WATER QUALITY IN THE GRAND RIVER: A SUMMARY OF CURRENT CONDITIONS (2000-2004) AND LONG TERM TRENDS

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Executive Summary

Generally, nutrient concentrations in the Grand River tend to be high where as metal concentrations generally comply with guidelines.

The inherent geology and current landuse practices appear to drive some of the chronic surface water quality issues within the Grand River watershed. For example, subwatersheds draining the clay and till plains tend to have the highest suspended sediment concentrations and nutrient loads (e.g. Nith River, Fairchild Creek). Subwatersheds with intensive agricultural production or urban development also contribute to the overall high nutrient levels within the Grand. Water quality in the lower reaches of the Grand River reflects the cumulative impact of the upstream watershed and the underlying geology as it tends to progressively deteriorate as it travels from the Shand Dam (upper middle Grand) towards Brantford (lower Grand).

The central portion of the Grand River, including the major tributaries draining into this reach such as the Canagagigue Creek, Conestogo River and lower Speed River tends to be the area within the watershed where water quality is most impaired. Land use including intensive agricultural production, urban development and wastewater treatment plant effluents in this area likely contribute to the degradation in water quality. Sites experiencing nutrient enrichment tend to be downstream of the major urban areas with the exception of the intensive agricultural areas in the Canagagigue Creek. High levels of phosphorus and nitrogen contribute to prolific aquatic plant growth in locations where conditions are right (e.g. good substrate, shallow, low flows etc) which can lead to depletion of dissolved oxygen levels.

Dissolved oxygen is an important indicator of the river's ability to sustain aquatic life. Certain reaches in the Grand River watershed experience stress with low dissolved oxygen levels (e.g. Grand River at Blair, Speed River at Road 32). However, in 2004 temperatures were cooler and dissolved oxygen levels tended to be above the 4.0 mg/L target.

The impact of the urban development on the Grand River is reflected by the significant increase in the concentrations of phosphorus, total ammonium and chloride as the river flows through the Region of Waterloo from Bridgeport to Blair. Similar impacts are also found within the Speed River below Guelph.

In general, suspended solids appear to be low throughout the upper and middle Grand River reaches when compared to the lower Grand River. A distinct change in water quality is evident below Brantford as significantly higher levels of suspended solids are seen in the river at the Newport Bridge which is likely a result of high suspended solid contributions from the Nith River. As the river flows into the southern clay plain, it picks up colloidal clay particles that virtually always remain in suspension (GRBWMS 1979) making it highly turbid. Suspended solids and phosphorus increase again in the river at Dunnville likely due to the significant contributions from Fairchild's and MacKenzie Creeks and river impoundments which makes the river almost lake-like. Most of the nitrate in the Grand River originates in the upper middle region of the watershed, likely from high concentrations found in Irvine Creek, Canagagigue Creek and Conestogo River. However, it is evident that contributions from other sources such as shallow groundwater high in nitrates (likely the source of elevated levels in both Whitemans and Alder Creeks) and wastewater treatment plant effluent are also impacting the nitrate concentration within the watershed.

Chloride levels in the lower Speed River are among the highest in the Grand River watershed. Sources include road de-icing and likely water softener discharges in the municipal wastewater effluent.

Two surveys conducted on the river for pesticides and other trace organics in 2003 and 2004 reveal that pesticides may not be a widespread issue in the watershed. Pesticides were detected in one intensive agricultural watershed and two urban watersheds. However, two surveys likely do not adequately characterize this issue and additional, targeted surveys are required to understand the breadth of this issue in the watershed.

A preliminary assessment of the benthic macroinvertebrate community monitoring in 1999-2001 indicates that most of the watershed experiences low to moderate organic enrichment (pollution). The sites where the invertebrate community indicates moderate pollution are consistent with the sites with poor water quality from very high nutrient concentrations.

Bacteria and pathogen monitoring is not done on a regular basis. Research indicates that bacteria and pathogens are common in the river which is not surprising and generally decrease in concentrations from the upper middle Grand River to the lower reaches of the River.

Very little current information exists on the three major reservoirs in the Grand River watershed. Historic monitoring data suggest that the Guelph and Conestoga Lake reservoirs are eutrophic with very high phosphorus levels in the euphotic zone while the Belwood Lake reservoir is meso-eutrophic with moderately high phosphorus levels.

Spills and wastewater treatment plant bypassess are a significant threat to downstream water users in the Grand River watershed. They represent an acute and immediate impairment to water quality that can compromise drinking water treatment. There were over 70 spills in the Grand River watershed in 2004 of which most were wastewater treatment bypasses of secondary treated wastewater. Therefore, it is imperative to have an effective spills response protocol and accurate river information for timely response.

Water quality conditions have greatly improved in the watershed since the 1930's and 40's when minimally treated sewage was dumped into the river. In the 1970's many parts of the Grand River and its tributaries were considerably stressed from wastewater treatment plants. A preliminary analysis of temporal trends in nutrient concentrations from 1981-2001 illustrates that total phosphorus concentrations are decreasing however nitrate concentrations are increasing at selected sites. Therefore, continued pro-active

planning and implementation by municipal water managers, agricultural producers and watershed residents will help to speed up improvements and slow down further deterioration of water quality in the river so that watershed residents can continue to enjoy the Grand River.

Introduction

The Grand River watershed has some of the fastest growing urban centres in Canada. As well, it also has some of the most valued and productive agricultural land in southwestern Ontario. These land use pressures can affect the quality and health of the Grand River.

The quality of the Grand River is a fundamental aspect of a healthy watershed and the health of the communities in the watershed. Consequently, it is important to document the state of water quality, identify issues, and recommend actions to improve the state of the river. The purpose of this report is to compile existing water quality information and analyze current and historic data to characterize the state of water quality in the Grand River watershed. The report is not exhaustive but provides insight into the chemical and physical aspects of river water quality. It does not summarize groundwater quality in the watershed.

The Provincial Water Quality Monitoring Network (PWQMN) provides invaluable data when evaluating ambient conditions and long term trends. Therefore, much of this report focuses on characterizing nutrients, suspended sediment, metals and major ions at 28 long term monitoring sites within the watershed. However, bacteria/pathogens, pesticides, dissolved oxygen, and temperatures are also important water quality indicators and therefore information from other programs and/or research initiatives are also included in this report.

Watershed Characteristics

The Grand River watershed is comprised of 6,965km² of southern Ontario. Most of the watershed drains rich agricultural land (76%) and forested areas (17%) (Figure 1). Urban areas are concentrated in the central portion of the watershed and cover about 5% of the total watershed area. The Grand River has eight major tributaries: Speed/Eramosa, Fairchild, Boston/McKenzie, Whitemans, Nith, Canagagigue, Conestogo, and Irvine Rivers and many other smaller tributaries. Approximately 900,000 people live in the watershed and 26 sewage treatment plants service about 80% of the total population the remaining 20% are serviced by on-site wastewater treatment systems (e.g. septic systems) (Figure 2). Most (52%) of the watershed residents are serviced by conventional municipal wastewater treatment facilities, while about 27 % of the watershed population is serviced with more advanced tertiary treatment (Figure 3). Conventional wastewater treatment removes most of the phosphorus and suspended sediment while tertiary treatment includes the removal of nitrogen compounds such as ammonia.

The Grand River and its tributaries flow through three geologically distinct areas (Figure 4). The northern till plain drains the upper Conestogo and Grand Rivers and facilitates a significant amount of runoff. Two of the four major reservoirs, Belwood and Conestogo Lakes capture most of this runoff, which is used to augment river flows during low flow periods. These reservoirs are also critical in mitigating flood events. The central watershed region, the major urban growth area, is comprised mostly of highly permeable sands and gravels (e.g. Paris-Galt moraine system). This part of the watershed has significant groundwater reserves, which are used for drinking water supplies. In many areas, groundwater discharges into surface waters creating coldwater or coolwater

streams and rivers. The Grand River finally traverses the southern clay plain, which also generates significant runoff, prior to empting into Lake Erie.

A combination of the land cover/use, intrinsic geology and anthropogenic sources (e.g. wastewater treatment plants) all contribute to water quality issues in the Grand River watershed.

Major Water Uses in the Grand River Watershed

Water quality is generally evaluated according to the primary use of the water body. Issues arise when these uses are compromised. Designated uses include drinking water supplies, aquatic habitat, industrial/commercial uses, agricultural uses and recreation. The Grand River and its tributaries are used as a drinking water supply for four communities in the watershed (Figure 5); water supplies for irrigation and livestock; industrial and commercial uses; and for supporting native (e.g. brook trout), non-native (e.g. brown trout) and endangered (e.g. wavy rayed lampmussel) aquatic species that are important to the natural heritage of the river as well as to local economies. Furthermore, the river is used to assimilate waste from 26 wastewater treatment plants, recharge shallow groundwater aquifers and recreation (MOE 1990). The Grand River is one of the most used waterways in Ontario for recreational pursuits including canoeing and kayaking.

Objective of Report

The objective of this report is to summarize the chemical and physical characteristics of the Grand River and its tributaries and to identify or reaffirm the water quality issues in the basin. The goals of this report are to:

- 1. Describe the current state of water quality in the Grand River and its tributaries; and
- 2. Identify long term trends in key water quality attributes and to determine if water quality is improving, deteriorating or staying the same over time.



Figure 2. Land cover in the Grand River watershed.



Figure 3. Wastewater treatment plants in the Grand River watershed and the population estimates (2001) the plants service.



Figure 4. Percentage of the population receiving wastewater treatment in the Grand River Watershed.



Figure 5. Surficial geology of the Grand River watershed.



Figure 6. Location of the drinking water treatment plants using surface water in the Grand River watershed. Note: the intake in the Eramosa River is for shallow aquifer recharge; the intake for Dunnville is located in Lake Erie.

Methods

Water Quality Monitoring

Routine Chemistry, Nutrients and Metals

There are 28 long term monitoring sites in the Grand River watershed that are part of the Provincial Water Quality Monitoring Network (PWQMN) (Table 1; Figure 6). Appendix A describes the location of the active and inactive PWQMN sampling sites and the period for which samples have been taken at each site. The sites monitored in the Grand River watershed have between 23 and 38 years of data. The Ministry of Environment (MOE) is responsible for the laboratory analysis while the Grand River Conservation Authority (GRCA) is responsible for collecting eight samples per year between March and November. Prior to 1996, 12 samples per year were taken at each site. Samples are taken more frequently at site 16018403502 (the bridge in Dunnville) by the MOE to get a better estimate of contaminant loading to Lake Erie. Samples are analyzed for routine chemistry, nutrients and metals (Table 2). Method detection limits are described in Appendix B.

Water samples were collected using standard bridge-sampling techniques. A stainless steel pail is used to collect water samples. Water is poured into bottles, preserved if necessary, stored on ice and couriered to the laboratory.

Dissolved Oxygen, Conductivity, pH and Temperature

Dissolved oxygen, conductivity, pH and temperature are collected in the field at each PWQMN site using a handheld YSI data sonde. These parameters are also monitored continuously at seven monitoring stations (separate from the PWQMN) in the Grand River watershed using HydrolabTM or YSITM data sondes (Figure 8). The data are primarily collected to support the Grand River Simulation Model (GRSM), which models the assimilative capacity of the Grand and Speed Rivers, as well as to provide information on the state of the river with respect to the protection of aquatic health.

Data collected at continuous water quality stations are relayed back to the GRCA administration office on a real-time basis, organized into relational databases and plotted to the website for easy public access.

PWQMN Identification Number	Short ID Number	Site Description			
Grand River					
16018403902	39	Downstream of Grand Valley			
16018403702	37	Below Shand Dam			
16018410302	103	West Montrose			
16018401502	15	Bridgeport			
16018401202	12	Blair			
16018401002	10	Glen Morris			
16018402702	27	Brantford			
16018409202	92	York			
16018403502	35	Dunnville			
Irvine River					
16018410402	104	Irvine River			
Canagagigue Creek					
16018405102	51	Upper Canagagigue Creek			
16018401602	16	Lower Canagagigue Creek			
Conestogo River					
16018409102	91	Moorefield Creek			
16018410002	100	Upper Conestogo River			
16018407702	77	Conestogo River below Reservoir			
16018402902	29	Conestogo River near mouth			
Speed River					
16018410202	102	Eramosa River			
16018409902	99	Upper Speed River			
16018403602	36	Speed River at Road 32			
16018410102	101	Speed River at Preston			
Nith River					
16018403802	38	Alder Creek			
16018403202	32	Upper Nith River below New Hamburg			
16018400902	9	Nith River at mouth			
Fairchild's Creek					
16018404402	44	Upper Fairchild's Creek			
16018409302	93	Fairchild's Creek near mouth			
Whitemans Creek					
16018410602	106	Whitemans Creek			
Boston/MacKenzie Ci	reek				
16018409502	95	Boston Creek			
16018409602	96	MacKenzie Creek			

Table 1. List of the 28 long term water quality monitoring sites with their PWQMN siteidentification number, short identification number and site description.

Water Quality Variable Category	Water Quality Variables			
Nutrients	Dissolved Nutrients: ammonia, nitrate+nitrite; phosphate			
	Total Nutrients: Total phosphorus, Total Kjeldahl nitrogen			
Solids	Total Suspended solids; Total dissolved solids			
Major Ions/Anions	Calcium; Magnesium, Sodium, Potassium; Hardness; Chloride			
Routine Chemistry	pH; Alkalinity; Conductivity			
Metals	Aluminum; Barium, Beryllium; Cadmium; Chromium, Copper; Iron; Manganese; Molybdenum; Nickel; Lead; Strontium; Titanium; Vanadium; Zinc			
Routine Physical Pesticides*^	Turbidity; Temperature Phenoxy Acid Herbicides°; Triazine Herbicides°; Organophosphorus insecticides°			

Table 2. List of water quality variables analyzed in PWQMN stream/river samples.

* only sampled at one site: 16018403502 (at Bridge in Dunnville) as part of MOE's Enhanced Tributary Monitoring Program

° includes currently registered and phased out products

^ for a complete list of pesticide products, see Appendix E



Figure 7. Provincial water quality monitoring network in the Grand River watershed.



Figure 8. Grand River real-time water quality monitoring network.

Bacteria and Pathogens

River water samples are not routinely collected at long term river monitoring sites for bacteria or pathogens. Significant variability in sampling and analysis methodologies provides for some hesitation of including these parameters as part of a long term monitoring program. However, river water samples are collected weekly from the Grand River through the Elora Gorge Conservation Area during the summer months (May – August) and analyzed for E. coli. The water samples are submitted to an accredited laboratory for analysis. Although these data are from one location in the Grand River, they do provide some insight into the range of E. coli concentrations found in the upper-middle Grand River.

Pesticides

River samples collected at the PWQMN site 16018403502 (Dunnville Bridge) are routinely analyzed for pesticides and other contaminants of concern. In addition, river/stream water samples were collected from 18 sites in 2003 and 2004 in partnership with the MOE and the Ontario Ministry of Agriculture and Food (OMAF) (Figure 8). Appendix C describes the location of these sites. Pesticide monitoring sites were chosen to represent smaller subwatersheds that had either agricultural or urban landuses. Surveys were completed in November in 2003 and June and August in 2004. The purpose of the June survey was to target a pre-application period while the August survey was targeted as a post application period. Effort was made to sample wet weather events. A list of the pesticide products that are analyzed by the University of Guelph laboratory is listed in Appendix E.

Data Analysis

Current water quality conditions in the Grand River watershed were graphically presented or statistically analyzed for selected water quality parameters using pooled data from 2000 to 2004. For preliminary long term trend assessment, data from 1981 to 2001 were used. This time frame coincides with Statistics Canada population and agricultural census years. Due to limitations of the water quality data, statistical trend analysis was limited to 1981 and 1995 for total nitrate and total ammonia as there was a change in laboratory analytical methods in 1996. Water quality parameters included: nutrients, major ions, metals, physical characteristics (e.g. dissolved oxygen, temperature, pH, and conductivity), bacteria and pesticides.

Streamflow, Precipitation and Climate

Monthly precipitation, streamflow and climate data (e.g. air temperature) were summarized to characterize the study period since water quality, in rivers is strongly influenced by these parameters (e.g. the amount and timing of rainfall and snowmelt).

Monthly levels of precipitation for 1998-2004 from selected monitoring sites were plotted against the long-term monthly average precipitation (40 year normal) to determine whether the years between 2001 and 2004 were wetter or dryer than usual.



Figure 9. Pesticide monitoring sites in 2003 and 2004 in the Grand River watershed.

Similarly, long-term average monthly river flows were calculated (1948-2000) and graphed against recent (2001-2004) river flow monthly means to determine whether any particular year was a wetter or dryer than normal period. Summer (June, July and August) air temperatures for a long term weather monitoring station in the watershed was summarized and compared against the five year running average air temperatures.

Exploratory Analysis

10th and 90th percentiles.

Detailed statistical summaries (e.g. minimum, maximum, percentiles, median, mean etc) are presented in Appendix D. EXCEL TM and SIGMAPLOT TM were used to calculate summary statistics and graphically plot the dataset. Box and whisker and time series plots were used to present the data graphically. Box and whisker plots can illustrate the distribution and statistics of a dataset (Figure 9). The box in the box-whisker plot shows the 25th and 75th percentiles of the dataset, called the lower and upper quartiles, and the median (the 50th percentile). The whiskers represent the range of the data set to the 90th and 10th percentile (Sigma Plot 8.0 2002). The circles illustrate outliers beyond the



Figure 10. Box and whisker plot illustrating the 10th, 25th, 50th (median) 75th and 90th percentiles and outliers of the 2000-2004 dataset.

Compliance with Water Quality Guidelines and Basin Water Quality Targets

Provincial water quality objectives, federal guidelines and other relevant criteria were used to evaluate whether river water quality meets specified uses (e.g. protection of aquatic life). The level of compliance was determined by calculating the percentage or frequency of samples meeting objectives, guidelines or criteria for the data collected between 2000 and 2004. Objectives, guidelines or relevant criteria used to evaluate compliance are listed in Table 3.

Dissolved oxygen levels in the river at the real-time monitoring stations are evaluated using the target derived by the Grand River Implementation Committee (GRIC) for the Grand River basin study. The Grand River basin study established this target to ensure that aquatic life in the river would be minimally impacted. The target is that dissolved oxygen would not fall below 4.0 mg/L more than 5% of the time (GRIC 1982).

For those water quality parameters that do not have an associated guideline or objective, referenced levels were extracted from the literature to be used as a benchmark. For chloride, a benchmark concentration of 250 mg/L was used, which is a chronic toxicity level for aquatic life (Environment Canada 2001).

For Total Suspended Solids (TSS), a benchmark of 25 mg/L was used as this is a level where there is no evidence of harmful effects on fish or fish habitat (EIFAC 1964, as sited in DFO 2001). However, it is acknowledged that a better measure of the effects of suspended sediment on aquatic life should include an assessment of concentration and duration of exposure (Caux et al 1997, and Newcombe and MacDonald 1991, as sited in

DFO 2000). Unfortunately, the monitoring design for the PWQMN in which only periodic grab sampling is done, inhibits the application of this approach.

Constituent	Water quality objective or criteria used	Jurisdiction
Total Phosphorus	0.030 mg/L	Ontario Ministry of Environment
Total Nitrate as Nitrogen	2.93 mg/L (13 mg/L Nitrate ion)	Canadian Environmental Quality Guidelines
Chloride	250 mg/L	Benchmark identified in Environment Canada report ¹ ; Drinking Water Quality Guideline
pH	6.5-8.5	Ontario Ministry of Environment
Nitrite	0.060 mg/L	Canadian Environmental Quality Guidelines
Total Suspended Solids	25.0 mg/L^2	n/a
Total Ammonia	pH and temperature dependant	Ontario Ministry of the Environment
1 Environment Cana	$\frac{1}{2}(2001) = 2$ DEO (2000)	

Table 3. Water quality variables and corresponding Federal or Provincial water quality guidelines/objectives.

Environment Canada (2001) 2. DFO. (2000)

Statistical and Trend Analysis

Typically, water quality data are not normally distributed (Helsel and Hirsch 1992). possess missing values, are collected at uneven time intervals; and have frequent occurrence of outliers (Trkulja 1997). To reduce the influence of outliers and not violate the assumptions required for parametric tests, nonparametric statistical analyses were used to evaluate differences between sampling sites and determine monotonic time trends. Nonparametric statistical tests are more powerful when applied to non-normally distributed data, and almost as powerful (under certain conditions) as parametric tests when applied to normally distributed data (Helsel and Hirsch 1992).

Microsoft EXCELTM with the Analyze-It TM (Analyze-it Software 2003) add-in was used for nonparametric comparisons between upstream and downstream sites while trend analyses were performed using WQStat PlusTM (Intelligent Decision Technologies Inc, Co., US).

The nonparametric analysis of variance (Kruskal-Wallis test) was used to compare the median values between three or more sites while the nonparametric Mann-Whitney rank sum test was used to determine statistical pairwise differences between medians. A significance level of 5% (e.g. p=0.05) was used in all comparisons. It is important to note that statistically significant differences are not always environmentally consequential (Larned et al 2005).

Two fundamental approaches have evolved for time-trend analysis of difficult surface water quality time series including formal statistical approaches and graphically oriented numerical procedures that permit the visual assessment of data series behaviour (as cited in Bodo 1991 by Trkulja 1997). The graphical approach used in this analysis includes a smoothing technique that was used on time series plots of selected water quality parameters to identify whether a trend over time was obvious. Smoothing is an exploratory technique, having no simple equation or significance test associated with it and is used to highlight trends or patterns in the data on a scatterplot (Helsel and Hirsch 2002). The smoothing technique LOWESS (Locally Weighted Scatterplot Smoothing) describes the relationship between Y and X without assuming linearity or normality of residuals and is a robust description of the dataset (Helsel and Hirsch 2002).

To further investigate the trends visible through the afore mentioned exploratory method, a formal statistical analysis was carried out to determine if there were any significant trends evident. Since river water quality can be influenced by stream flow and time of year (e.g. seasonality) water quality data were graphically plotted against flow and a Kendall Rank Correlation test was used to determine if the two datasets (flow and quality) were associated. If flow effects were detected, the water quality data were flowadjusted using WQStat PlusTM prior to performing the statistical trend analysis. However, an inherent trend detected in streamflow may influence whether a trend is detected in the water quality data if it is corrected for flow. Consequently, the complete flow data set and the subset of flow data that corresponds with water quality sampling dates for each monitoring site was tested for the presence of trends. If a trend was detected in both the complete data set and the water quality data subset, the flow data were detrended prior to evaluating trends in the water quality data. If a trend was detected in the water quality data subset yet not in the full dataset, again the flow data were detrended prior to evaluating trends in the water quality data however, it was noted that a sampling bias likely has occurred.

The nonparametric Seasonal Kendall trend test was used to determine statistically significant (p < 0.05) monotonic (i.e. single) trends in datasets that had seasonal effects (Helsel and Hirsch 1992). The test, which is a generalization of the Mann-Kendall test (Mann, 1945; Kendall, 1975) reduces the adverse effect that seasonal differences in the relation of concentration to discharge may have on trend detection by only making comparisons of data from similar season (Putnam and Pope 2003). There are four distinct time periods in which flows change in the Grand River watershed. Springtime is characterized by high flows; summer time is characterized by lower river flows yet experience sporadic peaks in discharge from significant rainfall events; high flows tend to characterize flows during the fall; and low flows under ice characterize the winter. Consequently, four seasons were assigned to the water quality datasets (Table 4). In datasets that were not affected by season, the SenSlope trend test was used at the same level of significance. The null hypothesis is that no trend exists.

Season	Timeframe	
Spring	March 1 – May 31	
Summer	June 1 – August 31	
Fall	September 1 – November 30	
Winter	December 1 – February 28	

 Table 4. Definition of the four seasons specified in the Seasonal-Kendall nonparametric test for monotonic trends for the Grand River watershed.

Estimation of Mass Loads and Total Export

Tributary mass loads were estimated using the model FLUX vers. 5.1 (Walker 1999). The model estimates mass nutrient or suspended sediment loads from grab sample concentration data and continuous (e.g., average daily) flow records. Five algorithms are used to estimate mass loads. The method that produced an estimate of mass load with the least variability (i.e. Coefficient of variation <0.10) was used to determine the relative mass loads generated at the sampling site.

The mass load or transport, expressed as a unit of weight/unit of time, is the total amount of material that passes by a given location over a given time period. For watershed evaluations, mass loads are usually standardized for drainage basin areas and flow volumes. To standardize mass load by drainage basin area, total mass loads are divided by drainage basin areas (mass unit/surface area unit) to determine the total mass export per unit area. Further, flow-weighted mean concentrations, expressed as the total mass/total volume over a given time period, were used to standardize mass transport for flow.

Water Quality Index

The Canadian Council for Ministers of the Environment (CCME) adopted a water quality index (WQI) to help communicate complex water quality information to the public and provide a broad overview of environmental performance (CCME 2001). A modification of the CCME WQI was used to determine the relative ranking of each PWQMN site for nutrients and metals. Since the Grand River and its tributaries generally have elevated levels of phosphorus and nitrogen in the river, the water quality index for nutrients was modified to incorporate only the F2 (Frequency of excursions from benchmark) and F3 (Amplitude of the excursion) factors of the index formula. This was done as the F1 factor (Scope – number of variables whose benchmarks are not met) would routinely saturate (i.e. all five variables would exceed benchmarks) and mask the relative differences among sampling sites. The formula used for the modified CCME water quality index for nutrients is shown in Equation 1. The standard CCME WQI formula was used for evaluating metal concentrations at the 28 sampling sites is Equation 2.

Water Quality Index Score =
$$100 - \left(\frac{\sqrt{F_2^2 + F_3^2}}{1.414}\right)$$
 Equation 1

Water Quality Index Score =
$$100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732}\right)$$
 Equation 2

Basin specific water quality benchmarks for nutrients were established to evaluate the relative status of water quality at the 28 PWQMN sampling sites in the Grand River watershed. The benchmarks were established based on the median concentrations of all sampling sites between 1978 and1982. The Grand River Basin study was completed during this time period and serves as a good benchmark from which to evaluate progress

made in reducing impacts to the river. Table 5 and Table 6 outline the nutrient and metal concentrations, respectively, used in the WQI as basin-specific benchmarks to make relative comparisons among the PWQMN sampling sites.

The WQI generates a score between 0 and 100. Zero indicates poor water quality while 100 indicates ideal water quality. The CCME WQI is used to give an overall rating of the general or ambient water quality for nutrients and metals; it does not determine the quality of water for specific uses. To provide a relative ranking of the scores calculated for each site within the watershed, scores were grouped into categories based on those derived by CCME (2001) (excellent, good, fair, marginal & poor). However, due to the nature of the index it is not possible to determine if a calculated score is as a result of one very high excursion or frequent small excursions away from the benchmark. Therefore further inspection of the data is needed to fully understand what is driving the results.

Table 5. Nutrients and corresponding water quality benchmarks used in the water quality index.

Constituent	Water quality criteria*
Total Ammonia (mg/L)	0.0435
Total Nitrate+Nitrite (mg/L)	2.043
Total Kjeldahl Nitrogen (mg/L)	0.78
Total Phosphorus (mg/L)	0.078
Phosphate (mg/L)	0.021

* water quality benchmarks were based on the median concentration between 1978-1982

 Table 6. Metals and corresponding water quality benchmarks used in the water quality index.

Constituent	Water quality criteria*
Cadmium (µg/L)	$0.2 - 0.5^{\wedge}$
Copper (µg/L)	1.0 - 5.0^
Iron (μ g/L)	300
Lead (µg/L)	1.0 - 5.0^
Mercury (µg/L)	0.1
Nickel (µg/L)	25
Zinc (µg/L)	30

* water quality benchmarks based upon PWQO's due to toxic effects of metals

^ dependant upon hardness

Spills

All spills reported to the Grand River Conservation Authority are recorded in a log book. Since spills can impact river water quality, a summary of the number and type of spills that occurred in the watershed in 2004 is presented.

Results

Precipitation, Climate and Streamflow

Monthly precipitation at the Shand Dam fluctuated at or slightly above the long term average conditions between 2000 and 2002 however, starting in June 2002, precipitation

fell below long term average conditions (Figure 11). This drought condition carried into the winter months of 2003. With the exception of a few months, monthly precipitation levels approached or exceeded normal conditions starting in May 2003 and continued to increase throughout much of 2004.



Figure 11. Monthly precipitation at the Shand Dam, 1998-2004, shown as a percentage of the 40 year normal.

The cumulative impact of the dry conditions in the late 1990's, the sporadic levels of precipitation between 2000 and 2002 and low snow pack in 2003 are reflected in the below average stream flows found within the Grand River watershed for that time (Figure 12). However, stream flows recover to average conditions in late 2003 and into 2004 as a result of a wet summer in 2003 and higher than average precipitation levels throughout much of 2004. The hot dry temperatures in the summer of 2002 (Figure 13) likely had an impact on dissolved oxygen levels in the river (see dissolved oxygen section)



Figure 12. Streamflow as shown as a percentage of the 30 year long term average annual flow at four flow gauging stations on the Grand, Nith and Speed rivers from 1998-2004.



Figure 13. Yearly average summer (June, July and August) (blue line) air temperatures compared to the five year running average (red line), at Kitchener, Ontario.

Sampling Regime

The Provincial Water Quality Monitoring Network (PWQMN) is the monitoring program from which most of the water quality information in the Grand River watershed is acquired. Figure 14 illustrates the number of sampling sites in the watershed and the average number of samples taken per site since the inception of the PWQMN in 1964. In 2004, there were 30 sampling sites at strategic locations throughout the watershed however, historically there were up to 43 sampling sites in the watershed.

On average, eight samples per year are collected at each sampling site, generally between March and November, with the exception of the Enhanced Tributary Monitoring site located at the mouth of the Grand River at Dunnville where an average of 20 samples are taken per year (Figure 15). However, the number of samples collected each year is down considerably from the historic high of over 20 samples per year per site.



■ Total No. Sites ■ Ave No. Samples

Figure 14. Total number of water quality monitoring sites; average number of samples per site per year for the Provincial Water Quality Monitoring Network in the Grand River watershed.

In general, most of the stream and river samples taken over the past five years have been collected during low river flows (Figure 16). In 2003, a change in the monitoring strategy targeted the collection of samples during high flow events such as spring runoff and summer rainfall events in addition to summer low flows. Figure 17 illustrates that the water quality sampling regime over the past five years characterizes the lower river flows but does not characterize the higher river flows as well.

Figure 15. Total number of samples collected at the Enhanced Tributary Monitoring Network site at Dunnville (site 35).

Figure 16. Water quality sampling events as they relate to river flow at Brantford (site 27) from 2000 to 2004.

Figure 17. Cumulative frequency of water quality samples collected at various stream flows from 2000 to 2004 at Brantford (site 27).

Nutrients, Suspended Sediments and Major Ions

Total Phosphorus

Median phosphorus levels are at or above the provincial water quality objective (PWQO) of 0.030 mg/L throughout the watershed with the exception of Irvine Creek, upper Speed and Eramosa Rivers and Whitemans Creek (Figure 18) (Refer to Figure 6 for site location). Between 2000 and 2004, total phosphorus concentrations ranged from as low as 0.005 mg/L in the Eramosa River to as high as 0.822 mg/L in the Canagagigue Creek watershed. All sampling sites had at least one sample that did not meet the PWQO ranging from 13% in the Eramosa River to 100% at several sites. Generally, some of the highest total phosphorus concentrations are found in the Canagagigue and Nith Creek subwatersheds. Phosphorus levels across the watershed tend to be the highest during the spring.

Generally, phosphorus levels are the lowest in the upper headwater regions of the watershed and progressively increase as the river flows toward the mouth near Dunnville with one exception: phosphorus levels in the Grand River significantly decrease (p=0.0032) between the Shand Dam and West Montrose (Table 7). Phosphorus levels increase significantly between West Montrose and Bridgeport (p= 0.0319) and again between Bridgeport and Blair (p<0.0001). Levels remain similar in the river from Blair through to York where levels increase significantly between York and Dunnville (p<0.0001). A similar pattern is seen in both the Conestogo and Speed Rivers with levels significantly higher at the outlet when compared to upstream sites.

Conversely, phosphorus levels are significantly lower at the mouth of the Nith River when compared to sites in the upper Nith near New Hamburg and Alder Creek (Table 7).

Figure 18. Total phosphorus concentrations between 2000-2004 at 28 long term monitoring sites in the Grand River watershed. Note log scale.

Parameter		Total Ammonium	Chloride	Total Nitrates	Total Phosphorus	Total Suspended Sediment	Sodium	Total Kjeldahl Nitrogen
Grand Rive	Grand River Sites							
39 vs 37	p	<0.0001	0.0283	0.4993	0.1506	0.6668	0.1083	0.0721
37 vs 103	p	<0.0001	<0.0001	<0.0001	0.0032	0.1776	<0.0001	0.0721
103 vs 15	p	0.3320	<0.0001	0.0015	0.0319	0.4154	<0.0001	0.0721
15 vs 12	p	<0.0001	<0.0001	0.0622	<0.0001	0.6412	<0.0001	<0.0001
12 vs 10	p	0.0011	0.1713	0.4916	0.0686	0.8869	0.0887	0.0002
10 vs 27	p	0.0617	0.0320	0.2889	0.1657	0.0015	0.0887	0.0012
27 vs 92	p	0.3966	0.0330	0.6990	0.1079	0.0515	0.0887	0.0088
92 vs 35	p	0.0163	0.0689	0.1049	<0.0001	<0.0001	0.0517	<0.0001
Canagagigu	e Cı	reek Sites						
51 vs 16	p	0.0190	<0.0001	0.5583	0.4029	0.0240	<0.0001	0.0024
Conestogo H	Rive	r Sites	-	_			-	
77 vs 29	р	0.3591	0.0002	0.7907	0.1854	0.4743	<0.0001	0.6947
77 vs 100	p	0.1632	0.5145	0.0024	<0.0001	0.2675	0.5493	0.4685
77 vs 91	p	0.0427	0.0499	0.3211	<0.0001	<0.0001	0.1107	0.0483
Speed / Erai	mos	a Rivers Sites	-	_			-	
36 vs 101	p	0.0285	0.3564	0.5648	0.9634	0.7137	0.4179	0.1080
99 vs 36	p	<0.0001	<0.0001	<0.0001	<0.0001	0.0219	<0.0001	<0.0001
102 vs 36	р	<0.0001	<0.0001	<0.0001	<0.0001	0.0010	<0.0001	<0.0001
102 vs 99	p	0.2450	<0.0001	0.4876	0.0179	0.6598	<0.0001	0.0002
Nith River	Site	s			•			
9 vs 32	p	0.0003	0.7499	0.9063	<0.0001	<0.0001	0.6896	<0.0001
9 vs 38	p	0.3063	<0.0001	0.7161	0.0003	0.2530	<0.0001	0.0043
Fairchild Creek Sites								
44 vs 93	р	0.4685	0.3031	<0.0001	0.2869	0.0018	0.1771	0.6563
Boston vs MacKenzie Creeks Sites								
95 vs 96	p	0.1963	0.0006	0.4913	0.0074	<0.0001	0.0006	0.0053
Eramosa Ri	ver	vs Upper Gran	nd	1		1	1	r
102 vs 39	p	0.0597	<0.0001	0.0025	<0.0001	0.5527	<0.0001	<0.0001

Table 7. Summary of Mann Whitney pairwise comparisons between upstream and downstream sampling sites in the Grand River watershed. Bold indicates significant difference with 95% confidence (p<0.05).

Total and Unionized Ammonia

Generally, the highest average total ammonia levels tend to be in the Grand River at Blair and Glen Morris and the upper Canagagigue Creek watershed (Figure 19). These watersheds also experience the most exceedances of the PWQO (0.0165 mg/L) for unionized ammonia with 47, 14, and 32 percent respectively, of the samples exceeding the objective (Appendix F) (Figure 21). Ammonia levels tend to be highest during the winter months (e.g. February) (Figure 20) in the Grand River at Blair while they are the highest during spring runoff and summer storm events (e.g. March and July) (Figure 21) in the Canagagigue Creek watershed. Concentrations ranged from as low as near the detection limit to 5.560 mg/L at Blair in March 2003.
Total ammonia levels tend to be the highest in the central Grand River region. Similar to phosphorus, total ammonia levels decrease significantly between the Shand Dam and West Montrose (p<0.0001) (Table 7). Conversely, there is a substantial increase in ammonia levels between Bridgeport and Blair (p<0.0001). Levels decrease (p<0.0001) between Blair and Glen Morris and then remain similar among sampling sites between Glen Morris and Dunnville.

Total ammonia levels in the Canagagigue Creek watershed are among the highest in the watershed. Levels are significantly higher at the upper Canagagigue Creek monitoring site when compared to the site near the mouth yet these levels do not exhibit a strong influence on the Grand River as there is no significant difference in total ammonia levels between West Montrose and Bridgeport.

Total ammonia levels on the Speed River at Road 32 below the City of Guelph are the highest in the Speed River basin and are significantly higher when compared to levels in the upper Speed and Eramosa Rivers. Levels decrease in the Speed River between Road 32 and the Preston (p=0.0285). Total ammonia levels in the Speed River in Preston are significantly lower (p = <0.0001) than in the Grand River at Blair.



Figure 19. Range of total ammonia concentrations between 2000-2004 at 28 long term sampling sites in the Grand River watershed. Note log scale.



Figure 20. Monthly concentrations of total ammonia in the Grand River at Blair (site 12).



Figure 21. Monthly concentrations of total ammonia in the upper Canagagigue Creek watershed (site 51).



Figure 22. Range of unionized ammonia concentrations between 2000-2004 at 28 long term sampling sites in the Grand River watershed. Note log scale.

Total Nitrate

Total nitrate levels tend to be high throughout the Grand River watershed with the exception of the headwaters of the Grand and Speed Rivers, lower Fairchild's Creek and Boston and MacKenzie Creeks (Figure 23). In the Grand River watershed, nitrate levels range from below the detection limit (0.001 mg/L) in the Boston/Mackenzie Creek watersheds to 13.6 mg/L in the Canagagigue Creek watershed near the mouth. Generally, total nitrate levels tend to be the highest in the Canagagigue Creek and Conestogo River subbasins.

All but one sampling site (e.g. Grand River below Shand Dam) had samples that did not meet the Canadian environmental quality guideline for nitrate (2.93 mg/L nitratenitrogen) (Appendix F). Whitemans and Alder Creeks had the most samples that did not meet this guideline (86 and 100%, respectively). In general, the highest levels of total nitrate in Whitemans and Alder Creeks are found during December and January when groundwater contributes to the flow in these creeks (Figure 24).

Total nitrate levels tend to progressively increase in the Grand River from the Shand Dam to Bridgeport. A significant increase in total nitrate levels between the Shand Dam and West Montrose (p<0.0001) and again between West Montrose and Bridgeport (p=0.0015)



Figure 23. Box and whisker plots showing the range of total nitrate concentrations between 2000-2004 at 28 long term sampling sites in the Grand River watershed.



Figure 24. Box and whisker plots showing the range of monthly total nitrate concentrations in Whitemans Creek (site 106).

(Table 7) suggests that the high levels in Irvine Creek, Canagagigue Creek and Conestogo River contribute to the high levels found in the Grand River through these reaches. Median total nitrate levels at sampling sites on the Grand River between Bridgeport and Dunnville remain around the federal guideline and are similar among the sampling sites.

Total nitrate levels are higher below the Conestogo Reservoir when compared to the Conestogo River near Drayton although levels in Moorefield Creek are similar to downstream levels. The upper Speed and Eramosa Rivers also have significantly lower total nitrate levels when compared to the Speed River at Road 32 yet there is no difference between median total nitrate levels in the Speed River between Road 32 and King Street in Preston. There is also a significant difference between the monitoring sites on Fairchilds Creek below St. George and near the mouth with higher levels found below St. George (Table 7).

Total Nitrite

Nitrite concentrations in the Grand River watershed range from below the detection limit (0.001 mg/L) to as high as 0.840 mg/L. The highest concentration was found in Moorefield Creek in September 2000. This level is 14 times the PWQO of 0.060 mg/L and is likely toxic to aquatic organism. Median nitrite concentrations tend to be above the federal guideline of 0.06 mg/L in the Grand River at Blair and Glen Morris, Canagagigue Creek watershed, Moorefield Creek and Conestogo River below the dam, lower Speed River and upper Nith River (Figure 25; Appendix F).



Figure 25. Box and whisker plots showing the range of nitrite concentrations between 2000-2004 at 28 long term sampling sites in the Grand River watershed. Note log scale.

Total Kjeldahl Nitrogen

Total kjeldahl nitrogen (TKN), a measure of total organic nitrogen plus total ammonia, is a good measure of organic pollution. TKN levels range from 0.08 mg/L in the Eramosa River to as high as 7.53 mg/L in the Grand River at Blair (Figure 26). Generally, median concentrations are below 1.0 mg/L with the exception of both sites in the Canagagigue Creek, the Grand River at Blair and Dunnville. There are significant increases in TKN levels between Bridgeport and Blair, Brantford and York and York and Dunnville (Table 7). Conversely, there is a significant decrease in TKN levels between Blair and Glen Morris and again between Glen Morris and Brantford.

TKN levels are significantly lower in the lower Canagagigue Creek when compared to the upper Canagagigue Creek. Similarly, levels are lower in the lower Nith River when compared to sites downstream of New Hamburg and in Alder Creek (Table 7). However, levels are higher downstream of the City of Guelph at Road 32 on the Speed River when compared to sites in the upper Speed and Eramosa Rivers. There is no difference in TKN concentrations in the Speed River between Road 32 and King Street in Preston.



Figure 26. Box and whisker plots showing the range of data for total kjeldahl nitrogen between 2000-2004 for the 28 long term monitoring sites it the Grand River watershed.

Total Nitrogen

Total nitrates make up most of the total nitrogen pool found in the Grand River watershed (Figure 27) ranging from just under half of the total nitrogen pool (49%; MacKenzie Creek) to almost 90% of the total nitrogen pool (Whitemans Creek). Organic nitrogen

ranges from 11% (Whitemans Creek) to 51% (MacKenzie Creek) of the total nitrogen pool whereas ammonia ranges from 1% (several streams) to 11% (Grand River at Blair) of the total nitrogen pool.



Figure 27. Composition of average total nitrogen concentrations between 2000-2004 at 28 long term sampling sites in the Grand River watershed.

Total Suspended Solids

Total suspended solids ranged from below 1.0 mg/L in the Irvine River to 370 mg/L in Fairchild Creek between 2000 and 2004. The very high suspended solids concentrations in Fairchild Creek occurred in June 2000 during the initial stages of a significant rainfall event (Figure 28). Exceedances of the benchmark, 25 mg/L, ranges from 0 (Grand River below Shand Dam; Eramosa River) to 81% (Fairchild and MacKenzie Creeks) (Appendix F).

Generally, concentrations of total suspended solids do not significantly differ from sites in the headwater region of the Grand River to Glen Morris; however, levels significantly increase between Glen Morris and downstream of Brantford and again between York and Dunnville (Table 7). Similarly, total suspended solid concentrations significantly increase between the upper Speed and Eramosa Rivers and lower Speed River as well as the upper monitoring site on Fairchild Creek and at the mouth. Levels also significantly differ between Boston and MacKenzie Creeks. Conversely, total suspended solid concentrations significantly decrease between the upper Canagagigue Creek and lower Canagagigue Creek as well as between the upper Nith River and the sampling site near the mouth (Table 7).



Figure 28. Box and whisker plots showing the range of total suspended solids concentrations at 28 long term sampling sites in the Grand River watershed between 2000 and 2004. Note the log scale.

Chloride

Median chloride levels in the Grand River watershed range from 13 mg/L in the upper Grand River to 103 mg/L in the lower Speed River. In general, the levels tend not to exceed a benchmark of 250 mg/L (Environment Canada 2001) with the exception of a few events during high spring flows (Appendix F). Levels reached as high as 326 mg/L in Fairchild Creek during spring runoff in 2004. Chloride levels tend to be the lowest in the Conestogo River basin while they tend to be the highest in the middle and lower Speed River.

Chloride levels progressively increase as the Grand River flows from Grand Valley to Blair with significant increases between all sampling sites. Chloride levels between Blair and Glen Morris are similar while levels decreased slightly between Glen Morris and Brantford. Levels increased significantly again between Brantford and York and decreased slightly between York and Dunnville (Table 7). Significantly increasing chloride levels between upstream sites and downstream sites is also seen in the Canagagigue Creek, Conestogo and Speed River watersheds.



Figure 29. Box and whisker plots showing the range of chloride concentrations at 28 long term monitoring sites in the Grand River watershed between 2000 and 2004.

Sodium

The spatial pattern of sodium concentrations is similar to that of chloride. Median sodium concentrations range from 7.0 mg/L in the upper Grand to 63.0 mg/L in the lower Speed River. The maximum sodium level found between 2000 and 2004 was 191 mg/L in the lower Fairchild Creek watershed during spring runoff in 2004. Sodium levels tend to be high (> 20.0 mg/L, drinking water standard for advising local health unit) in the Grand River starting at Blair through to the mouth; lower Canagagigue Creek, lower Speed River, Upper Nith River and Fairchild Creek. The lowest levels of sodium are found in the headwater regions (e.g. upper Grand, upper Speed River).

Sodium levels significantly increased between each successive sampling site within the Grand River from the Shand Dam to Blair. Continuing downstream from Blair to Dunnville sampling sites had sodium concentrations similar to that of Blair. Sodium concentrations increased significantly at the downstream sampling sites in the Canagagigue and Speed River basins when compared to the upstream sites. Also, levels significantly increased between the sampling site below the Conestogo Reservoir and the mouth (Table 7).



Figure 30. Box and whisker plots showing the range of sodium concentrations at 28 long term monitoring sites in the Grand River watershed between 2000 and 2004.

Total Metals

In general, there were more frequent exceedances of the PWQO's for aluminum, iron, and lead than any other metal (Appendix G). These exceedances usually occurred downstream of urban areas or at the outlet of the Grand to Lake Erie. The Eramosa River experienced the most exceedances of the guideline for zinc $(30\mu g/L)$ with 86 percent of the samples collected exceeding the guideline (Figure 31).

Aluminum concentrations exceeding the PWQO are somewhat misleading due to the fact that the PWQO is based on the aluminum concentration in clay-free samples. Samples collected as part of the PWQMN are not filtered and therefore are not considered clay-free. Elevated levels of aluminum in unfiltered samples are associated with sediment particles composed of naturally occurring aluminosilicate minerals.

Lead concentrations that appear to exceed the PWQO should also be interpreted with caution. Although lead concentrations have been reported as being above the analytical detection limit, the precision of the analytical technique is poor and it is unlikely that lead concentrations actually exceed the PWQO.



Figure 31. Box and whisker plots showing the range of zinc concentrations at 28 long term monitoring sites in the Grand River watershed between 2000 and 2004.

Dissolved Oxygen and Temperature

Dissolved oxygen (DO), temperature, conductivity and pH were measured continuously at seven real-time monitoring stations in the Grand and Speed Rivers in 2004 (Figure 7). In general, weather and precipitation conditions were near average conditions in 2004. Consequently, there were very few exceedances of the dissolved oxygen target at the five monitoring stations (Table 8). However, there was an apparent diurnal fluctuation in the dissolved oxygen concentrations. This fluctuation was more pronounced in some areas (e.g. Rd. 32 on the Speed River) and demonstrates that in some locations organisms could be experiencing a wide range of DO concentrations (Figure 32). Furthermore, the percentage of time between June and September that water temperatures rose above 24°C ranged from one percent in the Speed River at the Hanlon to nine percent in the Grand River at Glen Morris (Table 8). Generally, temperatures tend to be warmer in the Grand River as opposed to the Speed River (Figure 33).

Water Quality Monitoring Station	% of time DO > 4		% of time Temp > 24	
	2003	2004	2003	2004
Grand River at Blair	96%	100%	10%	4%
Grand River at Bridgeport	100%	99%	20%	6%
Grand River at Glen Morris	100%	100%	22%	9%
Speed River at Hanlon	100%	100%	9%	1%
Speed River at Rd 32	100%	100%	9%	3%

Table 8. The percent of time dissolved oxygen fell below 4.0 mg/L and the percent of time stream temperature was above 24°C in 2003 and 2004.



Figure 32. Diurnal variation in dissolved oxygen at an upstream (Hanlon) and downstream (Rd 32) site along the Speed River.



Figure 33. Maximum daily water temperatures at the five continuous water quality stations in the Grand and Speed Rivers in 2004.

Bacteria and Pathogens

Bacteria (e.g. E. coli) are not routinely monitored at any of the long term river monitoring sites in the Grand River watershed. However, some samples are collected in the Grand River at the Elora Gorge Conservation Area through the summer months. E. coli levels are highly variable at this site, ranging from 10 to over 4,000 CFU/100mL (Figure 34). During the 2000-2004 sampling period the guideline for contact recreation (100 CFU/100mL) is frequently not met. There doesn't appear to be a relationship between flow and E. coli concentrations (Kendall tau 0.15; p = 0.0859) in the river at this site.



Figure 34. Escherichia coli concentrations in the Grand River at the Elora Gorge Conservation Area between 2000 and 2004.

Pesticides

No pesticides were detected in the 2003 survey however; four pesticides (3 phenoxy herbicides and 1 triazine herbicides) were detected at three sampling sites in June 2004. 2,4-D and MCPP were detected in Schneider's Creek while dicamba was detected in Canagagigue Creek. Atrazine $(3.6\mu g/L)$ was detected above the Federal Environmental Quality Objective of $1.5\mu g/L$ in Fairchild Creek. Diazinon, an organophosphorus insecticide, was detected once in Laurel Creek in August of 2004.

Total Mass Loads and Export of Total Suspended Sediment and Total Phosphorus

Total Suspended Sediments and Total Phosphorus appear to be the most serious loading issue within the Grand River watershed. Suspended sediment and total phosphorus concentrations tend to be strongly related to stream flow. Therefore, samples must be collected at various flows to adequately characterize the variability of concentrations found in a river. Since sampling has historically focused on lower stream flows (e.g. Figure 4), a preliminary analysis illustrating a relative comparison of the total mass load among the major subbasins can be made. Further monitoring is required to adequately characterize high river flows and thus, get a more accurate account of the total mass load delivered by each major subbasin.

A relative comparison of the major subbasins illustrates that Fairchild Creek contributes the most suspended sediments to the Grand River per square kilometer than any other major tributary in the Grand River watershed (Figure 35). MacKenzie and Boston Creeks and the Nith River also contribute a relatively greater amount per square kilometer of suspended sediment to the Grand River than the other major subbasins in the watershed.



Figure 35. Total suspended sediment export (kg/km²/yr) from the major subbasins in the Grand River watershed.

The export of total phosphorus is highest from Canagagigue and Fairchild's Creeks relative to the other major subbasins in the watershed (Figure 36). High suspended sediment and high total phosphorus export from Fairchild Creek suggest that most of the total phosphorus exported from Fairchild Creek is attached to sediment. Kendall correlations between suspended sediment and total phosphorus in Fairchild's and Canagagigue Creeks (Figure 37) confirms a stronger association between suspended sediment and total phosphorus in Fairchild Creek (tau=0.66; p < 0.0001) than Canagagigue Creek (tau=0.19; p < 0.0001).



Figure 36. Relative total phosphorus export (kg/km²/yr) from the major subbasins in the Grand River watershed.



Figure 37. Kendall Correlation between total suspended sediment and total phosphorus in (A) Fairchild's Creek near the mouth (tau = 0.66; p < 0.0001) and (B) Canagagigue Creek downstream of Elmira (tau=0.19; p < 0.0001). Data from 1981-2001.

Preliminary Trend Analysis

LOWESS smoothing plots were used to visually inspect the datasets to determine whether an obvious trend was present. Figure 38, Figure 39 and Figure 40 illustrate examples of the LOWESS smoothing curves for total phosphorus, total nitrates and chloride, respectively at selected sites.



Figure 38. Total phosphorus concentrations in the Grand River at Glen Morris (site 10). Grey line indicates the LOWESS smoothing curve; red line is the PWQO for Total Phosphorus (0.030 mg/L).



Figure 39. Total nitrate concentration in the Grand River at Cockshutt Bridge (site 27). Grey line indicates the LOWESS smooth of the data illustrating an increasing trend. Red line indicates the Canadian guideline for nitrate (2.93 mg/L) (red line).



Figure 40. Chloride concentrations in the Speed River at Highway 8 in Preston (site 101). Grey line is the LOWESS smooth of the data illustrating an increasing trend. Red line is the 250 mg/L benchmark.

Statistical Trend Analysis

Upon visual inspection of the data a few trends became apparent. Thus, a more rigorous statistical analysis was performed to determine if these trends were in fact occurring. Table 9 summarizes the results of this more rigorous statistical trend analysis using the Seasonal Mann Kendall Trend test for nutrients, suspended sediments and chloride. Exact statistical results can be found in Appendix H.

In general, chloride concentrations are increasing, total phosphorus levels are decreasing and total ammonium levels are not changing over the specified monitoring periods (Appendix H). Total nitrate levels tend to be increasing at many sampling sites, specifically those sites downstream of major urban areas and in intensive agricultural areas (e.g. Whitemans Creek). Total ammonium concentrations have not changed significantly between 1981 and 1995 with the exception of a few sites downstream of major urban areas (e.g. Speed River at Road 32, Highway 8 in Preston and in the Grand River at Blair) where they are increasing. Increasing concentrations of chloride are found throughout the watershed with the exception of more rural locations (e.g. upper Conestogo River). Figure 40 illustrates an increasing chloride trend in the Speed River at Preston. The magnitude of this trend at this site is the greatest in the watershed (1.78 mg/L/yr).

Water Quality Index

Nutrient Water Quality Index

An overall rating of nutrient concentrations in the watershed indicates that the headwaters, in the upper Grand, Speed and Eramosa Rivers have the best water quality for nutrients with levels at or below the water quality benchmark (Figure 41). The monitoring sites throughout the upper middle Grand River, upper Conestogo River and Whitemans Creek scored in the 'Fair' category. In general, these monitoring sites have high levels of either phosphorus or nitrate. The monitoring sites which scored in the 'marginal' category had very high concentrations of phosphorus and nitrate while those sites that scored in the 'poor' category had very high phosphorus, nitrate and ammonia levels. In all, three sites scored in the 'good' category; seven sites scored in the 'poor' category for nutrients. Two sites were newly started in 2004 and therefore didn't have sufficient information to produce a nutrient score. For maps showing the 75th percentile concentrations of individual nutrients and chloride, see Appendix H.

Metal Water quality Index

The overall score for metal concentrations in the Grand River watershed indicate that the level of metal concentrations generally comply with water quality guidelines or objectives. As a result, the overall score for metal concentrations in the watershed are rated as good to excellent. Generally, most (15) of the sites scored in the 'Excellent' category, 11 sites were categorized in the Good category while two sites were in the "Fair" category. Site 35, the Grand River at Dunnville scored in the Fair category due to several samples exceeding guidelines for iron, copper, cadmium and lead while site 95, MacKenzie Creek had several samples exceed the guideline for iron.

Elevated concentrations of zinc, exceeding the PWQO, are commonly observed in the Eramosa River due to naturally high levels of zinc in groundwater. This also results in frequent exceedances of the PWQO in the Speed River downstream of the Eramosa confluence (see Appendix G).

Concentrations of iron exceeding the PWQO occur frequently at many sites throughout the watershed. Iron is extremely prevalent in rock-forming minerals and elevated iron concentrations are typically associated with elevated suspended solids.

As mentioned previously, lead concentrations are often reported to exceed the PWQO but the precision of the analytical method is poor and it is not possible to say with certainty whether the concentration exceeds the PWQO.

Site	Total Phosphorus	Total Ammonium	Total Nitrates	Chloride	Total Suspended Sediment		
Concentrations							
Grand River							
16018403902	\leftrightarrow	\leftrightarrow	\leftrightarrow	↑	Ļ		
16018403702	\leftrightarrow	\leftrightarrow	\leftrightarrow	1	\leftrightarrow		
16018410302	\downarrow	\leftrightarrow	\leftrightarrow	1	\leftrightarrow		
16018401502	\downarrow	\downarrow	\leftrightarrow	\leftrightarrow	\downarrow		
16018401202	\downarrow	↑	\leftrightarrow	↑	\leftrightarrow		
16018401002	\downarrow	\leftrightarrow	\leftrightarrow	1	\downarrow		
16018402702	\downarrow	\leftrightarrow	↑	1	\leftrightarrow		
16018409202	\downarrow	\leftrightarrow	↑	↑	\downarrow		
16018403502	\leftrightarrow	\leftrightarrow	↑	 ↑	\leftrightarrow		
Irvine River			•	•			
16018410402	\downarrow	\leftrightarrow	\leftrightarrow	↑	Ļ		
Canagagigue Cre	ek	•	•				
16018405102	\leftrightarrow	\leftrightarrow	\leftrightarrow	↑	n/a		
16018401602	\downarrow	\leftrightarrow	\leftrightarrow	\leftrightarrow	\leftrightarrow		
Conestogo River							
16018409102	\downarrow	\leftrightarrow	n/a	\leftrightarrow	Ļ		
16018410002	\downarrow	\leftrightarrow	\leftrightarrow	↑	\leftrightarrow		
16018407702	\leftrightarrow	\leftrightarrow	\leftrightarrow	\leftrightarrow	\downarrow		
16018402902	\downarrow	\leftrightarrow	\leftrightarrow	↑	\downarrow		
Speed River							
16018410202	\leftrightarrow	\downarrow	↑	↑	\leftrightarrow		
16018409902	↑	\leftrightarrow	\leftrightarrow	↑	↑		
16018403602	\downarrow	↑	↑	↑	\leftrightarrow		
16018410102	\downarrow	↑	↑	1	\leftrightarrow		
Nith River							
16018403802	n/a	n/a	n/a	n/a	n/a		
16018403202	\downarrow	\leftrightarrow	↑	\leftrightarrow	\downarrow		
16018400902	\downarrow	\leftrightarrow	\leftrightarrow	↑	\leftrightarrow		
Fairchild's Creek							
16018404402	n/a	n/a	n/a	n/a	n/a		
16018409302	\downarrow	\leftrightarrow	↑	↑	\downarrow		
Whitemans Cree	K						
16018410602	\leftrightarrow	\leftrightarrow	↑	↑	\leftrightarrow		
Boston/MacKenz	ie Creek		·	•			
16018409502	\leftrightarrow	\downarrow	\leftrightarrow	↑	\downarrow		
16018409602	\leftrightarrow	\leftrightarrow	\leftrightarrow	↑ 1	\leftrightarrow		

 Table 9.
 Summary of results: Seasonal Mann Kendall trend analysis for nutrients, suspended sediment and chloride. Detailed statistical results in Appendix I.

↑ Concentrations are increasing (deteriorating trend); \downarrow Concentrations are decreasing (improving trend); \leftrightarrow no change



Figure 41. Overall rating of nutrient levels (2000-2004) at the water quality sampling sites in the Grand River watershed.



Figure 42. Water quality index scores for metals (2000-2004) at the water quality sampling sites in the Grand River watershed

Spills

There were a total of 79 spills recorded by the Grand River Conservation Authority staff in 2004. Most of these spills (58%) were related to wastewater collection and treatment, whereby secondary or tertiary treatment processes were bypassed or raw sewage was

released from pumping stations or blocked sewer mains. There were four incidents in which raw unchlorinated sewage was discharged to the river and three incidents when chlorinated raw sewage was discharged into the river. The remainder of the spills consisted of a range of incidents that included drainage from fire fighting events and a tanker truck spills, including a major gasoline spill in July 2004 in which more than 5000L of gasoline was spilt adjacent to the Grand River in Cambridge.

Discussion

Data Limitations

Environmental monitoring is imperative to good environmental decision-making (ECO 1997). However, the interpretation of results from monitoring programs can be strongly influenced by the quality of data gathered. Therefore it is important to be transparent about the limitations of the data used in decision-making. This is not to say that we should hold-off investigating an issue until better data presents itself. In contrast, using the best available data at the time of investigation allows gaps in our existing datasets to be identified and thus better direct future data gathering expeditions.

Two of the most common data limitations found in environmental studies are the quantity (number of samples taken spatially and temporally) and quality (time and location of sampling event) of the data available.

Data Quantity Limitations

The Provincial Water Quality Monitoring Network (PWQMN) is a fundamental monitoring network for Ontario to characterize and track water quality in streams and rivers. Currently, the MOE, in partnership with local Conservation Authorities collect water quality samples at more than 350 stream sites across Ontario (A. Todd, pers communication). The number of sites is down from a high of 730 sampling sites in 1995 and up from 240 sites in 2000 (ECO 2002). The drastic reduction in the number of monitoring sites in the mid 1990's limited the spatial distribution of the data collection across Ontario.

In the Grand River watershed, the number of monitoring sites fell from a high of 43 in 1995 to a low of 27 sites in 2000. Although the Grand River Conservation Authority prioritized the collection of water quality samples at 27 sites through the mid to late 1990's, many Conservation Authorities lost many, if not all of their sites. The current 28 long term monitoring sites characterize water quality in the Grand River watershed fairly well at a large watershed scale; however, some spatial gaps exist and water quality issues that are specific to the major subbasins of the watershed (e.g. Speed River, Nith River etc) are not adequately characterized. Since 2003, the GRCA has added two additional long term sites to fill some of these spatial gaps within the watershed.

The number of annual samples taken per site has also declined over the years from a high of over 20 to an average of eight. Water quality is highly variable and is sensitive to

season, time of day, temperature, flow-stage, spills, soil types, basin topography and many other factors and must be collected over the range of streamflows that are representative of the stream at the sample-collection site (ECO, 2002; Painter *et al* 2000). Consequently, many samples are required to adequately characterize water quality over a range of environmental conditions. Painter *et al* (2000) recommends that at least 10 samples be taken per year to adequately characterize ambient surface water quality in streams while Maybeck *et al* (1996) suggest 12 samples per year for a multipurpose monitoring program, such as the PWQMN. Eight samples per year per site limits the ability to characterize water quality over a full range of environmental conditions. Therefore, any interpretation of the PWQMN data must be in context of the flow and seasonal conditions represented by the data.

Considering this and the limited sampling frequency at each site, water quality for the Grand River watershed is summarized on an aggregation of five years of data. This increases the likelihood of characterizing the full range of flow and climatic conditions. This approach also reduces the strong year-to-year variability from extremes in climate (e.g. wet and dry periods).

Statistical methods for detecting changes in water quality over time have greatly improved throughout the years (Hirsch, R.M et al 1991). Nonparametric statistical methods can accommodate data that are not normally distributed, are robust against outliers, and have missing data (Hrynkiw et al 2003). These characteristics are typical of water quality time series (Trkulja 1997). Although sampling frequency has fluctuated over the years, the long term nature of the PWQMN warrants the evaluation of long term monotonic trends to determine whether conditions are imporving or deteriorating. Furthermore, this is one of the objectives of the network (A. Todd, pers. Communication).

Although preliminary statistical analyses were performed on the PWQMN data for five key water quality variables over a twenty year period (using the LOWESS technique), it is cautioned that the bias in the sampling frequency (eight samples per year) and timing (i.e. samples collected during low to moderate flows) likely influences the power of the statistical test to detect a trend or detects a trend when a trend does not exist (e.g. Type I error). It is also cautioned that finding a statistically significant result does not necessarily imply that one has found an environmentally significant result (Griffith et al 2001; Trkulja 1997). Trkulja (1997) evaluated long term trends of total phosphorus in the Grand River at Dunnville, a site where more frequent samples are typically taken per year, and suggested that trend estimates based on monthly sampling is less reliable than estimates based on daily and weekly sampling schemes. Consequently, the results of the trend analysis presented in this report are considered preliminary and more detailed analyses are required.

Data Quality Limitations

Generally, water quality samples collected at sites in the Grand River watershed are collected during low to moderate flows. This was likely a result of limited manpower and of the logistical challenges of sampling high flow events (e.g. priority is given to flood forecasting during spring runoff; summer rainfall events occurring on weekends etc).

The determination of contaminant loads or 'fluxes' is critical to understand the contribution of nonpoint sources of contaminants to a waterbody since most of these contaminants are mobilized during runoff events. It is not uncommon for 80-90% or more of the annual load to be delivered during 10% of the time with the highest discharges (Richards 2002). As a result, it is important that water quality sampling be targeted to characterize both high and low flows. Painter *et al* (2000) suggests that as few as 30 to as many as 75 or more samples may be used to estimate river loads using various estimator techniques (e.g. statistical or regression approaches etc) however, censored data must be kept to a minimum of 50 percent.

Since only eight samples per year are collected at PWQMN sites, accurate annual loads cannot be made with any certainty. However, a regression or ratio estimator technique, such as in the model 'FLUX' (Walker 1996), which establishes a relationship between flow and concentration to estimate load, can be used to estimate a <u>relative</u> load from each sampling site given the consistency of the sampling bias. However, these methods tend to underestimate the 'true' load (Richards 2002).

To determine where most of the nonpoint source contributions are coming from in the Grand River watershed, an estimate of the <u>relative</u> total suspended solids and total phosphorus loads was calculated for the outlets of the major subbasins (Figure 42) in the Grand River watershed. Although these estimates do not describe the absolute contaminant flux from these subbasins, it provides insight into which subbasin may likely deliver a greater nonpoint nutrient load to the Grand River and where beneficial management practices can be directed to reduce overall nutrient and suspended solid loads. More frequent and targeted sampling of both high and low flows over the long term is required to adequately characterize both ambient water quality and contaminant fluxes from these subbasins.

Water Quality Conditions in the Grand River Watershed

There is great interest among the public, government and other agencies in understanding the water quality conditions of the Grand River and its tributaries. Currently, conditions are described according to chemical and physical characteristics of river water. However, biological indicators such as benthic macroinvertebrates and fish species should also be used in conjunction with chemical and physical characteristics to further describe the overall health of the Grand River. The following sections describe the current chemical and physical conditions in the major subbasins (Figure 42) in the Grand River watershed:

Upper Grand River

Only one current, long term sampling site exists in the upper Grand River watershed above Belwood Lake. Water quality at this site tends to be good. Nutrient levels are at or slightly above provincial guidelines; suspended solids and chloride levels tend to be



Figure 43. The six major sub-basins and the location of the 28 PWQMN monitoring sites within the Grand River watershed.

low. The low-intensive agriculture, high proportion of wetlands and forested lands and minor urban impacts likely contributes to the overall good water quality in the Upper Grand.

Belwood Lake tends to have high phosphorus levels (> 0.030 mg/L) in the euphotic zone (MOE 1996; MOE unpublished data). The high phosphorus levels suggest that the lake is eutrophic and can experience regular algal blooms. Of particular concern are blooms of potentially toxic blue-green algae (i.e. cyanobacteria) similar to the bloom that occurred in the fall of 2004. Belwood Lake is the source water for the middle Grand River region, supplying water for drinking water supplies, a successful brown trout fishery and assists with assimilating wastewater from nine municipal sewage treatment plants.

Middle Grand River

The middle Grand River basin extends from the tailwater of the Shand Dam to the Newport Bridge below Brantford. The land use in this area is characterized by some of the most intensive agricultural production and urban development in the watershed.

Generally, water quality tends to progressively deteriorate as the Grand River flows from the Shand Dam to Brantford. Three major tributaries drain into the upper middle Grand River including Irvine Creek, Canagagigue Creek and Conestogo River.

Twenty four degrees generally defines the water temperature threshold that can sustain cool and warm water fish species (Stoneman and Jones 1996). Cold water being discharged from the Shand Dam has facilitated the introduction of a successful brown trout fishery in the Grand River (OMNR 2004). Average maximum daily water temperatures between the Shand Dam and West Montrose are below 24°C (GRCA, unpublished data). Cool water temperatures, combined with relatively good water quality help to sustain this fishery. Temperatures rise above 25°C in the Grand River as the river flows from West Montrose toward Brantford, which supports a warm water fishery.

Irvine Creek empties into the Grand River near Salem and drains mostly non-intensive agricultural land. Although high nitrate levels in Irvine Creek tend to have a negative impact on the Grand River, low phosphorus and total ammonium levels tend to improve water quality in the Grand River. Consequently, efforts should be directed toward protecting the Irvine Creek watershed so that this creek can continue to improve water quality in the upper middle Grand River. Also, beneficial management practices that reduce nitrate movement off the land should be promoted in this watershed.

In contrast, high levels of total phosphorus, chloride and nitrates in the Canagagigue Creek and Conestogo River, tend to negatively impact the Grand River as these levels significantly increase between West Montrose and Bridgeport.

As in the 1970's, the Canagagigue Creek continues to have some of the highest levels of phosphorus and nitrogen in the watershed. Second only to Fairchild's Creek,

Canagagigue Creek delivers a significant amount of total phosphorus per square kilometer to the Grand River. However, the low suspended solids loads from this creek suggest that most of the total phosphorus in the creek is in the dissolved form. A high proportion of dissolved phosphorus relative to the total phosphorus pool suggests that much of the phosphorus originates from agricultural (livestock) sources (Cooke and Prepas 1998).

Most of the nitrate in the Grand River originates in the upper middle region of the watershed, likely from high concentrations (on average, above 3.5 mg/L) found in Irvine Creek, Canagagigue Creek and Conestogo Rivers. Nitrate levels in tile drainage tend to be very high (Flemming et al 1998). Since the Canagagigue and Conestogo watersheds tend to have a high density of tile drainage (Statistics Canada 2001), the high nitrates found in these rivers could be from extensive tile drainage in these watersheds.

The impact of the urban development on the Grand River is obvious. Although phosphorus, total ammonium and chloride levels in the Grand River at Bridgeport tend to be already elevated, there is a significant increase in these concentrations as the river flows through the Region of Waterloo from Bridgeport to Blair. The Grand River receives the effluent from the two municipal sewage treatment plants (Waterloo and Kitchener) and numerous small urban tributaries. As a result, average phosphorus levels in the river double, total ammonium levels increase by 13-fold and chloride levels at Blair are 2.6 times higher than at Bridgeport. Also, most of the pesticides detected in a high-level survey of the watershed were in creeks draining urban development and most of these pesticides were herbicides (e.g. 2,4-D, MCPP). This finding is different from the 1986-87 Ministry of Environment study that identified Lindane (BHC-gamma), an organochlorine insecticide and fumigant, as the most prevalent pesticide detected in the Grand River (MOE 1990).

Similarly, sodium levels in the Grand River increase dramatically between Bridgeport (15 mg/L) and Blair (45 mg/L). Median sodium levels in the Grand River remain above 40 mg/L through to Dunnville. Sodium levels in the river are generally not a concern to aquatic organisms yet can be a concern if the surface water is used for a drinking water supply. The levels in the Grand River are well below the aesthetic guideline of 200 mg/L. However, since the sodium levels are above 20 mg/L, the City of Brantford notifies the Brant County Medical Officer so that this information is passed onto medical practitioners and concerned residents (City of Brantford 2005).

The significant diurnal fluctuations of dissolved oxygen in the Grand River at Blair are indicative of the high primary productivity (e.g. abundant aquatic macrophyte and algae growth) seen in this reach of the river. It is likely due to substantial nutrient loading to this reach, especially during the summer months when growing conditions are optimal. Low dissolved oxygen levels have historically been seen in the Grand River at Blair with luxuriant growth of filamentous green algae where the physical characteristics of the river are suitable for algal growth (Sandilands 1971; OTB 1971). However, currently dissolved oxygen levels only fall below 4.0 mg/L periodically, where as in the 1970's levels were routinely below 1.0 mg/L (OTB 1971) and were below 4.0 mg/L as frequent

as 25% of the time (GRBWMS 1979). The improvement is likely attributable to phosphorus removal in 1974 at all of the watershed's wastewater treatment plants (Hore and Ostry 1978).

The Speed River flows into the Grand River below Blair in Cambridge. Historically this contrasts the quality of the river in the 1970s when the lower Speed River was in such poor shape that the Grand River was adversely affected for at least fifteen miles downstream (Sandilands 1971). Although the Speed River has high levels of phosphorus, nitrates and total ammonium, it doesn't appear to negatively impact the Grand River given that there is no difference between phosphorus and total nitrate levels between Blair and Glen Morris. Furthermore, levels of total ammonium and total kjeldahl nitrogen decrease between Blair and Glen Morris. Additional monitoring downstream of the Speed/Grand confluence is needed however, to confirm this since Glen Morris is a substantial distance downstream of Blair.

Total ammonium is an energy-efficient source of nitrogen for plants and is assimilated by plants more readily than nitrate (Wetzel 1983). The lower total ammonium and total kjeldahl nitrogen levels at Glen Morris suggest that this reach is highly productive as plants and algae are actively using up these nitrogen sources. Semi-quantitative aquatic plant surveys confirm the highly productive nature of this reach (GRCA unpublished data).

In general, suspended solids appear to be low throughout the upper and middle Grand River reaches when compared to the lower Grand River. The significant increase in suspended solids concentrations is seen between Glen Morris and Newport Bridge below Brantford is likely due to the southern clay plain within which the river begins to flow. Furthermore, the median concentration of suspended solids in the Nith River is higher than in the Grand River at Glen Morris. Another potential source of TSS to the Grand River is the Nith, given its higher concentrations than the Grand River at Glen Morris and its identification as the second highest TSS load when compared to all other major tributaries. However, due to the sampling bias toward low to moderate flows (as discussed earlier), more targeted sampling of higher flows is required to confirm or dispute this finding.

The Nith River and Whitemans Creek flow into the Grand River between Glen Morris and Brantford. These rivers do not appear to negatively impact the phosphorus, total ammonium or chloride levels in the Grand River. Although median nitrate levels in the Nith River and Whitemans Creek tend to be higher than the Grand River, there isn't a significant increase in nitrate levels in the Grand River between Glen Morris and Brantford.

Although there is a lack of long-term monitoring for bacteria and pathogens in the Grand River watershed, researchers have intensively studied bacteria and pathogen levels more recently. Dorner (2004) has recently completed an exhaustive study characterizing waterborne pathogens in the central Grand River region. This study characterized the levels of *Escherichia coli*, fecal coliforms, *Campylobacter* spp., *Cryptosporidium* spp.

and *Giardia* spp. Even though laboratory methodologies and sampling protocols for accurately quantifying pathogen levels are fraught with inherent error, this study provides invaluable information on the current levels of pathogens in the watershed.

Bacteria and pathogens in natural waters tend to be highly variable. Lakes, rivers and creeks surveyed within the United States and Canada had occurrences of *Cryptosporidium* spp. 5 - 87 % of the time (Mador et al 1987; Chauret et al 1995) while *Giardia* spp. was found to occurr 10 to 75% of the time (Hibler 1988; Chauret et al 1995). Throughout the Grand River watershed bacteria and pathogen levels are highly variable however, relatively higher levels were found in the Canagagigue and Laurel Creeks. Dorner (2004) found that, in general, concentrations of E. coli increased with stream flow and were correlated with turbidity whereas no clear relationship was evident between pathogens, stream flow and turbidity. Furthermore, Dorner (2004) illustrated that E. coli levels tend to decrease in a downstream direction at a watershed scale.

Lower Grand River

Water quality in the lower Grand River reflects the cumulative impact of the upstream watershed and the underlying geology. Suspended solids and phosphorus levels in the Grand River at Dunnville are among the highest in the watershed. Total phosphorus levels are about 4 times the PWQO while median suspended solids concentrations approach 50 mg/L (twice the benchmark). Consequently, the Grand River is a significant impact on the eastern basin of Lake Erie (MOE, 2002)

A distinct change in water quality is evident below Brantford as significantly higher levels of suspended solids are found in the river at the Newport Bridge. As the river flows into the southern clay plain, it picks up colloidal clay particles that virtually always remain in suspension (GRBWMS 1979) giving it a highly turbid, chocolate brown colour. Suspended solids and phosphorus increase again in the river at Dunnville likely due to the significant contributions from Fairchild's and MacKenzie Creeks and river impoundments which makes the river almost lake-like. The slower moving water between Brantford and Dunnville also suggest that sediment is being deposited and resuspended during high flows (Hore and Ostry 1978) which can yield maximum suspended solid concentrations of over 340 mg/L during high flow events.

Fairchild's Creek is the largest source of total suspended solids and total phosphorus per square kilometre, relative to the other major tributary to the Grand River. Consequently, beneficial management practices that reduce erosion should initially be targeted to Fairchild's Creek.

Conestogo River

Phosphorus and nitrate levels throughout the Conestogo River tend to be high with concentrations above provincial and federal guidelines. Nutrient concentrations tend to be lower above the reservoir than downstream of the reservoir where they negatively impact the Grand River. Although the lower Conestogo River basin drains intensive

agricultural production, phosphorus and nitrate levels appear to be heavily influenced by the reservoir as there are no significant differences in median concentrations of phosphorus and nitrogen between the monitoring site directly below the reservoir and the site at the mouth, near St. Jacobs. Therefore, improving water quality in the reservoir will likely improve water quality in the lower Conestogo River.

Conestogo Lake is eutrophic. Phosphorus levels in the euphotic zone are above the PWQO and results in regular algal blooms. For example, a substantial bloom of *Aphanizomenon* (potentially toxic cyanobacteria species) occurred in the fall of 2004. Anoxic conditions frequently exist in the hypolimnion following stratification (MOE, unpublished data 1996). Consequently, phosphorus-rich waters are likely discharged from the dam into the lower Conestogo River.

Speed River

Phosphorus and nitrogen levels in the Eramosa and upper Speed Rivers are among the lowest in the Grand River watershed. Phosphorus levels increase three fold between monitoring sites on the upper Speed and Eramosa Rivers and the monitoring site downstream of the City of Guelph.

Urban development, including the wastewater treatment plant, has a significant negative impact on the lower Speed River. With the exception of total ammonium, water quality in the lower Speed River did not recover between Road 32 and Preston as phosphorus, nitrate and chloride levels remained high. Similar to the significant decrease in total ammonium between Blair and Glen Morris in the Grand River, the decrease in total ammonium levels between Road 32 and Preston along the Speed River is likely due to the high productivity in this reach. Abundant macrophyte and attached algae (e.g. *Cladophera*) growth is evident in this reach of the Speed and contributes to dramatic diurnal fluctuations in dissolved oxygen. Although dissolved oxygen in the lower Speed River would be depleted at night up to 60% of the time during the 1970's (Sandilands 1971; GRBWMS 1979), now dissolved oxygen only occasionally (< 5% of the time) falls below the 4.0 mg/L guideline. The improvement in river water quality is attributed to the implementation of the Guelph reservoir (circa 1978) to help augment river flows during the summer months to assimilate wastewater as well as substantial investment in advanced wastewater treatment by the City of Guelph over the past 10-15 years.

Chloride levels in the lower Speed River are among the highest in the entire Grand River watershed. Sources include road deicing and likely water softener discharges in the municipal wastewater effluent.

Similar to Conestogo Lake, Guelph Lake is eutrophic with high levels of phosphorus in the euphotic zone (MOE, unpublished data, 1996). The long term monitoring site downstream of Guelph Lake was discontinued in 1996. Consequently, it is not possible to determine whether the reservoir impacts the Speed River.

Nith River

The Nith River is the largest, unregulated tributary in the Grand River watershed. Unlike the Grand River where there is a progressive deterioration in water quality as the river flows from the headwaters to the mouth, water quality in the Nith River is generally better at the mouth in Paris than in the upper watershed. Upstream urban impacts (e.g. New Hamburg) and geology likely contribute to this phenomenon. The upper Nith River drains a silty till plain whereas the lower Nith River traverses through the Paris-Galt moraine. The discharge of shallow groundwater into the Nith River in this region likely facilitates the improvement in water quality in the Nith River at the mouth in Paris. However, within a watershed context the Nith River is a tributary that delivers the second largest annual mass load of suspended solids and the third largest amount of total phosphorus to the Grand River. Targeted sampling of higher flows will help to characterize the variability in water quality in the Nith River at the mouth.

Alder Creek, a tributary of the Nith River, drains a portion of the waterloo moraine. Historically, this creek was tremendously overloaded by an industrial plant (Sandilands 1971) however; this industry was decommissioned in the late 1980's. Total phosphorus and nitrates continue to remain high in Alder Creek. High nitrate levels in the creek are likely due to high nitrate levels in the local groundwater that discharges to this creek ROW 2005).

Trends in Water Quality

To determine whether water quality conditions are improving or deteriorating proves to be particularly difficult as there are confounding variables that must be considered before statistically analyzing the data (Helsel and Hirsch 2002). For example, water quality time series data tend to be non-normally distributed, have large variability, are influenced by season, and have covariate effects (e.g. flow) (Trkulja 1997). Water quality data collected for the Provincial Water Quality Monitoring program routinely are affected by these confounding variables. The current trend analysis addressed some of these confounding variables (e.g. flow, seasonality) however, the bias in the sampling strategy towards base flows in the late 1990's likely influences whether a trend truly exists. Despite the sampling bias, the period of record selected for trend analysis (1981-2001) is of sufficient length to evaluate net or global monotonic trends over time however, it is cautioned that a more detailed analysis is required in the future following a change in the sampling regime which will encompass higher flows.

Although drastic decreases in total phosphorus were seen in the 1970's due to the removal of phosphates in detergent and improvements in wastewater treatment; total phosphorus concentrations have only slightly decreased (e.g. 0.001-0.003 mg/L/yr) over the study period (1981-2001) at some sites. Whether this statistically significant decrease is of environmental importance is in question as most of the sites in the Grand River have phosphorus levels well above the PWQO. At the current rate of decrease, it might take decades to see any environmental improvements in the Grand River using current phosphorus reduction strategies. Current urban development and agricultural

intensification pressures in the watershed will likely negate any small improvements in total phosphorus concentrations that are currently seen in the watershed.

Similarly, some statistically significant decreasing concentrations of suspended sediment were also detected over the study period. However it is not known whether this is as a result of the sampling bias toward low flows which does not adequately describe the true variability of suspended solids.

On the other hand, increasing concentrations of nitrate and chloride are obvious throughout the watershed. Simple LOWESS graphs illustrate this increasing trend. To mitigate these increasing trends, reduction strategies must be implemented now to curb the rise of these concentrations into the future. The Region of Waterloo is well underway with road salt management, chloride reduction strategies and nitrate source inventories (ROW 2001; ROW 2005).

Spills

Reported discharges into the river include accidental spills and wastewater treatment bypasses. Spills and wastewater treatment bypasses continue to be a threat to the water quality in the river. The impact of these releases can be devastating to downstream aquatic communities, and in some cases the effects may persist in stream sediments for years. Although most spills are small in the Grand River watershed, there is the risk that a large spill may occur which may threaten the ecological integrity of the river system.

Wastewater treatment bypasses constitute the largest number of reported spills in the watershed. Most of these bypasses are tertiary, meaning that advanced treatment (e.g. advanced nitrogen and phosphorus removal) is bypassed. These bypasses represent less of a threat to downstream users than do bypasses diverting raw sewage. Nonetheless, with improved wastewater treatment and improved capacity at all of the watershed's 26 wastewater treatment plants, this risk can be reduced.

Spills continue to be a significant risk to the three drinking water treatment plants that take water from the Grand River for drinking water supplies. Better information is required on river travel times to provide better early warning and better response to spills in general.

Summary and Conclusions

The Provincial Water Quality Monitoring Network is an important long term monitoring network for Ontario. However, financial cutbacks by the province over the last decade along with limited capacity at Conservation Authorities compromize the utility of the data. For example, estimating mass loads, completing thorough trend analysis and characterizing the full range of variability in chemical and physical water quality of streams and rivers in Ontario is significantly limited by the number of samples taken each year and the timing at which samples are taken. Nonetheless, the data provide for a preliminary assessment of the conditions and trends that may be occurring in stream water quality.

Generally, nutrient concentrations in the Grand River tends to be high likely as a result of the underlying geology, intensive agricultural production and growing urban development in the watershed. Conversely, metal concentrations generally comply with guidelines. Recent pesticide surveys suggest that the occasional insecticide or herbicide is detected in creeks draining mostly urban areas but atrazine was detected in an agricultural catchment. Pesticide detections are usually below guidelines. More thorough pesticide surveys are required to track pesticides in the watershed however, the cost for analyzing for pesticides in environmental samples is prohibitive.

Bacteria and pathogens in the Grand River tend to be highly variable likely as a result of the diverse landuse within the watershed. Dorner (2004) identified both agricultural and urban watersheds as areas that have a high occurrence of pathogens.

The middle reach of the Grand River, including the major tributaries draining into this reach such as the Canagagigue Creek, Conestogo River and lower Speed River tends to be the area in the watershed where water quality is most impaired. Land use including intensive agricultural production, urban development and wastewater treatment plant effluents in this area likely contribute to the degradation in water quality. On the other hand, the nutrient enrichment and high suspended solid concentrations found within the lower reaches of the Grand River are mainly influenced by the cumulative impact from the upstream watershed and underlying geology.

Spills and wastewater treatment plant bypassess are a significant threat to downstream water users in the Grand River watershed. They represent an acute and immediate impairment to water quality that can compromise drinking water treatment. Therefore, it is imperative to have an effective spills response protocol and accurate river information for timely response.

The Grand River and its tributaries have improved greatly since the 1970's when the Canagagigue Creek was extremely polluted by toxic industrial wastes and organic matter and the Speed River showed gross organic contamination below Guelph and Hespler (OTB 1971). Although statistically significant, improving water quality trends since the 1980's may not be as environmentally significant as the drastic improvements since the 1970's. For example, phosphate removal was mandated at all wastewater treatment plants in the watershed in 1974. As a result, phosphorus levels in the river drastically decreased. Alternatively, some variables (e.g. chloride and nitrate) are showing steady increasing trends (i.e. deterioration). Measures such as improved wastewater treatment, road salt management strategies and targetted implementation of agricultural beneficial management practices are needed to curb these increasing trends.

Recommendations

To improve our understanding of the water quality conditions of the Grand River and its tributaries, the following recommendations are made:

Sampling Regime

- 1. At a minimum, 12 samples per year should be taken at each long term monitoring site to characterize ambient water quality conditions. This will require additional financial resources from the province to complete the laboratory analysis as well as manpower resources from the Conservation Authority.
- 2. The sampling regime should be designed so that the range of flow conditions are sampled. For example, additional high flow samples should be targeted during spring runoff and summer rainfall events. This will characterize the range of environmental conditions that exist in the watershed.

Monitoring

- 3. Integrate chemical, physical and biological (e.g. benthic macroinvertebrate, fish community) monitoring.
- 4. Tiered monitoring is required to identify and track watershed-wide scale and local scale water quality issues. Additional long term ambient monitoring sites are required in addition to more intensive monitoring surveys (e.g. Rotation Basin surveys) to identify local, subbasin-specific water quality issues.
 - a. Additional long term monitoring sites are needed to gain better spatial coverage, at the watershed scale, so that upstream/downstream and pre/post implementation comparisons can be made. Additional recommended sites include:
 - i. Upper Grand River headwater region;
 - ii. Upper Grand River immediately above reservoir;
 - iii. Upper Nith River above New Hamburg;
 - iv. Speed River below Guelph Lake
 - v. Schneider's Creek urban
 - vi. Laurel Creek urban
 - vii. Boomer Creek agricultural creek to evaluate the long term implementation of Beneficial Management Practices
 - b. Intensive monitoring is required at the subbasin scale to identify local water quality issues. A "rotation-basin" approach in which intensive monitoring of chemical, physical and biological attributes would be collected in the following basins in a rotating basis (e.g. one year monitoring would focus on the Speed River basin; the next year monitoring would focus on the Upper Grand River basin etc):
 - i. Speed River basin including Guelph Lake
 - ii. Upper Grand River basin including Belwood Lake
 - iii. Conestogo River basin including Conestogo Lake
 - iv. Middle Grand River basin
 - v. Lower Grand River basin

- c. Site specific investigations including:
 - i. Additional monitoring downstream of the Speed/Grand confluence to determine the impact the Speed River has on the Grand River.
 - ii. Continuous monitoring for dissolved oxygen in selected river reaches.
- 5. Continue annual pesticides surveys and target high flow events, pre and post application. Target smaller agricultural and urban tributaries.
- 6. Further data analysis is required
 - a. evaluate relationships between land use and water quality to understand the mechanisms contributing to improvements or degradation in water quality;
 - b. mass load analysis to estimate mass loads from both point and nonpoint sources
- 7. Although bacteria and pathogen monitoring is fraught with difficulties and should remain in the research forum, a preliminary investigation into the variability of Escherichia coli in the Grand River would assist with understanding the range of concentrations seen in the watershed.

Reporting

- 1. Identify specific long term indicators that can be used for progress measurement. Target monitoring activities so that these indicators will be collected annually. Incorporate these indicators into the monitoring design.
- 2. Annual high-level reporting of current conditions to report on progress
- 3. Every five years, prepare an in-depth technical report.
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Appendices

Appendix A. List of active and inactive PWQMN monitoring sites and the year in which sampling commenced.

	Station ID	Station Description	Tributary	Start	End	Total
	Station ID	Sution Description	IIIbutui y	Year	Year	year
1	16018409502	2 First Conc. East of Hwy 6	Boston Creek	1978	2004	26
2	16018401602	2 First Bridge d/s of Elmira STP	Canagagigue Creek	1966	2004	38
3	16018405102	2 First Conc. North of Elmira	Canagagigue Creek	1973	2004	31
4	16018402902	2 Waterloo County Rd. 22	Conestogo River	1970	2004	34
5	16018407702	2 Steel Bridge, Glen Allan	Conestogo River	1975	2004	29
6	16018409102	2 County Rd 10, Village of Moorefield	Conestogo River	1977	2004	27
7	16018410002	2 Wellington County Rd. 7	Conestogo River	1978	2004	26
8	16018404402	2 First Conc. d/s St. George	Fairchild Creek	1972	2004	32
9	16018409302	2 Lot G, South of Hamilton Rd.	Fairchild Creek	1977	2004	27
10	16018401002	2 Glen Morris Bridge	Grand River	1965	2004	39
11	16018401202	2 Blair Bridge	Grand River	1965	2004	39
12	16018401502	2 Bridgeport Bridge	Grand River	1965	2004	39
13	16018402702	2 Cocksutts Bridge, Brantford	Grand River	1970	2004	34
14	16018403702	2 First Conc. d/s of Belwood Lake	Grand River	1972	2004	32
15	16018403902	2 East Luther-Amaranth Twp Line	Grand River	1972	2004	32
16	16018409202	2 Bridge, York	Grand River	1977	2004	27
17	16018403502	2 at Bridge in Dunville	Grand River	1980	2004	24
18	16018410302	2 Highway 86	Grand River	1980	2004	24
19	16018410402	2 William St Salem	Grand River	1980	2004	24
20	16018409602	P First Conc. East of Hwy 6	MacKenzie Creek	1978	2004	26
21	16018400902	2 Highway 24A Paris	Nith River	1965	2004	39
22	16018403202	P First Bridge d/s from New Hamburg	Nith River	1970	2004	34
	10010103202		Alder Creek/ Nith	1770	2001	51
23	16018403802	2 First Conc. South of New Dundee	River	1972	2004	32
24	16018403602	2 Wellington Rd. #32	Speed River	1972	2004	32
25	16018409902	Armstrong Mills, above Guelph Lake	Speed River	1978	2004	26
26	16018410102	2 Highway #8. Cambridge	Speed River	1979	2004	25
27	16018410202	2 Wellington Country Rd. 41. Arkell	Speed River	1979	2004	25
28	16018410602	2 First Conc. West of Hwy 24A	Whiteman Creek	1980	2004	24
			Alder Creek/Nith			
29	16018402602	2 Bleams Rd, Reg Rd 4, Mannheim	River	1970	1996	27
20	1 (010 40000		Baden Creek/ Nith	1070	1007	10
30	16018409802	Bleams Rd, dwnstrm Baden STP	River	1978	1996	19
21	1 (0 1 0 4 0 0 7 0 7	Weter Wenter Deale Contheside	Brantford Water	1070	1007	10
31	16018409702	water works Park footbridge	Works Canal	19/8	1996	19
32	16018405202	Reg Rd 19, Floradale	Canagagigue Creek	1973	1996	24
33	16018410502	2 Waterloo Reg Rd 86, E of West Montrose	Cox Creek	1980	1998	18
34	16018402402	2 Blossom Ave, Newport	Grand River	1969	1996*	30
35	16018402802	2 Hwy 7, Breslau	Grand River	1970	1998	28
36	16018404102	2 King St E, Kitchener	Grand River	1972	1998	26
37	16018406702	2 13th Ln, NW of Marsville	Grand River	1975	1996	21
38	16018409002	2 Sideroad 27-28, Leggatt	Grand River	1977	1996	20
39	16018403302	Brant-Oxford Twnln, dwnstrm Avr	Nith River	1970	1997	28
10	1 (010 10 10 100	Township Rd 2, E of Reg Rd 5, SE of		1072	1007	
40	16018404502	Wellesley	Nith River	1972	1996	25

Station ID Station Description	Tributary	Start Year	End Year	Total year
41 16018403402 Edinburgh Rd, Guelph	Speed River	1970	1996	27
42 16018404302 Woodlawn Rd, Guelph	Speed River	1972	1996	25

* resumed sampling in 2004

Variable	Detection Limit	Units
Alkalinity - TFE	0.2	mg/L as CaCO3
Ammonia nitrogen	0.002	mg/L as N
Calcium	0.05	mg/L
Conductivity, 25C	1	mS/cm
Copper	0.0002	mg/L
Dissolved Solids	2	mg/L
Hardness	0.2	mg/L
Lead	0.0005	mg/L
Magnesium	0.02	mg/L
Nickel	0.0005	mg/L
Nitrate + Nitrite Nitrogen	0.005	mg/L as N
Nitrite nitrogen	0.001	mg/L as N
Potassium	0.01	mg/L
Reactive Phosphorus	0.0005	mg/L as P
Sodium	0.02	mg/L
Suspended Solids	1	mg/L
Total Kjeldahl Nitrogen	0.02	mg/L as N
Total Phosphorus	0.002	mg/L as P
Total Solids	2	mg/L
Zinc	0.0005	mg/L

Appendix B. Current method detection limit at MOE laboratory for various water quality variables.

Site Name	Easting	Northing	Site ID Number
Schneiders Creek	547309	4804814	16018411702
Laurel Creek	541809	4814525	16018403002
Canagagiue Creek First Bridge	535495	4829347	16018401602
Canagagiue Creek Floradale	533870	4831371	16018405202
Fairchild Creek	561515	4786728	16018404402
McKenzie Creek	585539	4765156	16018409602
Boston Creek	585623	4763797	16018409502
Whitemans Creek	550136	4774999	16018410602
Speed River	558867	4832131	16018409902
Eramosa River	566054	4821993	16018410202
Grand River East Luther-Amaranth Townline	556227	4860333	16018403902
Conestogo River	529200	4847855	16018410002
Moorefield Creek	520234	4844982	16018409102
Nith River	513300	4814596	16018411902
Alder Creek	536510	4805068	16018402602
Horner Creek	537326	4778920	16018412002
Cox Creek	544705	4825872	16018410502
Swan Creek	545151	4832082	16018412102

Appendix C. Site locations, GPS coordinate and site ID numbers for the pesticide sampling.

			Phosphorus				Total A	mmonia	
			(m	ig/L)			(m	ig/L)	_
Site	n	Min	Mean	Median	Max	Min	Mean	Median	Max
Grand River									
16018403902	35	0.014	0.034	0.032	0.113	0.002	0.032	0.024	0.140
16018403702	38	0.012	0.039	0.032	0.164	0.002	0.092	0.078	0.394
16018410302	37	0.014	0.035	0.023	0.162	0.002	0.042	0.014	0.564
16018401502	38	0.016	0.055	0.032	0.253	0.002	0.046	0.019	0.289
16018401202	36	0.036	0.107	0.077	0.714	0.009	0.630	0.316	5.560
16018401002	37	0.040	0.090	0.057	0.625	0.002	0.312	0.078	4.160
16018402702	28	0.024	0.095	0.051	0.538	0.002	0.098	0.034	0.832
16018409202	39	0.020	0.106	0.065	0.662	0.002	0.166	0.046	2.110
16018403502	83	0.038	0.119	0.118	0.282	0.002	0.142	0.098	0.932
Irvine River									
16018410402	36	0.008	0.035	0.018	0.161	0.002	0.036	0.016	0.285
Canagagigue Creek									
16018405102	34	0.016	0.139	0.134	0.424	0.002	0.316	0.220	0.982
16018401602	36	0.028	0.159	0.113	0.822	0.002	0.199	0.076	0.917
Conestogo River									
16018409102	35	0.012	0.047	0.032	0.216	0.002	0.043	0.032	0.282
16018410002	37	0.016	0.051	0.032	0.278	0.002	0.046	0.036	0.182
16018407702	36	0.020	0.071	0.056	0.300	0.000	0.071	0.036	0.339
16018402902	36	0.022	0.086	0.052	0.367	0.002	0.067	0.024	0.353
Speed River									
16018410202	38	0.005	0.020	0.016	0.084	0.002	0.026	0.016	0.160
16018409902	35	0.009	0.046	0.020	0.485	0.002	0.029	0.014	0.404
16018403602	36	0.014	0.062	0.060	0.108	0.006	0.201	0.096	1.640
16018410102	35	0.037	0.077	0.058	0.290	0.004	0.118	0.044	0.864
Nith River									
16018403802	37	0.024	0.092	0.068	0.492	0.002	0.096	0.036	0.857
16018403202	37	0.056	0.168	0.100	0.810	0.002	0.102	0.056	0.879
16018400902	37	0.012	0.098	0.032	0.599	0.002	0.059	0.019	0.958
Fairchild's Creek									
16018404402	35	0.022	0.119	0.096	0.500	0.002	0.069	0.036	0.516
16018409302	37	0.040	0.140	0.116	0.598	0.002	0.081	0.047	0.703
Whitemans Creek									
16018410602	42	0.005	0.049	0.022	0.295	0.002	0.050	0.016	0.632
Boston/MacKenzie Creek									
16018409502	36	0.010	0.117	0.082	0.756	0.002	0.034	0.016	0.323
16018409602	37	0.050	0.138	0.132	0.368	0.002	0.042	0.027	0.344

Appendix D. Summary statistics for the 2000-2004 dataset for all the water quality parameters at the 28 long term PWQMN monitoring sites in the Grand River watershed.

		Total	Nitrates		Nitrite			
		(m	ng/L)			(m	ng/L)	
Site	Min	Mean	Median	Max	Min	Mean	Median	Max
Grand River								
16018403902	0.113	1.041	0.77	3.50	0.004	0.013	0.012	0.029
16018403702	0.073	1.173	1.37	2.32	0.007	0.034	0.024	0.157
16018410302	0.480	2.272	2.28	4.62	0.005	0.029	0.017	0.392
16018401502	0.926	3.466	3.40	6.38	0.005	0.027	0.026	0.071
16018401202	2.250	4.047	3.85	7.02	0.002	0.293	0.220	0.831
16018401002	2.310	3.836	3.66	6.45	0.018	0.137	0.096	0.628
16018402702	0.029	3.579	3.48	6.77	0.001	0.062	0.042	0.360
16018409202	1.880	3.506	3.49	6.26	0.009	0.046	0.033	0.189
16018403502	0.336	3.155	3.01	6.49	0.001	0.054	0.045	0.189
Irvine River								
16018410402	0.835	3.728	3.55	8.46	0.004	0.024	0.021	0.085
Canagagigue Creek								
16018405102	0.634	5.495	5.43	10.20	0.003	0.141	0.111	0.579
16018401602	1.400	6.351	6.07	13.60	0.045	0.129	0.113	0.331
Conestogo River								
16018409102	0.267	4.323	4.24	10.40	0.010	0.071	0.034	0.840
16018410002	0.005	3.076	3.11	10.20	0.002	0.026	0.021	0.104
16018407702	1.100	4.482	4.43	8.29	0.020	0.092	0.068	0.270
16018402902	1.300	4.605	4.30	9.58	0.007	0.039	0.037	0.096
Speed River								
16018410202	0.530	1.482	1.44	3.50	0.003	0.010	0.009	0.024
16018409902	0.799	1.611	1.41	5.23	0.003	0.012	0.011	0.040
16018403602	0.101	3.681	3.60	9.58	0.001	0.100	0.071	0.400
16018410102	1.750	3.404	3.02	7.83	0.017	0.077	0.058	0.290
Nith River								
16018403802	2.580	4.187	3.87	7.51	0.021	0.080	0.066	0.293
16018403202	0.100	4.669	4.96	12.20	0.009	0.053	0.041	0.150
16018400902	1.960	4.402	4.07	9.62	0.008	0.030	0.021	0.157
Fairchild's Creek								
16018404402	0.015	3.278	3.37	5.83	0.006	0.047	0.031	0.242
16018409302	0.009	2.040	1.65	4.93	0.004	0.044	0.033	0.128
Whitemans Creek								
16018410602	3.010	5.273	4.39	13.10	0.006	0.033	0.023	0.181
Boston/MacKenzie Cree	ek							
16018409502	0.005	1.317	0.77	5.21	0.001	0.027	0.016	0.128
16018409602	0.005	0.869	0.60	3.22	0.001	0.022	0.014	0.087

Total Kjeldahl Nitrogen					Total Nitrogen				
		(m	g/L)			(r	ng/L)		
Site	Min	Mean	Median	Max	Min	Mean	Median	Max	
Grand River									
16018403902	0.57	0.87	0.85	1.20	0.78	1.91	1.64	4.57	
16018403702	0.14	0.83	0.84	1.24	0.72	2.01	2.15	3.41	
16018410302	0.54	0.81	0.78	1.68	1.02	3.08	3.06	5.66	
16018401502	0.56	0.83	0.77	1.56	1.49	4.29	4.32	7.34	
16018401202	0.60	1.61	1.29	7.53	3.27	5.67	5.32	10.63	
16018401002	0.60	1.13	0.87	4.98	3.07	4.97	4.50	9.57	
16018402702	0.29	0.83	0.71	2.55	0.45	4.40	4.47	7.57	
16018409202	0.64	1.06	0.83	2.95	2.63	4.57	4.30	7.78	
16018403502	0.40	1.04	1.04	1.76	1.21	4.20	4.05	7.35	
Irvine River									
16018410402	0.16	0.76	0.70	1.44	1.00	4.49	4.31	9.38	
Canagagigue Creek									
16018405102	0.60	1.43	1.34	2.52	1.53	6.93	6.91	11.56	
16018401602	0.66	1.13	1.01	1.96	2.84	7.49	7.22	14.88	
Conestogo River									
16018409102	0.48	0.77	0.68	1.30	0.75	5.10	5.28	11.36	
16018410002	0.49	0.82	0.78	1.29	0.60	3.90	3.91	11.44	
16018407702	0.54	0.82	0.81	1.41	1.88	5.31	5.04	9.05	
16018402902	0.54	0.86	0.77	1.53	1.88	5.47	5.13	10.32	
Speed River									
16018410202	0.08	0.51	0.50	0.92	1.06	1.99	1.87	4.12	
16018409902	0.12	0.70	0.60	2.30	0.92	2.31	2.08	7.53	
16018403602	0.52	0.92	0.83	2.70	0.74	4.60	4.50	10.39	
16018410102	0.64	0.88	0.78	2.50	2.79	4.26	3.94	8.68	
Nith River									
16018403802	0.41	0.89	0.79	2.73	3.21	5.08	4.95	7.92	
16018403202	0.54	1.13	0.96	4.39	0.94	5.80	5.74	13.68	
16018400902	0.20	0.83	0.63	3.22	2.38	5.23	5.01	10.88	
Fairchild's Creek									
16018404402	0.47	0.84	0.77	2.01	0.84	4.12	4.13	7.03	
16018409302	0.44	0.92	0.80	2.43	0.81	2.96	2.49	6.64	
Whitemans Creek									
16018410602	0.31	0.68	0.59	2.17	3.72	5.95	5.08	13.94	
Boston/MacKenzie Cree	ek								
16018409502	0.28	0.77	0.69	1.67	0.30	2.08	1.52	6.85	
16018409602	0.47	1.00	0.84	4.26	0.49	1.86	1.70	4.86	

		Total Sus	pended Solid	S		Cł	nloride	
		(mg/L)			(r	ng/L)	
Site	Min	Mean	Medain	Max	Min	Mean	Median	Max
Grand River								
16018403902	1.0	7.2	5.5	39.5	7.2	13.6	13.2	27.6
16018403702	1.4	6.2	5.5	18.8	9.2	14.6	14.1	21.1
16018410302	1.9	9.7	4.3	61.1	14.8	24.3	23.8	42.0
16018401502	1.1	12.8	6.1	66.4	18.0	31.0	29.3	67.2
16018401202	1.8	17.9	6.5	147.0	32.8	81.5	73.9	296.0
16018401002	1.1	14.6	7.0	93.6	23.3	91.1	84.8	294.0
16018402702	0.9	29.1	13.6	187.0	22.8	70.4	67.8	118.0
16018409202	2.4	44.8	22.5	340.0	24.2	84.3	80.8	241.0
16018403502	2.0	47.2	44.9	180.0	6.1	73.3	72.6	153.0
Irvine River								
16018410402	0.8	8.8	2.8	64.4	13.6	24.7	25.9	33.0
Canagagigue Creek								
16018405102	4.0	25.5	19.3	121.0	22.0	28.4	27.2	40.9
16018401602	2.9	20.3	12.5	142.0	17.2	75.9	75.5	191.0
Conestogo River								
16018409102	1.5	6.9	3.8	40.3	10.6	25.9	22.9	115.0
16018410002	4.0	18.6	9.8	163.0	11.2	22.5	21.8	49.8
16018407702	2.5	11.3	8.7	61.8	12.2	24.3	19.1	87.4
16018402902	2.0	14.6	6.0	89.3	17.4	29.1	26.3	83.2
Speed River								
16018410202	1.2	5.8	5.6	22.5	23.6	35.2	33.8	98.4
16018409902	1.0	17.7	4.5	297.0	14.2	24.5	24.6	42.1
16018403602	2.6	10.2	8.4	33.0	32.4	103.0	97.2	236.0
16018410102	2.8	12.2	7.5	85.0	40.8	111.7	103.0	299.0
Nith River								
16018403802	2.5	18.5	14.5	91.5	31.8	52.6	51.8	108.0
16018403202	4.8	47.3	32.0	205.0	14.0	37.6	37.6	60.5
16018400902	2.6	35.1	9.5	220.0	15.4	38.1	40.2	68.8
Fairchild's Creek								
16018404402	8.0	37.1	25.1	282.0	25.8	54.2	52.4	98.6
16018409302	9.0	58.3	48.0	370.0	28.4	65.5	57.2	326.0
Whitemans Creek								
16018410602	1.4	10.1	3.5	77.5	20.4	38.5	37.6	86.7
Boston/MacKenzie Cre	ek							
16018409502	1.4	18.1	10.0	92.2	16.3	36.6	37.7	78.2
16018409602	9.2	47.9	45.0	140.0	10.9	29.7	30.6	63.9

	Sodium				Aluminum				
		()	ng/L)			(μ	g/L)		
Site	Min	Mean	Median	Max	Min	Mean	Median	Max	
Grand River									
16018403902	3.5	7.0	6.7	13.8	14.80	79.30	55.45	352.00	
16018403702	4.5	7.1	7.2	10.2	26.70	81.49	61.40	215.00	
16018410302	6.5	12.5	12.4	21.9	22.00	85.90	48.80	429.00	
16018401502	8.2	16.4	15.0	40.7	25.80	122.65	67.15	557.00	
16018401202	17.2	49.0	45.1	179.0	21.00	127.63	66.40	742.00	
16018401002	12.8	54.6	51.6	180.0	20.30	115.07	70.60	586.00	
16018402702	10.9	41.1	39.4	69.7	48.40	259.08	139.00	1390.00	
16018409202	11.7	49.4	46.2	144.0	59.60	310.58	218.00	1630.00	
16018403502	10.5	42.8	40.5	73.2	28.70	304.38	283.00	771.00	
Irvine River									
16018410402	4.6	11.1	11.1	18.2	6.81	94.06	33.40	614.00	
Canagagigue Creek									
16018405102	10.7	14.4	14.2	22.8	31.30	225.50	183.00	499.00	
16018401602	8.2	45.7	46.4	121.0	38.50	157.12	136.00	590.00	
Conestogo River									
16018409102	4.2	12.4	10.6	67.4	18.50	97.06	54.60	527.00	
16018410002	5.0	11.2	10.6	28.0	77.90	203.30	134.50	762.00	
16018407702	5.6	12.6	9.5	62.8	44.40	144.29	118.00	461.00	
16018402902	8.5	15.2	13.4	49.8	18.60	163.06	93.30	700.00	
Speed River									
16018410202	13.0	18.2	16.8	58.2	12.00	24.71	19.70	82.40	
16018409902	6.6	11.0	11.1	21.0	11.70	101.36	32.50	1390.00	
16018403602	16.6	60.1	60.1	148.0	13.80	53.09	34.70	213.00	
16018410102	22.5	66.1	63.1	188.0	22.20	69.93	40.90	399.00	
Nith River									
16018403802	17.8	30.6	30.3	64.3	16.50	152.50	104.50	623.00	
16018403202	7.2	21.0	20.6	36.3	6.39	410.73	298.50	1200.00	
16018400902	6.9	20.1	20.7	38.6	44.30	258.80	98.00	1460.00	
Fairchild's Creek									
16018404402	12.8	28.6	25.6	59.3	58.40	262.78	196.50	1050.00	
16018409302	14.6	35.2	30.1	191.0	149.00	408.22	334.00	1600.00	
Whitemans Creek									
16018410602	9.8	18.2	18.3	44.8	12.00	117.69	39.30	844.00	
Boston/MacKenzie Cre	ek								
16018409502	7.1	19.6	19.3	45.1	41.40	366.35	246.00	1260.00	
16018409602	5.6	14.8	14.1	33.0	160.00	513.28	464.50	1250.00	

	Cadmium				Iron			
		(µç	g/L)			(h	ıg/L)	
Site	Min	Mean	Median	Max	Min	Mean	Median	Max
Grand River								
16018403902	-0.91	-0.03	-0.03	0.47	67.00	140.35	122.00	299.00
16018403702	-1.13	-0.04	-0.01	0.78	39.50	165.07	135.00	1100.00
16018410302	-0.70	0.04	-0.02	0.94	32.60	115.05	67.40	495.00
16018401502	-1.82	0.01	0.03	1.79	32.90	136.89	85.40	589.00
16018401202	-1.43	0.15	0.03	1.76	41.40	187.06	115.00	1100.00
16018401002	-0.79	0.07	0.07	0.91	35.00	164.13	95.60	935.00
16018402702	-0.73	0.13	0.14	0.85	51.60	253.64	145.00	1320.00
16018409202	-0.85	0.15	0.12	1.12	59.60	368.39	239.00	2250.00
16018403502	-1.48	0.03	0.09	0.81	7.89	409.54	404.50	1160.00
Irvine River								
16018410402	-0.56	0.01	-0.01	0.64	17.00	101.97	61.30	462.00
Canagagigue Creek								
16018405102	-1.36	0.01	-0.01	1.32	50.60	315.68	258.00	1150.00
16018401602	-0.96	0.04	0.08	1.04	62.90	234.64	179.00	682.00
Conestogo River								
16018409102	-1.48	0.08	0.10	1.29	40.60	136.73	115.00	354.00
16018410002	-0.80	0.06	0.04	0.80	98.90	210.91	165.50	666.00
16018407702	-1.25	-0.06	0.00	0.76	32.90	139.79	125.00	403.00
16018402902	-1.13	-0.05	0.05	1.04	27.60	147.13	107.00	524.00
Speed River								
16018410202	-2.04	0.07	0.06	0.84	22.30	69.40	60.90	233.00
16018409902	-1.02	-0.01	0.00	0.74	39.20	182.99	94.05	1990.00
16018403602	-0.82	-0.01	0.05	0.53	73.20	128.42	104.00	356.00
16018410102	-0.83	0.14	0.12	1.49	62.20	177.52	139.50	718.00
Nith River								
16018403802	-1.32	0.00	0.06	0.72	66.10	210.36	178.50	752.00
16018403202	-0.62	0.04	0.06	0.79	6.99	394.19	314.00	1460.00
16018400902	-0.45	0.03	0.01	0.90	52.40	270.06	111.00	1610.00
Fairchild's Creek								
16018404402	-0.62	0.15	0.15	0.98	141.00	428.29	323.50	1280.00
16018409302	-1.38	0.04	0.06	1.06	170.00	568.67	537.50	1330.00
Whitemans Creek								
16018410602	-0.65	-0.01	-0.02	0.59	29.00	154.15	105.00	709.00
Boston/MacKenzie Cree	ek							
16018409502	-0.85	0.11	0.02	1.05	36.90	306.09	202.00	821.00
16018409602	-1.05	-0.03	0.03	0.50	209.00	618.69	542.50	1130.00

	Lead				Magnesium				
		(há	g/L)			(μ	g/L)		
Site	Min	Mean	Median	Max	Min	Mean	Median	Max	
Grand River									
16018403902	-7.46	0.91	0.47	16.50	10.60	15.30	16.00	21.80	
16018403702	-9.27	0.01	-0.21	7.69	9.68	14.72	14.45	20.50	
16018410302	-8.92	0.16	-0.34	12.60	11.30	16.67	16.45	23.00	
16018401502	-9.11	-0.42	-0.46	10.80	13.20	19.22	18.90	26.70	
16018401202	-12.00	1.07	1.61	12.10	10.70	20.31	20.70	28.90	
16018401002	-8.34	1.93	1.86	16.80	11.80	21.11	21.75	30.10	
16018402702	-14.00	1.41	0.82	8.29	10.80	21.66	21.70	37.60	
16018409202	-13.30	0.96	1.51	13.70	10.50	22.08	23.05	29.50	
16018403502	-15.70	0.11	-0.24	17.10	15.10	22.00	22.20	26.50	
Irvine River									
16018410402	-11.20	0.07	0.92	9.45	10.90	20.72	21.50	24.70	
Canagagigue Creek									
16018405102	-5.97	0.19	0.17	6.65	15.20	21.28	20.85	27.80	
16018401602	-8.76	0.09	-0.06	11.60	17.50	24.66	24.55	34.90	
Conestogo River									
16018409102	-12.10	-0.78	-0.48	6.22	14.40	25.75	26.60	30.20	
16018410002	-10.80	-0.27	0.50	6.99	12.40	22.52	23.30	27.00	
16018407702	-10.20	1.38	1.25	28.50	12.50	19.23	18.35	28.60	
16018402902	-6.19	0.71	0.17	12.80	13.70	19.99	19.55	29.40	
Speed River									
16018410202	-16.40	0.64	1.05	15.70	16.50	22.66	23.70	28.40	
16018409902	-5.91	1.05	0.80	12.00	10.50	19.17	20.00	23.50	
16018403602	-14.00	0.11	0.81	7.36	14.90	22.50	22.60	29.30	
16018410102	-18.40	1.40	2.34	9.48	13.20	22.89	22.90	30.70	
Nith River									
16018403802	-12.10	0.10	0.27	9.15	8.46	22.54	23.40	26.30	
16018403202	-16.60	-0.10	-0.36	10.00	8.46	19.52	20.10	24.60	
16018400902	-6.21	0.03	0.65	5.62	8.52	23.42	24.40	30.30	
Fairchild's Creek									
16018404402	-18.50	0.04	0.02	9.24	12.10	28.06	29.10	32.70	
16018409302	-7.51	1.08	0.68	12.50	7.24	23.94	25.40	30.60	
Whitemans Creek									
16018410602	-7.93	-0.14	0.26	10.50	6.98	22.03	23.15	26.60	
Boston/MacKenzie Cree	ek								
16018409502	-10.80	1.19	0.23	17.30	5.52	28.09	26.10	48.60	
16018409602	-8.44	2.68	1.05	30.80	6.58	21.61	23.20	31.70	

	Manganese					Zinc			
		(H	ıg/L)			(μ	g/L)		
Site	Min	Mean	Median	Max	Min	Mean	Median	Max	
Grand River									
16018403902	7.80	39.56	35.70	122.00	0.40	1.92	1.62	5.09	
16018403702	7.30	65.38	45.80	271.00	0.32	1.39	1.02	4.57	
16018410302	10.90	27.19	17.70	159.00	0.41	3.20	1.99	29.10	
16018401502	4.86	20.15	13.95	80.40	0.77	2.66	1.61	12.70	
16018401202	7.38	31.91	20.20	180.00	1.86	6.48	4.505	29.40	
16018401002	4.44	30.00	21.80	138.00	4.40	9.42	7.68	27.50	
16018402702	11.00	34.81	23.30	149.00	0.99	6.39	5.21	22.10	
16018409202	11.00	47.94	32.60	263.00	2.94	8.10	5.28	40.80	
16018403502	0.13	56.56	55.85	149.00	1.63	7.85	6.905	21.30	
Irvine River									
16018410402	1.77	10.88	6.84	47.10	0.25	1.67	1.2	5.94	
Canagagigue Creek									
16018405102	16.90	104.79	66.70	447.00	0.57	3.18	2.59	16.20	
16018401602	21.90	57.20	48.40	219.00	0.73	4.86	4.07	13.80	
Conestogo River									
16018409102	5.67	15.99	14.50	32.30	0.42	2.65	1.595	18.30	
16018410002	5.98	24.20	20.85	92.50	0.53	2.14	1.555	7.86	
16018407702	4.51	34.16	21.80	146.00	0.18	2.38	1.35	15.90	
16018402902	4.99	19.52	15.40	64.40	0.64	5.69	2.63	56.30	
Speed River									
16018410202	5.55	26.06	24.40	67.50	11.30	30.92	31.1	69.50	
16018409902	6.18	33.87	23.95	191.00	0.47	3.19	1.91	17.30	
16018403602	16.90	31.66	28.90	65.40	15.60	27.73	25	55.10	
16018410102	12.30	38.10	28.20	148.00	10.10	20.02	15.4	74.80	
Nith River									
16018403802	8.27	35.89	27.15	141.00	0.15	3.64	2.43	9.90	
16018403202	0.32	50.25	45.95	163.00	1.20	5.50	4.46	16.20	
16018400902	6.04	32.33	18.00	175.00	-0.40	3.28	1.775	15.10	
Fairchild's Creek									
16018404402	34.10	84.86	68.70	314.00	1.33	4.38	3.625	18.40	
16018409302	38.00	114.45	110.00	342.00	1.92	7.80	6.27	47.00	
Whitemans Creek									
16018410602	5.96	26.49	21.90	113.00	-0.50	1.85	1.34	6.94	
Boston/MacKenzie Cree	ek								
16018409502	11.30	33.09	27.10	84.50	0.31	3.27	2.14	9.02	
16018409602	26.30	92.03	90.15	210.00	1.03	4.47	3.945	12.20	

Pesticide Category	Pest Management Regulatory Agency (PMAR) Status (2003)			
Phenoxy Herbicides:				
Dicamba	currently registered			
MCPA	currently registered			
MCPB	currently registered			
Mecoprop	currently registered			
2,4 Dichlorophenoxyacetic	currently registered			
2,4 Dichlorophenoxybutyric	currently registered			
2,4 DP	phased out			
2,4,5 Trichlorophenoxyacetic	phased out			
Triazine Herbicides:				
Alachlor	phased out			
Metalachlor	currently registered			
Atrazine	currently registered			
Cyanazine	currently registered			
Atrazine de-ethylated	currently registered			
Sencor	phased out			
Prometone	phased out			
Simazine	currently registered			
Oganophosphorus Insecticides:				
Chlorofenvinphos	phased out			
Demeton	phased out			
Diazinaon	currently registered			
Dursban	phased out			
Ethion	currently registered			
Guthion	phased out			
Malathion	currently registered			
Phosalone	currently registered			
Parathion	phased out			
Phosmet	currently registered			

Appendix E. Pesticide products analyzed in PWQMN/Enhanced Tributary Monitoring Program samples. Note: Pesticide analysis is done on samples from site 16018403502 (at bridge in Dunnville), on the Grand River.

Percent of Samples that do not meet guidelines/objectives							
Site Objective:	Total Phosphorus 0.030	Total Nitrates 2.93	Nitrite 0.060	Total Suspended Solids 25.0 mg/l	pH <6.5 -	Chloride 250.0	Unionized Ammonia 0.0165 mg/l
16018400002	5.4	70	nig/L	111g/L	20.5	nig/L	0
16018400902	34 100	/U 91	0	14	5 41	0	0
16018401002	100	81 92	04 02	14	41 o	2	14
16018401202	100	85	92	19	8	3	4/
16018401502	55 07	03	5 02	18	55 17	0	0
16018401602	97	81	92	28	1/	0	0
16018402702	82	54	32	25	4	0	0
16018402902	78	72	14	17	58	0	0
16018403202	100	65	32	76	5	0	0
16018403502	100	51	28	77	0	0	5
16018403602	92	64	53	6	0	0	3
16018403702	58	0	11	0	3	3	0
16018403802	97	86	51	19	3	0	3
16018403902	54	6	0	6	6	0	0
16018404402	97	54	23	51	3	0	0
16018405102	97	76	82	35	18	0	32
16018407702	89	81	58	6	39	0	0
16018409102	51	66	20	6	17	0	0
16018409202	97	62	18	41	3	0	3
16018409302	100	24	19	81	3	3	0
16018409502	72	14	11	31	0	0	0
16018409602	100	5	5	81	0	0	0
16018409902	29	3	0	14	9	0	0
16018410002	59	51	8	22	11	0	0
16018410102	100	63	49	9	40	3	9
16018410202	13	3	0	0	11	3	0
16018410302	30	30	5	14	62	0	3
16018410402	22	56	6	8	22	0	3
16018410602	36	100	10	12	0	0	0

Appendix F. Compliance summary for nutrients and chloride with PWQO's or other relevant water quality criteria (2000-2004).

* Alberta Total Nitrogen objective of 1.0 mg/L

Percent of Samples that do not meet guideline/objective							
Site	Aluminum	Cadmium	Copper	Iron	Lead	Nickel	Zinc
	75	0.5	5.0	300	5.0	25	30
Objective	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L
16018400902	64	11	3	25	3	0	0
16018401002	43	9	3	14	14	0	0
16018401202	44	18	6	15	21	0	0
16018401502	44	8	0	8	8	0	0
16018401602	71	6	0	29	9	0	0
16018402402	82	0	0	18	18	0	9
16018402702	89	11	4	15	30	0	0
16018402902	63	3	0	11	14	0	3
16018403202	97	11	6	53	19	0	0
16018403502	96	6	1	73	14	0	0
16018403602	17	3	0	3	11	0	29
16018403702	41	3	0	11	11	0	0
16018403802	61	11	0	17	11	0	0
16018403902	29	0	0	0	9	0	0
16018404402	97	12	3	53	15	0	0
16018405102	91	9	0	36	6	0	0
16018407702	77	9	0	6	14	0	0
16018409102	32	21	0	6	6	0	0
16018409202	95	11	8	22	16	0	5
16018409302	100	11	6	92	17	0	3
16018409502	66	9	0	43	20	0	0
16018409602	100	3	0	92	19	0	0
16018409902	21	9	3	12	15	0	0
16018410002	100	11	0	17	8	0	0
16018410102	21	9	6	9	15	0	15
16018410202	3	19	0	0	8	0	51
16018410302	29	6	0	9	6	0	0
16018410402	26	3	0	9	9	0	0
16018410602	34	2	0	12	15	0	0

Appendix G. Compliance summary for metals at the 28 monitoring sites in the Grand River watershed (2000-2004).



Appendix H. Nutrient and chloride concentrations (75th percentiles) for 2000 – 2004 at the 28 Provincial Water Quality Monitoring Sites in the Grand River watershed.











Site	Time Period	Flow	NH3*	ТР	NO3*	CHLORIDE	TSS
16018400902	1981-2001	-0.052	-0.001	-0.001	0.035	0.92	-0.093
16018401002	1981-2001	-0.179	0.001	-0.002	0.022	1.69	-0.191
16018401202	1981-2001	-0.241	0.015	-0.001	0.049	1.314	-0.160
16018401502	1981-2001	-0.105	-0.002	-0.001	0.046	0.167	-0.233
16018401602	1981-2001	-0.011	-0.005	-0.006	0.052	-0.170	-0.169
16018402702	1981-2001	-0.489	-0.001	-0.001	0.040	1.538	-0.021
16018402902	1981-2001	-0.062	0.000	-0.002	0.032	0.488	-0.357
16018403202	1982-2001	-0.031	-0.003	-0.030	0.102	0.166	-0.185
16018403502	1985-1996	-1.976	0.012	0.001	0.048	1.541	0.464
16018403602	1981-2001	-0.011	0.005	-0.002	0.042	2.318	0.020
16018403702	1981-2001	-0.008	0.001	0.000	0.002	0.287	0.014
16018403802	N/A	N/A	N/A	N/A	N/A	N/A	N/A
16018403902	1981-1990	-0.014	0.000	0.000	0.002	0.336	-0.034
16018404402	N/A	N/A	N/A	N/A	N/A	N/A	N/A
16018405102	1981-2001	0.002	0.007	-0.001	-0.031	0.392	N/A
16018407702	1981-2001	-0.040	0.000	-0.001	0.004	0.833	-0.272
16018409102	1981-2001	-0.031	-0.003	-0.003	N/A	0.166	-0.185
16018409202	1981-2001	-0.661	-0.002	-0.001	0.042	1.345	-0.296
16018409302	1981-2001	-0.041	0.001	-0.001	0.022	1.284	-0.804
16018409502	1981-2001	-0.020	-0.0005	0.000	0.014	0.698	-0.146
16018409602	1981-2001	-0.018	-0.00	0.000	0.008	0.667	-0.166
16018409902	1981-2001	-0.010	0.000	0.001	N/A	0.816	0.125
16018410002	1981-2001	-0.002	0.000	-0.001	0.010	0.447	-0.088
16018410102	1981-2001	-0.113	0.003	-0.002	0.035	1.788	-0.023
16018410202	1981-2001	-0.023	0.000	0.000	0.012	0.630	0.000
16018410302	1981-2001	-0.028	-0.007	-0.00	0.007	0.463	-0.017
16018410402	1981-2001	-0.004	-0.001	-0.001	0.008	0.453	-0.082
16018410602	1981-2001	-0.061	0.000	0.000	0.043	0.623	-0.050

Appendix I. Seasonal Kendall slopes for nutrients, total suspended solids, and chloride. Significant (p = 0.05) trends are bolded.

Bold indicates significant trend; '-' slope indicates decreasing concentrations (improving trend); '+' slope indicates increasing concentrations (deteriorating trend); * Trends for total nitrates and total ammonia are for 1981-1995