# FACTORS INFLUENCING WATER QUALITY IN A LARGE RIVERINE SYSTEM

# A LANDSCAPE APPROACH TO EVALUATE SOURCES OF NUTRIENT AND SEDIMENT TO THE NOTTAWASAGA RIVER, A TRIBUTARY OF GEORGIAN BAY, LAKE HURON

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## LAY ABSTRACT

Eutrophication from agricultural runoff is a global problem, often resulting in formation of anoxic zones. The Nottawasaga River Watershed is dominated by agricultural land-use, and is a major source of nutrients and sediment to Georgian Bay, Lake Huron. The objective of our study was to develop a holistic understanding of sources and processes that influence spatial variation of water quality across the Nottawasaga River. We found that landscape features (drainage area, pasture, wetland), tributary inputs, and in-stream processes (riffles, substrate) significantly influence water quality. Our results will enhance restoration initiatives to improve health of riverine systems at a watershed scale.

## GENERAL ABSTRACT

Eutrophication from agricultural runoff is a global problem, often resulting in formation of anoxic zones in receiving water bodies. The Nottawasaga River Watershed (2,900 km$^2$) is dominated by agricultural land-use, and is a major source of nutrients and sediment to Nottawasaga Bay, Georgian Bay (Lake Huron). The primary objective of our study was to develop a holistic understanding of the different sources and processes that influence spatial variation of water quality across the Nottawasaga River (121 km). In our first chapter, we use landscape features to develop 6 models that predict daily base flow loading rates of total phosphorus (TP) and total suspended solids (TSS) from 11 sub-watersheds. We found that drainage area and % pasture land were the most significant predictive variables driving spatial variability in TP and TSS loading. We also found a significant positive relationship between TP and % wetland, suggesting that the Minesing Wetlands (largest inland wetland in southern Ontario) are a source of nutrients to the river. In our second chapter, we evaluate how tributary inputs and in-stream processes contribute to the longitudinal variation in water quality along the Nottawasaga River. We found that tributary concentration and discharge significantly predict downstream turbidity (TURB), but do not predict downstream TP. We also found that riffles improve water clarity, and that silt and clay substrate is significantly associated with high TURB. In our third chapter, we develop a Stream Water Quality Index (SWQI) using 13 variables collected at 15 stations along the Nottawasaga River. To predict SWQI scores for any site, we have provided 9 equations that use various combinations of available variables. Understanding landscape variables, as well as tributary and in-stream processes that

influence water quality will enhance the development of restoration initiatives to improve ecosystem health in lotic systems at a watershed scale.

## ACKNOWLEDGEMENTS

There are many individuals whom I would like to acknowledge for making the completion of this thesis possible. First and foremost, I would like to thank my supervisor Pat for all her guidance over the past few years. I don’t think there are many supervisors out there who would dedicate an entire day of their winter vacation to work through my dataset to tease out the story of the Nottawasaga River and the Minesing Wetlands, and for that I am grateful. Pat’s passion for ecology is inspirational, which keeps our lab motivated. She is always ready to head over to the Phoenix for a drink with us, which makes long days in the lab not only rewarding, but also a lot of fun. I would also like to thank Mike Waddington for his help during committee meetings, and Susan Dudley for chairing my defence.

The Nottawasaga Valley Conservation Authority was a huge help throughout the field season, and provided us with delineated watersheds and land cover data for our study area. Dave Featherstone and Fred Dobbs provided their expertise and experience working in the Nottawasaga River to help us determine monitoring stations and access points to the river. In particular, I would like to thank Ian Ockenden for all his help throughout this project. Ian was always quick to answer any questions I had, provide us with data, and lend us equipment. Ian and his team were vital to the success of our continuous monitoring efforts in Willow Creek, where he lent and deployed a YSI in the Minesing Wetlands for us. He also helped us measure stream discharge in unwadable parts of the river, and collected all of our storm flow samples.

Each spring, my father Terry Rutledge and boyfriend Sean Arscott put their crafty engineering skills to good use and helped me design and build contraptions for our field equipment. Without their assistance, our loggers likely would not have been able to withstand the high flows of the Nottawasaga River. My mother Terie Rutledge was my number one supporter, and was always ready with a motivational speech any time I needed one. I would like to extend a huge thank you to all the amazing graduate students and field technicians that helped me collect data and process water samples during the 2014 and 2015 field seasons. Without the hard work and paddling finesse of Dan Weller, James Marcaccio, Nick Luymes, Chantel Markle, Chris Biberhofer, and Massimo Narini, we would have never been able to sample all 15 of our sites in one week each month. Stuart Campbell, Mike Bredin, and Steve Savoie were vital to the success of my last field season. They battled the Minesing Wetlands (which earned the name “The Menacing” Wetlands) with me countless times; facing swarms of mosquitos and deerflies, and dodging burns from giant hogweed and climbing poison ivy. A special thanks to Dan, Nick, Stuart and Steve for paddling the entire 121 km of the Nottawasaga River in a week to complete the longitudinal survey (sorry for not warning you about the mini waterfall). Overall, I think that we can all agree that the Nottawasaga River is definitely “Notty”, not nice! Once again, thank you all so much for tackling the Nottawasaga River and Minesing Wetlands with me.

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| | |
|---|---|
| AGC | Agricultural (crop) land-use |
| AGP | Agricultural (pasture) land-use |
| BAR | Barren land cover |
| BMP | Best Management Practise |
| BN | Boyne River |
| BR | Bear Creek |
| *C* | Concentration |
| CANWET | Canadian Nutrient and Water Evaluation Tool |
| CEQG | Canadian Environmental Quality Guidelines |
| CHL | Chlorophyll-α |
| $Cl^-$ | Chloride |
| COND | Conductivity |
| dArea | Drainage area |
| DO | Dissolved Oxygen |
| FOR | Forest land cover |
| GIS | Geographic Information System |
| IN | Innisfil Creek |
| *L* | Loading rate |
| MB | Mad River Breach |
| ML | Marl Creek |
| MR | Mad River |

| | |
|---|---|
| mSg | Mean slope gradient |
| MT | McIntyre Creek |
| N | Nitrogen |
| NAESI | National Agri-Environmental Standards Initiative |
| NRW | Nottawasaga River Watershed |
| NVCA | Nottawasaga Valley Conservation Authority |
| OLS | Ordinary Least Squares |
| P | Phosphorus |
| PCA | Principal Components Analysis |
| PN | Pine River |
| PWQMN | Provincial Water Quality Monitoring Network |
| PWQO | Provincial Water Quality Objective |
| $Q$ | Discharge rate |
| sOrg | Organic soils |
| sSand | Sandy soils |
| SWQI | Stream Water Quality Index |
| TAN | Total Ammonia Nitrogen |
| TC | Thornton Creek |
| TEMP | Temperature |
| TN | Total Nitrogen |
| TNN | Total Nitrate Nitrogen |
| TOSS | Total Organic Suspended Solids |

| | |
|---|---|
| TP | Total Phosphorus |
| TSS | Total Suspended Solids |
| TURB | Turbidity |
| UN | Upper Nottawasaga River |
| URB | Urban land cover |
| WET | Wetland land cover |
| WL | Willow Creek |
| WQI | Water Quality Index |

## DECLARATION OF ACADEMIC ACHIEVMENT

This thesis is composed of three chapters. Dr. Patricia Chow-Fraser and I designed the field monitoring programs conducted in each chapter. Storm flow water sample collection and YSI deployment in Willow Creek was carried out by the Nottawasaga Valley Conservation Authority (NVCA). I led the collection of all other samples, as well as the deployment and maintenance of monitoring equipment. I completed all sample processing, and carried out all landscape and geospatial analyses in a Geographic Information System. Land cover data and delineated sub-watersheds were generously provided to us by the NVCA. Dr. Patricia Chow-Fraser and I performed all statistical analyses described in this thesis.

## GENERAL INTRODUCTION

Rivers are dynamic systems that play a crucial role in the global hydrological cycle. They transport nutrients and sediment between regions, creating river sections with distinct physical and chemical characteristics that support a variety of organisms (Smith & Hollibaugh, 1993; Aufdenkampe et al., 2011). Since most of the Earth's surface drains into rivers, increasing anthropogenic land-uses are altering natural loading (Das Gupta, 2008). Intensification of agricultural practices, including fertilizer application, tilling, and cattle grazing have led to significant increases in loading of nitrogen (N), phosphorus (P), and sediment in many riverine systems throughout the world (Sharpley et al., 1994, 2003; Carpenter et al., 1998; Goolsby et al., 2000; Dieleman & Chow-Fraser, 2012). This loading can be visualized as a dark plume of sediment entering bays and estuaries. Such a plume has been seen flowing out of the Nottawasaga River into Nottawasaga Bay, Georgian Bay (Lake Huron), which spreads northeast along the shoreline towards Woodland Beach or southwest along the shoreline towards Wasaga Beach. The runoff not only affects the ecology of the near-shore ecosystem of Nottawasaga Bay, it also threatens the socio-economic vitality of Wasaga Beach, the longest freshwater beach in the world, which attracts millions of visitors and seasonal residents each year.

Pollutants in the plume are more pronounced after storm events. The high nutrient inputs from runoff can lead to nuisance algal blooms. When the algae die, their decomposition can lead to anoxic zones near the substrate, a condition that favours proliferation of resident type E botulism bacteria (*C. botulinum*; Yule et al., 2005). Biomagnification of this neurotoxin has caused substantial avian and fish kills throughout

Wasaga Beach and Tiny Township, including 120 Lake Sturgeon during the fall of 2011 (Hopper, 2011). Most recently, avian kills reached 78 in October 2015 (Rowe, 2015). Algal blooms have yet to be observed in the bay, but have been reported in the lower section of the river due to high P concentrations and low flow velocities.

*Site description*

The Nottawasaga River Watershed (NRW) drains 2,900 $km^2$ of the Lake Huron sub-basin into the Nottawasaga River, which eventually flows into Nottawasaga Bay in southeastern Georgian Bay. About half of the NRW is agricultural land-use, 70% of which is specialty crops (Post, 2014), and is the probable source of sediment and nutrient enrichment in the river and in the bay. This has become an environmental concern because Nottawasaga Bay features one of the most popular stretches of beach in Ontario, with many summer resorts and cottages. The river also bisects the Minesing Wetlands, a Ramsar site and the largest contiguous inland wetland (6,000 ha) in southern Ontario (Ramsar, 1996; Frazier, 1999). The river itself is also very unique, flowing through a variety of geological landscapes (Niagara Escarpment, Simcoe Uplands, Oak Ridges and Oro Moraines) and is the only tributary of Georgian Bay with confirmed spawning populations of Lake Sturgeon, which is currently listed as a species at risk within Ontario.

The functions of the Minesing Wetlands are critical. Every year, they hold back large volumes of water from spring melt and prevent flooding in low-lying downstream areas such as the town of Wasaga Beach. The vast wetland complex provides various habitats that support diverse assemblages of plant and animal species, including species at risk (lake sturgeon, Blanding’s turtle, wood turtle, Hine’s emerald dragonfly; Bowles et al., 2007), all of which require good water quality in order to persist. Due to its large size and difficult terrain for field campaigns, research in the Minesing Wetlands has been scarce, but recent studies have shown that water quality on the more accessible northern portion of the wetland is impaired (Post et al., 2010; Brown et al., 2011), with significantly higher concentrations of total phosphorus (TP), turbidity (TURB), and chlorophyll-$\alpha$ (CHL) as the river exits the Minesing Wetlands compared with levels in upstream segments of the Nottawasaga River (Chow-Fraser, 2006). Given that the Nottawasaga River is the largest tributary that discharges into Georgian Bay, it has the potential to greatly impact the water quality of Nottawasaga Bay and Georgian Bay itself.

*Thesis objectives*

The overall goal of this thesis is to present a comprehensive understanding of the Nottawasaga River system. In the first chapter, we will examine how landscape features (geomorphology and land cover) drive spatial variation in nutrient and sediment loading from 11 sub-watersheds to the Nottawasaga River. The second chapter will relate how tributary loading and other in-stream processes (riffles, substrate, dissolved oxygen) contribute to the longitudinal variation in water quality along with middle and lower reaches of the Nottawasaga River. Finally, in the last chapter we use 13 water quality variables to develop a Stream Water Quality Index (SWQI) to identify critical areas in the NRW that are most at risk. This thesis will provide environmental agencies with useful information to help implement management strategies to improve the health of riverine systems at a watershed scale.

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## CHAPTER 1

## Landscape characteristics driving spatial variation in total phosphorus and sediment loading from sub-watersheds of the Nottawasaga River, a tributary of Georgian Bay, Lake Huron

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**Abstract**

Eutrophication from agricultural runoff is a global problem, often resulting in formation of anoxic zones in receiving water bodies. The Nottawasaga River Watershed (NRW) is dominated by agricultural land-use, and drains into Nottawasaga Bay, Georgian Bay (Lake Huron). A fundamental feature of the NRW is the Minesing Wetlands, a Ramsar site and the largest inland wetland in southern Ontario. We used total phosphorus (TP) and discharge data (including storm flows) to estimate annual loading from six sub-watersheds and compared these against published nutrient export, landscape, and CANWET models. Our results were consistently overestimated by published models, which did not offer a way to account for the unique properties of the Minesing Wetlands. We were able to accurately predict measured daily summer base-flow loading rates of TP ($r^2$ = 0.76, $p$ = $<$0.0001) and total suspended solids (TSS; $r^2$ = 0.65, $p$ = $<$0.0001) for 11 sub-watersheds using geomorphic and land-cover variables. Drainage area and % pasture land were the most significant predictive variables driving spatial variability in TP and TSS loading rates among sub-watersheds. The positive relationship between TP and % wetland ($r^2$ =0.22, $p$ = 0.0063) also suggested that the Minesing Wetlands are a source of nutrients to the Nottawasaga River. Watershed geomorphology (e.g. slope) was a good predictor of land cover, and produced accurate loading estimates. This study is the first to offer a new approach to predict TP and TSS loading rates during the growing season using readily available geospatial data.

**Key words:** phosphorus, suspended solids, loading, watershed, Minesing Wetlands

**Introduction**

Eutrophication is strongly influenced by agricultural runoff, and has become a major environmental problem globally (Matson et al., 1997; Smith, 2003). The positive relationship between nutrient loading and agricultural land-use is well documented (Carpenter et al., 1998); the primary nutrients, phosphorus (P) and nitrogen (N), originate from both pasture land (including livestock) and crop land, with pollutants entering watercourses through runoff contaminated with fertilizers and livestock manure (Reckhow et al., 1980; Beaulac & Reckhow, 1982; Johnes, 1996; Chambers & Dale, 1997). Both practices also increase sediment loading through livestock grazing and tilling, which loosens soil particles and leads to soil erosion from pasture and crop land respectively (Fullen, 1985; Dunne et al., 2011).

The Nottawasaga River Watershed (NRW), located in south central Ontario, is a relatively small (2,900 $km^2$) watershed, but a major source of nutrients and sediment to Nottawasaga Bay (Chow-Fraser, 2006; Brown et al., 2011) because of its predominant agricultural land-use (Greenland International Consulting Ltd., 2006). The runoff not only affects the ecology of the near-shore ecosystem of Nottawasaga Bay, it also threatens the socio-economic vitality of the region since the outflow of the Nottawasaga River is adjacent Wasaga beach, which attracts millions of visitors and seasonal residents each year. Another unique feature of the NRW is the Minesing Wetlands, a Ramsar site and Provincially Significant Wetland, and the largest contiguous inland wetland in southern Ontario (6,000 ha; Ramsar, 1996; Frazier, 1999). Although wetlands are known to filter out nutrients and sediment from upstream sources, Chow-Fraser (2006) found elevated levels of phosphorus, turbidity, and chlorophyll-α in the Nottawasaga River after it ran through the Minesing Wetlands, and hypothesized that the wetlands no longer provide nutrient and sediment filtration as an ecosystem function.

A simple and inexpensive approach to determine the total nutrient or sediment budget for a watershed is to apply published export coefficients to areal extent of specific land-use (human-altered; agriculture, urban) or land cover (natural; forest, wetland) classes (Johnes, 1996; Winter & Duthie, 2000). For these calculations, many export coefficients have been published for a variety of agricultural practices, but most of these have been developed with data from U.S. watersheds, and only a few exist for Canadian watersheds (Jones et al., 2001). The few exceptions include Chambers and Dale (1997), which examined nutrient loading from non-point sources in northern Canada (Alberta and Northwest Territories), and Dillon and Kirchner (1975), which measured phosphorus export in predominantly forested watersheds in southern Ontario. To date, no published studies have examined geomorphic and land-cover influences on total phosphorus (TP) and total suspended solids (TSS) loading for agricultural land-uses in Ontario, nor has any considered the potential influences of a large inland freshwater wetland complex. Perhaps a more serious problem is that many coefficients have been developed with base flow data, without any consideration of storm flow, which could greatly elevate nutrient and sediment concentrations in the river. The extent to which these information gaps may impede accurate assessment of the impact of pollutant loading to Nottawasaga Bay is unknown, and should be investigated given the ecological and socio-economical importance of this region.

The objectives of this study are four-fold. First, we will determine if existing loading models can be applied directly to the NRW. Secondly, we will determine how inclusion of storm flow data may improve the predictive power of annual loading models. Thirdly, we will develop predictive landscape models for TP and TSS that are specific to the NRW and lastly, we will use readily available geospatial data to estimate nutrient and sediment loading for the NRW. Specifically, we test the hypothesis that watershed geomorphology drives spatial variation in TP and TSS loading rates and that larger sub-watersheds with high proportions of agricultural land-use (crop and pasture land) will contribute to higher TP and TSS loading. This is the first comprehensive study of an agriculturally dominant watershed in south central Ontario in which we model nutrient and sediment loading based solely on geomorphic and land-cover features at a regional scale. Results from this study will reveal landscape characteristics that are most influential to nutrient and sediment loading within south central Ontario and permit environmental management agencies to implement appropriate conservation strategies at the scale of sub-watersheds.

## Methods

### *Study area*

We monitored 11 sub-watersheds of the NRW, all of which drain fourth or fifth order streams and eventually discharge into the main branch of the Nottawasaga River (Table 1.1; Figure 1.1). These sub-watersheds include the Upper Nottawasaga River (UN), Innisfil Creek (IN), Boyne River (BN), Thornton Creek (TN), Pine River (PN), Bear Creek (BR), the Mad River where it breaches the natural bank (MB), Mad River

(MR), Willow Creek (WL), Marl Creek (ML), and McIntyre Creek (MT).

*Sampling procedures*

In a preliminary study conducted in 2014, Rutledge et al. (2015) determined that base flow TP concentrations in the Nottawasaga River were highest during July; therefore, we sampled 11 tributaries for TP and TSS once during this month to capture maximal base flow loading rates. We ensured that samples and discharge measurements were representative of loading rates from the entire sub-watershed by locating the sampling site of each tributary as close as possible to its outflow to the Nottawasaga River. We measured discharge within tributaries of the 11 sub-watersheds during base flow conditions at the time of sample collection. Following the Ontario Stream Assessment Protocol (OSAP; Stanfield, 2010), we used the velocity-area method and a SonTek FlowTracker Acoustic Doppler Velocimeter (ADV™) to measure tributary discharge.

We used a Van Dorn sampler to collect discrete samples at each station in freshly acid-washed Corning™ snap-seal containers or Nalgene™ bottles for measurements of TP and TSS (Lind, 1974; Crosbie & Chow-Fraser, 1999). Once collected, all water samples were stored on icepacks in a cooler and placed in a freezer (within 6 hours) for storage until they could be transferred back to McMaster University for processing. All grab samples were taken from mid-depth against the current to ensure the samples were thoroughly mixed (Barton, 1977; Shelton, 1997; Poor & McDonnell, 2007).

Willow Creek flows through a substantial portion of the Minesing Wetlands before it discharges into the Nottawasaga River. As no previous studies have accounted for potential influences of the Minesing on the water quality of this tributary, we carried out additional studies to compare dissolved oxygen (DO) concentrations in Willow Creek with those in several tributaries that do not drain the Minesing Wetlands (Innisfil Creek, Marl Creek and Pine River). We obtained daytime measurements of DO once each month during July and August 2015 using a YSI 6920 V2 sonde with an optical DO sensor. We also installed an ISCO 6712 automatic sampler and a YSI EXO1 sonde in Willow Creek to continuously monitor TP and DO from June to August 2015 inclusive. The ISCO sampler was programed to collect 250 mL of water every 6 hours, which filled a 1 L sample bottle over a 24-hour period. Daily composites were collected every 4 – 14 days, and were replaced with freshly acid-washed 1 L bottles. Sub-samples from daily composites were transferred into acid washed Corning™ snap-seal containers, which were kept frozen until they could be processed. Sub-samples were representative of mean daily TP concentrations. We programed the YSI EXO1 to record DO in situ every two hours, taking simultaneous measurements when the ISCO collected water samples. Prior to analyses, we calculated mean daily DO concentrations.

*Sample processing*

All nutrient and sediment samples were processed in triplicate. TP concentrations were determined with the molybdenum blue method (Murphy & Riley, 1962) following potassium persulfate digestion in an autoclave for 50 minutes (120°C, 15 psi). Absorbance values were read with a Genesys 10 UV Spectrophotometer and final TP concentrations were calculated with a standard curve. Known aliquots of river water was filtered through GC filters (0.45 µm) and subsequently used to calculate concentrations of

TSS. All filters were pre-weighed before samples were filtered. Filters were then folded in half and kept in small plastic petri plates and placed in a freezer. When we were ready to process the TSS samples, filters were retrieved from the freezer and placed on a crucible of known weight to be dried in the oven for 1 hour at 100°C; subsequently, they were placed in a dessicator for an additional hour, and then weighed to the nearest 0.1 mg.

*Landscape analysis*

All landscape variables were analyzed in a Geographic Information System (GIS; ArcMap 10.3; ESRI Inc., Redlands, California). Landscape variables included both geomorphic and land-cover variables (Table 1.2). Geomorphic variables included drainage area (dArea; area of the sub-watershed), mean slope gradient (mSg; the average slope within the sub-watershed), as well as the percent of sandy (sSand) and organic (sOrg) soils within the sub-watershed. We followed a standardized global reference system to reclassify the NRW into seven main types of land cover (refers to both human-altered land-uses and natural areas in this paper): crop (AGC), pasture (AGP), urban (URB; built-up pervious and impervious surfaces, golf courses, recreational areas), forest (FOR), wetland (WET), barren (BAR; beaches, transitional areas, extraction), and water (note that this category included <1% of the total watershed area and was subsequently removed from further analyses). We subsequently determined the total area and percent cover of each land-cover class within each sub-watershed (Table 1.2).

*Loading calculations*

Use of export coefficients in models to estimate loading has been widely practiced in North America and Europe (Dillon & Kirchner, 1975; Reckhow et al., 1980; Beaulac & Reckhow, 1982; Johnes et al., 1996). The basic equation that describes the export coefficient model is as follows:

$$L_x = \sum_{i=1}^{m} c_i \, A_i \qquad \text{Eq. (1)}$$

where $L$ is the loading rate of constituent $x$ (TP or TSS) from land (kg/year), $m$ is the number of land-cover classes, $c_i$ is the export coefficient for land cover class $i$ (kg/ha/year), and $A_i$ is the area of land-cover class $i$ (ha) (Soranno et al., 1996). We applied export coefficients from published studies to this equation to calculate TP and TSS loading rates for each sub-watershed (Table 1.3).

Jones et al. (2001) published a landscape model in the Chesapeake Bay Basin that predicted TP and TSS loading rates. Two equations developed by their model are as follows:

$$\log(\text{TP}) = 0.840 + 0.025 \text{ purb} - 0.026 \text{ ripf} \qquad \text{Eq. (2)}$$

$$\log(\text{TSS}) = 8.472 + 0.079 \text{ purb} - 0.116 \text{ pwetl} - 0.038 \text{ ripf} \qquad \text{Eq. (3)}$$

where TP and TSS represent the annual loading rate (kg/ha/year), purb and pwetl are the percent of urban and wetland land cover in the sub-watershed respectively, and ripf is the percent of riparian forest adjacent to the stream edge (within a 30m x 30m buffer).

We collected field data and amalgamated federal climate and discharge data to estimate annual loading rates in the NRW. We compared these estimates to annual loads predicted with published export coefficients (Table 1.3; Dillon & Kirchner, 1975; Reckhow et al., 1980; Van Vliet & Hall, 1991; Chamber & Dale, 1997; Winter & Duthie, 2000) and loading models (Jones et al. 2001; Greenland International Consulting Ltd., 2006). We did not have data for five of the tributaries because federal gauges were only installed in six tributaries including Upper Nottawasaga River, Innisfil Creek, Boyne River, Pine River, Mad River, and Willow Creek. To estimate annual loading rates within the NRW, we first developed tributary-specific equations to predict TP concentrations from amount of precipitation (mm) during storm events. A team from the Nottawasaga Valley Conservation Authority (NVCA) collected water samples 24 hours after a storm event (to account for a lag period) at Provincial Water Quality Monitoring Network (PWQMN) stations located closest to our base flow monitoring stations (Figure 1.1). It is important to note that PWQMN stations were not situated in the same locations as our base flow monitoring stations; in particular, PWQMN stations for the Mad River and Willow Creek were located before the tributaries drain through the Minesing Wetlands.

In total, we had TP concentrations following four storm events (varied from 5 – 50 mm of rain), and one base flow event (reference condition from our sampling in July). We obtained daily precipitation data ($P_r$; mm) during the 24-hour period prior to storm-flow sample collection from the closest federal climate station (Table 1.1; Figure 1.1). We regressed storm flow TP concentrations against precipitation intensity (mm of rain in 24-hour period) for each tributary to produce six predictive equations (Table 1.4). We used these equations to estimate daily TP concentrations using daily precipitation data from the climate station closest to each tributary (Table 1.1). Finally, we obtained hourly discharge data from each tributary and calculated mean daily discharge rates during the 24-hour period prior to storm flow sample collection. In order to estimate annual loads from the six sub-watersheds (Table 1.4), we used the following equation:

$$L_x = C_x Q \qquad \text{Eq. (4)}$$

where $L$ is the loading rate of constituent $x$ (TP or TSS; kg/year), $C$ is the concentration of the constituent $x$ in water (TP or TSS; kg/L), and $Q$ is the rate of discharge of water ($m^3$/s).

*Description of the CANWET model*

Greenland International Consulting Ltd. (2006) produced TP and TSS loading models for the NRW using the Canadian Nutrient and Water Evaluation Tool (CANWET) interface within a geographic information system (GIS). CANWET models did not include water quality measurements from tributaries of the Nottawasaga River that flow through the Minesing, nor did the models consider water-chemistry data following storm events. Additionally, the Willow Creek sub-watershed, which drains a substantial portion of the Minesing Wetlands, was mislabeled as Matheson Creek (a low order stream that flows into Willow Creek). To account for this misrepresentation, we added the loads predicted for both Willow Creek and Matheson Creek together. PWQMN stations were not located at the base of sub-watersheds, and gauge stations were not situated where water samples were collected. The PWQMN does not monitor Thornton Creek or the Mad River Breach (included in our study); therefore, the CANWET model did not produce loads for these tributaries.

*Data analysis*

We used R and RStudio (v.3.2.3) to perform a breakpoint analysis on the segmented linear regression between TP and DO in Willow Creek. We also used JMP 12 software (SAS Institute Inc., Toronto, ON, Canada), to perform multivariate correlation analyses, Principal Components Analysis (PCA), and Ordinary Least Squares (OLS) regressions. Dependent variables were first log (TSS) or box-cox (TP) transformed to achieve normality. We arcsine-transformed all variables expressed as a percent (land-cover variables, percent soil) to normalize variances. Prior to performing OLS regression, we used Pearson's correlation analysis to identify collinearity between independent landscape variables. To reduce redundancy, variables that correlated highly with the primary factors identified in the PCA (e.g. slope, crop land, etc.) were removed from subsequent OLS regression analyses. The OLS regression models were chosen based on lowest AIC values for all possible combinations. Where ΔAIC was less than 2 between models, the model with the fewest predictive variables was chosen to minimize degrees of freedom and to create a simpler model.

**Results**

The size of sub-watersheds in this study spanned two orders of magnitude from 42 to 498 $km^2$; consequently, stream discharge and daily summer base-flow loadings to the Nottawasaga River also varied widely (Table 1.5). Concentrations of TP varied from 6.1 to 44.2 µg/L while concentrations of TSS ranged from 2.8 to 40.1 mg/L. Since tributaries with higher discharge rates had a greater volume of water entering the Nottawasaga

River, they contributed a higher loading of TP and TSS to the river on a daily basis. This is why we cannot make appropriate interpretations of stream concentrations without corresponding discharge rates (e.g. Marl Creek had a high TP concentration but a low overall loading because of the low discharge rate).

Because the NRW covers a large geographic area, both geomorphology and land-cover characteristics varied widely for the 11 sub-watersheds (Table 1.2). Despite this variability, agriculture consistently accounted for the greatest amount of land cover in all sub-watersheds, with proportion of crop land being higher than that of pasture land in most cases. It is also important to point out that the Minesing Wetlands accounted for a large portion of wetland land-cover class in the Mad River and Willow Creek sub-watersheds (17 and 21% respectively).

*Application of existing loading models to the NRW*

We used three different approaches to predict annual loading rates of TP and TSS from the 11 sub-watersheds of the NRW. We used (1) published export coefficients (Table 1.3), (2) the landscape model of Jones et al. (2001) (Eq. 2 and 3), and (3) the CANWET model (Greenland International Consulting Ltd., 2006) to determine annual loading rates for the 11 sub-watersheds (Figure 1.2). We also estimated annual TP loads using precipitation regressions for 6 sub-watersheds with available field data from storm flow samples and gauge stations that measured discharge (Table 1.4). The CANWET model produced TP loads that were most similar to those we estimated with field data, but it still produced overestimates that were higher by 2300 to 3900 kg/year. The landscape model of Jones et al. (2001) consistently over-estimated TP loading in all sub-watersheds by an order of magnitude compared to all other approaches. We did not have any TSS loads of our own to compare with those estimated by the three approaches. TSS loading rates estimated by the three published approaches were relatively similar, although the landscape model still tended to produce the highest values. This comparison indicated that all published models would overestimate TP loading rates for our tributaries, and in some cases, by an unacceptably large amount. Although use of export coefficients and the CANWET model appeared to be better options, there was no consistencies in how they ranked loading rates associated with the tributaries.

To determine the potential impact of the Minesing Wetlands on water quality of Willow Creek, we compared the daytime DO measurements of Willow Creek with those measured in Innisfil Creek, Marl Creek and Pine River. DO concentrations in Willow Creek were <4 mg/L, compared with >8.5 mg/L for the other three tributaries (Figure 1.3). Through continuous monitoring, we also found that TP concentrations of Willow Creek during the summer (June to August 2015) ranged from 12.1 to 180.8 µg/L. These extremely high TP concentrations in Willow Creek were 5 – 30 times higher than those measured in the tributaries at monitoring stations during base flow conditions (Table 1.5). When we performed the segmented regression analysis of daily TP against daily DO concentrations, we found a breakpoint at a DO concentration of $0.101 \pm 0.087$ mg/L; below this, there a significant negative correlation between TP and DO, and above this there was no linear relationship (Figure 1.4).

*Development of loading models specific to the NRW*

To develop our own loading model for the NRW, we first performed a PCA to identify linear combinations of landscape variables that would explain the greatest amount of variation across all sub-watersheds. The first three Principal Components (PC; eigenvalues >1) together explained 82% of the total variation in the dataset (Table 1.6). PC1 alone accounted for 44% of the variation, and was strongly and positively correlated with mean slope gradient (0.81) and negatively correlated with crop land (–0.95) (Table 1.6; Figure 1.5). The negative correlation with crop land explains why there was a positive correlation between PC1 and undeveloped land classes such as forests (0.76), wetlands (0.64) and barren land (0.64). PC2 explained 23% of the remaining variation, and ordinated watersheds according to proportion of urban land (0.84) and sandy soils (0.62). PC3, which accounted for 15% of the remaining variance, was most highly correlated with the proportion of barren land (0.73). Based on these correlations, it appears that land-cover classes depended on watershed geomorphology. When we grouped mean slope gradients in the NRW into three classes (gentle, moderate, steep), crop land occupied the highest proportion of gently sloped areas, while pasture land occurred on a greater proportion of moderate and steeply sloped areas compared to crops. The majority of the steeply sloped areas in the NRW were covered by forest (Figure 1.6).

The PCA confirmed the importance of land-cover and geomorphic variables in explaining variation in the dataset. When we regressed daily TP and TSS loading rates for each sub-watershed against corresponding PC1 scores, we found highly significant positive relationships that explained 46% and 37% of the variation, respectively (Figure

1.7). Willow Creek, Mad River breach, and Mad River had high PC1 scores, presumably because of the relatively large proportion of their sub-watersheds that drain wetlands (16 to 21%; Table 1.2), and were associated with high TP loads. By contrast, Bear Creek, with 19% wetland cover in its sub-watershed, was associated with a much smaller TP load. It is important to note that Willow Creek, Mad River, and the Mad River breach all drain the Minesing Wetlands Complex, whereas Bear Creek does not.

*OLS regression models*

We performed OLS regression models on all possible combinations of independent landscape variables. Three separate models were run with different combinations of predictive landscape variables (Table 1.7). One model included geomorphic variables only (slope, drainage area, % sandy soils, and % organic soils); a second model included land-cover variables (% crop land, % pasture land, % urban land, % forested land, % wetland, and % barren land); a third model included all landscape variables (i.e. both geomorphic and land-cover variables). These three models were developed for TP and TSS loading rates for a total of six predictive equations (Table 1.8).

OLS regression analysis identified significant predictive relationships for both TP and TSS for all three models (Table 1.7). The landscape model explained the greatest amount of variation in TP for the 11 sub-watersheds ($r^2$ = 0.76; $AIC_c$ = 117.5), and included drainage area ($p$ = <0.0001), % wetland ($p$ = 0.0076), and % pasture land ($p$ = 0.0111) as the most important significant predictive variables. The geomorphic model explained a little less of the overall variation ($r^2$ = 0.71; $AIC_c$ = 123.7), with drainage area ($p$ = <0.0001), % organic soils ($p$ = 0.002), and % sandy soils ($p$ = 0.0452) emerging as significant predictive variables. By contrast, the land-cover model explained the least amount of variation ($r^2$ = 0.56; $AIC_c$ = 134.5), and included % pasture land ($p$ = <0.0001) and % wetland ($p$ = 0.0308) as the most significant land-cover variables. In this direct comparison, the combination of geomorphic and land-cover variables together made the best predictive model for TP.

Overall, predictive models for TSS had lower $r^2$ values compared to predictive models for TP. The geomorphic model explained the greatest amount of variation ($r^2$ = 0.67; $AIC_c$ = 82.6), which included drainage area ($p$ = <0.0001), % sandy soils ($p$ = 0.0109), and % organic soils ($p$ = 0.0208) as the most important significant predictive variables. The landscape model only explained slightly less of the variation ($r^2$ = 0.65; $AIC_c$ = 81.5), which included drainage area ($p$ = 0.0002) and % pasture land ($p$ = 0.0115) as the most significant predictors. The land-cover model for TSS explained the least amount of variation ($r^2$ = 0.54; $AIC_c$ = 91.1). Land-cover variables that were most important for predicting TSS loads were % pasture land ($p$ = <0.0001), and % forested land ($p$ = 0.0239). These results indicate that geomorphic and landscape models were better predictors of TSS loading in the NRW than was the model using only land-cover variables.

*Comparison of model estimates*

Overall model performance was determined by comparing measured daily base flow loads to model estimates (Figure 1.8). Predictive equations generated by OLS regression analyses (Table 1.8) were used to generate estimates for all six models. Willow Creek was associated with the largest discrepancy among the three TP loading models, but it is important to note that all models under-estimated daily loads for this creek. By contrast, all three models over-estimated TP loading for the Upper Nottawasaga River, Bear Creek, the Mad River, and McIntyre Creek. The land-cover model severely under-estimated TP loading from the Innisfil and Pine River sub-watersheds. Consistent with the TP predictions, all three models over-estimated TSS loading from the Upper Nottawasaga River, Mad River, and McIntyre Creek sub-watersheds (Figure 1.8). All three models under-estimated TSS loading from the Mad River breach, and the land-cover model under-estimated TSS loading from Innisfil Creek.

We regressed measured TP and TSS loads against significant predictor landscape variables. Drainage area of sub-watersheds was significantly associated with the loading rates of TP ($r^2 = 0.59$; $p = <0.0001$) and TSS ($r^2 = 0.57$; $p = <0.0001$) (Figure 1.9). A strong positive relationship also existed between % pasture land and the loading rates of TP ($r^2 = 0.49$; $p = <0.0001$) and TSS ($r^2 = 0.45$; $p = <0.0001$) (Figure 1.10). % Wetland significantly predicted TP loading ($r^2 = 0.22$; $p = 0.0063$); however, the relationship was not as strong as that of the other two landscape variables (Figure 1.11). These results indicate that drainage area and pasture land are the main landscape variables driving spatial variability in TP and TSS loading rates among sub-watersheds.

## Discussion

In this study, we applied three published approaches (export coefficient, landscape model by Jones et al. (2001), CANWET) to estimate TP and TSS loading for the Nottawasaga River Watershed. Compared to our measured data, all three approaches over-estimated TP loads, and there was no consistency in how they ranked sub-watersheds with respect to loadings. These discrepancies point out the inappropriateness of using existing models to produce reliable annual loading estimates for the NRW, and underscore the need for us to create a model specifically for our sub-watersheds. In developing our model, we wanted to account for all possible contributions of nutrients from the Minesing Wetlands to the Mad River and Willow Creek sub-watersheds. This necessitated sampling the tributaries after they flowed through the Minesing Wetlands, rather than at the PWQMN stations, which are located upstream of the Minesing.

Of the three models we developed, the landscape model, which incorporated both geomorphic and land-cover variables, was the best predictor for both TP and TSS loading. Drainage area, and proportion of pasture land were the most significant predictors of daily base flow TP and TSS loading rates. Sub-watershed area was important because it is directly related to the volume of water that discharges into tributaries, with larger watersheds contributing higher volumes and thus higher loads. This is particularly important following storm events, where loading is amplified (Brezonik & Stadelmann, 2002). We also found that proportion of pasture land in sub-watersheds was a significant predictor of nutrient and sediment loading. This is not surprising, since manure contains a very high amount of organic P (Beaulac & Reckhow, 1982), and cattle grazing loosens soil and increases erosion (Dunne et al., 2011). Grazing also compacts soil, which decreases vegetation cover and root structure, thus increasing loading (Menzel et al., 1978; Reckhow et al., 1980).

Watershed geomorphology has a major impact on runoff characteristics and nutrient dynamics (Govindaraju & Hantush, 2003; Salvia-Castellvi et al., 2005). The effect of slope on runoff has been well documented in the literature (Chen et al., 2001; Fu et al., 2004; Long et al., 2006); however, few studies have addressed how the degree of slope can dictate land cover within a watershed. In the NRW, crop land and forests were almost exclusively found in areas with gentle and steep slopes, respectively. Although Fu et al. (2006), reported similar findings, they did not distinguish between crop and pasture land. Our study indicated that compared to crops, pasture land was more evenly distributed between gentle and moderately sloped areas, and were even found on some steeply sloped areas. Since watershed geomorphology is a good predictor of land cover in addition to being a fundamental feature controlling runoff, it is not surprising that the geomorphic models produced good estimates of TP and TSS loading from sub-watersheds. The model suggests that larger sub-watersheds with greater proportions of organic soils, and lower proportions of sandy soils would yield higher loading rates. This is likely because organic soils have limited nutrient retention capacity, and can increase rate of runoff. Conversely, sandy soils are more porous and allow water to percolate downwards, which can decrease erosion and allow nutrients to adsorb to soil particles (Beaulac & Reckhow, 1982).

We found a positive relationship between TP loading and % wetland cover, which was largely driven by Willow Creek, the Mad River, and the Mad River breach. This was counterintuitive because wetlands are assumed to function as nature's kidneys, filtering out nutrients and sediment from non-point source runoff, which is particularly important for agricultural watersheds (Weller et al., 1996). This positive relationship implies that the Minesing wetlands are sources rather than sinks of phosphorus, and are no longer able to filter out nutrients and sediments. Fisher & Reddy (2001) found that impaired wetlands, particularly those dominated by agricultural land-use, and that are subjected to prolonged nutrient loading, may be a source of nutrients under certain conditions. This is because excess loading leads to the accumulation of nutrients in wetland soil over time, particularly in the soluble form. Soluble P can be released to the water column under anoxic conditions (0 mg/L DO; Carpenter et al., 1998). We found TP concentrations in Willow Creek rapidly increased when DO reached 0.101 mg/L. This increase in TP appeared to be unrelated to point source pollution, and did not coincide with storm events. We hypothesize that internal loading during anoxic periods was responsible for the spikes in TP recorded in Willow Creek, and we recommend that this hypothesis be properly addressed in future studies of the Minesing Wetlands.

The largest inconsistency between predicted and measured daily loading rates for TP was in Willow Creek. The measured load was approximately twice as large as those predicted. This is likely due to internal P loading that is suspected to be occurring in the Minesing during the summer months. The largest discrepancy for the TSS models existed for the Mad River Breach. Measured TSS loadings were almost double those predicted. During high spring flows in 2000, the Mad River broke its natural levee and carved out a new channel that discharged into the Nottawasaga River at the southern end of the Minesing Wetlands. Scouring of the new channel increased bank erosion and lead to the development of a crevasse splay, where sediment is deposited in the Nottawasaga River.

This new channel comprised 70% of the Mad River's natural base flow by 2012, leading to a high discharge rate, which increased overall TSS loading (Rootham & Featherstone, 2014).

We also found the land cover model under-estimating TP and TSS loads from the Innisfil Creek sub-watershed. This may be because of the disproportionately high cropland in the Innisfil Creek sub-watershed, and the relatively low TP and TSS loading associated with cropland in this study relative to those reported in the literature (Beaulac & Reckhow, 1982). Most sub-watersheds in our study with a high proportion of crop land were associated with smaller drainage areas, which results in a lower discharge rate. The Innisfil Creek sub-watershed on the other hand has a large drainage area, which may explain the higher TP and TSS loads that we measured. Further research into nutrient and sediment export from crop and pasture land in south central Ontario is necessary to better understand loading rates from agricultural sub-watersheds.

**Conclusion**

Our study identified watershed drainage area and proportion of pasture land as the main drivers of variation in TP and TSS loading within the NRW. Independent of these two variables, sub-watersheds that drained through the Minesing Wetlands were also associated with high TP loads, implicating the wetland complex as a major source of nutrients to the Nottawasaga River. Watershed geomorphology was a good predictor of land-cover classes, since steeper slopes coincided with pasture land and forest, while gentle slopes coincided with crop land. These relationships underlie the reasons why geomorphic models made accurate predictions of daily TP and TSS loadings rates. Therefore, if land-cover data (which can be difficult to acquire) were not readily available, geospatial data (drainage area, slope, soil) could be used to estimate TP and TSS loading across sub-watersheds. We have provided base-flow loading rates of phosphorus and sediment during the growing season when agricultural practises are most intense, but future studies should evaluate annual loading rates throughout the season, including storm flows during the remainder of the year. Since our study area extended across several sub-watersheds with varying landscape features, our loading models should be applicable to other mixed agricultural watersheds, and we recommend that future studies be carried out to validate the usefulness of our models for south central Ontario watersheds.

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**Table 1.1:** Summary of base flow tributary monitoring stations and their associated federal gauge and climate stations used to estimate annual loading rates using Eq. 4. Tributaries are listed in order from furthest upstream to furthest downstream. †Indicates tributaries that drain through the Minesing Wetlands; tributaries listed above and below drain into the middle and lower Nottawasaga River reaches respectively.

| Site code | Monitoring Station | Latitude, Longitude | Federal Gauge Station | Federal Climate Station |
|---|---|---|---|---|
| UN | Upper Nottawasaga R. | 44.13648, -79.81020 | Nottawasaga R. at Hockley (02ED026) | Mono Centre (6157000) |
| IN | Innisfil Cr. | 44.13532, -79.80868 | Innisfil Cr. near Alliston (02ED029) | Egbert CS (611E001) |
| BN | Boyne R. | 44.16919, -79.81576 | Boyne R. at Earl Rowe Park (02ED102) | Egbert CS (611E001) |
| TN | Thornton Cr. | 44.24819, -79.81990 | -- | -- |
| PN | Pine R. | 44.33138, -79.87441 | Pine R. near Everett (02ED014) | Borden AWOS (611B002) |
| BR | Bear Cr. | 44.33403, -79.87095 | -- | -- |
| MB† | Mad R. breach | 44.36003, -79.87987 | -- | -- |
| MR† | Mad R. | 44.40856, -79.89931 | Mad R. below Avening (02ED015) | Borden AWOS (611B002) |
| WL† | Willow Cr. | 44.41880, -79.88382 | Willow Cr. near Minesing (02ED032) | Barrie Landfill (6110556) |
| ML | Marl Cr. | 44.44141, -79.89180 | -- | -- |
| MT | McIntyre Cr. | 44.46916, -80.04650 | -- | -- |

**Table 1.2:** Summary of key landscape variables (include both geomorphic and land-cover variables) for sub-watersheds in the study (see Table 1.1 for sub-watershed site codes).

| | | | Sub-watershed | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Variable | Description | UN | IN | BN | TN | PN | BR | MB | MR | WL | ML | MT |
| Geomorphology | mSg | Mean slope gradient (°) | 3.8 | 2.5 | 3.1 | 1.6 | 3.4 | 2.1 | 3.1 | 2.8 | 2.3 | 1.4 | 1.4 |
| | dArea | Drainage area ($km^2$) | 338 | 498 | 236 | 42 | 346 | 91 | 356 | 447 | 306 | 87 | 118 |
| | sSand | Sandy soils in sub-watershed (%) | 80 | 61 | 65 | 89 | 70 | 81 | 72 | 71 | 85 | 54 | 49 |
| | sOrg | Organic soils in sub-watershed (%) | 7 | 6 | 6 | 1 | 6 | 13 | 11 | 11 | 13 | 2 | 2 |
| Land Cover | AGC | Crop land-use in watershed (%) | 23 | 48 | 31 | 53 | 20 | 26 | 22 | 25 | 13 | 35 | 58 |
| | AGP | Pasture land-use in watershed (%) | 19 | 16 | 23 | 13 | 15 | 9 | 28 | 25 | 21 | 16 | 15 |
| | URB | Urban land-use in watershed (%) | 6 | 7 | 9 | 9 | 7 | 17 | 3 | 3 | 9 | 5 | 8 |
| | FOR | Forest land cover in watershed (%) | 26 | 12 | 15 | 12 | 35 | 21 | 24 | 22 | 26 | 26 | 7 |
| | WET | Wetland land cover in watershed (%) | 11 | 9 | 10 | 7 | 8 | 19 | 16 | 17 | 21 | 11 | 7 |
| | BAR | Barren land cover in watershed (%) | 15 | 8 | 11 | 5 | 14 | 9 | 7 | 7 | 9 | 7 | 5 |

**Table 1.3:** Published export coefficients associated with total phosphorus (TP) and total suspended solids (TSS) that best represent landscape characteristics in the study area. Eq. 1 was used to estimate total annual loads.

| Land | Export Coefficient (kg/ha/year) | | Published study | |
|---|---|---|---|---|
| Cover | TP | TSS | TP | TSS |
| Crop | 0.3 | 1000 | Chambers & Dale (1997) | Van Vliet & Hall (1991) |
| Pasture | 0.2 | 515 | Chambers & Dale (1997) | Reckhow et al. (1980) |
| Urban | 0.5 | 209 | Winter & Duthie (2000) | Reckhow et al. (1980) |
| Forest | 0.1 | 253 | Dillon & Kirchner (1975) | Reckhow et al. (1980) |

**Table 1.4:** Annual total phosphorus loads ($L_{TP}$; kg/year) estimated with Eq. 4 for Nottawasaga River tributaries with federal gauge stations. To account for differential effects of storm events on TP concentrations in each stream, we produced tributary-specific relationships between TP concentrations to precipitation amount. Daily precipitation ($P_r$) data were then obtained from the closest federal climate station for each sub-watershed (see Figure 1.1) and applied to these linear regression equations.

| Site code | Linear regression equation | $r^2$ | $p$-Value | $L_{TP}$ |
|---|---|---|---|---|
| UN | log(TP) = 1.504 + 0.121 $P_r$ | 0.82 | **<0.0001** | 1314 |
| IN | log(TP) = 3.908 + 0.048 $P_r$ | 0.83 | **<0.0001** | 4707 |
| BN | log(TP) = 3.199 + 0.044 $P_r$ | 0.64 | **0.0004** | 1639 |
| PN | log(TP) = 2.625 + 0.074 $P_r$ | 0.75 | **<0.0001** | 1701 |
| MR† | log(TP) = 1.274 + 0.129 $P_r$ | 0.86 | **0.0001** | 1118 |
| WL† | log(TP) = 2.730 + 0.045 $P_r$ | 0.79 | **<0.0001** | 1363 |

† Estimated loadings do not account for potential influences of the Minesing Wetlands

**Table 1.5:** Summary of Nottawasaga River tributary site codes (see Table 1.1), base flow discharge rates ($m^3/s$), as well as measured concentrations and loading rates of total phosphorus (TP) and total suspended solids (TSS). Eq. 4 was used to calculate daily loading rates.

| Site Code | Base flow | TP (µg/L) | TP (kg/day) | TSS (mg/L) | TSS (kg/day) |
|---|---|---|---|---|---|
| UN | 2.28 | 6.1 | 1.20 | 2.8 | 549 |
| IN | 1.57 | 40.4 | 5.48 | 27.9 | 3775 |
| BR | 2.51 | 19.0 | 4.13 | 5.8 | 1253 |
| TN | 0.12 | 12.8 | 0.14 | 10.5 | 113 |
| PN | 2.89 | 12.8 | 3.20 | 6.0 | 1500 |
| BR | 0.26 | 23.4 | 0.53 | 14.0 | 318 |
| MB | 2.41 | 32.5 | 6.76 | 40.1 | 8354 |
| MR | 1.45 | 44.2 | 5.55 | 15.3 | 1913 |
| WL | 3.74 | 31.5 | 10.18 | 4.4 | 1422 |
| ML | 0.48 | 41.0 | 1.69 | 31.2 | 1289 |
| MT | 0.26 | 20.0 | 4.44 | 8.0 | 177 |

**Table 1.6:** Correlation coefficients (*r*) between independent landscape variables and principal component (PC) axes for all sub-watersheds in the study. Only PCs with eigenvalues >1, and correlations >0.5 are displayed.

| Axis | Variance Explained (%) | Eigenvalue | Variable | *r* | *p*-Value |
|---|---|---|---|---|---|
| PC1 | 44 | 4.40 | mSg | 0.81 | <0.0001 |
| | | | sOrg | 0.76 | <0.0001 |
| | | | FOR | 0.76 | <0.0001 |
| | | | WET | 0.64 | <0.0001 |
| | | | BAR | 0.64 | <0.0001 |
| | | | dArea | 0.63 | <0.0001 |
| | | | AGP | 0.54 | <0.0001 |
| | | | AGC | –0.95 | <0.0001 |
| PC2 | 23 | 2.30 | URB | 0.84 | <0.0001 |
| | | | sSand | 0.62 | <0.0001 |
| | | | WET | 0.53 | <0.0001 |
| | | | AGP | –0.56 | <0.0001 |
| | | | dArea | –0.51 | <0.0001 |
| PC3 | 15 | 1.54 | BAR | 0.73 | <0.0001 |
| | | | WET | –0.53 | <0.0001 |
| | | | AGP | –0.52 | <0.0001 |

**Table 1.7:** Summary of predictive Ordinary Least Squares (OLS) regression models based on A) geomorphic B) land-cover and C) landscape variables.

| Parameter (kg/day) | Model type | $AIC_c$ | Signif. F | $r^2$ | $\beta_0$ | Predictor Variables | Estimate ±SE | *p*-Value |
|---|---|---|---|---|---|---|---|---|
| TP | A) | 123.7 | <0.0001 | 0.71 | 0.056 | dArea | 9.44e-5 ±1.88e-5 | <0.0001 |
| | | | | | | sOrg | 25.28 ±7.46 | 0.0020 |
| | | | | | | sSand | –3.40 ±1.63 | 0.0452 |
| | B) | 134.5 | <0.0001 | 0.56 | –5.25 | AGP | 27.46 ±5.62 | <0.0001 |
| | | | | | | WET | 14.56 ±6.43 | 0.0308 |
| | C) | 117.5 | <0.0001 | 0.76 | –4.96 | dArea | 8.88e-5 ±1.82e-5 | <0.0001 |
| | | | | | | WET | 13.90 ±4.84 | 0.0076 |
| | | | | | | AGP | 13.77 ±5.08 | 0.0111 |
| TSS | A) | 82.6 | <0.0001 | 0.67 | 6.81 | dArea | 4.87e-5 ±1.01e-5 | <0.0001 |
| | | | | | | sSand | –2.37 ±0.87 | 0.0109 |
| | | | | | | sOrg | 9.78 ±4.00 | 0.0208 |
| | B) | 91.1 | <0.0001 | 0.54 | 3.35 | AGP | 14.03 ±2.82 | <0.0001 |
| | | | | | | FOR | 4.55 ±1.91 | 0.0239 |
| | C) | 81.5 | <0.0001 | 0.65 | 4.24 | dArea | 4.55e-5 ±1.08e-5 | 0.0002 |
| | | | | | | AGP | 7.92 ±2.94 | 0.0115 |

**Table 1.8:** Summary of Ordinary Least Squares (OLS) predictive equations for estimating daily total phosphorus (TP; kg/day) and total suspended solids (TSS; kg/day) loading rates using A) geomorphic B) land-cover and C) landscape models.

| | Model | Eq. | Predictive Equation |
|---|---|---|---|
| TP | A) | 5 | box-cox(TP) = 0.056 + 9.44e-5*dArea + 25.28*sOrg – 3.40*sSand |
| | B) | 6 | box-cox(TP) = -5.25 + 27.46*AGP + 14.56*WET |
| | C) | 7 | box-cox(TP) = -4.96 + 8.88e-5*dArea + 13.9*WET+ 13.77*AGP |
| TSS | A) | 8 | Log(TSS) = 6.81 + 4.87e-5*dArea – 2.37*sSand + 9.78*sOrg |
| | B) | 9 | Log(TSS) = 3.35 + 14.03*AGP + 4.55*FOR |
| | C) | 10 | Log(TSS) = 4.24 + 4.55e-5*dArea + 7.92*AGP |

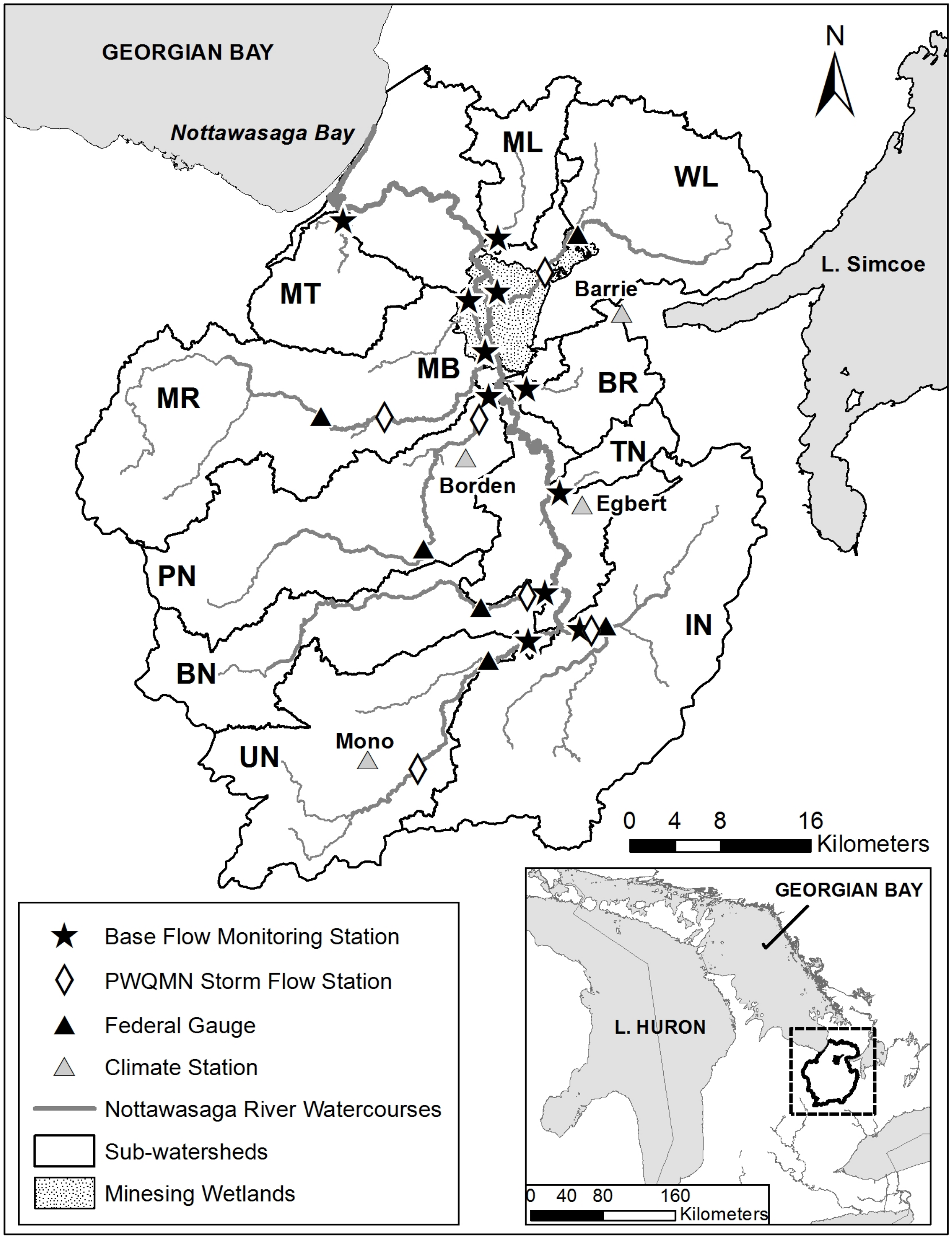


**Figure 1.1:** The Nottawasaga River watershed study area. Sub-watersheds included in the study are labeled with the site code (see Table 1.1). See Methods for description of monitoring stations.

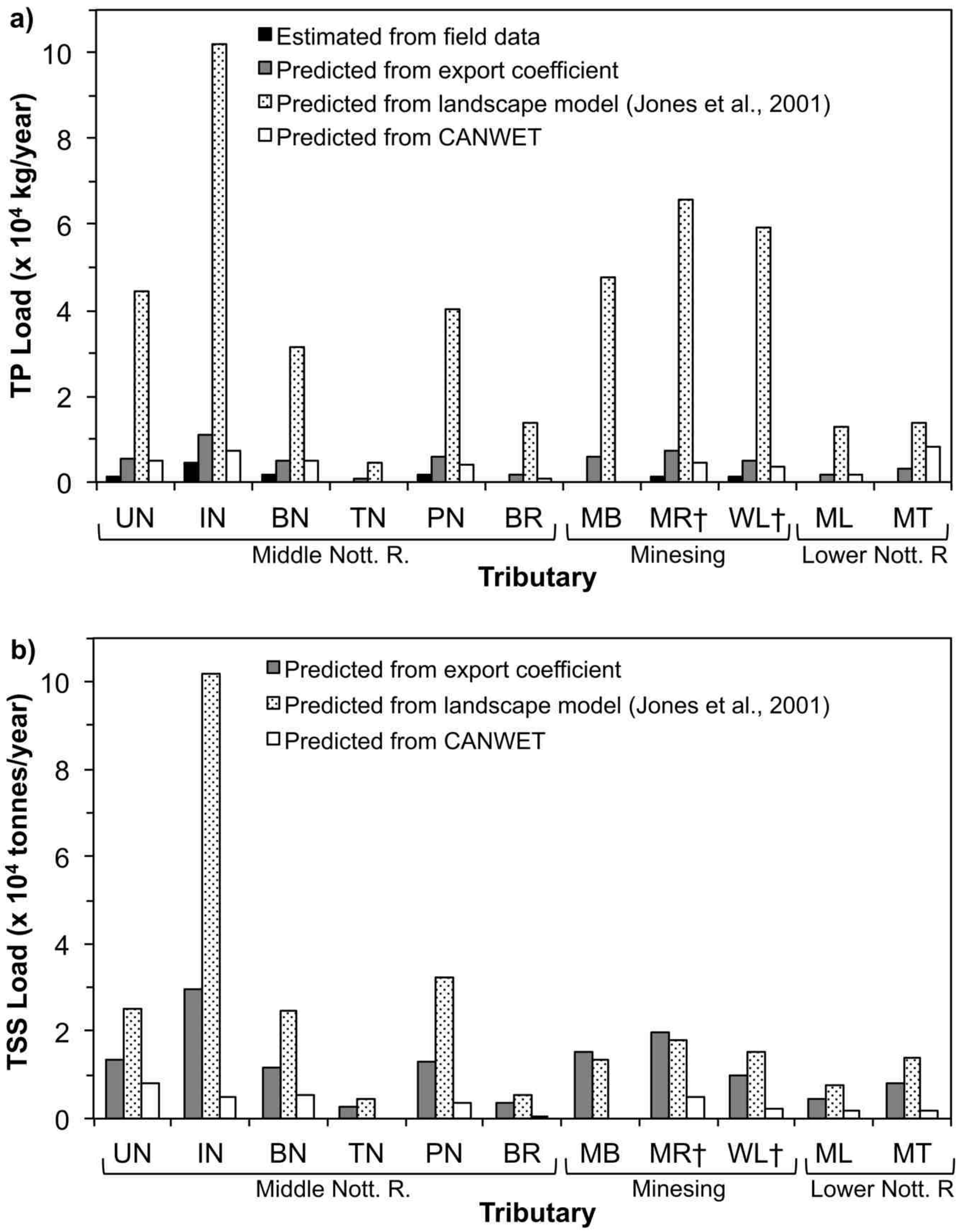


**Figure 1.2:** Comparison of a) total phosphorus (TP) and b) total suspended solids (TSS) annual loads calculated with different models for all tributaries (see Table 1.1). Field data refers to TP loads calculated with regression equations relating TP concentration and available continuous discharge data (see Table 1.4). †Indicates that estimated loads were calculated with regressions that do not account for potential influences of the Minesing Wetlands.

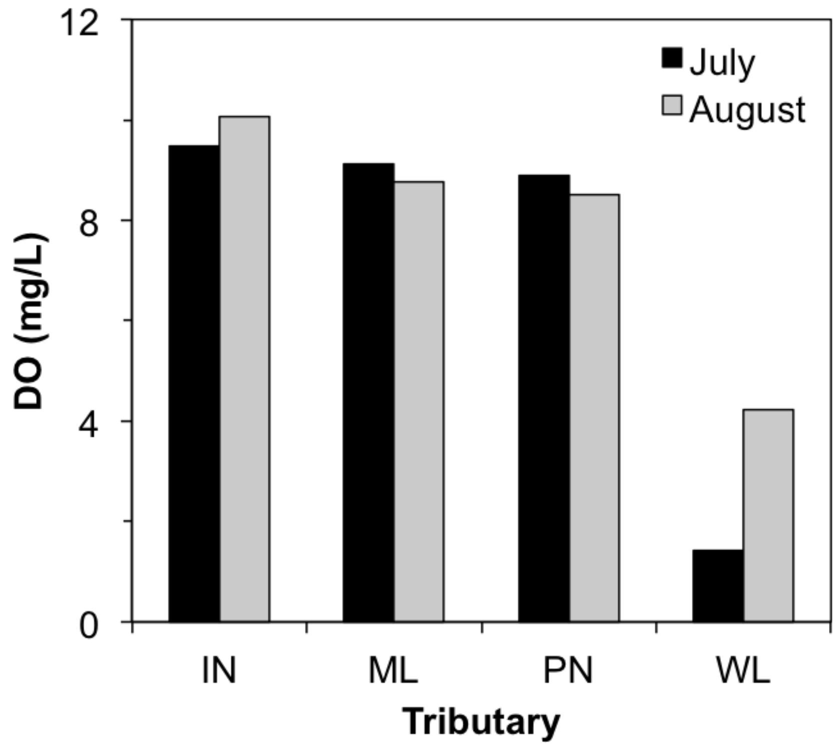


**Figure 1.3:** Comparison of daytime dissolved oxygen readings (DO; mg/L) in four tributaries (Innisfil Creek, Marl Creek, Pine River, and Willow Creek) measured once during July and August 2015.

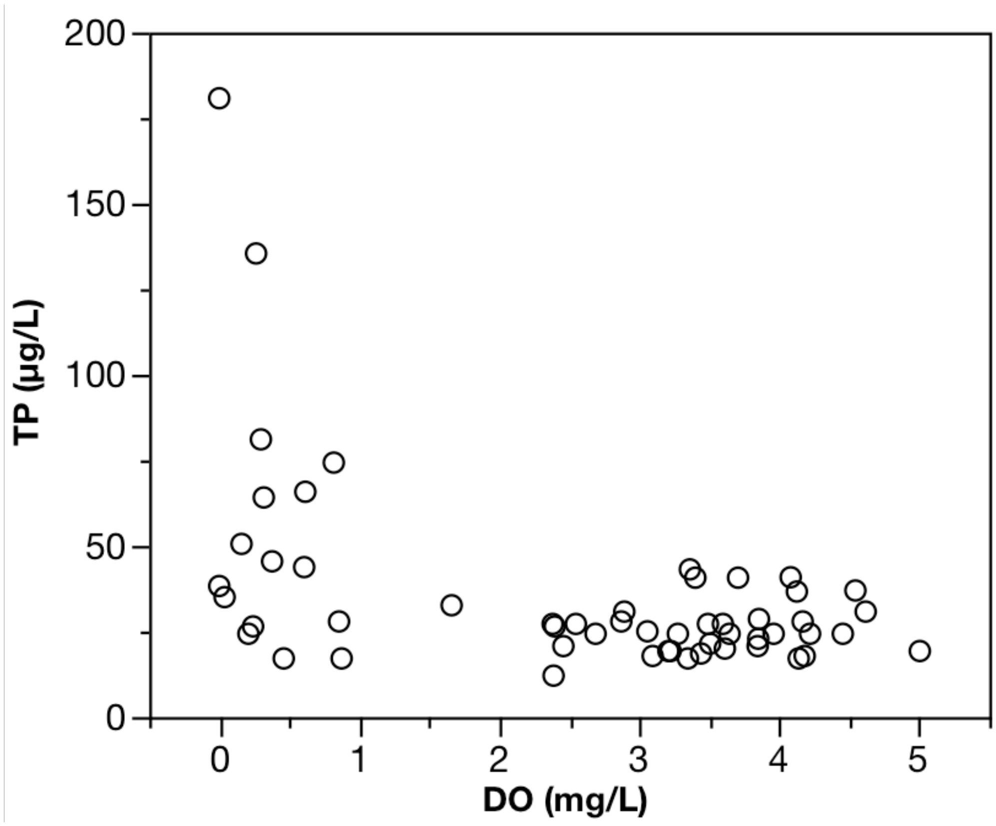


**Figure 1.4:** Mean daily total phosphorus concentration (TP; µg/L) versus dissolved oxygen (DO; mg/L) measured from June to August 2015 inclusive in Willow Creek.

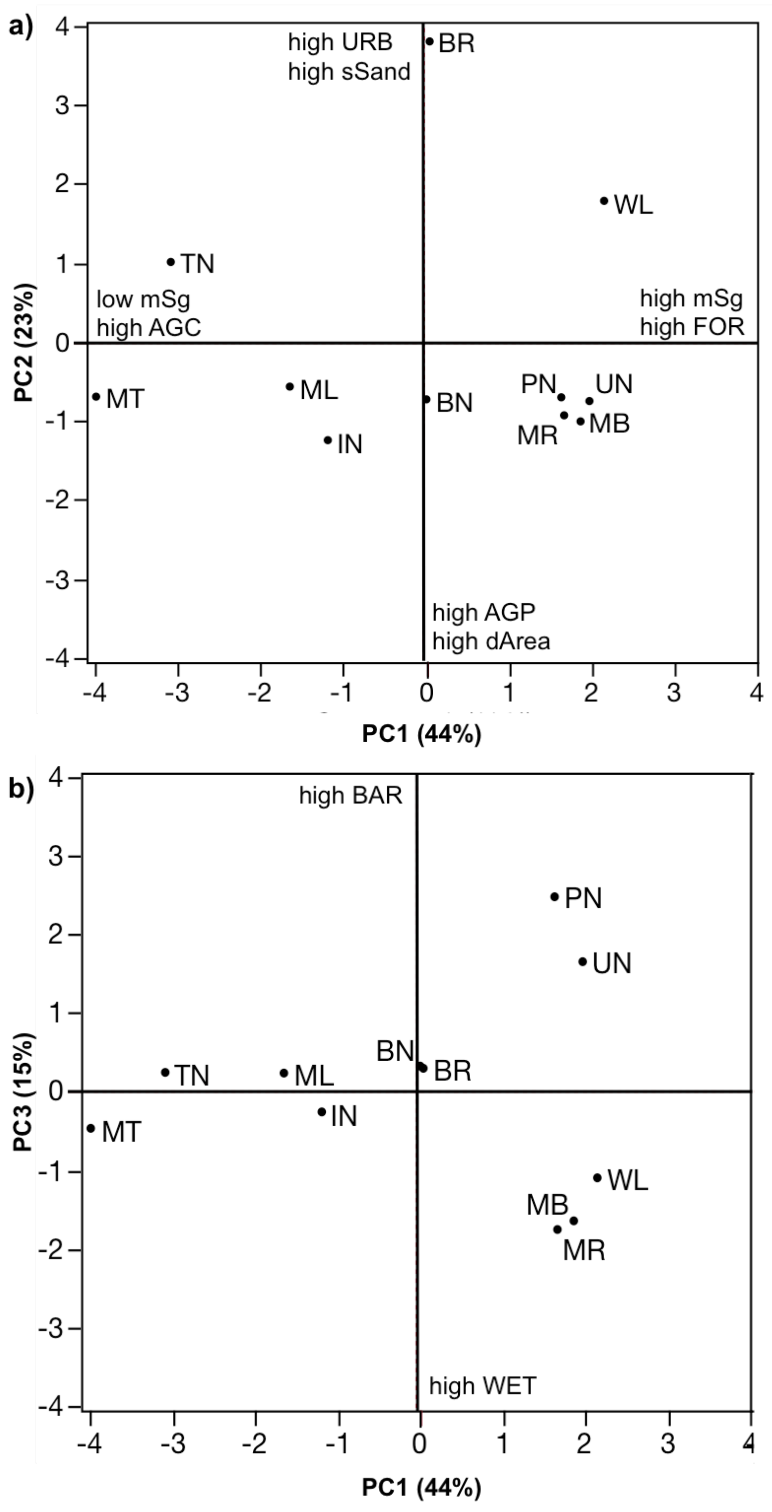


**Figure 1.5:** Biplot of PC1 scores versus a) PC2 scores and b) PC3 scores for independent landscape variables. Points are associated with site codes for sub-watersheds (see Table 1.1).

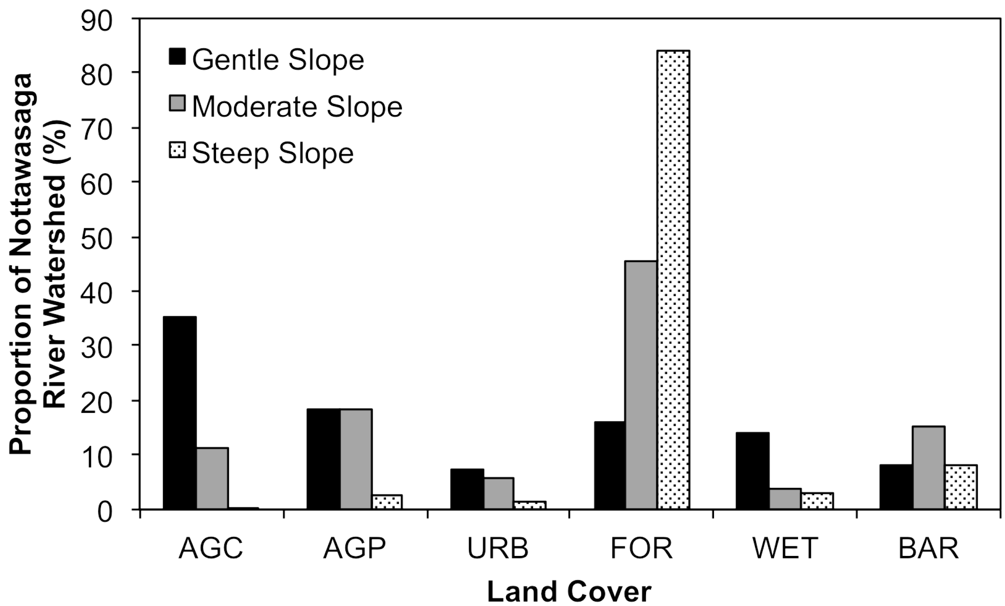


**Figure 1.6:** Proportion of land-cover classes (see Table 1.2) that exist on gentle (0 – 5°), moderate (5 – 16.5°), and steep (>16.5°) slope classes within the Nottawasaga River watershed.

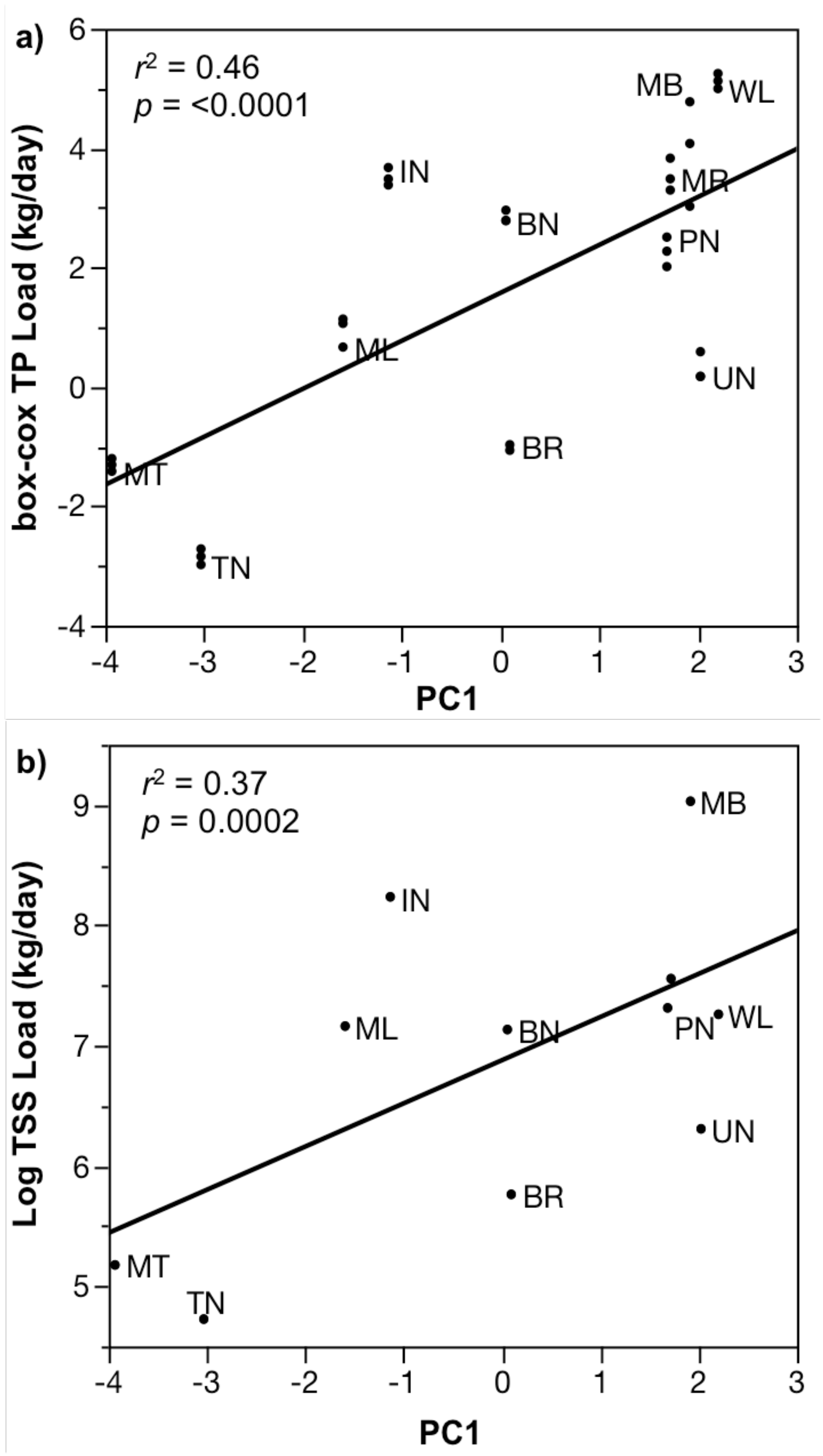


**Figure 1.7:** Measured daily loading rates for a) total phosphorus (TP; kg/day) and b) total suspended solids (TSS; kg/day) plotted against PC1 scores. Points are associated with site codes for sub-watersheds (see Table 1.1).

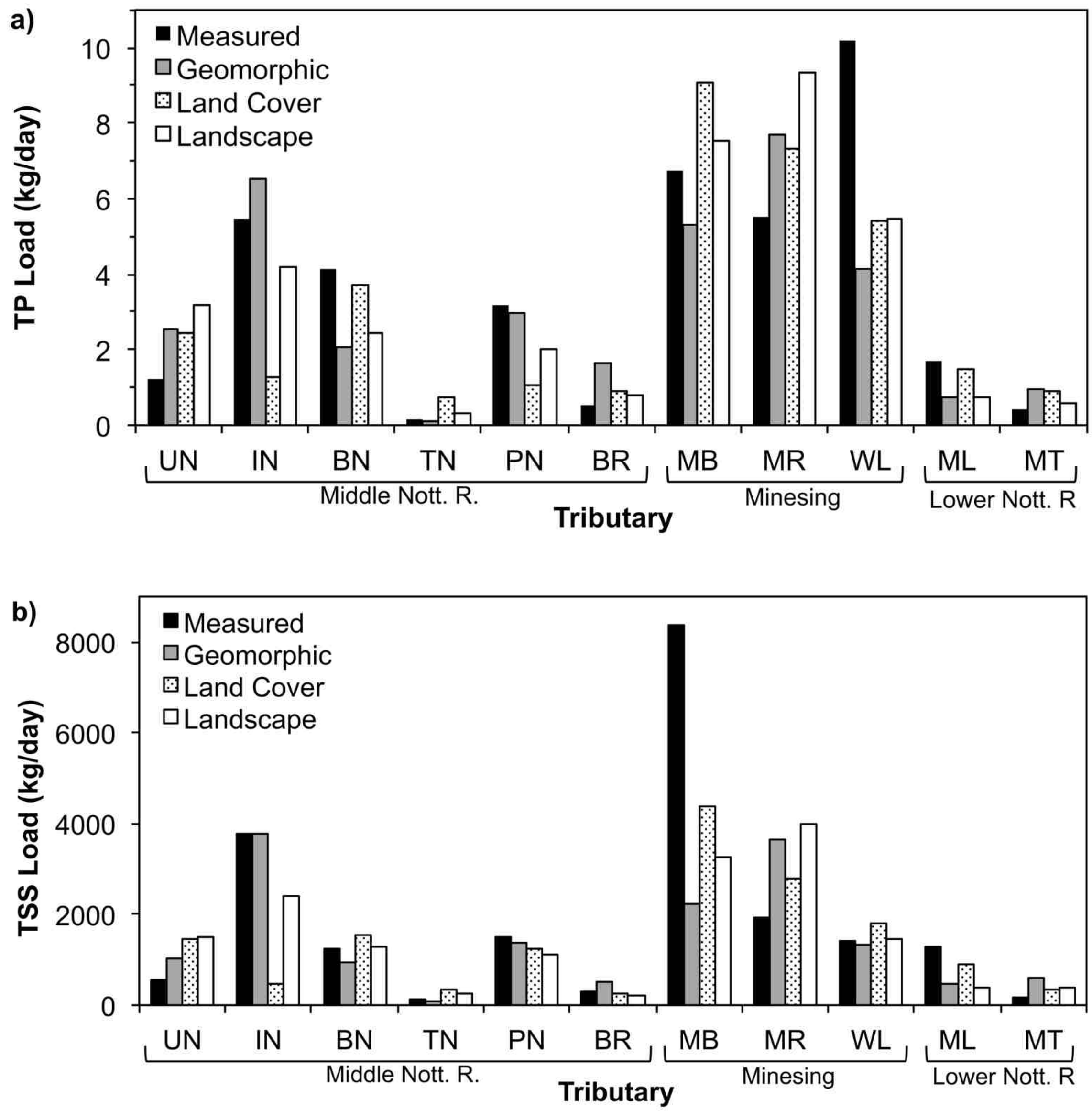


**Figure 1.8:** Comparison of a) total phosphorus (TP; kg/day) and b) total suspended solids (TSS; kg/day) daily summer base flow loading rates predicted by the geomorphic, land-cover, and landscape models for all tributaries (see Table 1.1 for site codes).

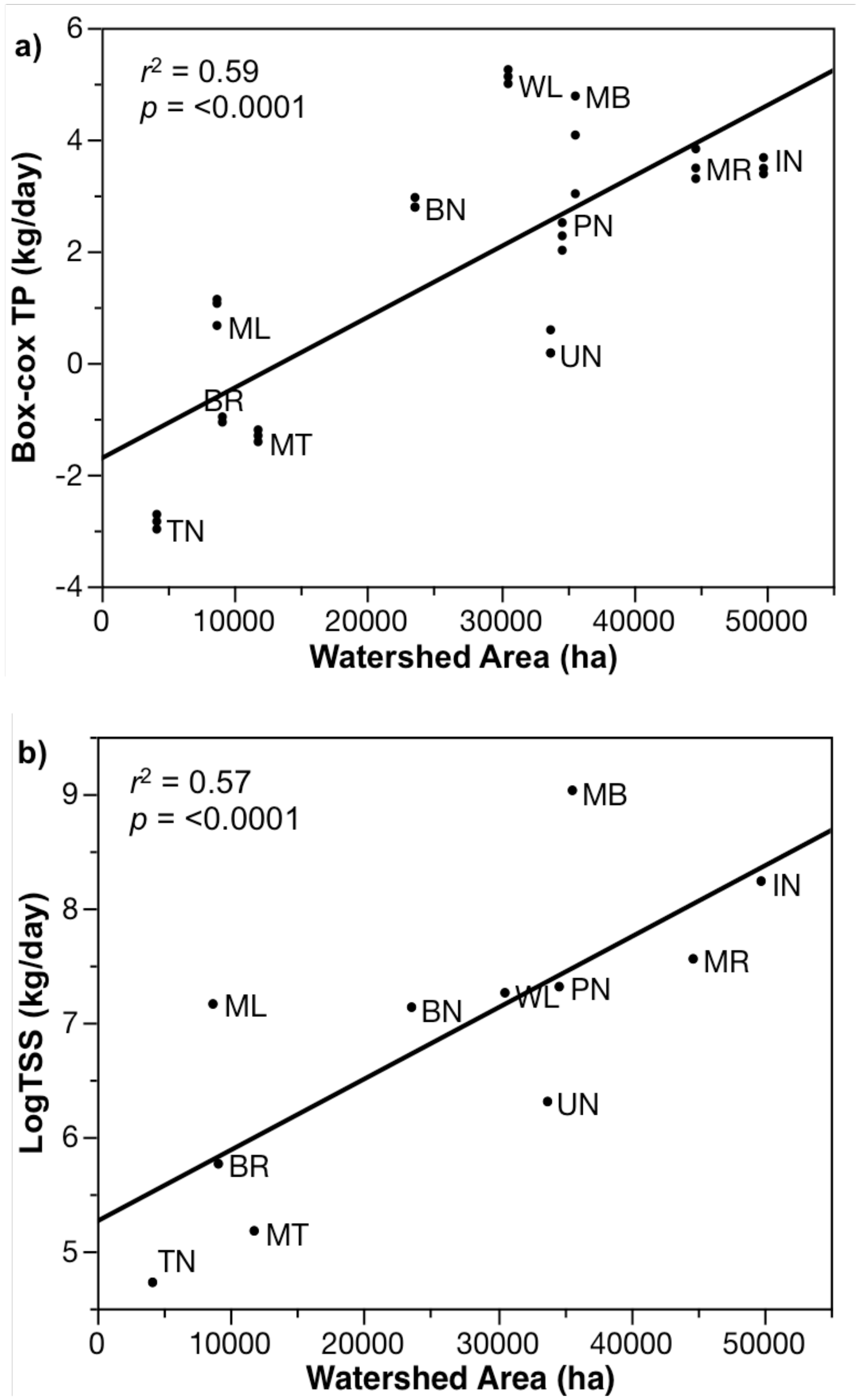


**Figure 1.9:** Linear regression of a) total phosphorus (TP; kg/day) and b) total suspended solids daily loads (TSS; kg/day) against watershed area (dArea; ha). Points are associated with site codes for sub-watersheds (see Table 1.1).

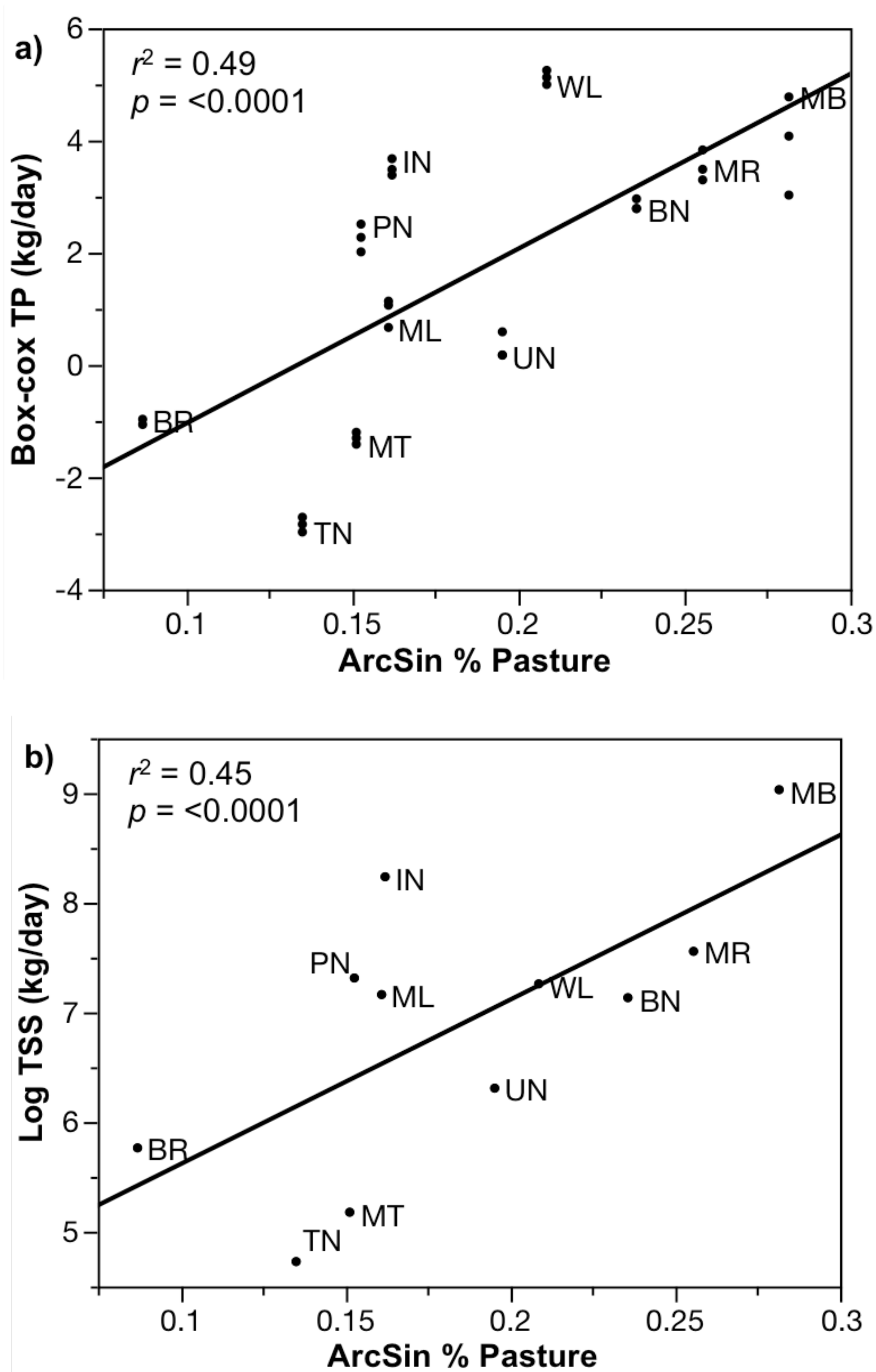


**Figure 1.10:** Linear regression of a) total phosphorus (TP; kg/day) and b) total suspended solids (TSS; kg/day) daily loads against proportion of pasture land (%) within the sub-watershed. Points are associated with side codes for sub-watersheds (see Table 1.1).

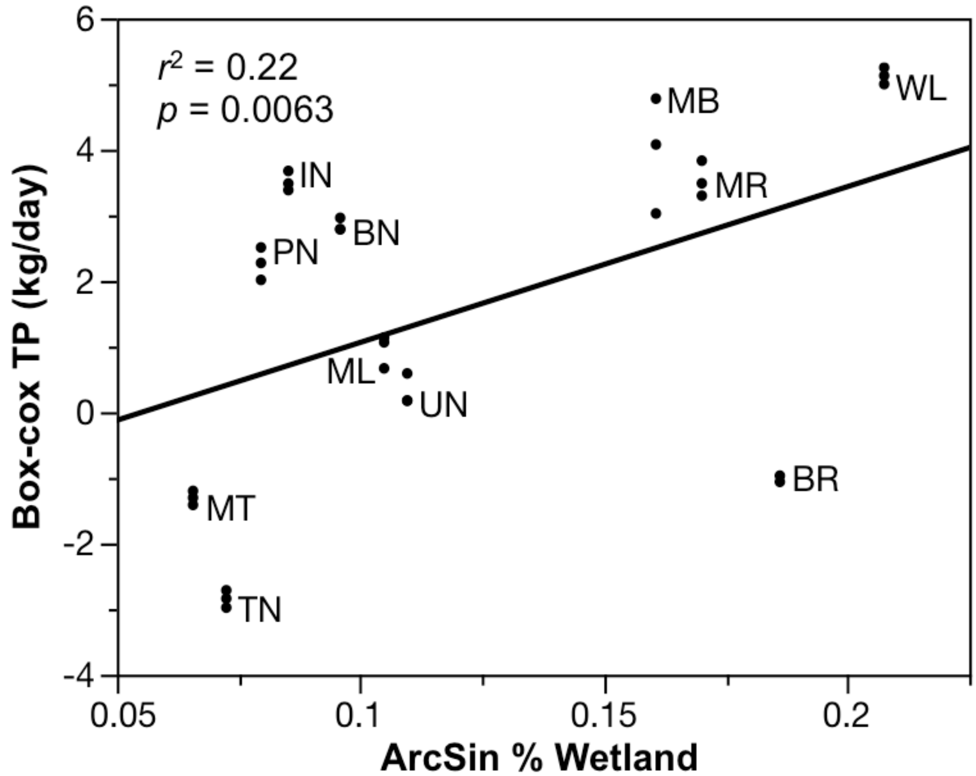


**Figure 1.11:** Linear regression of total phosphorus (TP; kg/day) daily loads against proportion of wetland (%) within the sub-watershed. Points are associated with site codes for sub-watersheds (see Table 1.1).

# CHAPTER 2

## Impacts of tributary loading and in-stream processes on surface water quality of the Nottawasaga River, a tributary of Georgian Bay, Lake Huron

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**Abstract**

Many factors, including tributary inputs and in-stream processes, can influence the longitudinal variation in water quality of riverine systems. Few studies have examined these factors at a large spatial scale. Here, we examine the Nottawasaga River system, a sixth-order stream, with a complex hydrological network that flows through a variety of geological and land-cover features, including Ontario's largest inland wetland complex, before it discharges into Georgian Bay, Lake Huron. We collected turbidity (TURB), total phosphorus (TP), and substrate samples from 11 tributaries, and sampled above and below confluences with the main river. Tributaries that had high TURB concentrations and a wide range of discharge rates significantly increased concentrations downstream, whereas tributaries that had high discharge rates and low TURB significantly reduced downstream concentrations. As a comparison, tributary inputs did not generally influence downstream TP concentrations. Both TP ($r^2$=0.72; $p$ = <0.0001), and TURB ($r^2$ = 0.74; $p$ = <0.0001) were significantly and positively related to proportion of silt+clay particles in tributary substrate. We conducted an intensive longitudinal survey to measure changes in TURB along the Nottawasaga River, and determined that both the presence and length of riffle sections significantly improved water clarity downstream. By studying the complexity of riverine ecosystems, we can provide insight into some of the more important factors that contribute to spatial variation in water quality at a landscape scale.

**Keywords:** tributary loading, in-stream processes, total phosphorus, turbidity, riffles

## Introduction

Anthropogenic loading of nutrients and sediment from urban and agricultural land-uses have become key drivers impacting surface water quality in watersheds. These also result in nutrient enrichment and sedimentation, which are two of the most severe problems facing the ecological health and integrity of lotic systems globally (Sabater et al., 1990; Jordan et al., 1997; Thornton et al., 1999; Kronvang et al., 2005). Though algal blooms associated with excess phosphorus (P) occur frequently in lakes, they sometimes occur in rivers (Hecky & Kilham, 1988; Correll, 1998), and can lead to the same detrimental ecological effects, including reduced light penetration and depletion in dissolved oxygen (DO) concentrations. In turn, anaerobic conditions can lead to internal loading of soluble P from the streambed substrate, thus forming a positive feedback loop (Carpenter et al., 1998). Increased sediment loading, consisting mostly of fine particulate matter such as silts and clay (<0.063 mm; Waters, 1995), can lead to increased water turbidity (TURB) that can reduce light penetration and macrophyte diversity (Steffen et al., 2013), interfere with feeding by invertebrates and fish (Langer, 1980; Bilotta & Brazier, 2008) and suffocate fish eggs and reduce survival of fish populations (Cobb et al., 1996; Culp, 1996). Turbid systems frequently lead to channel infilling, and can release nutrients or harmful chemicals that are easily adsorbed to fine sediments (Lloyd et al., 1987; Miller, 1997; Kronvanget al., 2003).

Nutrient and sediment loading is a common problem in large lotic systems, such as the Nottawasaga River, a sixth-order stream that drains into Nottawasaga Bay, Georgian Bay. The Nottawasaga River Watershed (NRW) is dominated by agricultural land-use, which is a major source of nutrient and sediment loading to the system. In addition to agricultural land-use in the watershed, other geological and land cover features such as the Niagara escarpment and the Minesing Wetlands can also influence water quality in the complex tributary network that drains into the Nottawasaga River. Previous studies have shown how spatial variation in water quality of lotic systems are influenced by tributaries (Rice et al., 2001; McDowell et al., 2002; Change, 2004; Kiffney et al., 2006). It is important to note, however, that tributaries alone cannot explain longitudinal changes in water quality; many other in-stream processes, such as uptake of soluble P by river substrate and macrophytes, and interactions with the hyporheic zone, can influence water quality along rivers (House & Warick, 1998; Ranalli & Macalady, 2010).

Although past studies have documented longitudinal trends in water quality, few have explored the mechanisms that govern these, making it difficult to develop effective restoration strategies when sources of sediments and nutrients vary across landscapes. In this paper, we employ first principles to examine factors influencing spatial variation in water quality. Our goal is to explore how tributary loading and various in-stream processes contribute to the longitudinal variation of total P (TP) and TURB along the main branch of the Nottawasaga River. We hypothesize that downstream nutrient and sediment concentrations will be dependent on the concentration of the tributary and its discharge and make the following predictions: 1) Tributaries with high discharge and high TP and TURB will increase downstream concentrations in the Nottawasaga River 2) Tributaries with high discharge and low TP and TURB concentrations will dilute concentrations in the Nottawasaga River below the confluence and 3) Tributaries with low discharge would have no effect on TP and TURB concentrations below the confluence. Secondly, we hypothesize that riffles would improve water clarity in tributaries, and we predict that TURB values will decrease below riffle sections in the Nottawasaga River. Thirdly, we hypothesize that stream substrate would influence TURB levels in tributaries; we predict that tributaries with substrate composed of a high proportion of silt and clay particles will have high TP and TURB concentrations, compared with those that have a high proportion of sand particles. Finally, we investigate the possibility that internal P loading may occur in areas that experience oxygen depletion; accordingly, areas in the river with high TP concentrations and no obvious point source of nutrient should be associated with periodic anoxic conditions.

**Methods**

*Study area*

Our study takes place in the Nottawasaga River Watershed (~2,900 km$^2$), which encompasses parts of Simcoe and Dufferin County in south central Ontario. More specifically, this paper examines water-quality parameters along the main branch of the Nottawasaga River, as well as 11 of its main tributaries (Figure 2.1). The main branch of the Nottawasaga River is a sixth-order stream, which starts at the confluence of the Upper Nottawasaga River (UN) with Innisfil Creek (IN), and flows 121 km to the mouth located in Wasaga Beach where the river drains into Nottawasaga Bay, Georgian Bay (Lake Huron). All tributaries sampled were fourth- or fifth-order streams. From upstream to the mouth, monitored tributaries include: the Upper Nottawasaga River (UN), Innisfil Creek

(IN), Boyne River (BN), Thornton Creek (TN), Pine River (PN), Bear Creek (BR), the Mad River where it breaches the natural bank (MB), Mad River (MR), Willow Creek (WL), Marl Creek (ML), and McIntyre Creek (MT).

*Site selection*

We used ArcGIS 10.3 (ESRI Inc., Redlands, California), the Ontario Hydro Network (OHN) stream layer (OMNR, 2012), and orthophotos of the study area (Muskoka and Simcoe County Orthophotos, 2008; SCOOP, 2013) to select tributary monitoring stations (Figure 2.1; Table 2.1). All locations were field validated and adjusted accordingly to ensure river access was feasible prior to sampling. In an earlier study, Rutledge et al. (2015) sampled 15 monitoring stations in the main branch of the Nottawasaga River, and noted that two stations (station 10 and 13) had significantly higher TP, and significantly lower daytime DO concentrations compared to the other stations. Based on these findings, we set up continuous monitoring stations to measure diurnal changes in DO at these two stations (station 10 and 13) from June to August 2015, and compared results to a reference site (station 3), where DO was measured continuously for the month of June in 2014 (Figure 2.1; Table 2.3).

*Sampling procedures*

All tributary stations were sampled once from July 13 – 17, 2015 during base flow. At each station, we sampled for TP and TURB within the tributary, as well as in the Nottawasaga River above and below the confluence. We sampled sufficiently far upstream in each tributary to ensure there was no influence from backwash of the

Nottawasaga River, and sufficiently far downstream of the confluence to ensure water from the tributary and the main branch of the Nottawasaga River had mixed well. We used a Van Dorn sampler to collect discrete water samples in freshly acid-washed Corning™ snap-seal containers to measure TP (Lind, 1974; Crosbie & Chow-Fraser, 1999). Once collected, TP samples were stored on icepacks in a cooler until they could be processed or placed immediately in a freezer for storage until they can be processed in the laboratory at McMaster University. TURB readings were determined in situ and measured in triplicate with a HACH® 2199Q turbidimeter. All grab samples and measurements were taken from mid-depth against the current to ensure the sample was thoroughly mixed (Barton, 1977; Shelton, 1997; Poor & McDonnell, 2007).

We followed the methods outlined by the Ontario Stream Assessment Protocol (OSAP; Stanfield, 2010) and measured tributary discharge using the velocity-area method and a SonTek FlowTracker Acoustic Doppler Velocimeter (ADV™). In each tributary, we collected substrate samples from the streambed using a modified PVC pipe sampler (10 cm diameter x 50 cm deep). Samples were taken below the water surface halfway between the thalweg and bank to obtain a representative streambed sample for sediment-size analysis. The pipe was pushed straight down into the substrate to a minimum depth of ~15 cm (McNeil & Ahnell, 1964; Ramos, 1996; Bunte & Abt, 2001). The pipe was capped before it was removed from the water to ensure fine-grained sediment was retained in the sample. We emptied the contents of the pipe, including all the water in the tube (containing fine sediments), into a tightly sealed plastic sample bag. Streambed substrate samples were stored frozen until they could be analyzed in the laboratory.

*Sample processing*

All analyses were performed in triplicate for each variable. TP concentrations were determined with the molybdenum blue method (Murphy & Riley, 1962) following potassium persulfate digestion in an autoclave for 50 minutes (120 °C, 15 psi). Absorbance values were read with a Genesys 10 UV Spectrophotometer and final TP concentrations were calculated with a standard curve.

To analyze the particle size of substrate samples, we thawed streambed samples overnight and pre-treated them by thoroughly drying them in an oven at 100 °C over a 24-hour period. We ensured there were no large clumps or organic matter in the sample before sieving. We used the Wentworth scale of particle sizes to determine mesh sieve sizes (Wotton, 1994). We chose three square-mesh sizes to separate fine sand (0.123 mm), very fine sand (0.063 mm), silt (0.032 mm) and fine silts and clay (any sediment left in the bottom pan). An initial weight of 60 g of dried sample was measured with an electronic balance and placed in the top sieve mesh. The sieve pans were sealed shut, and shaken consistently for 10 minutes (Syvitski, 2007). Remaining soil in each sieve was carefully brushed out and weighed, and the percentage of soil passing through each sieve was calculated. We subsequently grouped very fine sand and fine sands into one category (representing % sand) and then silt, very fine silts, and clay into a second category (representing % silts+clay).

*Longitudinal survey of turbidity*

From August 10 – 14 in 2015, we documented longitudinal changes in TURB down the main branch of the Nottawasaga River under base flow conditions (Figure 2.1).

Rutledge et al. (2015) determined that TURB in the Nottawasaga River did not vary significantly between June and September 2014; therefore, we chose to complete the survey in August to ensure we obtained base flow measurements. The survey covered the full extent of the river, from Innisfil Creek to the town of Wasaga Beach. We did not continue the survey all the way to the mouth of the river because water in this portion of the river is contaminated with water from Nottawasaga Bay. A sonde (YSI 600OMS V2) with an optical turbidity sensor was towed down the river by canoe, and set to take simultaneous measurements and GPS coordinates at 60-second intervals. The sonde was fastened to the canoe to ensure measurements were taken at the same depth and to prevent rocks or large debris from damaging the sensor. An additional component of the longitudinal survey involved riffle mapping. GPS waypoints were taken every time a riffle was encountered. Subsequent analysis in a Geographic Information System (ArcGIS 10.3; ESRI Inc., Redlands, California) allowed us to group individual riffles into 14 sections based on maximum distance separating them (riffles separated by <500 m were considered one riffle section), and to determine length of the riffle sections. We sorted the river segments by geographic location into upper, middle and lower Nottawasaga River before we performed statistical analyses.

*Tributary monitoring*

In order to evaluate the impact of tributary loading on water quality in the Nottawasaga River, we measured TP and TURB within the main branch of the Nottawasaga River both above and below 11 tributary inputs (Table 2.1). Based on the expectation that both tributary discharge and parameter concentration will influence downstream water quality, we created four tributary scenarios to test our assumptions (Table 2.2). Scenario A predicts that inputs from a tributary with a high parameter concentration and a high discharge rate would greatly increase downstream concentrations (++). Scenario B predicts that inputs from a tributary with high parameter concentration and low discharge would increase downstream concentration, but not as much as that in Secnario A (+). Scenario C predicts that inputs from a tributary with low parameter concentration and high discharge would decrease downstream concentrations (–). Finally, scenario D predicts that inputs from tributaries with both low discharge and low parameter concentration would have no significant effect on downstream concentration (0).

*Continuous monitoring of dissolved oxygen*

Continuous monitoring devices were deployed at stations 10 and 13 from June until the end of August 2015 (Figure 2.1). A continuous logger was also deployed at Station 3 during the month of June in 2014 and served as a reference. At each station, loggers (Onset HOBO U26) were deployed mid-depth in the water column to ensure underlying substrate did not influence DO measurements. Loggers were secured in PVC pipes with holes to prevent any damage to the sensor, while allowing water to readily pass through. The PVC pipes with secured loggers were attached to metal stakes, which we used to anchor into the streambed. We could adjust the height of the PVC pipe on the metal stake to ensure DO loggers were taking measurements at mid-depth in the stream at each station. DO measurements were recorded every hour and were left submerged for the duration of the study period. Every two to four weeks, loggers were temporarily removed to facilitate data download and maintenance (if needed), and were recalibrated before they were redeployed.

*Data analysis*

All statistical analyses were conducted with JMP 12 software (SAS Institute Inc., Toronto, ON, Canada). Where data did not meet assumptions of normality and equal variance, we transformed variables using box-cox and arcsine functions. We used ANOVA and Tukey-Kramer comparisons to classify tributaries as being "high" or "low" with respect to discharge and parameter concentrations. Paired t-tests were used to detect significant changes in mean downstream water quality following tributary inputs and riffle sections. Linear regression analysis was used to determine relationships between tributary substrate and water-quality variables.

## Results

*Longitudinal turbidity changes*

The most turbid section of the Nottawasaga River was at the confluence of Innisfil Creek (IN; >25 NTU) and the Upper Nottawasaga tributaries (UN), where they formed the main branch of the Nottawasaga River (Figure 2.1). High discharge combined with very low TURB concentrations in the Upper Nottawasaga diluted the high levels of TP and TURB in Innisfil Creek, and resulted in much lower TURB concentrations throughout the rest of the upper and middle river segments (11 mapped riffle sections; Figure 2.1). TURB values decreased in the main branch of the Nottawasaga River after inputs from Pine River (PN). We also noted increased TURB (>15 NTU) near the inflow of the Minesing Wetlands, which corresponded to inputs from the Mad River Breach (MB); this increased TURB remained evident as the river flowed through much of the Minesing Wetlands. Very high TURB (>25 NTU) was observed at the confluence with Marl Creek (ML), although this was such a short segment of the river that it was difficult to discern without zooming into this region (see inset; Figure 2.1). Downstream of this section, TURB increased to make this section of the lower Nottawasaga River the most turbid section during base flow conditions (15 – 25 NTU). TURB levels decreased again once the Nottawasaga River reached the lower river segment containing riffle sections. Water in the final stretch of the Lower Nottawasaga River was reduced to TURB levels <10 NTU, mostly because of dilution and mixing from the very clear water of Nottawasaga Bay.

*Tributary influences on downstream water quality*

Tributaries classified as having "high" discharge rates included Willow Creek (WL; 4.32 $m/s^2$), Pine River (PN; 2.89 $m/s^2$), Boyne River (BN; 2.51 $m/s^2$), Mad River Breach (MB; 2.41 $m/s^2$) and the Upper Nottawasaga River (UN; 2.28 $m/s^2$), while those with "low" discharge included Thornton Creek (TN; 0.12 $m/s^2$), Bear Creek (BR; 0.26 $m/s^2$), McIntyre Creek (MT; 0.26 $m/s^2$), Marl Creek (ML; 0.48 $m/s^2$), Mad River (MR; 1.45 $m/s^2$), and Innisfil Creek (IN; 1.57 $m/s^2$) (Table 2.1). Tributaries with significantly higher TP concentrations included the Mad River (MR; 44.2 μg/L), Marl Creek (ML; 41.0 μg/L), Innisfil Creek (IN; 40.4 μg/L), and Mad River Breach (MB; 32.5 μg/L). Most of these tributaries also had significantly higher TURB (Marl Creek (ML; 48.9 NTU), Innisfil Creek (IN; 35.0 NTU) and Mad River Breach (MB; 27.4 NTU)).

Tributary inputs influenced downstream water quality in different ways, depending on the variable of interest (Figure 2.2). For TP concentrations, predictions associated with the four scenarios (Table 2.2) were only applicable for two of our tributaries. As expected, the high concentration of TP in Innisfil Creek increased TP concentrations downstream of the confluence by 16.2 μg/L (Scenario A; paired t-test; $p$ <0.05). Similarly, given the large discharge of the Upper Nottawasaga and low concentration of TP, we predicted that TP concentrations downstream of the confluence would decrease, and this was supported by a drop in TP concentration of 18.0 μg/L (Scenario C; paired t-test; $p$ <0.05). For the remainder of the tributaries, tributary inputs had no significant effect on downstream TP concentrations in the main river.

By contrast, the four scenarios accurately described how downstream TURB concentrations would be affected by tributary inputs. Following the confluence of the Mad River Breach, TURB levels in the Nottawasaga River significantly increased by 5.37 NTU (Scenario A; paired t-test; $p$ <0.05). Consistent with Scenario B, two of the three tributaries with low discharge and high TURB levels significantly increased downstream values (12.7 and 2.8 NTU, respectively for Innisfil and Marl Creek; paired t-test; $p$ <0.05). Inputs from the four tributaries with high discharge and low TURB all decreased downstream concentrations of the Nottawasaga River (Scenario C; -4.24 NTU for Boyne River; -2.37 NTU for Pine River, -19.4 NTU for the Upper Nottawasaga River, and -10.8 for Willow Creek; paired t-test; $p$ <0.05). Inputs from Bear Creek, Thornton Creek, and McIntyre Creek were not associated with any significant changes in TURB (Scenario D; paired t-test; $p$ >0.05).

*Effects of in-stream processes on water quality*

To determine the effect of riffles on water clarity, we compared TURB values above and below riffle sections along the main branch of the Nottawasaga River. To account for differences in bedrock geology that might affect water clarity along the Nottawasaga River, we first categorized riffle sections as belonging to the upper, middle or lower river segments. TURB readings decreased significantly following riffle sections in all river segments (Figure 2.3). The greatest decrease occurred within the lower river segment by 1.21±0.13 NTU (paired t-test; $p$ <0.0001); values decreased by 0.7±0.22 NTU in the middle river section (paired t-test; $p$ = 0.0059), compared with only 0.51±0.061 NTU decrease in the upper river segment (paired t-test; $p$ <0.0001).

We found a positive relationship between ΔTURB and TURB measured above riffle sections ($r^2$ = 0.61, $p$ = <0.0001; Figure 2.4), which suggests that the "cleansing" power of riffles is dependent on the TURB of upstream water. Since water quality in the lower river segment was generally more turbid, riffles had a greater impact on water clarity there than in the upper river segment. We also found a significant positive relationship between ΔTURB and riffle section length ($r^2$ = 0.26, $p$ = 0.0008; Figure 2.5), with longer riffle sections associated with greater decreases in downstream TURB. Two outliers in our regression suggested that the effect of riffle length eventually plateaus, which is why these points were excluded from the regression analysis.

We determined the effects of substrate on stream water quality by regressing TP and TURB against the proportion of sand particles (0.0625 – 2 mm) and silt+clay particles (<0.0039 mm – 0.0625 mm) in substrate samples from 11 tributaries monitored in 2015. We found significant negative relationships between TP and sand particles ($r^2$ = 0.67; $p$ = <0.0001; Figure 2.6a), and by implication, a significant positive relationship between TP and proportion of silt+clay particles ($r^2$ = 0.72, $p$ = <0.0002; Figure 2.6b). Similar trends were observed for TURB; there was a significant negative relationship between TURB and proportion of sand particles ($r^2$ = 0.77; $p$ = <0.0001; Figure 2.7a), and a significant positive relationship between TURB and silt+clay particles ($r^2$ = 0.74, $p$ = <0.0001; Figure 2.7b).

During 2015, continuous loggers were deployed from June through August inclusive, at stations 10 and 13, that had previously been identified as having significantly higher TP concentrations and significantly lower DO relative to other stations (Figure 2.8). DO concentrations fluctuated diurnally throughout the sampling period, with greater fluctuations occurring during the first half of the growing season (June to end of July). During this period of more extreme daytime maxima and nighttime minima, substantial periods of hypoxia (<4 mg/L), and in some instances, anoxia (<1 mg/L) occurred. Over this period, mean DO concentrations measured at station 10 and 13 were 6.01 mg/L and 5.85 mg/L respectively (Table 2.3). For comparison, minimum DO concentrations obtained at Station 3 (associated with low mean seasonal TP concentrations) during the month of June in 2014 never dropped below 7.25 mg/L (Figure 2.9), and the mean concentration over the entire sampling period was 8.60 mg/L (Table 2.3). This comparison indicates that parts of the Nottawasaga River can and do remain well oxygenated for the entire summer, whereas the two stations associated with high TP concentrations (10 and 13) experienced periods of hypoxia and anoxia during the summer.

**Discussion**

Presence of intricate tributary networks, channel morphology, substrate type, amount of groundwater flow, and land cover features are all major factors that can influence the water quality of large rivers. Consistent with basic mass balance principles, almost all 11 tributaries sampled followed our discharge-concentration matrix predictions for TURB. As illustrated by Mad River Breach, a tributary with high discharge and TURB concentrations will increase downstream concentrations (Scenario A). The magnitude of this change was clearly reflected in results of the longitudinal survey (Figure 2.1), where an abrupt spike in TURB coincided with where the Mad River broke its natural levee and discharged into the Nottawasaga River. Although McIntyre Creek also had a low discharge but high TURB, downstream conditions were significantly lower than expected. This may be explained by the positive influence of riffles located both upstream and downstream of the confluence. Since detailed mass-balance studies are time-consuming and expensive to undertake, they are seldom conducted in large river systems occurring over a large spatial scale. Our method offers a simple and effective means to predict how downstream TURB might change as a result of tributary inputs.

Only inputs from two tributaries occurring in the upper portion of the Nottawasaga River (Innisfil Creek and Upper Nottawasaga) had the expected effect on downstream TP concentrations (Scenario A and C, respectively; Table 2.3). For the other tributaries, we were unable to accurately predict the outcome of tributary inputs based on discharge rate and concentrations. McDowell et al. (2002) found that TP concentrations increased as the proportion of fine particles in the sediment increased, and that tributary confluences were locations of turbulence, where there was a shift in particle size to coarser sediments. Since soluble P is the main form associated with coarse-grained sediments (Baldwin et al., 2002), tributaries of the Nottawasaga River with high discharge are likely to provide sufficient energy to suspend coarse sediments in the water column, and result in temporarily lower TP concentrations, followed by rapid release of soluble P as the sediment becomes continually resuspended (McDowell et al., 2002). Since this is the form readily taken up by primary producers, algal biomass would tend to peak at tributary confluences (Kiffney et al., 2006). Furthermore, various studies illustrate that tributary confluences are sites of disturbance that create locations of high biological productivity and increased habitat complexity (Polis et al., 1997; Power & Dietrich, 2002; Benda et al., 2004; Kiffney et al., 2006). Increased habitat complexity, including more primary producers that take up bioavailable P from suspended coarse-sized particles, may be an additional reason why our study did not reveal significant changes in downstream TP concentrations.

Following tributary input from the Mad River Breach, TURB remained high through a substantial portion of the Minesing Wetlands. This stretch of relatively high TURB did not include additional tributary inputs; therefore, we speculate that the high TURB was maintained through in-stream processes. Historically, this southern portion of the Minesing Wetlands had been used for pasture land until the 1930s (Brown et al., 2011). Soil compaction from cattle grazing destroyed riparian habitat, and recovery of vegetation in this area has been slow. Lack of vegetation promoted bank erosion and sedimentation, which may explain the high TURB in this stretch of river. In the absence of additional tributary influences, the decrease in TURB identified by the longitudinal survey is likely due to dilution from groundwater, which flows slowly through the wetland in a northwesterly direction, and eventually enters the Nottawasaga River (Post et al., 2015). The most turbid section appeared in the Lower Nottawasaga River (20-25 NTU), which decreased slightly (15-20 NTU) as it flowed through Jack's Lake, a widening in the river. Jack's Lake is more representative of a lentic system, with low flow and abundant vegetation, conditions that likely lead to settling out of suspended solids. This explains why we observed a decrease in TURB as the Nottawasaga River flowed through Jack's Lake.

Consistent with our hypothesis, we found that TURB decreased below riffle sections. Riffles are characterized by declines in elevation and coarser, cobble substrates. Periphyton, or attached algae, which grows on substrate in riffle sections, is vital for nutrient uptake (Burkholder et al., 1990; Flemming, 1995). Sabater et al. (2002) found that periphyton or "biofilms" can efficiently assimilate both inorganic and organic nutrients, and are important natural water purifiers. Because riffles have been found to decrease nutrient concentrations, it is possible that reduced inorganic P following riffle sections decreased planktonic algal growth, an organic component of TURB. A reduction in planktonic algae might explain the decrease in TURB observed following riffle sections in the Nottawasaga River. In addition, many studies report down-welling of river water at the head of a riffle, and upwelling at the end of a riffle (White et al., 1987; Hill et al., 1998; Kasahara & Hill, 2006). This leads to hyporheic exchange between surface and ground water. Upwelling of surface waters from the hyporheic zone is mixed with groundwater, which may dilute turbid stream surface water and thus lead to decreasing TURB in the Nottawasaga River after flowing through the riffles.

Our results suggest that tributaries with a greater proportion of silt and clay sediment in streambed have higher TP and TURB concentrations. Based on Stoke's law, larger particles (ie. sand) should settle out of water more quickly than smaller particles (ie. silt and clay) (Gordon et al., 2004), and therefore, substrate with higher proportions of silt and clay can be more easily re-suspended and should be associated with higher TURB. By contrast, substrate with a higher percentage of sand particles are more likely to move by rolling or saltating along the streambed, and should be associated with lower TURB (Petts & Foster, 1985). TP concentration in tributaries followed a similar pattern, with higher concentrations associated with greater proportions of silt and clay particles in substrate. Depending on its sediment composition, tributary substrate can either function as a source or sink for dissolved P to satisfy the sediment equilibrium P concentration (EPC) (Froelich 1988; Sharpley et al. 2002; Haggard & Sharpley, 2006). Generally, silt and clay sediments act as a sink (Baldwin et al., 2002) because they have a relatively large surface area that allows easier adsorption of nutrients (Stone & Droppo, 1994).

The periods of hypoxia and anoxia at stations 10 and 13 occurred during the months of June and July in 2015, particularly late at night when respiration was highest. This has implications for fish that rely on the Nottawasaga River for important spawning and nursery habitat. Sediments are known to release soluble P under anoxic conditions (Mortimer, 1942; Holdren & Armstrong, 1980; Baldwin & Williams, 2007; Hupfer & Lewandowski, 2008), and this may be the primary mechanism by which TP concentrations have accumulated at these sites. Station 13 occurs after the Nottawasaga River flows through Jack's Lake, which has qualities more similar to that of a wetland than a river, whereas station 10 occurs after inputs from Willow Creek, within the Minesing Wetlands. High organic matter and dissolved organic carbon at these stations likely contribute to the low DO conditions. We suspect that internal loading, when it happens, are restricted to areas that undergo anoxia, and contributes to the spatial variation of TP along the Nottawasaga River.

**Conclusion**

Riverine systems encompass dynamic interactions between terrestrial and aquatic ecosystems. It is vital that we understand landscape and in-stream processes that influence water quality in lotic environments in order to maintain ecosystem health. Our study reveals that tributary loading significantly influences TURB in the Nottawasaga River according to tributary discharge and TURB concentrations. We identified tributaries with high discharge and high concentrations as having the most detrimental impacts on downstream TURB. Conversely, tributaries with high discharge and low TURB improved downstream water clarity. These results have implications for best management practises (BMPs) aimed at reducing sediment loads to large rivers. By targeting individual tributaries with high discharge, agencies can improve TURB in the main river through dilution with clear tributary water. Given that phosphorus is the most limiting nutrient in freshwater ecosystems, it is important to account for effects of TP loading from tributaries; however, our results suggest nutrient cycling at the tributary-river confluence are too dynamic to enable a prediction based on tributary concentration and discharge rate.

The longitudinal survey was an effective approach for identifying reaches of the Nottawasaga River where sedimentation and erosion was greatest. This has implications for restoration of riparian habitat and stabilization of riverbanks. We also found that presence of riffle sections significantly decreased TURB in tributaries and that proportions of sand was negatively related to TP and TURB. These findings imply that constructed riffles, consisting of sand substrate, may be used to improve water quality in turbid stretches of tributaries and the main river. Finally, continuous monitoring identified two locations in the main river that developed anoxic conditions for at least part of the growing season. Though this is unusual for riverine systems, we have shown that rivers with slow flow velocities can become anoxic, and potentially contribute P internally through remineralization of soluble P from the sediment. The periods of hypoxia are of concern because of implications for sport fish that require DO >4 mg/L to survive. This is particularly important in the Nottawasaga River, as it is the only tributary of Georgian Bay with confirmed spawning populations of lake sturgeon, a threatened species in Ontario.

We recommend that future studies investigate TP loading at tributary junctions to improve our understanding of phosphorus cycling in these important areas. Additionally, further research should be conducted in natural riffle sections to evaluate the in-stream processes (biotic and abiotic) responsible for the observed decline in TURB. It would also be valuable to determine if riffle sections have similar effects on TP cycling. Understanding the influences of both tributary loading and in-stream processes will enhance the development of BMPs and restoration initiatives to improve water quality and ecosystem health in lotic systems at a watershed scale.

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**Table 2.1:** Tributary coordinates, discharge ($Q_{trib}$; $m^2/s$), mean TP (µg/L), and TURB (NTU) sampled within each tributary (trib), as well as above and below the confluence within the main branch of the Nottawasaga River. Bold values indicate tributary discharges and parameter concentrations that are significantly highest as indicated by ANOVA. n/a=not available.

| Trib | Latitude, Longitude | $Q_{trib}$ | TP Trib | TP Above | TP Below | TURB Trib | TURB Above | TURB Below |
|---|---|---|---|---|---|---|---|---|
| UN | 44.13648, -79.81020 | **2.28** | 6.08 ±0.48 | n/a | n/a | 3.0 ± 0.2 | n/a | n/a |
| IN | 44.13532, -79.80868 | 1.57 | **40.4 ±1.4** | 6.08 ± 0.48 | 22.4 ±0.5 | **35.0 ±0.7** | 3.0 ±0.2 | 15.7 ±0.2 |
| BN | 44.16919, -79.81576 | **2.51** | 19.0 ±0.5 | 19.0 ±1.0 | 17.6 ±1.3 | 6.3 ±0.2 | 12.9 ±0.3 | 8.6 ±0.3 |
| TN | 44.24819, -79.81990 | 0.12 | 12.8 ±0.8 | 26.2 ±1.0 | 22.9 ±0.0 | 11.7 ±0.1 | 11.8 ±0.5 | 11.2 ±0.6 |
| PN | 44.33138, -79.87441 | **2.89** | 12.8 ±0.8 | 22.4 ±1.3 | 22.4 ±0.5 | 8.8 ±0.2 | 23.0 ±0.8 | 20.6 ±0.3 |
| BR | 44.33403, -79.87095 | 0.26 | 23.4 ±0.5 | 22.9 ±0.0 | 24.3 ±0 | 16.4 ±0.4 | 20.6 ±0.4 | 20.1 ±0.4 |
| MB | 44.36003, -79.87987 | **2.41** | **32.5 ±6.2** | 23.8 ±0.5 | 21.9 ±1.0 | **27.4 ±0.6** | 21.1 ±0.4 | 26.4 ±1.3 |
| MR | 44.40856, -79.89931 | 1.45 | **44.2 ±2.9** | 22.9 ±0.8 | 24.3 ±2.2 | 15.0 ±1.2 | 18.3 ±0.2 | 18.5 ±0.3 |
| WL | 44.41880, -79.88382 | **4.32** | **31.5 ±0.8** | 28.6 ±2.2 | 30.6 ±2.5 | 8.4 ±0.2 | 26.6 ±0.2 | 15.8 ±0.2 |
| ML | 44.44141, -79.89180 | 0.48 | **41.0 ±3.0** | 26.7 ±0.5 | 28.6 ±0.8 | **48.9 ±0.9** | 15.2 ±0.4 | 18.0 ±0.1 |
| MT | 44.46916, -80.04650 | 0.26 | 20.0 ±0.8 | 23.8 ±1.3 | 24.3 ±0.8 | 14.7 ±0.5 | 11.9 ±0.2 | 11.4 ±0.2 |

**Table 2.2:** Matrix describing four sets of conditions relating discharge ($\boldsymbol{Q}_{\mathbf{trib}}$) and concentration of constituents in the tributary ($\boldsymbol{C}_{\mathbf{trib}}$). Each scenario (A to D) is a prediction of how downstream concentrations would change below the confluence of the tributary and main river branch. The four possible outcomes include a large increase (++), an increase (+), a decrease (–), and no change (0) in downstream parameter concentration.

| | | $\boldsymbol{Q}_{\mathbf{trib}}$ | |
|---|---|---|---|
| | | **High** | **Low** |
| $\boldsymbol{C}_{\mathbf{trib}}$ | **High** | ++ (A) | + (B) |
| | **Low** | – (C) | 0 (D) |

**Table 2.3:** Summary of location, total phosphorus (TP; µg/L), and dissolved oxygen (DO; mg/L) concentrations from continuous monitoring stations. TP values represent means of samples collected monthly from June to September in 2014. DO values for station 10 and 13 were measured continuously from June to August 2015, and DO for station 3 was measured continuously during the month of June in 2014.

| Stn | Location | Latitude, Longitude | TP | DO Min | DO Max | DO Mean |
|---|---|---|---|---|---|---|
| 3[†] | Downstream confluence with IN | 44.13699, -79.80843 | 31.1 | 7.25 | 10.4 | 8.60 |
| 10 | Downstream confluence with WL | 44.42848, -79.89464 | 39.8 | -0.02 | 9.88 | 6.00 |
| 13 | Downstream Jack's Lake | 44.47552, -80.00853 | 42.1 | 0.05 | 11.5 | 5.85 |

[†] Indicates reference station.

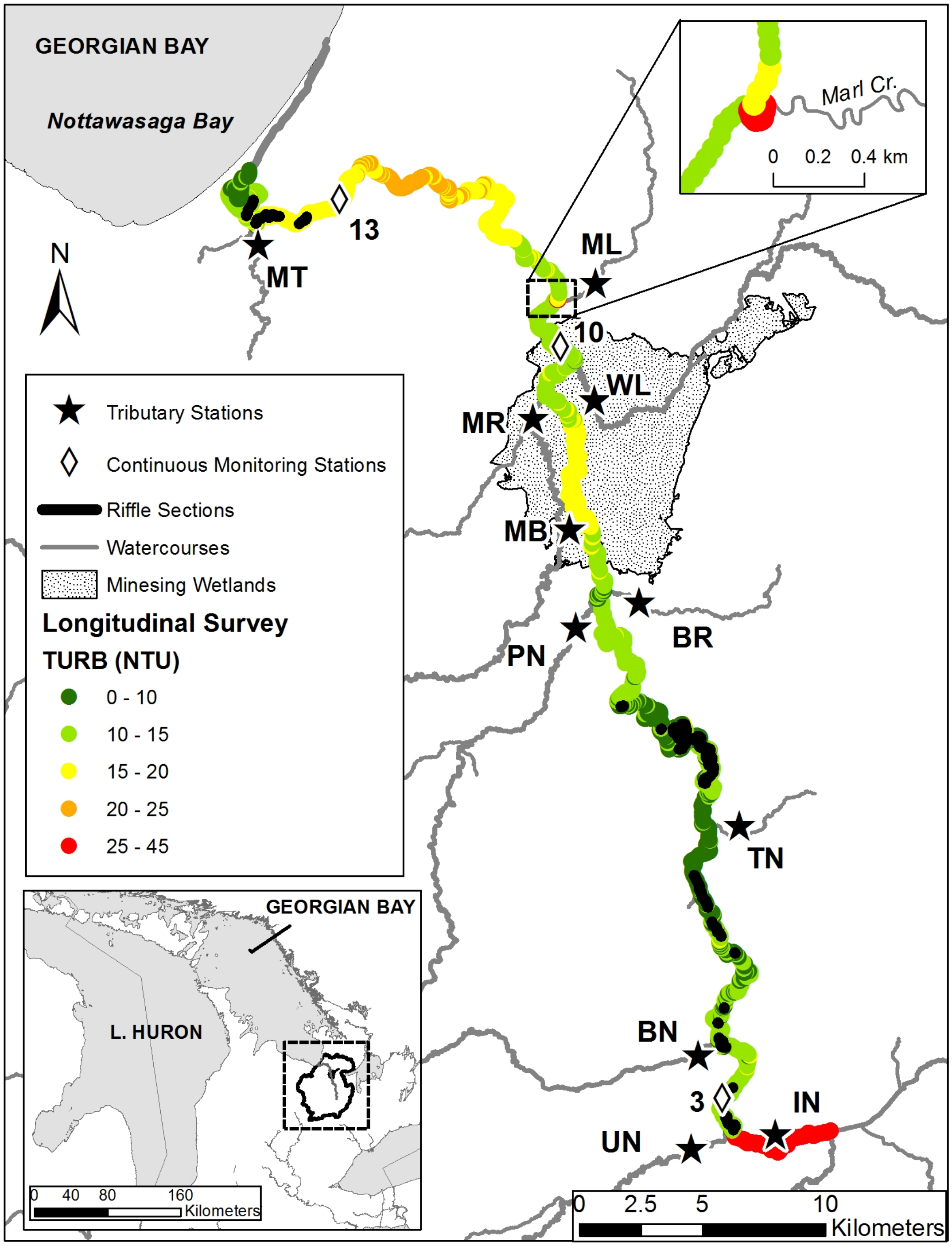
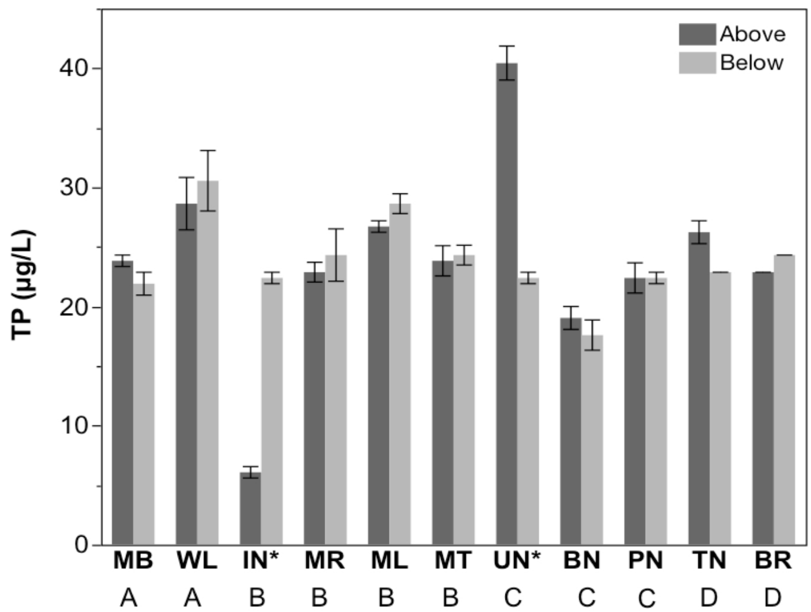



**Figure 2.1:** Map showing location of monitoring stations (*black stars*), continuous monitoring stations (*white diamonds*), and 14 riffle sections (*black circles* in the river channel) in the Nottawasaga River. Inset shows a close-up of the confluence between Marl Creek and the main branch of the river.

a)




b)

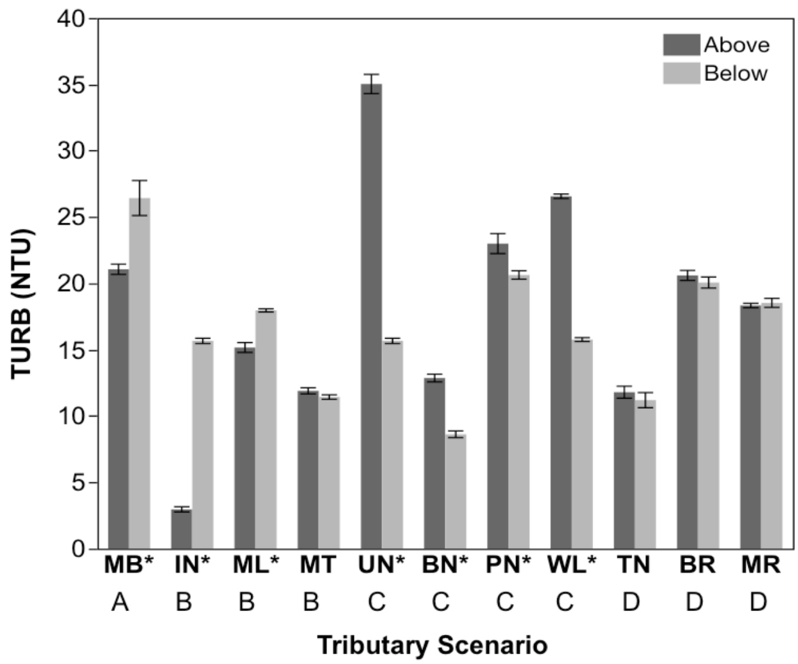



**Figure 2.2:** Mean difference between a) total phosphorus (TP; µg/L) and b) turbidity (TURB; NTU) concentrations in the Nottawasaga River above and below confluence with each tributary. Corresponding concentration-discharge scenarios (A – D) are indicated below each tributary. The asterisk (*) indicates statistically significant differences between upstream and downstream concentrations.

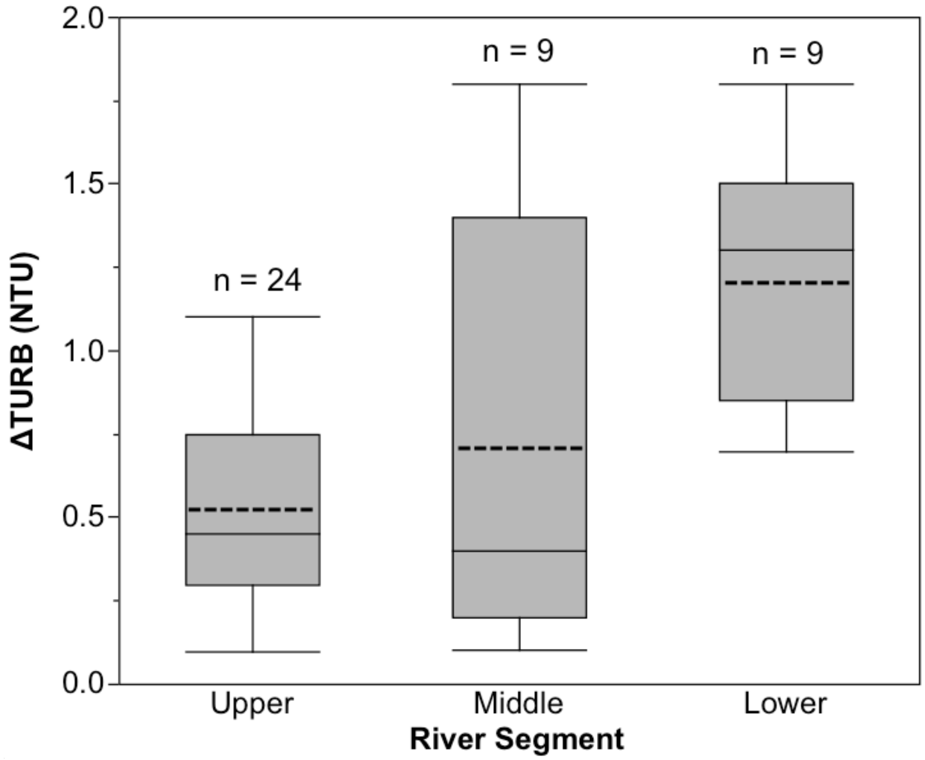



**Figure 2.3:** Box-whisker plot illustrating mean (*dotted black line*) and median (*solid black line*) for Δ turbidity (TURB; NTU) measured above and below riffle sections. Data are sorted by location of the riffle sections in the upper, middle, and lower segments of the Nottawasaga River.

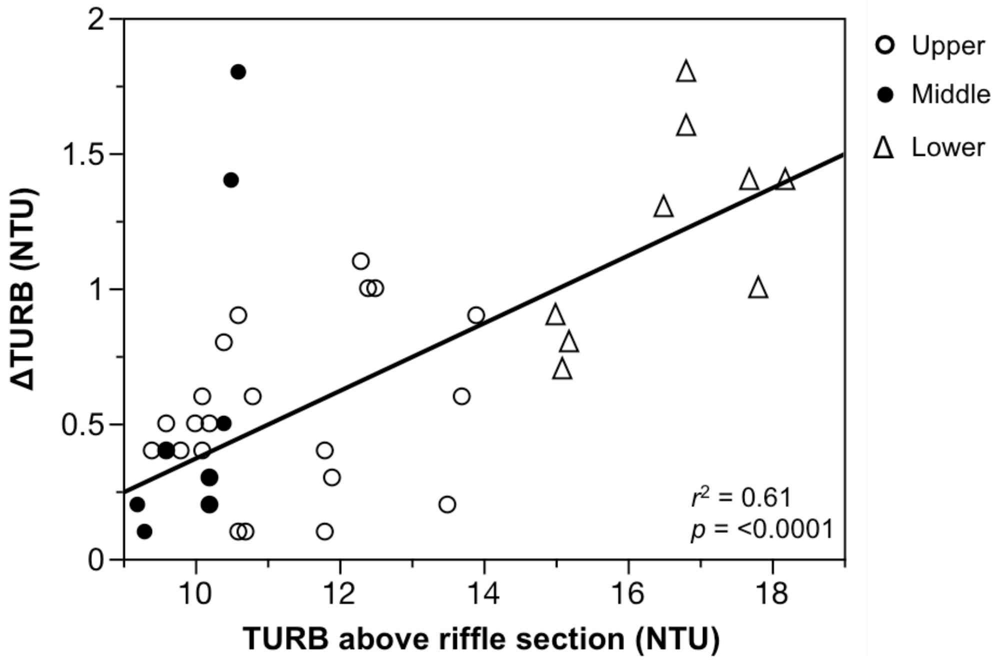



**Figure 2.4:** Relationship between changes in turbidity (ΔTURB; NTU) measured above and below riffle sections and TURB measured above riffle sections. Open circles, closed circles, and triangles represent riffle sections located within the upper, middle, and lower river segments respectively.

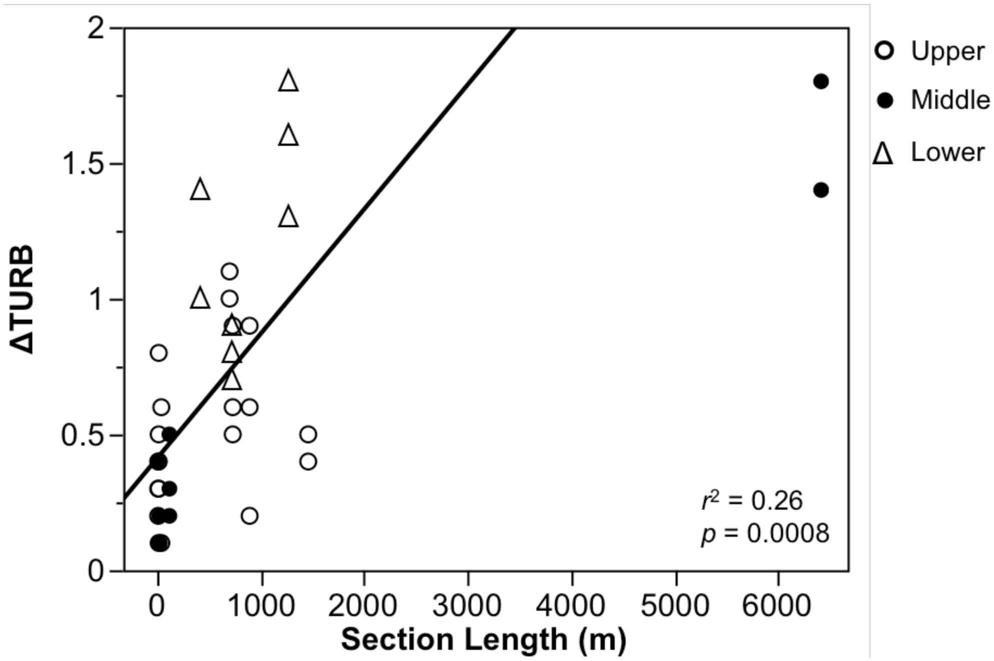
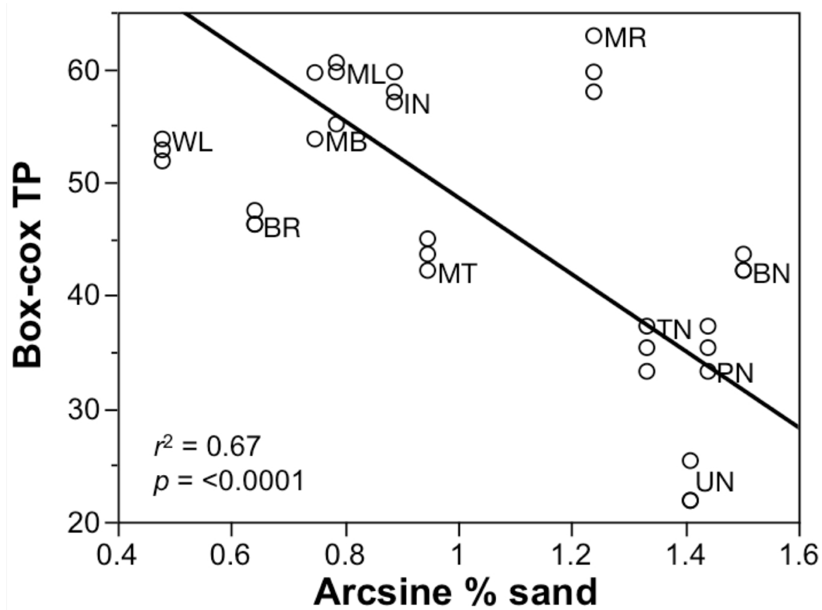



**Figure 2.5:** Relationship between changes in turbidity (ΔTURB; NTU) measured above and below riffle sections and riffle section length (m). Open circles, closed circles, and triangles represent riffle sections located within the upper, middle, and lower river segments respectively.

**a)**




**b)**

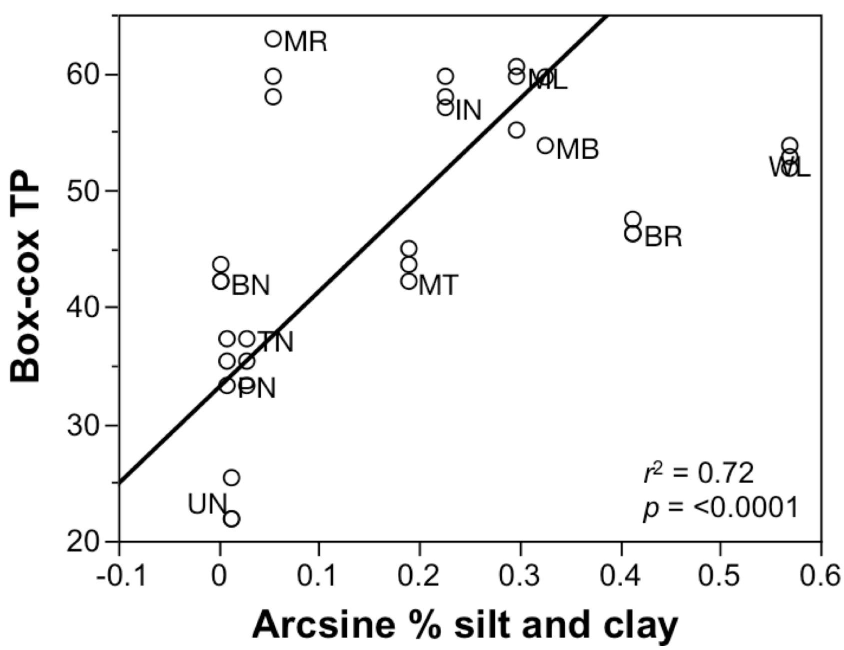
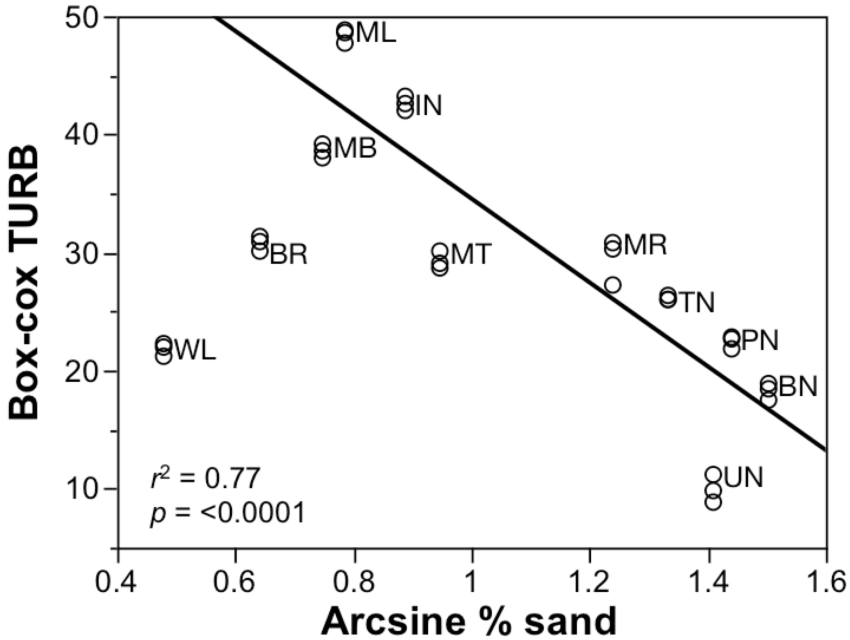



**Figure 2.6:** Linear regression of total phosphorus (TP; box-cox transformed) against proportion (arcsine transformed) of a) sand particles (0.0625 – 2 mm) and b) silt+clay particles (<0.0039 mm – 0.0625 mm) in tributary substrate. Outliers (MR, WL, BR) are shown, but were excluded from the regression analysis.

**a)**




**b)**

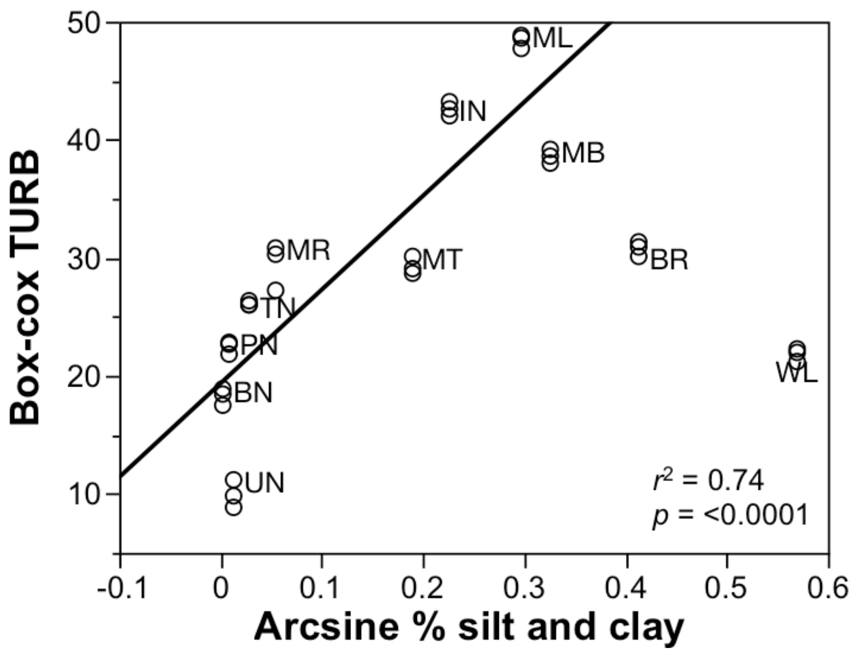
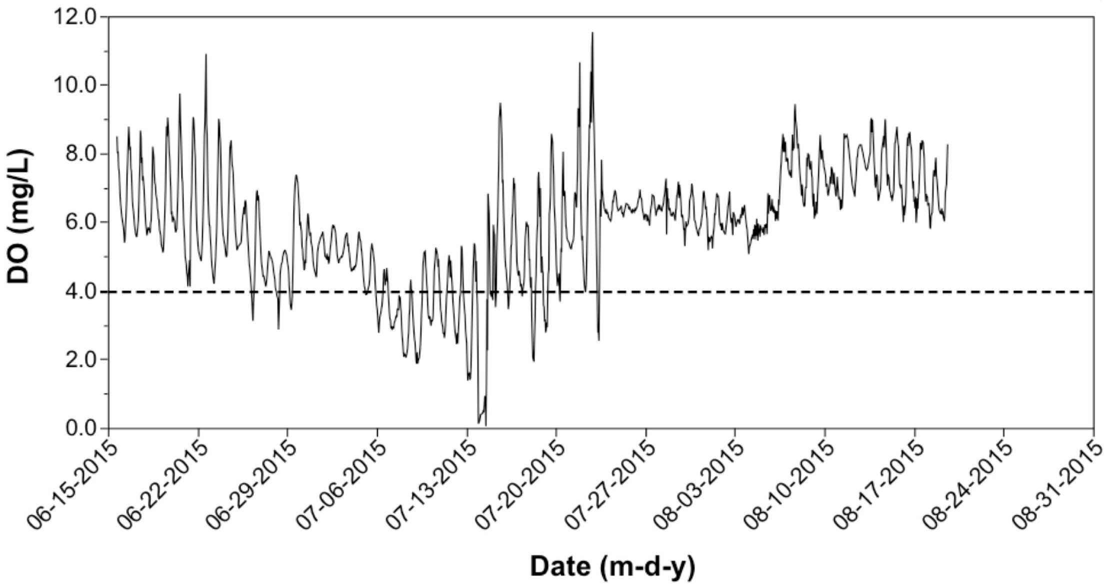



**Figure 2.7:** Linear regression of turbidity (TURB; box-cox transformed) against proportion (arcsine transformed) of a) sand particles (0.0625 – 2 mm) and b) silt+clay particles (<0.0039 mm – 0.0625 mm) in tributary substrate. Outliers (WL, BR) are shown, but were excluded from the regression analysis.

**a)**




**b)**

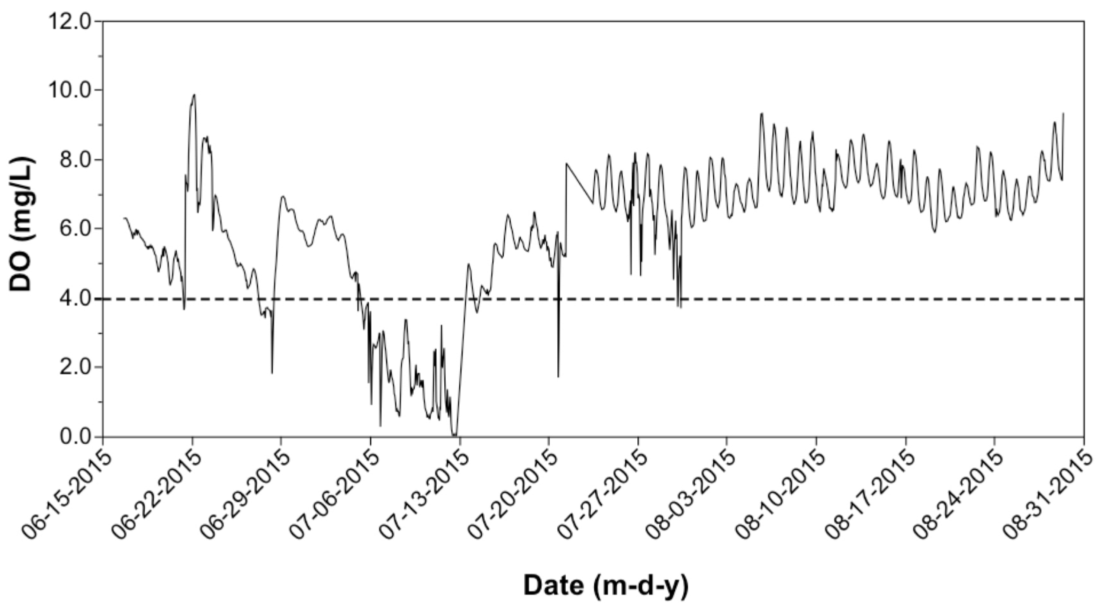



**Figure 2.8:** Diurnal fluctuations in dissolved oxygen (DO) at stations a) 13 and b) 10 from June to August 2015. The dashed line indicates the PWQO for DO (4 mg/L).

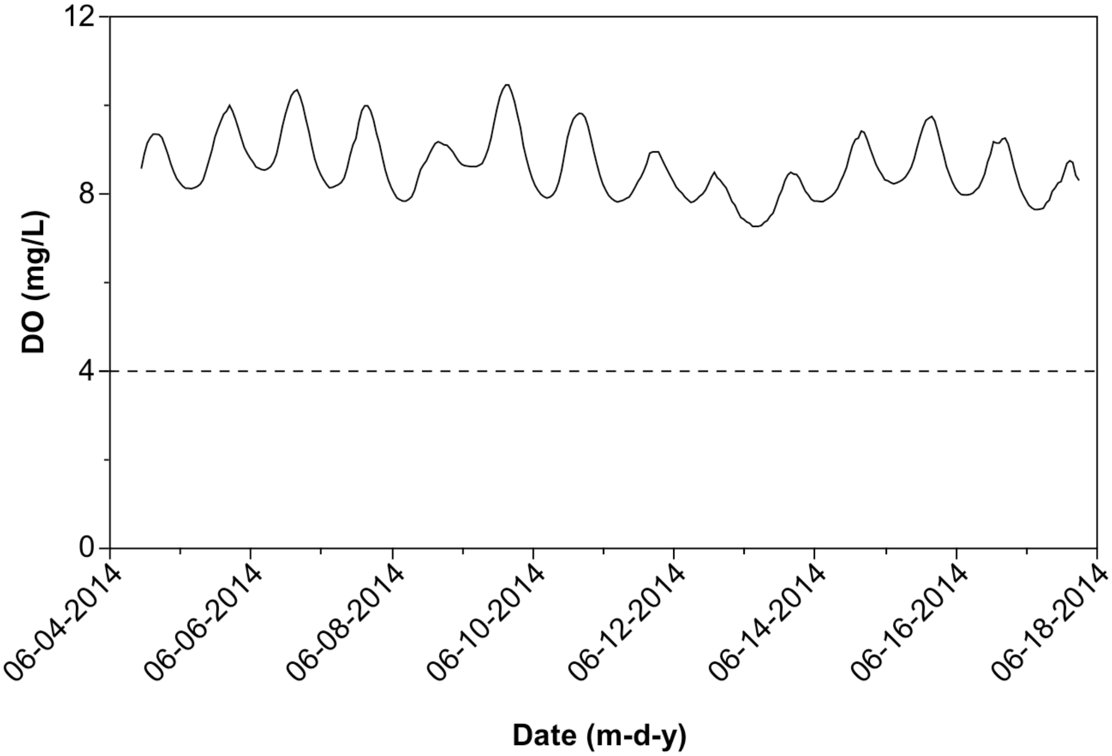



**Figure 2.9:** Diurnal fluctuations in dissolved oxygen (DO) at reference station 3 monitored June 4 to 18, 2014. The dashed line indicates the PWQO for DO (4 mg/L).

# CHAPTER 3

## Development of the Stream Water Quality Index (SWQI) to evaluate surface water quality of the Nottawasaga River, a tributary of Georgian Bay, Lake Huron

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**Abstract**

Good water quality is vital for sustaining the health and biodiversity of lotic systems, which are commonly degraded by conversion of natural areas to urban and agricultural land-use. Such water quality impairment has been noted in the watershed of the Nottawasaga River, a major tributary of Georgian Bay (Lake Huron), which is dominated by agricultural land-use, and which also drains the Minesing Wetlands, a Ramsar site and the largest contiguous inland wetland in southern Ontario. We initiated a study to assess the extent of impairment along 15 locations of the main branch of the Nottawasaga River (121 km) and found that nearly all stations exceeded published water-quality targets and nutrient guidelines. Using multivariate techniques, we developed the Stream Water Quality Index (SWQI) specifically for the Nottawasaga River, which relies on 13 variables commonly available in routine monitoring programs. To predict SWQI scores for any site, we have provided 9 equations that use various combinations of available variables. SWQI scores calculated for most of the 15 stations were categorized as fair or poor, 2 were deemed degraded, and only 1 station in the headwaters was classified as being in very good condition. We applied the SWQI to main tributaries of the Nottawasaga River and found that it was effective for determining the degree of impairment in watersheds with mixed land uses. The SWQI is a valuable tool that conservation authorities and land managers can use to identify tributaries or river stretches that require rehabilitation.

**Keywords:** Nottawasaga River, water quality index, tributary impairment

**Introduction**

Good water quality is vital for sustaining the health and biodiversity of lotic systems. Healthy tributaries have ecosystems that reflect sustainable and resilient conditions, allowing them to maintain ecosystem structure and function. With an exponentially increasing human population, natural areas continue to be converted to urban and agricultural land-uses within watersheds. This has altered natural loading of nutrients and sediment to watercourses (Das Gupta, 2008), which has led to increased cases of eutrophication and anoxia globally (Matson et al., 1997; Smith, 2003). Such increased loading is known to degrade water quality in tributaries, and have negative impacts on aquatic organisms and overall biodiversity.

Although use of biological indices to track overall stream health and habitat quality is widely used by agencies (Karr, 1981; Hilsenhoff, 1982; Wichert & Rapport, 1998), index scores reflect the state of the environment but may obscure the source of pollution (Suter, 2001). Since anthropogenic stressors on streams are primarily related to nutrient and sediment loading, a monitoring program based on water-quality parameters is best for identifying effects of these stressors. Over the past two decades, a number of Water Quality Indices (WQI) have been developed to assess overall water quality conditions of surface waters in Canada (Munger, 1996; CCME, 2001; Chow-Fraser, 2006). These provide a standardized way for environmental managers to identify critical areas to focus rehabilitation efforts. The CCME WQI (2001) has been applied to data collected across Ontario and has shown relatively good discrimination between streams in distinct regions; however, the method for determining index scores is complex, incorporating scope, frequency, and amplitude of water quality variables, which may not be available for short term monitoring projects.

Water-quality impairment has been noted in the Nottawasaga River, a major tributary that drains into Nottawasaga Bay, Georgian Bay (Lake Huron). The river mouth is located in Wasaga Beach, a popular tourist destination and the longest freshwater beach on the world. The Nottawasaga River Watershed is dominated by agricultural land-use, and is the probable source of nutrient and sediment enrichment. Since rivers are important corridors connecting terrestrial and lake ecosystems (Fisher et al., 1998), high concentrations of nutrients and sediment in the Nottawasaga River can have major influences on water quality in the near-shore zone of Nottawasaga Bay, particularly following storm events. This has implications for botulism-induced avian and fish kills, which have been reported in the bay in 2011 and 2015 (Yule et al., 2005; Hopper, 2011).

The Nottawasaga River is unique in a number of respects. Firstly, it bisects the Minesing Wetlands, a Ramsar site and the largest contiguous inland wetland (6,000 ha) in southern Ontario (Ramsar, 1996; Frazier, 1999). To date, no study has documented the water quality of the river through this vast wetland complex; however, water quality in the outflow has been observed to be more degraded than that in the inflow, prompting speculation that the Minesing Wetlands no longer function as a natural filter of sediment and nutrients (Chow-Fraser, 2006; Brown et al., 2011). Secondly, the river flows through a variety of geological landscapes (Niagara Escarpment, Simcoe Uplands, Oak Ridges and Oro Moraines) that contribute to natural variations in water quality. Finally, the Nottawasaga River is also the only tributary of Georgian Bay with confirmed spawning populations of Lake Sturgeon, currently listed as a species at risk in Ontario. Therefore, sustaining the health and biodiversity of the Nottawasaga River is crucial, as the river hosts a wide array of aquatic life, is a popular recreational destination, and can have substantial impacts on downstream water quality at Wasaga Beach in Nottawasaga Bay.

The primary goal of this paper is to develop a Stream WQI (SWQI) specifically for the Nottawasaga River and its watershed. In developing this index, we wanted it to 1) provide a useful and informative way to integrate a large number of water-quality variables into a single value that reflects the overall condition of the river, and 2) identify degraded areas that could be targeted for rehabilitation within a standardized framework. Previous studies have shown that biomass of benthic algae (McNair & Chow-Fraser, 2003), species richness of submersed aquatic vegetation (Lougheed et al., 2001), type of wetland zooplankton (Lougheed & Chow-Fraser, 2002) and type of wetland fish (Seilheimer & Chow-Fraser, 2007) are strongly related to water-quality variables. These suggest that good water-quality conditions, reflected by high SWQI scores, should be associated with high biodiversity, and can be used to evaluate the overall ecosystem health of the Nottawasaga River.

## Methods

### *Study area and site selection*

Our study was conducted along the main branch of the middle and lower reaches of the Nottawasaga River, a major tributary that drains into Nottawasaga Bay, Georgian Bay. We used ArcGIS 10.3 and orthophotos of the study area (Muskoka and Simcoe County Orthophotos, 2008; SCOOP, 2013) to strategically select 15 monitoring stations along the river (Table 3.1; Figure 3.1). Stations were chosen to confirm previous trends and include new areas not previously sampled, particularly the stretch of river that flows through the Minesing Wetlands (Chow-Fraser, 2006; Brown et al., 2011). Station 1 started in the Upper Nottawasaga River, Station 2 was located in Innisfil Creek, and station 3 marked the first site located within the Middle Nottawasaga River following confluence with stations 1 and 2. The remaining stations were separated to capture various stream habitats, land cover influences, and tributary inputs that contribute to longitudinal variation in water quality. Lastly, station 15 is located along the final stretch of the Nottawasaga River close to the mouth at Wasaga Beach. The spatial distributions of these stations are representative of overall water quality across the main branch of the Nottawasaga River. As part of another study, we sampled major tributaries (fourth- and fifth-order streams) that discharged into the Nottawasaga River (Figure 3.1). All locations were field validated and adjusted accordingly to ensure river access was feasible prior to sampling.

*Sampling procedures*

Following the sampling procedures outlined by Crosbie and Chow-Fraser (1999), we designed a monthly sampling program (June – September 2014) to measure physical and chemical variables, as well as primary nutrients at 15 stations in the Nottawasaga River during base flow conditions (total of 13 parameters). We used a Van Dorn sampler to collect discrete samples at each station in freshly acid-washed Corning™ snap-seal containers or Nalgene® bottles to measure total suspended solids (TSS; mg/L), total organic suspended solids (TOSS; mg/L), total phosphorus (TP; μg/L), total ammonia nitrogen (TAN; mg/L), total nitrate nitrogen (TNN; mg/L), total nitrogen (TN; mg/L), chloride ($Cl^-$; mg/L), and chlorophyll-α (CHL; μg/L) (Lind, 1974; Crosbie & Chow-Fraser, 1999). We also collected *Escherichia coli* (*E. coli*; CFU/100 mL*)* samples in sterile Whirl-Pak® bags at all 15 stations once during the month of July 2014. Once collected, all samples were stored on icepacks in a cooler until they could be processed or stored in a freezer prior to analyses.

A YSI 6920 V2 sonde was calibrated prior to each sampling week and used to measure conductivity (COND; μS/com), temperature (TEMP), and dissolved oxygen (DO; mg/L) at each station. To confirm accuracy of YSI values, we filled a BOD bottle with sample water and HACH® chemicals to determine DO using the Winkler titration method. Turbidity (TURB; NTU) readings were measured in situ with a HACH® 2199Q turbidimeter in triplicate. All grab samples and measurements were taken from mid-depth against the current to ensure samples were thoroughly mixed (Barton, 1977; Shelton, 1997; Poor & McDonnell, 2007).

*Sample processing*

Unless otherwise indicated, all water quality analyses were performed in triplicate for each variable. We used the molybdenum blue method to determine TP concentrations (Murphy & Riley, 1962) following potassium persulfate digestion in an autoclave for 50 minutes (120°C, 15 psi). Absorbance values were read with a Genesys 10 UV spectrophotometer, and final TP concentrations were calculated with a standard curve. TNN and TN samples were also processed in the laboratory and read with a DR 2800 spectrophotometer following the HACH® cadmium reduction and TNT 826 methods, respectively. Samples collected for $Cl^-$ were titrated following the mercuric nitrate method (HACH method 8206). A HACH® DR 850 colorimeter was used to read TAN in the field according to HACH® method 8155.

Known aliquots of river water was filtered through GC filters (0.45 µm) and subsequently used to calculate concentrations of TSS, TOSS and CHL. All filters used for TSS and TOSS were pre-weighed before samples were filtered. Filters were then folded in half and kept in small plastic petri plates and placed in a freezer. When we were ready to process the TSS samples, filters were retrieved from the freezer and placed on a crucible of known weight to be dried in the oven for 1h at 100°C; subsequently, they were placed in a dessicator for an additional hour, and then weighed to the nearest 0.1 mg. The same filters were used to determine concentrations of TOSS by burning the dried filter in a muffle furnace for 1 h at 550°C, placing it in a dessicator for an additional hour, and then re-weighed. Filters for CHL determination were folded, then wrapped in aluminum foil and placed in a freezer until they were processed. CHL was extracted from filters in 90% reagent grade acetone in a freezer over a 24 h period. Following extraction, samples were acidified with hydrochloric acid (0.1 N), and fluorescence was read with a Turners Design Trilogy fluorometer.

We used Coliplate™ kits from Bluewater Biosciences to determine the most probable number of colony forming units (CFU) in a 100 mL sample at each monitoring station. Once all the wells were completely filled with sample water and excess water was removed from the top of the plate, the Coliplates™ were incubated at 35 °C over a 24-hour period. Following incubation, we identified the number of *E. coli* CFU's by counting the number of blue fluorescing wells under a UV light (366 nm).

*Statistical analyses and index development*

All statistical analyses were conducted in JMP 12 software (SAS Institute Inc., Toronto, ON, Canada). Monthly measurements (June – September) of all water quality parameters were averaged for each station prior to analyses to represent mean values for the growing season. We used ANOVA and Tukey-Kramer comparisons ($\alpha = 0.05$) to determine which monitoring stations had the highest values for variables of interest. Following methods outlined by Chow-Fraser (2006) as a guideline, we performed a Principal Components Analysis (PCA) using all 13 water quality variables to create the Stream Water Quality Index (SWQI). PCA is an ordination technique that extracts eigenvalues and eigenvectors from the original set of variables. It produces as many Principal Components (PCs) as there are variables, which are weighted linear combinations of the original 13 water quality variables (Singh, 2004; Table 3.2). All data were $\log_{10}$ or box-cox transformed to achieve normality, and subsequently z-transformed to standardize variables to a mean of zero. To ensure all variables were on the same scale, we multiplied dissolved oxygen by -1 (–DO) so that all high values indicated more degraded water quality, and all low values indicated more pristine water quality.

To account for the greatest amount of variability in the dataset as possible, we used all 13 PCs to calculate SWQI scores for each station. SWQI scores were calculated by multiplying the PC score for each station by the relative weight of the eigenvalue for each variable. We summed the products for each variable to determine the SWQI score at each station. Final index scores were multiplied by -1 so that degraded stations would have a negative score, and more pristine stations would have positive scores. We divided the scores into five categories that describe the degree of water quality impairment (very good, good, fair, poor, degraded; Table 3.3). We used least squares multiple linear regressions to create predictive models that can be used to generate SWQI scores using various combinations of water quality parameters (Table 3.4). Different combinations of variables were chosen based on those most routinely monitored by agencies, such as the Provincial Water Quality Monitoring Network (PWQMN), those that are easiest to collect, such as sonde variables, or those that tell us something unique about the stream in question.

To assess the usefulness of the SWQI, we collected TURB, TSS, TOSS, and TP from the main tributaries (fourth- and fifth-order) of the Nottawasaga River during the summer of 2015. We used water-quality data from these tributary stations and applied the SWQI predictive Eq. 8 to determine SWQI scores. From upstream to the mouth of the Nottawasaga, monitored tributaries included: the Upper Nottawasaga River (UN), Innisfil Creek (IN), Boyne River (BN), Thornton Creek (TN), Pine River (PN), Bear Creek (BR), the Mad River where it breaches the natural bank (MB), Mad River (MR), Willow Creek (WL), Marl Creek (ML), and McIntyre Creek (MT) (Table 3.1; Figure 3.1).

**Results**

*Water quality trends in the Nottawasaga River*

To evaluate differences in water quality and trophic status among sites in the Nottawasaga River, we compared parameter means at each station to published water quality targets and nutrient guidelines (Table 3.5; Table 3.6). We could not make comparisons for some variables that did not have a pre-determined provincial or federal water quality target. Provincial Water Quality Objectives (PWQO) exists for TAN (0.02 mg/L), TP (30 μg/L), *E. coli* (100 CFU/100 mL), and DO (>4 mg/L) (MOE, 1994), while the Canadian Environmental Quality Guidelines (CEQG) exist for TNN (3.0 mg/L) (CCME, 2001). Almost all monitoring stations exceeded the PWQO for TP, TAN, and *E. coli* (Table 3.5). The PWQO for TP was exceeded at all stations except 1, 4 and 7. TAN was exceeded at every station, and *E. coli* was exceeded at stations 1, 2, 3, 6, 7, 13 and 14. Non-regulatory performance standards have been developed for the National Agri-Environmental Standards Initiative (NAESI) for TN (1.06 mg/L), TP (26 μg/L), TSS (3.6 mg/L), and TURB (6.1 NTU) in southern Ontario (Culp et al., 2009; Chambers et al., 2011). These standards indicate nutrient and sediment concentrations that protect ecological integrity and health of streams in agricultural settings. All 15 monitoring stations in the Nottawasaga River exceeded the NAESI standards for TN, TP, TSS, and TURB (Table 3.5).

Smith et al. (1999) summarized nutrient and CHL concentrations for different trophic states in stream environments (Table 3.6). The Nottawasaga River is unique in that it can be classified into three different trophic states depending on which indicator variable is used. TN levels indicated that the Nottawasaga River is eutrophic (>1.5 mg/L) across all 15 monitoring stations, whereas low planktonic CHL concentrations across all stations suggest that it is oligotrophic (<10 μg/L). By comparison, TP concentrations were more variable, and most stations were classified as mesotrophic (25 – 75 μg/L), whereas stations 1, 4, 7 were classified as oligotrophic (<25 μg/L).

We used ANOVA and Tukey-Kramer comparisons to identify which stations had the highest concentrations of the parameters of interest ($\alpha = 0.05$; Table 3.7). Station 2 had significantly higher TURB (41.4 NTU), TSS (29.1 mg/L), and TOSS (6.65 mg/L) compared to all other monitoring stations. TURB and TSS were high across most stations in the Nottawasaga River (TURB generally >10 NTU). The inorganic portion of suspended solids accounted for the majority of TSS at all stations except at station 15 (Figure 3.2). TP was significantly higher at stations 2 (48.2 μg/L), 13 (42.1 μg/L), 10 (39.8 μg/L), and 12 (37.3 μg/L), while TN was significantly higher at stations 4 (2.38 mg/L) and 5 (2.29 mg/L). COND was significantly higher at stations 2 (668 μS/cm) and 4 (582 μS/cm), and $Cl^-$ was significantly higher at stations 2 (53.8 mg/L) and 5 (39.8 mg/L). DO concentrations measured at station 10 and 13 were relatively low (6.52 and 6.11 mg/L, respectively). TEMP (21.8 °C), TAN (0.08 mg/L), and *E. coli* (2424 CFU/100 mL) were all significantly highest at station 14. Overall, significantly higher mean water-quality variables and significantly lower DO were found at stations 2, 4, 5, 10, 12, 13, and 14 (Table 3.6).

We entered all 13 water quality variables (Table 3.5) into a PCA to determine which parameters were the most meaningful. Of the 13 axes fit by the PCA, the first 4 (eigenvalues >1) explained a cumulative 87% of the total variation in the dataset (Table 3.8). PC1 alone explained 39% of the total variation, and was highly and significantly correlated with variables associated with particulate matter and dissolved ions in the water column (Table 3.8). TURB was most highly correlated with PC1 (0.89), followed by TP (0.88), TSS (0.84), TOSS (0.83), $Cl^-$ (0.81), COND (0.79), and CHL (0.75). PC2, which accounted for 19% of the variation, and was positively and negatively correlated with variables that reflect anaerobic conditions and aerobic conditions respectively. Variables positively correlated with PC2 included DO (i.e. low DO concentrations; 0.71), TAN (0.60), and TEMP (0.53), and those negatively correlated included TN (–0.70) and TNN (–0.59). PC3 explains 17% of the variation in the dataset, and was positively correlated with variables associated with urbanization. TEMP (0.80) and TN (0.56) were most correlated with PC3. PC4, which only accounted for 11% of the variation, was strongly positively correlated with *E. coli* (0.94), which was associated with livestock waste and septic systems.

The PC scores reflected the weighted linear combinations of the 13 original variables, which, taken together, described the degree of water-quality impairment. Monitoring stations with high, positive PC scores represented a higher degree of impairment and more degraded water-quality conditions. On the other hand, comparatively low negative PC scores indicated a lower degree of impairment, and suggested good water-quality conditions (Figure 3.3). Station 2 had the highest PC1 score, indicating that it had the highest concentrations of particulate content (TURB, TSS, TP, CHL), while station 1 had the lowest PC1 score, and had the lowest TURB, TSS, TP, and CHL. The highest PC2 scores corresponded to stations 13 to 15, which were all stations with low DO and high TAN. PC3 scores were highest for stations 4, 5, 14 and 15, all of which had warmer temperatures and high concentrations of TN. Stations with the highest PC4 scores were 14 and 1, which had extremely high concentrations of *E. coli*.

*Calculation of SWQI scores*

We determined SWQI scores for all 15 monitoring stations in the main branch of the Nottawasaga River sampled in 2014 (Table 3.9; Figure 3.4). Based on the classes we developed for this study (Table 3.3), two stations were classified as “degraded” (2, 13), four were classified as “poor” (14, 5, 6, 12), eight as “fair” (15, 4, 10, 7, 8, 3, 11, 9), none as “good”, and only one as “very good” (station 1). We also applied the SWQI to data obtained from the main tributaries of the Nottawasaga River using predictive Eq. 8 (Table 3.4). SWQI scores calculated for main tributaries of the Nottawasaga River indicated that Upper Nottawasaga (UN; 4.63) and Pine Creek (PN; 2.74) were both in very good condition, Thornton Creek (TN; 1.59) and the Boyne River (BN; 1.29) were in good condition, and Bear River (BR; –0.06), Willow Creek (WL; –0.15), McIntyre Creek (MT; –0.46), and the Mad River Breach (MB; –0.64) were all in poor condition. Those that were deemed degraded included the Mad River (MR; –1.62), Innisfil Creek (IN; –1.83), and Marl Creek (ML; –2.68) (Table 3.10; Figure 3.5).

The Nottawasaga Valley Conservation Authority (NVCA) has provided Health Check report cards on the sub-watersheds of the Nottawasaga River since 2007. We compared our SWQI impairment categories measured in 2015 with grades reported for stream health of corresponding sub-watersheds documented in the 2013 report cards (Table 3.10). NVCA uses three water quality parameters as indicators of stream health (benthic invertebrates, TP, *E.* coli), but TP is the variable most frequently sampled. NVCA uses TP concentrations to rate tributary health as “very good”, “good”, “fair”, “poor”, and “very poor”. To enable proper comparison, we decided that “very poor” in the NVCA scheme was equivalent to “degraded” in ours. In 2013, NVCA classified the Upper Nottawasaga River as being in very good condition, and the Pine River, Willow Creek, and Mad River as being in good condition. Boyne River and Innisfil Creek were classified as being in fair and degraded conditions respectively. The remaining tributaries in our study had not been assessed individually by NVCA; therefore, we were unable to carry out the comparison.

**Discussion**

The main goal of this paper was to develop an index specifically to classify the degree of impairment along the main branch of the Middle and Lower Nottawasaga River. Development of our own model for this system was necessitated because other guidelines and objectives (e.g. PWQO, NAESI, CCME WQI) could not be used to resolve differences in quality among stations in the main river and tributaries to determine priorities for rehabilitation. In developing the SWQI, we wanted the index to reflect the overall water-quality condition of monitoring stations based on the 13 variables. Stations with high concentrations of nutrients, sediment, dissolved ions, and *E. coli* should have low index scores reflecting degraded water-quality conditions, whereas stations with low concentrations of these constituents should have high index scores to reflect relatively good water-quality conditions.

Meeting provincial or federal guidelines for water quality variables is an effective way to improve ecosystem health; however, when guidelines are overly stringent, they cease to have relevance for management purposes. When we applied these federal and provincial guidelines to the Nottawasaga River, we found exceedances for almost all stations (i.e. all stations were deemed to be "impaired"). We had an equally difficult time classifying sites according to trophic state because depending on the variable used (TP, TN, or CHL; Smith et al., 1999), we obtained conflicting results that showed the river as being mesotrophic, eutrophic, or oligotrophic respectively. Even though majority of the stations in the Nottawasaga River are obviously impaired, some of the stations were better than others and this information is important for ranking rehabilitation priorities. Using the SWQI, we were able to discriminate the most degraded sites (only a third of the stations) from majority of the stations that we classified as fair, and one was in fact found to be in very good condition. Since the SWQI was developed with weighted PC scores of 13 variables, we have confidence that the final index scores incorporated variables that explained the greatest amount of variation in the dataset.

Even though TP concentrations were high in the Nottawasaga River, CHL concentrations of planktonic algae were generally low. There is a well-known positive relationship between phosphorus and algal concentrations for lakes (Dillon & Rigler, 1974; Carlson, 1977); however, this relationship is much more variable in stream environments (Jones et al., 1984; Lohman & Jones, 1999; Winterborn et al., 1992). Turbidity is a major factor limiting algal growth in streams, as it decreases light attenuation and does not favour photosynthesis (May et al., 2003). Since the Nottawasaga River tends to be very turbid, CHL concentrations may be limited by light availability rather than by TP concentration. Our analyses indicate that inorganic matter constituted the majority of TSS at all river stations, except for station 15, which was most likely influenced by water of Nottawasaga Bay. This suggests that the high TURB in the river is due to inorganic sediments rather than algae, and accounts for the low CHL concentrations measured.

The SWQI classified stations 2, 5, 6, 13, and 14 as being the most degraded. These stations had the highest concentrations of nutrients and sediment. Using ANOVA alone to determine which stations had statistically higher pollutant concentrations relative to others, we came up with a similar list of sites that had impaired water quality (2, 4, 5, 10, 12, 13, and 14; Table 3.7), but this list did not provide a way to rank stations according to degree of impairment. By comparison, we could use the SWQI to determine the rank of stations based on their overall impaired condition, and thus allow managers to identify river segments that are in most need of rehabilitation. As an example, the SWQI identified stations 2 and 13 as being the most degraded, while there was no way to quantify this using results of the ANOVA.

The cause of degradation in our stations is high loading of nutrients and sediments. Station 2 (Innisfil Creek) had the highest PC1 score, which is associated with high particulate content and dissolved ions. The Innisfil Creek sub-watershed currently has the highest proportion of agricultural land-use, most of which is crop land, compared to all other sub-watersheds. Crops are known to be associated with high TP and sediment loading from watersheds (Reckhow et al., 1980; Chambers & Dale, 1997; Carpenter et al., 1998). Stations 13, 14, and 15 had the highest PC2 scores, which were positively correlated with low DO and high TAN concentrations, and negatively correlated with TN and TNN concentrations. These results are reflective of anaerobic conditions, because it is known that nitrification (conversion to nitrate) does not occur in the absence of oxygen.

This means that when no oxygen is present, nitrates are transformed and become ammonia (Kemp & Dodds, 2002). In addition, ammonification could lead to even higher concentrations of ammonia if organic matter in substrate is high. This could pose an environmental threat to fish or other aquatic organisms at high enough concentrations (Thurston et al., 1981). Stations highly correlated with PC2 and PC3 (stations 4, 5, 13, 14, 15) are located near urban areas, such as Baxter, Angus, and Wasaga Beach. TN concentrations are high across all stations, presumably from fertilizers associated with the high proportion of agricultural land in the watershed. These stations draining parts of urban areas likely have even higher nitrogen loading from increased surface runoff and erosion from industry, fossil fuels, sewage and septic systems (Mitsch et al., 2001). Stations 1 and 14 had the highest PC4 scores, reflecting river locations with the highest concentrations of *E. coli*, and are associated with residential areas and pasture land.

Based on the SWQI score, station 1 was deemed to be in very good condition because of low concentrations of almost all variables, except *E. coli*, which was extremely high. The high coliform count likely reflects the disproportionately high pasture land in the sub-watershed, and the known association between livestock manure and *E. coli* concentrations in watercourses (Gerba & Smith, 2005). Another station that had a high count of *E. coli* was Station 14, which is located in the town of Wasaga Beach, the fastest growing rural and small town municipality in Ontario (Mitchell, 2009). It may be that upgrade and development of sewage infrastructure has not kept pace with the population growth in the area, and leakage from septic systems and sewage by-passes may have resulted in increased *E. coli* contamination to the river (Whitlock et al., 2002).

This is one of the first studies to examine the water quality of surface waters in the portion of the Nottawasaga River that flows through the Minesing Wetlands. Previous studies had reported elevated concentrations of TP at a station after the Nottawasaga drained the Minesing, but relatively low concentrations before it drained the wetland complex (Chow-Fraser, 2006; Brown et al., 2011). We were able to confirm these findings with quantitative scores. The SWQI scores for the Minesing stations (7, 8, 9, 10) were all classified as fair, but scores generally improved as the river flowed from station 7 to 9 until station 10. Station 10 had a higher PC1 and PC2 score compared to the other Minesing stations. This is because TP increased, and DO decreased at station 10. This station is located after the confluence of Willow Creek (WL; Figure 3.1), which Rutledge & Chow-Fraser (2016) identified as a potential site of internal loading, given that it experienced episodes of anoxia associated with spikes in TP. This suggests that water quality in the Nottawasaga River improved slightly as it flowed through the Minesing Wetlands, but became degraded following inputs from Willow Creek (i.e. DO decreased and TP increased).

We provided a list of predictive equations (Table 3.4) using different combinations of water quality variables that other agencies can use to calculate SWQI scores. Depending on which parameters are most routinely collected or useful, agencies can determine SWQI scores to categorize stream impairment. All 9 predictive equations should generate comparable results because $r^2$ values are high (>0.915). We successfully applied the SWQI to data obtained from the main tributaries of the Nottawasaga River. Low SWQI scores were obtained for many of the tributaries that had high levels of

TURB, TSS, TOSS and TP, whereas high SWQI scores were obtained for a few tributaries that had clear water and low levels of nutrients and sediments. This comparison demonstrates that the SWQI may be applicable to similar subwatersheds with mixed land uses and land cover in Ontario. We have provided predictive equations using various combinations of the most commonly measured variables in monitoring programs in hopes that management agencies will be able to use these to calculate SWQI scores for their sites (Table 3.4).

We wanted to see how the SWQI performs relative to other established assessment approaches developed for the Nottawasaga River watershed. We found relatively high concordance between SWQI impairment categories and grades assigned to tributaries in the 2013 NVCA health check report card (Table 3.10). The major discrepancies were for the Mad River and Willow Creek, which both drained through the Minesing Wetlands. The reason for this discrepancy is likely due to differences in location of sampling sites. We collected our samples in the portion of Willow Creek within the Minesing Wetlands. By contrast, NVCA collected their samples further upstream of the tributary before it enters the Minesing. Rutledge & Chow-Fraser (2016) found extremely high levels of TP in a segment of Willow Creek that flows through the Minesing Wetlands, and attributed this to internal loading of P during periods when the river became depleted of dissolved oxygen. We therefore speculate that TP concentrations measured by NVCA were lower because their sample did not reflect the in-stream influences of the Minesing Wetlands.

**Conclusion**

Water quality in the Nottawasaga River is generally impaired and needs to be rehabilitated. Nutrient and sediment concentrations have exceeded published guidelines at almost all monitoring stations, and areas with low dissolved oxygen could limit use by juvenile lake sturgeon. Nutrient concentrations within the Minesing Wetlands initially decreased, but after inputs from Willow Creek, TP concentrations increased while DO concentrations decreased. Consequently, water quality in the Nottawasaga River is slightly more degraded as it exits the Minesing Wetlands. The SWQI identified one third of the monitoring stations as being in poor or degraded condition. These stations are associated with high concentrations of nutrients, sediment, dissolved ions, and *E. coli*, and are likely stations most impacted by anthropogenic sources, such as agricultural and urban land-uses. Only one station, located in the upper Nottawasaga River, was categorized as being in very good condition. The remaining stations were categorized as fair, which indicates that water quality must be improved before the river can be classified as good. We demonstrated that the SWQI could be effectively applied to individual sub-watersheds using the predictive equations we developed, which suggests the potential for the SWQI to be used in other mixed agricultural watersheds in south central Ontario. We outlined a practical method for developing a WQI, which can be followed by other agencies to create an index specific to other watersheds. Management agencies can use the SWQI to objectively identify rehabilitation priorities in a large watershed such as the Nottawasaga River Watershed.

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**Table 3.1:** Summary of locations of monitoring stations (presented from furthest upstream to the mouth of the river) and year sampled. Station codes 1 to 15 were located within the main branch of the Nottawasaga River, while all others were located in the main tributaries.

| River Section | Station Code | Station Name | Latitude | Longitude | Year Sampled |
|---|---|---|---|---|---|
| Upper | 1 | | 44.13651 | -79.81014 | 2014 |
| | UN | Upper Nottawasaga R. | 44.13648 | -79.81020 | 2015 |
| Middle | 2 | | 44.13522 | -79.80849 | 2014 |
| | 3 | | 44.13699 | -79.80843 | 2014 |
| | 4 | | 44.27893 | -79.82343 | 2014 |
| | 5 | | 44.33105 | -79.87286 | 2014 |
| | 6 | | 44.33831 | -79.86975 | 2014 |
| | IN | Innisfil Cr. | 44.13532 | -79.80868 | 2015 |
| | BN | Boyne R. | 44.16919 | -79.81576 | 2015 |
| | TN | Thornton Cr. | 44.24819 | -79.81990 | 2015 |
| | PN | Pine R. | 44.33138 | -79.87441 | 2015 |
| | BR | Bear Cr. | 44.33403 | -79.87095 | 2015 |
| | MB | Mad R. Breach | 44.36003 | -79.87987 | 2015 |
| Minesing | 7 | | 44.37127 | -79.88529 | 2014 |
| | 8 | | 44.38924 | -79.88478 | 2014 |
| | 9 | | 44.41955 | -79.88461 | 2014 |
| | 10 | | 44.42848 | -79.89464 | 2014 |
| Minesing | MR | Mad R. | 44.40856 | -79.89931 | 2015 |
| | WL | Willow Cr. | 44.41880 | -79.88382 | 2015 |
| Lower | 11 | | 44.43693 | -79.89922 | 2014 |
| | 12 | | 44.44291 | -79.89152 | 2014 |
| | 13 | | 44.47552 - | 80.00853 | 2014 |
| | 14 | | 44.47506 | -80.05029 | 2014 |
| | 15 | | 44.52349 | -80.01639 | 2014 |
| | ML | Marl Cr. | 44.44141 | -79.89180 | 2015 |
| | MT | McIntyre Cr. | 44.46916, | -80.04650 | 2015 |

**Table 3.2:** Summary of eigenvalues and proportion of variance explained of 13 principal components (PC) used to create the Stream Water Quality Index (SWQI) for the Nottawasaga River.

| PC axis | Eigenvalue | Variance explained (%) | Cumulative variance explained (%) | *p*-value |
|---|---|---|---|---|
| 1 | 5.0909 | 39.160 | 39.160 | **<0.0001** |
| 2 | 2.5211 | 19.393 | 58.554 | **<0.0001** |
| 3 | 2.2701 | 17.463 | 76.016 | **<0.0001** |
| 4 | 1.3740 | 10.569 | 86.586 | **<0.0001** |
| 5 | 0.9931 | 7.639 | 94.225 | **0.0002** |
| 6 | 0.3977 | 3.059 | 97.284 | **0.0452** |
| 7 | 0.1181 | 0.908 | 98.192 | 0.3798 |
| 8 | 0.1038 | 0.798 | 98.991 | 0.3174 |
| 9 | 0.0561 | 0.432 | 99.422 | 0.3716 |
| 10 | 0.0482 | 0.370 | 99.793 | 0.2781 |
| 11 | 0.0181 | 0.139 | 99.932 | 0.3658 |
| 12 | 0.0080 | 0.062 | 99.993 | 0.2632 |
| 13 | 0.0009 | 0.007 | 100.000 | -- |

**Table 3.3:** Stream Water Quality Index (SWQI) scores and corresponding impairment categories.

| SWQI Score | Category |
|---|---|
| >2 | Very good |
| 1 to 2 | Good |
| 0 to 1 | Fair |
| 0 to –1 | Poor |
| <–1 | Degraded |

**Table 3.4:** Summary of regression equations to predict Stream Water Quality Index (SWQI) scores. Bold $r^2$ values and variables indicate models with significant variance and significant predictor variables respectively.

| Eq. | Variables in Model | $r^2$ | Predictive Equation |
|---|---|---|---|
| 1 | *All 13 PCA variables:* TURB, TSS, TOSS, TP, TAN, TNN, TN, $Cl^-$, COND, TEMP, DO, CHL, *E. coli* | **1.000** | +76.88379125332110<br>+0.95650542571126 * log TURB<br>-1.01289529186520 * log TSS<br>-5.48159381461230 * log TOSS<br>+0.34256775592687 * log TP<br>-0.76138056162880 * log TAN<br>+0.26146631281982 * log TNN<br>+0.11545059274682 * log TN<br>+0.24412444423647 * log $Cl^-$<br>-15.64687485750300 * log COND<br>-24.96850010939800 * log TEMP<br>+1.27547600597178 * (log DO * -1)<br>-0.19423162982200 * log CHL<br>-0.32513851361770 * log *E. coli* |
| 2 | *PWQMN variables:* **TP**, **SRP**, TAN, TNN, TN, $Cl^-$, COND, **TEMP**, DO, pH | **0.994** | +18.81466291998620<br>**-0.06842558417670 * TP**<br>**-0.13386208299070 * SRP**<br>-6.68526975155900 * TAN<br>-0.01002745243110 * TNN<br>+1.22675955123468 * TN<br>-0.05835248689990 * $Cl^-$<br>+0.00874514095847 * COND<br>**-0.33160549688270 * TEMP**<br>-0.31331435969270 * (DO * -1)<br>-2.14002344452470 * pH |
| 3 | *Simplified PWQMN variables:* **TURB**, **TP**, **TAN**, TNN, COND, **TEMP**, DO, **pH** | **0.987** | **+32.67270841486560**<br>**-0.04271612763420 * TURB**<br>**-0.07460165117400 * TP**<br>**-19.11812812709300 * TAN**<br>+1.10061265478229 * TNN<br>+0.00175744178523 * COND<br>**-0.31234515238800 * TEMP**<br>-0.36172619833690 * (DO * -1)<br>**-3.32956710809920 * pH** |

| Eq. | Variables in Model | $r^2$ | Predictive Equation |
|---|---|---|---|
| 4 | *4 variable model:*<br>**TURB**, **TP**, **TAN**, **TEMP** | **0.982** | **+23.06775003355390**<br>**-3.24383837198180 * log TURB**<br>**-1.90827356738330 * log TP**<br>**-1.17249161079320 * log TAN**<br>**-14.09568124985800 * log TEMP** |
| 5 | *5 variable model:*<br>**TURB**, **TAN**, **TNN**, **DO**, **CHL** | **0.980** | **1.66298685950116**<br>**-0.05760261774340 * TURB**<br>**-0.66777259627980 * CHL**<br>**-15.66506727380800 * TAN**<br>**-2.42594524863140 * TNN**<br>**-0.24775085075890 * (DO * -1)** |
| 6 | *3 variable model:*<br>**TURB**, **TAN**, **CHL** | **0.979** | **1.44934337375383**<br>**-2.49719763385610 * log TURB**<br>**-3.32909815798190 * log CHL**<br>**-1.93879805043410 * log TAN** |
| 7 | *Sonde variables:*<br>**TURB**, COND, **TEMP**, DO, pH | **0.960** | +28.68909883318740<br>**-3.87133839201290 * log TURB**<br>-8.81612337303200 * log COND<br>**-20.00314577984100 * log TEMP**<br>+1.49722522331034 * (log DO * -1)<br>+27.13731806322370 * log pH |
| 8 | *Agricultural runoff model:*<br>**TURB**, TSS, TOSS, **TP** | **0.919** | **+10.31762839550260**<br>**-5.40053615953870 * log TURB**<br>+2.35029151652254 * log TSS<br>+4.19972799943120 * log TOSS<br>**-6.35185733402610 * log TP** |
| 9 | *Nutrient model:*<br>**TP**, **SRP**, **TAN**, TNN | **0.915** | **+3.75102652442980**<br>**-0.07621992435450 * TP**<br>**-0.12257656410850 * SRP**<br>**-20.45731149273200 * TAN**<br>+0.21622125403500 * TNN |

**Table 3.5:** Summary of 13 water quality parameters for 15 monitoring stations in the Nottawasaga River. Bold numbers indicate values that exceed the provincial or federal water quality target. Variables with published targets include TURB (6.1 NTU; NAESI), TSS (3.6 mg/L; NAESI), TP (30 μg/L; PWQO), TAN (0.02 mg/L; PWQO), TNN (3.0 mg/L; CEQG), TN (1.06 mg/L; NAESI), DO (>4 mg/L; PWQO), *E. coli* (100 CFU/100 mL; PWQO).

| Stn | TURB | TSS | TOSS | TP | TAN | TNN | TN | $Cl^-$ | COND | TEMP | DO | CHL | *E. coli* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **8.3 ±2.9** | **6.9 ±2.4** | 2.96 ±0.83 | 12.2 ±4.9 | 0.010 ±0.003 | 0.061 ±0.028 | **1.90 ±0.19** | 18.4 ±3.2 | 517 ±7 | 18.9 ±1.3 | 8.03 ±0.15 | 1.54 ±0.65 | **388** |
| 2 | **41.4 ±9.1** | **29.1 ±5.5** | 6.64 ±0.44 | **48.2 ±6.8** | **0.050 ±0.009** | 0.043 ±0.006 | **1.88 ±0.27** | 53.8 ±2.2 | 668 ±19 | 19.7 ±1.1 | 8.05 ±0.27 | 4.43 ±0.42 | **587** |
| 3 | **15.9 ±4.5** | **15.1 ±4.8** | 4.88 ±1.15 | **31.1 ±4.4** | **0.020** ±0.012 | 0.043 ±0.015 | **1.63 ±0.16** | 25.0 ±4.5 | 563 ±16 | 18.7 ±1.1 | 8.44 ±0.29 | 2.90 ±1.01 | **375** |
| 4 | **12.3 ±1.8** | **10.9 ±2.2** | 4.03 ±0.45 | 29.7 ±7.0 | **0.029 ±0.013** | 0.245 ±0.099 | **2.38 ±0.05** | 37.6 ±1.4 | 582 ±10 | 20.1 ±0.7 | 8.34 ±0.38 | 2.75 ±0.53 | 79 |
| 5 | **16.7 ±1.7** | **13.7 ±1.2** | 4.36 ±0.42 | **30.2 ±7.9** | **0.029 ±0.008** | 0.081 ±0.051 | **2.29 ±0.17** | 39.8 ±6.9 | 579 ±10 | 20.8 ±0.5 | 7.90 ±0.20 | 3.73 ±1.29 | 79 |
| 6 | **19.3 ±3.4** | **15.9 ±1.9** | 5.49 ±0.44 | **33.9 ±7.9** | **0.029 ±0.014** | 0.204 ±0.103 | **2.17 ±0.17** | 26.9 ±3.9 | 543 ±10 | 19.9 ±0.4 | 7.96 ±0.15 | 2.80 ±0.57 | **451** |
| 7 | **15.1 ±1.0** | **13.6 ±0.8** | 5.31 ±0.07 | 28.0 ±8.0 | 0.016 ±0.007 | 0.120 ±0.044 | **2.22 ±0.17** | 27.0 ±3.5 | 543 ±6 | 19.4 ±0.8 | 7.79 ±0.27 | 3.33 ±0.73 | **200** |
| 8 | **12.6 ±1.2** | **12.2 ±1.1** | 4.81 ±0.23 | **30.2 ±6.6** | **0.026 ±0.01** | 0.152 ±0.082 | **2.20 ±0.14** | 26.6 ±4.0 | 547 ±5 | 19.6 ±0.8 | 7.75 ±0.28 | 3.09 ±0.55 | 98 |
| 9 | **13.3 ±1.2** | **16.2 ±3.3** | 4.89 ±0.62 | **33.4 ±9.0** | 0.015 ±0.005 | 0.036 ±0.019 | **1.89 ±0.16** | 25.2 ±2.6 | 532 ±6 | 19.2 ±0.4 | 7.64 ±0.39 | 2.85 ±0.59 | 87 |
| 10 | **11.7 ±0.6** | **18.7 ±2.5** | 5.47 ±0.44 | **39.8 ±8.0** | **0.030 ±0.014** | 0.057 ±0.020 | **2.04 ±0.19** | 26.2 ±2.5 | 538 ±6 | 18.7 ±0.3 | 6.51 ±0.56 | 2.70 ±0.29 | 65 |
| 11 | **13.8 ±1.5** | **15.6 ±3.6** | 4.91 ±0.44 | **34.4 ±11.4** | **0.021 ±0.008** | 0.080 ±0.018 | **1.90 ±0.08** | 25.5 ±3.2 | 544 ±6 | 19.2 ±0.1 | 6.58 ±0.36 | 2.63 ±0.4 | 69 |
| 12 | **15.5 ±1.4** | **17.4 ±3.8** | 5.48 ±0.24 | **37.3 ±9.6** | **0.040 ±0.016** | 0.042 ±0.017 | **1.73 ±0.16** | 27.2 ±3.2 | 542 ±6 | 19.1 ±0.1 | 6.54 ±0.39 | 2.61 ±0.31 | 79 |
| 13 | **15.6 ±1.2** | **13.2 ±0.2** | 5.23 ±0.6 | **42.1 ±5.5** | **0.035 ±0.016** | 0.059 ±0.010 | **1.70 ±0.17** | 24.3 ±2.4 | 531 ±11 | 21.3 ±0.7 | 6.11 ±0.74 | 3.92 ±1.02 | **451** |
| 14 | **11.7 ±0.7** | **10.0 ±1.1** | 3.75 ±0.44 | **32.7 ±7.5** | **0.080 ±0.007** | 0.093 ±0.042 | **1.78 ±0.19** | 25.0 ±2.9 | 531 ±11 | 21.8 ±0.9 | 6.85 ±0.47 | 3.39 ±0.91 | **2424** |
| 15 | **7.6 ±1.0** | **5.5 ±1.1** | 3.14 ±0.29 | **31.6 ±10.5** | **0.043 ±0.015** | 0.028 ±0.010 | **1.91 ±0.19** | 26.6 ±2.0 | 540 ±14 | 21.6 ±0.9 | 7.31 ±0.55 | 3.57 ±0.87 | 39 |

**Table 3.6:** Trophic status for different nutrient concentrations in stream ecosystems. This table is modified from Smith et al. (1999). Bolded values indicate the ranges that exist within the Nottawasaga River.

| Trophic Status | TP (μg/L) | TN (mg/L) | CHL (μg/L) |
|---|---|---|---|
| Oligotrophic | **<25** | <0.7 | **<10** |
| Mesotrophic | **25 – 75** | 0.7 – 1.5 | 10 – 30 |
| Eutrophic | >75 | **>1.5** | >30 |

**Table 3.7:** Summary of monitoring stations in the Nottawasaga River that were deemed to be impaired (bolded). "X" indicates that values for the corresponding station and variable were significantly higher as indicated by ANOVA.

| | | Station | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Variable | Target | 1 | **2** | 3 | **4** | **5** | 6 | 7 | 8 | 9 | **10** | 11 | **12** | **13** | **14** | 15 |
| TURB (NTU) | 6.1 (NAESI) | | X | | | | | | | | | | | | | |
| TSS (mg/L) | 3.6 (NAESI) | | X | | | | | | | | | | | | | |
| TOSS (mg/L) | -- | | X | | | | | | | | | | | | | |
| TP (μg/L) | 30 (PWQO) | | X | | | | | | | | X | | X | X | | |
| TAN (mg/L) | 0.02 (PWQO) | | | | | | | | | | | | | | X | |
| TNN (mg/L) | 3.0 (CEQG) | | | | | | | | | | | | | | | |
| TN (mg/L) | 1.06 (NAESI) | | | | X | X | | | | | | | | | | |
| $Cl^-$ (mg/L) | -- | | X | | | X | | | | | | | | | | |
| COND (μS/cm) | -- | | X | | X | | | | | | | | | | | |
| TEMP (°C) | -- | | | | | | | | | | | | | | X | |
| –DO (mg/L) | >4 (PWQO) | | | | | | | | | | X | | | X | | |
| CHL (μg/L) | -- | | | | | | | | | | | | | | | |
| *E. coli* (CFU/ 100 mL) | 100 (PWQO) | | | | | | | | | | | | | | X | |

**Table 3.8:** Correlation coefficients between Principal Component (PC) scores and water quality variables. Only PCs with eigenvalues >1 and variables with loadings >0.5 are shown.

| | Variance Explained (%) | Eigenvalue | Variable | Loading |
|---|---|---|---|---|
| PC1 | 39.16 | 5.09 | TURB | 0.89 |
| | | | TP | 0.88 |
| | | | TSS | 0.84 |
| | | | TOSS | 0.83 |
| | | | $Cl^-$ | 0.81 |
| | | | COND | 0.79 |
| | | | CHL | 0.75 |
| PC2 | 19.39 | 2.52 | –DO | 0.71 |
| | | | TAN | 0.60 |
| | | | TEMP | 0.53 |
| | | | TN | –0.70 |
| | | | TNN | –0.59 |
| PC3 | 17.46 | 2.27 | TEMP | 0.80 |
| | | | TN | 0.56 |
| PC4 | 10.57 | 1.37 | *E. coli* | 0.94 |

**Table 3.9:** Stream Water Quality Index (SWQI) score for each monitoring station sampled in the Nottawasaga River. Index scores are categorized as very good (>2), good (1 to 2), fair (0 to 1), poor (0 to –1), and degraded (<–1). Stations are presented in order from least to most impaired.

| Station | SWQI Score | Category |
|---|---|---|
| 1 | 2.309 | Very good |
| 9 | 0.609 | Fair |
| 11 | 0.390 | Fair |
| 3 | 0.380 | Fair |
| 8 | 0.304 | Fair |
| 7 | 0.251 | Fair |
| 10 | 0.236 | Fair |
| 4 | 0.231 | Fair |
| 15 | 0.207 | Fair |
| 12 | –0.064 | Poor |
| 6 | –0.212 | Poor |
| 5 | –0.412 | Poor |
| 14 | –0.938 | Poor |
| 13 | –1.051 | Degraded |
| 2 | –2.240 | Degraded |

**Table 3.10:** Stream Water Quality Index (SWQI) scores for main tributaries of the Nottawasaga River determined with predictive Eq. 8. SWQI scores are categorized as very good (>2), good (1 to 2), fair (0 to 1), poor (0 to –1), and degraded (<–1). Tributaries are presented in order from least to most impaired. The NVCA health status rating (using total phosphorus as the indicator) is shown for comparison. n/a = not available.

| Trib | TURB | TOSS | TSS | TP | SWQI Score | SWQI Category | NVCA Health Status |
|---|---|---|---|---|---|---|---|
| UN | 3.0 | 1.6 | 2.8 | 6.1 | 4.627 | Very good | Very good |
| PN | 8.8 | 4.5 | 5.8 | 12.8 | 2.735 | Very good | Good |
| TN | 11.7 | 2.5 | 10.5 | 12.8 | 1.587 | Good | n/a |
| BN | 6.3 | 2.4 | 5.8 | 19.0 | 1.295 | Good | Fair |
| BR | 16.4 | 3.3 | 14.0 | 23.4 | –0.059 | Poor | n/a |
| WL | 8.4 | 4.0 | 4.4 | 31.5 | –0.153 | Poor | Good |
| MT | 14.7 | 2.5 | 8.0 | 20.0 | –0.462 | Poor | n/a |
| MB | 27.4 | 4.3 | 40.1 | 32.5 | –0.640 | Poor | n/a |
| MR | 15.0 | 3.1 | 15.3 | 44.2 | –1.622 | Degraded | Good |
| IN | 35.0 | 5.2 | 27.9 | 40.4 | –1.826 | Degraded | Degraded |
| ML | 48.9 | 4.8 | 31.2 | 41.0 | –2.675 | Degraded | n/a |

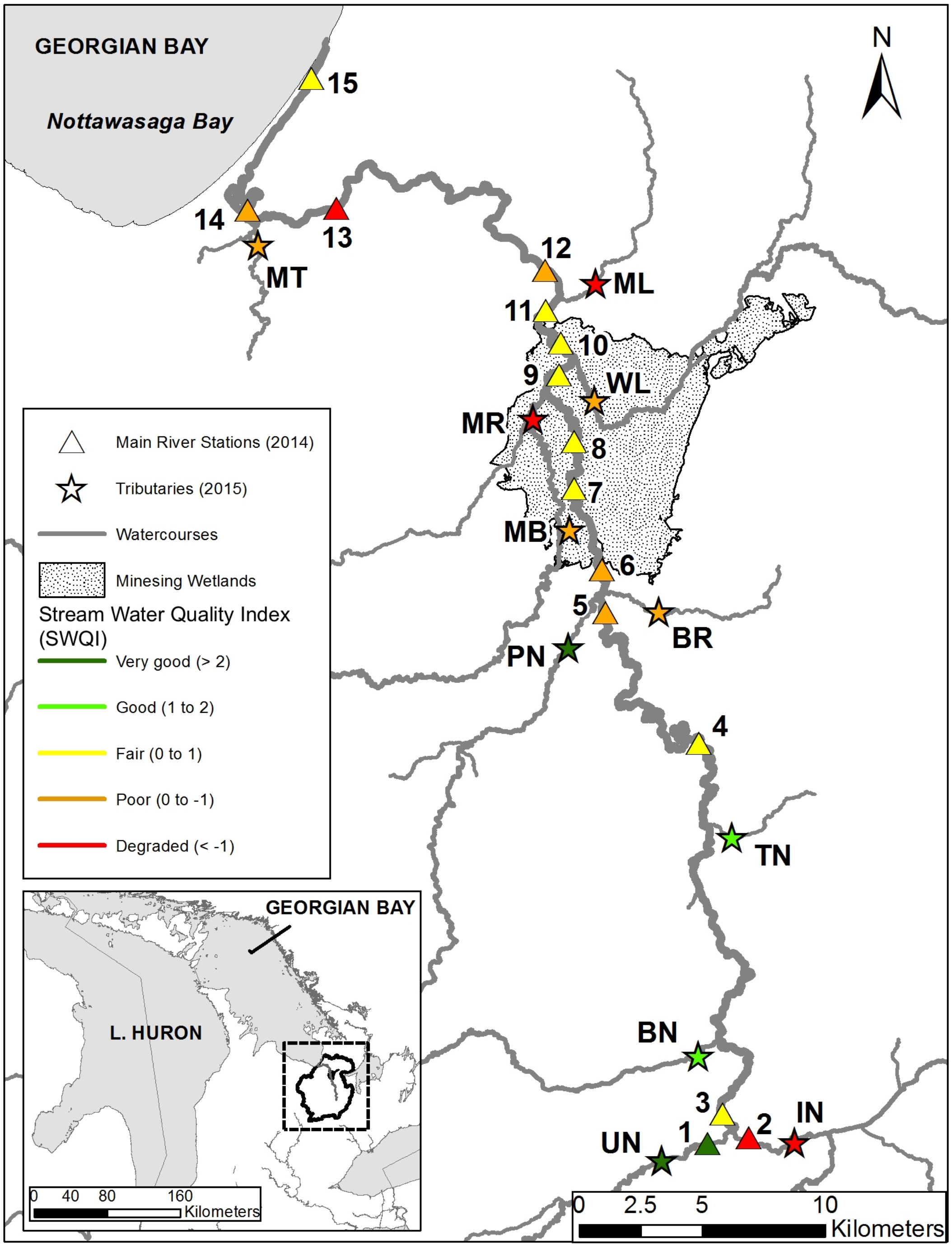


**Figure 3.1:** Map showing locations of monitoring stations in tributaries sampled in 2015 (*stars*), and in the main branch of the Nottawasaga River sampled in 2014 (*triangles*). Stations are coloured according to their score determined by the Stream Water Quality Index (SWQI; very good, good, fair, poor, degraded).

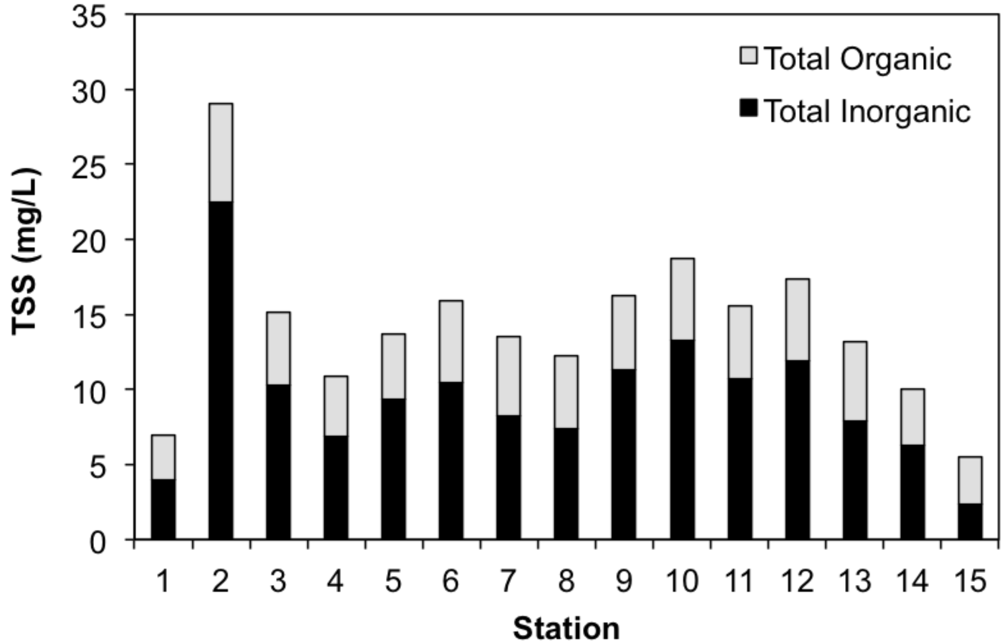


**Figure 3.2:** Relative contributions of organic (grey) and inorganic (black) constituents in total suspended solids (TSS) at monitoring stations (1 to 15) in the Nottawasaga River.

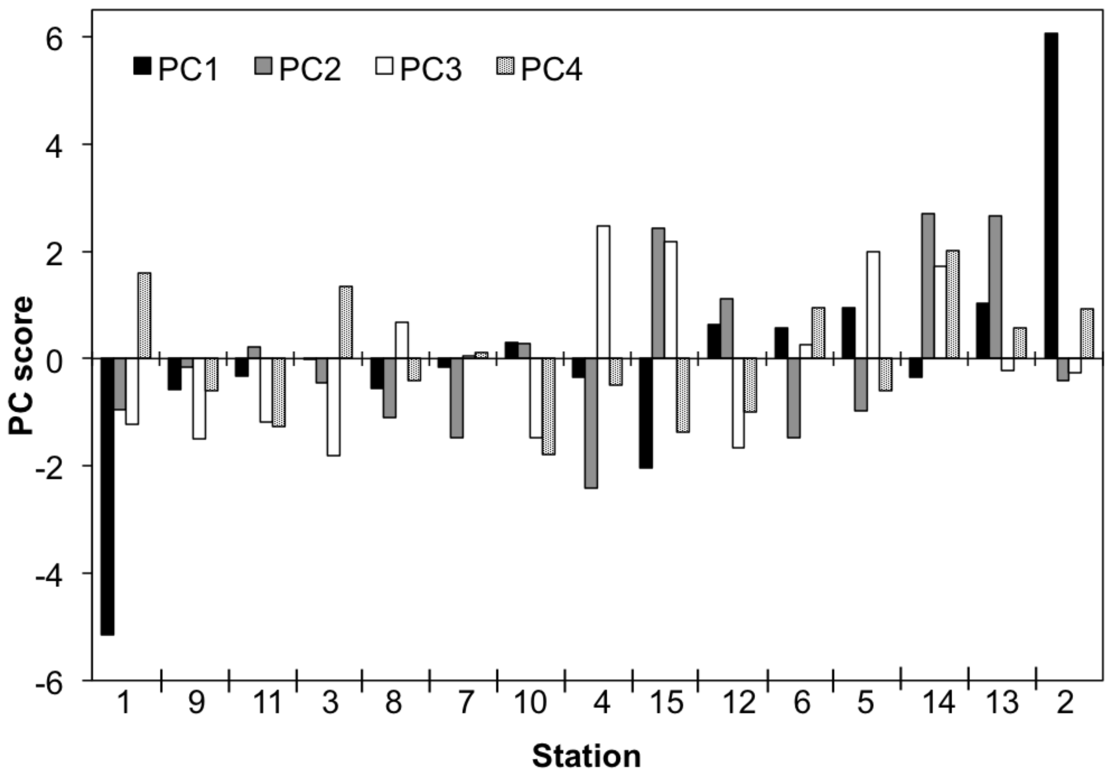


**Figure 3.3:** Principal component (PC) scores for the first four axes presented for each station. Stations are presented in order from least impaired (low PC scores) to most impaired (high PC scores).

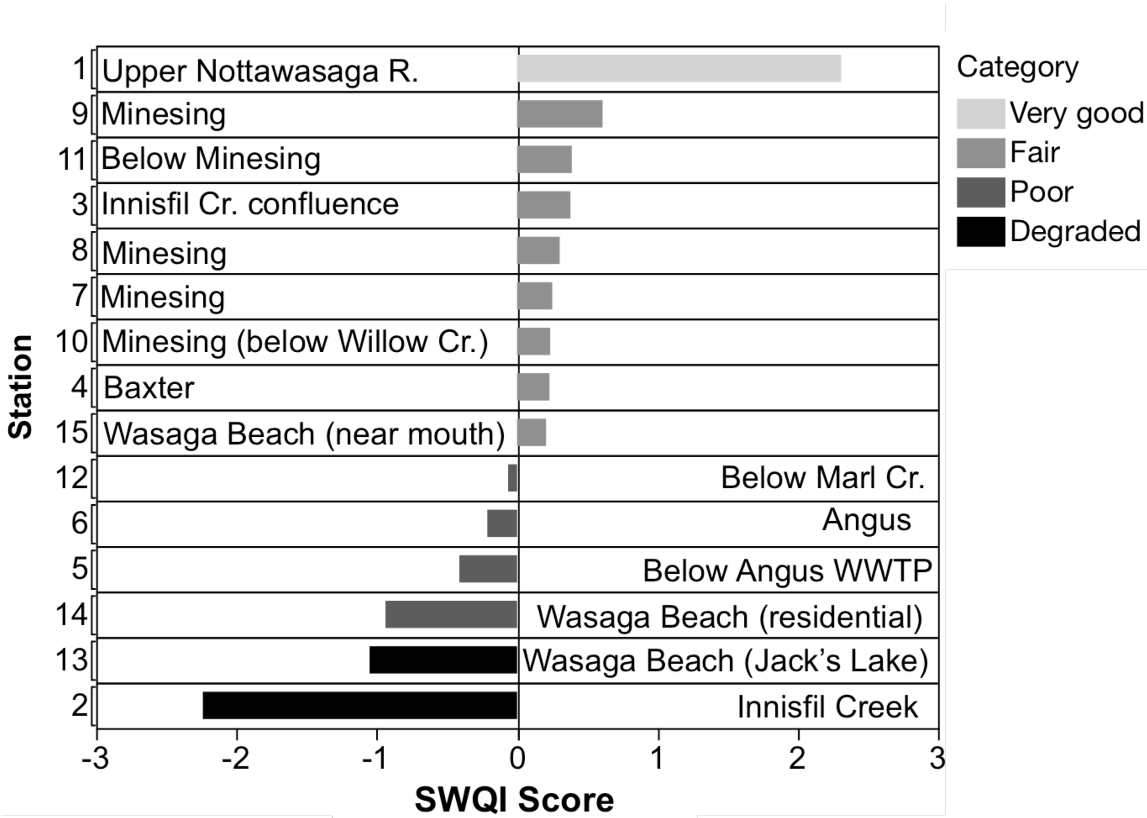


**Figure 3.4:** Stream Water Quality Index (SWQI) score for each monitoring station sampled in the Nottawasaga River. SWQI scores are categorized as very good (>2), good (1 to 2), fair (0 to 1), poor (0 to –1), and degraded (<–1). Stations are presented in order from least to most impaired.

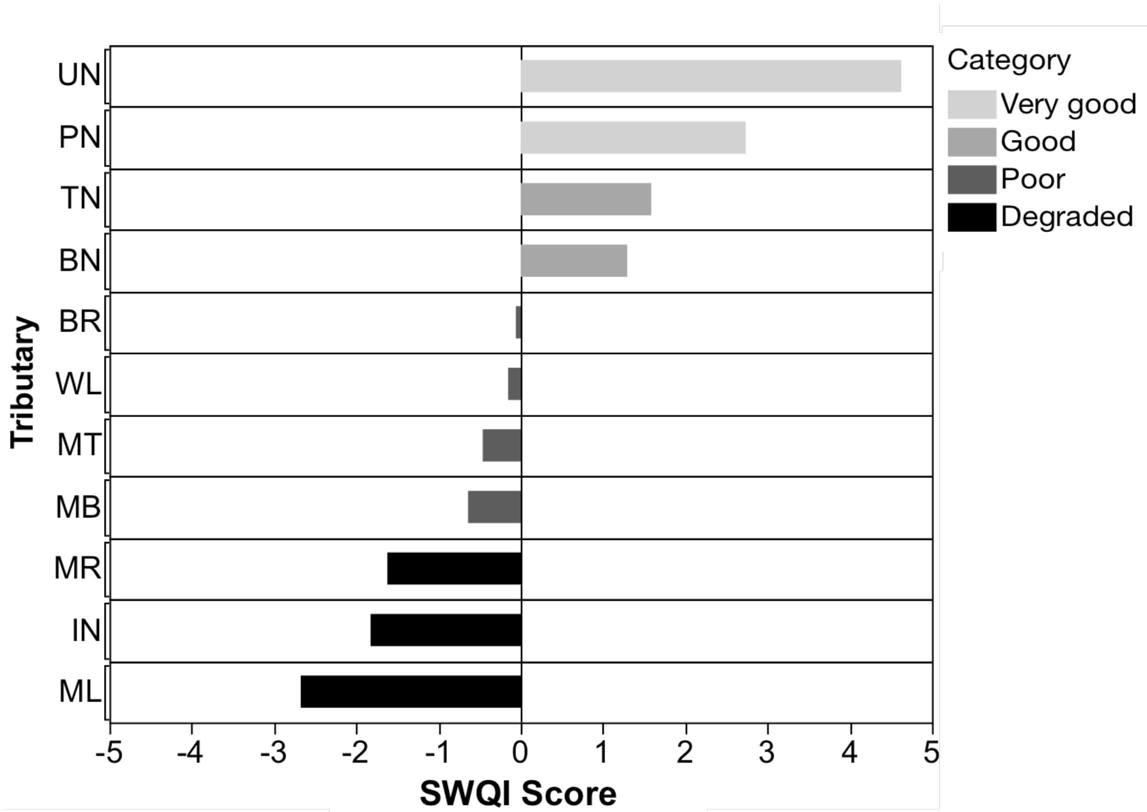


**Figure 3.5:** Stream Water Quality Index (SWQI) scores for main tributaries of the Nottawasaga River determined using predictive Eq. 8. Index scores are categorized as very good (>2), good (1 to 2), fair (0 to 1), poor (0 to –1), and degraded (<–1). Tributaries are presented in order from least to most impaired.

## GENERAL CONCLUSION

The overall goal of this thesis was to use a landscape approach to better understand the different sources and processes that influence spatial variation in water quality across the Nottawasaga River Watershed. Both watershed geomorphology and land cover independently influenced tributary loading, but a landscape model that used both variables was the best predictor of loading rates (Chapter 1). More specifically, drainage area and the proportion of pasture land in sub-watersheds were the main drivers of variation in TP and TSS loading within the river. Our predictive models revealed that sub-watersheds that drained through the Minesing Wetlands were significantly associated with high TP loads, suggesting that the wetland complex is a source of nutrients to the Nottawasaga River. The effectiveness of the geomorphic model illustrated that in the absence of land-cover data (which can be difficult to acquire), readily available geospatial data such as area, slope, and soil can be used to estimate TP and TSS loading across sub-watersheds. Sub-watersheds in our study that contributed the highest base flow TP loads to the Nottawasaga River included Willow Creek, Mad River Breach, Mad River (all three drain through the Minesing Wetlands), and Innisfil Creek (highly agricultural). TSS loading was highest for the Innisfil Creek and the Mad River Breach sub-watersheds. BMPs aimed towards decreasing nutrient and sediment loading to the Nottawasaga River and Nottawasaga Bay should target these sub-watersheds.

Tributary loading can influence the longitudinal variation in water quality of large rivers. In our second chapter, we found that tributary discharge and concentration significantly predicted downstream TURB concentrations in the Nottawasaga River.

More specifically, we found that tributaries with high discharge and high TURB increased downstream concentrations, tributaries with high discharge and low TURB diluted concentrations below the confluence, and tributaries with low discharge had no effect on TURB concentrations below the confluence. Conversely, tributary discharge and concentration did not predict downstream TP concentrations. Given that phosphorus is the most limiting nutrient in freshwater ecosystems, it is important to account for effects of TP loading from tributaries; however, our results suggest nutrient cycling at the tributary-river confluence are too dynamic to enable a prediction based on tributary concentration and discharge rate. Our results have implications for BMPs aimed at reducing sediment loads to the Nottawasaga River. By targeting individual tributaries with high discharge, agencies can improve TURB in the main river through dilution with clear tributary water. For example, the Mad River Breach has a high discharge rate and high TURB; therefore, targeting this tributary as part of a stream restoration strategy could reduce sediment loading, and therefore reduce downstream TURB in the Nottawasaga River.

The longitudinal survey identified stretches of the Nottawasaga River with high TURB. This was an effective way to determine where rehabilitation efforts should be focused. For example, we identified the stretch of river that flows through the Minesing Wetland as having high TURB, which is likely because of erosion of the riverbank where pasture land used to exist. Restoration of riparian habitat in this area may therefore decrease bank erosion and decrease TURB through the Minesing. Additionally, the longitudinal survey identified that riffle sections improved water clarity along the Nottawasaga River, and that the "cleansing" power of riffles was stronger in river segments that were more turbid. We also found a significant negative relationship between sandy substrate and TURB. These findings imply that constructed riffles, consisting of sandy substrate, may be used to improve water quality in turbid stretches of tributaries and the main river. Since most of the Nottawasaga River is relatively deep, it would be beneficial to target turbid tributaries with high discharge, since they are relatively shallow. Improved water clarity in high discharge streams could lead to a dilution effect following confluence with the main branch of the Nottawasaga River. The second chapter identifies two locations in the Nottawasaga River (downstream of Willow Creek and Jack's Lake) that develop anoxic conditions for part of the growing season. This is not only an environmental hazard for aquatic organisms and fish species that rely on sufficient DO (>4mg/L) to survive, but it also has the potential to release soluble P from substrate, which increases TP concentrations. Our results suggest that Willow Creek and Jack's Lake are potential sources are P under anoxic conditions.

Our study shows that landscape variables influence tributary loading, and tributary loading as well as in-stream processes contribute to the spatial variation in water quality observed across the middle and lower reaches of the Nottawasaga River. In our third chapter, we showed that water quality in the main branch of the Nottawasaga River was generally impaired, with most measured variables exceeding provincial standards and guidelines. Meeting provincial or federal guidelines for water quality variables is an effective way to improve ecosystem health; however, when guidelines are overly stringent, they cease to have relevance for management purposes. For this reason, we developed our own model (SWQI) for the Nottawasaga River system using 13 variables to resolve differences in water quality among stations to determine priorities for rehabilitation. By using a wide range of variables, we were able to capture the overall water-quality condition at each monitoring station. The SWQI identified one third of the monitoring stations as being in poor or degraded condition. The most impaired stations in the Nottawasaga River were located below Marl Creek (station 12), downstream of Angus (station 6), below the Angus wastewater treatment plant (5), in the town of Wasaga beach within a residential area (station 14), and below Jack's Lake (station 13), as well as Innisfil Creek (station 2). These stations were associated with high concentrations of nutrients, sediment, dissolved ions, and *E. coli*, and are likely stations most impacted by anthropogenic sources, such as agricultural and urban land-uses. Only one station, located in the upper Nottawasaga River, was categorized as being in very good condition. The remaining stations were categorized as "fair", which indicates that water quality must be improved before the river can be classified as "good".

When we applied the SWQI to main tributaries of the Nottawasaga River, we found that the most impaired tributaries were Marl Creek, Innisfil Creek, Mad River, Mad River Breach, McIntyre Creek, Willow Creek, and Bear Creek. We demonstrated that the SWQI can be effectively applied to individual sub-watersheds, and was able to identify the most impaired tributaries and river sections in the Nottawasaga River. We recommend that the SWQI be applied to similarly large mixed agricultural watershed so that management agencies can objectively identify rehabilitation priorities.