted to non-point sources from animal manure. Historically, non-point fertilizer application might have controlled the PP loads in the Grand River but more recently, other factors such as land use may be affecting it as well. Higher SRP loads and concentrations are observed in the CGR due to the high population and urbanization. While SRP and PP loads increase from upstream to downstream due to nutrient accumulation, the increase in PP concentration in the LGR can be attributed to its clay-dominated basin.

Chapter 5

Conclusion

Phosphorus loadings were examined in this thesis to gain a better understanding of what has occurred in the Grand River watershed historically. Long-term historical nutrient data available through the PWQMN were examined from 1965 to 2010 to identify any indications of changing phosphorus loads spatially and temporally. TP, SRP, and PP were analyzed as all three nutrients are important in determining the fate of the water quality in the Grand River. Other environmental and physical attributes in the Grand River amassed from different sources were also examined in anticipation of identifying possible factors that may be driving the patterns that were observed.

Increases in animal farming, population, land cover alteration and decrease in fertilizer are observed in the Grand River watershed over the years. These changes over time may have affected the biogeochemistry of the river temporally. Generally, TP, SRP, and PP had about three distinct time periods where changes were observed over time. SRP loads were high before the phosphorus ban in detergents in 1973, they decreased in the 1970's after the ban; in the 1980's they stayed more or less stable despite the constant increase in population which may have been due to improvements to WWTPs; and in the 2000's the loads started to increase again which could have been due to increasing population and a distinct increase in animal farming. PP loads were high prior to the late 1970's due to high fertilizer application, the loads then began to decrease in the 1980's which may correspond to the declines in fertilizer application after 1980; they also seems to be on an increasing trend in the 2000's which may be due to land alteration and a legacy effect of intensive historical fertilizer application. The PP:SRP ratio was high prior to the mid 1970's because there was more PP from fertilizer and less SRP from WWTPs, it decreased in the 1980's which may have been caused by the decline of fertilizer application after 1980, and in more recent years it seems to be increasing but we cannot confirm this until more statistical tests are done for it. Daloğ lu et al., (2012) found that two watersheds in the Lake Erie basin have experienced an increase in phosphorus loads from 2000 to 2010, which corresponded with an increase in extreme storms events. Seasonal variation is an essential factor in phosphorus dynamics and it should be examined in greater detail to determine whether or not seasonal phosphorus trends have shifted over the years and what implications this change may have on the concentration and load patterns.

Spatial patterns observed were as predicted. TP, SRP, and PP concentrations and loads increase from upstream regions to downstream regions. This can be explained by the differences in land-use and geology between the three parts of the watershed as well as the accumulation of nutrients and sediments by the river as it travels downstream from the headwaters. The highest TP and SRP loads and concentrations fluctuated between the CGR and the LGR which is expected since the largest WWTP and most tile drainages are located in the middle of the watershed but the LGR receives nutrient accumulated from the upper reaches. The LGR had higher PP loads due to a more clay-dominated basin.

This thesis contributes to the understanding of the impact of land use and climate change on an important nutrient that contributed to water quality degradation. It is the first detailed long term analysis carried out on phosphorus in the Grand River which is home to almost a million people and is culturally and economically important. This study provides a historical framework in which to assess ongoing efforts to restore water quality in the watershed and prevent it from further exacerbation.

Appendix A
Tables

Table 2. Characteristics of the three regions in the Grand River watershed, the UGR, CGR, and the LGR.

Region	Area (km^2)	% Area	Main Stem Length (km)	% Urban Land-use
UGR	585	9	35	4
CGR	3167	47	110	56
LGR	3015	45	138	40
Total	6767	100	283	100

Table 3. Population and WWTP characteristics in the three regions of the Grand River Watershed, the UGR, CGR, and the LGR.

Region	Pop. Density (people/km^2)	Number of WWTP	Population Served	Total Capacity (m^3/day)
UGR	113	2	2889	1.73E+03
CGR	170	13	420404	3.29E+05
LGR	122	14	103184	1.10E+05
Total		29	526477	4.41E+05

Table 4. Percent land-use in the three regions of the Grand River Watershed, the UGR, CGR, and the LGR for the year 2007.

Land Cover	UGR	CGR	LGR
Agriculture	70	69	72
Urban	5	12	9
Wetland	22	12	10
Forest	3	7	8
Total	100	100	100

Table 5. UGR, CGR, and LGR characteristics.

Region	Station numbers	Data coverage	Gaps	Elevation (m.a.s.l)	Slope Erosion (km2)	% Slope Erosion
UGR	9002, 3902	1977-2010	1978, 1994	530-475	0.29	0.04957265
CGR	1002, 1102	1965-2009		475-310	20	0.631512472
LGR	3502, 3583	1974-2010		310-170	34	1.127694859

Table 6. Abbreviation used in this thesis and their definitions.

Abbreviation	Antonym
TP	Total Unfiltered Phosphorus
SRP	Soluble Reactive Phosphorus
PP	Particulate Phosphorus
WWTP	Wastewater Treatment Plant
GRCA	Grand River Conservation Authority
PWQMN	Provincial Water Quality Monitoring Network

Appendix B
Figures

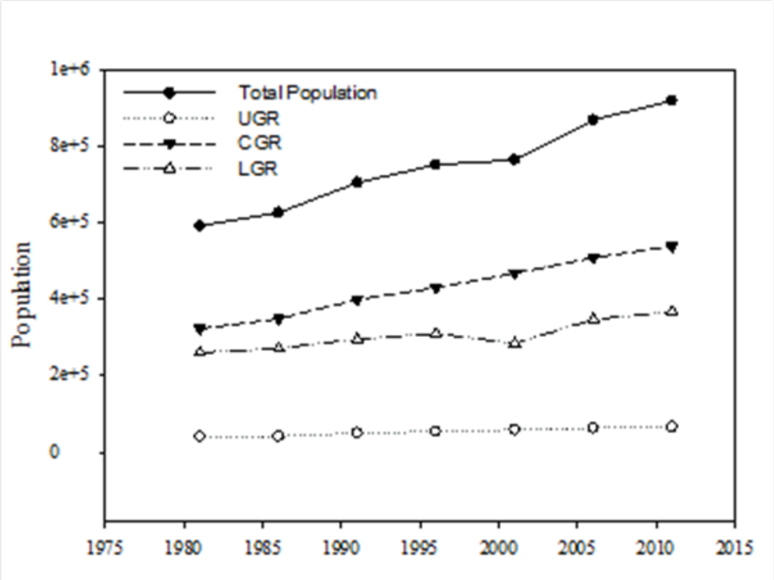

Figure 4. Census population in the Grand River watershed from 1981-2011 in 5 year intervals. Each region's population is a percentage of the counties within that watershed. The exception is the middle region where the major cities lie and their populations were included separately from their associated counties.

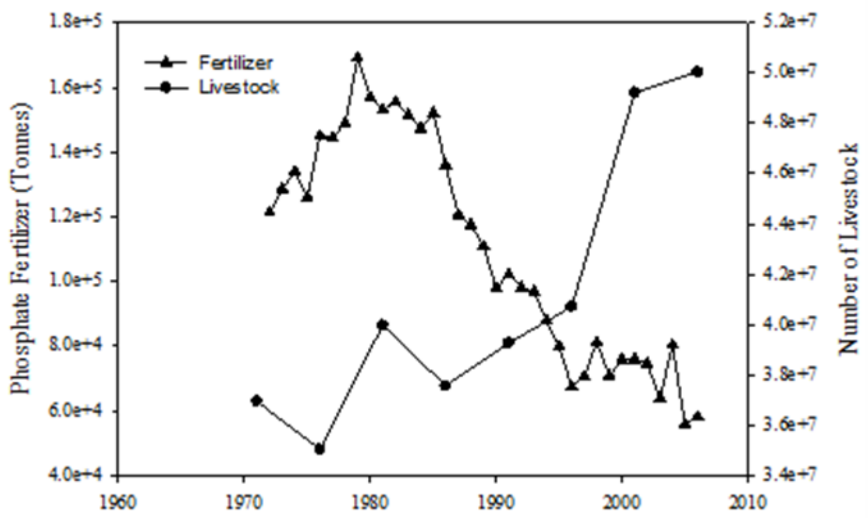

Figure 5. Phosphate fertilizer sales in Ontario from 1972-2006 and total number of farmed animals (Cows, pigs, and chickens) number in 5 year intervals years from 1971-2006. Source: z- 1972-2002 (Korol, 2002), 2003-06 (CFIS, 2011); total livestock number (Statistics Canada, retrieved on May 16th 2012 from (http://odesi1.scholarsportal.info.proxy.lib.uwaterloo.ca/webview/)

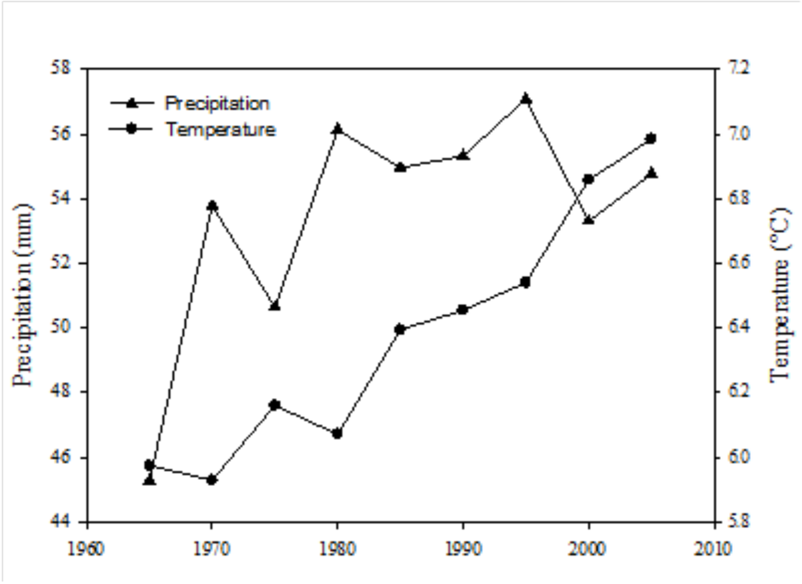

Figure 6. Temperature and total precipitation of a single station in the western basin of the Grand River, over 5-6 year time periods from 1965-2009. This station was chosen to represent the temperature and precipitation in the whole watershed because it was far from any cities where anthropogenic warming may influence the results.

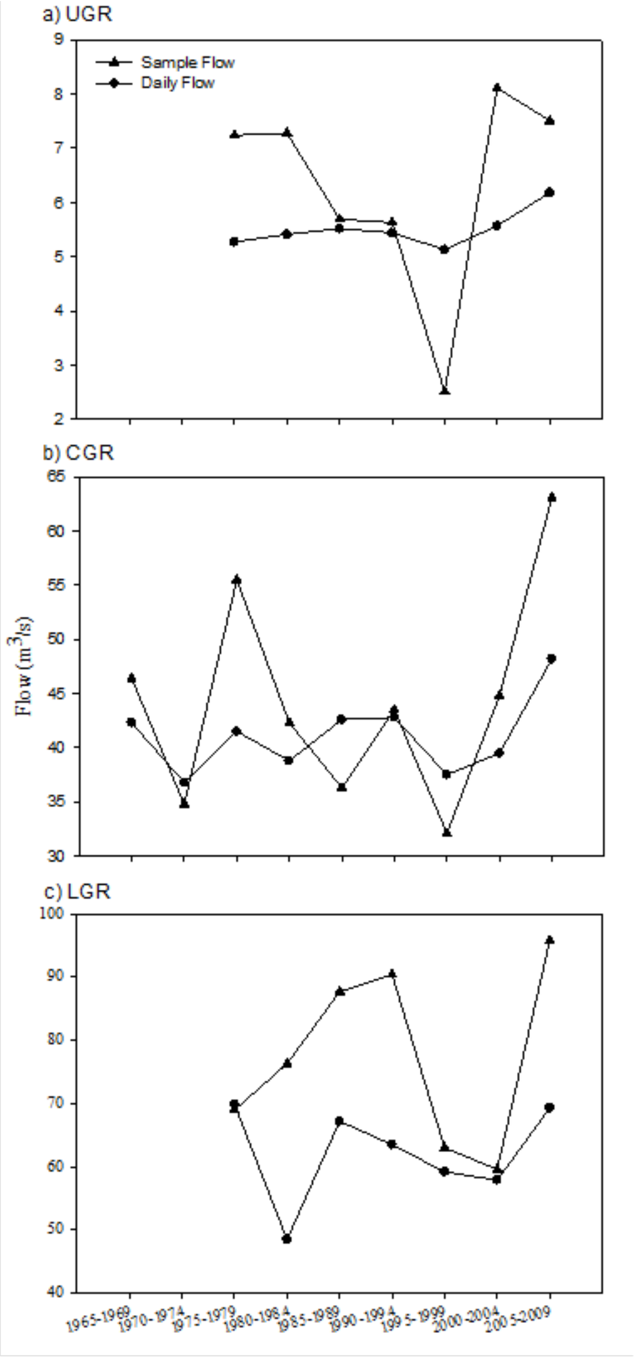

Figure 7. Flow corresponding concentrations and daily flow averages, samples in the three regions of the Grand River from 1975-2009 displayed on a time scale of 5 year intervals. Note: There are missing years in the flow corresponding concentrations for the UGR (1978, 1994).

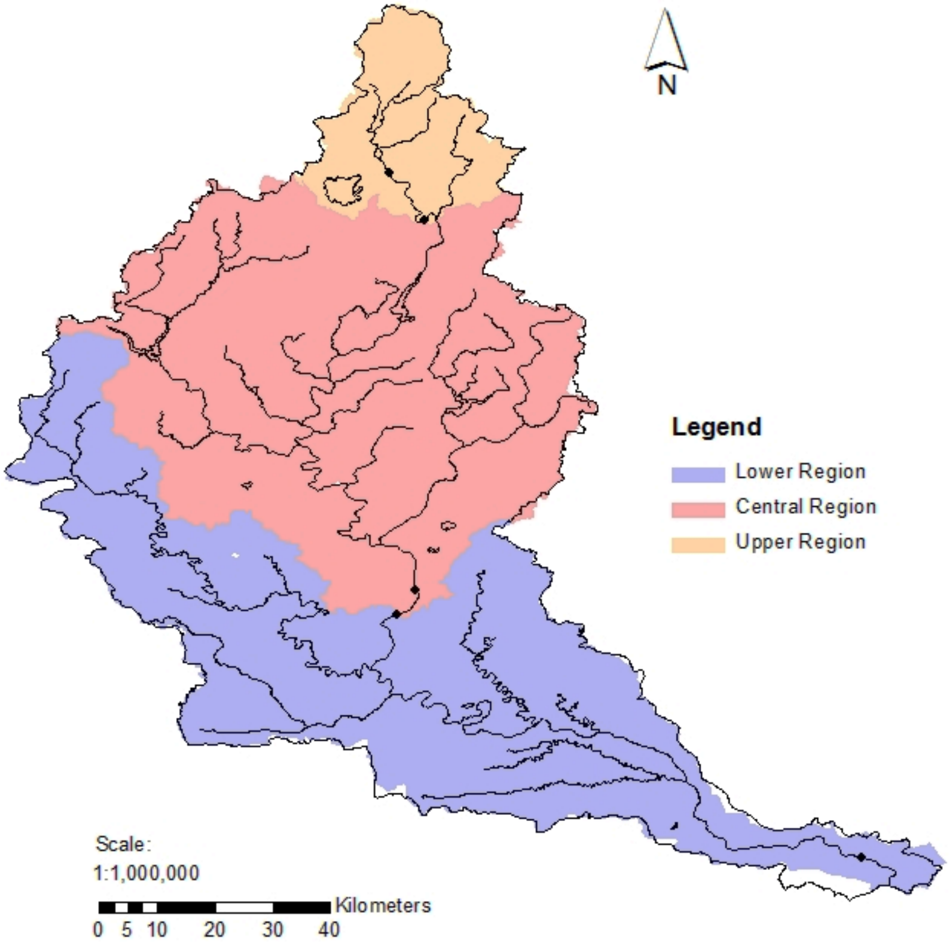

Figure 8. The Grand River watershed and the regions we explored for the long-term nutrient trend. The black dots are the sites analyzed in this project.

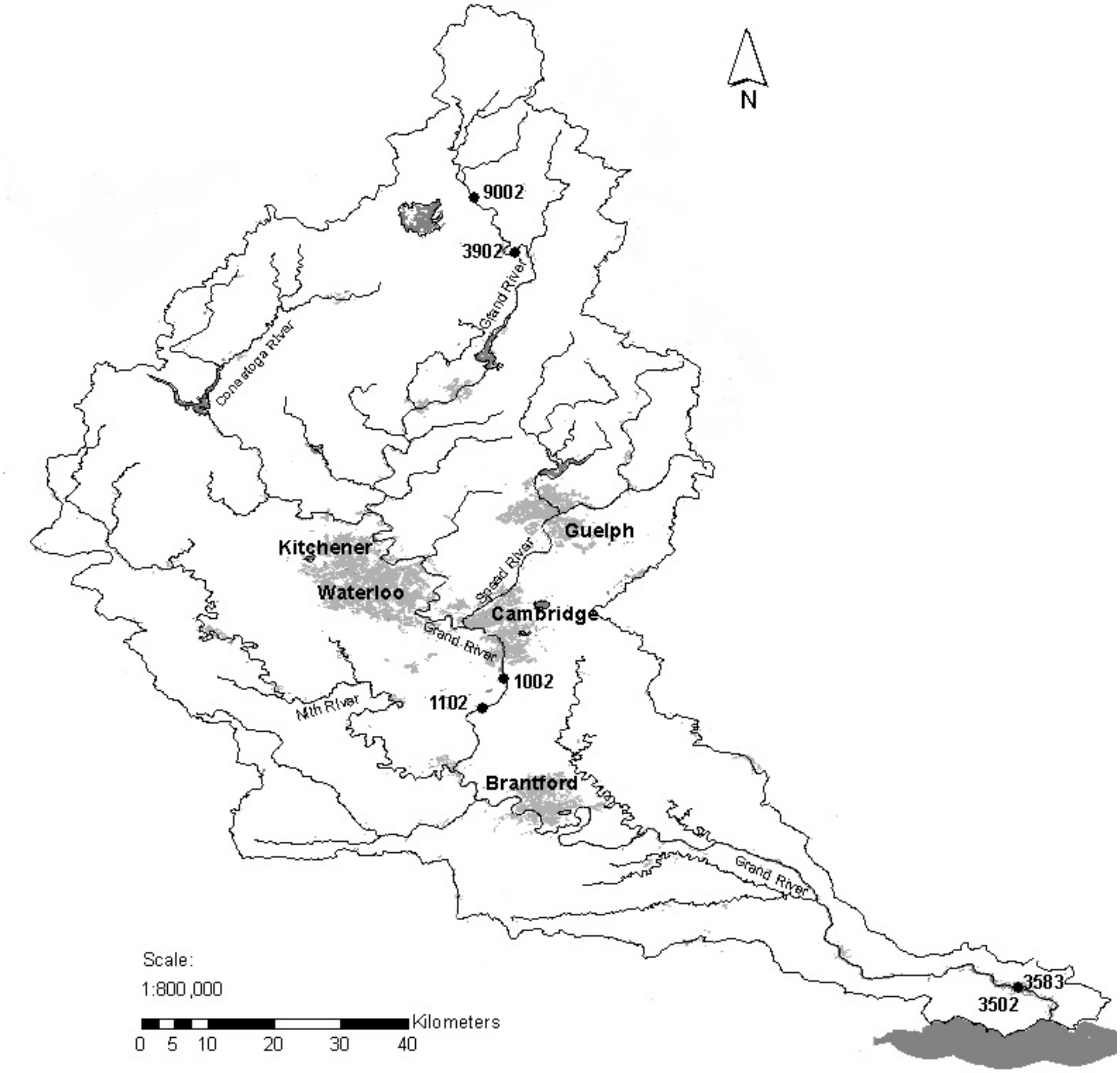

Figure 9. Grand River watershed map with sites, major cities, and major tributaries.

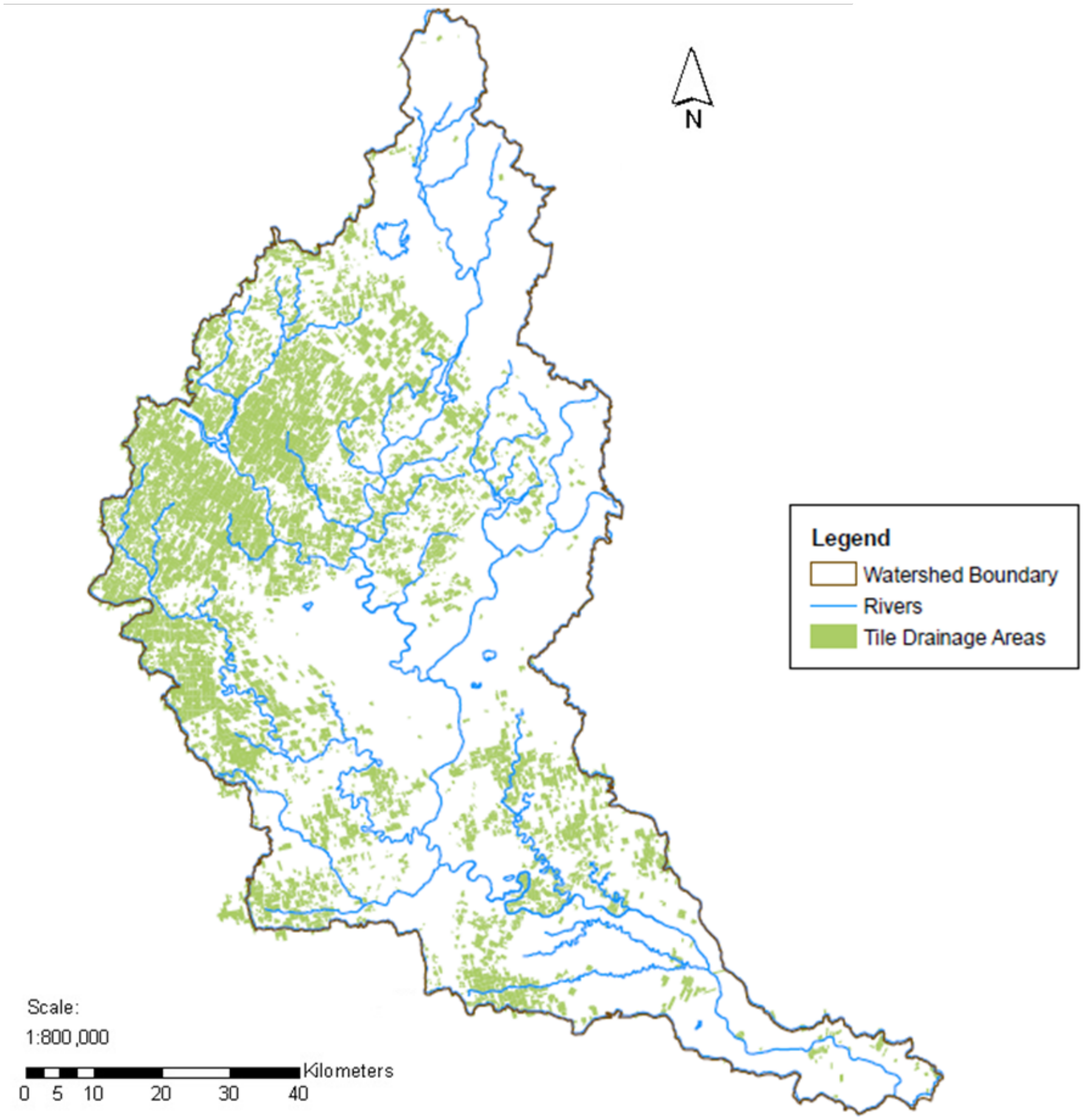

Figure 10. Tile drainage areas in the Grand River watershed.

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