Water Quality in the Conservation Halton Watershed: 1964-2014

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Conservation
Halton

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Executive Summary

Water quality sampling in the Conservation Halton watershed has been ongoing since 1964 and can provide valuable information about the impact of changes to land use within the watershed over time. To this end, temporal trends for seven parameters were examined at 19 monitoring locations using data collected through the grab sampling program. The analysis focussed on significant increases or decrease in each parameter over two time periods: 1975-1996 and 2002-2014. In addition, seasonal differences were examined for samples collected in spring, summer and fall. A Water Quality Index (WQI) score was calculated for each station at five year intervals.

Data analysis provided the following general conclusions:

- Chloride concentrations are increasing across the watershed.
- Total phosphorus concentrations are decreasing, with many stations below the water quality objective.
- Total suspended solids have remained consistently low, although higher levels are seen during rain events.
- Nitrate has remained low across the watershed, with notable decreases seen within Grindstone Creek.
- Copper, iron and zinc are consistently below the water quality objective and are therefore not currently of concern. However, increasing trends in both iron and zinc indicate that they may become problematic in the future. All three metal concentrations are strongly correlated with total suspended solids and a reduction of TSS levels will likely result in improvements of metal concentrations.
- The majority of water quality index scores fall within the “Fair” category

Further improvements to storm water management with a focus on methods to capture chlorides and reduce the movement of sediment during rain events would be beneficial to all streams within the CH jurisdiction. Working with landowners, municipal staff, farmers and developers to protect and improve riparian buffers and reduce or manage the movement of materials entering a stream will be essential to further reductions in the parameters discussed above.

Introduction & Background

Conservation Halton Jurisdiction and Land Uses

The Watershed

Conservation Halton's area of jurisdiction (also known as its watershed) encompasses an area of approximately 1,000 km^2 and includes the watersheds of 23 streams flowing into the Lake Ontario drainage basin; from Joshua's Creek in the east to Grindstone Creek and small tributaries along the north shore of Hamilton Harbour to the west. Also included is approximately 26 km of Lake Ontario shoreline and 80 km of the Niagara Escarpment. The three largest watersheds within the Conservation Halton jurisdiction include the Sixteen Mile Creek, Bronte Creek, and Grindstone Creek watersheds.

The Land Uses

The Conservation Halton (CH) watershed supports one of the most rapidly growing urban areas in Canada. By the year 2031, the population of the Halton Region is expected to grow by 50% to 752,537 people from the most recent (2011) population estimate of 501,669 (Statistics Canada 2011). Most of this urban growth is expected to take place in the Sixteen Mile Creek watershed in the Towns of Milton and Oakville. This portion of Halton Region has been designated as an urban growth area under the Provincial *Places to Grow Act (2005)*.

In addition to urban development, agricultural and rural land uses dominate much of the area within the watershed. The Sixteen Mile and Grindstone Creek watersheds provide the majority of agricultural land, used predominantly for crops, nurseries and horse farms. Pits and quarries make up a small percentage of land use, most notably within the Bronte and Sixteen Mile Creek watersheds where Dufferin (a division of CRH Canada Group Inc.), Nelson Aggregates, Hanson Brick, Sherman Sand and Gravel and Halton Crushed Stone extract sand, gravel and bedrock for various road and construction projects.

The protection of natural spaces by Conservation Halton and other public and private landowners in the watershed has resulted in approximately 26.4% of forested and 8.7% of wetland area across the watershed (Conservation Halton 2013). Other natural communities in earlier stages of succession are also present, and together these natural areas play a key role in protecting water quality throughout the watershed. These locations also act as important wildlife refuge and contain many of the species at risk found within the watershed.

The different types of land uses all have different impacts on the aquatic ecosystem and the biota living within CH streams. General understanding of land uses is essential for understanding changes seen in aquatic communities, and is aided by the collection of data at specific locations in quantifying changes seen over time.

Conservation Halton Aquatic Monitoring Program

Long-term Environmental Monitoring Program

In 2005, Conservation Halton began its Long-term Environmental Monitoring Program (LEMP) that includes both terrestrial and aquatic components. This program was designed to detect changes in the aquatic ecosystem by using standard protocols to examine biotic communities (benthic macroinvertebrate and fish communities) and abiotic features (channel morphology and water temperature and quality) over time. The program uses stations monitored annually and biennially across the Conservation Halton watershed to assess the health of the aquatic community against a standard set of metrics.

An important part of the assessment of aquatic communities is the assessment of water quality, as it can provide insight into changes seen in the biological community and provide early detection of stressors to aquatic ecosystems. Due to the high cost of water quality laboratory analysis, CH does not monitor water quality at all the aquatic monitoring stations. Instead, in partnership with the Ontario Ministry of the Environment and Climate Change (OMOECC), CH monitors water quality at 11 stations under the umbrella of the Provincial Water Quality Monitoring Network (PWQMN).

History of the PWQMN

The PWQMN was established across Ontario in 1964 by the OMOECC to collect water quality information from streams and rivers throughout the province. Samples are typically collected by partner agencies and sent to the OMOECC laboratory for analysis of a standard set of analytes. Program cutbacks in the 1990's have greatly reduced the number of locations sampled and station locations have changed throughout the province over the 50 years of monitoring. The program was revamped in 2002 and most stations have been monitored consistently since that time.

The program was designed to collect information on ambient conditions over a long time period and does not provide information on nutrient loading. In addition, samples collected on a monthly basis provide a point-in-time snapshot of conditions. While this is useful for assessing chronic impairment by certain analytes, it does not provide information on acute impairment occurring as a result of high concentrations over a short time period, such as those experienced during a storm event. The purpose of this report is to assess how ambient water quality conditions have changed at various locations throughout the watershed over time and to determine if chronic impairment is occurring.

Methods

Collection Methods

The timing and location of sample collection has varied over the 50 years of monitoring with 28 stations sampled within the CH watershed at various times. This variation has ranged from bi-weekly sampling to bi-monthly sampling, with as few as four locations sampled to as many as 20 locations sampled in a given year. Table 1 provides a description of how sampling frequency has changed over the 50 years of monitoring. Monitoring has occurred at a minimum of four stations during all 50 years with the exception of 1998 when no samples were collected.

Table 1: Sampling frequency over the 50 years of monitoring

Time Period	Sampling Frequency	Start	End
1964-1965	Variable	March	December
1966-1972	Bi-weekly	January	December
1973-1995	Monthly	January	December
1996-1997	Monthly	April	November
1998	Not Sampled	N/A	N/A
1999-2002	Five times per year	April	November
2003-2014	Eight times per year (7 stations)	March	November
2003-2014	Four times per year (4 stations)	March	November

At each location sampled since 2003 four grab sample bottles were collected, ensuring that each bottle was pre-washed with stream water three times before a sample was collected. A YSI multi-meter sonde collected additional data at each location including stream temperature, conductivity, dissolved oxygen and pH. Samples were collected during both dry and wet events.

All stations sampled since 2003 were sampled within a maximum of eight hours from each other. Samples were kept in a cooler on ice and delivered to the OMOECC laboratory for analysis within 6 to 24 hours of collection. Samples were analyzed for a variety of nutrients and metals which are presented in Appendix A.

Data Analysis Methods

Stations of Interest

Due to the variation in sample timing over the 50 years of monitoring, analysis focused on samples collected between March 1 and November 30 each year with samples collected between December and February removed from the analysis. This was done to help reduce the potential influence of winter values on the data analysis as winter samples have not been collected since 1995. In addition, analysis has been scoped to stations with long-term data sets as well as those currently sampled as part of Conservation Halton's LEMP program, resulting in the analysis of 19 stations. Table 2 provides a description of each station analyzed and Figure 1 provides a map of their locations. Stations in all charts and graphs are organized from west to east and from south to north.

Table 2: PWQMN monitoring locations

Watershed	Station	Location	Start	End	Dominant Land Use*
Grindstone	GRN-114^{M}	Valley Inn Road	1964	1996	Natural/Urban
	GRN-5	Unsworth Avenue	2002	Ongoing	Natural/Urban
	GRN-18	Waterdown Road	1964	1996	Urban
Sheldon	SHL-48^{M}	Lakeshore Road	2007	Ongoing	Urban
Bronte	BRO-19^{M}	Lakeshore Road	1964	2001	Urban
	BRO-119	Petro Canada Park	2000	Ongoing	Natural/Urban
	BRO-264	Appleby Line	1965	2001	Agriculture
	BRO-16	Indian Creek at Appleby Line, north of Zimmerman	2000	Ongoing	Agriculture
	BRO-265	Indian Creek at Tremaine Road., south of Britannia Road	1979	1996	Agriculture/Urban
	BRO-2	Mountsberg Creek at Hwy 401, above Mountsberg Reservoir	1975	Ongoing	Agriculture/Natural
Fourteen Mile	FOR-58^{M}	Lakeshore Road	1972	Ongoing	Urban
Sixteen Mile	SXM-143^{M}	Hogsback Park	1964	Ongoing	Urban
	SXM-216	West Sixteen Mile Creek at Lower Base Line	2002	Ongoing	Natural
	SXM-537	West Sixteen Mile Creek at Derry and Hwy 25	1965	1996	Urban
	SXM-61	West Sixteen Mile Creek downstream of Kelso	1975	1996	Natural
	SXM-63	West Sixteen Mile Creek at Limestone Road	1975	Ongoing	Natural
	SXM-205	East Sixteen Mile Creek at Lower Base Line	1975	Ongoing	Natural

Watershed	Station	Location	Start	End	Dominant Land Use*
Sixteen Mile	SXM-349	East Sixteen Mile Creek at 5th Line	2002	Ongoing	Agriculture
	SXM-556	East Sixteen Mile Creek at Hwy 25, south of Scotch Block	1973	1996	Agriculture

^{M} indicates station located at or near the mouth of a creek

*Dominant land use identified within the reaches immediately upstream of station

Figure 1: PWQMN Monitoring Locations

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Analytes of Interest

While 42 analytes were analyzed in the lab (Appendix A), data analysis focused on those listed in Table 3, as these parameters have been analyzed with the highest consistency over the monitoring period and across sampling locations. In addition, all analytes have either a provincial or federal water quality objective associated with them. A water quality objective is set based on laboratory assessments of impacts for each parameter on both vertebrate and invertebrate populations. The objective is set so that concentrations below the objective are likely to have minimal to no effect on aquatic ecosystems, while concentrations above the objective indicate that a given analyte may be impacting the aquatic ecosystem (CCME 1999).

Table 3: Analytes of interest

Analyte Category	Analyte	Objective	Units	Years Sampled
General	Chloride	120 [C]	mg/L	1965 – Present
	Total Suspended Solids	25 [C]	mg/L	1964 – Present
Nutrient	Nitrate	2.93 [C]	mg/L	1964 – Present
	Phosphorus	0.03 [P]	mg/L	1964 – Present
Metal	Copper	5 [P]	µg/L	1980 – Present
	Iron	300 [P]	µg/L	1965 – Present
	Zinc	20[P]	µg/L	1980 – Present

[C] Denotes an objective derived from the Canadian Water Quality Objectives (CCME 1999)
[P] Denotes an objective derived from the Provincial Water Quality Objectives (OMOEE 1994)

Laboratory analysis of the three metals (copper, iron and zinc) does not provide information about speciation or bioavailability of these elements. All analysis is completed on total unfiltered concentrations found within the water sample. Eisler (1998) states that up to 88% of total copper measured within a water sample is “associated with suspended solids and not available to biota”. The PWQO for copper has been set based on toxicity measured with total copper concentrations and is therefore a conservative approach as higher levels of unavailable copper could have no effect on aquatic organisms (OMOE 1979). Similar to copper, the availability of iron and zinc depend on their speciation within a water body. Insoluble iron and zinc concentrations increase with increasing dissolved oxygen and therefore higher levels may not have an impact on aquatic biota if they are present with higher dissolved oxygen concentrations (OMOE 1979).

It should also be noted that laboratory methods have changed over the last 50 years with an increased ability to detect analyte concentrations at very low levels as well as an increased accuracy of detection. Analytes with dramatic methodology changes have been noted in the sections below, but an overall understanding that changes over time could be a result of either actual changes in concentrations within the stream or changes in the ability to detect concentrations is important and must be recognized.

Statistical Analysis

Each parameter at each station was summarized by calculating the median for each year sampled. The median was used because it more accurately represents annual conditions at a station as it is not as influenced by potentially high values collected during wet events. Five year averages of annual median values were then calculated and compared against the water quality objective for each parameter. The five year averages were graphed to provide a visual assessment of general trends over time, however statistical analysis of five year averages was not completed as the intent of five year averages was to gain an understanding of how parameters may be changing at a coarse time scale.

To statistically assess trends over time, a Mann-Kendall trend analysis was used to determine if parameter annual medians were increasing or decreasing, with a significance level of $p<0.05$. The Mann-Kendall trends were assessed for three separate time periods for each station – one for all dates monitored, one for data between 1975 and 1996, and one for data between 2002 and 2014. These time periods were chosen to allow for comparison of trends between stations as standardizing the time frame removes the influence of stations having a longer or shorter monitoring history. Many of the historical stations were sampled consistently between 1975 and 1996, with less consistency before this period. Four of the current stations were not sampled prior to 2002, so accurate comparisons between current stations could only be made for the 2002 to 2014 time period. Comparisons between stations for their entire monitoring period were not made due to the wide variation in sampling time frames.

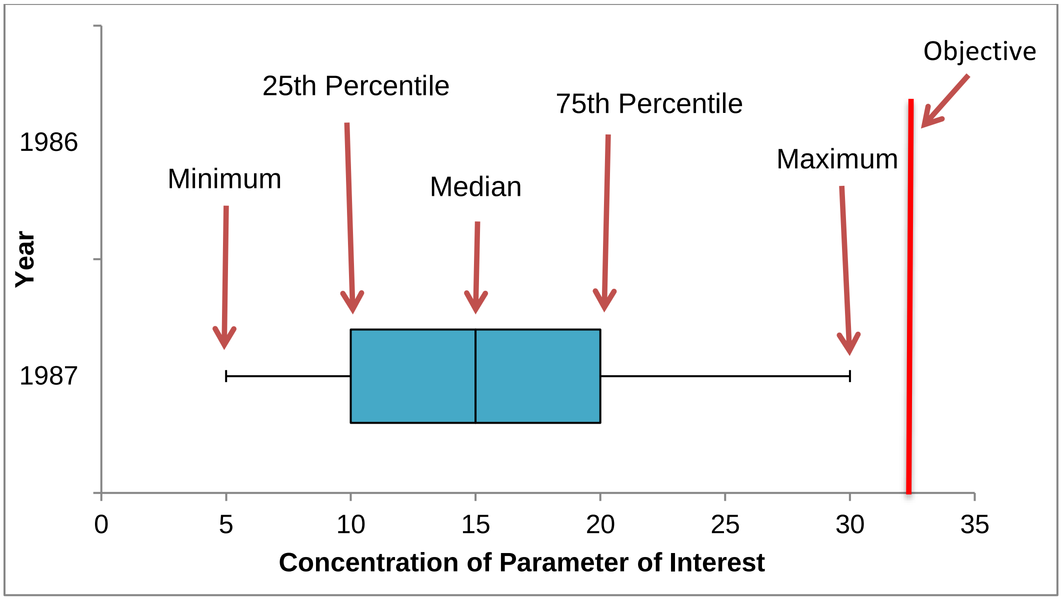
Differences between seasons were analyzed using a Kruskal-Wallis test. The purpose of seasonal analysis was to determine if season influenced parameter concentrations as this knowledge would provide guidance to management decisions regarding mitigation techniques for parameters of concern. Seasons were set as Spring (March, April, May), Summer (June, July, August) and Fall (September, October, November). Comparisons were made between pairs of seasons (i.e. Spring vs. Summer, Spring vs. Fall and Summer vs. Fall) regardless of sampling year, so that data from all years for one season was aggregated and compared against data from all years of another season. Only data from 2002 to 2014 were used for between-season analysis because the goal of between-season analysis was to guide management decisions and therefore seasonal differences present early in the monitoring period that no longer exist were not of interest. Seasonal differences were considered significant if the Kruskal-Wallis statistic (K) had a p-value <0.05 (Helsel and Hirsch 2002).

Correlation coefficients were calculated to describe the relationship between total suspended solids and the three metals (copper, iron and zinc). Spearman's rho was used as scatter plots indicated the data showed a nonlinear monotonic relationship. Correlations were considered significant if $p<0.05$.

Spatial comparisons were made between the stations located at or near the mouths of the creeks, with the exception of Sheldon Creek as it was not monitored prior to 2008. Monitoring locations at the mouths of Grindstone and Bronte Creeks was discontinued in 1996 and stations were respectively relocated 2.6 and 1.3 km upstream in 2002. Neither creek has major contaminant sources between the two station locations so data for both stations was combined to provide a complete 50 year data set for each creek for the purposes of spatial comparisons between creek mouth stations.

Box plots of the minimum, median, maximum and 25th/75th percentiles were used to describe trends in parameters annually at the four creek mouth stations. Years without data are represented by a gap in the graph, while years with a single data point are represented by a dashed line at the value of the data point. To allow for the best graphical representation of annual variation in each parameter the scale of each parameter concentration was set at a defined limit. This resulted in some very high values beyond the scope of the graph and can be seen when the maximum error bar line extends to the edge of the graph without a cap. These values, along with all the values for all box plots, are presented in Appendix B. A standard box plot is presented in Figure 2, with the blue box representing data falling between the 25th and 75th percentiles and the line splitting the box representing the median annual value. Minimum and maximum values are represented by the caps located at the end of the error bars. A red line denotes the water quality objective associated with each parameter.

Figure 2: Standard box plot



Water Quality Index

The Canadian Council of the Ministers of the Environment Water Quality Index (WQI) was used to assess general water quality and provide an overall rating at each station. This index measures values of each water quality parameter against set objectives to determine if impairment to freshwater ecosystems is probable. Index values are calculated by determining the frequency and amplitude of exceedances for each parameter as well as the number of parameters for each station that exceed objectives. The WQI requires that a minimum of four parameters be used to calculate the index and as a result years where less than four parameters were monitored were removed from the analysis to ensure that all scores were calculated with the greatest accuracy (CCME 2001). The water quality parameters and associated objective from Table 3 were used in calculating the index values. The final rating for a site falls into one of five categories ranging from poor to excellent as described in Table 4.

Table 4: Water Quality Index Values and Interpretations*

Rating	WQI Value	Description
Excellent	95-100	Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels
Good	80-94	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels
Fair	65-79	Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels
Marginal	45-64	Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels
Poor	0-44	Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels

*Adapted from CCME 2001

Results and Discussion

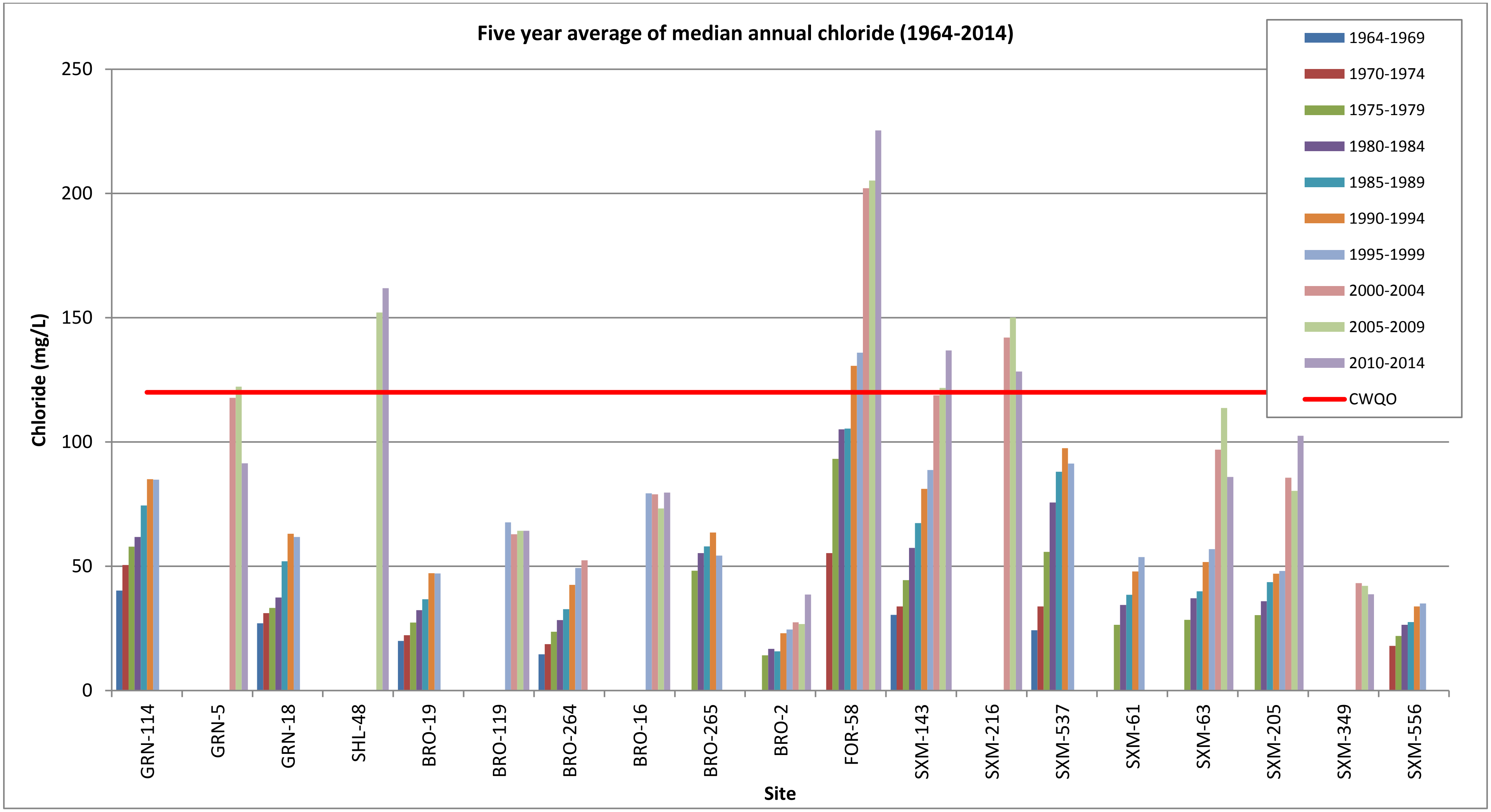
Chloride

Changes in chloride concentrations in aquatic environments are often associated with increasing urbanization, as anthropogenic sources associated with winter application for de-icing account for the majority of the chloride detected within a stream system not affected by sea water (CCME 2011, Stone *et al.* 2010). Chloride impacts biological life cycles of both fish and invertebrates and can bioaccumulate in the food chain causing concerns for terrestrial species (CCME 2011). Two objectives are used for determining chloride impacts on aquatic ecosystems, one for short-term (acute) exposure and one for long term (chronic) exposure. The short term objective is 640 mg/L and is designed to provide protection for aquatic organisms during a short term event such as a spill. The long term objective is 120 mg/L and is designed to provide protection for aquatic organisms such that continued exposure below the objective would be unlikely to cause negative effects (CCME 2011). References to the CWQO in the section below refer to the long term objective of 120 mg/L.

Trend Analysis

Median annual chloride concentrations have increased over the 50 years of monitoring. Although decreases in five year averages have been seen at four stations (GRN-5, SXM-216, SXM-349, and SXM-63) in recent years, the majority of stations have had increasing values, with four stations exceeding the chronic exposure CWQO of 120 mg/L for chloride during at least one of the five year intervals. Increases in chloride can be seen when moving from upstream stations downstream, following the pattern of urbanization which is more heavily concentrated at downstream locations. Three of the four stations with five year averages exceeding the CWQO between 2010 and 2014 (SHL-48, FOR-58, SXM-143) were located along Lakeshore Road, near the mouth of a creek. In addition, the station near the mouth of Grindstone Creek (GRN-5) was above the CWQO for the 2005-2009 sampling period. Figure 3 presents the changes in the five year average of median chloride concentrations at all stations.

Figure 3: Five year average of median annual chloride concentrations (1964-2014)



A statistically significant increase in median annual chloride concentrations was seen at 12 of the 19 stations when analyzed over their entire sampling period, with an additional two stations showing an increasing, but not statistically significant, trend.

When examining the three time frames (1965-2014, 1975-1996 and 2002-2014), the majority of stations which showed a statistically significant increase over their entire monitoring period also showed a significant increase in one or both of the shorter time frames. Twelve of the 13 stations monitored between 1975 and 1996 showed a significant increase, while only one (BRO-2) of the 11 stations monitored between 2002 and 2014 showed a significant increase. No stations showed a significant decrease. Table 5 summarizes the results of the Mann-Kendall analysis for chloride concentration, with test statistics provided in Appendix C. Time periods where "No trend" were found still showed increases over time, however these were not statistically significant at $p<0.05$.

Table 5: Median annual chloride trend analysis results

Watershed	Station	Overall Trend	1975-1996	2002-2014
Grindstone	GRN-114	Increasing	Increasing	--
	GRN-5	No trend	--	No Trend
	GRN-18	Increasing	Increasing	--
Sheldon	SHL-48	No trend	--	No Trend
Bronte	BRO-19	Increasing	Increasing	--
	BRO-119	No trend	--	No Trend
	BRO-264	Increasing	Increasing	--
	BRO-16	No trend	--	No Trend
	BRO-265	No trend	No Trend	--
	BRO-2	Increasing	Increasing	Increasing
Fourteen Mile	FOR-58	Increasing	Increasing	No Trend
Sixteen Mile	SXM-143	Increasing	Increasing	No Trend
	SXM-216	No trend	--	No Trend
	SXM-537	Increasing	Increasing	--
	SXM-61	Increasing	Increasing	--
	SXM-63	Increasing	Increasing	No Trend
	SXM-205	Increasing	Increasing	No Trend
	SXM-349	No trend	--	No Trend
	SXM-556	Increasing	Increasing	--

Seasonal differences in chloride were inconclusive, with each season having higher concentrations than the other two seasons at different locations. These differences showed that spring was significantly lower than summer at four stations (GRN-5, BRO-119, SXM-216 and SXM-63), while it was higher than summer at one station (SXM-205). Comparing between spring and fall showed mixed results with three stations (BRO-119, SXM-63 and SXM-349) showing lower concentrations in the spring and three stations (FOR-58, SXM-143 and SXM-205) showing lower concentrations in the fall. Summer and fall showed significant differences at three stations, two (GRN-5 and SXM-143) showed higher concentrations in the summer while one (SXM-349) showed higher concentrations in the fall. Three stations (SHL-48, BRO-16 and BRO-2) did not show significant differences between seasons. Table 6 provides the summary of the Kruskal-Wallis test results at all stations with test statistics presented in Appendix D.

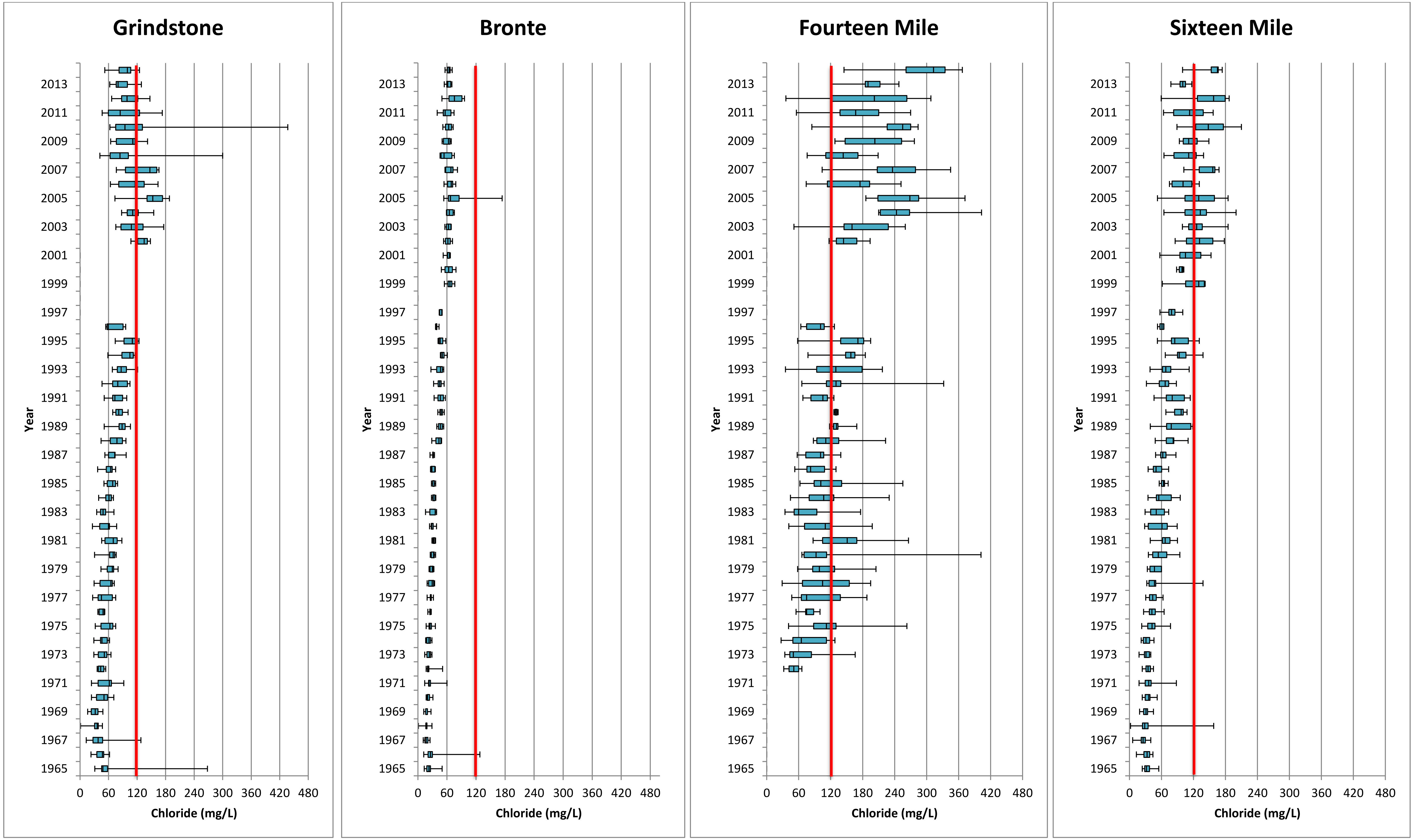
Table 6: Seasonal differences in median chloride concentrations (2002-2014)

Station	Spring vs. Summer	Spring vs. Fall	Summer vs. Fall	Seasonal Difference
GRN-5	Different	No difference	Different	Summer higher
SHL-48	No difference	No difference	No difference	
BRO-119	Different	Different	No difference	Spring lower
BRO-16	No difference	No difference	No difference	
BRO-2	No difference	No difference	No difference	
FOR-58	No difference	Different	No difference	Fall lower
SXM-143	No difference	Different	Different	Fall lower
SXM-216	Different	No difference	No difference	Spring lower
SXM-63	Different	Different	No difference	Spring lower
SXM-205	Different	Different	No difference	Spring higher
SXM-349	No difference	Different	Different	Fall higher

Spatial Comparison

Figure 4 shows how chloride concentrations have changed at the mouths of Grindstone, Bronte, Fourteen Mile and Sixteen Mile Creeks over the last 50 years. Concentrations within Grindstone Creek increased at a small but stable rate prior to 2002. Since that point, multiple years have had median concentrations above the CWQO, although decreases have been seen in the last six years. Maximum values continue to exceed the long term CWQO each year. Similar to Grindstone Creek, Sixteen Mile Creek saw small annual increases in chloride concentrations prior to 2002 at which point the increases became larger, with the majority of median concentrations exceeding the CWQO. Annual maximum concentrations greater than the CWQO have been seen 13 times in the last 14 years, with only 2013 not exceeding the CWQO at least once. Bronte Creek has consistently had concentrations below the CWQO with only two exceedances, once in 1966 and again in 2005. While concentrations have increased over time, the increase is small, with little variation between years. Chloride concentrations within Fourteen Mile Creek have increased substantially since monitoring began in 1972. Maximum concentrations over the CWQO have been seen during every sampling year except two (1972 and 1976), with concentrations since 1992 having exceeded the CWQO for at least half of the annual sampling events for the majority of years sampled. This indicates that chloride within the Fourteen Mile Creek watershed is likely causing aquatic impairment and negatively impacting the aquatic organisms within this watershed as they are chronically exposed to chloride levels in excess of the long term objective. No samples at the creek mouths have exceeded the short term objective of 640 mg/L.

Figure 4: Chloride concentrations at GRN-5, BRO-119, FOR-58 and SXM-143 (1964-2014)



Discussion

Significant increases in chloride seen throughout the watershed are likely a result of increasing density of roadways and the corresponding increasing use of road salt (Kelting *et al.* 2012). As Figure 3 showed, steady increases have been seen at nearly all stations over the last 50 years, with especially high results near the mouths of creeks. The last 13 years have seen multiple stations with median annual concentrations over the water quality objective for the long-term protection of aquatic health, indicating that aquatic organisms across the watershed are likely being negatively impacted by chloride as they are consistently exposed to high concentrations. One would expect chloride concentrations to be significantly higher during the spring melt, when excess road salt is being flushed into the creeks, however seasonal chloride analysis showed chloride concentrations to be variable over the season indicating that chloride is likely being stored on the landscape and released over time.

Currently, wastewater and stormwater technologies are unable to remove chlorides from water sources. As a result, continued efforts to reduce chloride use throughout the watershed should be encouraged in an effort to reduce concentrations in the stream environment. New methods of capturing chloride before it enters waterways should also be investigated.

Total Phosphorus

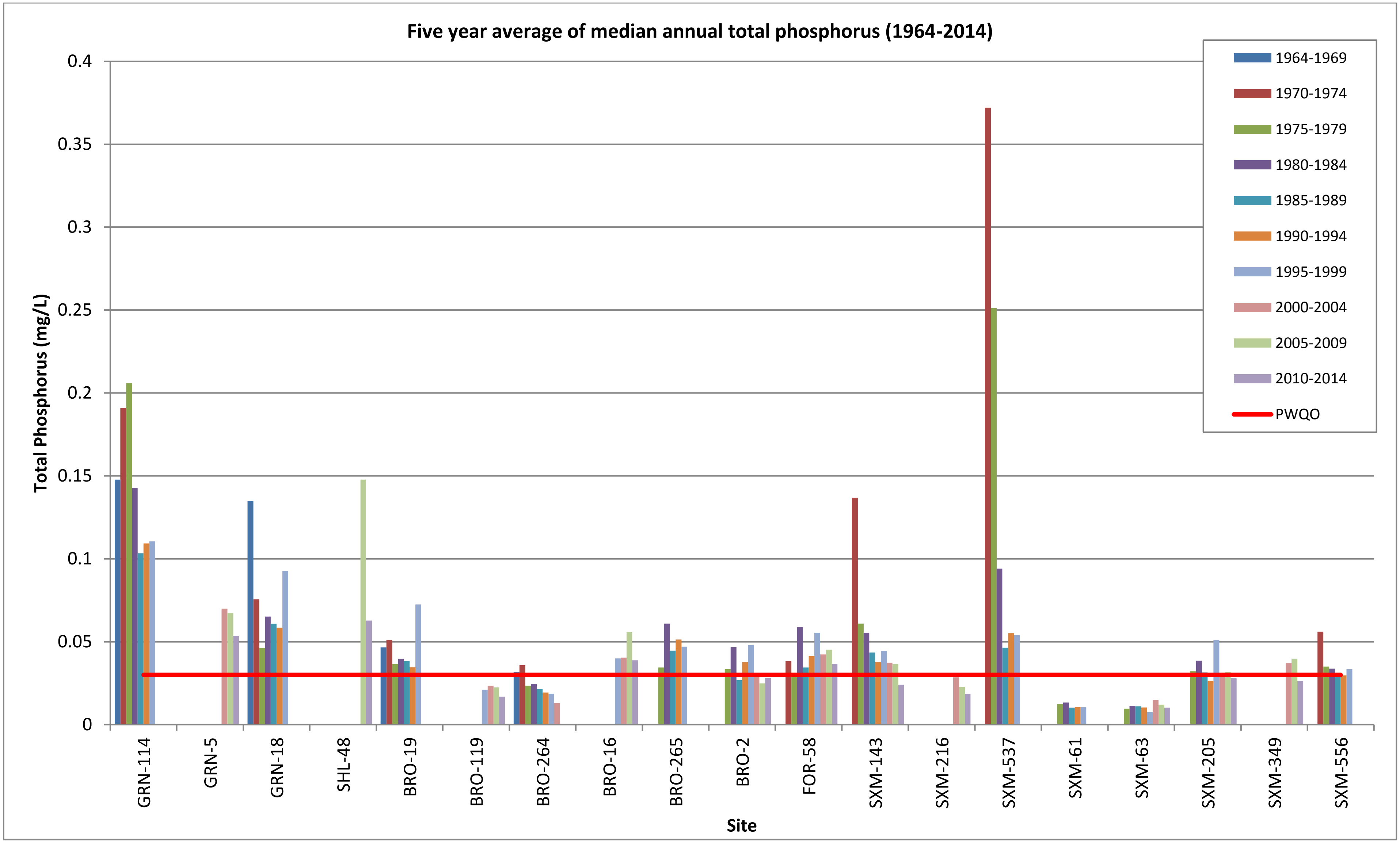
Sources of total phosphorus inputs to aquatic ecosystems include natural geologic weathering, municipal wastewater and agricultural application (Kolzau *et. al.* 2014). The effects of phosphorus in the aquatic environment have been widely studied, with the major issue pertaining to the increase in plant growth and eutrophication of an ecosystem, not direct toxicity of phosphorus to aquatic organisms (CCME 2004, Correll 1998, Rabalais 2002, Kolzau *et al.* 2014). While increases in plant growth can be beneficial, after a certain point it can result in decreases in ecologically sensitive species as species more tolerant to the changes in plant communities and oxygen regimes move in. In addition, changes in biota and decreases in biodiversity have been noted with increases in phosphorus (CCME 2004). Natural total phosphorus concentrations in streams are highly variable and setting an objective for all systems is not feasible as total phosphorus is not associated with toxicity levels but rather with indirect impacts of changes in plant communities.

The OMOECC provides a PWQO of 0.03 mg/L as a general guide for streams as levels below this point should prevent nuisance plant growth (OMOEE 1994). It should be noted that creeks within the CH watershed with total phosphorus concentrations over the PWQO do not necessarily represent impairment, but instead indicate areas where further study is required to understand the impact that total phosphorus may be having on the ecosystem.

Trend Analysis

Median annual total phosphorus concentrations have been decreasing over the last 50 years, with many stations at or below the PWQO. Figure 5 illustrates the changes in the five year average of median annual total phosphorus concentrations at all stations. Grindstone Creek has consistently had samples over the PWQO at all stations sampled during all five year time frames. The upper reaches of Bronte Creek (BRO-16, BRO-265, and BRO-2) have also seen elevated total phosphorus concentrations. In contrast to this, multiple stations (SXM-143, SXM-537, and SXM-556) within Sixteen Mile Creek have shown decreases in total phosphorus levels, with the majority of stations in this watershed having a five year average below the PWQO for 2010-2014.

Figure 5: Five year average of median annual total phosphorus concentrations (1964-2014)



A statistically significant decrease in median annual total phosphorus concentrations was seen at four of the 19 stations, while an additional 11 stations had decreasing, but not significant, trends. Table 7 summarizes the results of the Mann-Kendall analysis for total phosphorus over the entire monitoring period as well as the 1975-1996 and 2002-2014 time frames, with test statistics provided in Appendix C. All trends indicated in Table 7 were found to be statistically significant at $p<0.05$, stations which showed "No trend" still showed increases or decreases over time but were not statistically significant.

When examining the three separate time frames, two stations showed a statistically significant trend in the shorter time frames that was not seen over the entire monitoring period. FOR-58 was significantly increasing between 1975 and 1996, while SXM-63 was significantly decreasing between 2002 and 2014. Three of the four stations with a significant trend during the entire monitoring period also had significant trends during at least one of the shorter time frames. No stations have shown a significantly increasing trend in the last 13 years, although one station (SXM-205) did have an increasing, but not statistically significant trend, over this time.

Table 7: Median annual total phosphorus trend analysis results

Watershed	Station	Overall Trend	1975-1996	2002-2014
Grindstone	GRN-114	Decreasing	Decreasing	--
	GRN-5	No trend	--	No Trend
	GRN-18	No trend	No Trend	--
Sheldon	SHL-48	No trend	--	No Trend
Bronte	BRO-19	No trend	No Trend	--
	BRO-119	No trend	--	No Trend
	BRO-264	Decreasing	No Trend	--
	BRO-16	No trend	--	No Trend
	BRO-265	No trend	No Trend	--
	BRO-2	No trend	No Trend	No Trend
Fourteen Mile	FOR-58	No trend	Increasing	No Trend
Sixteen Mile	SXM-143	Decreasing	Decreasing	Decreasing
	SXM-216	No trend	--	No Trend
	SXM-537	Decreasing	Decreasing	--
	SXM-61	No trend	No Trend	--
	SXM-63	No trend	No Trend	Decreasing
	SXM-205	No trend	No Trend	No Trend
	SXM-349	No trend	--	No Trend
	SXM-556	No trend	No Trend	--

Seasonal differences in total phosphorus were examined using a Kruskal-Wallis test, and showed that summer was significantly higher at three stations (BRO-2, SXM-63 and SXM-349) and significantly lower at three stations (BRO-119, BRO-16 and SXM-205). One station, SXM-63, had significant differences between all 3 seasonal pairs, with the highest total phosphorus concentrations seen in the summer, followed by the fall with the lowest concentrations observed in the spring. Table 8 provides between season differences as well as a description of which season was different from the others. Test statistics are provided in Appendix D.

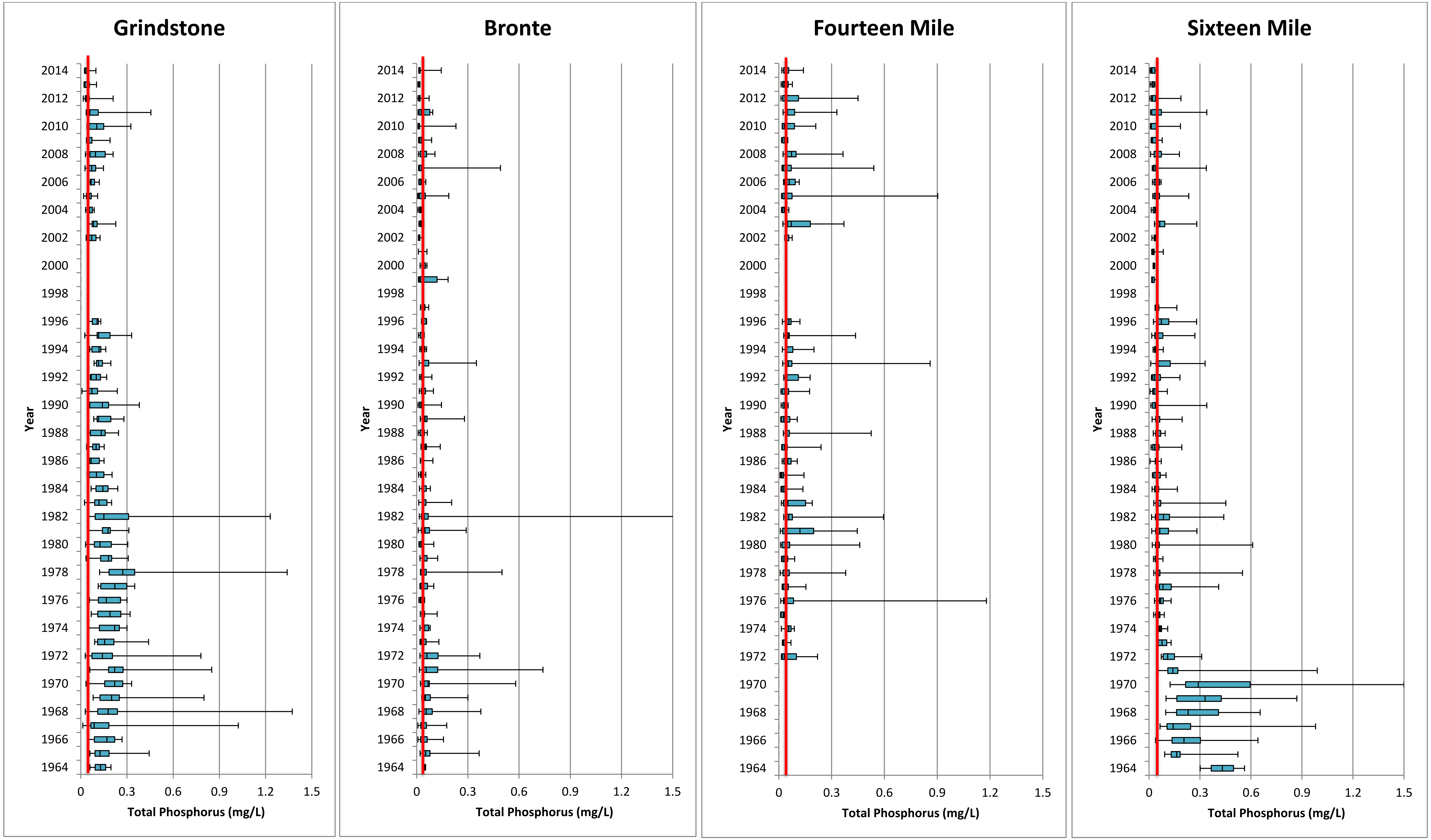
Table 8: Seasonal differences in median total phosphorus concentrations (2002-2014)

Station	Spring vs. Summer	Spring vs. Fall	Summer vs. Fall	Seasonal Difference
GRN-5	No difference	No difference	No difference	
SHL-48	No difference	No difference	No difference	
BRO-119	Different	No difference	Different	Summer lower
BRO-16	No difference	No difference	Different	Summer lower
BRO-2	Different	No difference	Different	Summer higher
FOR-58	No difference	No difference	No difference	
SXM-143	No difference	No difference	No difference	
SXM-216	No difference	No difference	No difference	
SXM-63	Different	Different	Different	Summer highest, spring lowest
SXM-205	Different	No difference	No difference	Summer lower
SXM-349	No difference	No difference	Different	Summer higher

Spatial Comparison

Figure 6 shows how total phosphorus concentrations have changed near the mouths of Grindstone, Bronte, Fourteen Mile and Sixteen Mile Creeks. Concentrations in Grindstone Creek have decreased since the beginning of the 1980's. Median concentrations are above the PWQO for the entire monitoring period, however they have been only slightly elevated during the last five years. The spread of values in the 1970's and 1980's was large, with maximum values close to 50 times higher than the PWQO. The overall spread has decreased over the last 50 years, although maximum values 10 times higher than the PWQO are still occurring. Concentrations in Bronte Creek have remained relatively stable, with only small decreases since 1975. Despite these decreases, values continue to fluctuate around the PWQO. During most years the spread of values over the season was small with few high measurements of total phosphorus. Concentrations in Fourteen Mile Creek have remained stable over the entire monitoring period, and continue to exceed the PWQO on a regular basis. The spread of values is large each year, with maximum concentrations more than 10 times greater than the PWQO. Concentrations in Sixteen Mile Creek decreased dramatically between 1965 and 1972, and have remained relatively stable since that time. Similar to Bronte Creek, the spread of values over the season was small, with higher maximum values seen in the 1970's and 1980's.

Figure 6: Total phosphorus concentrations at GRN-5, BRO-119, FOR-58 and SXM-143 (1964-2014)



Discussion

Decreases in total phosphorus concentrations over the last 50 years have occurred across the watershed. In general, decreases have been seen in both agricultural and urban areas. Dramatic decreases in urban areas in the early 1970's have occurred, likely as result of the Phosphorus Concentration Regulations (1989) which restricted the use of phosphorus in laundry detergent (Government of Canada 1999). The implementation of stormwater management ponds in the 1980's may have further reduced the amount of phosphorus entering streams as water containing phosphorus was detained on the landscape for a longer period. This would provide time for phosphorus to bind to suspended sediment and settle to the bottom of the pond, therefore reducing the amount of phosphorus within the stream. In addition to the reduction of phosphorus in detergent, wastewater treatment plants (WWTP) in the 1970's typically had effluent limits around 1mg/L. This was further decreased in the 1990's when limits were reduced to 0.5 mg/L. As WWTPs are upgraded or expanded these limits are often decreased again to less than 0.1mg/L (Kraemer 2015). Reduction of effluent limits results in decreases of total phosphorus at a point source, however non-point sources continue to provide TP to streams.

The highest watershed-wide phosphorus concentrations have been seen in Grindstone Creek, likely as a result of nutrient application to the many agricultural areas throughout this watershed. Although concentrations are high, there have been decreases at all stations monitored in Grindstone Creek, with significant decreases seen at GRN-114. Sampling completed by the Royal Botanical Gardens over the last 15 years has continued to show decreasing trends at their sampling station at the mouth of Grindstone Creek, approximately 20 m downstream of GRN-114 (Bowman 2016).

Decreases at SXM-537 within the west branch of Sixteen Mile Creek are likely associated with the Milton Wastewater Treatment Plant located upstream. Changes in phosphorus use as a result of the Phosphorus Concentration Regulations likely decreased the levels of total phosphorus entering the plant and therefore decreased the amount of total phosphorus present in the effluent leaving the plant. Although total phosphorus inputs at this station have decreased, impacts of high total phosphorus levels are still seen with excess macrophytes and algae present throughout this section of Sixteen Mile Creek. Abundance of algae decreases at SXM-216 although macrophytes and algae are still present each year.

Seasonal trends in total phosphorus do not provide conclusive evidence for when higher concentrations could be expected. Seasonal variation in total phosphorus concentrations is driven by both riparian and instream processes that can vary across geographic areas. Riparian areas can act as either a sink for phosphorus or a source of phosphorus depending on surrounding land use and sediment conditions, with phosphorus-starved sediment taking up inorganic phosphorus from streams, while anthropogenic application of phosphorus to riparian areas provides a source to streams. Instream processes such as uptake by plants, algae and microbes influences the availability of phosphorus within the water and can result in low phosphorus concentrations if it is the limiting factor. However, when phosphorus is abundant, uptake by aquatic communities will have little impact on the concentration of total phosphorus (Mulholland 1992). Site specific analysis of total phosphorus seasonal variation should be completed to help guide total phosphorus management decisions.

Total Suspended Solids

Total suspended solids (TSS) are made up of both organic and inorganic material such as silt, clay, plankton and microscopic organisms. The largest source of TSS is natural erosion followed by anthropogenic activities. Natural erosion rates are affected by extremity of precipitation events, destabilization of stream banks resulting from changes to riparian vegetation, natural slope of stream banks and soil type (CCME 2002). TSS affects biological processes in streams in part by affecting respiration in fish and creating unsuitable habitat for benthic macroinvertebrate populations, thereby changing the structure of the aquatic community (CCME 2002). TSS also affects the fluvial geomorphology of a stream by changing the supply of sediment to the stream. When the supply of sediment is greater than the ability of the stream to transport that sediment, deposits will occur in slower moving areas where the sediment is able to settle out. This can change the dynamics of the stream and further impact both physical and biological processes (Hogan and Luzi 2010). The CWQO for TSS uses both short and long term exposure objectives for water quality. In the short term the CWQO is 25 mg/L over background concentrations during a 24 hour period. In the long term the CWQO is 5 mg/L over background concentrations for exposure lasting longer than 30 days.

Methods for determining background concentrations are varied and include sampling prior to disturbance or sampling of reference locations (CCME 2003). Sampling prior to disturbance is not possible within the CH watershed as water quality sampling began after anthropogenic disturbances within the watershed had begun. Instead, three stations that would best represent reference conditions were used for determining background levels. The first station (BRO-2) is located upstream of Highway 401 in Bronte Creek, the second (SXM-63) is located upstream of Kelso Reservoir in Sixteen Mile Creek and the third (GRN-60) is located in Grindstone Creek downstream of the Fuciarelli wetland. Analysis of TSS at these three stations provided average concentrations of 2.75, 2.4 and 4.2 mg/L respectively over their entire monitoring period which results in a watershed average of 3.11 mg/L. Based on this, it is assumed that a water sample collected within any stream in the watershed would naturally contain 3.11 mg/L of TSS. To calculate the short term exposure CWQO, the background level was added to the short term exposure objective of 25 mg/L, resulting in a CWQO of 28.11 mg/L . It should be noted that the reference station sampled within Grindstone Creek was monitored outside of the PWQMN and was only sampled in 2013 and 2014. Sampling of TSS within CH streams has been sporadic, with only three stations (BRO-19, FOR-58 and SXM-143) sampled consistently between 1982 and 1994.

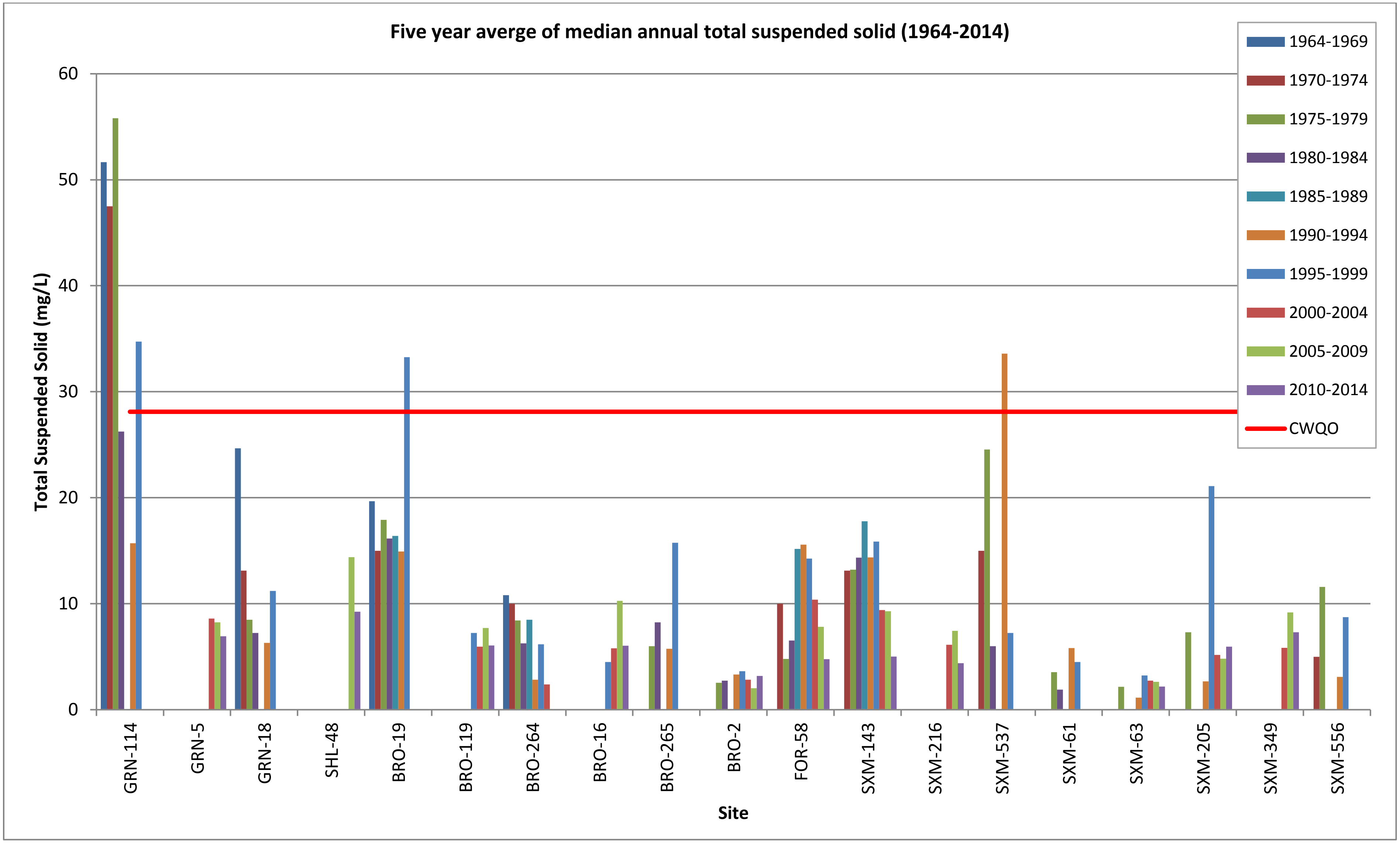
Trend Analysis

Accurately capturing changes in TSS trends is challenging because its largest source is natural erosion. During dry weather, natural erosion is likely to be minimal, with erosion rates increasing with higher levels of precipitation. Responses of watercourses to precipitation events follow a standard hydrograph pattern, with water levels increasing to a maximum point, and then decreasing to pre-event levels when the storm has concluded. Concentrations of TSS within a stream during a storm follow the same pattern as water levels, with highest levels expected during the peak of the hydrograph. Sampling at any time other than the peak will yield lower concentrations of TSS than were experienced by aquatic organisms at some point during the course of the storm.

The influence of precipitation on TSS often results in annual data with both very high and very low concentrations depending on the number and magnitude of storm events that were sampled. Years where storm events were sampled more often than dry events will have median concentrations much higher than years where dry events were sampled more often than storm events. Since 2002 sampling has been completed such that an even number of storm and dry events were sampled each year, however it is not known if this methodology was used prior to 2002. In addition, information about the magnitude (i.e. amount of precipitation) of each storm event was not recorded and it is possible that a given year may have many very small or very large storm events. High median values could be misinterpreted as anthropogenic impact at a given station when the reality may be a higher than average precipitation level or greater storm event sampling and caution should be used when examining these values. For the purpose of this report TSS was analyzed according to the same methods used for the analysis of all other parameters.

Median annual total suspended solid concentrations have been decreasing over the last 50 years, with many stations at or below the CWQO. Figure 7 represents the changes in the five year average of median annual total suspended solid concentrations at all stations. The mouth of Grindstone Creek (GRN-114) has consistently had samples in excess of the CWQO during most years, while most other stations have been below the CWQO.

Figure 7: Five year average of median annual total suspended solid concentrations (1964-2014)



A statistically significant decrease in median annual total suspended solid concentrations was seen at two of the 19 stations. An additional nine stations had decreasing, but not significant, trends.

When examining the three separate time frames, three stations showed a statistically significant trend in at least one of the shorter time frames that was not seen over the entire monitoring period. BRO-2 and FOR-58 were significantly increasing between 1975 and 1996, while GRN-114 was significantly decreasing over this time. SXM-143 had a significantly decreasing trend over the entire monitoring period, but only showed a decreasing trend over the 1975-1996 period. BRO-264 showed a decreasing trend over the entire period, but did not show a trend in either of the shorter time frames, indicating that samples taken prior to 1975 had a large influence on the trend analysis. No stations showed significant trends in the last 13 years. Table 9 summarizes the results of the Mann-Kendall analysis for total suspended solids, showing which stations had statistically significant trends at $p<0.05$. Test statistics are provided in Appendix C.

Table 9: Median annual total suspended solids trend analysis results

Watershed	Station	Overall Trend	1975-1996	2002-2014
Grindstone	GRN-114	No trend	Decreasing	--
	GRN-5	No trend	--	No Trend
	GRN-18	No trend	No Trend	--
Sheldon	SHL-48	No trend	--	No Trend
Bronte	BRO-19	No trend	No Trend	--
	BRO-119	No trend	--	No Trend
	BRO-264	Decreasing	No Trend	--
	BRO-16	No trend	--	No Trend
	BRO-265	No trend	No Trend	--
	BRO-2	No trend	Increasing	No Trend
Fourteen Mile	FOR-58	No trend	Increasing	No Trend
Sixteen Mile	SXM-143	Decreasing	Decreasing	No Trend
	SXM-216	No trend	--	No Trend
	SXM-537	No trend	No Trend	--
	SXM-61	No trend	No Trend	--
	SXM-63	No trend	No Trend	No Trend
	SXM-205	No trend	No Trend	No Trend
	SXM-349	No trend	--	No Trend
	SXM-556	No trend	No Trend	--

Seasonal changes in total suspended solids were examined using a Kruskal-Wallis test, which showed that spring was significantly higher than summer at four stations (GRN-5, SXM-143, SXM-216 and SXM-205), fall was significantly lower than spring and summer at three stations (BRO-2, SXM-63 and SXM-34) and summer was significantly lower than spring and fall at one station (BRO-16). Given the impact of precipitation on TSS concentrations, it is not surprising that spring would have higher concentrations of TSS as precipitation and runoff are expected to be higher during spring freshet and the magnitude of storm events sampled in spring is likely greater as well. Table 10 provides between season differences as well as a description of which season was different from the others, with test statistics provided in Appendix D.

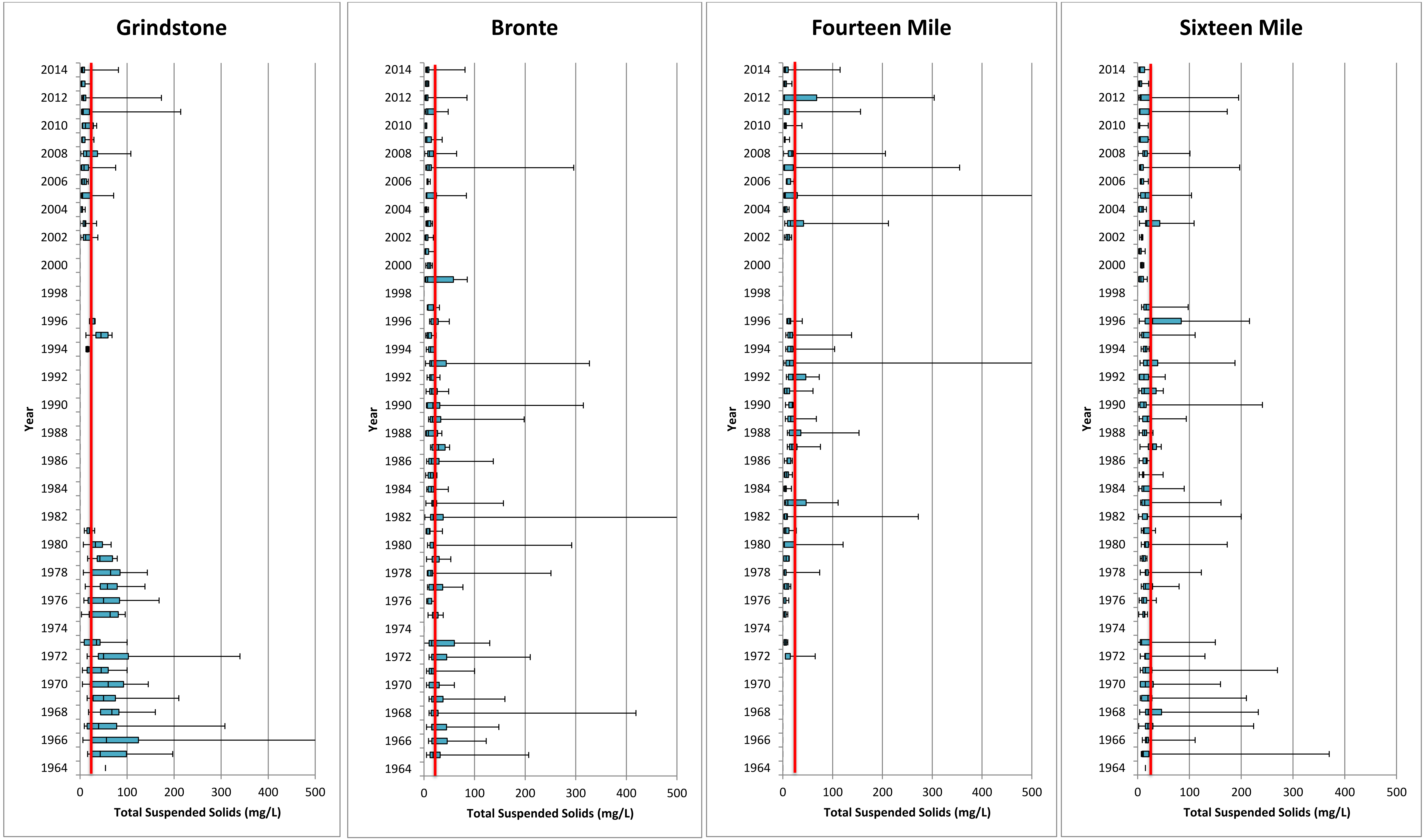
Table 10: Seasonal differences in median total suspended solid concentrations (2002-2014)

Station	Spring vs. Summer	Spring vs. Fall	Summer vs. Fall	Seasonal Difference
GRN-5	No difference	Different	No difference	Spring higher
SHL-48	No difference	No difference	No difference	
BRO-119	No difference	No difference	No difference	
BRO-16	Different	No difference	Different	Summer lower
BRO-2	No difference	Different	Different	Fall lower
FOR-58	No difference	No difference	No difference	
SXM-143	Different	Different	No difference	Spring higher
SXM-216	Different	No difference	No difference	Spring higher
SXM-63	No difference	Different	Different	Fall lower
SXM-205	Different	No difference	No difference	Spring higher
SXM-349	No difference	Different	Different	Fall lower

Spatial Comparison

Figure 8 shows how total suspended solid concentrations have changed at the mouths of Grindstone, Bronte, Fourteen Mile and Sixteen Mile Creeks over the last 50 years. Grindstone Creek has had decreasing concentrations of TSS over the last 50 years. Between 1964 and 1981 the spread of values was large, with maximum concentrations well above the CWQO of 28.11 mg/L. Since the early 2000's median concentrations within Grindstone Creek have been below the CWQO and the spread of values has been small. Median annual concentrations within Bronte Creek have remained below the CWQO for most years sampled. The spread of values each year has decreased, indicating that surges of sediment moving during rain events may be decreasing. Despite these results, sediment within Bronte Harbour continues to be an issue with plumes often seen in Lake Ontario after a large storm event. Further investigation into the load of sediment moving through the watershed should be conducted for a better understanding of TSS dynamics, but is beyond the scope of the PWQMN. Both Fourteen Mile and Sixteen Mile Creeks have shown TSS concentrations similar to Bronte Creek. Although maximum concentrations may exceed the CWQO on a regular basis, median concentrations remain below the CWQO and indicate that TSS is not likely to cause impairment at these stations. Further investigation of TSS levels across the watershed should be completed in areas where impact by TSS is expected, such as areas under development where riparian buffers have been removed and topsoil is exposed.

Figure 8: Total suspended solid concentrations at GRN-5, BRO-119, FOR-58 and SXM-143 (1964-2014)



Discussion

Total suspended solids do not appear to be causing aquatic impairment over the long term at the 19 stations sampled throughout the Conservation Halton jurisdiction. TSS concentrations exceeding the CWQO are typically associated with rain events when TSS is expected to be elevated. Average median concentrations of TSS have been well below the CWQO at all stations except GRN-114 at the mouth of Grindstone Creek. While this station consistently experienced high TSS concentrations in the 1980's and 1990's, monitoring upstream at GRN-5 has not continued to show this trend during the last 13 years. Sampling by the Royal Botanical Gardens at a station near GRN-114 has shown TSS concentrations have remained stable over the last 16 years with median annual concentrations around 25 mg/L (Bowman 2016). Influences of Common Carp within Carroll's Bay could account for the elevated concentrations seen early on in the monitoring period. In addition, soils within the Grindstone Creek watershed are more easily eroded than soils within other watersheds and are dominantly comprised of sand plains, till moraines and the Niagara Escarpment (Halton-Hamilton Source Protection 2011). This is especially true within the tributaries draining the Niagara Escarpment, where high gradients combined with erodible soils create an environment of higher natural erosion rates (Halton Region Conservation Authority 1998). Seasonal trends indicate that TSS tends to be higher in spring when concentrations are associated with spring freshet and rain event sampling. The low concentrations observed in fall sampling can be expected as vegetation helps to stabilize soil along stream banks.

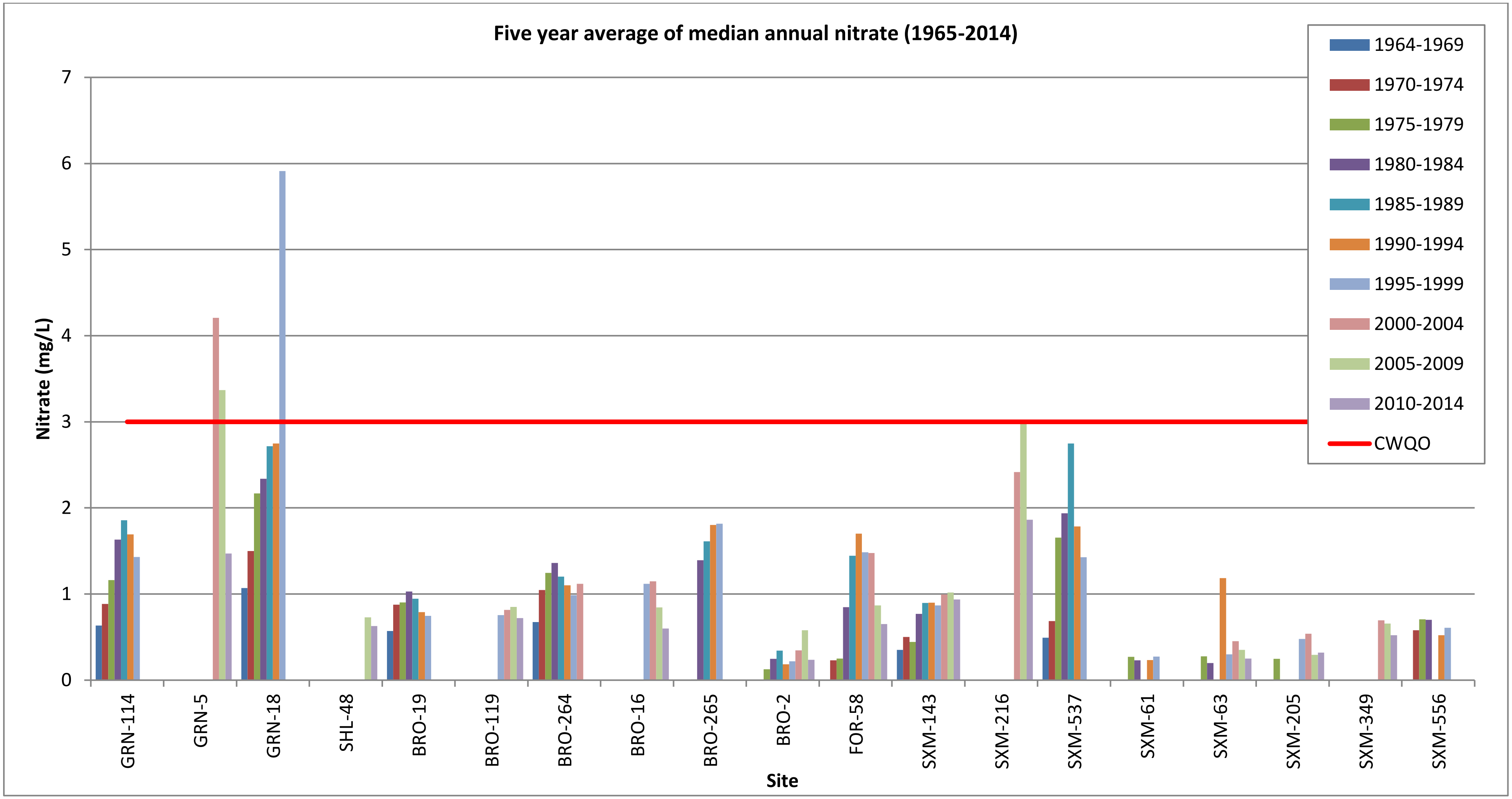
Nitrate

Anthropogenic nitrate sources include wastewater from municipal and industrial sources, septic beds, agricultural and urban runoff as well as lawn fertilizers and storm sewer overflows (CCME 2012). As an essential nutrient for plant growth, excess nitrate can result in increased algal and macrophyte growth which may lead to a decrease in water clarity and changes to biological communities as a result of the changes in water quality and habitat (CCME 2012). The CWQO for nitrate is 3 mg/L.

Trend Analysis

Median annual nitrate concentrations have shown both increasing and decreasing trends over the entire monitoring period. Concentrations increased during the 1970's and 1980's, then began to level off and have remained stable or decreased over the last 13 years. Only two stations (GRN-5 and GRN-18) have seen five year average concentrations over the CWQO of 3 mg/L. In addition, GRN-18 has consistently had increases in five year average concentrations, with each 5 year period having a higher average than the preceding one. Figure 9 illustrates the changes in the five year average of annual median nitrate concentrations at all stations.

Figure 9: Five year average of median annual nitrate concentrations (1965-2014)



Eight stations showed a statistically significant trend in median annual nitrate concentrations, with six stations showing an increase and two stations showing a decrease over the entire monitoring period.

When examining the three separate time frames, three stations showed a statistically significant trend in at least one of the shorter time frames that was not seen over the entire monitoring period. BRO-19 was significantly decreasing between 1975 and 1996, while SXM-63 and BRO-119 were significantly decreasing between 2002 and 2014. GRN-114, GRN-18, BRO-2, SXM-143 and SXM-537 had significantly increasing trends over the entire monitoring period, but did not show a trend in either of the shorter time frames. FOR-58 was unique in that it was significantly increasing during the first time frame (1975-1996), but significantly decreasing during the second time frame (2002-2014). Over the entire monitoring period it showed a significantly increasing trend. No stations showed a statistically significant increase in nitrate over the last 13 years. Table 11 summarizes the results of the Mann-Kendall analysis for nitrate. Test statistics are provided in Appendix C.

Table 11: Median annual nitrate concentration trend analysis results

Watershed	Station	Overall Trend	1975-1996	2002-2014
Grindstone	GRN-114	Increasing	No Trend	--
	GRN-5	Decreasing	--	Decreasing
	GRN-18	Increasing	No Trend	--
Sheldon	SHL-48	No trend	--	No Trend
Bronte	BRO-19	No trend	Decreasing	--
	BRO-119	No trend	--	Decreasing
	BRO-264	No trend	No Trend	--
	BRO-16	No trend	--	No Trend
	BRO-265	No trend	No Trend	--
	BRO-2	Increasing	No Trend	No Trend
Fourteen Mile	FOR-58	Increasing	Increasing	Decreasing
Sixteen Mile	SXM-143	Increasing	No Trend	No Trend
	SXM-216	No trend	--	No Trend
	SXM-537	Increasing	No Trend	--
	SXM-61	No trend	No Trend	--
	SXM-63	No trend	No Trend	Decreasing
	SXM-205	No trend	No Trend	No Trend
	SXM-349	Decreasing	--	Decreasing
	SXM-556	No trend	No Trend	--

Seasonal changes in nitrate were examined using a Kruskal-Wallis test, and similar to the temporal trend analysis showed variation across the watershed, with some stations showing higher concentrations in the spring while others showed lower concentrations in spring. Table 12 provides a summary of the results of the Kruskal-Wallis test, while test statistics are provided in Appendix D.

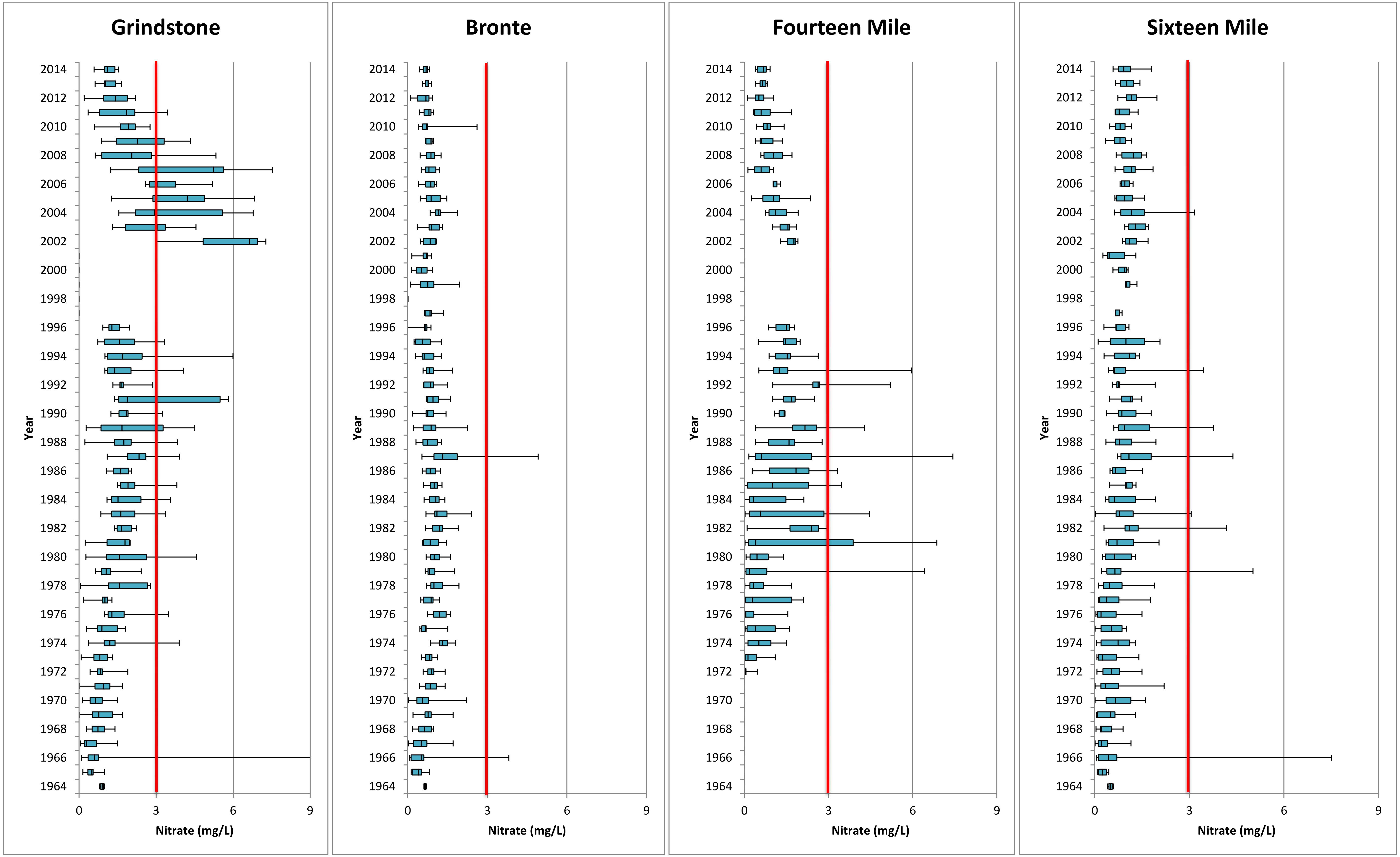
Table 12: Seasonal differences in median nitrate concentrations (2002-2014)

Station	Spring vs. Summer	Spring vs. Fall	Summer vs. Fall	Seasonal Difference
GRN-5	Different	Different	No difference	Spring lower
SHL-48	Different	Different	No difference	Spring higher
BRO-119	No difference	No difference	No difference	
BRO-16	No difference	No difference	Different	Summer lower
BRO-2	No difference	No difference	No difference	
FOR-58	No difference	No difference	No difference	
SXM-143	No difference	No difference	Different	Summer lower
SXM-216	Different	Different	No difference	Spring lower
SXM-63	No difference	No difference	No difference	
SXM-205	Different	Different	No difference	Spring higher
SXM-349	Different	Different	Different	Spring highest, fall lowest

Spatial Comparison

Figure 10 illustrates how nitrate concentrations have changed at the mouths of Grindstone, Bronte, Fourteen Mile and Sixteen Mile Creeks over the last 50 years. Nitrate concentrations within Grindstone Creek steadily increased from the beginning of monitoring in the 1960's up to the early 2000's. Since 2002, where median concentrations were more than double the CWQO, levels have begun decreasing, with no exceedances of the CWQO in the last six years. Nitrate concentrations within Bronte and Sixteen Mile Creeks have remained fairly stable over the entire monitoring period, and have rarely exceeded the CWQO. The spread of values each year at both stations has been small, with median concentrations around 1 mg/L. Nitrate within Fourteen Mile Creek was low in the 1970's, increased in the 1980's and 1990's, and has decreased again in the last 13 years. The last sample to exceed the CWQO at the mouth of Fourteen Mile Creek was in 1993.

Figure 10: Nitrate concentrations at GRN-5, BRO-119, FOR-58 and SXM-143 (1964-2014)



Discussion

Nitrate does not appear to be causing aquatic impairment at the stations monitored throughout the watershed. Although exceedances of the CWQO have been seen, they are at a low frequency and do not appear to be a regular occurrence. The analysis of seasonal trends of nitrate was inconclusive, with spring having higher concentrations for some stations while having lower concentrations for others. Coats and Goldman (2001) found nitrate in streams to be highest during winter with increases often associated with melt events. Stations which showed higher spring concentrations may be showing the influence of melt events on nitrate however further winter sampling would be required to determine if this accounts for the seasonal variation. Samples collected at the mouths of the creeks indicate that nitrate levels have been either consistently low or are decreasing.

Nitrate levels within Grindstone Creek have decreased dramatically between 2002 and 2014. GRN-5 is located downstream of the Waterdown wastewater treatment plant (WWTP) effluent tributary. The WWTP was taken offline in 2010 and initial analysis of the data indicates that this may have contributed to the decrease in nitrates seen at GRN-5 after this time. However comparison of data collected at GRN-18 upstream of the WWTP with data collected at GRN-114 located downstream between 1965 and 1996 shows GRN-18 having much higher concentrations during the same sampling events. This indicates that the WWTP was not the source of nitrate as concentrations in the creek were high before the WWTP effluent entered the stream. Further investigation into sources of nitrate within the watershed would have been necessary in the early 2000’s to determine causes of the decrease.

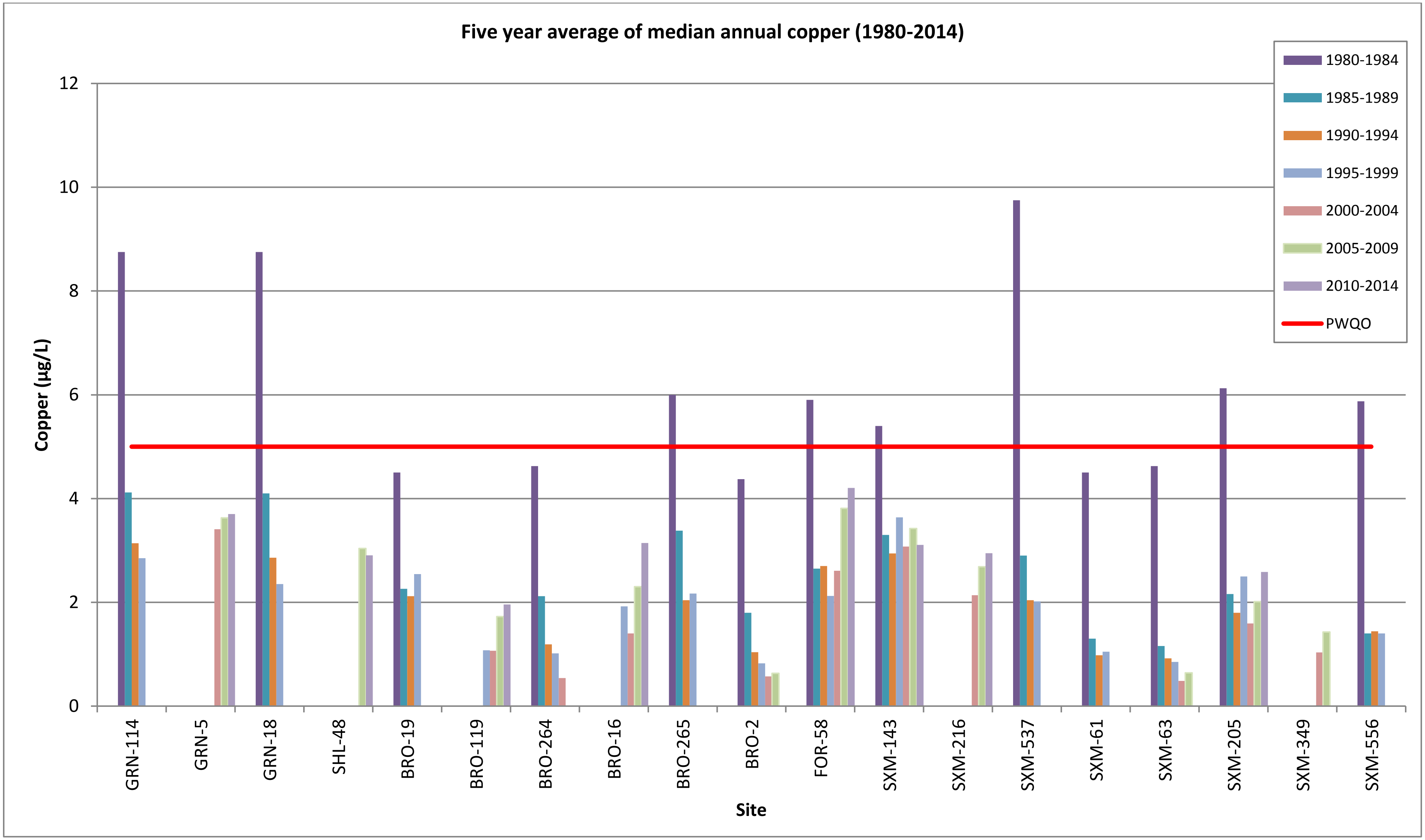
Copper

Copper is an essential metal for both aquatic and terrestrial organisms and is beneficial at low doses. As concentrations of copper increase, toxic effects can be seen such as damage to invertebrate gills and interference with osmoregulation in fish (Eisler 1998). Anthropogenic sources of copper inputs to aquatic ecosystems include mining, agricultural fertilizers, roads and parking lots, municipal waste and electronic equipment production (Eisler 1998, EPA 2007, Solomon 2009). The PWQO for copper is 5 µg/L at hardness levels greater than 20 mg/L (OMOEE 1994). Hardness levels within the Conservation Halton watershed have not been measured below 88 mg/L and were 274 mg/L on average over the entire monitoring period, therefore the objective of 5 µg/L applies across the watershed.

Trend Analysis

Copper has not been consistently sampled over the entire 50 years, and trend analysis will focus on samples collected between 1980 and 2014 as this time period has multiple samples collected per year at each station sampled. Median annual copper concentrations have decreased over the last 35 years, with five year average concentrations exceeding the PWQO only during the 1980-1984 time frame. Analysis methods at the laboratory changed in 1984 and likely explain the higher values before this time. To better assess trends over time, values between 1980 and 1984 were removed from the analysis so that trends seen represent changes in the environment not changes to laboratory methods. Figure 11 shows how the five year average of median annual copper concentrations has changed since 1980.

Figure 11: Five year average of median annual copper concentrations (1980-2014)



Changes in median annual copper concentrations over time at each station were examined using a Mann-Kendall test. Statistically significant trends were seen at 12 stations, with 10 stations showing a decreasing trend while two stations showed an increasing trend. Both stations showing an increasing trend were located within the Bronte Creek watershed, at BRO-119 and BRO-16.

When examining the three separate time frames, one station showed statistically significant trends over at least one of the shorter time frames that was not seen over the entire monitoring period. SXM-63 was significantly increasing between 1985 and 1996, but showed no trend for the entire monitoring period. Seven stations showing a trend in 1985-1996 were increasing, while one station (BRO-265) showed a decreasing trend during this period. Of the 11 stations that have been monitored since 2002, three have shown a significantly increasing trend while four have shown an increasing, but not statistically significant, trend in copper concentrations. Table 13 provides a summary of the Mann-Kendall tests, with test statistics provided in Appendix C.

Table 13: Median annual copper trend analysis results

Watershed	Station	Overall Trend	1985-1996	2002-2014
Grindstone	GRN-114	No trend	No trend	--
	GRN-5	No trend	--	No Trend
	GRN-18	No trend	No trend	--
Sheldon	SHL-48	No trend	--	No Trend
Bronte	BRO-19	Increasing	Increasing	--
	BRO-119	Increasing	--	Increasing
	BRO-264	No trend	No trend	--
	BRO-16	Increasing	--	Increasing
	BRO-265	Decreasing	Decreasing	--
	BRO-2	No trend	No trend	No Trend
Fourteen Mile	FOR-58	Increasing	Increasing	No Trend
Sixteen Mile	SXM-143	Increasing	Increasing	No Trend
	SXM-216	No trend	--	No Trend
	SXM-537	No trend	No trend	--
	SXM-61	Increasing	Increasing	--
	SXM-63	No trend	Increasing	No Trend
	SXM-205	Increasing	Increasing	Increasing
	SXM-349	No trend	--	No Trend
	SXM-556	Increasing	Increasing	--

Seasonal differences in copper concentrations were examined using a Kruskal-Wallis test. Three stations (BRO-119, BRO-16 and SXM-205) showed differences between seasons, with all stations showing higher copper concentrations in the spring. Both BRO-119 and BRO-16 showed higher concentrations only when compared with summer, while SXM-205 showed higher concentrations in spring than in summer and fall. Table 14 provides a summary of the seasonal differences, with test statistics provided in Appendix D.

Table 14: Seasonal differences in median copper concentrations (2002-2014)

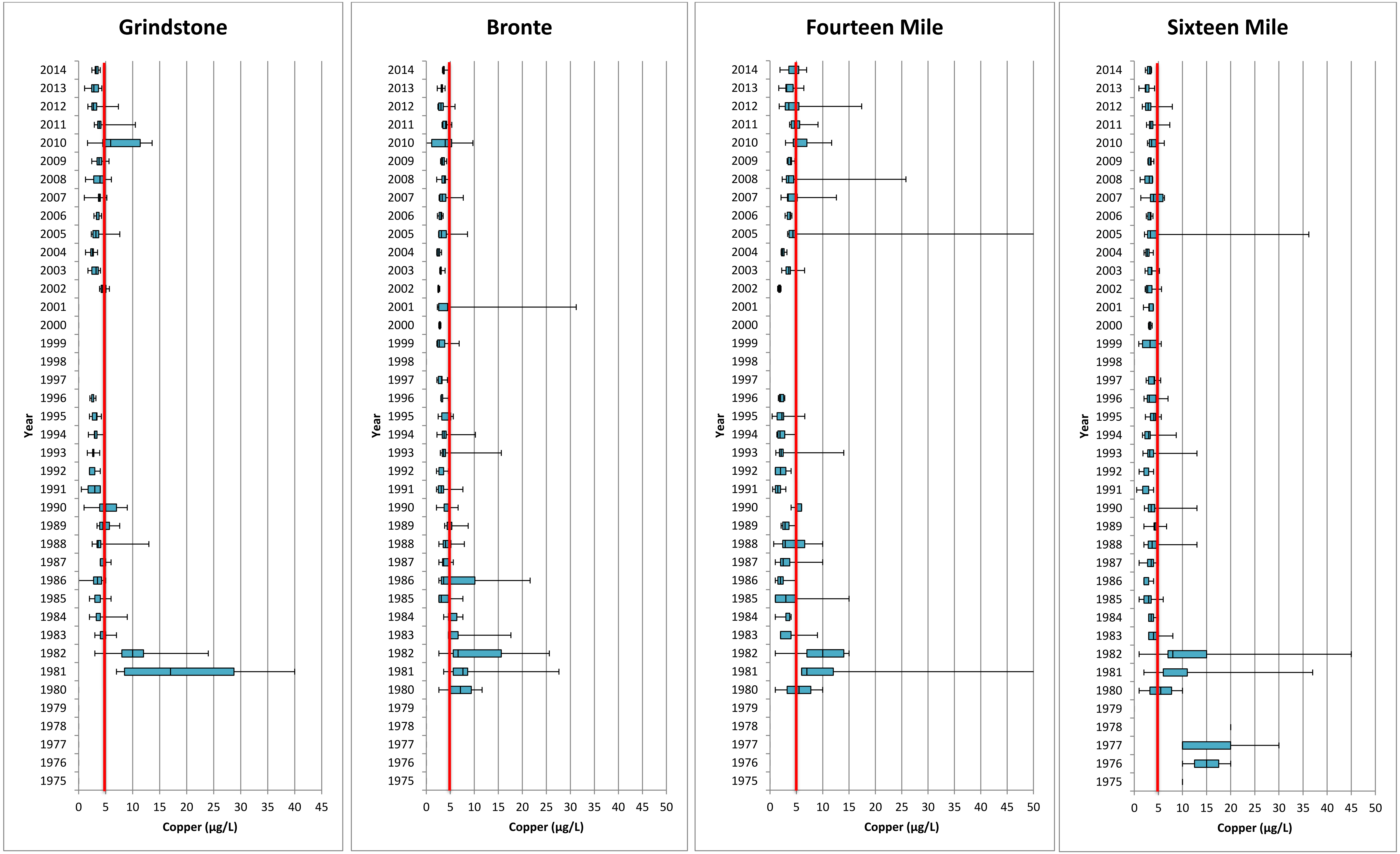
Station	Spring vs. Summer	Spring vs. Fall	Summer vs. Fall	Seasonal Difference
GRN-5	No difference	No difference	No difference	
SHL-48	No difference	No difference	No difference	
BRO-119	Different	No difference	No difference	Spring higher
BRO-16	Different	No difference	No difference	Spring higher
BRO-2	No difference	No difference	No difference	
FOR-58	No difference	No difference	No difference	
SXM-143	No difference	No difference	No difference	
SXM-216	No difference	No difference	No difference	
SXM-63	No difference	No difference	No difference	
SXM-205	Different	Different	No difference	Spring higher
SXM-349	No difference	No difference	No difference	

Correlation coefficients were calculated to better understand the relationship between copper and TSS. A significant positive correlation was found at 15 of the 19 stations indicating that higher levels of copper are seen in conjunction with higher levels of TSS as may be experienced during storm events. Stations which did not show a correlation between copper and TSS were BRO-2, SXM-556, SXM-61 and SXM-63. Correlation coefficients and test statistics are presented in Appendix E.

Spatial Comparison

Figure 12 shows how copper concentrations at the mouths of Grindstone, Bronte, Fourteen Mile and Sixteen Mile Creeks have changed over the entire monitoring period. Exceedances of the PWQO of 5 µg/L were common at all stations during the 1980's, with most years having median concentrations above this level. Since that time concentrations have decreased at all stations, although maximum values continue to exceed the PWQO during most years.

Figure 12: Copper concentrations at GRN-5, BRO-119, FOR-58 and SXM-143 (1975-2014)



Discussion

Copper is not currently a metal of concern within the watershed, as concentrations remain below the PWQO for most samples. There have been small increases in concentration over time, and if this trend continues copper could become a toxic factor within the aquatic ecosystem. Research shows that when copper is found in areas with high chloride concentrations, the chloride increases the bioavailability of copper, thus increasing the effect copper could have at a lower concentration (Warren and Zimmerman 2004). This causes concern for Fourteen Mile Creek where chloride concentrations continually exceed the CWQO and copper concentrations are also increasing and have exceeded the PWQO during at least one sampling event annually for the last five years.

Seasonal analysis showed spring had higher copper concentrations than both other seasons. This could be a result of increased runoff and a higher proportion of wet event sampling occurring in the spring. In addition, copper may be stored on the landscape over the winter and spring freshet could release this into the aquatic environment when runoff increases and metals are released from previously frozen surfaces. Hart (1982) found that total suspended sediment binds heavy metals and provides an important transport mechanism for metals to reach aquatic ecosystems. Once sediment with copper enters a stream the pH levels within the stream determine the availability of copper to the ecosystem, with higher pH levels resulting in copper remaining bound to the suspended sediment and being immobilized within the ecosystem (Bambric *et al.* 2006). pH levels within the CH watershed range from 6 to 9 for the majority of samples collected. At these levels Bambric *et al.* (2006) found that copper bound to sediment was 10-1000 times greater than soluble copper within stream water.

Future work to increase the capture of copper on the landscape during the spring would be beneficial to streams within the CH watershed, especially within Fourteen Mile Creek which is under additional stress due to high chloride concentrations. The use of bioretention ponds for capturing heavy metals has been widely studied, and has been shown to reduce the amount of copper entering creek systems following rain events (Davis *et. al* 2003, Li and Davis 2008, Jones and Davis 2013). Proper design and maintenance of these ponds is required to ensure they function at optimal capacity. The strong correlation between copper and TSS at the majority of stations in the watershed indicate that reducing TSS during rain events would provide the added benefit of reducing copper inputs to the aquatic environment.

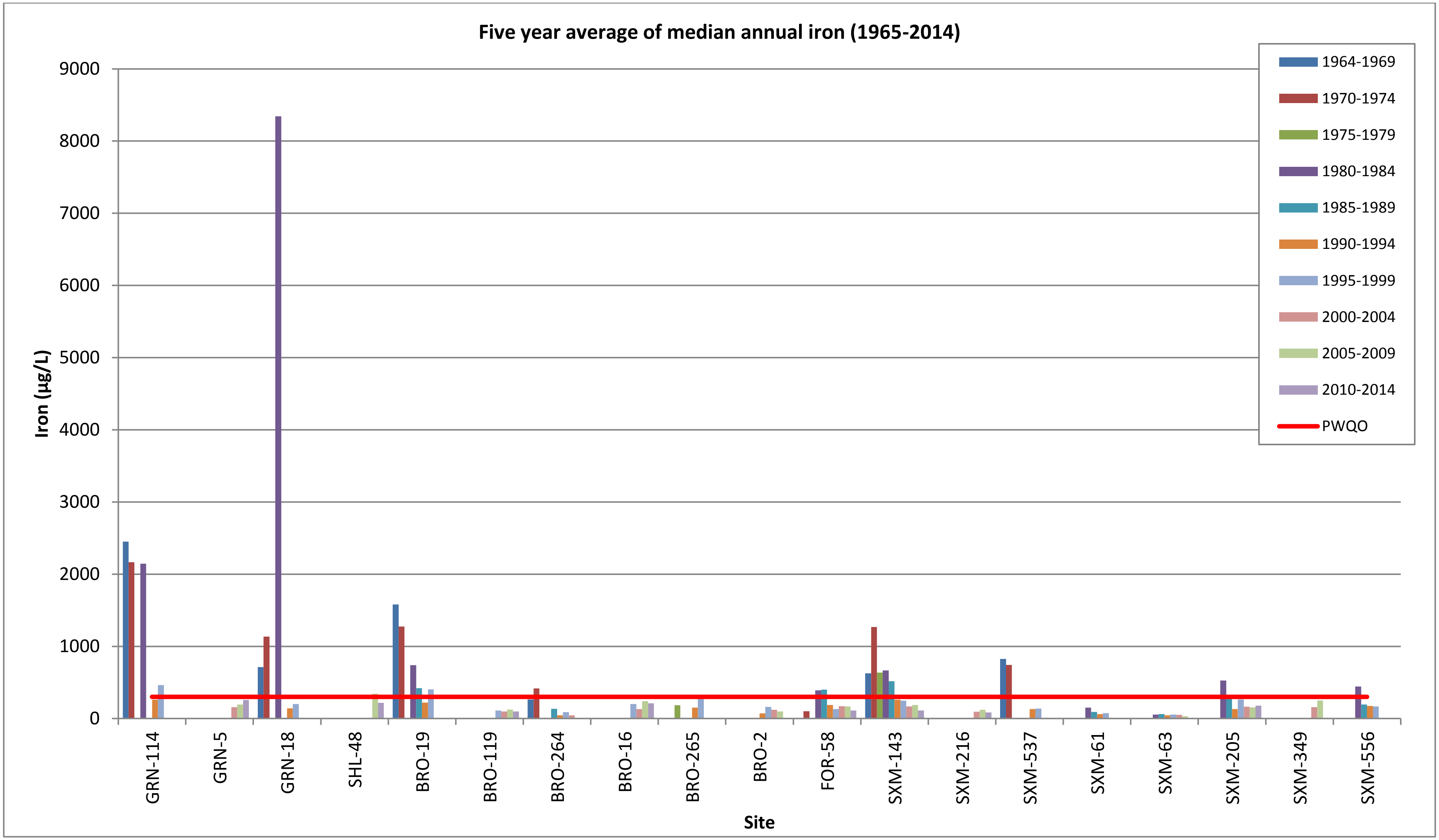
Iron

Iron is naturally found in high concentrations within rocks and soils and a common source to the environment includes the weathering of these materials. In addition, anthropogenic sources include burning of fossil fuels, mining and mineral processing, agricultural draining, forestry and the corrosion of iron products (OMOE 1979, Vuori 1995). Iron toxicity in aquatic ecosystems is seen through damage to fish and invertebrate gills leading to a reduced ability to uptake oxygen, as well as damage to DNA and membrane structures within biotic organisms (Vuori 1995). The PWQO for iron is 300 μg/L (OMOEE 1994).

Trend Analysis

Median annual iron concentrations have decreased over the 50 years of monitoring. Figure 13 shows the five year average of annual median iron concentrations. Most stations have been below the PWQO of 300 μg/L since the early 1990’s.

Figure 13: Five year average of median annual iron concentrations (1965-2014)



Changes in median annual iron concentrations over time were examined using a Mann-Kendall trend test. Nine stations showed a statistically significant decreasing trend over the entire monitoring period. No statistically significant increasing trends were seen.

When examining the three separate time frames, three stations (BRO-264, FOR-58 and SXM-537) did not show trends in either of the shorter time frames despite trends over the entire monitoring period. One station (SXM-205) showed a significantly decreasing trend between 1975 and 1996, but no trend overall. Table 15 summarizes the results of the Mann-Kendall test. Test statistics are provided in Appendix C.

Table 15: Median annual iron trend analysis results

Watershed	Station	Overall Trend	1975-1996	2002-2014
Grindstone	GRN-114	Decreasing	Decreasing	--
	GRN-5	No trend	--	No Trend
	GRN-18	No trend	No Trend	--
Sheldon	SHL-48	No trend	--	No Trend
Bronte	BRO-19	Decreasing	Decreasing	--
	BRO-119	No trend	--	No Trend
	BRO-264	Decreasing	No Trend	--
	BRO-16	No trend	--	No Trend
	BRO-265	No trend	No Trend	--
	BRO-2	No trend	No Trend	No Trend
Fourteen Mile	FOR-58	Decreasing	No Trend	No Trend
Sixteen Mile	SXM-143	Decreasing	Decreasing	Decreasing
	SXM-216	No trend	--	No Trend
	SXM-537	Decreasing	No Trend	--
	SXM-61	Decreasing	Decreasing	--
	SXM-63	Decreasing	No Trend	Decreasing
	SXM-205	No trend	Decreasing	No Trend
	SXM-349	No trend	--	No Trend
	SXM-556	Decreasing	Decreasing	--

Seasonal differences in iron concentrations were examined using a Kruskal-Wallis test. Eight stations showed differences between seasons, seven of which showed summer having lower concentrations. One station (SXM-349) had lower concentrations in the fall than in either spring or summer. Table 16 provides the summary results of the seasonal differences, with test statistics provided in Appendix D.

Table 16: Seasonal differences in median iron concentrations (2002-2014)

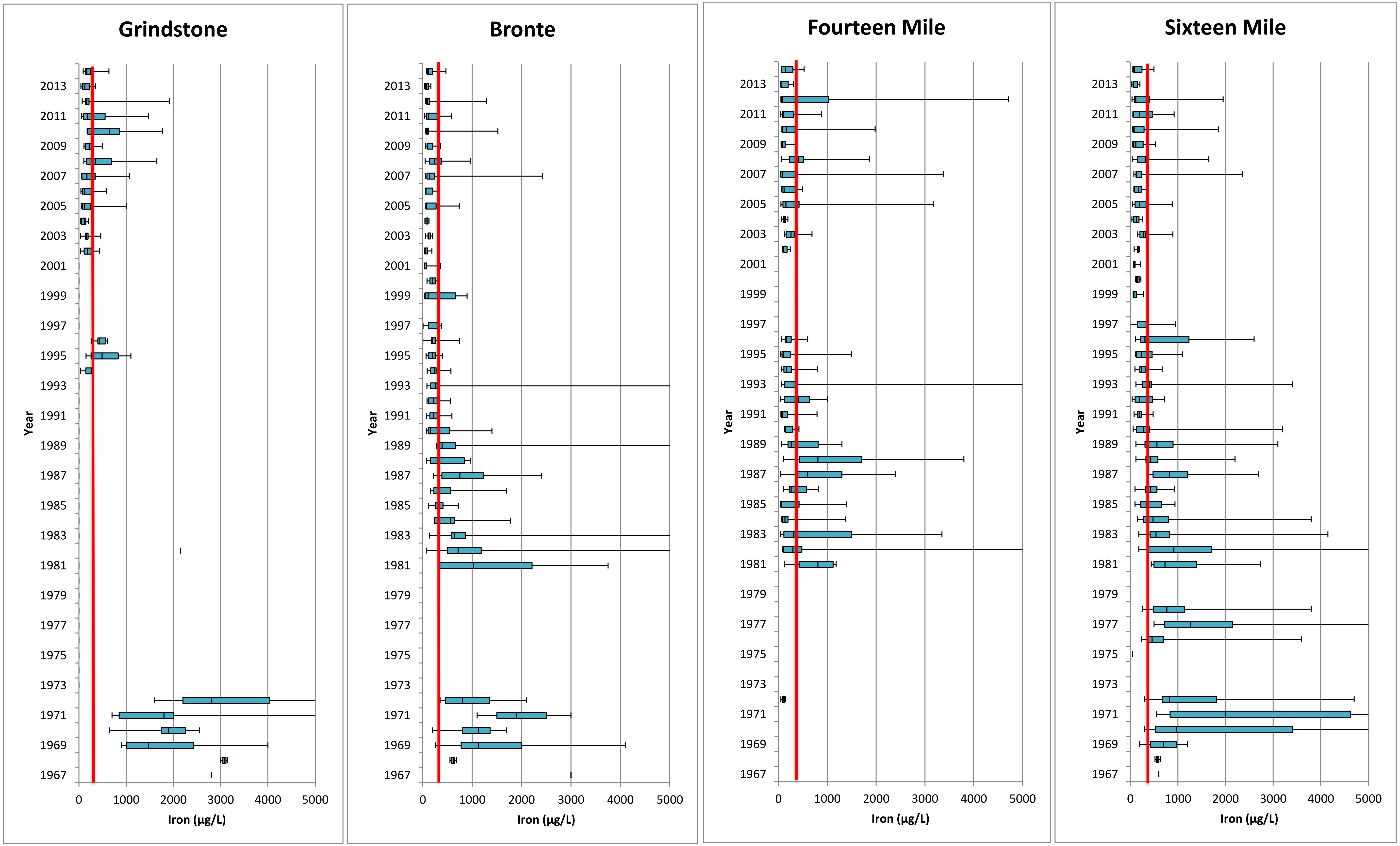
Station	Spring vs. Summer	Spring vs. Fall	Summer vs. Fall	Seasonal Difference
GRN-5	Different	No difference	No difference	Spring higher
SHL-48	No difference	No difference	No difference	
BRO-119	No difference	No difference	Different	Fall higher
BRO-16	Different	No difference	Different	Summer lower
BRO-2	No difference	No difference	Different	Fall higher
FOR-58	No difference	No difference	No difference	
SXM-143	Different	No difference	Different	Summer lower
SXM-216	Different	No difference	Different	Summer lower
SXM-63	No difference	No difference	No difference	
SXM-205	Different	No difference	No difference	Spring higher
SXM-349	No difference	Different	Different	Fall lower

The correlation coefficient between iron and TSS was strong, with only one station (SXM-61) not showing a significant correlation. The average correlation coefficient was 0.77 with all stations except SXM-61 having p-values less than 0.01 indicating a strong correlation between TSS and iron. Correlation coefficients and test statistics are presented in Appendix E.

Spatial Comparison

Figure 14 shows how iron concentrations have changed at the mouth of Grindstone, Bronte, Fourteen Mile and Sixteen Mile Creeks over the last 50 years. Iron concentrations have decreased at all creek mouth stations, although exceedances of the PWQO continue to occur. The spread of values had decreased since the 1970's and 1980's, however maximum values six times the PWQO have occurred in the last 5 years.

Figure 14: Iron concentrations at GRN-5, BRO-119, FOR-58 and SXM-143 (1967-2014)



Discussion

While iron concentrations have been decreasing across the watershed over the last 50 years, exceedances of the PWQO continue to occur on a regular basis, indicating that iron may be causing acute aquatic impairment at some locations if conditions, such as low dissolved oxygen, exist to change iron to its most bioavailable form. Because levels are not chronically high, the impact of iron is most significantly felt by sensitive taxa which have a low tolerance for small fluctuations in iron levels. Continued efforts to reduce iron inputs to aquatic environments should be encouraged.

Seasonal analysis showed summer had lower iron concentrations than spring and fall. This could be a result of increased runoff and higher proportion of wet event sampling occurring in the spring and therefore increased iron levels within spring samples. Future work to increase the capture of iron on the landscape during the spring and fall would be beneficial to streams within the CH watershed. As with copper, the use of bioretention ponds for capturing iron would help reduce the amount of iron entering streams following runoff events (Davis *et. al* 2003, Li and Davis 2008, Jones and Davis 2013). Iron showed a stronger correlation with TSS than copper, indicating that a reduction of TSS within streams during storm events would likely have a large impact on iron concentrations during storm events.

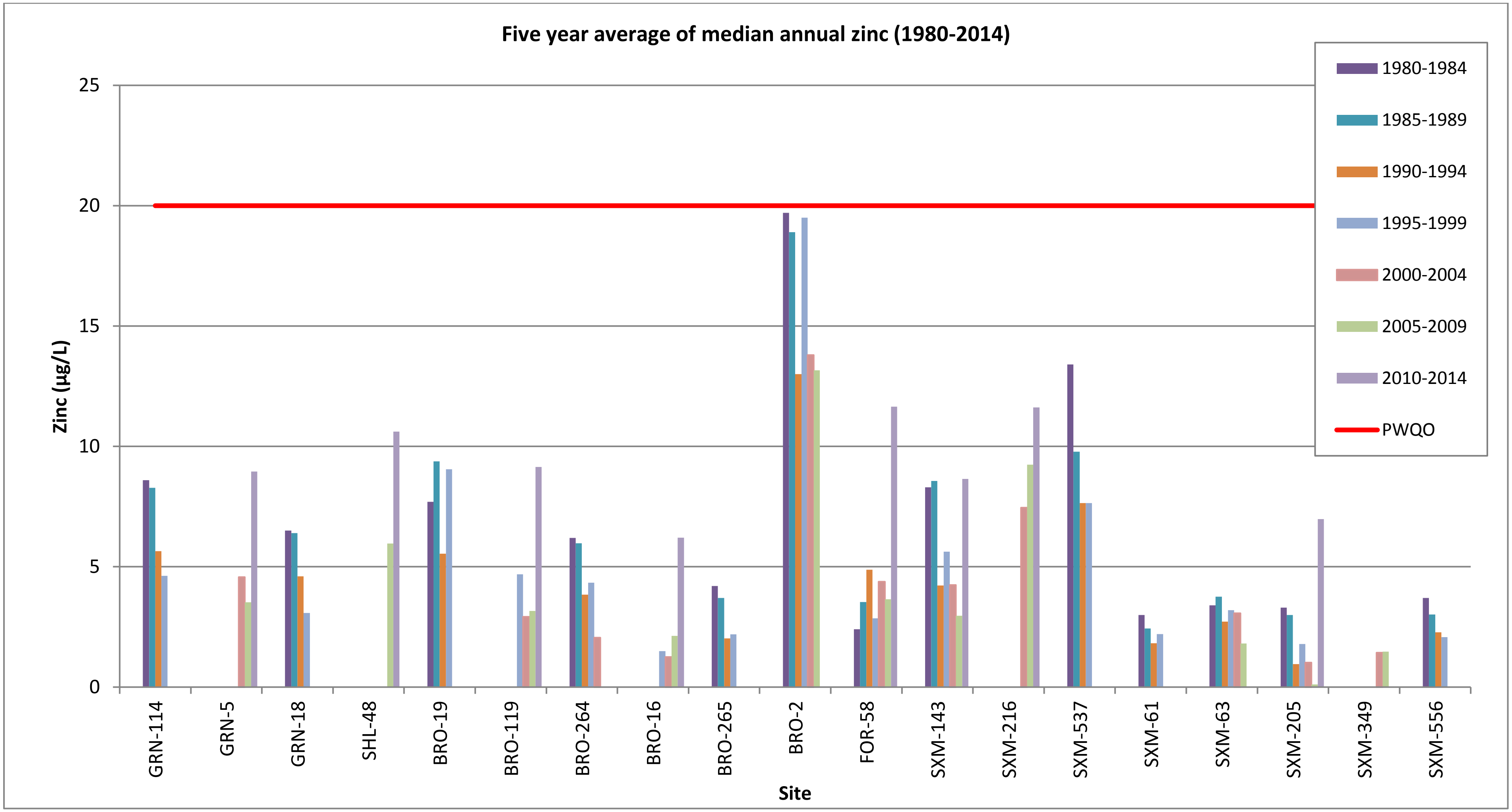
Zinc

Inputs of zinc to the aquatic environment are most commonly associated with natural weathering of rock, municipal wastewater, metal fabrication and coating, mining, paint, industrial cleaners and soaps as well as pharmaceutical products (OMOE 1979). Zinc toxicity is associated with impacts on RNA and DNA enzymes as well as metabolism (Eisler, 1993). The PWQO for zinc is 20 μg/L (OMOEE 1994).

Trend Analysis

Median annual zinc concentrations across the watershed have consistently been below the PWQO of 20 μg/L during the entire monitoring period. Concentrations have generally decreased or remained stable, with the exception of the 2010-2014 time frame where concentrations were typically higher than the previous time frames. Figure 15 shows how the five year average of median annual concentrations has changed over the last 35 years.

Figure 15: Five year average of median annual zinc concentrations (1980-2014)



Eight stations showed a statistically significant decrease in median annual zinc concentrations over the entire monitoring period. In contrast, two stations (BRO-16 and FOR-58) showed a statistically significant increase over the monitoring period.

When examining the three separate time frames, three stations (BRO-19, BRO-119 and SXM-205) showed a significant trend in one of the shorter time frames that was not seen over the entire monitoring period. Both BRO-19 and SXM-205 significantly decreased between 1980 and 1996, while BRO-119 significantly increased between 2002 and 2014. BRO-2 showed a decreasing trend over the entire monitoring period but did not show trends over the shorter time frames. Overall, concentrations between 1980 and 1996 decreased while concentrations between 2002 and 2014 increased, indicating that during the last 13 years sources of zinc to the aquatic environment have increased. Table 17 provides a summary of the trend analysis for zinc. Test statistics are provided in Appendix C.

Table 17: Median annual zinc trend analysis results

Watershed	Station	Overall Trend	1980-1996	2002-2014
Grindstone	GRN-114	Decreasing	Decreasing	--
	GRN-5	No trend	--	No Trend
	GRN-18	No trend	No Trend	--
Sheldon	SHL-48	No trend	--	No Trend
Bronte	BRO-19	No trend	Decreasing	--
	BRO-119	No trend	--	Increasing
	BRO-264	Decreasing	No Trend	--
	BRO-16	Increasing	--	Increasing
	BRO-265	Decreasing	Decreasing	--
	BRO-2	Decreasing	No Trend	No Trend
Fourteen Mile	FOR-58	Increasing	No Trend	Increasing
Sixteen Mile	SXM-143	Decreasing	Decreasing	No Trend
	SXM-216	No trend	--	No Trend
	SXM-537	Decreasing	Decreasing	--
	SXM-61	Decreasing	Decreasing	--
	SXM-63	No trend	No Trend	No Trend
	SXM-205	No trend	Decreasing	No Trend
	SXM-349	No trend	--	No Trend
	SXM-556	Decreasing	Decreasing	--

Seasonal differences in zinc concentrations were examined using a Kruskal-Wallis test. Similar to copper, zinc concentrations were higher in the spring. Three stations (BRO-119, BRO-16 and SXM-63) were higher in spring when compared with summer, while one station (SXM-349) was higher in spring than in fall. Table 18 provides the summary results of the seasonal differences, with test statistics provided in Appendix D.

Table 18: Seasonal differences in median zinc concentrations (2002-2014)

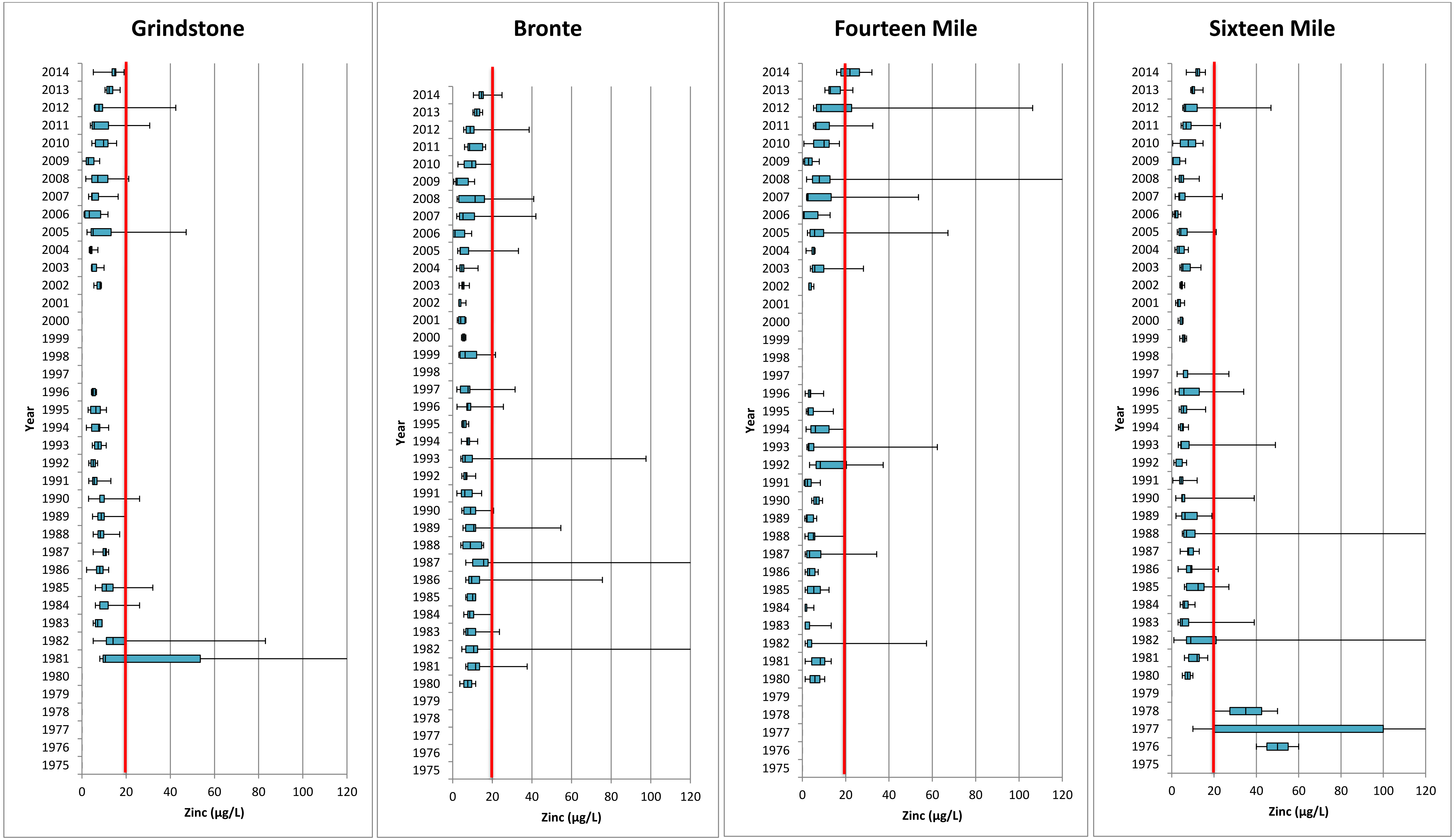
Station	Spring vs. Summer	Spring vs. Fall	Summer vs. Fall	Seasonal Difference
GRN-5	No difference	No difference	No difference	
SHL-48	No difference	No difference	No difference	
BRO-119	Different	No difference	No difference	Spring higher
BRO-16	Different	No difference	No difference	Spring higher
BRO-2	No difference	No difference	No difference	
FOR-58	No difference	No difference	No difference	
SXM-143	No difference	No difference	No difference	
SXM-216	No difference	No difference	No difference	
SXM-63	Different	No difference	No difference	Spring higher
SXM-205	No difference	No difference	No difference	
SXM-349	No difference	Different	No difference	Spring higher

Similar to both copper and iron, the correlation coefficient for the relationship between TSS and zinc was strong, with only 2 stations not significantly correlated (SXM-61 and SXM-216). Correlation coefficients and test statistics are presented in Appendix E.

Spatial Comparison

Figure 16 shows how zinc concentrations have changed at the mouth of Grindstone, Bronte, Fourteen Mile and Sixteen Mile Creeks over the last 50 years. All four stations had elevated zinc concentrations in the 1970's, but median concentrations have been consistently below the PWQO since the beginning of the 1980's, with only a small number of maximum values over the PWQO. Increases in zinc concentrations over the last six years have been seen at all stations, with FOR-58 having a median concentration above the PWQO in 2014.

Figure 16: Zinc concentrations at GRN-5, BRO-119, FOR-58 and SXM-143 (1975-2015)



Discussion

Zinc is not currently a metal of concern across the Conservation Halton watershed. Concentrations have consistently remained below the PWQO, indicating that it is not causing aquatic impairment. While significant decreases were seen during the first half of the monitoring period, increases have been seen since 2002, with nine stations showing increasing trends. Because concentrations are below the PWQO, this is not a cause for immediate concern, however it should be monitored to ensure that increases do not continue to occur or that the rate of increase does not escalate as this could cause impairment within a short time frame.

The zinc concentrations seen at BRO-2 in the upper reaches of the Bronte Creek watershed are of concern and require further investigation. When examining the five year average of median annual concentrations, each time frame is nearly double the levels seen at any other station. Land uses upstream of this station are predominantly agricultural and not associated with a large source of zinc so it is unknown why levels are high at this station.

Seasonal analysis showed spring had higher zinc concentrations than both other seasons. Similar to copper, the higher zinc concentrations in the spring could be a result of the binding of heavy metals to sediment and the increase in runoff and higher proportion of wet event sampling occurring during the spring. Also similar to copper, zinc may be stored on the landscape over the winter and spring freshet could release this into the aquatic environment. Future work to increase the capture of zinc on the landscape during the spring would be beneficial to streams within the CH watershed. Similar to other heavy metals, multiple studies have found that bioretention ponds were most effective for capturing zinc associated with runoff events (Davis *et al.* 2003, Li and Davis 2008, Jones and Davis 2013). This is further supported by the correlation between TSS and zinc, as bioretention ponds would reduce TSS levels in streams by providing an area for sediment to settle out, and removing zinc bound to sediment in the process.

Water Quality Index

The Water Quality Index (WQI) provides a general assessment of stream health based on the performance of a station against set water quality objectives. The objectives are defined by the user, and for the purpose of this report were set at the PWQO and CWQO concentrations for each parameter as described in previous sections. Table 19 shows the WQI rank for the last year monitored and provides the scores corresponding to each rank in Table 4. Statistical trend analysis was not completed as the OMOECC indicated that this is not a valid use of the data (G. Kaltenecker, personal communication, Feb. 2, 2017).

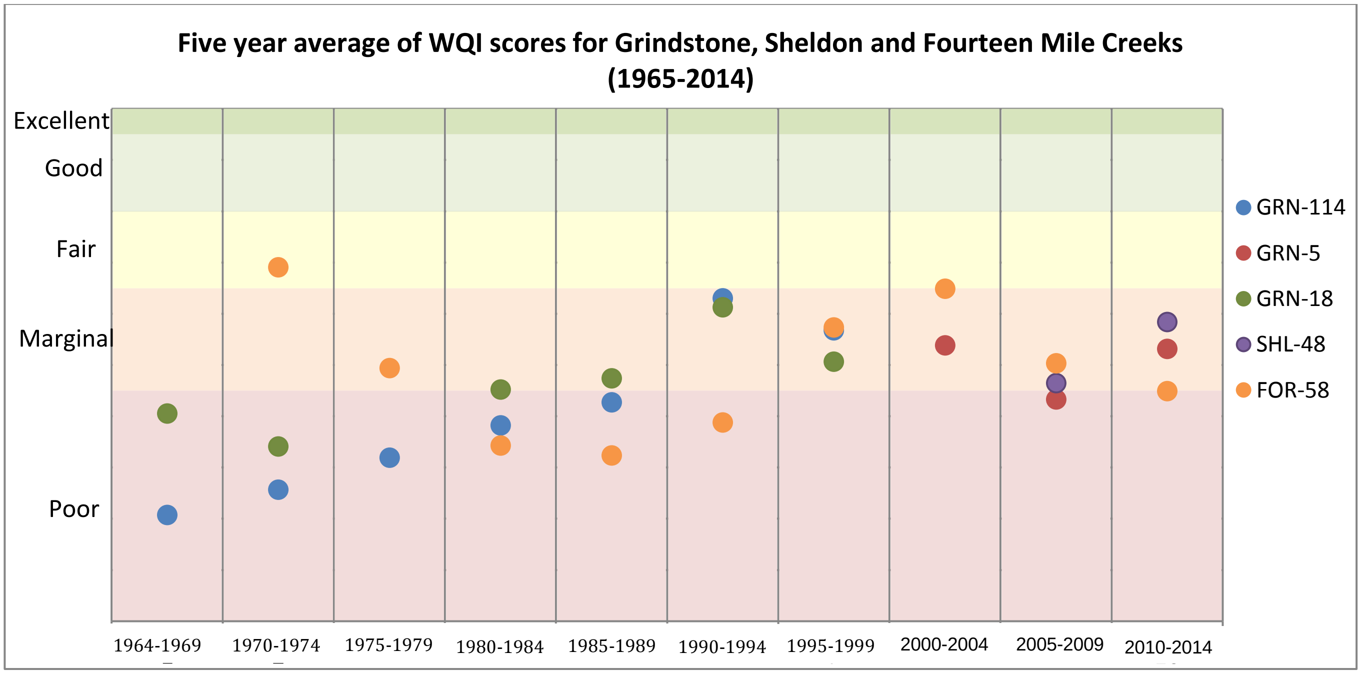
Table 19: Water Quality Index Scores for final year sampled

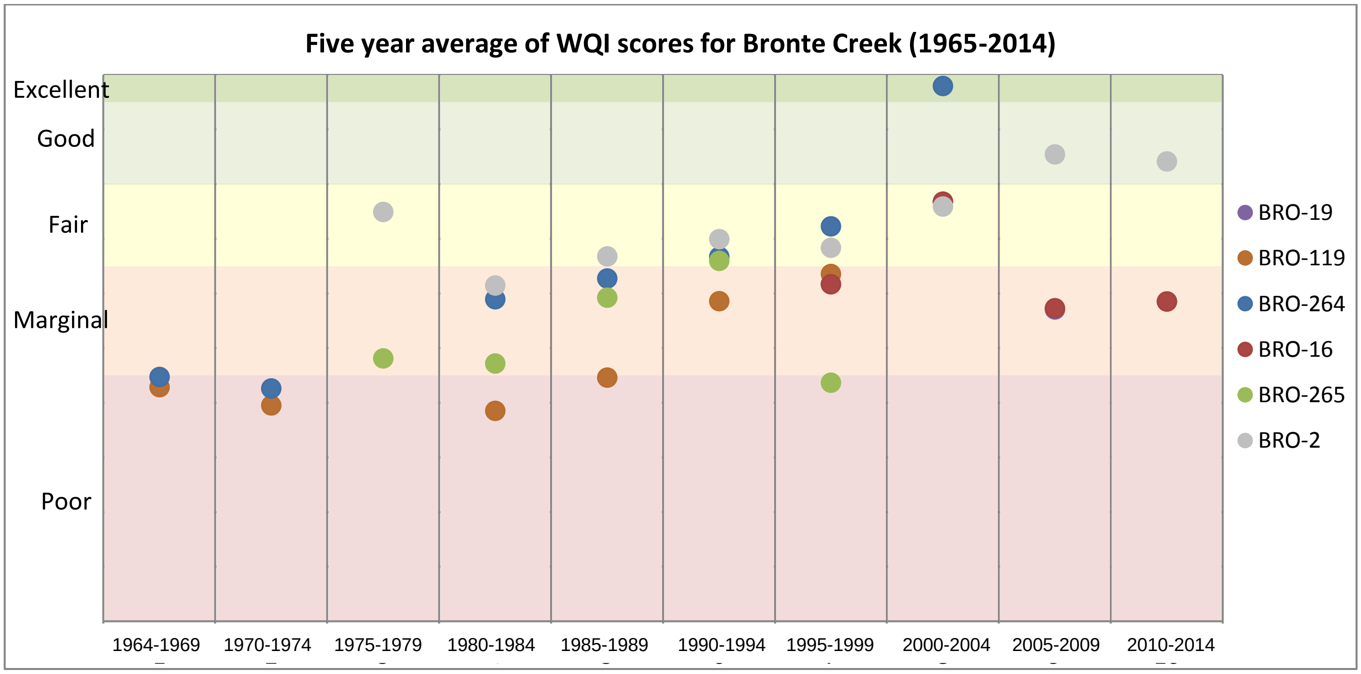
Watershed	Station	Year	Score	Rank
Grindstone	GRN-114	1996	66.0	Fair
	GRN-5	2014	64.9	Marginal
	GRN-18	1996	45.6	Marginal
Sheldon	SHL-48	2014	38.8	Poor
Bronte	BRO-19	1999	42.6	Poor
	BRO-119	2014	62.7	Marginal
	BRO-264	2001	100	Excellent
	BRO-16	2014	62.7	Marginal
	BRO-265	1996	35.5	Poor
	BRO-2	2014	84.6	Good
Fourteen Mile	FOR-58	2014	41.3	Marginal
Sixteen Mile	SXM-143	2014	72.3	Fair
	SXM-216	2014	75.0	Fair
	SXM-537	1996	72.8	Fair
	SXM-61	1996	91.6	Good
	SXM-63	2014	85.1	Good
	SXM-205	2014	72.8	Fair
	SXM-349	2014	84.9	Good
	SXM-556	1996	82.4	Good

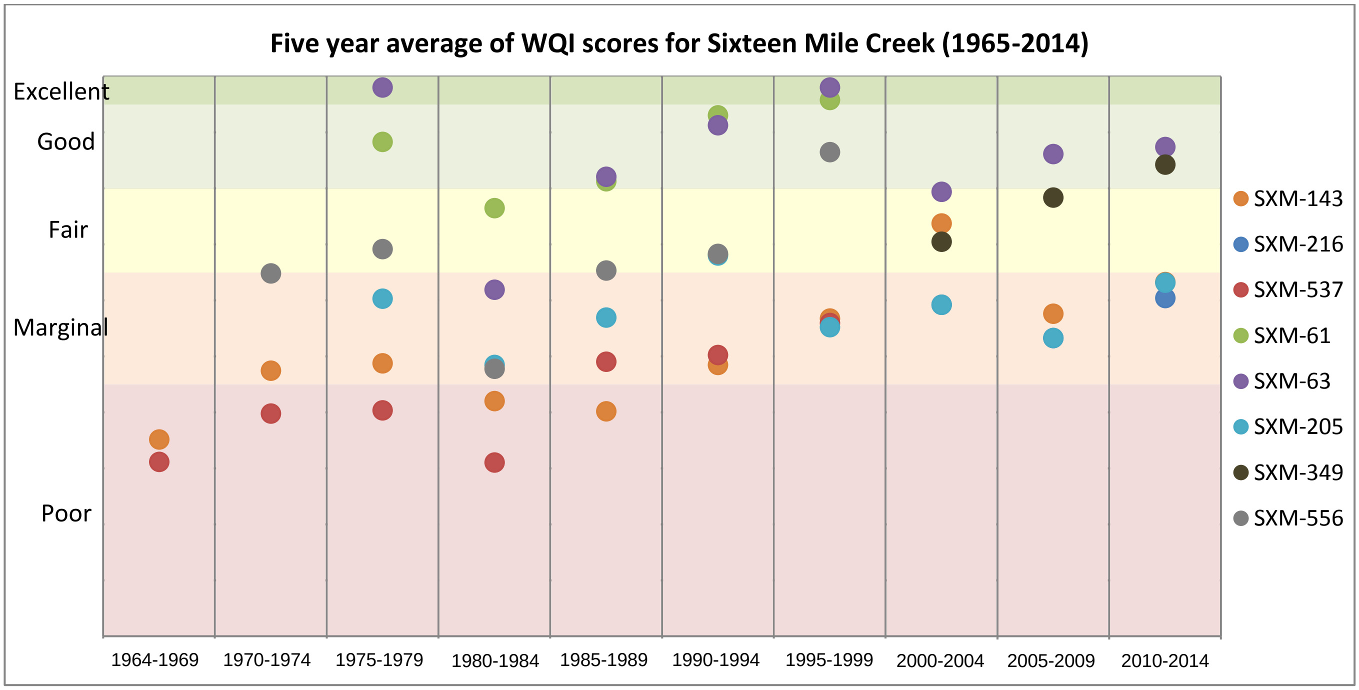
Trend Analysis

Water Quality Index scores across the watershed have been improving over the 50 years of monitoring at most stations. Figure 17 shows the five year average of annual WQI scores at each station. All stations monitored between 1964 and 1969 were ranked as poor, with scores improving since that time. Three stations (BRO-264, SXM-61 and SXM-63) have scored excellent during at least one of the five year time frames. SXM-61 and SXM-349 have consistently scored well, with no scores below a “Fair” ranking. No stations in Grindstone Creek have scored above a “Marginal” ranking, indicating that aquatic impairment is occurring at the stations sampled within this watershed. The majority of scores across all time frames and all stations fell within the “Marginal” ranking.

Figure 17: Five year average of annual water quality index scores (1964-2014)







Discussion

Water quality index values across the watershed are generally improving. This is a reflection of the decreases that have been seen in the parameters previously discussed in this report. With the exception of chloride, most parameters at most stations have been consistently below the objectives or are decreasing and the reductions are shown in the WQI scores. Continued effort to reduce road runoff, remove nutrients and metals from stormwater and wastewater, as well as reduce industrial sources of contaminants will help to further improve WQI scores in the future.

Considerations for Future Monitoring

The following actions are recommended based on the results of this report:

- Additional sampling of total suspended solids in areas suspected to be impacted by precipitation events (i.e. development areas with bare topsoil)
- Additional sampling of nutrient loading including sampling of water levels and flows in addition to 24-hr event sampling
- Further analysis of data related to stormwater management ponds and the potential implications of ponds to be heavy metal sinks and chloride sources; integration of data from developer-led monitoring programs with CH sampling
- Additional sampling of chloride in creeks within urban areas to determine if small urban watersheds are under similar pressures as Fourteen Mile Creek
- Further investigation into zinc sources to the upper reaches of Bronte Creek (BRO-2)
- Development of storm event sampling to determine acute impacts to aquatic ecosystems by spikes in metal and nutrient concentrations during these events
- Analysis of wet weather and dry weather sampling events separately, and integration with rainfall data for parameters highly correlated with storm events
- Winter water quality sampling to understand water quality conditions during the entire year

Conclusion and Recommendations

Water quality throughout the Conservation Halton watershed is generally improving. Decreases in nutrient and metal concentrations have been seen over the last 50 years and ambient conditions continue to improve, with many parameters below the water quality objectives for healthy aquatic communities. Aquatic organisms depend on clean water in much the same way that terrestrial organisms depend on clean air. While many are able to withstand degraded conditions for short time periods, long term exposure will reduce survivability and will ultimately change the biota found within a stream. As the origin of many contaminants is anthropogenic activities, mitigation and prevention of contamination must begin at the source. The use of low impact development and stormwater management are already proving to benefit aquatic ecosystems by helping trap metals and sediment before reaching streams. Further development of these technologies to filter chlorides will help to increase their benefits.

Additional recommendations for improving water quality in streams include:

- Help maintain healthy habitats by protecting stream banks from erosion by maintaining and improving riparian buffers
- Consider planting native trees and shrubs along the stream bank. Woody vegetation has strong root systems that hold together soil and resist erosion helping to reduce the amount of suspended sediment in the stream. Manicured lawns do a very poor job at stabilizing banks.
- Look for opportunities to capture and store runoff on properties through site grading. On large properties this can mean major works involving wetland creation but there are often other simple and relatively easy opportunities to make a difference, such as using rain barrels, permeable pavers and rain gardens.
- Avoid flushing pool water into storm sewers as this directly increases chlorides in streams.
- Reduce the use of salt in the winter to prevent excess salt from entering the stream.
- Encourage municipalities and commercial businesses to participate in “Smart About Salt” programs to better manage winter salt use to reduce chlorides.
- Identify areas where streams require large improvements to buffers and focus stewardship opportunities in those areas.
- Encourage academics to investigate and develop new ways to remove salt from watercourses and stormwater management ponds.
- Ensure best management practices and erosion and sediment controls are used on development sites to prevent runoff and excess sedimentation entering streams.
- Encourage the uptake of low impact development (LID) in new developments and evaluate opportunities to install LID’s in older neighbourhoods where stormwater management is limited or non-existent

References

Bambric, D.G., C.N. Alpers, P.G. Green, E. Fanelli and W.K. Silk. 2006. Seasonal and spatial patterns of metals at a restored copper mine site. I. Stream copper and zinc. Environmental Pollution. 144: 774-782.

Bowman, J.E. 2016. Water Quality Season Summary 2015. RBG Report No. 2016-10. Royal Botanical Gardens. Hamilton, Ontario. 38 pages.

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian water quality guidelines for the protection of aquatic life: Introduction. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2001. Canadian water quality guidelines for the protection of aquatic life: CCME Water Quality Index 1.0, User's Manual. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2002. Canadian water quality guidelines for the protection of aquatic life: Total Particulate Matter. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2003. Canadian water quality guidelines for the protection of aquatic life: Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2004. Canadian water quality guidelines for the protection of aquatic life: Phosphorus: Canadian Guidance Framework for the Management of Freshwater Systems. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2011. Canadian water quality guidelines for the protection of aquatic life: Chloride. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). 2012. Canadian water quality guidelines for the protection of aquatic life: Nitrate Ion. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Coats, R.N. and C.R. Goldman. 2001. Patterns of nitrogen transport in streams of the Lake Tahoe basin, California-Nevada. Water Resources Research, 37 (2): 405-415.

Conservation Halton. 2013. Halton Watershed Report Card 2013. 6 pages.

Correll, D.L. 1998. The role of phosphorus in the eutrophication of receiving waters: A review. J. Environ. Qual. 27:261-266.

Davis, A.P., M. Shokouhian, H. Sharma, C. Minami and D. Winogradoff. 2003. Water Quality Improvement through bioretetion: Lead, Copper, and Zinc Removal. Water Environmental Research, 75 (1) 73-82.

Eisler, R. 1993. Zinc hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Department of Interior Fish and Wildlife Service, Laurel, Maryland. 126 pages.

Eisler, R. 1998. Copper hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Geological Survey, Biological Resources Division, Biological Science Report USGS/BRD/BSR--1997-0002. 98 pages.

Environmental Protection Agency (EPA). 2007. Aquatic life ambient freshwater quality criteria – Copper: 2007 Revision. U.S. Environmental Protection Agency, Office of Water and Office of Science and Technology, Washington. 204 pages.

Government of Canada. 1999. Concentration of Phosphorus in Certain Cleaning Products Regulations. Canadian Environmental Protection Act. Ottawa, Ontario. 278 pages.

Halton-Hamilton Source Protection, 2011. Proposed Updated Assessment Report Halton Region Source Protection Area. 388 pages.

Halton Region Conservation Authority. 1998. Grindstone Creek Watershed Study: Our Legacy to Value: The Grindstone Creek. Milton, Ontario. 50 pages.

Hart, B.T. 1982. Uptake of trace metals by sediments and suspended particulates: a review. Hydrobiologia. 91: 299-313.

Helsel, D.R. and R.M. Hirsch. 2002. Statistical Methods in Water Resources Techniques of Water Resources Investigations, Book 4, chapter A3. U.S. Geological Survey. 522 pages.

Hogan, D.L. and D.S. Luzi, 2010. Chapter 10: Channel Geomorphology: Fluvial Forms, Processes, and Forest Management Effects. Compendium of forest hydrology and geomorphology in British Columbia. B.C. Min. For. Range, For. Sci. Prog., Victoria, B.C. and FORREX Forum for Research and Extension in Natural Resources, Kamloops, B.C. Land Manag. Handb. 331-371.

Jones, P. and A. Davis. 2013. Spatial Accumulation and Strength of Affiliation of Heavy Metals in Bioretention Media. Journal of Environmental Engineering. 10: 479-487.

Kelting, D.L., C.L. Laxson, and E.C. Yerger. 2012. Regional analysis of the effect of paved roads on sodium and chloride in lakes. Water Research. 46: 2749-2758.

Kolzau, S., C. Wiedner, J. Rucker, J. Kohler, A. Kohler and A.M. Dolman. Seasonal Patterns of Nitrogen and Phosphorus Limitation in Four German Lakes and the Predictability of Limitation Status from Ambient Nutrient Concentrations. PLoS One 9(4): e96065.

Kraemer, J. 2015. Current best practices for chemical phosphorus removal. Influents 10: 38-40.

Li, H. and A.P. Davis. 2008. Heavy Metal Capture and Accumulation in Bioretention Media. Environmental Science and Technology 42 (14): 5247-5253.

Mulholland, P.J. 1992. Regulation of nutrient concentrations in a temperate forest stream: Roles of upland, riparian, and instream processes. Limnology and Oceanology 37 (7): 1512-1526.

Ontario Ministry of the Environment (OMOE). 1979. Rationale for the Establishment of Ontario's Provincial Water Quality Objectives. Queen's Printer for Ontario. Toronto, ON. 244 pages.

Ontario Ministry Environment and Energy (OMOEE). 1994. Policies Guidelines and Provincial Water Quality Objectives of the Ministry of Environment and Energy. Queen's Printer for Ontario. Toronto, ON. 29 pages.

Province of Ontario. 2005. Places to Grow Act. Ontario Regulation 415/05: Growth Plan Areas

Rabalais N.N. 2002. Nitrogen in Aquatic Ecosystems. Ambio. 31 (2): 103-112.

Solomon, F. 2009. Impacts of Copper on Aquatic Ecosystems and Human Health. MINING.com. January Edition, 25 – 28.

Statistics Canada. 2011. Census of Population.

Stone, M., M.B. Emelko, J. Marsalek, J.S. Price, D.L. Rudolph, H. Saini and S.L. Tighe. 2010. Assessing the Efficacy of Current Road Salt Management Programs. University of Waterloo. 227 pages.

Vuori, K. 1995. Direct and indirect effects of iron on river ecosystems. Ann. Zool. Finnici. 32: 317-329.

Warren, L.A. and A.P. Zimmerman. 2004. The influence of temperature and NaCl on cadmium, copper and zinc partitioning among suspended particulates and dissolved phases in an urban river. Water Res. 28:1921–1931.

Appendix A: Analytes

Parameter	Units
Alkalinity	mg/L
Aluminium	µg/L
Ammonia+ammonium	mg/L
Barium	µg/L
Beryllium	µg/L
Bismuth	µg/L
Dissolved Organic Carbon	mg/L
Dissolved Inorganic Carbon	mg/L
Cadmium	µg/L
Calcium	µg/L
Chloride	mg/L
Chromium	µg/L
Cobalt	µg/L
Conductivity	µS/cm
Copper	µg/L
Hardness	
Iron	µg/L
Lead	µg/L
Lithium	µg/L
Magnesium	µg/L
Manganese	µg/L
Molybdenum	µg/L
Nickel	µg/L
Nitrate+nitrite	mg/L
Nitrite	mg/L
Total Kjeldahl Nitrogen	mg/L
pH	

Parameter	Units
Phosphate	mg/L
Total Phosphorus	mg/L
Potassium	µg/L
Selenium	µg/L
Silicon	mg/L
Silver	µg/L
Sodium	µg/L
Tin	µg/L
Total suspended solids	mg/L
Strontium	µg/L
Titanium	µg/L
Turbidity	µg/L
Uranium	µg/L
Vanadium	µg/L
Zinc	µg/L
Zirconium	µg/L

Appendix B: Values used in creating box plots

Red values indicate exceedances of the water quality objective associated with each parameter. When only one sample was collected in a year it is listed as the minimum. When two samples were collected they are listed as the minimum and maximum. For years with 3 or more samples the 25th/75th percentile and median were calculated using all available data.

Chloride

	Grindstone					Bronte					Fourteen Mile					Sixteen Mile				
Year	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max
1965	31	45.5	**48**	58	268	13	18.25	**23**	26	50						24	28.5	**32**	37.5	55
1966	23	35.25	**47**	49.75	62	12	21	**26**	30	128						13	27	**33**	38	44
1967	13	27.25	**38**	47.5	128	11	14.25	**17**	20.5	25						6	22	**25.5**	29.75	40
1968	1	30.5	**36**	38.25	47	1	16.25	**18**	18.75	29						2	24.5	**28.5**	35	158
1969	16	23.5	**32**	37.5	48	12	16	**16**	19.5	27						19	26.5	**31**	34	45
1970	24	34.75	**50.5**	58	71	17	19	**20**	24	31						24	29.5	**36**	38.5	52
1971	24	38	**61.5**	65.75	92	14	22	**23**	26	60						18	29.5	**36**	40.5	88
1972	36	38.5	**43.5**	50	54	17	19.5	**22**	22.75	51	32	42	**51**	51	66	24	31	**35**	39.5	45
1973	29	38.25	**51**	56.5	65	14	18.5	**23.5**	26.25	29	34	43.5	**50**	50	166	18	28	**31**	37.5	40
1974	29	43	**46**	57	62	16	18	**23**	26	29	27	49	**65**	65	128	22	26	**31**	38	46
1975	32	44	**63**	69	75	17	23	**25**	28	36	41	88	**112**	112	263	23	34.25	**42.5**	47.75	77
1976	37.5	40	**48.5**	51	52	20.5	24.5	**25.5**	25.5	27.5	55	73	**75**	75	100	26.5	37.25	**42**	48.5	65
1977	26.5	38	**45**	68	75	19	25.5	**27**	27.5	32	47	65	**75**	75	188	30.5	37.5	**43.5**	50.25	63
1978	29.5	42	**65**	68	72	19	22	**29.5**	32.5	34.5	29	67	**105**	105	195	32.5	36.75	**47**	49.25	138
1979	44	57.25	**68**	70.5	80	23	25	**30**	31.375	33	58	86.25	**99**	99	205	33.5	38.63	**47**	60	60
1980	30.5	62.25	**69.75**	73	76	25.5	27.5	**32.5**	34	36.5	66	70	**92.5**	92.5	402	35.5	43.5	**54**	70	94.5
1981	45.5	52.5	**70**	78	88	29	31	**33**	35.5	36.5	87	105	**151**	151	266	39	62	**67**	76	90
1982	26	41.5	**60**	62	77	24	27.4	**28.6**	31.4	38.4	41.5	71	**110**	110	198	28.5	35.2	**61**	71	89.5
1983	35	43.2	**48.3**	53.8	71.3	15.7	24.6	**35.9**	36.1	38.55	34.3	51.5	**60**	60	176.1	29.3	39.8	**50.3**	65.5	73.6
1984	39.11	54.22	**60.77**	65.88	70.2	27.96	30.47	**31.56**	35.14	37.01	44.55	79.74	**106.85**	106.85	229.75	34.79	50.42	**54.89**	78.41	95.26
1985	50.3	57.33	**68.48**	74.74	78.95	27.95	30.15	**33.75**	33.9	36.63	62.4	88.95	**101.45**	101.45	255.4	55.8	60.15	**63.9**	65.9	72.6
1986	37	55.25	**64.5**	67.75	74.85	26	27.05	**29**	34.8	36	52.7	75.5	**82.45**	82.45	130	35	44.8	**50**	60.45	73.5
1987	52.2	60	**73**	73.5	97	25	30.65	**30.9**	31.9	34.2	57.2	73.5	**101**	101	139	49	58.5	**62.5**	68.5	87.2
1988	44.2	63.7	**77.7**	89	96.5	28.6	37.2	**43.3**	47.6	48.9	87.6	94	**111**	111	223	48.3	69.1	**81.9**	83.3	110
1989	50.8	82.1	**88.5**	94.7	106	38.9	42.4	**46.5**	50.6	53.3	118	125.25	**131**	131	169	39.1	69.8	**78.4**	115	119
1990	68.7	75.3	**81.5**	89.1	101	41.1	45.4	**47.9**	50.6	54.4	126	128	**130**	130	134	68.3	84.6	**97.1**	101	108
1991	50.8	68.53	**73.2**	89.33	98.2	33.4	41.55	**46.4**	52.7	56.7	67.9	82.85	**105.5**	105.5	126	46.1	69.1	**80.05**	103	114
1992	46.2	68.7	**79.2**	99.6	105	32.4	41.8	**45.1**	47.9	54.1	65.9	112	**130**	130	332	31.8	56	**66.9**	73.6	88
1993	67.9	78.45	**86.3**	97.65	121	26.9	38.7	**46.7**	50.8	53.3	35.2	93.9	**129.6**	129.6	217	38.6	61.8	**68.3**	77.6	112
1994	58.6	88	**105**	112	116	46.4	47.3	**50.2**	53.9	60.7	77.4	148	**158**	158	185	67.2	90.2	**93.4**	106	138
1995	74	92.45	**110**	120.75	124	41.6	43.45	**46**	51.35	57.6	58	138.75	**171**	171	195	52.4	78.6	**84.95**	110.5	131
1996	54	56.8	**59.6**	90.4	96	36.4	37.2	**38.6**	39.2	43.6	64	74.8	**101**	101	127	52.6	57.25	**60.9**	64.25	64.6
1997						44	44.8	**49.4**	50	50						57.2	74	**79**	85.2	100
1998																				
1999						54.6	62.3	**66.3**	70.3	76.2						61.6	105.4	**130**	140.5	142
2000						48.4	55.95	**63.5**	71.05	78.6						88.4	93.4	**98.4**	100.2	102
2001						52.2	61	**61.4**	65.2	67						57	94.6	**105**	134	153
2002	107	121	**135**	141.5	148	53	56.83	**61.75**	66.9	71.4	117	130.5	**144**	144	194	85.7	106.93	**131.5**	156.25	178
2003	75.2	86.15	**108**	132.5	176	55.7	59.05	**63.1**	68.05	68.8	51.1	145	**160**	160	260	99.3	111	**126**	136.5	185
2004	87.4	99.33	**110.5**	122.5	155	58.9	59.6	**64.75**	72.93	75.3	210	213	**243.5**	243.5	403	64.6	104.125	**133**	144.25	200
2005	73.4	141	**153**	173.5	188	53.4	62.85	**67.25**	85.13	174	186	208.5	**268.5**	268.5	372	52.5	104.225	**130**	159.5	185
2006	63.8	81.4	**116**	135	164	53.9	61.33	**68.9**	71.98	78.2	74.1	114	**175**	175	252	75	79.83	**100.55**	117	131
2007	76.3	95.35	**147**	161.25	166	55.9	57.28	**68.05**	72.43	81.7	104	207.5	**236**	236	345	102	131	**156.5**	160.25	168
2008	41.7	63.33	**84.15**	101.4	300	45.7	47.7	**54**	70	75.2	75.9	110.75	**143.5**	143.5	209	64.7	83.63	**111**	125.25	139
2009	64.4	76.45	**111**	116	142	50	52.8	**63.2**	66.6	68.9	128	147	**203**	203	277	93.6	101	**111**	127	149
2010	62.8	75.05	**94.5**	131	437	51.5	56.95	**63.55**	69.48	72.8	84.7	226	**255**	255	284	89.1	124	**148**	176	210
2011	46.5	59.38	**84.25**	125	173	39.8	52.18	**56.2**	68.05	74.6	55.7	137.5	**167**	167	270	63.9	82.95	**113**	138.5	157
2012	66.5	87.53	**99**	121.5	147	49.6	64.3	**75.3**	91.08	96.2	36	120	**202**	202	308	59.5	127.5	**158**	179.5	187
2013	62.5	76	**80**	99.45	129	54.4	59.7	**61.65**	67.88	70.2	122	185	**190**	190	248	77.7	94.95	**100**	105	117
2014	52	82	**99.55**	106.75	125	56	61	**64.6**	66.38	70.8	145	261.5	**313**	313	367	99.6	153.25	**165**	166.5	174

Total Phosphorus

	Grindstone					Bronte					Fourteen Mile					Sixteen Mile				
Year	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max
1964	0.059				0.196	0.046				0.052						0.301				0.562
1965	0.059	0.092	**0.125**	0.183	0.444	0.02	0.039	**0.052**	0.078	0.366						0.092	0.131	**0.163**	0.183	0.523
1966	0.046	0.088	**0.17**	0.221	0.268	0.007	0.023	**0.039**	0.062	0.157						0.039	0.136	**0.206**	0.303	0.641
1967	0.013	0.065	**0.087**	0.182	1.023	0.007	0.024	**0.033**	0.057	0.176						0.065	0.107	**0.142**	0.245	0.98
1968	0.029	0.111	**0.178**	0.238	1.373	0.013	0.043	**0.056**	0.091	0.376						0.098	0.162	**0.231**	0.409	0.654

1969	0.08	0.125	**0.20**	0.25	0.80	0.03	0.045	**0.05**	0.08	0.30						0.10	0.164	**0.33**	0.425	0.87
1970	0.034	0.155	**0.22**	0.273	0.33	0.022	0.044	**0.066**	0.074	0.58						0.124	0.215	**0.29**	0.595	1.50
1971	0.058	0.18	**0.22**	0.275	0.85	0.016	0.039	**0.056**	0.123	0.74						0.054	0.111	**0.14**	0.17	0.99
1972	0.029	0.072	**0.14**	0.205	0.78	0.019	0.033	**0.06**	0.125	0.37	0.014	0.019	**0.032**	0.10	0.22	0.072	0.083	**0.11**	0.15	0.31
1973	0.09	0.109	**0.155**	0.215	0.44	0.019	0.026	**0.029**	0.055	0.13	0.02	0.025	**0.027**	0.042	0.069	0.05	0.054	**0.077**	0.104	0.13
1974	0.052	0.12	**0.220**	0.25	0.30	0.019	0.034	**0.045**	0.07	0.079	0.014	0.038	**0.056**	0.07	0.088	0.055	0.06	**0.067**	0.074	0.11
1975	0.068	0.11	**0.19**	0.26	0.32	0.021	0.030	**0.037**	0.046	0.12	0.01	0.013	**0.026**	0.031	0.035	0.027	0.04	**0.057**	0.065	0.09
1976	0.056	0.114	**0.166**	0.258	0.30	0.013	0.020	**0.024**	0.034	0.046	0.011	0.027	**0.03**	0.083	1.18	0.032	0.061	**0.068**	0.085	0.13
1977	0.113	0.13	**0.221**	0.299	0.35	0.019	0.024	**0.036**	0.064	0.10	0.019	0.02	**0.025**	0.054	0.154	0.04	0.061	**0.082**	0.131	0.41
1978	0.122	0.183	**0.272**	0.35	1.34	0.022	0.024	**0.043**	0.056	0.50	0.008	0.024	**0.039**	0.06	0.38	0.028	0.042	**0.055**	0.065	0.55
1979	0.034	0.129	**0.181**	0.201	0.308	0.019	0.032	**0.043**	0.061	0.123	0.015	0.019	**0.028**	0.05	0.09	0.026	0.036	**0.044**	0.051	0.082
1980	0.031	0.088	**0.125**	0.198	0.305	0.013	0.019	**0.029**	0.036	0.10	0.01	0.018	**0.042**	0.061	0.46	0.019	0.039	**0.042**	0.060	0.61
1981	0.044	0.14	**0.177**	0.192	0.312	0.009	0.028	**0.048**	0.075	0.29	0.009	0.022	**0.12**	0.198	0.446	0.016	0.04	**0.063**	0.115	0.282
1982	0.042	0.093	**0.15**	0.31	1.23	0.015	0.028	**0.044**	0.067	1.55	0.028	0.044	**0.057**	0.077	0.595	0.015	0.038	**0.085**	0.12	0.44
1983	0.024	0.09	**0.118**	0.17	0.20	0.012	0.035	**0.041**	0.054	0.205	0.014	0.026	**0.051**	0.152	0.19	0.028	0.041	**0.046**	0.069	0.452
1984	0.067	0.099	**0.144**	0.178	0.24	0.016	0.031	**0.036**	0.056	0.08	0.012	0.015	**0.025**	0.035	0.137	0.018	0.033	**0.041**	0.057	0.167
1985	0.041	0.053	**0.102**	0.15	0.203	0.011	0.023	**0.026**	0.037	0.053	0.007	0.011	**0.017**	0.027	0.143	0.02	0.027	**0.042**	0.066	0.10
1986	0.053	0.057	**0.067**	0.121	0.151	0.021	0.031	**0.034**	0.04	0.095	0.019	0.028	**0.051**	0.07	0.105	0.006	0.037	**0.044**	0.047	0.072
1987	0.038	0.078	**0.10**	0.12	0.152	0.025	0.048	**0.05**	0.057	0.138	0.016	0.019	**0.032**	0.048	0.24	0.012	0.021	**0.033**	0.059	0.193
1988	0.042	0.062	**0.133**	0.158	0.245	0.009	0.019	**0.034**	0.045	0.062	0.026	0.037	**0.044**	0.06	0.525	0.025	0.04	**0.048**	0.069	0.095
1989	0.084	0.106	**0.115**	0.195	0.28	0.021	0.04	**0.048**	0.061	0.28	0.011	0.015	**0.029**	0.062	0.105	0.018	0.04	**0.05**	0.063	0.195
1990	0.043	0.058	**0.14**	0.18	0.38	0.008	0.016	**0.026**	0.042	0.145	0.013	0.023	**0.033**	0.043	0.053	0.011	0.021	**0.037**	0.042	0.34
1991	0.008	0.045	**0.072**	0.109	0.237	0.015	0.027	**0.037**	0.051	0.098	0.012	0.02	**0.035**	0.056	0.175	0.006	0.022	**0.029**	0.052	0.108
1992	0.062	0.067	**0.101**	0.128	0.168	0.016	0.025	**0.038**	0.042	0.089	0.028	0.036	**0.041**	0.111	0.178	0.014	0.02	**0.031**	0.067	0.182
1993	0.086	0.102	**0.115**	0.14	0.195	0.014	0.032	**0.04**	0.07	0.35	0.022	0.04	**0.054**	0.074	0.86	0.01	0.042	**0.054**	0.125	0.33
1994	0.058	0.072	**0.118**	0.13	0.162	0.018	0.026	**0.032**	0.048	0.058	0.02	0.042	**0.044**	0.08	0.20	0.024	0.032	**0.038**	0.048	0.084
1995	0.026	0.106	**0.115**	0.19	0.33	0.01	0.020	**0.036**	0.037	0.044	0.028	0.039	**0.053**	0.06	0.436	0.016	0.034	**0.042**	0.081	0.27
1996	0.052	0.074	**0.106**	0.114	0.13	0.028	0.036	**0.04**	0.056	0.058	0.02	0.044	**0.058**	0.07	0.12	0.026	0.045	**0.073**	0.117	0.28
1997						0.022	0.03	**0.03**	0.048	0.07						0.036	0.038	**0.042**	0.058	0.164
1998																				
1999						0.01	0.014	**0.021**	0.120	0.184						0.016	0.016	**0.02**	0.031	0.052
2000						0.02				0.06						0.024	0.024	**0.024**	0.029	0.034
2001						0.01	0.016	**0.016**	0.016	0.06						0.016	0.022	**0.028**	0.03	0.084
2002	0.035	0.053	**0.071**	0.098	0.125	0.01	0.012	**0.013**	0.018	0.033	0.034	0.036	**0.037**	0.057	0.076	0.017	0.031	**0.037**	0.041	0.047
2003	0.053	0.073	**0.083**	0.106	0.227	0.013	0.019	**0.027**	0.039	0.042	0.023	0.05	**0.071**	0.179	0.370	0.032	0.052	**0.063**	0.093	0.281
2004	0.031	0.041	**0.056**	0.076	0.087	0.007	0.016	**0.022**	0.024	0.027	0.015	0.022	**0.031**	0.043	0.057	0.013	0.024	**0.034**	0.038	0.047
2005	0.018	0.037	**0.054**	0.068	0.109	0.006	0.012	**0.015**	0.051	0.188	0.015	0.022	**0.035**	0.075	0.903	0.022	0.03	**0.041**	0.062	0.234
2006	0.052	0.062	**0.067**	0.089	0.12	0.012	0.014	**0.025**	0.027	0.053	0.027	0.032	**0.06**	0.094	0.116	0.02	0.03	**0.041**	0.061	0.071
2007	0.027	0.053	**0.072**	0.096	0.147	0.011	0.013	**0.017**	0.029	0.491	0.018	0.021	**0.025**	0.071	0.54	0.019	0.026	**0.029**	0.04	0.337
2008	0.03	0.06	**0.095**	0.158	0.21	0.01	0.02	**0.038**	0.058	0.107	0.024	0.044	**0.073**	0.099	0.365	0.009	0.031	**0.052**	0.073	0.179
2009	0.037	0.043	**0.048**	0.073	0.19	0.011	0.013	**0.018**	0.029	0.088	0.015	0.022	**0.034**	0.037	0.051	0.012	0.016	**0.021**	0.047	0.078
2010	0.04	0.054	**0.104**	0.149	0.325	0.008	0.008	**0.011**	0.017	0.23	0.019	0.021	**0.031**	0.089	0.21	0.008	0.013	**0.014**	0.052	0.185
2011	0.035	0.047	**0.059**	0.114	0.455	0.008	0.015	**0.028**	0.077	0.094	0.024	0.04	**0.049**	0.09	0.330	0.009	0.016	**0.048**	0.073	0.34
2012	0.016	0.03	**0.038**	0.054	0.21	0.002	0.01	**0.015**	0.021	0.073	0.012	0.022	**0.036**	0.112	0.45	0.004	0.013	**0.021**	0.04	0.188
2013	0.021	0.025	**0.027**	0.056	0.102	0.007	0.012	**0.014**	0.016	0.019	0.013	0.021	**0.029**	0.054	0.077	0.007	0.017	**0.02**	0.029	0.035
2014	0.024	0.03	**0.04**	0.049	0.098	0.012	0.014	**0.017**	0.021	0.144	0.017	0.027	**0.039**	0.056	0.14	0.006	0.012	**0.018**	0.035	0.052

TSS

	Grindstone					Bronte					Fourteen Mile					Sixteen Mile				
Year	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max
1964	54					23										15				
1965	16	24.75	**43**	98.75	197	5	12	**18**	32	207						7	8.75	**11**	21.75	370
1966	6	22	**56**	124	658	9	15.5	**21.5**	45.75	123						9	15	**17**	20.75	111
1967	9	15	**39.5**	77.75	308	5	15	**15.5**	44.5	148						2	15	**20**	29.5	224
1968	18	43.5	**67.5**	82.75	160	10	14.25	**20**	27.75	419						4	15.25	**20.5**	46.25	233
1969	15	27.5	**50**	75	210	10	15	**20**	37.5	160						5	7.5	**20**	27.5	210
1970	5	21.25	**60**	92.5	145	5	10	**10**	30	60						5	5	**15**	30	160
1971	5	15	**45**	60	100	5	10	**15**	20	100						5	10	**15**	27.5	270
1972	15	38.75	**50**	102.5	340	10	15	**20**	45	210	5	5	**15**	15	65	5	13.75	**15**	25	130
1973	0	8.75	**35**	42.5	100	0	10	**15**	60	130	0	2.5	**5**	7.5	10	0	5	**7.5**	23.75	150
1974																				
1975	3	19.5	**64**	81.25	96	8	16.75	**20**	27.75	38	1	1.75	**3.5**	6.5	10	2	10	**13**	14	19
1976	8.1	17	**50**	84	168	5.3	7.5	**15**	15	22	0.9	1.6	**2.2**	6.2	12	2.9	7.95	**11**	17.5	36
1977	11	43	**58**	79	138	6.8	9.8	**19**	37	77	1.3	3.5	**8.7**	12	16	6.9	11	**15**	29	80
1978	7	23	**65**	85	143	6.5	8	**14**	17	251	0.4	2.4	**3.1**	6.6	74	5	14.5	**16**	20.5	123
1979	16	36.25	**42**	69	79	5	16	**21.5**	30	53	0.9	1.73	**6.5**	12.25	13	5	8.25	**11**	15.25	18
1980	7	23	**32.5**	47.75	66	7	12	**19**	20	292	1	2	**3**	23	121	7	13	**15**	21	173
1981	9				31	4	5.6	**10.8**	12	36.4	2	3.1	**5.9**	12.38	27	7	10.7	**12.5**	23.75	34.4

1982						1.66	12.9	**18.3**	37.8	1116	1.88	3.56	**7.92**	9.05	272	1.905	9	**18.3**	19.1	200
1983						3.76	15.6	**18**	24.9	157	3.29	5.58	**10.3**	46.8	111	5.74	8.27	**13.6**	26.5	161
1984						5.41	8.126	**14.64**	19.49	48.05	1.32	3.42	**5.543**	6.95	17.2	2.28	8.07	**11.88**	24.68	89.9
1985						3.28	8.27	**12.85**	18.47	25.49	2.63	4.09	**7.96**	11.47	19.2	2.89	9.44	**11.06**	11.81	49.15
1986						5.2	9.5	**14.9**	29.85	137	3.2	8.1	**8.8**	15.9	19	2.8	10.2	**16.5**	18.45	23.9
1987						12.8	15.75	**28.8**	41.58	50.6	9	13.45	**18.3**	28.4	75.5	4.5	20.5	**29.2**	36.2	45.5
1988						3.2	4.8	**8.8**	26.9	35.3	9.1	13	**24.9**	36.3	153	2.8	9.4	**13.4**	17.3	29.6
1989						9.1	12.4	**16.6**	33.2	198	5.1	10.2	**15.9**	25.58	67.3	2.9	9.7	**18.7**	26.6	93.9
1990						4.8	6.7	**17.8**	31.4	315	5.3	12.25	**19.2**	20	20.8	1.6	4.5	**12.3**	16.4	241
1991						4.1	11.5	**15.35**	26.38	48.8	2.5	3.5	**8.1**	13.7	60.6	2.5	7.48	**12.85**	35.68	49.5
1992						6.1	11.03	**13.85**	22.53	31.6	7.1	11.1	**20.6**	46.1	73.1	2.8	3.9	**12.3**	21	53.2
1993						3	11.3	**14.6**	43.9	327	2	6.2	**13.7**	21.8	620	4.6	11.3	**18.4**	38.6	188
1994	12.5	14.1	**15.7**	17.5	19.3	4.48	9.18	**13**	22.5	23	5.9	9.5	**16.3**	20.4	104	6.7	10.9	**15**	18.1	22
1995	12.4	33.5	**44.45**	59.5	68	3.33	6	**8.5**	14.75	24	6	10.32	**14.5**	19.93	138	4	7.75	**11.7**	26.725	111
1996	20	21	**25**	31	32	11	14	**20**	28	50	8	10	**14**	16	39	3	14.25	**29**	84.25	216
1997						6.5	8	**19**	20	30.5						7.5	12	**16.5**	25.5	97.5
1998																				
1999						2	3.5	**7.25**	58.25	85.5						2	3.125	**6.25**	11.375	18.5
2000						3.5				16.5						5.5	6.75	**8**	10	12
2001						2	2	**3.5**	9.25	22						1.5	3.38	**4.25**	7	14.5
2002	1.6	6.7	**11.8**	24.8	37.8	1.9	3.4	**4.15**	7.93	18.5	3	6.4	**9.8**	13.65	17.5	3.7	7.23	**8.5**	8.95	10
2003	0.7	6.3	**10.1**	12.3	35.1	3.8	5.75	**7.9**	13.58	16.7	3.9	9.1	**15.4**	41.5	212	3.5	15.35	**17.8**	42.7	109
2004	0.5	0.8	**3.9**	5.3	10.9	1.8	2.43	**4.15**	6	8.9	1.4	2.875	**5.15**	8.625	12.6	1.8	2.775	**8.45**	11.35	16.9
2005	1.6	3.63	**5.3**	23.33	71.4	4.1	4.38	**5.7**	24.75	83.8	1.9	3.15	**5**	29.2	1010	1.4	5.7	**14.55**	25.95	104
2006	2.8	4.53	**8.8**	13.73	17.4	5.9	5.98	**6.5**	8.325	12.3	7	7.85	**8.7**	15.5	22.3	4.9	5.5	**7.2**	11.675	20.6
2007	1.8	3.25	**8.4**	18.1	75.7	3.5	5.58	**10.05**	14.68	296	1.6	2.63	**3.4**	21.03	355	3.5	4.33	**6.1**	10.93	197
2008	1.6	7.03	**14.1**	37.08	108	1.4	7.2	**10.6**	18.9	64.5	1.4	10.68	**18.2**	20.83	206	1	10.1	**13.45**	18.7	101
2009	3.4	4.03	**4.65**	10.38	29.5	2.8	3	**5.7**	14.55	35.9	2.8	3.03	**3.8**	4.88	13.6	2.5	3.38	**5.2**	20.23	25.6
2010	4.4	5.425	**11.4**	28.25	35.3	2.2	2.5	**5.2**	5.5	5.6	2.6	3.25	**5.2**	7.075	38.4	1.4	2.55	**2.9**	4.075	20.4
2011	3.1	4.4	**6.7**	20.15	214	1.8	4.05	**7.6**	20.7	47.8	2.6	2.85	**5.8**	13.1	156	3.1	3.65	**4.5**	22.3	173
2012	3.4	5.88	**7.4**	12.33	173	2	3.15	**4.75**	7.93	85	0.6	2.275	**3.15**	67.98	304	1.9	4.5	**6.5**	24.275	195
2013	2	2.45	**3.6**	10.7	24	2.7	3.55	**6**	8.6	9.6	1	2.25	**4.4**	7.35	18.2	1.1	2.6	**4.3**	7.8	21.2
2014	2.5	4.15	**5.55**	9.475	81.6	3.4	5.48	**6.8**	9.85	81.1	2.3	3.2	**5.25**	10.9	115	2.3	3.6	**4.7**	13.3	24.5

Nitrate

	Grindstone					Bronte					Fourteen Mile					Sixteen Mile				
Year	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max
1964	0.8				1.0	0.6				0.7						0.40				0.6
1965	0.15	0.35	**0.5**	0.55	1.0	0.12	0.16	**0.4**	0.52	0.8						0.08	0.13	**0.25**	0.38	0.45
1966	0.1	0.35	**0.6**	0.76	10.0	0.06	0.12	**0.5**	0.6	3.8						0.05	0.12	**0.44**	0.7	7.5
1967	0.05	0.2	**0.3**	0.68	1.5	0.01	0.2	**0.5**	0.71	1.7						0.01	0.11	**0.21**	0.4	1.15
1968	0.3	0.51	**0.74**	1.0	1.4	0.16	0.41	**0.62**	0.88	0.96						0.04	0.18	**0.22**	0.53	0.9
1969	0.02	0.52	**0.77**	1.3	1.7	0.19	0.64	**0.76**	0.87	1.7						0.05	0.09	**0.5**	0.64	1.3
1970	0.13	0.43	**0.65**	0.9	1.5	0.01	0.34	**0.55**	0.78	2.2						0.01	0.36	**0.66**	1.15	1.6
1971	0.01	0.62	**0.94**	1.2	1.7	0.42	0.66	**0.84**	1.08	1.4						0.01	0.2	**0.34**	0.76	2.2
1972	0.43	0.71	**0.83**	0.9	1.9	0.57	0.75	**0.88**	0.97	1.4	0.01	0.01	**0.04**	0.06	0.46	0.07	0.26	**0.53**	0.79	1.5
1973	0.08	0.58	**0.81**	1.1	1.3	0.51	0.67	**0.81**	0.91	1.1	0.01	0.03	**0.13**	0.43	1.1	0.07	0.12	**0.25**	0.69	1.4
1974	0.36	0.98	**1.2**	1.4	3.9	0.84	1.2	**1.3**	1.5	1.8	0.01	0.13	**0.52**	0.95	1.5	0.05	0.2	**0.74**	1.1	1.3
1975	0.3	0.72	**0.89**	1.5	1.8	0.45	0.52	**0.65**	0.68	1.5	0.03	0.1	**0.39**	1.1	1.6	0.01	0.2	**0.52**	0.87	1.0
1976	0.99	1.13	**1.28**	1.75	3.49	0.74	0.97	**1.19**	1.44	1.6	0.01	0.01	**0.06**	0.34	1.55	0.04	0.09	**0.2**	0.68	1.5
1977	0.18	0.91	**1.01**	1.11	1.28	0.49	0.58	**0.88**	0.94	1.19	0.01	0.04	**0.29**	1.69	2.1	0.12	0.16	**0.38**	0.77	1.78
1978	0.05	1.15	**1.57**	2.66	2.79	0.69	0.86	**0.98**	1.31	1.92	0.02	0.2	**0.33**	0.68	1.68	0.12	0.28	**0.47**	0.87	1.9
1979	0.64	0.87	**1.06**	1.23	2.42	0.65	0.75	**0.82**	1.01	1.74	0.01	0.06	**0.19**	0.8	6.42	0.21	0.39	**0.64**	0.83	5.02
1980	0.27	1.08	**1.56**	2.64	4.58	0.69	0.85	**0.99**	1.2	1.61	0.06	0.2	**0.45**	0.85	1.39	0.24	0.34	**0.64**	1.17	1.29
1981	0.24	1.09	**1.79**	1.96	1.99	0.55	0.59	**0.84**	1.16	1.45	0.03	0.16	**0.41**	3.88	6.86	0.36	0.44	**0.71**	1.24	2.04
1982	1.37	1.48	**1.66**	2.04	2.24	0.66	0.92	**1.19**	1.3	1.89	0.1	1.63	**2.39**	2.65	2.95	0.3	0.96	**1.09**	1.38	4.18
1983	0.85	1.27	**1.63**	2.17	3.37	0.68	1.01	**1.09**	1.47	2.39	0.03	0.19	**0.57**	2.84	4.47	0.02	0.68	**0.78**	1.22	3.06
1984	1.09	1.27	**1.52**	2.41	3.56	0.61	0.8	**1.05**	1.17	1.39	0.0	0.19	**0.33**	1.48	2.12	0.34	0.45	**0.63**	1.3	1.93
1985	1.49	1.62	**1.91**	2.17	3.81	0.59	0.84	**0.99**	1.1	1.28	0.01	0.12	**1.0**	2.29	3.47	0.46	0.97	**1.02**	1.19	1.31
1986	1.08	1.34	**1.62**	1.94	2.03	0.54	0.68	**0.84**	1.04	1.22	0.28	0.89	**1.84**	2.3	3.33	0.49	0.57	**0.67**	0.99	1.51
1987	1.1	1.89	**2.34**	2.60	3.92	0.53	0.98	**1.31**	1.86	4.91	0.16	0.38	**0.62**	2.39	7.43	0.72	0.83	**1.09**	1.79	4.38
1988	0.23	1.38	**1.75**	2.03	3.82	0.3	0.56	**0.73**	1.1	1.26	0.4	0.87	**1.6**	1.8	2.77	0.36	0.66	**0.78**	1.18	1.94
1989	0.27	0.86	**1.67**	3.27	4.51	0.2	0.57	**0.87**	1.05	2.24	0.4	1.72	**2.16**	2.58	4.28	0.61	0.76	**0.94**	1.75	3.77
1990	1.24	1.56	**1.85**	1.91	3.26	0.17	0.68	**0.75**	0.96	1.43	1.06	1.24	**1.42**	1.44	1.45	0.37	0.76	**0.86**	1.31	1.79
1991	1.37	1.54	**1.9**	5.49	5.82	0.69	0.74	**0.94**	1.15	1.59	1.01	1.41	**1.68**	1.81	2.51	0.47	0.85	**1.14**	1.21	1.49
1992	1.32	1.59	**1.64**	1.72	2.87	0.58	0.6	**0.84**	0.97	1.48	1.0	2.44	**2.63**	2.68	5.20	0.56	0.7	**0.76**	0.78	1.92
1993	1.01	1.12	**1.39**	2.02	4.07	0.57	0.7	**0.81**	0.95	1.67	0.52	1.02	**1.25**	1.55	5.95	0.44	0.61	**0.64**	0.97	3.44
1994	1.01	1.11	**1.7**	2.45	6.0	0.29	0.54	**0.61**	0.98	1.26	0.88	1.12	**1.53**	1.64	2.63	0.3	0.63	**1.1**	1.3	1.43

1995	0.73	0.99	**1.58**	2.15	3.32	0.23	0.28	**0.55**	0.83	1.27	0.5	1.39	**1.47**	1.86	1.99	0.11	0.51	**0.99**	1.58	2.07
1996	0.93	1.17	**1.28**	1.57	1.96	-0.01	0.63	**0.65**	0.71	0.87	0.87	1.13	**1.5**	1.6	1.8	0.29	0.67	**0.68**	0.97	1.09
1997						0.62	0.65	**0.83**	0.89	1.35						0.65	0.66	**0.78**	0.79	0.87
1998																				
1999						0.09	0.48	**0.75**	0.97	1.95						0.97	0.98	**1.01**	1.12	1.34
2000						0.12				0.91						0.58	0.76	**0.95**	1.0	1.06
2001						0.14	0.57	**0.71**	0.73	0.89						0.26	0.4	**0.46**	0.95	1.31
2002	3.02	4.83	**6.65**	6.96	7.28	0.48	0.59	**0.83**	1.05	1.07	1.28	1.53	**1.77**	1.84	1.91	0.87	0.97	**1.1**	1.33	1.69
2003	1.29	1.8	**3.04**	3.36	4.55	0.37	0.8	**0.88**	1.19	1.3	0.99	1.28	**1.56**	1.61	1.87	0.95	1.08	**1.29**	1.62	1.71
2004	1.55	2.19	**2.93**	5.58	6.78	0.84	1.03	**1.14**	1.22	1.85	0.75	0.88	**1.1**	1.5	1.92	0.63	0.83	**1.17**	1.57	3.16
2005	1.26	2.88	**4.22**	4.89	6.84	0.46	0.7	**0.87**	1.21	1.46	0.25	0.66	**1.04**	1.26	2.36	0.64	0.69	**0.94**	1.19	1.58
2006	2.59	2.74	**3.04**	3.76	5.18	0.39	0.67	**0.86**	0.99	1.08	1.03	1.03	**1.04**	1.16	1.29	0.81	0.84	**0.96**	1.1	1.22
2007	1.21	2.33	**5.24**	5.63	7.53	0.5	0.66	**0.79**	1.05	1.17	0.13	0.37	**0.6**	0.89	1.03	0.64	0.93	**1.17**	1.28	1.85
2008	0.63	0.89	**2.06**	2.82	5.33	0.46	0.69	**0.86**	1.01	1.25	0.59	0.7	**1.04**	1.36	1.7	0.68	0.86	**1.22**	1.48	1.65
2009	0.86	1.46	**2.28**	3.31	4.33	0.66	0.68	**0.86**	0.91	0.95	0.4	0.57	**0.62**	1.02	1.36	0.35	0.62	**0.8**	0.97	1.17
2010	0.61	1.61	**1.92**	2.19	2.77	0.41	0.55	**0.71**	0.74	2.6	0.43	0.68	**0.81**	0.93	1.42	0.48	0.66	**0.81**	0.96	1.17
2011	0.35	0.78	**1.86**	2.17	3.44	0.44	0.6	**0.79**	0.87	0.95	0.33	0.37	**0.6**	0.92	1.68	0.65	0.67	**0.78**	1.1	1.38
2012	0.2	0.96	**1.43**	1.88	2.19	0.11	0.36	**0.67**	0.79	0.93	0.11	0.38	**0.52**	0.69	1.04	0.73	1.0	**1.17**	1.33	1.97
2013	0.63	0.98	**1.04**	1.42	1.67	0.55	0.65	**0.76**	0.78	0.88	0.4	0.56	**0.64**	0.77	0.83	0.66	0.82	**1.02**	1.23	1.43
2014	0.59	1.0	**1.11**	1.4	1.53	0.45	0.58	**0.68**	0.74	0.82	0.41	0.46	**0.68**	0.78	0.92	0.58	0.76	**0.92**	1.14	1.79

Copper

	Grindstone					Bronte					Fourteen Mile					Sixteen Mile				
Year	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max
1975																10				
1976																10				20
1977																10	10	**20**	20	30
1978																20				20
1979																				
1980						1				10	1				10	1				10
1981	7	8.5	**17**	28.75	40	2	4	**6**	7	26	6	6	**7**	12	80	2	6	**6**	11	37
1982	3	8	**10**	12	24	1	4	**5**	14	24	1	7	**10**	14	15	1	7	**8**	15	45
1983	3	4	**4**	5	7	3	3	**3**	5	16	2	2	**4**	4	9	3	3	**4**	5	8
1984	2	3.25	**4**	4	9	2	3	**3**	4.75	6	1	3	**3**	3.75	4	3	3	**3.5**	4	5
1985	2	3	**4**	4	6	1	1	**1.5**	3	6	1	1	**3**	5	15	1	2	**3**	3.5	6
1986	0	2.75	**3.5**	4.25	5	1	1.5	**2**	8.5	20	1	1.5	**2**	2.5	5	2	2	**2**	3	4
1987	4	4	**5**	5	6	1	1.75	**2**	3.25	4	1	2	**2.5**	3.75	10	1	2.75	**3.5**	4	5
1988	2.5	3.4	**3.6**	4.1	13	1	1.9	**2.4**	3.5	6.3	0.7	2.4	**2.9**	6.6	10	2	2.9	**3.7**	4.6	13
1989	3.4	3.9	**4.5**	5.7	7.6	2.2	2.7	**3.4**	3.7	7.1	2.1	2.4	**2.85**	3.6	5	2	4.1	**4.3**	4.6	6.7
1990	1	3.9	**5**	7	9	0.5	2.1	**3**	3	5	4	5	**6**	6	6	2.1	2.93	**3.5**	4.25	13
1991	0.5	1.75	**3**	4	4	0.5	0.88	**1.5**	2	6	0.5	1	**1.5**	2	3	0.5	1.75	**3**	3	4
1992	2	2	**2**	3	4	0.5	1	**2**	2	3	1	1	**2**	3	4	1	2	**2**	3	4
1993	1.6	2.6	**2.7**	2.83	3.9	1.3	1.7	**2**	2.4	14	1.1	1.8	**2.1**	2.5	14	1.8	2.8	**3.2**	4	13
1994	1.8	2.9	**3**	3.4	4.9	0.6	1.7	**2.1**	2.5	8.6	1.3	1.5	**1.9**	2.8	4.9	1.7	2.2	**3**	3.3	8.7
1995	2	2.53	**3.3**	3.4	4.2	0.85	1.6	**1.6**	3.45	4	0.4	1.33	**2.25**	2.6	6.6	2.3	3.35	**4.05**	4.45	5.6
1996	2.08	2.4	**2.4**	2.8	3.2	1.4	1.51	**1.8**	1.8	3	1.58	1.8	**2**	2.6	2.8	2.02	2.7	**3.1**	4.52	7
1997						0.58	0.89	**1.56**	1.68	2.79						2.46	2.96	**4.13**	4.21	5.48
1998																				
1999						0.58	0.73	**1.08**	2.22	5.22						0.93	1.7	**3.27**	4.83	5.59
2000						0.98				1.42						2.94	3.06	**3.17**	3.44	3.71
2001						0.68	0.95	**0.96**	2.84	29.6						1.90	3.01	**3.13**	3.92	3.97
2002	3.87	4.15	**4.43**	5.06	5.69	0.8	0.8	**0.86**	0.98	1.18	1.45	1.65	**1.84**	1.97	2.09	2.26	2.51	**2.81**	3.68	5.65
2003	1.72	2.45	**3.23**	3.65	4.04	1.18	1.27	**1.41**	1.51	2.29	2.22	3.03	**3.58**	3.88	6.56	2.24	2.82	**3.57**	3.68	5.21
2004	1.27	2.25	**2.57**	2.72	3.5	0.56	0.62	**0.89**	1.17	1.56	2.11	2.18	**2.41**	2.68	3.21	2.02	2.41	**2.69**	3.09	3.94
2005	2.34	2.66	**3.21**	3.74	7.62	0.94	1.02	**1.55**	2.54	6.96	3.34	3.6	**4.35**	4.94	66.0	2.12	2.77	**3.35**	4.82	36.2
2006	2.83	3.29	**3.3**	3.79	4.23	0.69	1.06	**1.43**	1.61	1.89	2.86	3.29	**3.81**	3.9	4.15	2.49	2.83	**3.32**	3.47	3.88
2007	1.05	3.66	**3.88**	4.01	5.22	1.05	1.22	**1.69**	2.44	6.08	2.09	3.30	**3.46**	5.14	12.6	1.36	3.35	**4.01**	5.96	6.26
2008	1.27	2.8	**3.96**	4.72	6.06	0.54	1.64	**2.16**	2.38	3.32	2.31	3.10	**3.54**	4.49	25.8	1.21	2.20	**3.12**	3.77	3.83
2009	2.43	3.41	**3.79**	4.27	5.62	1.36	1.53	**1.81**	2.17	2.63	3.25	3.42	**3.9**	4.09	4.73	2.82	2.92	**3.33**	3.52	4.06
2010	1.64	4.48	**5.92**	11.4	13.6	-1.62	-0.51	**2.34**	3.65	8.09	2.94	4.41	**4.8**	6.99	11.7	2.73	3.12	**3.61**	4.56	6.22
2011	2.9	3.53	**3.82**	4.13	10.5	1.66	1.84	**2.41**	2.62	3.69	3.71	4.03	**4.67**	5.63	9.11	2.54	3.16	**3.43**	3.87	7.37
2012	1.71	2.44	**2.74**	3.35	7.36	0.8	0.94	**1.42**	1.92	4.36	1.74	2.88	**3.56**	5.49	17.4	1.66	2.34	**2.89**	3.44	7.89
2013	1.10	2.42	**2.82**	3.66	4.29	0.66	1.48	**1.62**	1.77	2.29	1.66	3.01	**3.15**	4.39	6.42	0.97	2.26	**2.41**	3.06	4.21
2014	2.45	3.06	**3.22**	3.60	3.99	1.74	1.86	**2.02**	2.13	3.29	1.89	3.57	**4.84**	5.47	6.95	2.29	2.73	**3.20**	3.46	3.59

Iron

	Grindstone					Bronte					Fourteen Mile					Sixteen Mile				
Year	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	**25th**	Med	75th	Max
1967	2800					3000										600				
1968	3000				3150	550				680						520				630
1969	900	1012.5	**1475**	2425	4000	250	775	**1125**	2000	4100						200	**425**	700	975	1200
1970	650	1750	**1900**	2250	2550	200	800	**1125**	1362.5	1700						300	**525**	975	3412.5	5900
1971	700	850	**1800**	2000	7200	1100	1500	**1900**	2500	3000						550	**837.5**	2000	4625	7000
1972	1600	2200	**2800**	4025	6500	350	462.5	**800**	1350	2100	50				150	300	**675**	825	1812.5	4700
1973																				
1974																				
1975																50				
1976																230	**355**	460	695	3600
1977																500	**727.5**	1260	2145	13000
1978																260	**485**	770	1145	3800
1979																				
1980																				
1981						320	342.5	**1025**	2212.5	3750	120	420	**810**	1120	1180	440	**500**	730	1390	2740
1982	2145					70	495	**715**	1180	37000	75	100	**295**	480	13500	180	**390**	915	1700	46500
1983						135	580	**650**	865	5200	40	110	**315**	1500	3350	180	**415**	540	830	4150
1984						230	240	**570**	635	1775	65	81.25	**135**	195	1380	155	**276.25**	477.5	806.25	3800
1985						110	260	**340**	410	725	43	50.25	**70.5**	420	1400	100	**220**	345	655	940
1986						160	225	**330**	565	1700	96	225	**260**	575	820	100	**315**	430	560	930
1987						210	387.5	**750**	1225	2400	38	385	**595**	1300	2400	360	**477.5**	820	1200	2700
1988						75	150	**290**	840	960	110	430	**810**	1700	3800	120	**330**	430	580	2200
1989						270	340	**390**	660	5900	63	195	**260**	812.5	1300	120	**310**	560	900	3100
1990						70	110	**160**	540	1400	130	140	**150**	285	420	60	**127.5**	285	410	3200
1991						70	145	**220**	332.5	590	50	60	**85**	182.5	790	80	**147.5**	195	230	480
1992						86	120	**222**	300	560	40	120	**410**	640	1000	40	**100**	190	470	720
1993						84	160	**260**	300	5200	65	120	**130**	350	8700	120	**250**	410	450	3400
1994	33	146.5	**260**	265	270	89	160	**240**	270	570	59	110	**170**	270	800	99	**200**	230	330	670
1995	150	257.5	**490**	830	1100	67	110	**200**	255	400	40	73.25	**94.5**	240	1500	110	**127.5**	240	460	1100
1996	260	400	**438**	560	600	1.44	180	**200**	260	740	60	140	**167**	260	600	113	**220**	310	1232.5	2600
1997						4.73	117	**324**	338	374						6.27	**152**	366	391	951
1998																				
1999						40.1	47.63	**110.5**	662.75	896						61.4	**66.2**	77.35	133.43	273
2000						85.9				317						106	**129.5**	153	189	225
2001						34.8	38	**39.6**	79.3	364						69	**74.9**	98.2	103	220
2002	38.8	111.4	**184**	312.5	441	35.2	36.18	**52.95**	98.3	185	79.2	92.1	**105**	177	249	81.3	**147.08**	170	175.75	190
2003	28.7	139.5	**168**	194.5	463	52.4	107	**120**	154.75	197	129	156.5	**255**	322.5	687	157	**202.5**	285	314.5	895
2004	32.8	50.65	**117.5**	148	205	43	63.95	**66.1**	103.7	126	55.4	100.35	**118**	151	193	35.6	**73.8**	133	184.5	259
2005	47.8	69.48	**118.05**	244.25	1010	51.8	67.23	**76.95**	269	737	50.7	90.85	**153**	420.5	3170	49.4	**100.73**	192	334.75	883
2006	42.9	81.2	**114**	301	583	51.7	55.6	**63.4**	203	296	64.6	72.4	**114**	373	495	77.1	**94.2**	173	229	341
2007	54.9	62.25	**169**	343.25	1070	49.6	82.88	**142.5**	244.25	2420	37.5	50.18	**76.65**	385.25	3380	77.2	**120.5**	133	241	2360
2008	105	162	**354**	687.25	1650	47.8	131	**240**	375	966	64.2	226.25	**408.5**	517	1860	42.8	**157.75**	316	360.75	1650
2009	107	135.5	**221**	273.5	501	54.6	88.3	**91.8**	202.5	358	53.8	60.25	**83**	136	375	54.3	**67.5**	117	269.5	536
2010	173	191	**650**	859.5	1770	61	72.05	**93.05**	111.5	1520	70.4	80.95	**164**	350.5	1980	45.3	**63.4**	80.6	288.6	1850
2011	55.6	89.6	**176**	552.5	1470	35.3	78.1	**112**	311.5	580	39.4	84.45	**104**	312.5	884	55.7	**72.55**	191	463	921
2012	68.2	133.75	**168**	214.25	1920	60.7	80.48	**93**	136.5	1290	50.2	66.13	**78.6**	1023.75	4710	37.7	**90.38**	119	398.5	1950
2013	42.3	75.8	**128**	223	349	34.1	53.28	**74.95**	114.4	164	45.9	49.6	**53.3**	197	306	28.9	**59.7**	74	158.5	204
2014	89.1	137.5	**166**	246.25	635	75.8	96.33	**114**	192.25	469	55.5	59.375	**151.5**	294	524	54.8	**68.35**	95.45	247	498

Zinc

	Grindstone					Bronte					Fourteen Mile					Sixteen Mile				
Year	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max	Min	25th	**Med**	75th	Max
1975																20				
1976																40				60
1977																10	20	**20**	100	140
1978																20				50
1979																				
1980						2				10	1				10	5				10
1981	7	8.5	**9.5**	52.5	180	5	6	**10**	12	36	1	4	**8**	10	13	6	8	**12**	13	17
1982	4	10	**13**	19	82	3	5	**9**	11	150	1	2	**2**	4	57	1	7	**9**	21	160
1983	4	5	**6**	8	8	4	5	**6**	10	22	1	1	**1**	3	13	3	4	**5**	8	39
1984	5	7	**7**	10.75	25	4	6	**7**	9	18	1	1	**1**	1.75	5	4	5.25	**6**	7.75	11
1985	5	8	**10**	13	31	5	5.75	**8.5**	10	10	1	2	**5**	8	12	6	7	**12.5**	15.25	27
1986	1	5.5	**7**	8.5	11	5	6.5	**8**	12	74	1	2	**3**	5.5	7	3	7	**9**	9.5	22
1987	4	8.5	**9.5**	10	11	5	8.5	**14**	16.25	370	1	1.75	**3**	8.25	34	4	7.5	**8**	10.25	13

1988	4	6.2	**7.2**	8.8	16	2.5	3.5	**7.3**	13	14	0.9	2.4	**4.8**	5.4	19	5	5.7	**7**	11	910
1989	3.7	6.1	**7.7**	9	19	3.6	4.9	**9.1**	10	53	0.8	1.53	**1.85**	4.8	6.3	2	4.7	**6.3**	12	19
1990	1.9	7	**7**	9	25	3	4	**7.4**	10	19	4	5	**6**	7.5	9	1.9	4.75	**5**	6.1	39
1991	2	3.75	**4.5**	5.75	12	0.5	2.75	**4.5**	8.25	13	0.5	1	**2**	3.75	8	0.5	3.75	**4.5**	5.25	12
1992	2	3	**4**	5	6	3	4	**5**	5.6	10	3	6	**8**	20	37	1	2	**2**	5	7
1993	3.6	4.6	**6.25**	7.65	9.9	2.5	3.4	**4.7**	8.3	96	1.8	2.4	**2.7**	5	62	3.1	4.3	**4.5**	8.2	49
1994	0.92	3.3	**6.5**	7	11	2.8	5.5	**6.1**	6.9	11	1.4	3.6	**5.7**	12	19	3.2	4	**5.1**	5.5	7.9
1995	1.7	2.875	**5.25**	7.25	10	3	3.3	**4**	5.15	6.5	1.5	2.175	**2.5**	4.75	14	3.5	4.45	**5.5**	7.05	16
1996	3.21	3.5	**4**	5	5.5	0.58	5.5	**6**	7.5	24	1	2.5	**3.21**	3.5	9.5	1.62	3.5	**5.75**	13.03	34
1997						0.49	2.27	**6.21**	7.11	29.9						2.52	5.51	**5.51**	7.49	27
1998																				
1999						1.51	2.13	**4.69**	10.49	20						3.8	5.04	**5.74**	6.28	7.01
2000						2.84	3.39	**3.95**	4.5	5.05						3.02	3.96	**4.89**	5.13	5.36
2001						0.71	1.42	**2.45**	4.59	5.1						1.84	2.74	**3**	4.14	6.05
2002	4.31	5.72	**7.13**	7.43	7.72	1.52	1.53	**1.63**	2.57	5.1	2.69	2.71	**2.73**	3.86	4.99	3.84	4.33	**4.6**	5.05	6.08
2003	3.2	3.35	**3.51**	5.52	8.92	1.63	3.01	**3.51**	4.15	6.82	3.39	4.26	**5.43**	9.62	27.9	3.85	4.56	**5.29**	8.74	13.8
2004	2.22	2.65	**3.06**	3.41	6.13	0.35	2.03	**3.06**	4.01	11.2	1.39	4.13	**4.98**	5.24	5.58	1.52	2.5	**3.46**	5.88	7.85
2005	1.2	3.1	**3.94**	12.1	46.10	0.93	2.11	**2.23**	6.42	31.6	2.04	3.26	**5.35**	9.51	66.9	2.61	3.39	**4.27**	7.27	21
2006	-0.15	0.29	**2.26**	7.36	10.7	-1.59	-1.38	**-0.41**	4.45	7.97	-0.31	0.1	**0.5**	6.89	12.50	0.49	1.34	**1.78**	2.94	4.26
2007	1.93	3.32	**3.49**	6.41	15.3	0.45	1.79	**3.65**	9.39	40.4	1.63	1.78	**2.3**	12.99	53.3	1.62	3.37	**3.69**	6.26	23.9
2008	0.64	3.33	**6.08**	10.66	20.10	0.63	1.48	**9.72**	14.40	39.3	1.63	4.36	**7.51**	12.45	142	1.7	3.47	**4.43**	5.6	13
2009	-1.08	0.83	**1.83**	4.35	6.93	-1.09	-0.06	**0.63**	6.28	9.45	0.15	0.76	**2.58**	4.23	7.51	0.154	0.4	**0.64**	3.79	6.54
2010	3.39	4.97	**8.67**	10.72	14.6	1.04	4.23	**8.05**	10.09	18	0.4	4.89	**9.71**	12.1	16.8	0.438	4.05	**7.84**	11.3	14.8
2011	2.71	3.52	**4.49**	10.94	29.60	4.38	6.09	**6.94**	13.55	15	4.8	5.54	**5.94**	12.12	32.2	4.43	5.25	**6.86**	9.17	23
2012	4.52	4.81	**6.63**	8.23	41.40	3.95	5.2	**7.24**	9.16	37	4.85	6.22	**8.31**	22.4	106	5.19	5.84	**6.53**	12	46.9
2013	9.36	10.16	**11.2**	12.85	16.2	8.62	9.42	**10.55**	12.08	13.5	10.1	11.9	**12.6**	17.25	23	8.97	9.51	**9.86**	10.75	14.8
2014	4.06	12.55	**13.8**	14.28	18	8.85	11.68	**12.95**	13.90	23.3	15.5	17.45	**21.7**	26.03	31.80	6.88	11.43	**12.15**	13.2	15.9

Appendix C: Results of Mann-Kendall Test

Watershed	Station	Chloride									Total Phosphorus									Total Suspended Sediment									Nitrate								
		Overall Trend			1975-1996 Trend			2002-2014 Trend			Overall Trend			1975-1996 Trend			2002-2014 Trend			Overall Trend			1975-1996 Trend			2002-2014 Trend			Overall Trend			1975-1996 Trend			2002-2014 Trend		
		N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P
Grindstone	GRN-114^{M}	32	5.21	<0.01	22	3.55	<0.01	--	--	--	33	-2.80	0.01	22	-3.38	<0.01	--	--	--	20	-1.88	0.06	11	-2.15	0.03	--	--	--	33	4.76	<0.01	22	1.44	0.15	--	--	--
	GRN-5	13	-1.89	0.06	--	--	--	13	-1.89	<0.01	13	-1.53	0.13	--	--	--	13	-1.53	0.13	13	-1.16	0.25	--	--	--	13	-1.16	0.25	13	-3.60	<0.01	--	--	--	13	-3.60	<0.01
	GRN-18	32	5.82	<0.01	22	4.79	<0.01	--	--	--	34	-1.22	0.22	22	1.24	0.21	--	--	--	21	-1.90	0.06	11	0.54	0.59	--	--	--	34	3.96	<0.01	22	0.79	0.43	--	--	--
Sheldon	SHL-48^{M}	8	0.37	0.71	--	--	--	8	0.37	0.71	8	-0.87	0.39	--	--	--	8	-0.87	0.39	8	-0.87	0.39	--	--	--	8	-0.87	0.39	8	-0.12	0.90	--	--	--	8	-0.12	0.90
Bronte	BRO-19^{M}	34	6.69	<0.01	22	4.26	<0.01	--	--	--	35	-1.49	0.14	22	0	1.00	--	--	--	34	-1.36	0.17	22	-1.75	0.08	--	--	--	35	0.80	0.43	22	-2.17	0.03	--	--	--
	BRO-119	16	0.14	0.89	--	--	--	13	0.18	0.85	16	-0.95	0.34	--	--	--	13	-0.43	0.67	16	0.32	0.75	--	--	--	13	0.55	0.58	16	-0.86	0.39	--	--	--	13	-2.81	0.01
	BRO-264	35	6.93	<0.01	21	4.68	<0.01	--	--	--	35	-3.96	<0.01	22	-1.72	0.09	--	--	--	23	-2.59	0.01	11	0.23	0.82	--	--	--	35	1.24	0.22	22	-1.75	0.08	--	--	--
	BRO-16	16	-0.63	0.53	--	--	--	13	-0.37	0.71	16	0.23	0.82	--	--	--	13	-0.55	0.58	16	0.90	0.37	--	--	--	13	-0.12	0.90	16	-0.59	0.56	--	--	--	13	-1.16	0.25
	BRO-265	18	0.83	0.40	18	0.83	0.40	--	--	--	18	0.91	0.36	18	0.91	0.36	--	--	--	6	0.75	0.45	6	0.75	0.45	--	--	--	18	1.25	0.21	18	1.25	0.21	--	--	--
	BRO-2	35	5.41	<0.01	22	3.47	<0.01	13	2.26	0.02	35	-1.46	0.14	22	0.99	0.32	13	-0.24	0.81	23	0.42	0.67	10	3.22	<0.01	13	0	1	35	2.26	0.02	22	1.04	0.30	13	-1.28	0.20
Fourteen Mile	FOR-58^{M}	38	5.97	<0.01	22	2.62	0.01	13	0.31	0.76	38	1.16	0.25	22	2.06	0.04	13	-0.37	0.71	37	0.04	0.97	22	3.55	<0.01	13	-1.16	0.25	38	2.09	0.75	22	3.38	<0.01	13	-2.75	0.01
Sixteen Mile	SXM-143^{M}	49	7.20	<0.01	22	3.98	<0.01	13	0.37	0.71	50	-5.53	<0.01	22	-1.95	0.05	13	-2.14	0.03	49	-3.37	<0.01	22	0.99	0.32	13	-1.89	0.06	50	4.82	<0.01	22	2.76	0.01	13	-1.16	0.25
	SXM-216	13	-0.49	0.63	--	--	--	13	-0.49	0.63	13	-1.22	0.22	--	--	--	13	-1.22	0.22	13	-0.61	0.54	--	--	--	13	-0.61	0.54	13	-1.40	0.16	--	--	--	13	-1.40	0.16
	SXM-537	32	5.76	<0.01	22	3.21	<0.01	--	--	--	32	-5.11	<0.01	22	-3.75	<0.01	--	--	--	19	-1.33	0.18	10	-1.25	0.21	--	--	--	32	3.58	<0.01	22	0.23	0.82	--	--	--
	SXM-61	22	4.40	<0.01	22	4.40	<0.01	--	--	--	22	-1.83	0.07	22	-1.83	0.07	--	--	--	10	-1.25	0.21	10	-1.25	0.21	--	--	--	10	-1.70	0.09	10	-1.70	0.09	--	--	--
	SXM-63	34	5.63	<0.01	21	4.11	<0.01	13	-1.4	0.16	35	0.87	0.39	22	0.09	0.93	13	-2.38	0.02	21	0	1	8	0.62	0.54	13	-1.46	0.14	23	-0.48	0.63	10	0.98	0.33	13	-3.17	<0.01
	SXM-205	33	5.93	<0.01	21	3.29	<0.01	12	1.44	0.15	34	0.25	0.80	22	-0.17	0.87	12	0.07	0.95	20	-0.45	0.65	8	0.62	0.54	12	1.17	0.24	21	0.51	0.61	9	-0.31	0.75	12	-0.21	0.84
	SXM-349	13	-1.89	0.06	--	--	--	13	-1.89	0.06	13	-1.71	0.09	--	--	--	13	-1.71	0.09	13	0.31	0.76	--	--	--	13	0.31	0.76	13	-2.38	0.02	--	--	--	13	-2.38	0.02
	SXM-556	23	5.04	<0.01	21	4.59	<0.01	--	--	--	24	-1.51	0.13	22	-0.48	0.63	--	--	--	9	-0.83	0.40	8	-1.73	0.08	--	--	--	11	0.23	0.82	9	0.00	1.00	--	--	--

Number of Samples (N), Test Statistic (S), P value (P)

Watershed	Station	Copper									Iron									Zinc									Water Quality Index								
		Overall Trend			1975-1996 Trend			2002-2014 Trend			Overall Trend			1975-1996 Trend			2002-2014 Trend			Overall Trend			1975-1996 Trend			2002-2014 Trend			Overall Trend			1975-1996 Trend			2002-2014 Trend		
		N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P	N	S	P
Grindstone	GRN-114^{M}	12	1.30	0.19	12	1.30	0.19	--	--	--	10	-2.59	0.01	4	-3.06	<0.01	--	--	--	16	-2.84	<0.01	16	-2.84	<0.01	--	--	--	33	4.76	<0.01	22	3.27	<0.01	--	--	--
	GRN-5	13	-0.06	0.95	--	--	--	13	-0.06	0.95	13	0.12	0.90	--	--	--	13	0.12	0.90	13	1.77	0.08	--	--	--	13	1.77	0.08	13	0.79	0.43	--	--	--	13	0.79	0.43
	GRN-18	12	1.03	0.30	12	1.03	0.30	--	--	--	10	-0.72	0.47	4	-0.34	0.73	--	--	--	16	-1.22	0.22	16	-1.22	0.22	--	--	--	34	1.33	0.18	22	-0.11	0.91	--	--	--
Sheldon	SHL-48^{M}	8	0.12	0.90	--	--	--	8	0.12	0.90	8	-0.87	0.39	--	--	--	8	-0.87	0.39	8	1.36	0.17	--	--	--	8	1.36	0.17	8	0.12	0.90	--	--	--	8	0.12	0.90
Bronte	BRO-19^{M}	14	3.89	<0.01	12	3.84	<0.01	--	--	--	24	-3.52	<0.01	16	-2.93	0.00	--	--	--	19	-1.08	0.28	17	-1.98	0.05	--	--	--	35	2.49	0.01	22	1.97	0.05	--	--	--
	BRO-119	16	3.02	<0.01	--	--	--	13	2.5	0.01	16	0.68	0.50	--	--	--	13	1.04	0.30	16	1.85	0.06	--	--	--	13	2.5	0.01	16	-0.45	0.65	--	--	--	13	-0.61	0.54
	BRO-264	15	-0.20	0.84	12	1.17	0.24	--	--	--	13	-2.32	0.02	4	0.34	0.73	--	--	--	19	-2.80	0.01	16	-1.67	0.10	--	--	--	35	3.45	<0.01	22	0.96	0.34	--	--	--
	BRO-16	16	2.84	<0.01	--	--	--	13	2.5	0.01	16	1.49	0.14	--	--	--	13	0.92	0.36	16	2.12	0.03	--	--	--	13	2.01	0.04	16	-1.22	0.22	--	--	--	13	-0.18	0.85
	BRO-265	12	-10.63	<0.01	12	-10.63	<0.01	--	--	--	4	0.34	0.73	4	0.34	0.73	--	--	--	16	-12.56	<0.01	16	-12.56	<0.01	--	--	--	18	0.76	0.45	18	0.76	0.45	--	--	--
	BRO-2	19	-0.31	0.75	12	0.96	0.34	7	0	1.00	10	-0.09	0.93	3	1.04	0.30	7	0	1.00	23	-2.09	0.04	16	-1.31	0.19	7	0	1.00	35	3.38	<0.01	22	-0.45	0.65	13	2.14	0.03
Fourteen Mile	FOR-58^{M}	25	5.49	<0.01	12	2.74	<0.01	13	1.65	0.10	30	-2.43	0.02	16	-1.49	0.14	13	-1.16	0.25	30	2.28	0.02	17	0.29	0.77	13	2.5	0.01	38	0.20	0.84	22	-0.73	0.46	13	-0.79	0.43
Sixteen Mile	SXM-143^{M}	29	4.2	<0.01	12	7.54	<0.01	13	-0.31	0.76	43	-5.19	<0.01	20	-11.55	0.00	13	-2.07	0.04	38	-2.82	<0.01	21	-3.78	<0.01	13	1.89	0.06	50	2.87	<0.01	22	-0.06	0.96	13	0.31	0.76
	SXM-216	13	1.40	0.16	--	--	--	13	1.40	0.16	13	-0.06	0.95	--	--	--	13	-0.06	0.95	13	1.16	0.25	--	--	--	13	1.16	0.25	13	1.16	0.25	--	--	--	13	1.16	0.25
	SXM-537	12	1.92	0.05	12	1.92	0.05	--	--	--	9	-2.40	0.02	3	0.00	1.00	--	--	--	16	-3.11	<0.01	16	-3.11	<0.01	--	--	--	32	2.04	0.04	22	1.52	0.13	--	--	--
	SXM-61	12	2.33	0.02	12	2.33	0.02	--	--	--	16	-3.60	<0.01	16	-3.60	0.00	--	--	--	16	-2.57	0.01	16	-2.57	0.01	--	--	--	22	0.59	0.55	22	0.59	0.55	--	--	--
	SXM-63	19	0.87	0.38	12	3.02	0.02	7	<0.01	1.00	23	-2.48	0.01	16	-0.45	0.65	7	-3	<0.01	23	-1.40	0.16	16	-0.63	0.53	7	-0.9	0.37	35	0.23	0.82	22	0.85	0.40	13	0.43	0.67
	SXM-205	24	3.42	<0.01	12	3.43	<0.01	12	2.13	0.03	28	-1.84	0.07	16	-2.30	0.02	12	1.03	0.30	28	-1.80	0.07	16	-2.75	0.01	12	1.44	0.15	34	2.31	0.02	22	0.62	0.54	12	-0.34	0.73
	SXM-349	7	0.30	0.76	--	--	--	7	0.30	0.76	7	0.00	1.00	--	--	--	7	0.00	1.00	7	-0.90	0.37	--	--	--	7	-0.90	0.37	13	1.28	0.20	--	--	--	13	1.28	0.20
	SXM-556	12	3.77	<0.01	12	3.77	<0.01	--	--	--	16	-3.02	<0.01	16	-3.02	0.00	--	--	--	16	-2.07	0.04	16	-2.07	0.04	--	--	--	24	1.61	0.11	22	1.97	0.05	--	--	--

Number of Samples (N), Test Statistic (S), P value (P)

Appendix D: Results of Kruskal-Wallis Test

Watershed	Station	Chloride									Total Phosphorus									Total Suspended Sediment									Nitrate								
		Spring vs. Summer			Spring vs. Fall			Summer vs. Fall			Spring vs. Summer			Spring vs. Fall			Summer vs. Fall			Spring vs. Summer			Spring vs. Fall			Summer vs. Fall			Spring vs. Summer			Spring vs. Fall			Summer vs. Fall		
		N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P
Grindstone	GRN-5	24	14.40	<0.01	24	2.29	0.13	26	4.23	0.04	24	0.87	0.35	24	1.24	0.27	26	1.87	0.17	24	2.87	0.09	24	4.78	0.03	26	2.35	0.13	24	7.57	0.01	24	8.22	<0.01	26	0.24	0.63
Sheldon	SHL-48	15	1.46	0.23	13	3.27	0.07	14	2.4	0.12	15	0.00	1.00	13	0.00	1.00	14	1.35	0.25	15	0.01	0.92	13	0.07	0.80	14	0.15	0.70	15	5.91	0.02	13	5.90	0.02	14	0.07	0.80
Bronte	BRO-119	24	8.39	<0.01	24	4.72	0.03	26	0.11	0.74	24	4.85	0.03	24	0.44	0.51	26	5.68	0.02	24	3.02	0.08	24	1.83	0.18	26	0.58	0.45	24	1.28	0.26	24	0.07	0.79	26	0.63	0.43
	BRO-16	24	0.01	0.93	23	0.46	0.50	25	0.96	0.33	24	2.27	0.13	23	0.98	0.32	25	8.00	<0.01	24	5.36	0.02	23	0.31	0.58	25	6.67	0.01	24	17.16	<0.01	23	2.37	0.12	25	4.27	0.04
	BRO-2	22	9.66	<0.01	21	2.80	0.09	23	0.91	0.34	22	4.91	0.03	21	3.69	0.05	23	14.15	<0.01	22	0.54	0.46	21	4.98	0.03	23	6.37	0.01	22	0.35	0.55	21	0.32	0.57	23	0.14	0.71
Fourteen Mile	FOR-58	24	1.670	0.19	24	7.26	0.01	26	3.50	0.06	24	0.57	0.45	24	1.06	0.30	26	1.74	0.19	24	1.21	0.27	24	0.74	0.39	26	0.05	0.83	24	3.12	0.08	24	0.14	0.71	26	2.78	0.10
Sixteen Mile	SXM-143	24	0.08	0.77	24	4.23	0.04	26	6.44	0.01	24	2.82	0.09	24	1.03	0.31	26	1.51	0.22	24	5.64	0.02	24	4.53	0.03	26	0.54	0.46	24	2.92	0.09	24	0.91	0.34	26	9.31	<0.01
	SXM-216	24	4.11	0.04	23	0.46	0.50	25	1.30	0.25	24	2.54	0.11	23	0.52	0.47	25	2.66	0.10	24	4.98	0.03	23	2.45	0.12	25	2.67	0.10	24	10.72	<0.01	23	8.73	<0.01	25	0.01	0.91
	SXM-63	23	15.75	<0.01	21	4.55	0.03	24	0.52	0.47	23	4.04	0.04	21	7.79	0.01	24	10.89	<0.01	23	2.10	0.15	21	10.14	<0.01	24	15.63	<0.01	23	1.11	0.29	21	2.74	0.10	24	0.81	0.37
	SXM-205	22	9.00	<0.01	21	10.04	<0.01	23	0.46	0.50	22	7.18	0.01	21	3.04	0.08	23	1.55	0.21	22	6.28	0.01	21	3.10	0.08	23	0.05	0.83	22	15.65	<0.01	21	9.60	<0.01	23	2.18	0.14
	SXM-349	23	1.28	0.26	21	6.73	0.01	24	7.90	<0.01	23	1.78	0.18	21	0.16	0.69	24	10.27	<0.01	23	0.00	0.98	21	6.39	0.01	24	9.25	<0.01	23	5.85	0.02	21	15.00	<0.01	24	11.10	<0.01

Number of Samples (N), Test Statistic (K), P value (P)

Watershed	Station	Copper									Iron									Zinc								
		Spring vs. Summer			Spring vs. Fall			Summer vs. Fall			Spring vs. Summer			Spring vs. Fall			Summer vs. Fall			Spring vs. Summer			Spring vs. Fall			Summer vs. Fall		
		N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P	N	K	P
Grindstone	GRN-5	24	14.40	<0.01	24	2.29	0.13	26	4.23	0.04	24	0.87	0.35	24	1.24	0.27	26	1.87	0.17	24	2.87	0.09	24	4.78	0.03	26	2.35	0.13
Sheldon	SHL-48	15	1.46	0.23	13	3.27	0.07	14	2.4	0.12	15	0.00	1.00	13	0.00	1.00	14	1.35	0.25	15	0.01	0.92	13	0.07	0.80	14	0.15	0.70
Bronte	BRO-119	24	8.39	<0.01	24	4.72	0.03	26	0.11	0.74	24	4.85	0.03	24	0.44	0.51	26	5.68	0.02	24	3.02	0.08	24	1.83	0.18	26	0.58	0.45
	BRO-16	24	0.01	0.93	23	0.46	0.50	25	0.96	0.33	24	2.27	0.13	23	0.98	0.32	25	8.00	<0.01	24	5.36	0.02	23	0.31	0.58	25	6.67	0.01
	BRO-2	22	9.66	<0.01	21	2.80	0.09	23	0.91	0.34	22	4.91	0.03	21	3.69	0.05	23	14.15	<0.01	22	0.54	0.46	21	4.98	0.03	23	6.37	0.01
Fourteen Mile	FOR-58	24	1.670	0.19	24	7.26	0.01	26	3.50	0.06	24	0.57	0.45	24	1.06	0.30	26	1.74	0.19	24	1.21	0.27	24	0.74	0.39	26	0.05	0.83
Sixteen Mile	SXM-143	24	0.08	0.77	24	4.23	0.04	26	6.44	0.01	24	2.82	0.09	24	1.03	0.31	26	1.51	0.22	24	5.64	0.02	24	4.53	0.03	26	0.54	0.46
	SXM-216	24	4.11	0.04	23	0.46	0.50	25	1.30	0.25	24	2.54	0.11	23	0.52	0.47	25	2.66	0.10	24	4.98	0.03	23	2.45	0.12	25	2.67	0.10
	SXM-63	23	15.75	<0.01	21	4.55	0.03	24	0.52	0.47	23	4.04	0.04	21	7.79	0.01	24	10.89	<0.01	23	2.10	0.15	21	10.14	<0.01	24	15.63	<0.01
	SXM-205	22	9.00	<0.01	21	10.04	<0.01	23	0.46	0.50	22	7.18	0.01	21	3.04	0.08	23	1.55	0.21	22	6.28	0.01	21	3.10	0.08	23	0.05	0.83
	SXM-349	23	1.28	0.26	21	6.73	0.01	24	7.90	<0.01	23	1.78	0.18	21	0.16	0.69	24	10.27	<0.01	23	0.00	0.98	21	6.39	0.01	24	9.25	<0.01

Number of Samples (N), Test Statistic (K), P value (P)

Appendix E: Correlation Coefficients

Watershed	Station	Copper			Iron			Zinc		
		rho	t-stat	p	rho	t-stat	p	rho	t-stat	p
Grindstone	GRN-114	0.57	2.58	0.02	0.76	6.97	0.00	0.56	2.54	0.02
	GRN-5	0.39	3.95	0.00	0.85	14.82	0.00	0.50	5.25	0.00
	GRN-18	0.67	3.39	0.00	0.84	9.42	0.00	0.96	12.23	0.00
Sheldon	SHL-48	0.67	5.04	0.00	0.90	11.43	0.00	0.50	3.20	0.00
Bronte	BRO-19	0.36	3.89	0.00	0.79	15.66	0.00	0.69	11.03	0.00
	BRO-119	0.46	5.11	0.00	0.85	15.52	0.00	0.58	6.87	0.00
	BRO-264	0.78	6.67	0.00	0.84	10.89	0.00	0.78	6.61	0.00
	BRO-16	0.51	5.54	0.00	0.82	13.41	0.00	0.45	4.72	0.00
	BRO-265	0.67	3.36	0.00	0.77	5.44	0.00	0.74	4.15	0.00
	BRO-2	0.16	1.13	0.27	0.50	4.01	0.00	0.33	2.36	0.02
Fourteen Mile	FOR-58	0.23	3.10	0.00	0.79	18.50	0.00	0.44	7.11	0.00
Sixteen Mile	SXM-143	0.32	4.72	0.00	0.85	26.60	0.00	0.50	8.92	0.00
	SXM-216	0.39	3.83	0.00	0.87	15.66	0.00	0.16	1.45	0.15
	SXM-537	0.85	6.08	0.00	0.76	7.00	0.00	0.77	4.46	0.00
	SXM-61	-0.01	-0.05	0.96	0.39	1.56	0.14	0.26	1.00	0.33
	SXM-63	0.28	1.99	0.05	0.77	7.97	0.00	0.64	5.55	0.00
	SXM-205	0.56	6.41	0.00	0.80	12.98	0.00	0.54	6.16	0.00
	SXM-349	0.59	3.84	0.00	0.84	8.04	0.00	0.82	7.64	0.00
	SXM-556	0.39	1.58	0.14	0.66	3.25	0.01	0.65	3.20	0.01