# WATER QUALITY OF THE ST. MARY'S RIVER WATERSHED:

# A DETAILED ANALYSIS.

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# EXECUTIVE SUMMARY


Water quality data in the St. Mary's River watershed, Guysborough County, has been collected as far back as 1966. This report presents a comprehensive analysis of water quality in the St. Mary's River to identify potential parameters of concern from ecological and drinking water perspectives. The St. Mary's River drains a large area (1,350 $km^2$) and is comprised of three branches – the East Branch, West Branch, and Main Branch. The East and West Branches are fundamentally different in many respects of water quality due to differences in bedrock geology and soils. Eleven data sources, ranging from 1975 to 2009 and using data from 1966 to 2009 were used in this analysis. These data sources included a large variety of water quality parameters (DO, pH, temperature, ionic composition, hardness/alkalinity, turbidity, colour, specific conductance, nutrients, and metals). Data sources were reviewed, compiled and analyzed. Water quality parameters were interpreted in comparison with Canadian Council of Ministers of the Environment Guidelines for the Protection of Aquatic Life and with Health Canada Drinking Water Quality Guidelines.

Water temperature was greater in the West Branch than either the East or Main Branches, and there was high variability on the West Branch relative to the other two. There is little evidence of consistent, directional heating or cooling in summer months between early 1990s and late 2000s. The Main and East Branches show some evidence of increases in frequency of maximum temperatures between 1990s and 2000s, but West Branch does not show this. The maximum temperatures occur in early- to mid-July. Cold water refugia have been identified which may help ameliorate effects of temperature extremes. Turbidity is equal among the three branches, and is generally low (<1.0 JTU or <1.0 NTU). The period of greatest frequency of high turbidity is November, December, March and April of each year. Turbidity has been measured using two, incomparable, units (NTU and JTU) which limits inferences. There is some evidence of long-term decreases in turbidity. Levels of turbidity observed in the St. Mary's are not expected to be problematic for biota. In terms of colour, the East Branch is clearer than the West or Main Branch. The dark colour of the West Branch water is likely due to tannins and humic acids derived from bogs and wetlands on this branch. Colour has been measured using three, incomparable, units (Apparent, True, Hazen) which limits inferences.

East Branch pH is significantly greater than the West and Main Branches, with the latter two being equal. There is considerable variability among tributaries within a branch. There is no evidence of increasing or decreasing trend in pH over 35+ years. pH is generally higher in winter than in summer, and commonly ranges over 1.5 to 2.0 pH units over the period of a year. pH varies on weekly and monthly time scales with the West Branch being more variable than the East or Main Branches. Low pH can affect all freshwater stages of Atlantic salmon, with fry being the most sensitive. Salmon appear largely unaffected at pH >5.4, and show mortality and population declines below this value. pH occasionally is recorded as <5.4 units on the West Branch which may impact Atlantic salmon locally, but pH depressions of this level are infrequent and so not likely to exert a population-level depression effect.

Levels of alkalinity are greater in the East Branch than the West Branch, which are in turn greater than the Main Branch. Variability of alkalinity appears higher in the West Branch than East or Main. There is no evidence of change in alkalinity over time, and the values recorded are at the low end of the range, implying sensitivity to acidification. Similar to alkalinity, hardness

is greater in the East Branch than the West Branch, and in turn greater than the Main Branch. Variability of hardness is higher in the East Branch than Main or West. Overall mean hardness is 6.6 mg/L $CaCO_3$, implying this is a soft-water system. Specific conductance is greater in the East Branch than the Main or West Branches. Variability of specific conductance is higher in the East Branch than Main or West. There is no evidence of change in specific conductance over time. Eleven individual ionic constituents (bicarbonate, calcium, carbon, carbonate, chloride, fluoride, humic acid, potassium, silica, sodium and sulphate) contributing to alkalinity, hardness and specific conductance are briefly summarized. Dissolved oxygen concentrations are unlikely to be an issue of concern except perhaps in highly localized areas of specialized conditions (deeper water and larger masses of decaying matter).

There is no difference in phosphorous concentrations among branches, and phosphorous is present at low (usually <0.01 mg/L) concentrations. There is some evidence of change over time, appearing to be elevated in 1970s, depressed in 1980s and increasing again since the 1990s. According to CCME classification, based on the phosphorous concentrations, the system is mesotrophic or meso-eutrophic, though at the low end of this classification. Four forms of nitrogen have been monitored (total nitrogen, nitrate/nitrite, nitrate, and ammonia). Total nitrogen appears elevated relative to phosphorous and concentration, in general, are lower in summer and higher in winter. Total nitrogen concentrations appear to have increased significantly in 2006-2008 relative to previous years. Nitrate/nitrite concentrations are greater in the East Branch than the Main and West Branches. They peak in winter months and are lowest in summer. There is large variation for a given month among years, and no evidence of increasing or decreasing trend over time. Nitrate concentrations peak in winter and are low in summer, and the maximum concentration do not exceed CCME guidelines. There no evidence of increasing or decreasing trends over time, but the annual cycle of nitrate (peaks and valleys within a year,) are noticeable. Ammonia has only been measured infrequently (small sample size) and measured as dissolved ammonia, while CCME guidelines are as total ammonia making comparison problematic. Based on the small sample size the three branches have similar concentrations of ammonia. Further sampling is recommended to increase sample size and to sample total ammonia and so allow comparison with CCME guideline. Nutrient concentrations do not appear to be of concern in the St. Mary’s River, though phosphorous is most likely the limiting nutrient to stream productivity here.

Concentrations of twelve metals (aluminum, arsenic, cadmium, chromium, copper, iron, lead, mercury, molybdenum, nickel, silver and zinc) were analyzed in detail. Concentrations of nine metals (arsenic, barium, beryllium, cobalt, magnesium (dissolved), manganese, strontium, titanium, and vanadium) were considered “low priority” given sample sizes <20 and lack of CCME guidelines yet developed. Seven metals (boron, magnesium (extractable), rubidium, selenium, thallium, tin, and uranium) were of insufficient sample size to conduct a meaningful analysis.

- Aluminum concentrations are elevated in the St. Mary’s River in all branches. The CCME guideline for the protection of aquatic life is exceeded in every measurement, but the Health Canada Drinking Water quality guideline only rarely exceeded. There is no indication of changing aluminum concentration over time. The metal is considered a parameter of concern in the St. Mary’s River.

- Arsenic concentrations are generally low, almost always less than CCME and Health Canada guidelines. There is some (weak) evidence for a decrease in concentration over time. Arsenic is considered an element not of concern in the St. Mary's River.
- Cadmium concentrations are below analytical detection limit which minimizes the ability to compare concentrations with independent guidelines. Concentrations are very low, but cadmium is highly toxic as evidenced by the very low guideline values. There is uncertainty due to the guidelines being less than analytical detection limits, and so cannot determine from existing data whether cadmium should be considered a parameter of concern in the St. Mary's River.
- Chromium data had a very small sample size. Most concentrations were below analytical detection limit. The data are not sufficient to conclude risk associated with this parameter due to small sample size.
- Copper concentrations in the East and West Branches are greater than in the Main Branch, but this is likely an artefact of sampling and differing analytical detection limits among sampling regimes. There was a lower analytical detection limit for copper post-2006 relative to pre-2006 which gives the appearance of decreasing copper concentrations over time. This is likely not real as the pre-2006 detection limits were not sufficiently low to detect low concentrations. Copper exceeds the CCME guidelines approximately 10% of the time, but there is difficulty in interpretation as most available data are as extractable copper while CCME guidelines are as total copper. Copper may be an issue in the St. Mary's River with respect to aquatic ecology but there is no evidence that it is of concern from a human health perspective.
- Iron concentrations are equivalent in all the branches though there are large (order-of-magnitude) fluctuations in concentration over time. There is no evidence of change over time. There is some exceedance of the CCME and Health Canada guidelines, but it is a relatively benign and common metal in aquatic systems. Iron is considered an element not of concern in the St. Mary's River.
- Lead concentrations are low but still appear to be elevated relative to CCME guidelines. However, analytical detection limits are less than guidelines which makes interpretation problematic. Lead should be considered a metal of concern unless future sampling shows it to be consistently less than guidelines. Future sampling of lead is recommended.
- Mercury has a very small sample size associated with it. Analytical detection limits were less than CCME guidelines and historical data measured mercury as total but the guidelines are presented as methylmercury. These issues confound interpretation of the small sample size. Future sampling of mercury in the St. Mary's River is recommended.
- Molybdenum also has a very small sample size. The maximum sampled value is two orders-of-magnitude less than the CCME guideline. Molybdenum is considered an element not of concern in the St. Mary's River.
- Nickel also has a very small sample size. The maximum sampled value is an order-of-magnitude less than the CCME guideline. Nickel is considered an element not of concern in the St. Mary's River.
- Silver also has a very small sample size. All samples were measured with high resolution (low analytical detection limit) and were less than CCME guideline. Silver is considered an element not of concern in the St. Mary's River.
- Zinc concentrations in the Main Branch were less than those of the East and West (but very small sample sizes limit this inference). There is no evidence of long-term trend or

change over time. The maximum zinc concentration is an order of magnitude less than the CCME guideline and two orders of magnitude less than Health Canada guideline. Zinc is considered an element not of concern in the St. Mary's River.

Additionally, antimony, barium, magnesium and manganese were analyzed despite being originally classified as "low priority". They were analyzed despite not having associated guidelines, because they were of sufficient sample size to allow detailed analysis.

- Antimony suffers from small sample size, preventing meaningful interpretation of results. However, it has high potential toxicity and so future sampling of this metal is recommended.
- Barium is not of concern in the St. Mary's River
- Magnesium is not of concern in the St. Mary's River
- Manganese is elevated relative to Health Canada aesthetic objectives, but not elevated compared to water quality criteria from another jurisdiction (British Columbia). This element is not considered a concern in the St. Mary's River.

The 16 metals considered in some depth here may be classified into four general categories:

1. Metals of concern (aluminum)
2. Metals of high toxicity with analytical issues compromising interpretation (cadmium, copper, lead)
3. Metals with insufficient data requiring monitoring in the future (antimony, chromium, mercury, nickel, silver)
4. Metals likely not of concern (arsenic, barium, iron, manganese, magnesium, molybdenum, zinc)

Lakes have been sampled to a limited degree in the St. Mary's and that limited data presented here. It is difficult to draw conclusions regarding the lakes given the very limited sampling, but Lochaber Lake does appear to have sporadic and localized elevations of fecal coliforms exceeding guideline values. Groundwater in the St. Mary's River watershed has only been sampled twice. None of the 22 sampled parameters with associated Health Canada guidelines exceeded their respective limits. Based on this analysis of a very small sample size, there does not appear to be any parameters to be concerned about in the groundwater in this area of the St. Mary's River.

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## 1.0 INTRODUCTION

Water quality data have been collected for the St. Mary's River, Guysborough County, since at least 1966 and various reports have provided reviews of these data (Green et al. 1986; Farmer et al., 1988; Rutherford and Associates, 1988; Hart Buckland-Nicks 1995). None, however, have compiled all of the available data and attempted a comprehensive analysis of all data. Such a comprehensive analysis has been an ongoing project of the St. Mary`s River Association (SMRA) who appreciated not only the role of water quality in affecting riverine ecology but also the need for confidence by people in its use as a drinking water source. This project began in 2008-09 with data gathering, compilation and preliminary analyses, and was completed in 2011.

The purpose of this report is to provide a comprehensive analysis of water quality in the St. Mary`s River in order to identify potential parameters which may be of concern from an ecological or drinking water perspective. In conducting this analysis and developing this report, it is hoped that all interested parties will be able to agree on the priorities of water quality issues in the watershed and work together, as required, to remediate issues.

## 2.0 STUDY AREA

The St. Mary's River, Guysborough County, drains an area of approximately 1,350 $km^2$, flowing into a flooded-river-valley type estuary at Sherbrooke, Nova Scotia (45$^o$08'00"N, 61$^o$59'01"W). This river is a large system with a mean annual flow of 45.6 $m^3/s$ at Stillwater (Mitchell, 2009) and includes an estimated 118 tributaries ranging from 1$^{st}$ to 4$^{th}$ order and 132 lakes. Elevations within the watershed range from 0 m (sea level) to 260 m (Mount Adam in the Garden River system).

There are three major branches to the St. Mary's River (Figure 1):

(1) The East Branch extending from the headwaters of Moose River, Garden River and Eden Lake to Glenelg (27 km long; drainage area 389 $km^2$). Communities along the East Branch include Garden of Eden, Willowdale, East River St. Mary's, Newtown and Denver. In this report, the "North Branch" (Lochaber, Lochiel and Wallace lakes; 27 km long; drainage area 82 $km^2$) is also considered part of the East Branch. Land use along the East Branch has historically been agriculture and forest harvesting

(2) The West Branch extending from the headwaters near Trafalgar (Nelson and North Nelson Rivers) to Glenelg (56 km long; drainage area 470 $km^2$). Communities along the West Branch include Cameron Settlement, Caledonia, Lower Caledonia and Smithfield. Land use along this branch has historically been forest harvesting.

(3) The Main Branch extending from Glenelg downstream to Sherbrooke (19 km long; draining entire watershed). Communities along this branch include Melrose, Stillwater, and Sherbrooke. Land use is agriculture, forestry, roading and residential.

The watershed is mapped as having three different ecodistricts (Neily et al., 2003): (*i*) Pictou Antigonish Highlands Ecodistrict north of the East Branch, (*ii*) St. Mary's River Ecodistrict between the East and West Branches, and (*iii*) Eastern Interior Ecodistrict south of the West Branch. Landforms associated with these ecodistricts are largely hills and hummocky landscape.

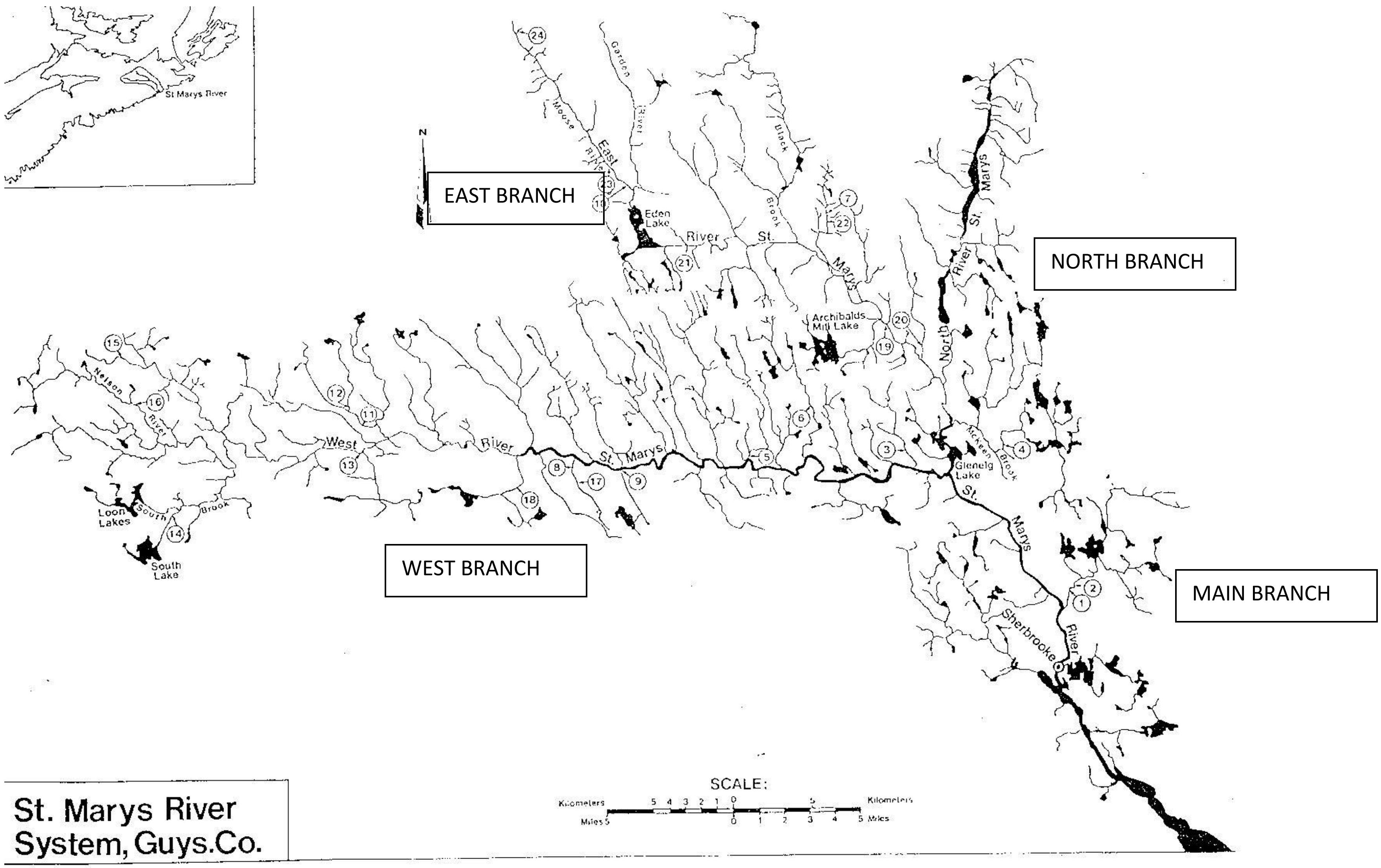


Figure 1: St. Mary's River watershed illustrating four "branches" of river. Circled numbers are electrofishing sites and not relevant to the report presented here. (Figure from Mitchell, 2010)

The East and West Branches differ in fundamental ways including bedrock geology (see below). One of the differences is that bogs and peatlands are common draining into the West Branch but are infrequent on the East Branch. Thus the water of the West Branch tend to be dark ("tea-coloured") due to tannins and humic acids while the water of the East Branch tends to be clear.

Due to water leaching through soils and picking up dissolved and particulate matter from the rock, bedrock geology and soils are important in understanding water quality characteristics. The geology of the St. Mary's River watershed is quite complex as it is a large system and flows over various geological assemblages (the following from Roland 1982). The Chedabucto Fault, running through the St. Mary's River watershed, is a primary geological feature in Nova Scotia as it represents the joining together of the Avalon and Meguma Terranes in the Devonian to Permian period (300-400 mya). North of this fault, the East Branch originates in the Pictou-Antigonish Highlands in which the bedrock geology is Hadrynian-Cambrian age (greater than 500 million years old) siltstones, shales, greywacke, volcanic tuff and ash. South of this fault is a wide band of early Carboniferous shale, sandstone and conglomerate (Horton Group, ~350 mya). The West Branch St. Mary's flows along the southern edge of this Horten band. South of the band of the Horton Group (i.e., south of the West Branch) is the Southern Upland. This consists of Cambrian age shales and limestones, Devonian and Carboniferous age igneous rock (granite, diorite, granodiorite) and Cambrian/Ordovician age conglomerates and siltstones.

The soils throughout the watershed are dominated by two types, with the exception of the river floodplain and low areas along the main rivers (the following from Hilchey, 1964). Most of the watershed is comprised of Halifax soils. The second dominant soil type is the Shulie Series, forming an intruding triangle with vertices at McDonald Brook on the West Branch, Crows Nest on the Main Branch and Lochiel Lake. Along the rivers the soils are mostly Millbrook and Cumberland series. Millbrook and Shulie soils are strongly acid throughout their profile and all upland soils in Guysborough County are considered low in natural fertility (particularly low in available calcium, magnesium, potassium and phosphorous).

The geology in this watershed has supported mineral exploration and extraction, indicating relatively high concentrations of some metals and elements. A lead mine was operated for a very short period of 1930-1931 on the west Branch of the River (Hurley Fisheries Consulting, 1988). There is a mine at Cochrane Hill which was worked historically and exploratory work conducted in the 1980's to evaluate the feasibility of reopening the operation. However, mining exploration and working in the St. Mary's River area has been surprisingly light relative to other Atlantic Coast watersheds. The Nova Scotia Department of Natural Resources Abandoned Mine Openings database[1] shows only seven known mine-related openings on the West Branch, five on the North Branch, one on the Main Branch, and none on the East Branch.

In addition to geology and soils, other sources of introduced material affecting water quality parameters are licensed effluent sources to waterways. Permitted effluent introductions which may influence water quality are

[1] This database available at: http://www.gov.ns.ca/natr/meb/links/amolinks.asp. Accessed September 29, 2011.

## 3.0 REVIEW OF PAST STUDIES

Eleven data sources were collected, compiled and used in this review of water quality data for the St. Mary's River. Descriptions of these data sources are provided below in chronological order.

1. In 1972 and 1973 water quality sampling was conducted by MacPhail and Alpert (1975) in several areas of the St. Mary's as part of an assessment for potential development of semi-natural rearing areas for Atlantic salmon (*Salmo salar*). In 1972 they sampled 14 sites between June 27 and October 25 with individual sites being sampled repeatedly, from 6 to 18 times in this period. In 1973 five sites were sampled between June 21 and November 1, with 15 to 19 sampling periods per site in this time frame. Parameters sampled were dissolved oxygen, pH, and temperature.

2. Water quality was again assessed in 1982 (reported by Farmer et al., 1988) as part of a Nova Scotia-wide project collecting information on the chemical characteristics of 15 rivers to facilitate Atlantic salmon enhancement planning and allow selection of suitable sites for hatchery-reared salmon releases. Samples were collected in the St. Mary's on April 13 (19 sites) and October 14 (22 sites) reflecting Spring and Autumn conditions. Parameters sampled were pH, total alkalinity, total hardness, specific conductance, and apparent colour. Two additional samples (one each for the West and East Branches) were collected in April for analysis of calcium, magnesium, chloride, and sulphate. Analogous two location sampling in October was for chloride, sulphate, and aluminum.

3. Water samples were collected in August 1984 (date not provided) at seven sites, January 31, 1985 at seven sites, and September 2, 1985 at three sites (locations unspecified). Parameters measured in this sampling were pH, acidity, hardness, specific conductance, alkalinity and apparent colour. These data have not been published in report form before, but are on file with the St. Mary's River Association.

4. Historical water quality data (Environment Canada NAQUADAT data, 1966-1985) was summarized by Green et al. (1986) from a long-term monitoring site at Stillwater. Parameters included major ions (specific conductance, sodium, potassium, calcium, chloride, sulphate), a few metals (aluminum, magnesium, manganese, iron), pH, total alkalinity, colour, turbidity, nitrates, and dissolved organic carbon.

5. The St. Mary's River Association conducted a large-scale water sampling program between 1990 and 1993 (methods and results reported in Hart Buckland-Nicks, 1995). Monthly samples of pH and specific conductance were collected from August 1990 to August 1991 at 26 sites. Detailed water chemistry (including nutrients, iron, manganese, copper, zinc and aluminum) was sampled in October, 1990, and January, April, and July 1991 from 10 sites. Sample sites were selected to largely coincide with those of Farmer et al. (1988) to allow comparison over time. Further, pH and specific conductance sampling in 1992 and 1993 included 15 sites sampled monthly from May to November (1992) and April to August (1993). Water temperature was recorded daily in the East and West Branches from June 12 to September 25, 1991, and in the Main Branch from June 5 to October 18, 1992.

6. Between 1992 and 1994, water quality samples were routinely collected by DFO[2]. Samples were collected in September and November (1992; at the Ford Pool), May, August, September and November (1993; adjacent to DNR Picnic Park on Highway 7), and May, August and November (1994; adjacent to DNR Picnic Park on Highway 7). Parameters measured were pH, specific conductance, dissolved oxygen, water temperature, dissolved organic carbon, nutrients, dissolved metals, particulate metals, and major ions.

7. In 1995, Taylor reported on a relatively comprehensive study conducted on Lochaber Lake. Biweekly water quality sampling was conducted between April and October, 1994 at five stations on the lake and up to three depths per station. Additionally, inlet and outlet streams were sampled. Parameters measured were water temperature, dissolved oxygen, Secchi depth, nutrients, chlorophyll concentrations, metals, major ion concentration, and fecal coliform concentrations. The focus of this study was on determining nutrient levels and associated trophic state of the lake.

8. Environment Canada has collected water quality data in the St. Mary's River as far back as 1966 at a station at Stillwater.[3] Historical water quality data for the sampling station at Stillwater is available on line at Environment Canada, Atlantic Envirodat Water Quality Database[4] for the period 1974 to 2009, with sampling having taken place between three and five times per year. Parameters measured were pH, hardness, alkalinity, ionic composition, colour, turbidity, specific conductance, nutrients, and metals. Additionally, Environment Canada has collected limited data on Lochaber Lake (2000), Black Brook Lake (1998), Ellen Brown Lake (1997), Moose Lake (1997) and Eden Lake (2000). Environment Canada also has limited data on groundwater, (alkalinity, colour, pH, specific conductance, turbidity, nutrients, ionic composition, and metals) sampled from a well at the Sherbrooke High School in 1972.

9. The Nova Scotia Department of Environment and Labor sampled groundwater quality at a well in Stillwater on December 13, 2006[5]. This well has been in operation since 1987, recording groundwater level but has only been sampled for water quality this once. Parameters analyzed were pH, hardness, alkalinity, ionic composition, colour, turbidity, specific conductance, nutrients, and metals.

10. A large scale pH survey was undertaken by the St. Mary's River Association in 2009. Four index sites were sampled approximately weekly between March 10 and November 9. Twelve sites on the East Branch and 15 sites on the West Branch were sampled on a monthly basis between March 18 and October 28, 2009. This design was intended to allow nesting of the index sites (frequent sampling to capture weekly variation) within

[2] This data source is herein referred to as Dalziel (1994); it was a personal communication of unpublished data collected under the Green Plan Program from J. Dalziel (DFO) to the St. Mary's River Association.

[3] Environment Canada water quality sampling station is: NS01EO0001 located at St. Mary's River at the Highway 7 bridge at Stillwater.

[4] Atlantic Envirodat Water Quality Database: http://map.ns.ec.gc.ca/envirodat/root/main/en/extraction_page_e.asp

[5] Groundwater Observation Well ID Number 055; Nova Scotia Department of Environment and Labor Well Number 871263; UTM coordinates Easting 579938, Northing 50004212; year started monitoring 1987; well depth 36.0 m.

broader geographic sampling at lower intensity reflecting large-scale variation on a monthly basis.

11. Finally, water temperature was monitored hourly using automatic data loggers by the St. Mary's River Association annually between 2008 and 2010. In 2008 data loggers collected data for variable time periods between April 17 and December 31 in each of the East, Main and West Branches. Temperature was recorded between April 9 and December 31, 2010 for each of the West and Main Branches. Data were also collected in 2009 but, unfortunately, the data were subsequently lost.

## 4.0 METHODS

Water quality data were compiled from reports, unpublished data in files, and data available on-line; the sources for each parameter analyzed are clearly described in the following analysis. The Environment Canada data from Stillwater only includes to 2008 as that was the most recent data at time of data compilation.

The data are presented in both parametric form (mean, standard deviation, coefficient of variation (mean/SD *100), 95% confidence intervals) as well as non-parametric form (median, interquartile ($10^{th}$-$90^{th}$ percentile) range). The data were not tested for conformation to assumptions of normality and the non-parametric variables were included to exclude the influence of extreme values which may affect the parametric estimates. When data were reported as less than analytical detection limit, the data point was assigned a value equal to the detection limit (e.g., <0.001 set to 0.001). This may bias results high as the "true" concentration is less than the assigned value. Statistical comparisons for each parameter were made by Analysis of Variance (ANOVA) when more than two comparisons were involved, and by comparing 95% confidence intervals, either as follow up tests to significant ANOVA results or when comparing two means. Comparing confidence intervals is equivalent to conducting Student's t-tests. The author is fully aware of the issues related to potential violations of assumptions and family-wise error rates associated with this approach, but chose to do so for ease of comparison and interpretation given the amount of, and diversity of, data analyzed. The purpose of this analysis was to highlight the most important parameters, not necessarily to produce a definitive statistical analysis of these data. Examination of trends over time was based on (1) visual analysis of scatterplots of data, (2) fitting linear regressions, and (3) comparison with historical mean estimates from 1966-1985 by Green et al. (1986).

To assist in interpreting values of water quality parameters, Environmental Quality Guidelines for the Protection of Aquatic Life from the Canadian Council of Ministers of the Environment (CCME) and Drinking Water Quality Guidelines from Health Canada were compiled and use. These guidelines[6] are derived by expert review of all relevant toxicological information for a given parameter to determine concentrations at which exposure impacts aquatic biota (CCME) or human health (Health Canada). Guidelines for the protection of aquatic life are based on the most sensitive species and/or the most appropriate conditions and are then subject to expert

[6] CCME guidelines available at: http://ceqg-rcqe.ccme.ca/
Health Canada Drinking Water Quality guidelines available at: http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/2010-sum_guide-res_recom/index-eng.php

review before approval. Drinking water guidelines are also based on expert review of toxicological studies, usually based on animals rather than humans, and then the concentration at which negative effects begin to be seen divided by a factor between 1 and 10 (depending upon the parameter) to provide a safety margin to account for uncertainty and risk. For example, a concentration showing impact at 1.0 mg/L might be divided by 10 to give a guideline of 0.1 mg/L. Health Canada Drinking Water Guidelines are given as Maximum Acceptable Concentration (MAC), an "Aesthetic Objective"[7] based on taste and odour, or an Operational Guideline.

For purposes of classifying parameters into categories of interest, the following comparisons with CCME and Health Canada guidelines were used.

- 0% of data exceeding guidelines: No concern
- 1-15% of data exceeding guidelines: Some concern but occasional exceedance acceptable
- >15% of data exceeding guidelines: Of concern

## 5.0 WATER QUALITY ANALYSES

The following analyses are divided into three major sections: (1) River Water (the greatest bulk of the analyses), (2) Lakes, and (3) Groundwater. Within each section, the relevant water quality data are analyzed and interpreted in terms of ecological and human health.

### 5.1 RIVER WATER

#### *5.1.1 Physical Parameters*

Water Temperature

Water temperature is a very important parameter as it influences rates of chemical processes and governs distribution of aquatic organisms as each taxa has thermal tolerance, and when that is exceeded the organism will move or suffer mortality. Water temperature also affects life cycles of some organisms. For example, some benthic invertebrates can switch from completing one life cycle in a year (univoltine) to two (bivoltine) under elevated thermal regimes. Temperature may be considered a controlling variable in stream ecology.

Water temperature has been recorded in a variety of studies, and these may be divided into those which did spot sampling (MacPhail and Alpert, 1975 (N=294); Dalziel, 1994 (N=9); SMRA unpublished (N=51); and Environment Canada (N=287)) and those which conducted continuous recording using some method of datalogger (Buckland-Nicks, 1995; SMRA unpublished 2008-2010). For the purpose of this analyses, spot samples are excluded and the analyses limited to

[7] An aesthetic objective (AO) applies to certain substances or characteristics of drinking water that can affect its acceptance by consumers or interfere with practices for supplying good water. For certain parameters, both AOs and health-related guidelines (maximum acceptable concentrations, or MACs) have been derived. Where only AOs are specified, the values are below those considered to constitute a health hazard. )From health Canada (1995) *Part I Approach to the Derivation of Drinking Water Guidelines*). Available at: http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/index-eng.php#tech_doc

only the continuous sampling that took place in 1991, 1992, 2008, and 2010. In 1991 the East and West branches were monitored, in 1992, the Main Branch only. In 2008 all three branches were monitored and in 2010 the West and Main Branches. This inconsistent sampling prevents comparison among branches for every year.

Differences in mean daily water temperature between branches was assessed by regressing mean daily temperature of one branch on another for data from the years 1991, 2008 and 2010. If branches did not differ in mean daily temperature, the slope of the regression should be unity (1.0). Results of these regressions are presented in Table 1. The West Branch is slightly warmer than the East and Main Branches. In 1991 the East and West Branches were of similar temperature, but in 2008 the West was slightly (~3%) warmer than the East. The West Branch was 6-10% warmer than the Main Branch in both 2008 and 2010. The East and Main branches were of similar temperature in 2008. Thus, in general, the West Branch is slightly warmer than the East Branch. However, it is important to recognize that there is large variability within a branch as well. There are cold streams, cold groundwater inputs, shallow stretches which heat in the sun, deep pools where water may cool, etc. All of these create spatial variability. This variability <u>within</u> a branch is likely as great as that <u>among</u> branches.

Table 1: Regression equations of water temperature ($^{o}C$) in one branch as it relates to another branch. P-value of each regression <<< 0.0001.

| | Regression equation | 95% CI of slope | $r^2$ (N) |
|---|---|---|---|
| West Branch versus East Branch (1991) | West = 1.050 * East Branch – 0.725 | 0.099 – 1.106 | 0.931 (104) |
| West Branch versus East Branch (2008) | West = 1.123 * East Branch – 1.248 | 1.087 – 1.158 | 0.973 (108) |
| Main Branch versus West Branch (2008) | Main = 0.871 * West Branch + 2.359 | 0.835 – 0.907 | 0.942 (146) |
| Main Branch versus West Branch (2010) | Main = 0.910 * West Branch + 0.983 | 0.874 – 0.946 | 0.908 (250) |
| Main Branch versus East Branch (2008) | Main = 1.016 * East Branch + 0.407 | 0.988 – 1.044 | 0.973 (155) |

To evaluate whether there has been a noticeable change in river temperature between the early 1990s and late 2000s (i.e., over about 18 years), monthly mean temperatures were calculated (Figure 2). Based on 95% confidence intervals, in the East Branch, temperatures in June and September of 2008 were less than 1991, but equivalent in July and August in these two years. In the West Branch, in July and September of 1992, 2008, and 2010 the temperatures were equivalent among years, August 2008 was cooler than 1992 and 2010 which were equivalent to each other, and June 2008 was intermediate to 1991 and 2010. For the Main Branch, in June, the 1991, 2008 and 2010 temperatures were equal, July 1991 was cooler than 2008 and 2010, and

August and September 1991 were equivalent to 2008, and both of these cooler than 2010. From these results there is little evidence of consistent, directional heating or cooling of months for these two decades. It is more likely that these data simply reflect variability of climate but the temperatures have not changed meaningfully between 1991-92 and 2008-10.

Temperature maxima are of concern as organisms in this part of the world are generally adapted to cold water conditions and there is concern that climate change is increasing water temperatures. Frequency of occurrence of daily maximum temperatures were assessed by cumulative frequency distributions (Figure 3). The Main and East Branches show evidence of increasing frequency of high temperatures (>20 $^{o}$C, >24 $^{o}$C, >27 $^{o}$C, and >30 $^{o}$C) between the early 1990s and late 2000s. However, there is no evidence of increasing frequency on the West Branch; indeed 2008 stands out as being a cooler year, at least with respect to maximum temperatures, than 1991 or 2010 in this branch. The overall maximum temperature recorded was 33.2 $^{o}$C (East Branch, July 18, 2008) and 30 $^{o}$C has been exceeded on three days (East Branch), 14 days (West Branch) and zero days (Main Branch). The period of maximum temperatures is quite consistent between years, occurring in early to mid-July. Exceedances of 30$^{o}$C occurred between July 19-25 (1991); July 6-18 (2008), and July 8-9 & September 3 (2010).

Turbidity

Turbidity is the cloudiness or haziness of a fluid caused by individual particles (suspended solids) that are generally invisible to the naked eye. Turbidity in the St. Mary's River has been measured using two different units. Jackson Turbidity Units (JTU) have been used by Environment Canada (N=292, measured at Stillwater), and Nephelometric Turbidity Units (NTU; N=49) reported by Dalziel (1994; N=15) and Hart Buckland-Nicks (1995; N=34). The two units are not directly comparable or interchangeable. For the analyses described here, the NTU data are used for the spatial analysis and JTU data for temporal analysis.

Spatially, there is no significant difference (ANOVA p=0.093) in turbidity among the three branches (Table 2). There is, however, high variability in turbidity at two locations on the East Branch - the outflow of Wallace Lake (suspect point of 3.06 NTU when 90% of values less than 1.03) and Moose River (suspect point of 4.90 NTU when 90% of values less than 1.03). Overall mean turbidity is 0.87 NTU (SD=0.78; N=48; range 0.25-4.90 NTU). There was one anomalous data point (21 NTU recorded at Lochiel Lake outflow in October, 1990), which was excluded from this analysis as that measurement is five-times greater than the next greatest value of 4.90 NTU (Moose River, October, 1990), which is, itself, a suspect point.

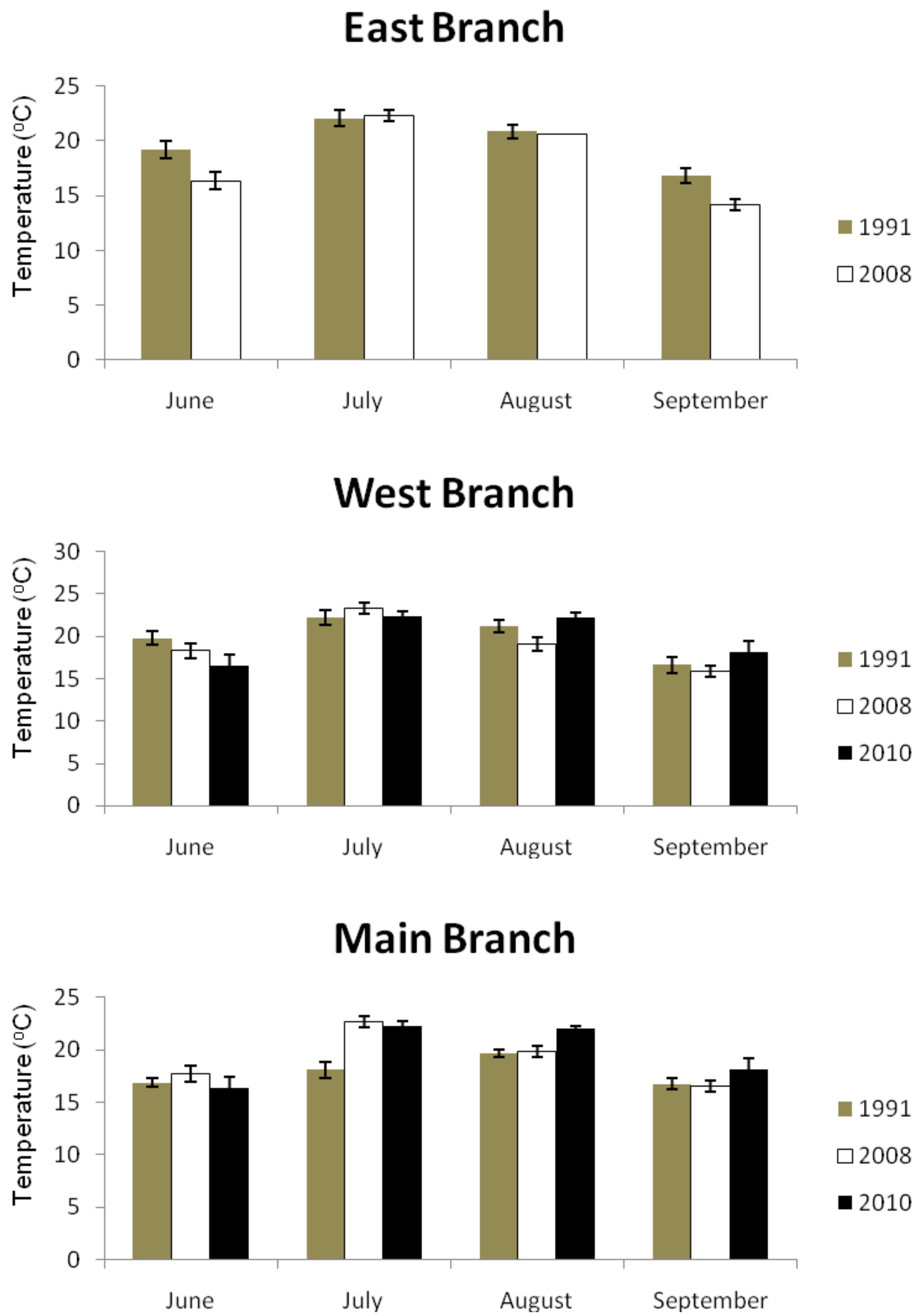


Figure 2: Mean monthly summer temperatures for each branch and year of record. Error bars are 95% confidence intervals.

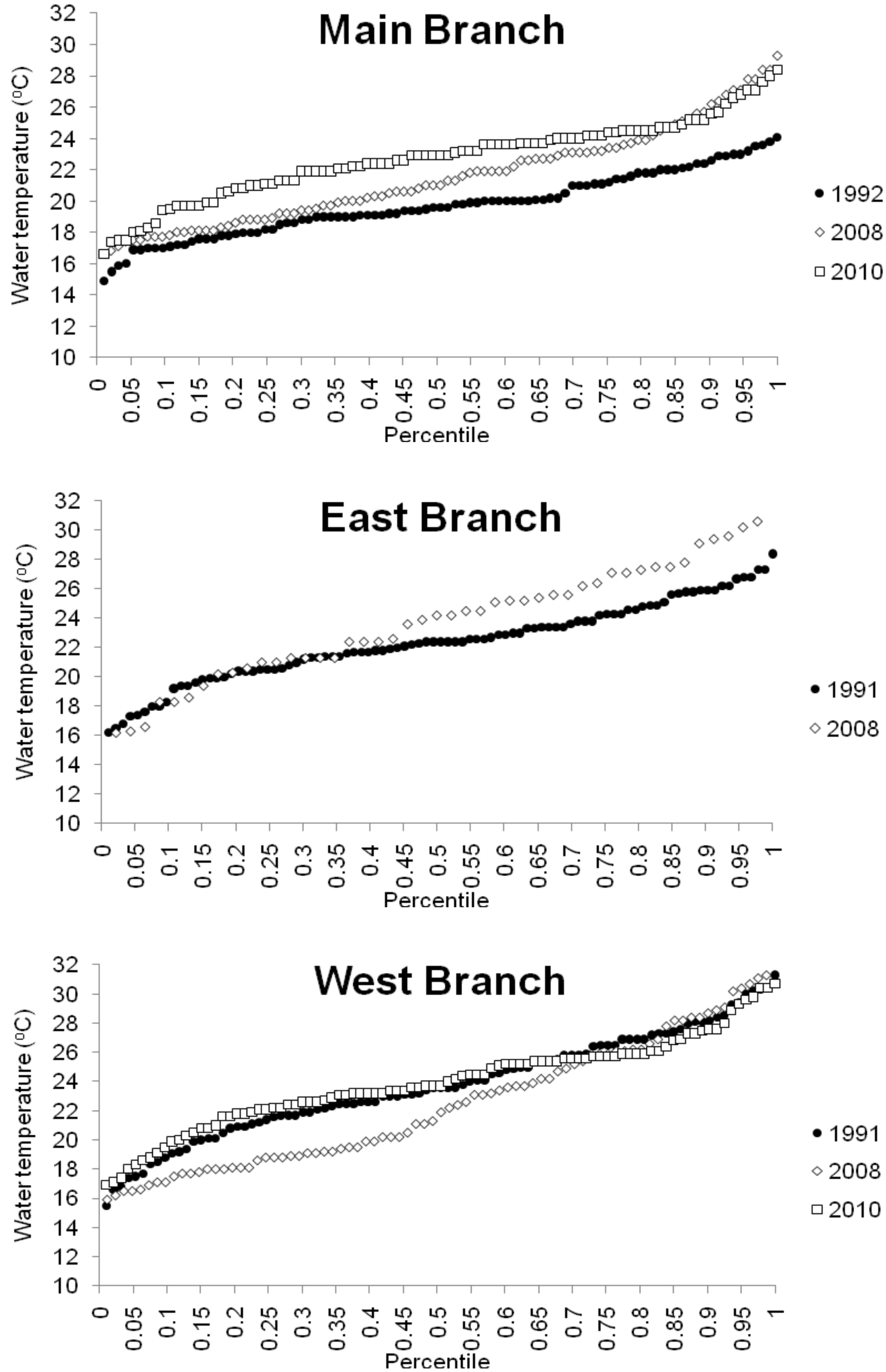


Figure 3: Cumulative distribution of maximum daily temperatures, June 15-Sept. 15, for each branch and year of record.

Table 2: Summary statistics of turbidity and colour in the St. Mary's River. Data from Hart Buckland-Nicks (1995), Dalziel (1994), and Environment Canada (Stillwater).

| | Mean (SD); N | Range | Median | $10^{th}$-$90^{th}$ percentile |
|---|---|---|---|---|
| **Turbidity** | | | | |
| East Branch (NTU) | 1.16 (1.07); 19 | 0.46 – 4.90 | 0.83 | 0.57 – 1.73 |
| Main Branch (NTU) | 0.76 (0.53); 15 | 0.37 – 2.52 | 0.65 | 0.37 – 0.97 |
| West Branch (NTU) | 0.59 (0.31); 14 | 0.25 – 1.20 | 0.56 | 0.27 – 1.03 |
| Main Branch at Stillwater (JTU) | 0.78 (0.70); 292 | 0.20 – 7.30 | 0.60 | 0.40 – 1.20 |
| **Colour** | | | | |
| **Apparent (Relative Units)** | | | | |
| East Branch | 27.75 (12.90); 21 | 15 – 55 | 25.0 | 15 – 45.5 |
| Main Branch | 44.50 (13.20); 10 | 20 – 60 | 45.0 | 24.5 – 55.5 |
| West Branch | 35.80 (18.90); 29 | 15 - 75 | 25.0 | 20 - 66 |
| Main Branch at Stillwater | 27.07 (15.20); 299 | 5 - 90 | 25.0 | 10 - 50 |
| **True (True Colour Units)** | | | | |
| East Branch | 22.60 (13.50); 28 | 3 – 63 | 18.0 | 11.0 – 37.4 |
| Main Branch | 31.30 (13.10); 17 | 8 – 55 | 33.0 | 15.4 – 48.6 |
| West Branch | 33.90 (18.20); 31 | 14 - 74 | 26.0 | 15.0 – 60.0 |

There are 292 turbidity measurements at Stillwater by Environment Canada (Table 2; Figure 4). Between February, 1974 and October, 2008 turbidity ranged between 0.2 and 7.3 JTU, with a median turbidity of 0.6 JTU and 95% of measurements <1.8 JTU. The greatest values of turbidity (>3.0 JTU) were recorded December 17 (1990), February 28 (2002), March 14 (1985), March 19 (1980), and April 19 (1985). Approximately 68% of turbidity measurements in excess of 1.0 JTU occurred in the four months of November, December, March or April, periods of typically high water. Only 16% of turbidity measurements in excess of 1.0 JTU occurred between June and September, indicating low-flow baseline turbidity is generally <1.0 JTU. There is no evidence of change over time for turbidity (linear regression; slope = 0.00001; $p=0.625$; $r^2 = 0.001$). Green et al. (1986) reported mean turbidity values at Stillwater (1966-1985) of 1.1 JTU (SD=1.0; N=189) and range of 0.1 to 7.3 JTU. There is a significant difference in mean turbidity concentrations at Stillwater (based on 95% confidence intervals) between the period 1966-1985 and 1974-2008 indicating a slight decrease in mean turbidity between the two periods, though this is not reflected in the long-term trend.

## Colour

Similar to the various measurement units of turbidity in the St. Mary's River, three classes of colour have been reported – Apparent Colour (relative units; N=58), True Colour (TCU; N=374), and Hazen Units (N=188). Apparent colour was reported by Dalziel (1994) and Hart Buckland-Nicks (1995); True Colour by Dalziel (1994), Hart Buckland-Nicks (1995), and Environment Canada at Stillwater; and Hazen Units by Green et al. (1986). Apparent colour is the colour of the whole sample, including dissolved and suspended material. True colour is the colour after filtering (removal of suspended material) and reflecting only the dissolved materials in the water.

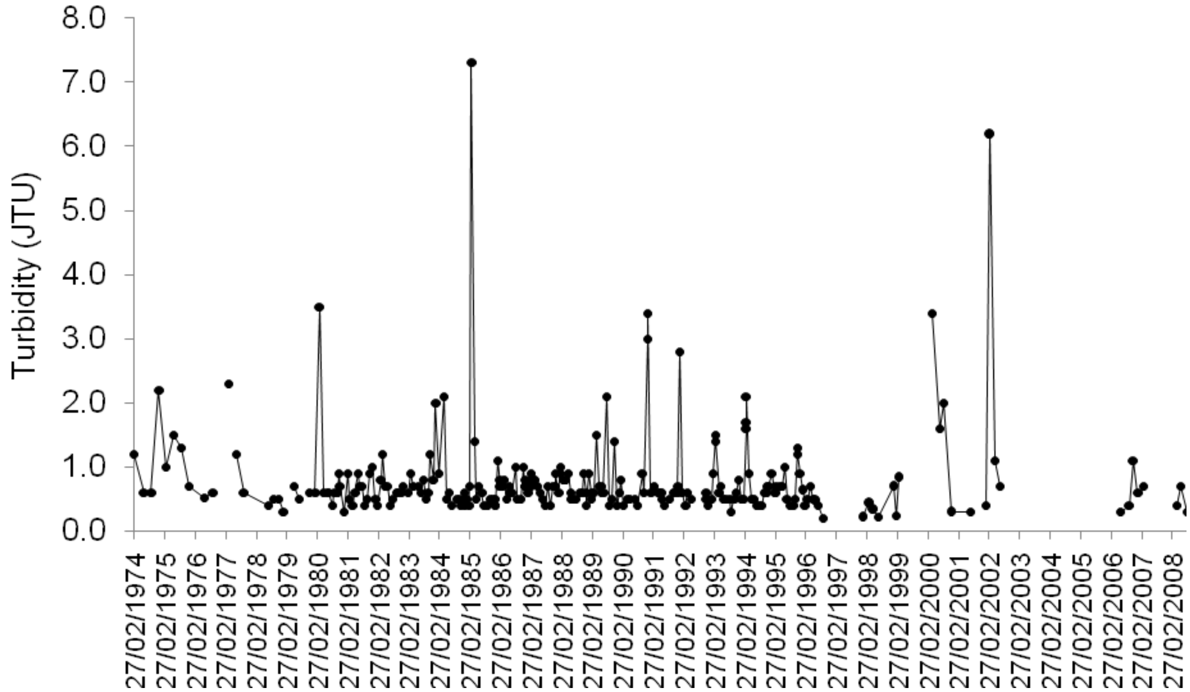


Figure 4: Turbidity over time (1974-2008) measured at Stillwater by Environment Canada.

There are significant differences in color among branches of the St. Mary's River (apparent color ANOVA p=0.030; True Colour ANOVA p=0.022). For Apparent Colour, the Main Branch is greater than the East, but equal to the West, and the East and the West are similar (Table 2; Figure 5). For True Colour, the Main and West branches are greater than the East Branch. That is, the East Branch is significantly clearer than the other two branches.

Of 299 Apparent Colour measurements made by Environment Canada at Stillwater between February 1974 and October, 2008 the median color is 25 relative units (range 5-90) and 95% of all measurements are below 59.1 relative units (Figure 6). Color fluctuates over time, and over the period of sampling at Stillwater by Environment Canada there is weak indication of long term increase (linear regression slope = 0.0021, $p << 0.001$; $r^2 = 0.138$). The regression is statistically significant but the slope is very low (i.e., equivalent to a change of one colour unit per century) and the amount of variation explained also very low suggesting little confidence be placed in it. Green et al. (1986) reported mean colour (Hazen Units) values at Stillwater (1966-1985) of 25.0 units (SD=13.0; N=188) and range of 5.0 to 80.0 units. These data cannot be compared with the later Environment Canada sampling due to the change in measurement units between the two sampling periods.

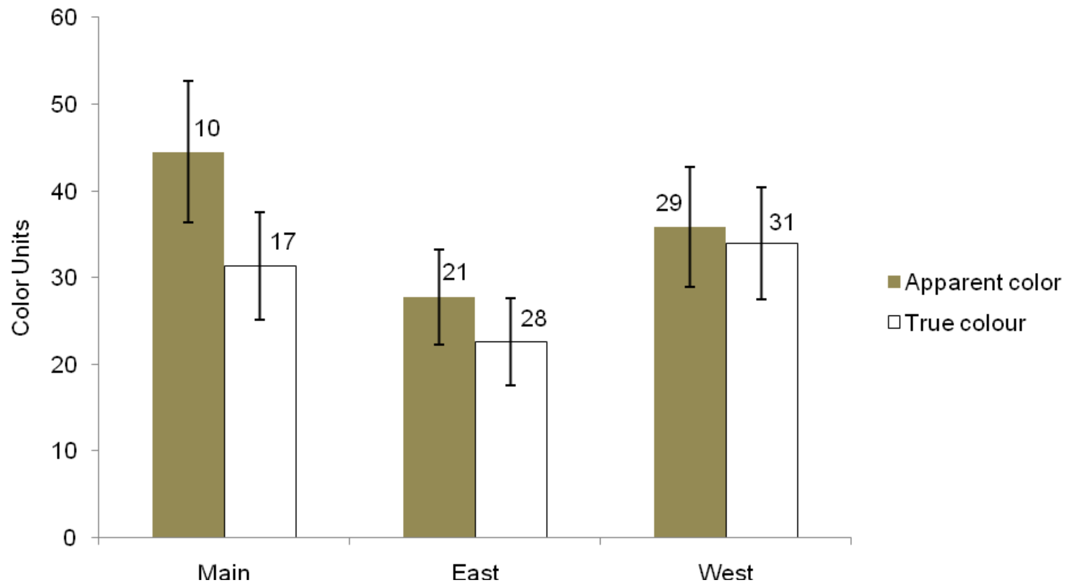


Figure 5: Mean colour of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate. Values represent sample size used to calculate means.

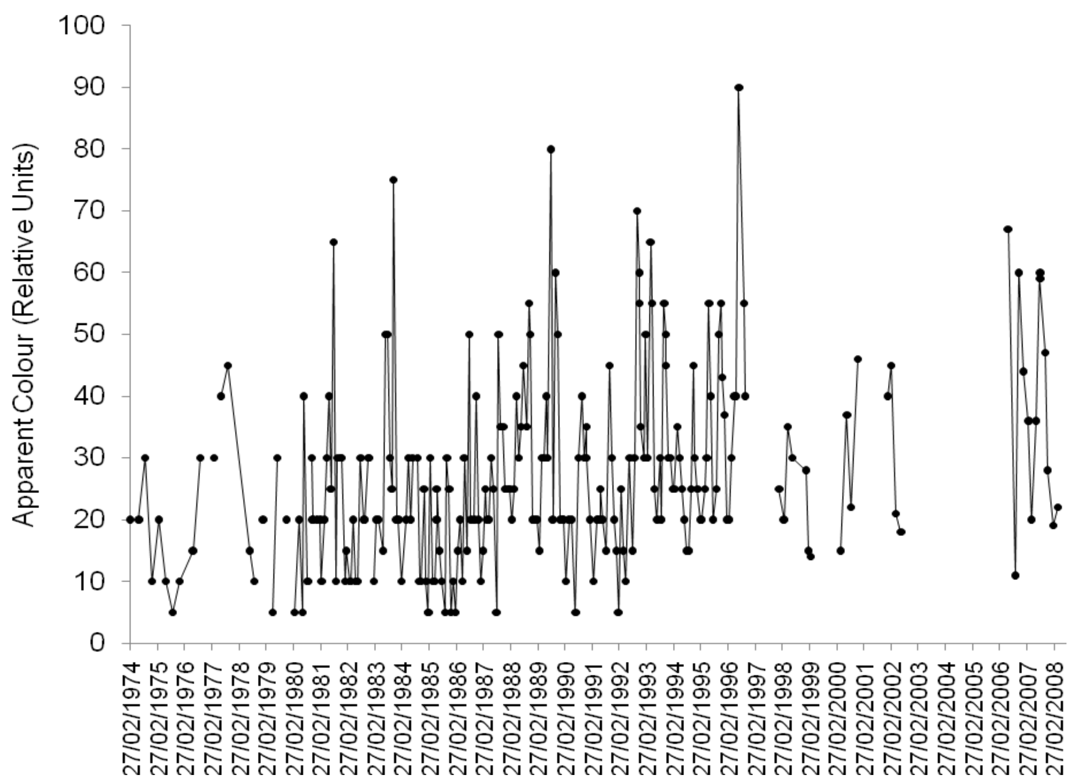


Figure 6: Apparent colour over time (1974-2008) measured at Stillwater by Environment Canada.

### *5.1.2 Chemical Parameters*

pH

pH in the St. Mary's River has been measured extensively, both spatially and temporally; it is probably the most frequently measured water quality parameter in the watershed. pH data have been recorded by MacPhail and Alpert (1975; N=188), Farmer et al. (1988; N=41), unpublished 1984-85 SMRA data (N=19), Hart Buckland-Nicks (1995; N=365), Dalziel (1994; N=36), 2009 unpublished SMRA data (N=289), and Environment Canada at Stillwater (N=300), for a total sample size of 1,238 measurements.

There are significant differences of mean pH among branches with pH in the East Branch being significantly greater than the Main or West Branches (Table 3, Figure 7), based on 95% confidence intervals. The Main and West Branches are statistically of equal pH. Within each branch, mean pH varies among areas (mainstem and tributaries). In the East Branch, of 19 locations, mean values range between 5.8 (Archibald Mills Brook) and 7.0 (Two Mile Brook – Fishers Mills) (Figure 8). Of 20 locations on the West Branch, mean pH ranges between 5.2 (Mitchell Brook) and 6.1 (Cross Brook) and of three locations on the Main Branch between 5.4 (Archibald's Brook) and 6.3 (DNR picnic site). There is little overlap in pH values between the East and West Branches; almost all locations sampled on the West Branch are of lower pH than locations on the East Branch.

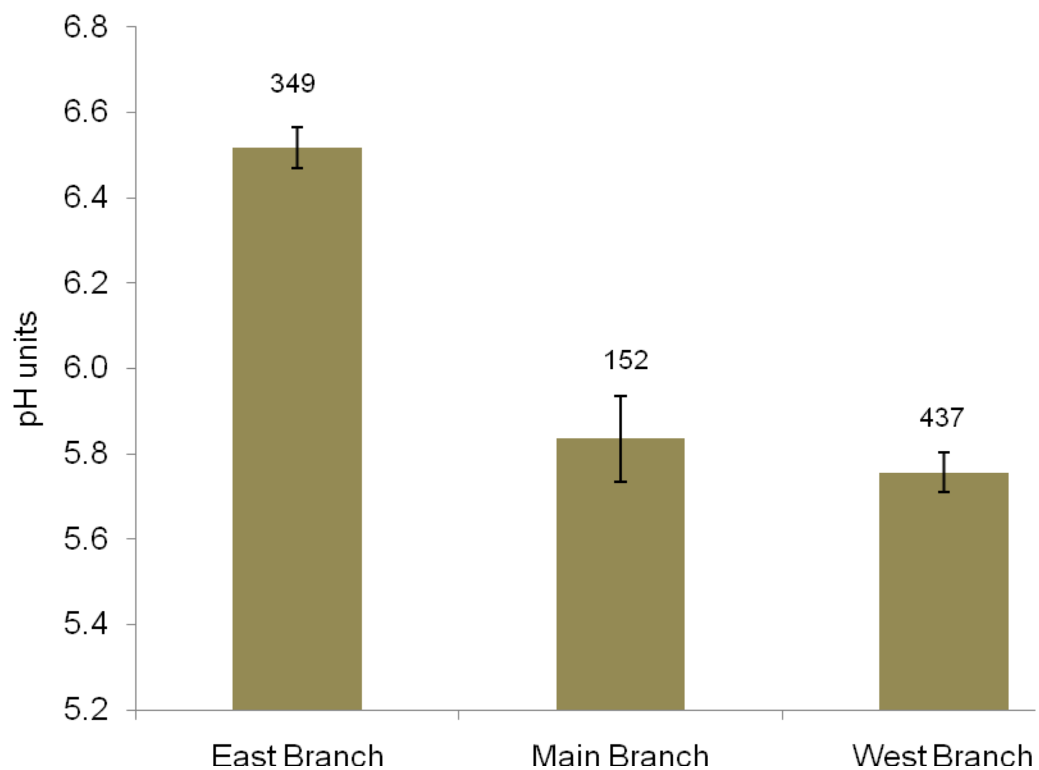


Figure 7: Mean pH of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate. Values represent sample size used to calculate means.

Between February 1974 and October 2008, pH at Stillwater has ranged between 4.5 and 7.2 units (mean 6.2 pH units; SD=0.30; N=300) (Figure 9). There is a single anomalously low value (4.5 units; September 12, 1987); exclusion of this data point as an anomaly does not change the mean or SD of the data set. There is no evidence of a positive or negative change over time (linear regression: slope <0.0001, $p = 0.972$; $r^2 < 0.005$). pH measured at Stillwater has been quite stable over the last 35 years, with the interquartile range (i.e., range from 10th percentile to 90th percentile) being between 5.8 and 6.5 pH units. This is a range for the great majority of the measurements of only 0.7 units. Green et al. (1986) reported on Environment Canada pH data for this station from 1966 to 1985. They reported a mean of 6.0 pH units (SD=0.4), with a range of 3.8-7.2 units. The very low value (3.8) reported by them occurred as part of a dip (including two other values < 5.0 units) in 1969 (dates not provided by Green et al. (1986)). The 1966-1985 mean calculated by Green et al. is not significantly different from that calculated here for 1974-2008, indicating the long-term mean pH at Stillwater 1966-2008 is 6.0-6.2 pH units.

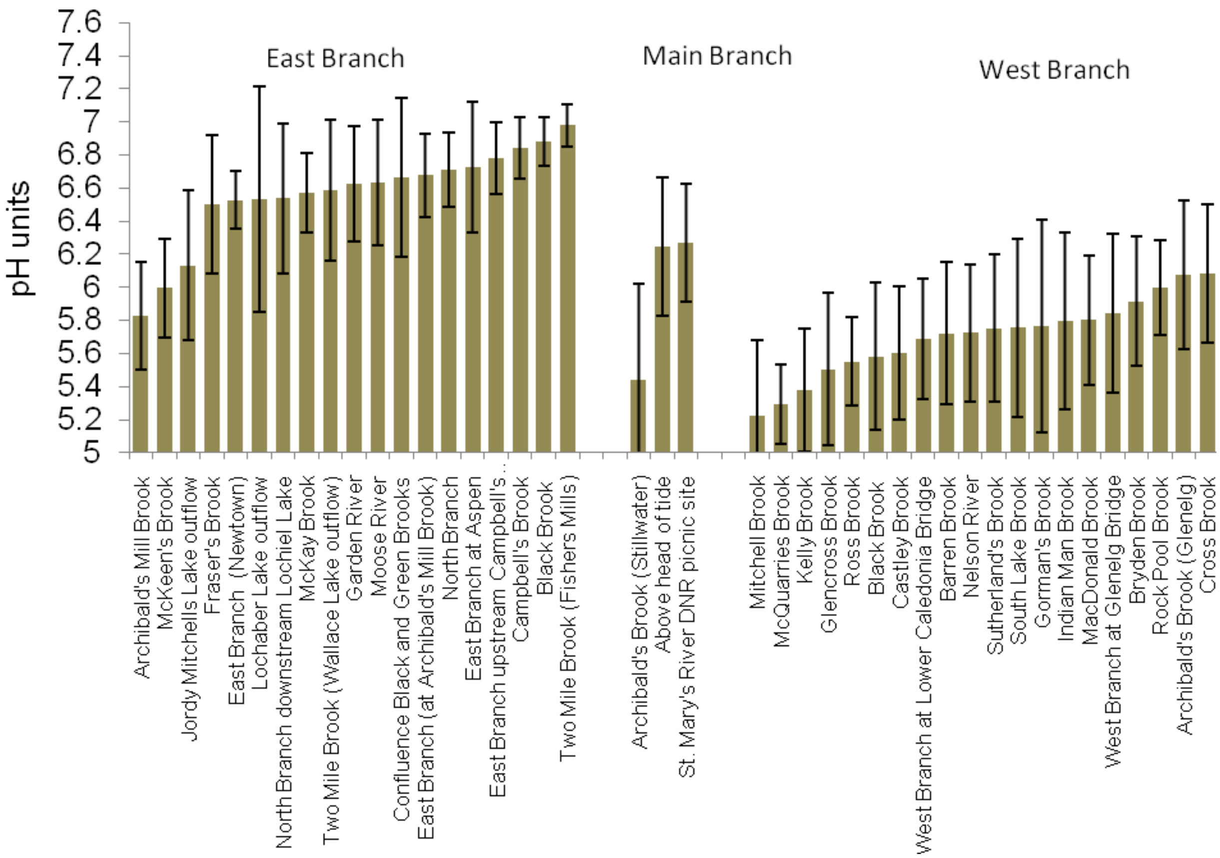


Figure 8: Mean pH of tributaries of St. Mary's River by branch. Error bars represent standard deviation of mean estimate. Only those tributaries where sample size ≥ 5 are shown.

Table 3: Summary statistics of pH distribution in the St. Mary's River. Spatial summary is by river branch analyzing data over time. Temporal summary uses the monthly sampling of Hart Buckland-Nicks (1995) and 2009 unpublished SMRA data to assess month-to-month and week-to-week changes in mean branch pH over time. Data from MacPhail and Alpert (1975), Farmer et al. (1988), unpublished 1984-85 SMRA data, Hart Buckland-Nicks (1995), Dalziel (1994), 2009 unpublished SMRA data, and Environment Canada (Stillwater).

| | Mean (SD); N | Range | Median | $10^{th}$-$90^{th}$ percentile |
|---|---|---|---|---|
| **Spatial Summary** | | | | |
| East Branch | 6.52 (0.46); 349 | 5.30 - 7.90 | 6.57 | 5.84 - 7.00 |
| Main Branch | 5.84 (0.64); 152 | 4.63 - 7.40 | 6.00 | 4.90 - 6.55 |
| West Branch | 5.76 (0.50); 437 | 4.51 - 7.50 | 5.70 | 5.10 - 6.40 |
| Main Branch at Stillwater | 6.17 (0.31); 300 | 4.50 - 7.20 | 6.20 | 5.80 - 6.50 |
| **Temporal Summary** | | | | |
| <u>Month-to-month changes</u> | | | | |
| East Branch | -0.06 (0.55); 163 | -1.3 – 2.3 | -0.10 | -0.74 - 0.55 |
| Main Branch | -0.02 (0.48); 28 | -1.2 – 0.8 | 0.05 | -0.60 – 0.59 |
| West Branch | -0.08 (0.59); 210 | -1.9 – 1.9 | 0.00 | -0.81 – 0.53 |
| <u>Week-to-week changes</u> | | | | |
| East Branch | 0.009 (0.23); 83 | -0.54 – 0.58 | 0.00 | -0.30 – 0.30 |
| Main Branch | 0.022 (0.25); 52 | -0.64 – 0.89 | 0.00 | -0.27 – 0.26 |
| West Branch | -0.019 (0.49); 90 | -1.80 – 1.50 | 0.00 | -0.59 – 0.59 |

pH in natural waters varies seasonally. Hart Buckland-Nicks (1995) reported on monthly pH sampling of 22 stations between August 1990 and November 1992, and the SMRA conducted monthly sampling of 21 locations from March to October, 2009 (Figure 10). In general, pH is higher in winter and lower in summer. The range over which mean pH varied over a year approached 1.5-2.0 pH units and over the summer season (March-October) is on the order of 0.8-1.0 pH units. Maximal month-to-month changes in pH values among measurements in the St. Mary's River are on the order of 1.2-1.9 pH units (Table 3). The majority of the month-to-month variation (i.e., the interquartile range) are changes of ± 0.5-0.8 pH units. pH variation also occurs on a weekly basis. The East and Main branches fluctuate less dramatically from week-to-week than the West Branch (Table 3). Mean weekly change for all branches is on the order of <0.02 pH units with the interquartile range on the order of +/- 0.3 units for the East and Main branches and +/- 0.6 units for the West Branch. That is, the West Branch appears to be more variable on a week-to-week basis than other parts of the river.

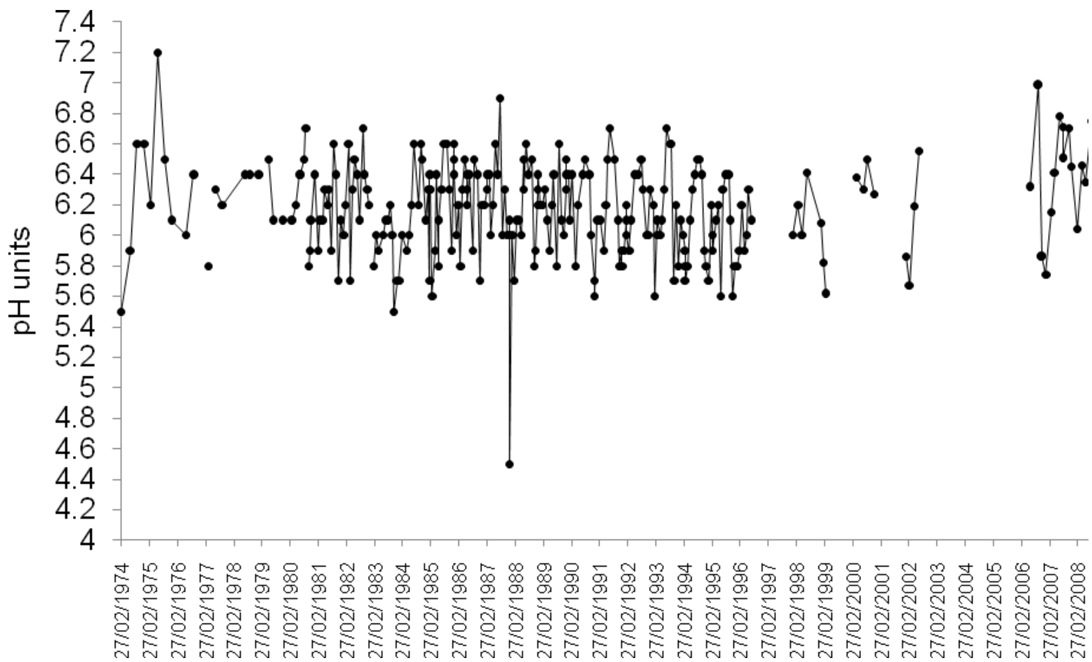


Figure 9: pH over the period 1974-2008, as measured by Environment Canada at Stillwater.

Of 1,238 pH measurements, 154 (12.4%) have been less than 5.4 pH units and so potentially problematic for Atlantic salmon (see *Discussion* for pH toxicity and Atlantic salmon). Of these 154 values, 67.5% were in the West Branch, 30.5% in the Main Branch, and 1.3 % in the East Branch. Considering only the West Branch, 104 of 437 (23.8%) of measurements have been < pH 5.4. These low values have occurred primarily in: Mitchell Brook (n=19), Indian Man Brook (n=15), South Lake Brook (n=11), Glencross Brook (n=8), Kelly Brook (n=6) and Black Brook (n=6). Only 21 of these 437 (4.8%) measurements have been < pH 5.0, so while low pH may potentially be an issue within some areas of the West Branch St. Mary's, the magnitude of the pH depressions is quite small and so unlikely to exert a population level depressing effect on Atlantic salmon.


Figure 10: Monthly mean pH values illustrating fluctuations in East and West Branches, St. Mary's River during two periods (1990-91 and 2009). 1990-91 data from Hart Buckland-Nicks (1995); 2009 data from SMRA unpublished.

<u>Alkalinity</u>

Alkalinity refers to the kind and quantity of compounds present which collectively shift the pH to the alkaline (Wetzel, 1975), and is measured as mg $CaCO_3$/L, treating all alkaline substances as though they are $CaCO_3$. Alkalinity data for the St. Mary's River comes from Farmer et al. (1988; N=41), unpublished 1984-85 SMRA data (N=17), Hart Buckland –Nicks (1995; N=38), Dalziel (1994; N=11), and Environment Canada at Stillwater (N=155). Based on data collected from various areas in the watershed between 1982 and 1994 (N=105 measurements), the East Branch has significantly greater alkalinity values than the Main Branch, which in turn is significantly greater than the West Branch (ANOVA $p<<0.0001$; Figure 11; Table 4). Variability among measurements within a branch were greater for the West Branch (CV=83%) compared to East or Main Branches (CV= 54% and 48%, respectively). Alkalinity values ranged between 0.5 and 14.0 mg/L $CaCO_3$. These values are at the low end of the alkalinity range, implying sensitivity to acid inputs.

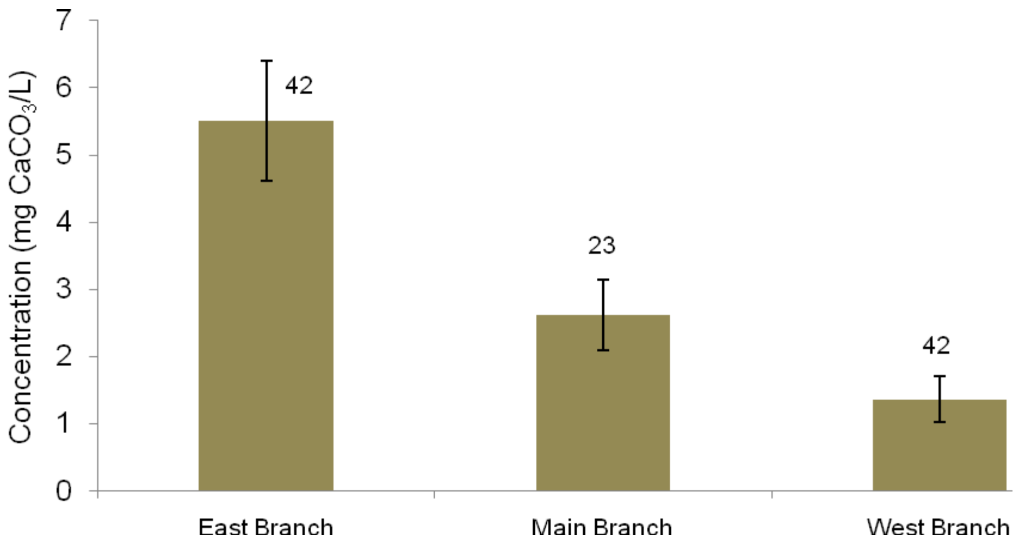


Figure 11: Mean alkalinity of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate. Values represent sample size used to calculate means.

Table 4: Summary statistics of alkalinity, hardness and specific conductance distribution in the St. Mary's River. Data from Farmer et al. (1988), unpublished 1984-85 SMRA data, Hart Buckland-Nicks (1995), Dalziel (1994), and Environment Canada (Stillwater).

| | Mean (SD); N | Range | Median | 10th-90th percentile |
|---|---|---|---|---|
| **Alkalinity (mg/L $CaCO_3$)** | | | | |
| East Branch | 5.51 (2.96); 42 | 0.7 – 14.0 | 5.1 | 2.0 – 9.8 |
| Main Branch | 2.62 (1.28); 23 | 0.5 – 5.0 | 2.5 | 1.0 – 4.0 |
| West Branch | 1.36 (1.14); 42 | 0.5 – 7.0 | 1.0 | 0.5 – 2.3 |
| Main Branch at Stillwater | 2.88 (1.90); 136 | 0.5 – 18.1 | 2.6 | 1.4 – 3.8 |
| **Hardness (mg/L $CaCO_3$)** | | | | |
| East Branch | 10.0 (5.5); 42 | 0.6 – 25.9 | 9.2 | 4.1 – 16.6 |
| Main Branch | 5.3 (1.9); 24 | 1.5 – 7.5 | 5.8 | 2.6 – 7.3 |
| West Branch | 3.9 (1.4); 43 | 1.3 – 7.2 | 3.9 | 2.2 – 5.5 |
| **Specific Conductance (µS/cm)** | | | | |
| East Branch | 42.8 (24.5); 143 | 16 – 177 | 36.5 | 25.0 – 69.0 |
| Main Branch | 28.4 (11.9); 86 | 15 – 108 | 27.0 | 19.4 – 36.4 |
| West Branch | 25.6 (9.7); 343 | 13 - 73 | 23.0 | 17.0 – 36.9 |
| Main Branch at Stillwater | 31.1 (5.4); 301 | 21 - 76 | 31.0 | 25.8 – 37.0 |

Temporally, alkalinity has been measured by Environment Canada at Stillwater between 1974 and 1991 and again in 2002-2008 (Figure 12). Mean alkalinity over 136 measurements was 2.88 mg/L (Table 4). This analysis excludes data after 2006 as that data are simply reported as ">20 mg/L" which are of questionable validity. The maximum of the previous 136 measurements or the 107 measurements from sources other than Environment Canada, was 18.1 mg $CaCO_3$/L. To then have 19 measurements between 2006 and 2008 which are greater than 20 mg/L suggests these latter values are in error. The greatest values of alkalinity (>6 mg $CaCO_3$/L) occurred on September 18, 1974, March 19, 1975, and August 27, 1980; apart from these points, alkalinity has been very stable and constant at Stillwater between 1.4 mg/L (10$^{th}$ percentile of distribution) and 3.8 mg/L (90$^{th}$ percentile of distribution). There is no evidence of a positive or negative change in alkalinity over time (linear regression: slope = -0.0001, p = 0.152; $r^2$ = 0.015). Green et al. (1986) reported on 170 alkalinity measurements at Stillwater between 1966 and 1985, and gave a mean of 2.5 mg/L (SD=1.5) and range of 0.5 – 12.6 mg/L, which is very similar to that reported for 1974-2008. The estimates for the two time periods are not statistically different based on overlapping 95% confidence intervals.

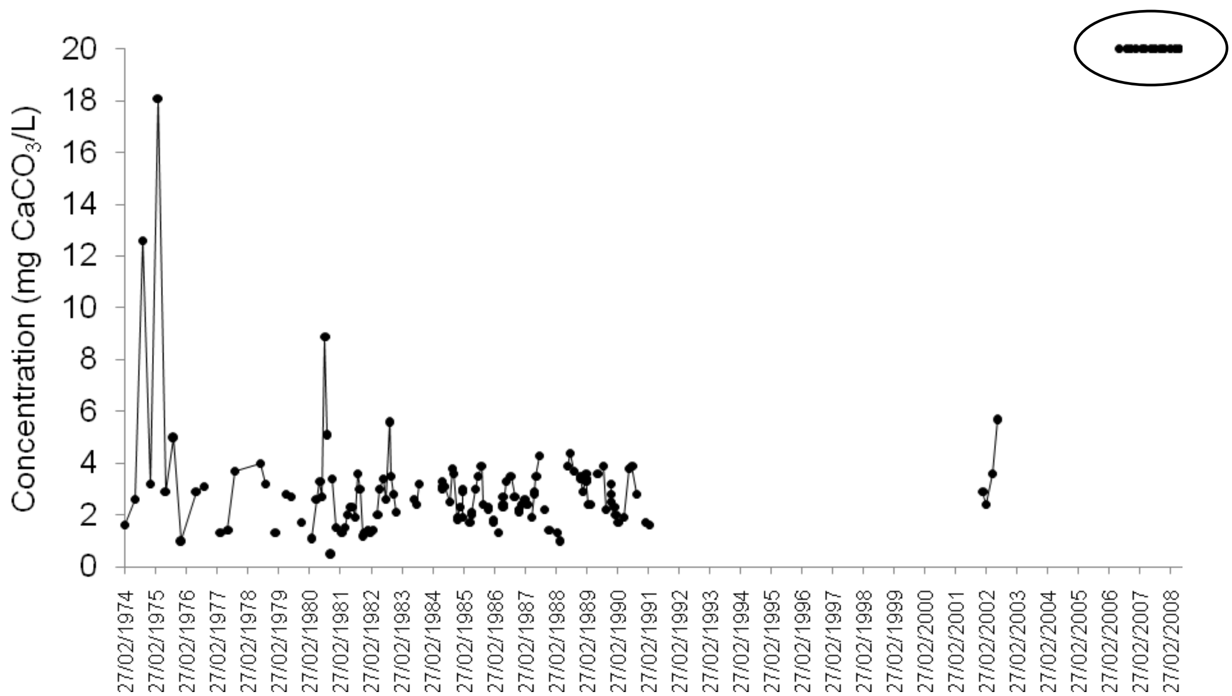


Figure 12: Alkalinity over the period 1974-2008 (mg/L $CaCO_3$) as measured by Environment Canada at Stillwater. Note grouping circled in upper right corner simply reported as "> 20 mg/L" and so of questionable validity (see text).

## Hardness

The hardness of water is used as an assessment of the quality of water supplies and is governed by the content of calcium and magnesium salts, bicarbonates, carbonates, sulphates and chlorides (Wetzel, 1975). Units of hardness are mg $CaCO_3$/L, treating all hardness substances as though they are $CaCO_3$. Water hardness data for the St. Mary's River comes from Farmer et al. (1988; N=41), unpublished SMRA data (N=19), Hart Buckland–Nicks (1995; N=38), and Dalziel (1994; N=11). Hardness has not been measured at the Stillwater Station by Environment Canada. Hardness is significantly greater (ANOVA $p<<0.0001$; Figure 13) in the East Branch than in the other two branches, and the Main Branch has significantly greater hardness values than the West Branch; this is the same pattern as that shown by alkalinity. Hardness values ranged between 0.6 and 25.9 mg $CaCO_3$/L (Table 4). Variability among measurements within a branch was greater for the East Branch (CV=55%) compared to West or Main Branches (CV= 34% and 36%, respectively). Overall mean hardness for all branches combined is 6.6 mg/L (SD=4.5, N=109). Water hardness of 0-60 mg/L $CaCO_3$ is classified as "soft water" and hence the St. Mary's River may be interpreted as a soft water system.

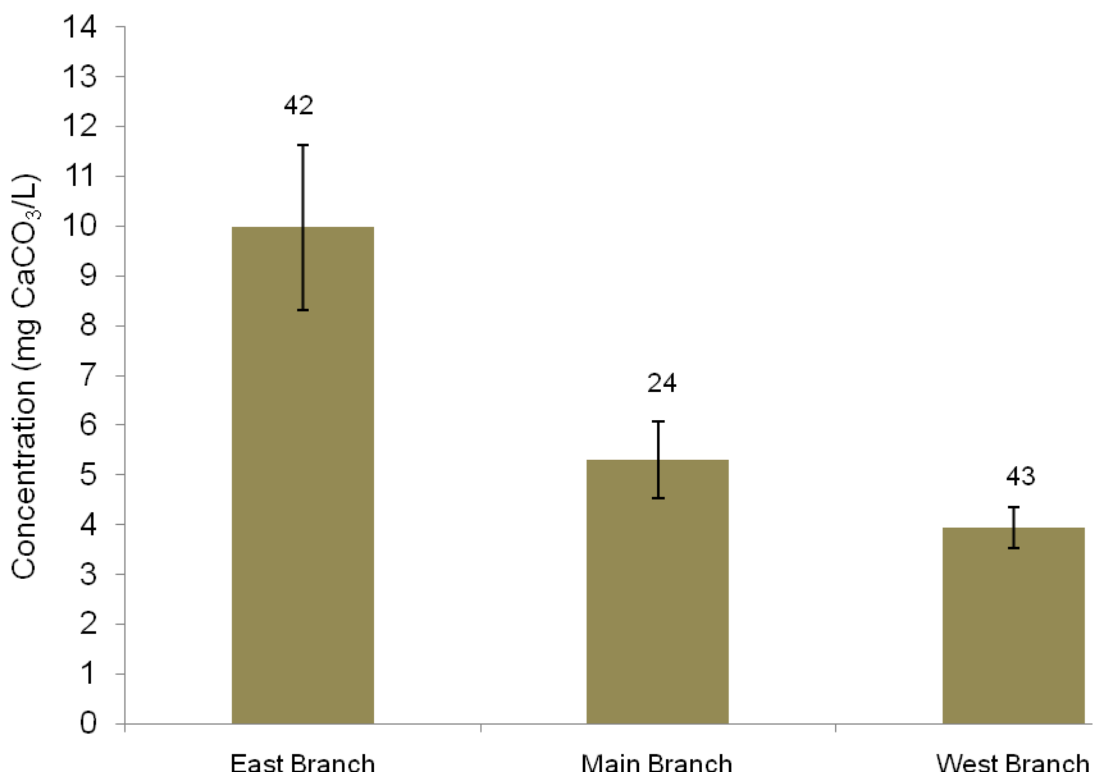


Figure 13: Mean water hardness of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate. Values represent sample size used to calculate means.

<u>Specific Conductance</u>

Specific conductance is a measure of the resistance of water to an electric current, with resistance decreasing as concentration of ionized salts increases (Wetzel, 1975); thus specific conductance is a measure of the concentration of aggregate ionic components in the water. Units of specific conductance are microsiemens/cm (µS/cm). Specific conductance data for the St. Mary's River come from Farmer et al. (1988; N=41), unpublished 1984-85 SMRA data (N=19), Hart Buckland –Nicks (1995; N=466), Dalziel (1994; N=20), and Environment Canada at Stillwater (N=301). Based on data collected from various areas in the watershed between 1982 and 1994 (N=573 measurements), the East Branch has significantly greater values of specific conductance than the Main Branch, which equal to the West Branch (ANOVA $p<<0.0001$; Figure 14; Table 4). Variability among measurements within a branch was greater for the East Branch (CV=87%) compared to West or Main Branches (CV= 38% and 42%, respectively).

Temporally, specific conductance measurements have been made by Environment Canada at Stillwater between 1974 and 2008 (Figure 15). Mean specific conductance over 301 measurements was 31.1 mg/L µS/cm (Table 4). The highest values of specific conductance (>50 µS/cm) occurred on September 17, 1975, July 16, 1984, and December 9, 1987; all other values ranged between 21 and 43 µS/cm. There is no evidence of increasing or decreasing trend in specific conductance over time (linear regression: slope = -0.0002, p = 0.115; $r^2$ = 0.008). Green et al. (1986) reported on 188 conductance measurements at Stillwater between 1966 and 1985, and gave a mean of 31.0 µS/cm (SD=9.0) and range of 20 – 99 µS/cm, which is not statistically different from that reported for 1974-2008.

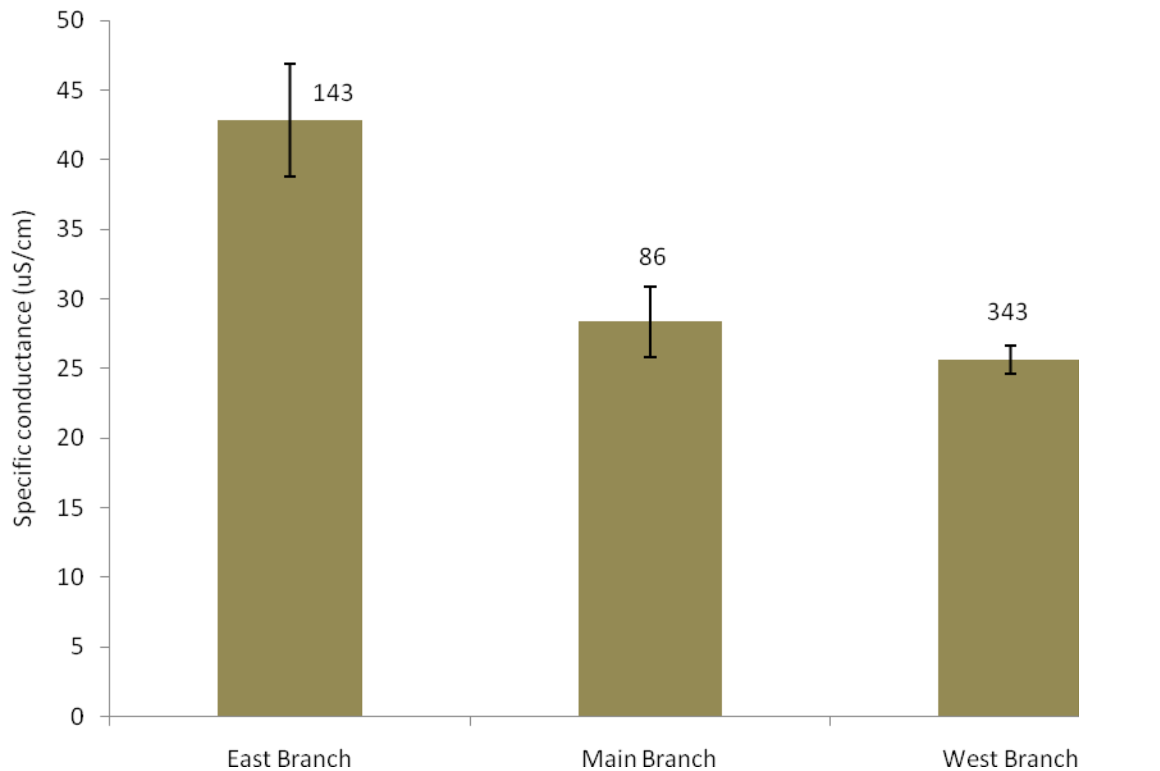


Figure 14: Mean specific conductance of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate. Values represent sample size used to calculate means.

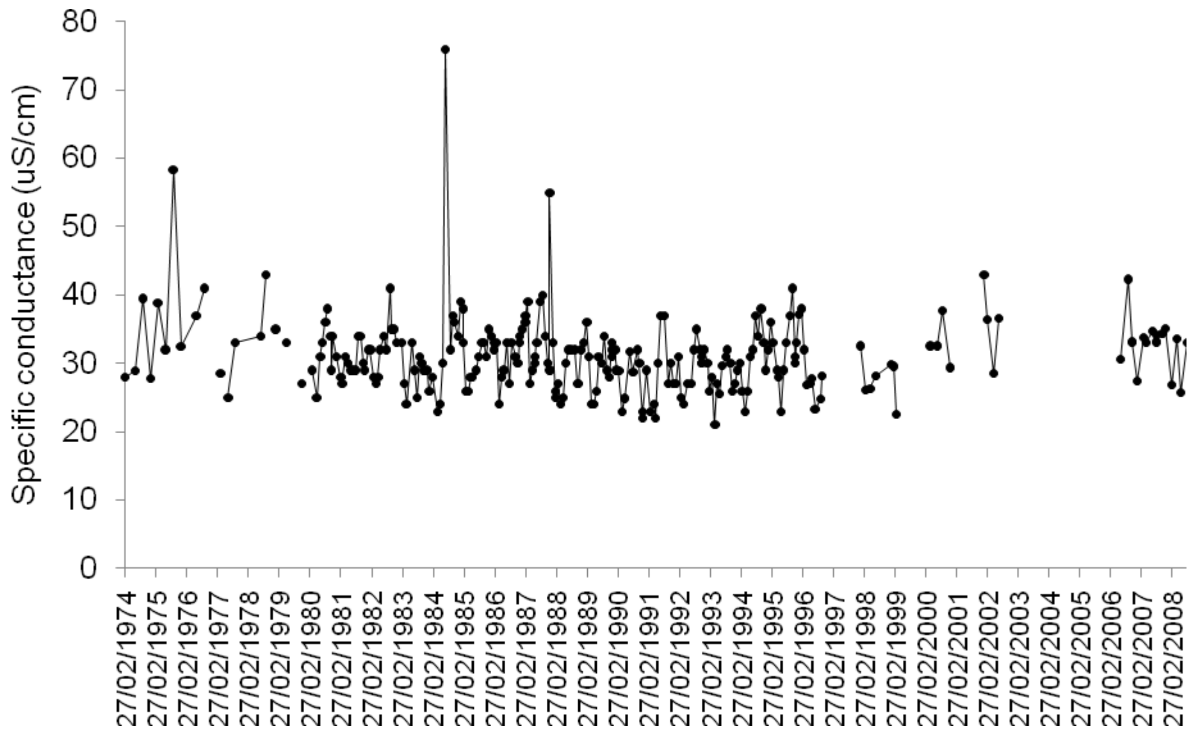


Figure 15: Specific conductance over the period 1974-2008 as measured by Environment Canada at Stillwater.

<u>Individual Ionic Constituents</u>

Eleven individual ionic components contributing to alkalinity, hardness and specific conductance have been measured in the St. Mary's River (Table 5). These have measured using various variables (e.g., carbon as four variables – Dissolved Inorganic, Dissolved Organic, Total Inorganic, and Total Organic). It is beyond the scope of this review, and would be tedious, to evaluate each of these parameters in detail. Summary statistics of these components are provided for the reader in Table 5.

Table 5: Summary statistics of individual ionic components contributing to alkalinity, hardness and specific conductance. Data from Farmer et al. (1988), Dalziel (1994), Hart Buckland-Nicks (1995), and Environment Canada sampling at Stillwater.

| | Mean (SD); N | Range | Median | $10^{th}$-$90^{th}$ percentile |
|---|---|---|---|---|
| **Bicarbonate (mg/L)** | | | | |
| Various areas through watershed | 3.41 (3.57); 44 | 0 - 14 | 2.15 | 0.00 – 7.14 |
| **Calcium (mg/L)** | | | | |
| Various areas through watershed | 1.53 (1.34); 51 | 0.20 - 6.24 | 1.02 | 0.40 – 2.90 |
| Main Branch at Stillwater (dissolved) | 1.38 (0.34); 297 | 0.14 - 3.20 | 1.40 | 1.00 – 1.70 |
| Main Branch at Stillwater (extractable) | 1.18 (0.27); 6 | 0.96 - 1.64 | 1.06 | 0.97 – 1.51 |
| **Carbon (mg/L)** | | | | |
| Dissolved Inorganic Carbon (DIC) Main Branch at Stillwater | 0.81 (0.64); 63 | 0.5 – 4.0 | 0.6 | 0.50 – 1.10 |
| Dissolved Organic Carbon (DOC) various areas through watershed | 4.87 (2.32); 3 | 2.2 - 6.4 | 6.0 | 2.96 – 6.32 |
| Dissolved Organic Carbon (DOC) Main Branch at Stillwater | 4.06 (1.51); 181 | 0.7 – 10.0 | 3.9 | 2.40 – 5.90 |
| Total Inorganic Carbon (TIC) Main Branch at Stillwater | 0.81 (0.34); 117 | 0.5 – 2.0 | 0.7 | 0.50 – 1.30 |
| Total Organic Carbon (TOC) various areas through watershed | 4.07 (2.50); 49 | 1.4 – 11.0 | 3.2 | 1.70 – 7.50 |
| Total Organic Carbon (TOC) Main Branch at Stillwater | 6.02 (1.98); 77 | 1.8 – 14.0 | 6.0 | 3.66 – 8.40 |
| Total Organic Carbon (TOC) (Non-purgeable) Main Branch at Stillwater | 5.21 (1.98); 45 | 2.4 - 10.5 | 5.0 | 2.84 – 7.94 |
| **Carbonate (mg/L)** | | | | |
| Various areas through watershed | 1.23 (3.15); 44 | 0 - 19 | 0.0 | 0.0 – 4.0 |
| **Chloride (mg/L)** | | | | |
| Various areas through watershed | 5.70 (5.54); 53 | 1.5 – 37.0 | 4.4 | 2.3 – 8.7 |
| Main Branch at Stillwater | 4.83 (0.97); 301 | 2.5 - 9.7 | 4.8 | 3.8 – 6.1 |
| **Fluoride (mg/L)** | | | | |
| Main Branch at Stillwater | 0.05 (0.003); 183 | 0.02 - 0.05 | 0.05 | 0.05 – 0.05 |
| **Humic Acid (mg/L)** | | | | |
| Main Branch at Stillwater | 7.31 (3.16); 54 | 1 - 15 | 6.85 | 4.12 – 12.00 |

Table 5 (Con't): Summary statistics of individual ionic components contributing to alkalinity, hardness and specific conductance.

| | Mean (SD); N | Range | Median | 10th-90th percentile |
|---|---|---|---|---|
| **Potassium (mg/L)** | | | | |
| Various areas through watershed | 0.34 (0.14); 49 | 0.2 - 0.8 | 0.30 | 0.20 – 0.53 |
| Main Branch at Stillwater (Dissolved) | 0.29 (0.12); 297 | 0.1 - 1.7 | 0.28 | 0.20 – 0.40 |
| Main Branch at Stillwater (Extractable/unfiltered) | 0.27 (0.06); 6 | 0.2 - 0.3 | 0.28 | 0.02 – 0.32 |
| **Silica (mg/L)** | | | | |
| Various areas through watershed (reactive silica) | 1.99 (0.75); 11 | 1.0 – 3.0 | 2.1 | 1.10 – 2.90 |
| Various areas through watershed (silica) | 2.66 (1.04); 38 | 1.2 - 5.3 | 2.2 | 1.78 – 4.18 |
| Main Branch at Stillwater (reactive silica) | 2.49 (0.95); 145 | 0.6 - 4.3 | 2.7 | 1.13 – 3.64 |
| Main Branch at Stillwater (silica dioxide) | 2.62 (0.94); 41 | 1.0 - 4.2 | 2.8 | 1.30 – 3.70 |
| **Sodium (mg/L)** | | | | |
| Various areas through watershed | 3.68 (3.98); 49 | 0.2 - 27.4 | 2.8 | 1.48 – 4.74 |
| Main Branch at Stillwater (dissolved) | 3.14 (0.51); 298 | 2.0 - 5.8 | 3.1 | 2.50 – 3.80 |
| Main Branch at Stillwater (extractable/unfiltered) | 3.33 (0.28); 6 | 3.0 - 3.6 | 3.4 | 2.99 – 3.61 |
| **Sulphate (mg/L)** | | | | |
| Various areas through watershed | 2.94 (0.95); 53 | 2.0 – 5.0 | 3.0 | 2.00 – 4.00 |
| Main Branch at Stillwater | 2.77 (0.64); 296 | 1.7 - 6.7 | 2.7 | 2.12 – 3.33 |

Dissolved Oxygen (DO)

Dissolved oxygen has been measured 339 times in the St. Mary's River watershed (153 measurements from Environment Canada; 183 from MacPhail and Alpert, 1975; 3 from Dalziel, 1994). Median concentration is 10.0 mg/L, with 95% of measurements in excess of 7.6 mg/L and 99% greater than 5.5 mg/L (Figure 16). CCME dissolved oxygen guidelines for the protection of aquatic life have been established as >9.5 mg/L for early stages of invertebrates and fish, and >6.5 mg/L for other life stages. Based on measurements for the St. Mary's River, DO exceeds 9.5 mg/L approximately 63% of the time and 6.5 mg/L approximately 97.5% of the time.

Throughout most of the watershed there is no reason to believe that low dissolved oxygen concentrations are of concern from an ecological perspective (see *Discussion*).

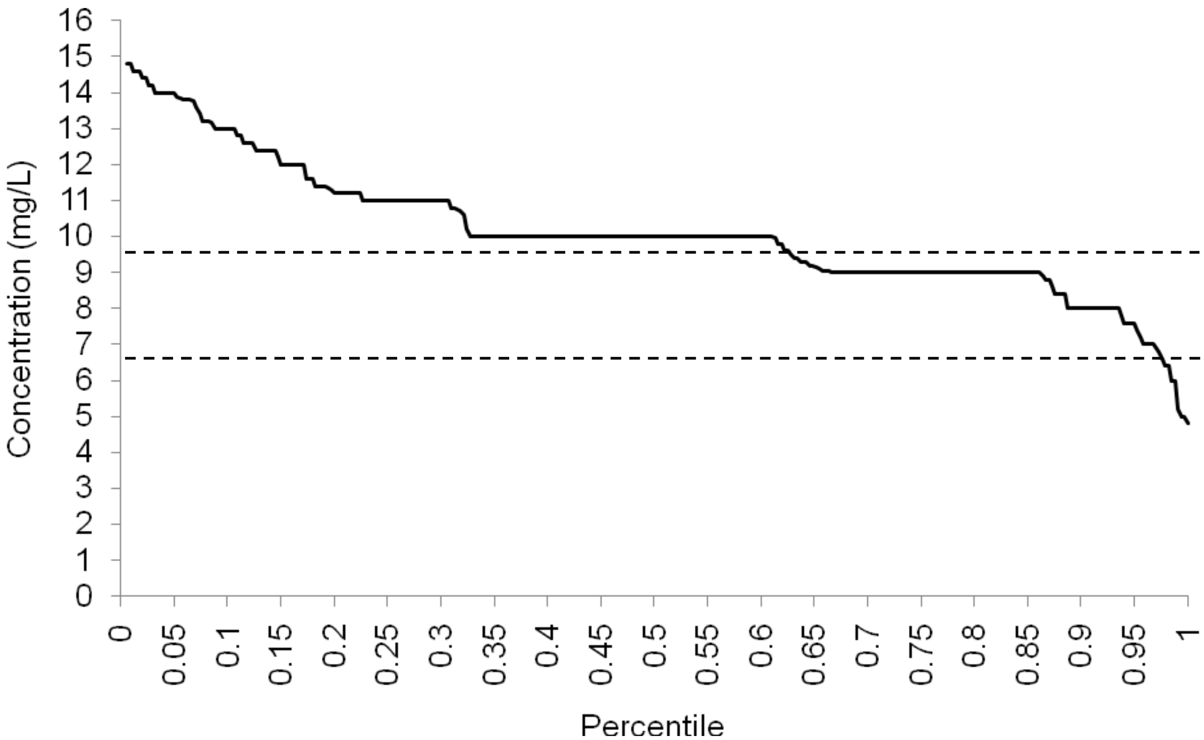


Figure 16: Cumulative distribution of dissolved oxygen measurements in St. Mary's River (N=339 measurements). Dashed lines represent CCME guidelines (6.5 and 9.5 mg/L).

### *5.1.3 Nutrients*

The two nutrients, nitrogen and phosphorous, are essential for life. Nitrogen is a principal structural component of amino acids and proteins, and phosphorous provides the cellular energy source for metabolism and activity. Therefore, availability of these elements at adequate concentrations is critical to living organisms for both structure and function. Furthermore, nutrient concentrations often control the ecology of a waterway, either by being at low concentrations, and so limiting (oligotrophic), or present at high concentrations and shifting the aquatic community to one dominated by plants and periods of low oxygen (eutrophic). Thus, nutrients are critical to the function, and state of, aquatic systems.

<u>Phosphorous</u>

Phosphorous concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=38 as ortho-phosphate), Dalziel (1994; N=11 as ortho-phosphate), and Environment Canada at Stillwater (N=280 as total phosphorous). Phosphorous concentrations in the water of the St. Mary's River watershed are low, almost always less than 0.01 mg/L (i.e., of 331 measurements, 287 (86.7%) were <0.01 mg/L). The concentrations do not differ among river branches (ANOVA p=0.075) with mean concentrations ranging between 0.011 mg/L (Main and West Branches) and 0.017 mg/L (East Branch) (Table 6). Maximum phosphorous concentrations reported have been 0.05 mg/L (East Branch).

Table 6: Summary statistics of nutrient distribution in the St. Mary's River. Data from Farmer et al. (1988), unpublished 1984-85 SMRA data, Hart Buckland-Nicks (1995), Dalziel (1994), and Environment Canada (Stillwater).

| | Mean (SD); N | Range | Median | 10th-90th percentile |
|---|---|---|---|---|
| **Phosphorous (mg/L)** | | | | |
| East Branch | 0.017 (0.014); 20 | 0.01 – 0.05 | 0.01 | 0.010 – 0.042 |
| Main Branch | 0.011 (0.004); 14 | 0.01 – 0.02 | 0.01 | 0.010 – 0.018 |
| West Branch | 0.011 (0.005); 17 | 0.01 – 0.03 | 0.01 | 0.010 – 0.010 |
| Main Branch at Stillwater | 0.010 (0.003); 279 | 0.001 – 0.027 | 0.005 | 0.002 – 0.01 |
| **Nitrogen (Total) (mg/L)** | | | | |
| Main Branch at Stillwater | 0.15 (0.07); 275 | 0.01 – 0.66 | 0.14 | 0.09 – 0.24 |
| **Nitrogen (Nitrate & Nitrite) (mg/L)** | | | | |
| East Branch | 0.13 (0.09); 20 | 0.05 – 0.39 | 0.125 | 0.05 – 0.21 |
| Main Branch | 0.06 (0.02); 15 | 0.05 – 0.13 | 0.050 | 0.05 – 0.06 |
| West Branch | 0.08 (0.03); 14 | 0.05 – 0.14 | 0.080 | 0.05 – 0.13 |
| Main Branch at Stillwater | 0.06 (0.06); 170 | 0.01 – 0.45 | 0.035 | 0.01 – 0.14 |
| **Nitrogen (Dissolved nitrate) (mg/L)** | | | | |
| Main Branch at Stillwater | 0.06 (0.04); 129 | 0.01 – 0.18 | 0.05 | 0.02 – 0.10 |
| **Nitrogen (Ammonia) (mg/L)** | | | | |
| East Branch | 0.052 (0.005); 20 | 0.05 – 0.07 | 0.05 | 0.05 – 0.06 |
| Main Branch | 0.050 (0.000); 14 | 0.05 – 0.05 | 0.05 | 0.05 – 0.05 |
| West Branch | 0.051 (0.003); 15 | 0.05 – 0.06 | 0.05 | 0.05 – 0.05 |
| Main Branch at Stillwater | 0.02 (0.02); 28 | 0.005 – 0.100 | 0.008 | 0.005 – 0.030 |

Temporally, over a period of sampling total phosphorous[8] by Environment Canada at Stillwater from February 1974 to October 2008, concentrations have remained low (i.e., 90th percentile of 280 samples were less than 0.01 mg/L) (Table 6). Eighteen of the 23 peaks in concentration exceeding 0.01 mg/L in this period occurred in November (7), June (5), January (3), or December (3). Monthly values of phosphorous concentration fluctuate but there is no apparent seasonal pattern (Figure 17). Each month shows a mean concentration between 0.004 and 0.008 mg/L with variation within a given month over years (i.e., Coefficient of Variation) on the order of 33%-82%. This suggests high variability for a given month from year-to-year. Over the long term there is slight indication of phosphorous having been higher in the 1970s, declining in the 1980s and then increasing again since the 1990s (Figure 18), but these data are very noisy and

[8] Dissolved inorganic phosphate was also sampled by Environment Canada, but only on 12 occasions, and thus that parameter is not analyzed here as the data are insufficient to draw conclusions.

the regression equation accounts for only a very small proportion of the variation (~18%). Re-evaluating these data as annual means (Figure 18, lower panel) makes the changes over time more apparent. Note, however, the years of lowest concentration are also those of largest sample size so it could be that increasing number of samples more accurately reflects true (low concentration) conditions, and concentrations only appear elevated when sampling effort is low. The evidence for decrease and increase over time is suggestive, but not strong. However, total nitrogen (see below) shows a similar pattern, suggesting that the recent increase may be real and significant.

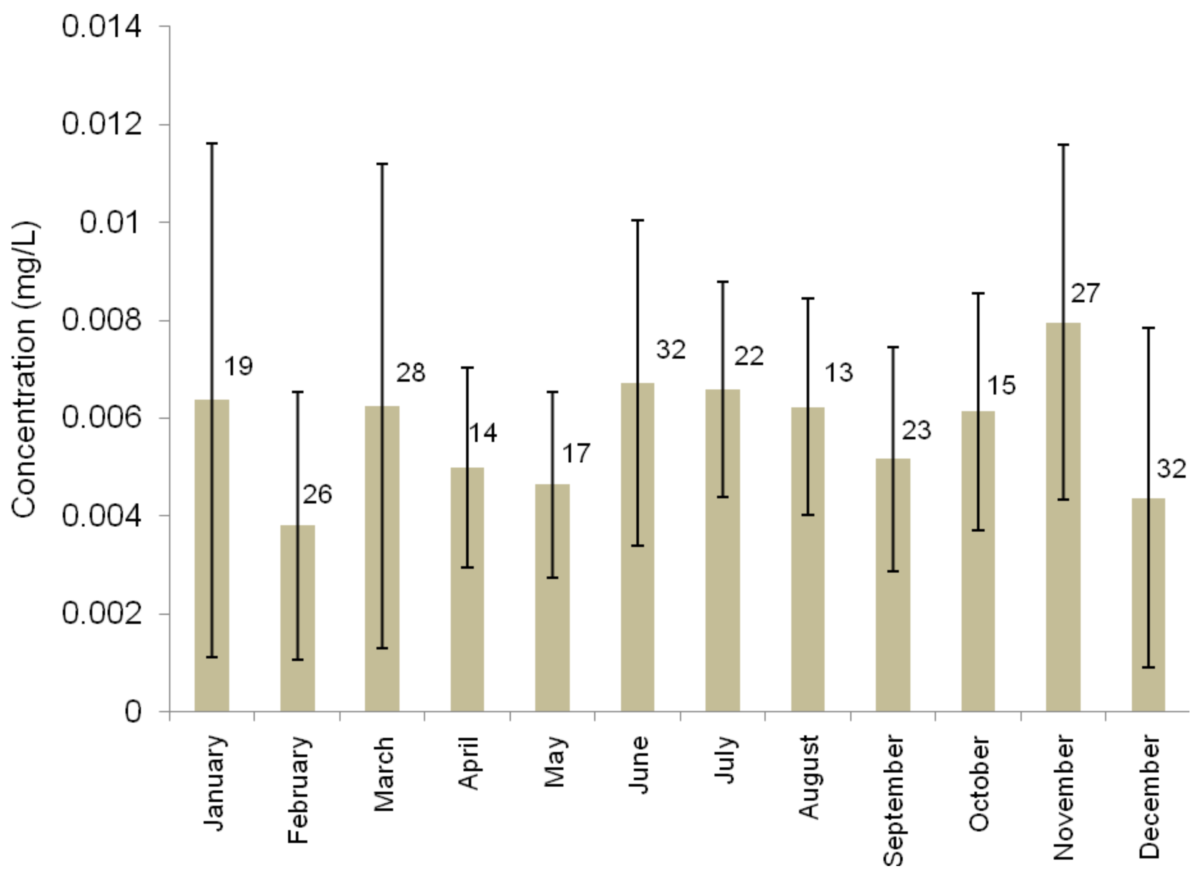


Figure 17: Mean phosphorous concentration reported by Environment Canada at Stillwater (1974-2008) arranged by month of sample. Error bars are standard deviation. Values are number of samples/month.

Neither the CCME nor Health Canada have guidelines for phosphorous concentrations. However, the CCME provide guidance on classifying water according to phosphorus concentration. Within the range of concentration shown by the St. Mary’s River (0.01-0.05 mg/L) the water would be considered mesotrophic or meso-eutrophic, though at the lower end of this classification.

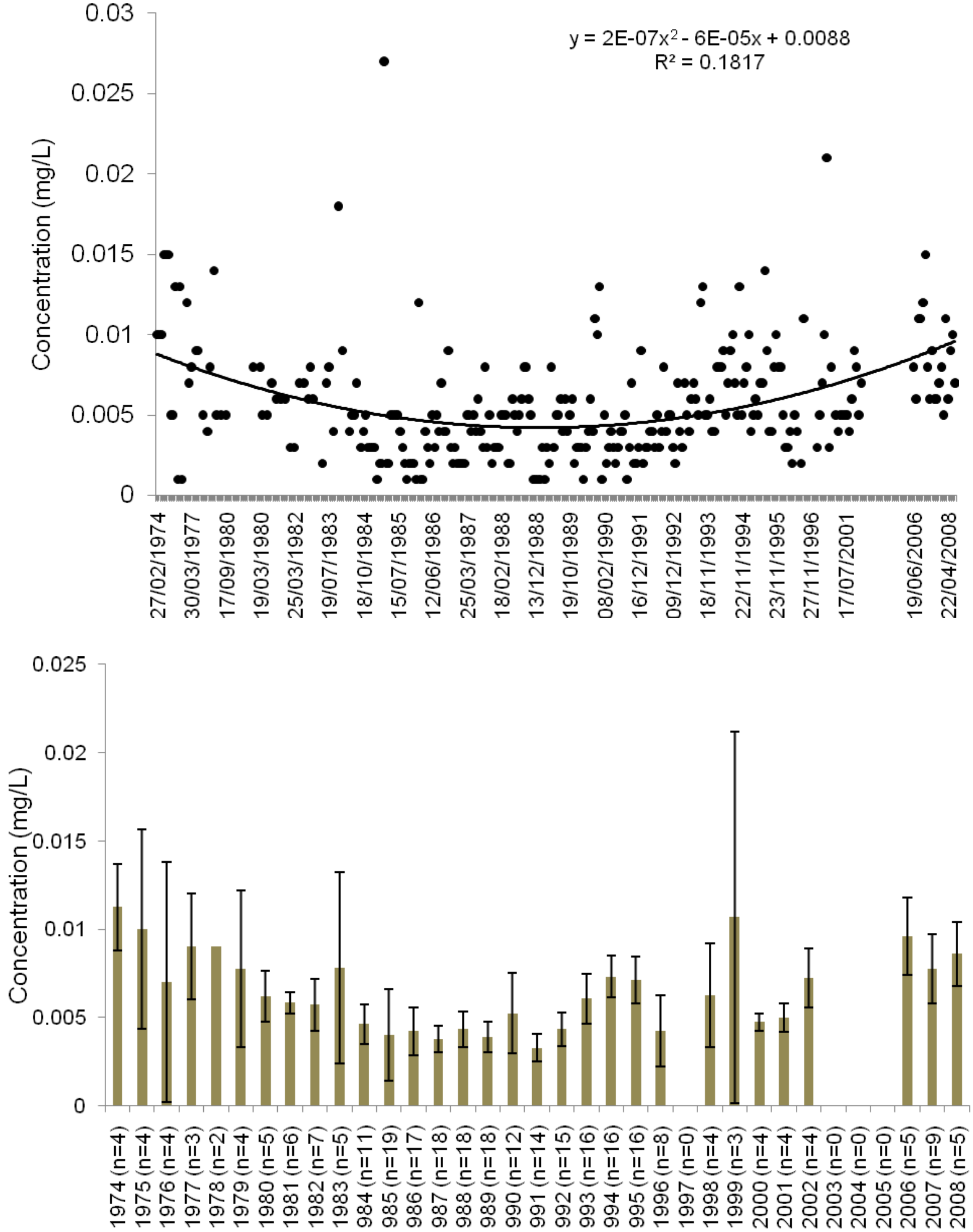


Figure 18: Upper Panel: Total phosphorous concentration over the period 1974-2008 as measured by Environment Canada at Stillwater. Lower Panel: Annual total phosphorous concentration over the period 1974-2008 as measured by Environment Canada at Stillwater. Error bars are 95% confidnece interval of mean estimate. Sample sizes provided on x-axis.

Nitrogen

Four forms of nitrogen have been sampled in the waters of the St. Mary's River watershed: (1) total nitrogen, (2) nitrate & nitrite nitrogen, (3) dissolved nitrate, and (4) ammonia.

(i) Total Nitrogen

Total nitrogen concentrations in the St. Mary's River have only been reported by Environment Canada at Stillwater (N=275), resulting in a lack of branch-specific data to allow analyses for differences among branches. Total nitrogen concentrations are elevated relative to phosphorus, with 50% of nitrogen measurements being in excess of 0.14 mg/L and 10% over 0.24 mg/L (Table 6). Maximum total nitrogen concentration was 0.66 mg/L. Total nitrogen appears to be at lowest concentration in May-June and greatest in August, January and February of a year (Figure 19). Mean monthly concentrations range from 0.10 (May) to 0.19 (February) mg/L. The coefficient of variation within a month among years ranged from 28% (January) to 55% (December). Nitrogen concentration at Stillwater appear to be elevated in the measurement period 2006-2008 (mean 0.26 mg/L; SD=0.086; N=19; 95% CI ± 0.04) relative to 1978-2002 (mean 0.14 mg/L; SD=0.06; N=256; 95% CI ± 0.008) (Figure 20), which are significantly different based on 95% confidence intervals. Thus, total nitrogen concentration appears to have risen recently over the long-term baseline. Prior to the 2006-2008 sampling there was no evidence of increasing or decreasing trend over time (linear regression slope <0.0001, $p = 0.114$; $r^2 = 0.01$).

There are not CCME Water Quality Guidelines nor Health Canada Drinking Water Quality Guidelines for Total Nitrogen for comparison with these concentrations.

(ii) Nitrate/Nitrite

Nitrate and nitrite nitrogen concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=38), Dalziel (1994; N=11), and Environment Canada at Stillwater (N=170). Nitrogen in the form of nitrate ($NO_3$) and nitrite ($NO_2$) combined ranges between <0.05 mg/L and 0.45 mg/L, and is generally at low concentrations, with 59 of 219 (26.9%) measurements reported as <0.05 or <0.01 mg/L (depending on detection level used in the analysis). Spatially, concentrations are greater (ANOVA p=0.001) in the East Branch than in the Main Branch (Table 6; Figure 21). Concentrations in the West Branch are intermediate between the East and Main branches and statistically equal to each of the other branches.

Seasonally, nitrate/nitrite concentrations peak in winter months (Jan-March) and are lowest in summer (Figure 22). Within month variation, as indicated by the coefficient of variation, ranges between 21% (January) and 160% (September); all other months are between 37% and 96%. Over time between 1974 and 1991 (Environment Canada not measuring nitrate/nitrite post-1991), nitrate/nitrite concentrations have fluctuated but not shown patterns of increase or decrease (Figure 23). The highest concentrations (>0.2 mg/L) occurred on September 17, 1980, November 23, 1982, February 13, 1985, December 9, 1987, and February 21, 1989. In the period 1974-1991, there was no evidence of increasing or decreasing trend over time (linear regression slope <0.001, $p = 0.076$; $r^2 = 0.019$). Green et al. (1986) reported $NO_x$ concentrations for Environment Canada data from Stillwater between 1966 and 1985. They reported a mean concentration of 0.054 mg/L (SD=0.094; N=164), with a range of 0.001 to 0.61 mg/L, which is not significantly different from the 1974-2008 mean, based on 95% confidence intervals.

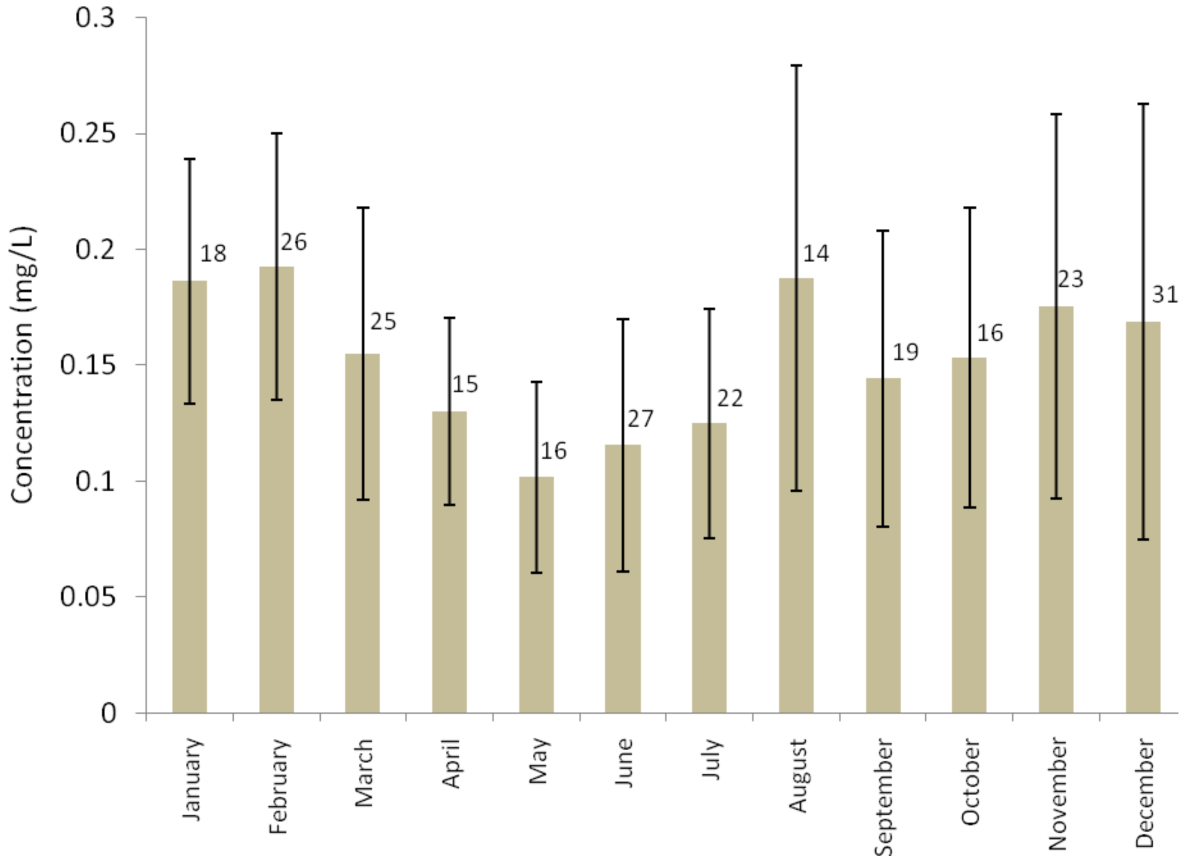


Figure 19: Total nitrogen concentration reported by Environment Canada at Stillwater (1974-2008) arranged by month of sample. Error bars are standard deviation. Values are number of samples/month.

The CCME has established water quality guidelines for the protection of aquatic life of 0.197 mg/L as nitrite and 13.0 mg/L as nitrate. Health Canada does not have drinking water quality guidelines for this parameter. Unfortunately, nitrate and nitrite are generally measured as combined species, so applying the CCME individual guidelines to nitrate/nitrite is problematic. Ideally, nitrate is measured concurrently with nitrate/nitrite and then nitrite concentrations may be estimated by subtraction of nitrate from nitrate/nitrite. Unfortunately, concurrent sampling of nitrate/nitrite and nitrate has not taken place in the St. Mary's River (nitrite/nitrate sampled prior to 1991; nitrate sampled post-1991 (see below)), preventing estimating of nitrite concentrations. In general the combined nitrate/nitrite is below the CCME guideline for nitrite only and thus elevated nitrate/nitrite concentrations are not considered to be an issue in the St. Mary's River watershed.

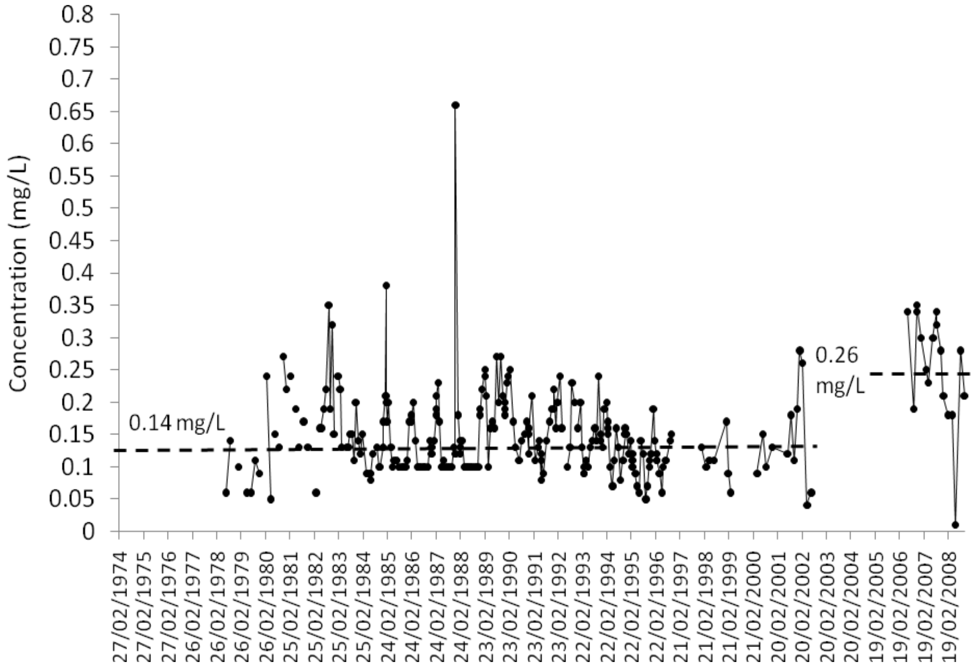


Figure 20: Total nitrogen concentration over the period 1974-2008 as measured by Environment Canada at Stillwater. Values indicate means over periods 1974-2002 and 2006-2008.

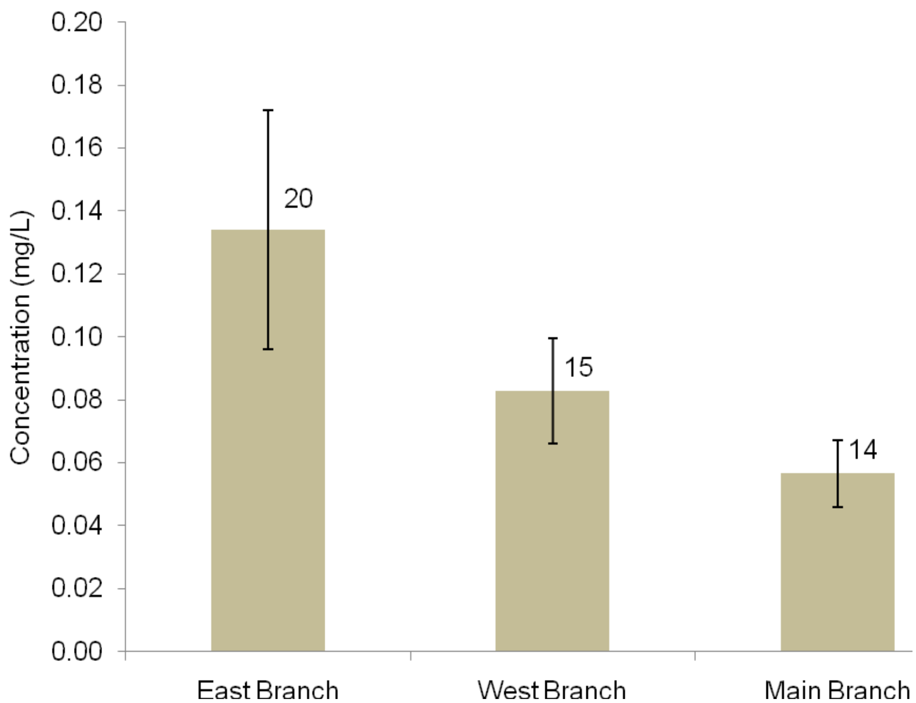


Figure 21: Mean dissolved nitrate/nitrite concentrations of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate. Values represent sample size used to calculate means.

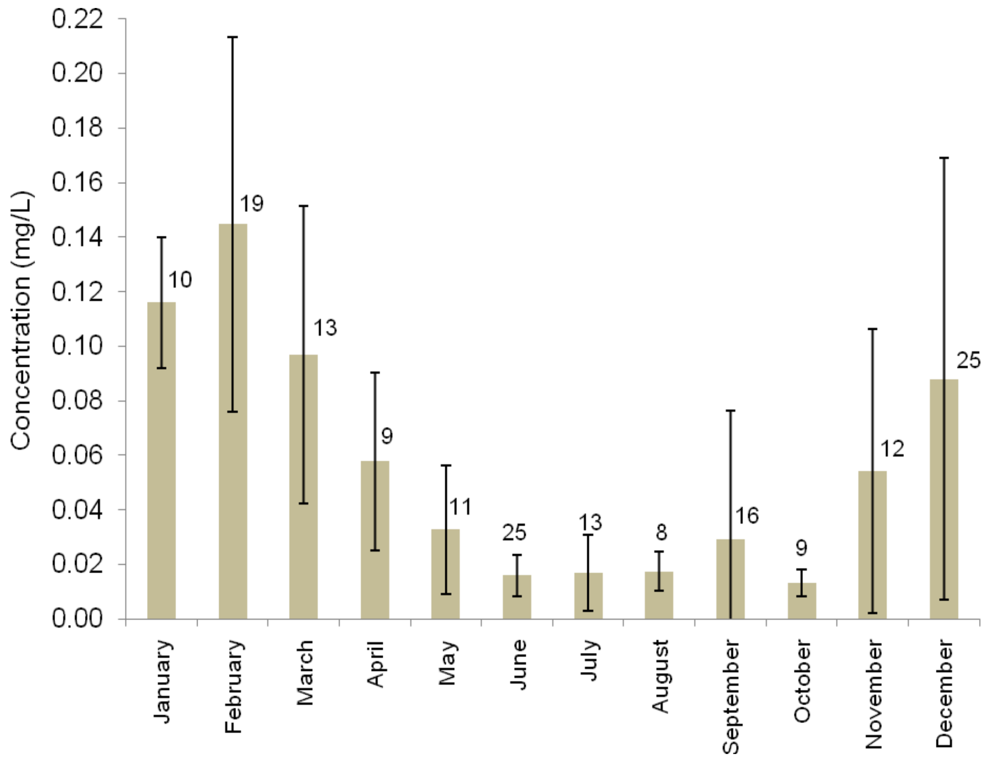


Figure 22: Dissolved nitrate/nitrite nitrogen concentration reported by Environment Canada at Stillwater (1974-2008) arranged by month of sample. Error bars are standard deviation. Values are number of samples/month.

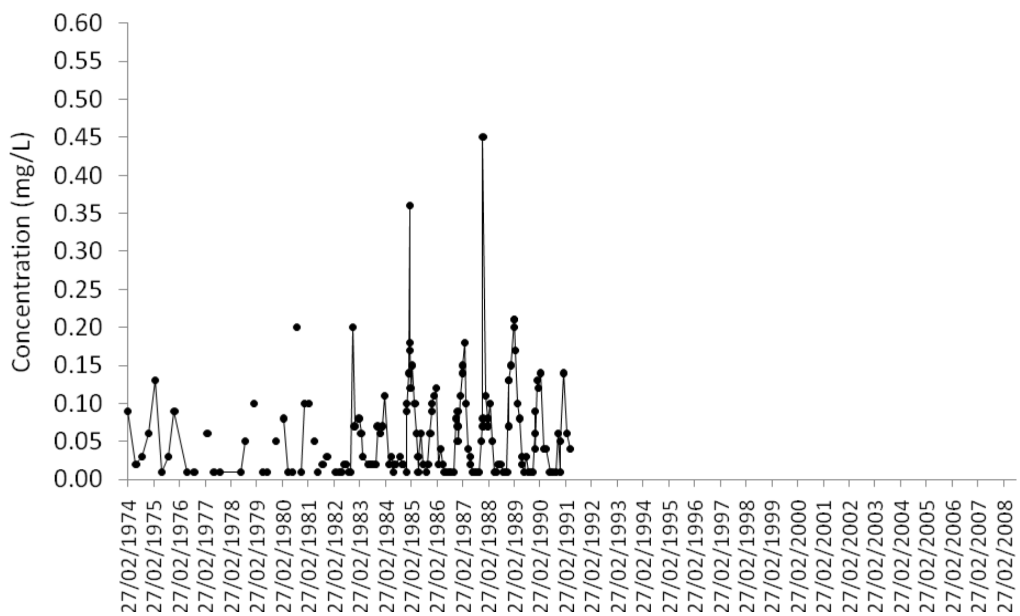


Figure 23: Dissolved nitrate/nitrite concentration over the period 1974-2008 as measured by Environment Canada at Stillwater. Note: this parameter not sampled by Environment Canada after 1991.

(iii) Dissolved Nitrate

Dissolved nitrate concentrations in the St. Mary's River have only been reported by Environment Canada at Stillwater (N=129), and the only between 1990 and 2008. Dissolved nitrate follows the same pattern as nitrate/nitrite with peak values in winter and low values in summer months (Figure 24). Variability among years for a given month (i.e., coefficient of variations) is moderate and stable for all months, ranging between 20.4% (May) and 57.1% (August). Nitrate values ranged between <0.01 and 0.18 mg/L with 90% of the 129 measurements <0.11 mg/L (Table 6). Nitrate shows regular annual fluctuations over the years of measurement (Figure 25) but no pattern of increase or decrease over this time (linear regression slope <0.0001, $p = 0.693$; $r^2 = 0.001$). These peaks and valleys represent changes through the year with peaks in winter months and low periods in summer.

The highest values of nitrate measured are two orders-of-magnitude less than the CCME Water Quality Guidelines of 13.0 mg/L nitrate. Health Canada MAC for nitrate is 45 mg/L.

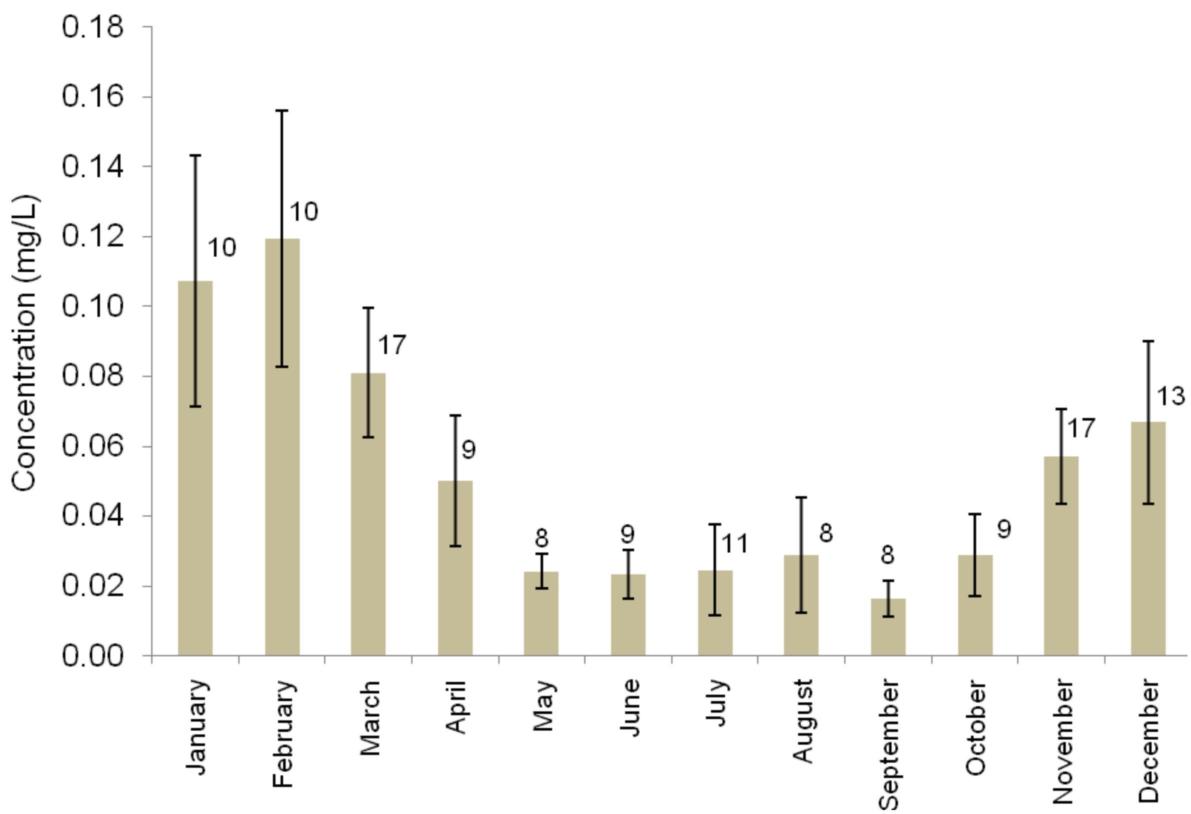


Figure 24: Dissolved nitrate nitrogen concentration reported by Environment Canada at Stillwater (1974-2008) arranged by month of sample. Error bars are standard deviation. Values are number of samples/month.

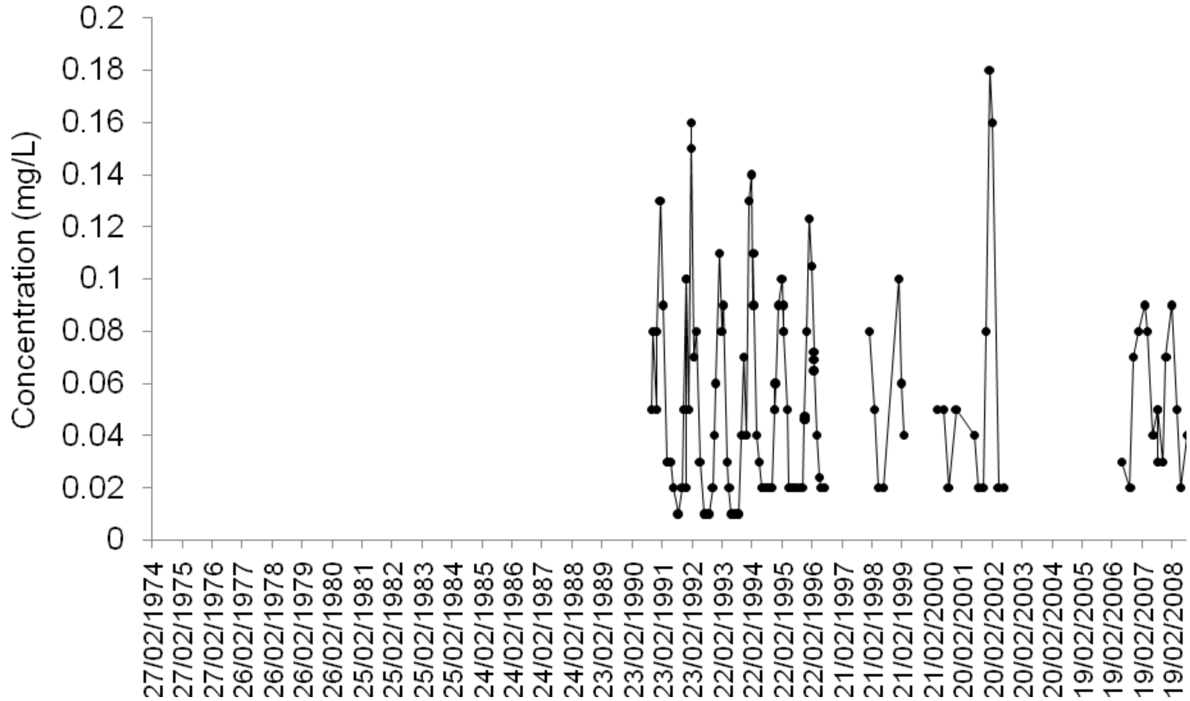


Figure 25: Dissolved nitrate concentration over the period 1974-2008 as measured by Environment Canada at Stillwater.

(iv) Ammonia

Ammonia nitrogen concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=38), Dalziel (1994; N=11), and Environment Canada at Stillwater (N=28). Dissolved ammonia concentrations in the St. Mary's River have not been measured as regularly as phosphorous and other forms of nitrogen (i.e., total of 77 ammonia measurements; Table 6). There is no significant difference in ammonia concentrations among the three branches of the river (ANOVA p=0.27), with each branch averaging between 0.05 and 0.052 mg/L. There are insufficient data to analyze ammonia concentrations over time, either seasonally (e.g., the four months of February, April, August and October have no data) or longer term (i.e., only nine years of data, 7 of which have 4 or less measurements in a year). However, based on the limited data available (maximum of 77 measured values = 0.07 mg/L; 95% of measurements <0.06 mg/L), ammonia concentrations are not likely to be of concern in the St. Mary's River when compared against CCME guidelines. The CCME guidelines have not been derived for waters of pH<6.0 (i.e., the West and Main branches in this system). Assuming an ammonia worst case scenario (pH 7.0, water temperature 25 $^{o}$C) the CCME guideline is 2.77 mg/L total ammonia. It is important to note that decreasing pH decreases ammonia toxicity, thus at reduced pH ammonia will be less of a risk. However, it is also important to emphasize that the data presented are dissolved ammonia while the CCME guidelines are total ammonia. Given the extremely low concentration of dissolved ammonia in the St. Mary's it is unlikely that total ammonia approaches its CCME guideline and therefore highly unlikely that ammonia is a parameter of concern in this watershed. There is no Health Canada drinking water quality guideline for this parameter.

Due to the discrepancy in form of ammonia sampled (dissolved) versus that with guidelines (total), it is recommended that total ammonia be sampled in the St. Mary's River watershed in the future (*Recommendation #1*).

### *5.1.4 Metals*

Metals concentrations in the St. Mary's River have been reported for the periods:

- October, 1990; January, April, and July, 1991 for 10 sites (Hart Buckland-Nicks, 1995).
- September and November, 1992 at the Ford Pool (Dalziel, 1994).
- May, August, September and November, 1993; May, August and November, 1994 at the DNR picnic site (Dalziel, 1994), and
- February 1974 to October 2008 at Stillwater (Environment Canada).

Twenty eight metals have been analyzed in these sampling programs but not all metals have been sampled as frequently as others. Sample sizes of the long-term Environment Canada sampling program have ranged from 4 (selenium, thorium, tin, uranium) to 298 (magnesium). A filtering approach was applied to the Environment Canada data to priorize metals for analysis. First, metals with <20 measurements between 1974 and 2008 (boron, magnesium (extractable), rubidium, selenium, thorium, tin, and uranium) were excluded due to very small sample size, leaving 21 metals. Those metals without Canadian Council of Ministers of the Environment (CCME) guidelines for the protection of aquatic life, but N>20, were then deemed low priority as guidelines have not yet been established, suggesting that these metals are likely fairly benign. This list included antimony, barium, beryllium, cobalt, magnesium (dissolved), manganese, strontium, titanium, and vanadium, leaving 12 metals to be analyzed in detail. The Environment Canada data was used to evaluate temporal patterns, while data from Dalziel (1994) and Hart Buckland Nicks (1995) was used, where data made possible, to evaluate spatial distribution of metals. The metals subjected to the detailed analyses were aluminum, arsenic, cadmium, chromium, copper, iron, lead, mercury, molybdenum, nickel, silver, and zinc.

Aluminum (Al)

Aluminum concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=38), Dalziel (1994; N=10), and Environment Canada at Stillwater (N=277). Aluminum concentrations are elevated in the St. Mary's River, with mean values ranging from 0.09 to 0.12 mg/L (Table 7). Aluminum concentrations are not significantly different among the three branches of the river (ANOVA p=0.56), indicating that this metal is elevated throughout the watershed.

Over the period of sampling at Stillwater by Environment Canada there is very weak indication of long term increase (Figure 26) (linear regression slope = 0.000049, p = 0.0002; $r^2$ = 0.050). The regression is statistically significant but the slope is very low implying an increase of 0.00049 mg/L per decade. As well, the very low $r^2$ indicates that the equation explains very little of the variability in the data. So, while the regression is statistically significant, it is unclear whether this relationship is significant in the field. Maximum concentrations of aluminum (>0.25 mg/L) occurred on October 15, 1982, March 14, 1985, January 14, 1999, March 17, 1999, and February 28, 2002. Aluminum appears to be elevated throughout the watershed and to have been so for the last three decades. Green et al. (1986) reported on aluminum in the St. Mary's River between 1966 and 1985 (N=39; mean concentration 0.082 mg/L (SD=0.035); range 0.02-0.19 mg/L), which is not significantly different from the Environment Canada data presented here (based on 95% confidence intervals), indicating no change in mean aluminum concentration between 1966-1985 and 1980-2008.

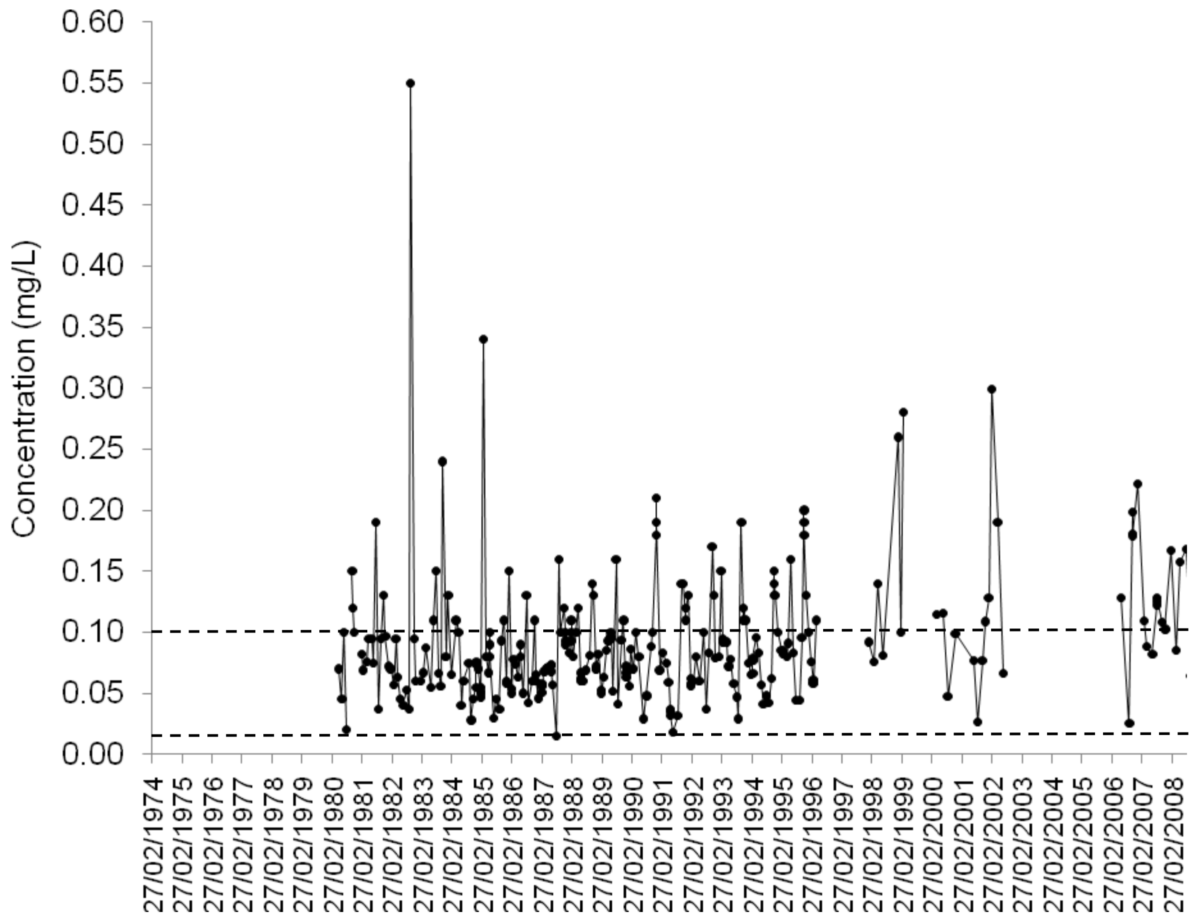


Figure 26: Aluminum concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed lines indicate CCME Water Quality Guidelines for pH<6.5 (lower line) and pH>6.5 (upper line).

The CCME aluminum guideline for the protection of aquatic life is 0.005 mg/L Al if the pH is less than 6.5 and 0.1 mg/L if pH greater than 6.5. Throughout most of the St. Mary's River the pH is less than 6.5 (e.g., 40% of pH measurements in East Branch, 87% in Main Branch, and 91% in West Branch <6.5 pH units) suggesting the appropriate CCME guideline is 0.005 mg/L of aluminum. Every aluminum measurement exceeded this guideline, indicating that aluminum is elevated in this watershed. The Health Canada guideline for drinking water is 0.2 mg/L Al, although this is based on water quality post-water treatment facility, not naturally occurring surface water. Of 227 measurements made by Environment Canada, 98% were <0.2 mg/L and 90% of the 48 data from Dalziel and Hart Buckland-Nick were <0.2 mg/L, suggesting that aluminum rarely is elevated sufficiently to be a concern from a drinking water perspective. This metal was also highlighted by Rutherford and Associates (1988) as being elevated.

Based on this review, aluminum is a parameter of concern in the St. Mary's River watershed.

Arsenic (As)

Arsenic concentrations in the St. Mary's River have been reported by Dalziel (1994; N=9 as dissolved As), and Environment Canada at Stillwater (N=143 as total As). Mean arsenic concentrations are low (Table 7), as is the maximum recorded value (0.014 mg/L). The majority of measurements are reported as being below the analytical detection limit, so the estimates of means and percentile distributions are likely biased high as the lowest values are not reported accurately but merely as the limit of detection ability. The data are not sufficient to assess for differences in arsenic concentration among the branches of the river. Over time at Stillwater arsenic has been consistently very low (Figure 27), with only three dates (June 19, 1974, March 30, 1977, and June 29, 1977) having measured arsenic concentrations greater than 0.005 mg/L. Over the period of sampling at Stillwater by Environment Canada there is weak indication of long term decrease (linear regression slope = -0.000006, $p << 0.001$; $r^2 = 0.380$). The regression is statistically significant but the slope is very low. Much of this regression may be due to the historically higher values in 1974-1979; since 1979, arsenic concentrations have been very low and stable. So, while the regression is statistically significant, it is unclear whether this relationship is significant in the field.

The CCME arsenic guideline for the protection of aquatic life is 0.005 mg/L (as total As). Of 143 measurements at Stillwater by Environment Canada, 95% of measurements are equal to or less than this guideline. The 9 measurements of Dalziel are all less than 0.0007 mg/L (dissolved) (unfortunately these data of Dalziel are not total As and so comparison with CCME guideline is not strictly appropriate). Health Canada has established a Maximum Acceptable Concentration (MAC) of 0.01 mg/L As for drinking water. This has been exceeded only once (June 29, 1977) in the St. Mary's River.

Based on this review, there is little evidence that arsenic is a parameter of concern in the St. Mary's River watershed. Following the classification laid out in *Methods*, arsenic is considered of some concern (historically) but occasional exceedances are acceptable.

Table 7: Summary statistics of metals distribution in the St. Mary's River. Data from Hart Buckland-Nicks (1995), Dalziel (1994), and Environment Canada (Stillwater).

| | Number samples below analytical detection level | Mean (SD); N | Range | Median | 10th-90th percentile |
|---|---|---|---|---|---|
| **Aluminum (mg/L)** | | | | | |
| East Branch | 8 (40%) | 0.11 (0.11); 20 | 0.01 – 0.57 | 0.10 | 0.055 – 0.131 |
| Main Branch | 0 (0%) | 0.10 (0.06);14 | 0.009 – 0.25 | 0.10 | 0.031 – 0.171 |
| West Branch | 5 (35.7%) | 0.12 (0.07); 14 | 0.01 – 0.30 | 0.10 | 0.025 – 0.184 |
| Main Branch at Stillwater | 0 (0%) | 0.09 (0.05); 277 | 0.01 – 0.55 | 0.08 | 0.045 – 0.150 |
| **Arsenic (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 3 (33%) | 0.0003 (0.0002); 9 | 0.0005 – 0.0060 | 0.0003 | 0.0005 – 0.0006 |
| Main Branch at Stillwater | 122 (85.3%) | 0.0009 (0.0020); 143 | 0.0001 – 0.0140 | 0.0005 | 0.0004 – 0.0006 |
| **Cadmium (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 0 (0%) | 0.000015 (0.000021); 9 | -0.00001 – 0.00006 | 0.00001 | 0.000 – 0.00003 |
| Main Branch at Stillwater | 285 (96.9%) | 0.0009 (0.0003); 294 | 0.0001 – 0.002 | 0.001 | 0.00098 – 0.001 |
| **Chromium (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 3 (33%) | 0.0002 (0.0002); 9 | 0.00004 – 0.0005 | 0.00009 | 0.00004 – 0.0005 |
| Main Branch at Stillwater | 21 (72.4%) | 0.0008 (0.0015); 29 | 0.0001 – 0.0082 | 0.0004 | 0.0004 – 0.001 |
| **Copper (mg/L)** | | | | | |
| East Branch | 20 (100%) | 0.01 (<0.00001); 20 | 0.01 – 0.01 | 0.01 | 0.01 – 0.01 |
| Main Branch | 6 (37.5%) | 0.006 (0.004); 16 | 0.0006 – 0.011 | 0.005 | 0.00075 – 0.01 |
| West Branch | 14 (100%) | 0.01 (<0.00001); 14 | 0.01 – 0.01 | 0.01 | 0.01 – 0.01 |
| Main Branch at Stillwater | 269 (91.5%) | 0.002 (0.0017); 294 | 0.0002 – 0.02 | 0.002 | 0.002 – 0.002 |
| **Iron (mg/L)** | | | | | |
| East Branch | 0 (0%) | 0.104 (0.102); 15 | 0.04 – 0.38 | 0.07 | 0.044 – 0.238 |
| Main Branch | 0 (0%) | 0.191 (0.104); 16 | 0.10 – 0.45 | 0.15 | 0.108 – 0.355 |
| West Branch | 0 (0%) | 0.144 (0.151); 10 | 0.02 – 0.56 | 0.11 | 0.065 – 0.209 |
| Main Branch at Stillwater | 0 (0%) | 0.179 (0.080); 280 | 0.05 – 0.56 | 0.16 | 0.100 – 0.270 |

Table 7 (Cont'd): Summary statistics of metals distribution in the St. Mary's River.

| | Number samples below analytical detection level | Mean (SD); N | Range | Median | 10th-90th percentile |
|---|---|---|---|---|---|
| **Lead (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 0 (0%) | 0.00011 (0.00013); 8 | 0.00004 – 0.0004 | 0.00007 | 0.00004 – 0.0002 |
| Main Branch at Stillwater | 289 (97.6%) | 0.002 (0.0018); 296 | 0.0001 – 0.028 | 0.002 | 0.002 – 0.002 |
| **Mercury (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 0 (0%) | 0.0024 (0.0026); 6 | 0.000007 – 0.0055 | 0.002 | 0.000054 – 0.005 |
| Main Branch at Stillwater | 44 (93.6%) | 0.000088 (0.0003); 47 | 0.00002 – 0.002 | 0.00005 | 0.00002 – 0.00005 |
| **Molybdenum (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 2 (25%) | 0.000027 (0.000034); 8 | 0.00001 – 0.00011 | 0.00002 | 0.00001 – 0.000047 |
| Main Branch at Stillwater | 0 (0%) | 0.00012 (0.000077); 29 | 0.0001 – 0.0005 | 0.0001 | 0.0001 – 0.00012 |
| **Nickel (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 0 (0%) | 0.0003 (0.0003); 8 | 0.00006 – 0.0009 | 0.0002 | 0.00009 – 0.0006 |
| Main Branch at Stillwater | 0 (0%) | 0.0008 (0.0016); 28 | 0.0002 – 0.009 | 0.0004 | 0.0003 – 0.0007 |
| **Silver (mg/L)** | | | | | |
| Ford Pool & DNR picnic site | 3 (37.5%) | 0.000009 (0.000010); 8 | 0.000001 – 0.00002 | 0.000008 | 0.000004 – 0.00002 |
| Main Branch at Stillwater | 27 (93.1%) | 0.00044 (0.0013); 29 | 0.0001 – 0.005 | 0.0001 | 0.0001 – 0.0001 |
| **Zinc (mg/L)** | | | | | |
| East Branch | 19 (95%) | 0.011 (0.007); 20 | 0.01 – 0.04 | 0.01 | 0.01 – 0.01 |
| Main Branch | 6 (42.8%) | 0.006 (0.004); 14 | 0.001 – 0.01 | 0.006 | 0.0017 – 0.01 |
| West Branch | 4 (100%) | 0.01 (0.000); 4 | 0.01 – 0.01 | 0.01 | 0.01 – 0.01 |
| Main Branch at Stillwater | 39 (13.3%) | 0.009 (0.006); 292 | 0.0001 - 0.08 | 0.01 | 0.002 – 0.01 |

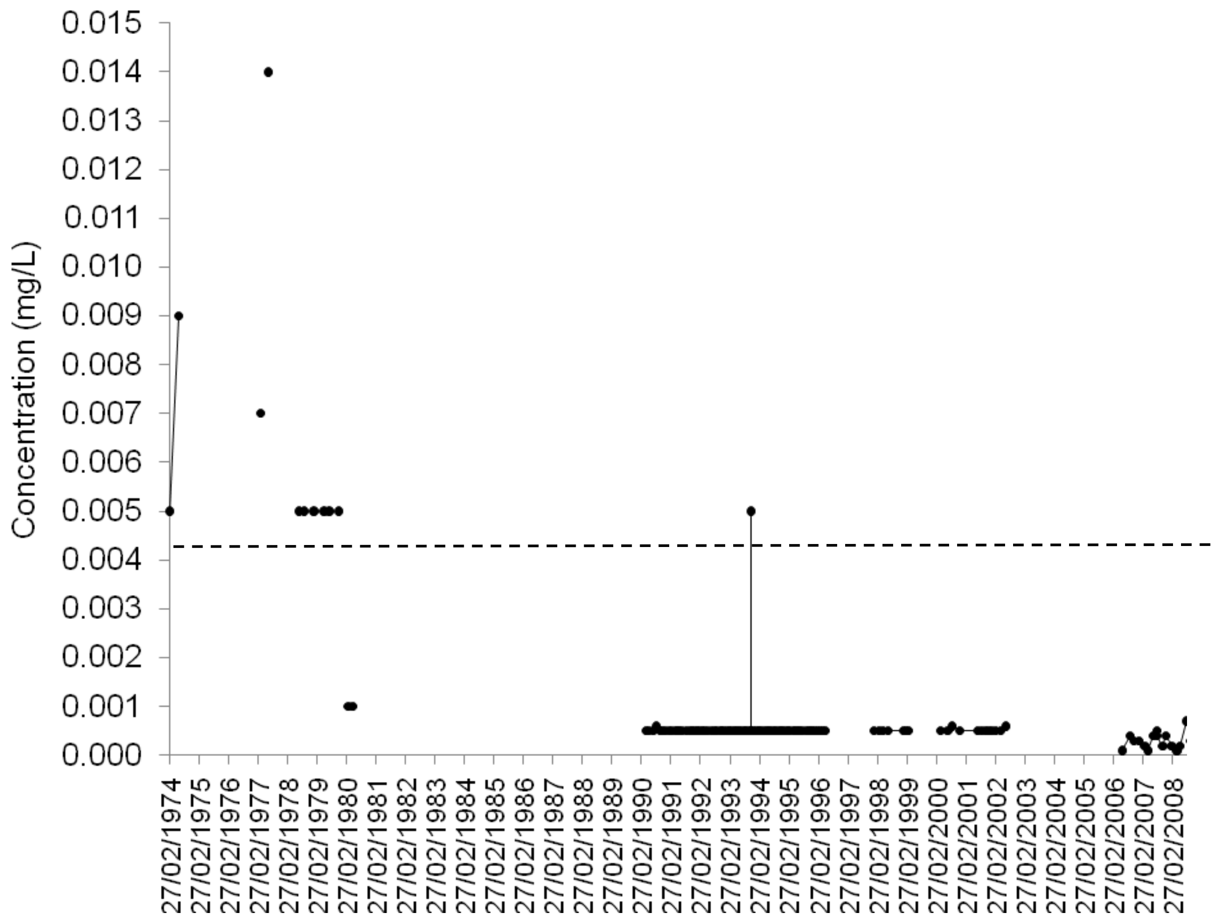


Figure 27: Arsenic concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed line indicates CCME Water Quality Guideline.

<u>Cadmium (Cd)</u>

Cadmium concentrations in the St. Mary's River have been reported by Dalziel (1994; N=9), and Environment Canada at Stillwater (N=294). Mean cadmium concentrations are very low (Table 7), as is the maximum recorded value (0.002 mg/L). The majority of measurements are reported as being below the analytical detection limit, so the estimates of means and percentile distributions are likely biased high as the lowest values are not reported accurately but merely as the limit of detection ability. The data are not sufficient to assess for differences in cadmium concentration among the branches of the river. Over time at Stillwater cadmium has been consistently very low (Figure 28), with only two dates (May 5, 1998, and May 7, 2002) having measured cadmium concentrations greater than 0.001 mg/L. Over the period of sampling at Stillwater by Environment Canada there is weak indication of long term decrease (linear regression slope = -0.0000007, $p << 0.001$; $r^2 = 0.439$). The regression is statistically significant but the slope is very low. Much of this regression may be due to the "step" in Figure 28 from 0.001 to 0.0001 mg/L in 2000. This step represents an order of magnitude decrease in analytical detection limit (i.e., methodological change), not a true reduction in chromium concentration.

So, while the regression is statistically significant, it is unclear whether this relationship is significant in the field.

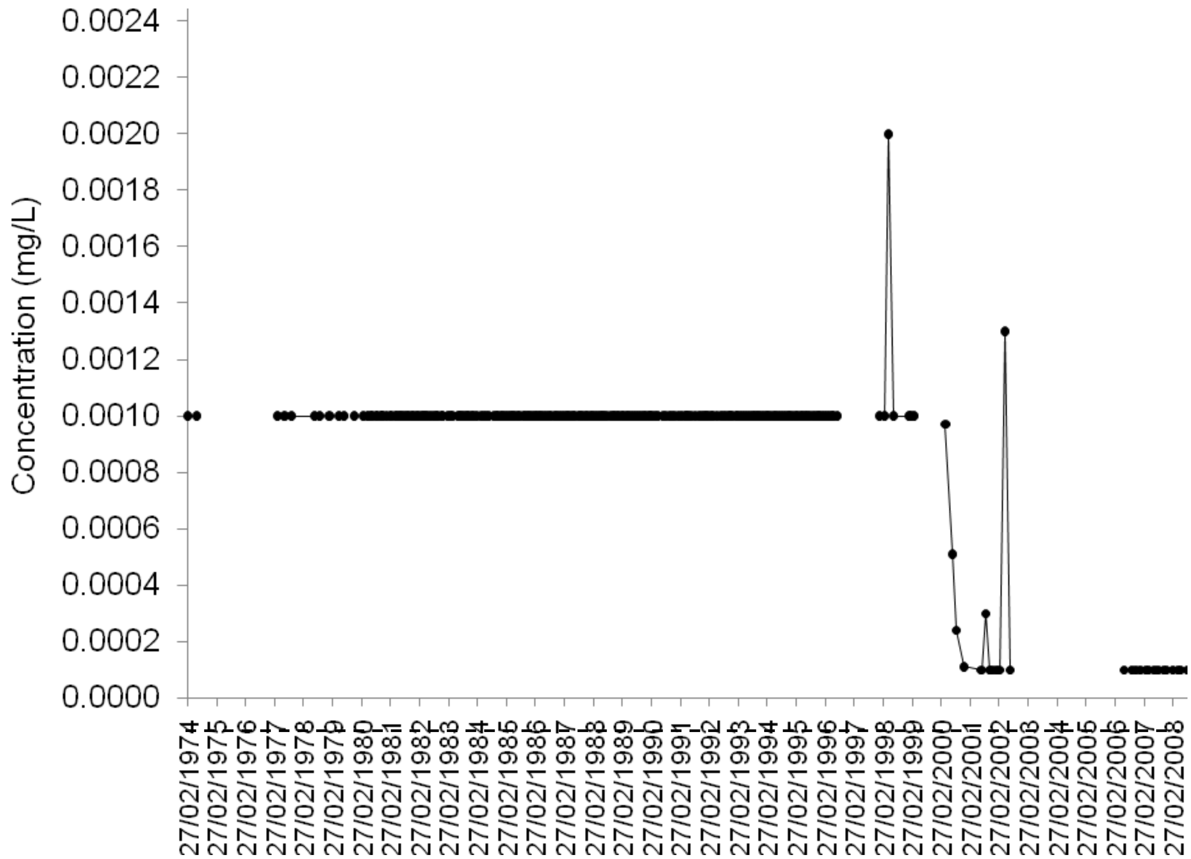


Figure 28: Cadmium concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed line indicates CCME Water Quality Guideline (0.000003 mg/L). Note: “Step” in year 2000 represents an order of magnitude decrease in analytical detection limit (i.e., methodological change), not a true reduction in chromium concentration.

The CCME cadmium guideline for the protection of aquatic life is 0.000003 mg/L (0.003 µg/L) Cd. This extremely low acceptable concentration highlights the very high toxicity of cadmium. This guideline is water hardness dependent[9] and for the St. Mary’s River a mean water hardness of 6.6 mg/L as $CaCO_3$ was used to calculate this cadmium guideline. Health Canada provides an MAC of 0.005 mg/L for drinking water, which has not been exceeded in the St. Mary’s River cadmium data. The extremely low CCME guideline is difficult to compare with the St. Mary’s River data as the analytical detection limit for the samples was 0.001 mg/L prior to 2000 and 0.0001 mg/L after 2000. These detection limits are orders-of-magnitude greater than the CCME

[9] CCME equation to determine cadmium guideline based on water hardness is:
Cadmium concentration = $10^{0.86[\log10(\text{hardness})]-3.2}$ µg/L

guideline making comparison impossible. The US Environmental Protection Agency (USEPA) provides criteria for cadmium concentration in both maximum concentration (0.00016 mg/L at water hardness 6.6 mg/L $CaCO_3$) and continuous concentration (0.000003 mg/L at water hardness 6.6 mg/L $CaCO_3$). Using the USEPA maximum concentration as a comparison, cadmium has only exceeded this value once (May 5, 1998) out of 294 measurements (0.3%).

Based on this review, there is little evidence that cadmium is a parameter of concern in the St. Mary's River watershed. There is, however, some uncertainty due the analytical detection limit being of greater value than the CCME guideline.

Chromium (Cr)

There are only 38 measurements of chromium in the St. Mary's River (29 from Environment Canada; 9 from Dalziel, 1994). Mean chromium concentrations are low (Table 7), as is the maximum recorded value (0.008 mg/L). The majority of measurements are reported as being below the analytical detection limit, so the estimates of means and percentile distributions are likely biased high as the lowest values are not reported accurately but merely as the limit of detection ability. The data are not sufficient to assess for differences in chromium concentration among the branches of the river. Over time at Stillwater chromium has been generally low, with only three dates (June 19, 1974, October 31, 2001, and January 17, 2002) having measured chromium concentrations greater than 0.001 mg/L. This conclusion must, of course, be tempered by the very small sample size. Peaks of chromium may have been missed by the sporadic sampling (2 samples in 1974; 27 samples between 2001 and 2008). Data are not sufficient to evaluate temporal trends for this parameter.

The CCME chromium guideline for the protection of aquatic life is 0.001 mg/L and the Health Canada drinking water MAC is 0.05 mg/L. Three of the 38 measurements exceeded the CCME guideline and none exceeded the Health Canada MAC. It is important to note that the Environment Canada sampling of chromium is not continuous and of small sample size, and so conclusions are tenuous at best.

Based on this review, there is little evidence that chromium is a parameter of concern in the St. Mary's River though the very small sample size and inconsistent sampling makes this conclusion preliminary. Chromium is potentially a highly toxic metal and the conclusions drawn here should be viewed as tentative only. Further sampling of chromium in the future should continue (*Recommendation #2*).

Copper (Cu)

Copper concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=38), Dalziel (1994; N=12), and Environment Canada at Stillwater (N=294). Mean values of copper concentrations range between 0.0002 and 0.011 mg/L among branches (Table 7). Copper concentrations differ among the three branches (ANOVA $p<<0.0001$; Figure 29) with the East and West Branches having significantly greater concentrations than the Main Branch. This, however, is likely an artefact of combining data sources, as the data of Dalziel (Main Branch) are measured at a lower detection limit that Hart Buckland-Nicks (East and West

Branches) and so while all of the data for the East and West Branches are reported as "<0.01 mg/L", much of the Main Branch data provides values below this cut-off value. In essence, the Main Branch is reported with greater accuracy than the other two branches and so the observed difference is more likely to be an artefact of analytical accuracy rather than true copper concentrations in the water.

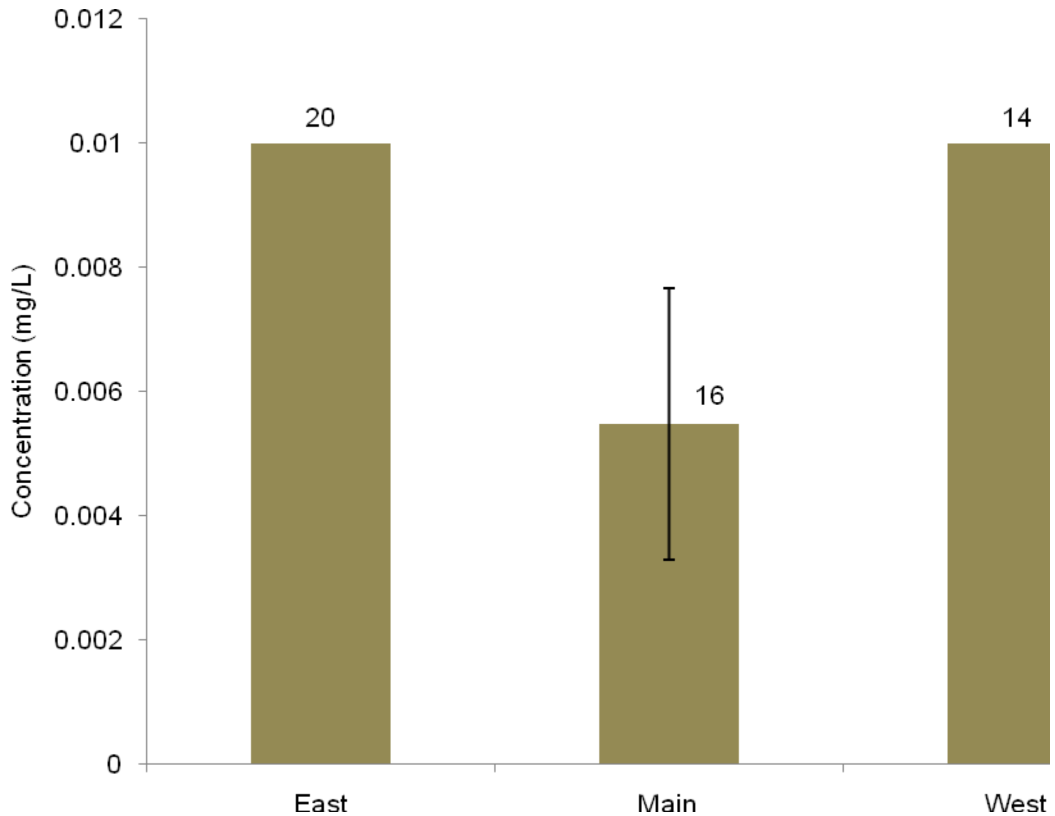


Figure 29: Mean copper concentrations of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate; error bars too small to be visible for East and West Branches. Values represent sample size used to calculate means.

Over the period of sampling at Stillwater by Environment Canada there is weak indication of long term decrease in copper concentration (linear regression slope = -0.00000009, $p = 0.025$; $r^2 = 0.017$). The regression is statistically significant but the slope is very low. Much of this regression may be due to the cluster of low values for the period 2006-2008 (Figure 30) which makes it appear than copper concentrations have decreased over time, but this is more likely a reflection of improved analytical accuracy (i.e., lower detection limit) than historically. Previously most measurements were simply given as "<0.002 mg/L", but after 2006 precise values below this limit were provided.

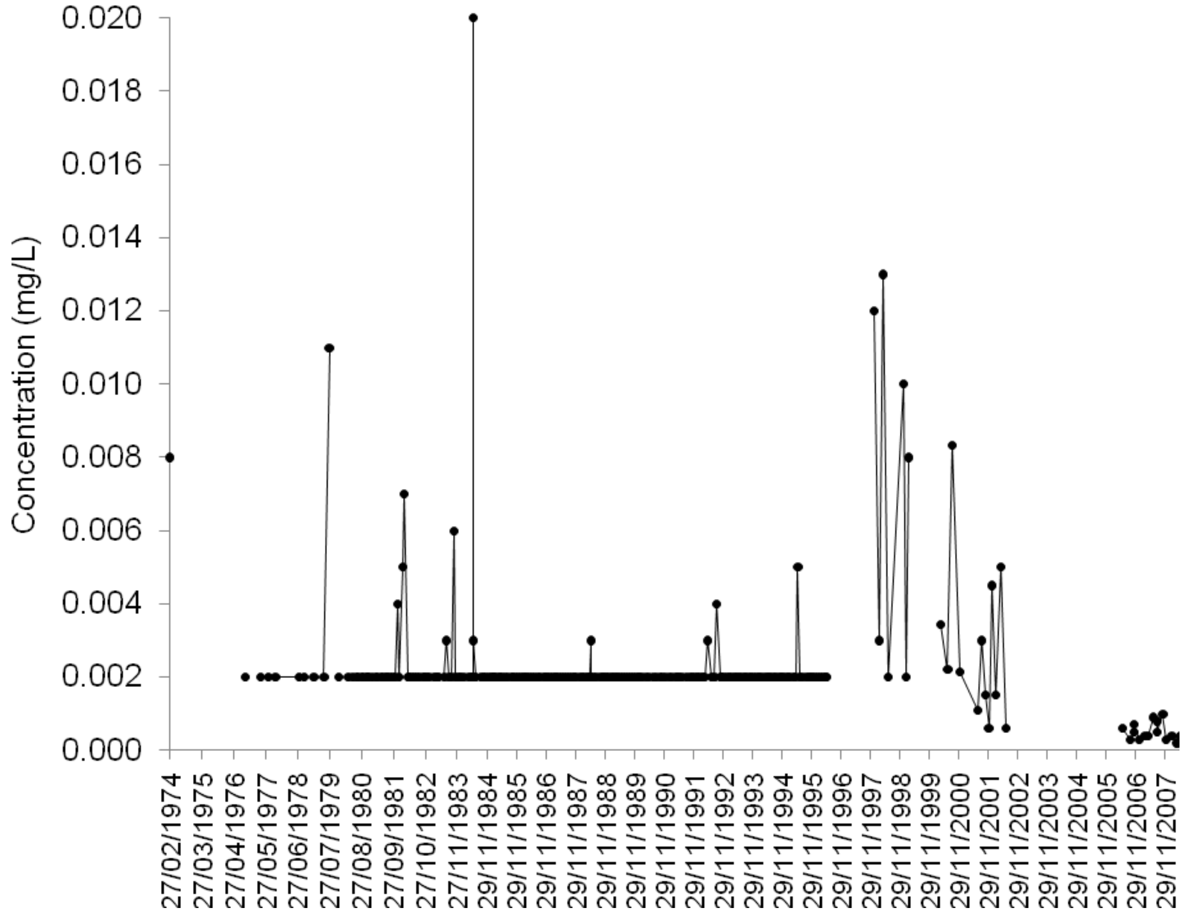


Figure 30: Extractable copper concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed line indicates CCME Water Quality Guideline (Total Copper).

The CCME copper guideline for the protection of aquatic life is 0.002 mg/L Cu (based on a mean water hardness of 6.6 mg/L $CaCO_3$)[10] and the Health Canada drinking water objective is ≤1.0 mg/L. Of the 294 measurements made by Environment Canada, 90% were less than or equal to 0.002 mg/L (Figure 30), and all were well below the Health Canada objective. Direct comparison with the CCME guideline is made problematic as the Environment Canada data are Extractable Copper, while the CCME guideline is in the form of Total Copper. It is probable that total copper in the St. Mary's is at greater concentrations than extractable copper and so guideline exceedance may be occurring more frequently than that determined here. Of 50 measurements made in other areas of the St. Mary's River by Dalziel and Hart Buckland-Nicks (Dissolved and Total forms), 40 were reported as being at the analytical detection limit of the time of 0.01 mg/L. The remaining 10 measurements ranged between 0.0006 mg/L and 0.0027 mg/L with only one greater than the CCME guideline. It appears that the CCME guideline is exceeded about 10% of the time in the St. Mary's River. Exceedance of the guideline occurred

[10] CCME equation to determine copper guideline based on water hardness is:
Copper concentration = $e^{0.8545[\ln(\text{hardness})]-1.465} * 0.2$ µg/L

fairly regularly between 1980 and 2002 (mean 1.04 times/yr (SD=1.17); N=22 years; number of samples/year 2-19), but has not occurred since 2002.

Copper should continue to be monitored, using the lowest detection limit possible and measuring Total Copper to make comparison with the CCME guideline possible (*Recommendation #3*). Guideline exceedance in 10% of occasions highlights this parameter of interest but it is not a human health concern.

Iron (Fe)

Iron concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=36), Dalziel (1994; N=13), and Environment Canada at Stillwater (N=280). Mean values of iron concentration range among branches between 0.10 and 0.19 mg/L, with no significant differences among branches (ANOVA p=0.32). Iron concentrations at Stillwater have fluctuated to a large degree (an order of magnitude, between 0.05 and 0.5 mg/L) over the period 1974-2008 (Figure 31). Over the period of sampling at Stillwater by Environment Canada there is weak indication of long term increase (linear regression slope = 0.000008, $p << 0.001$; $r^2 = 0.064$). The regression is statistically significant but the slope is very low and the amount of variation explained also very low suggesting little confidence be placed in it. Green et al. (1986) reported on iron in the St. Mary's River between 1966 and 1985 (N=94; mean concentration 0.17 mg/L (SD=0.08); range 0.001-0.40 mg/L), which is not significantly different from the Environment Canada data presented here (based on 95% confidence intervals), indicating no change in mean iron concentration between 1966-1985 and 1980-2008.

The CCME iron guideline for the protection of aquatic life is 0.3 mg/L Fe. In the data for the St. Mary's River 18 of 280 measurements (6.4%) exceeded this value at Stillwater and 10 of 49 measurements (20.4%) are in excess of this guideline from the data of Dalziel and Hart Buckland-Nicks. Health Canada has the same value for a drinking water objective (≤0.3 mg/L) as the CCME guideline for aquatic life. The maximum concentration recorded for iron in the St. Mary's River watershed was 0.56 mg/L (July, 1991). Over time, almost 40% of the guideline exceedances occurred between 2006 and 2008, and the other 60% between 1981 and 2002 (Figure 31).

Iron is a fairly benign metal as indicated by the high concentration guideline/objective of CCME and Health Canada, and the relatively few exceedances of these limits suggest that iron is likely not of great concern in the St. Mary's River. This metal should be identified as an element to be monitored, but it is unlikely, based on this review, to be a significant water quality issue in the St. Mary's.

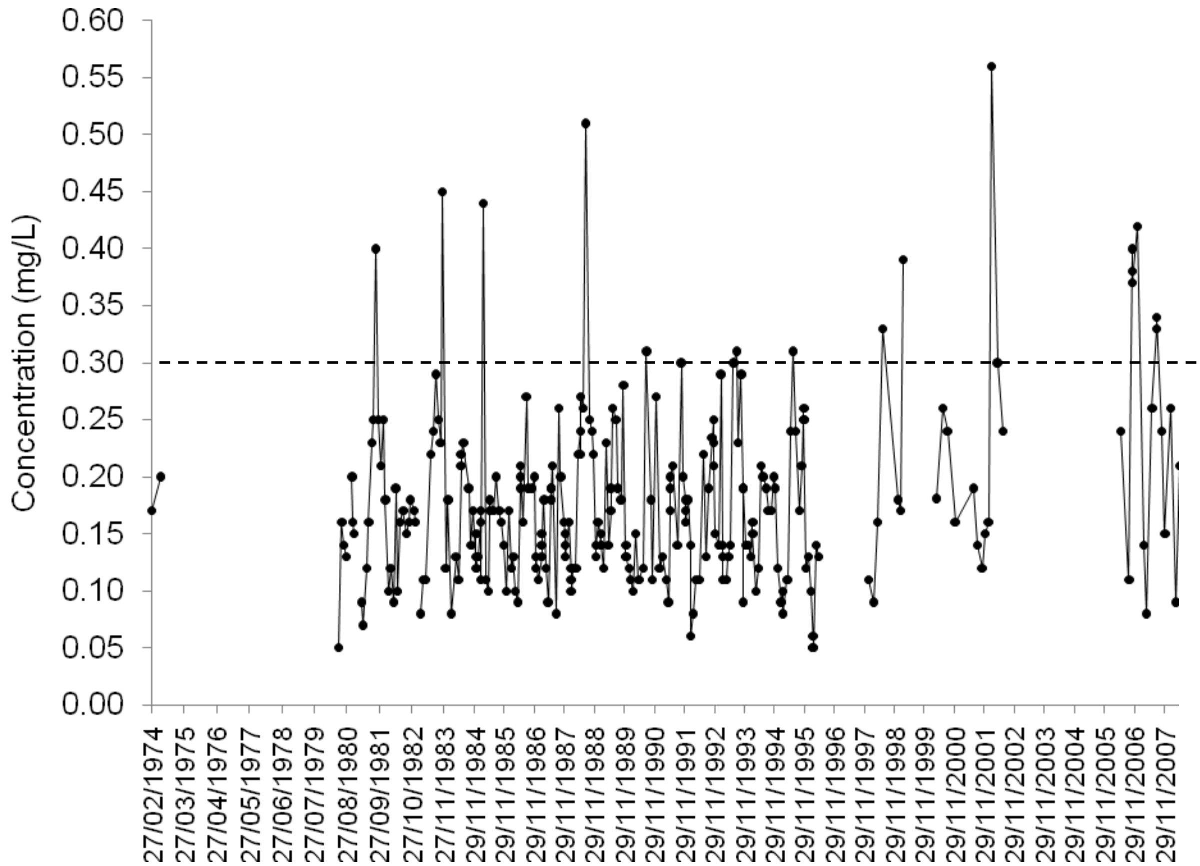


Figure 31: Iron concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed line indicates CCME Water Quality Guideline.

<u>Lead (Pb)</u>

Lead concentrations in the St. Mary's River have been reported by Dalziel (1994; N=8), and Environment Canada at Stillwater (N=296). Mean lead concentrations are low (Table 7), as is the maximum recorded value (0.028 mg/L). The majority of measurements are reported as being below the analytical detection limit, so the estimates of means and percentile distributions are likely biased high as the lowest values are not reported accurately but merely as the limit of detection ability. The data are not sufficient to assess for differences in lead concentration among the branches of the river. Over time at Stillwater lead has been consistently very low (Figure 32), with only seven dates (February 27, 1974, September 26, 1977, November 20, 1980, April 14, 1983, May 5, 1998, April 19, 2000, and May 7, 2002) having measured lead concentrations greater than 0.002 mg/L. Over the period of sampling at Stillwater by Environment Canada there is weak indication of long term decrease (linear regression slope = -0.0000001, p = 0.006; $r^2$ = 0.025). The regression is statistically significant but the slope is very low and the amount of variation explained also very low suggesting little confidence be placed in it.

The CCME lead guideline for the protection of aquatic life is 0.001 mg/L Pb, based on a water hardness of 6.6 mg/L $CaCO_3$[11], and the Health Canada drinking water MAC is 0.01 mg/L. Until 1999-2000 the analytical detection limit was 0.002 mg/L and so the majority of the historical data (268 of 296 measurements) could not accurately measure concentrations below 0.002 mg/L. Thus, direct comparison with the CCME guideline is not possible. Comparison with the Health Canada drinking water MAC shows only three data points (February 27, 1974; May 5, 1998; May 7, 2002) exceeding 0.01 mg/L (Figure 32). Since 2000 when the detection limit was reduced to below 0.002 mg/L, 6 of 31 (19.3%) measurements exceeded 0.001 mg/L.

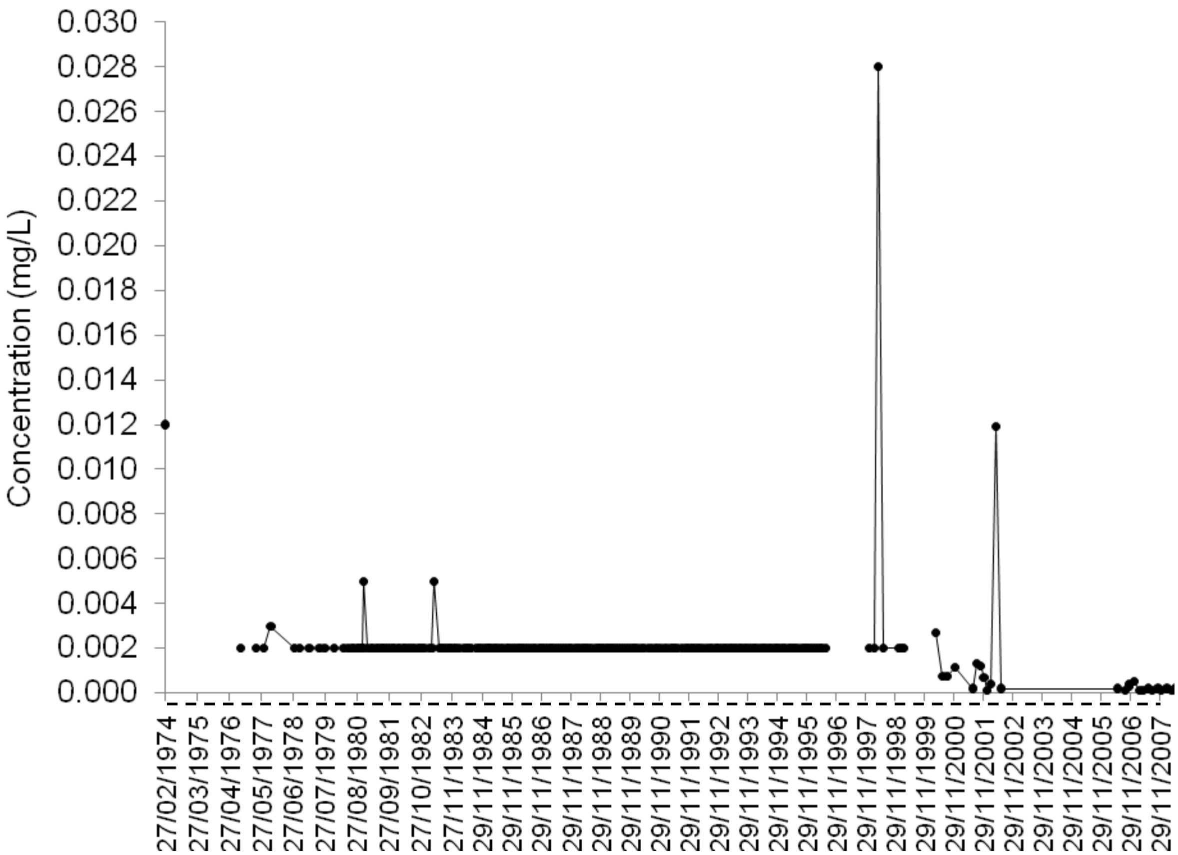


Figure 32: Lead concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed line indicates CCME Water Quality Guideline.

There is some evidence that lead concentrations are elevated in water of the St. Mary's River, but this is not surprising considering the bedrock geology, existence of a galena (lead) mine in the area, and depressed pH. This metal was also highlighted by Rutherford and Associates (1988) as being elevated. Lead does not appear to pose a risk for human consumption but may exceed guidelines for the protection of aquatic life. Given the frequency of guideline exceedance after

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[11] CCME equation to determine lead guideline based on water hardness is:
Lead concentration = $e^{1.273[\ln(\underline{hardness})]-4.705}$ µg/L

the analytical detection limit was reduced below the CCME guideline in 2000, lead should be considered a metal of concern until future sampling has sufficient sample size to re-assess (*Recommendation #4*).

Mercury (Hg)

Mercury concentrations in the St. Mary's River have been reported by Dalziel (1994; N=6), and Environment Canada at Stillwater (N=47). Mean mercury concentrations are low (Table 7), as is the maximum recorded value (0.0055 mg/L). The majority of measurements are reported as being below the analytical detection limit, so the estimates of means and percentile distributions are likely biased high as the lowest values are not reported accurately but merely as the limit of detection ability. The data are not sufficient to assess for differences in mercury concentration among the branches of the river. Nor has mercury been sufficiently sampled at Stillwater to conduct a meaningful analysis of mercury distribution over time at this station.

The CCME mercury guideline for the protection of aquatic life is 0.000004 mg/L (0.004 µg/L) as methylmercury and the Health Canada Drinking Water MAC is 0.001 mg/L. Given the significance and toxicity of mercury, it has been surprisingly undersampled in the St. Mary's River (total of 53 measurements). As with other metals, historical analytical detection limits (0.00002 and 0.00005 mg/L) were greater than the CCME guideline, thus making direct comparison impossible. Further, the CCME guideline is based on one form of mercury (methylmercury), whose concentration is pH dependent, and historical sampling was for total mercury; thereby making comparison inappropriate. Of the 53 samples for mercury, 4 (7.5%) exceeded the Health Canada MAC. Mercury sampling by Environment Canada has not been done since 1984.

The small sample size and inconsistency between sampled mercury (total) and guideline form (methylmercury) makes conclusions regarding mercury in the St. Mary's River tentative. Sampling should be conducted for mercury with spatial coverage to assess methylmercury and total mercury in the water and also tissue to determine whether mercury is an issue in the watershed (*Recommendation #5*). At present the data are insufficient to form informed conclusions about distribution or concentrations of mercury in the St. Mary's River.

Molybdenum (Mo)

Molybdenum concentrations in the St. Mary's River have been reported by Dalziel (1994; N=8), and Environment Canada at Stillwater (N=29). Mean molybdenum concentrations are low (Table 7), as is the maximum recorded value (0.0005 mg/L). The data are not sufficient to assess for differences in molybdenum concentration among the branches of the river. Nor has molybdenum been sufficiently sampled at Stillwater to conduct a meaningful analysis of distribution of this metal over time at this station.

The CCME molybdenum guideline for the protection of aquatic life is 0.073 mg/L. There is no Health Canada drinking water guideline/objective/MAC for this element. Within the St. Mary's River, molybdenum has received very little sampling attention, but from the little sampling that has been done, none of the 37 samples exceeded the CCME guideline.

Given the very low concentrations of molybdenum reported in past samples, this element is not likely to be of concern in the St. Mary's River. The maximum value of 37 samples (0.0005 mg/L) is two orders of magnitude less than the CCME guideline.

Nickel (Ni)

Nickel concentrations in the St. Mary's River have been reported by Dalziel (1994; N=8), and Environment Canada at Stillwater (N=28). Mean nickel concentrations are low (Table 7), as is the maximum recorded value (0.009 mg/L). The data are not sufficient to assess for differences in nickel concentration among the branches of the river. Nor has nickel been sufficiently sampled at Stillwater to conduct a meaningful analysis of nickel distribution over time at this station.

The CCME nickel guideline for the protection of aquatic life is 0.025 mg/L based on a water hardness of 6.6 mg/L $CaCO_3$[12]. There is no Health Canada drinking water guideline/objective/MAC for this element. Within the St. Mary's River, nickel has received very little sampling attention, but from the little sampling that has been done, none of the 36 samples have exceeded the CCME guideline.

Given the very low concentrations of nickel reported in past samples, this element is not considered of concern in the St. Mary's River. The maximum value of 36 samples is an order of magnitude less than the CCME guideline.

Silver (Ag)

Silver concentrations in the St. Mary's River have been reported by Dalziel (1994; N=8), and Environment Canada at Stillwater (N=29). Mean silver concentrations are low (Table 7), as is the maximum recorded value (0.005 mg/L). The data are not sufficient to assess for differences in silver concentration among the branches of the river. Nor has silver been sufficiently sampled at Stillwater to conduct a meaningful analysis of silver distribution over time at this station.

The CCME silver guideline for the protection of aquatic life is 0.0001 mg/L. There is no Health Canada drinking water guideline/objective/MAC for this element. Within the St. Mary's River, silver has received very little sampling attention. Two of these samples (1974) are reported as <0.005 mg/L which was the analytical detection limit of the time. Since then, all samples have been <0.0001 mg/L which is both the CCME guideline and the analytical detection limit. Thus, it is unknown how far below the CCME guideline the concentration of silver in the St. Mary's River is; only that it is less than guideline.

Given the very low concentrations of silver reported in past samples, this element is not considered of concern in the St. Mary's River. However, accurate values of concentrations are

[12] CCME equation to determine nickel guideline based on water hardness is:
Nickel concentration = $e^{0.76[\ln(\text{hardness})]+1.06}$ µg/L

not available, only the knowledge that silver is present below both detection limit and CCME guideline.

Zinc (Zn)

Zinc concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=28), Dalziel (1994; N=10), and Environment Canada at Stillwater (N=292). Mean values of zinc concentrations range between 0.006 and 0.011 mg/L among branches, with the Main Branch indicating significantly lower zinc concentrations than the East or West Branches (ANOVA p=0.024; Figure 33). However, the small sample sizes in this comparison (e.g., N=4 for West Branch) limit the reliance that should be placed on this conclusion. Zinc concentrations at Stillwater have been very stable and low over the period 1974-2008 (Figure 34), with only 6 measurements (2.0% of total measurements) in excess of 0.01 mg/L. There is no evidence of long-term increases or decreases in zinc concentration over time ((linear regression slope = 0.0000001, $p = 0.257$; $r^2 = 0.004$).

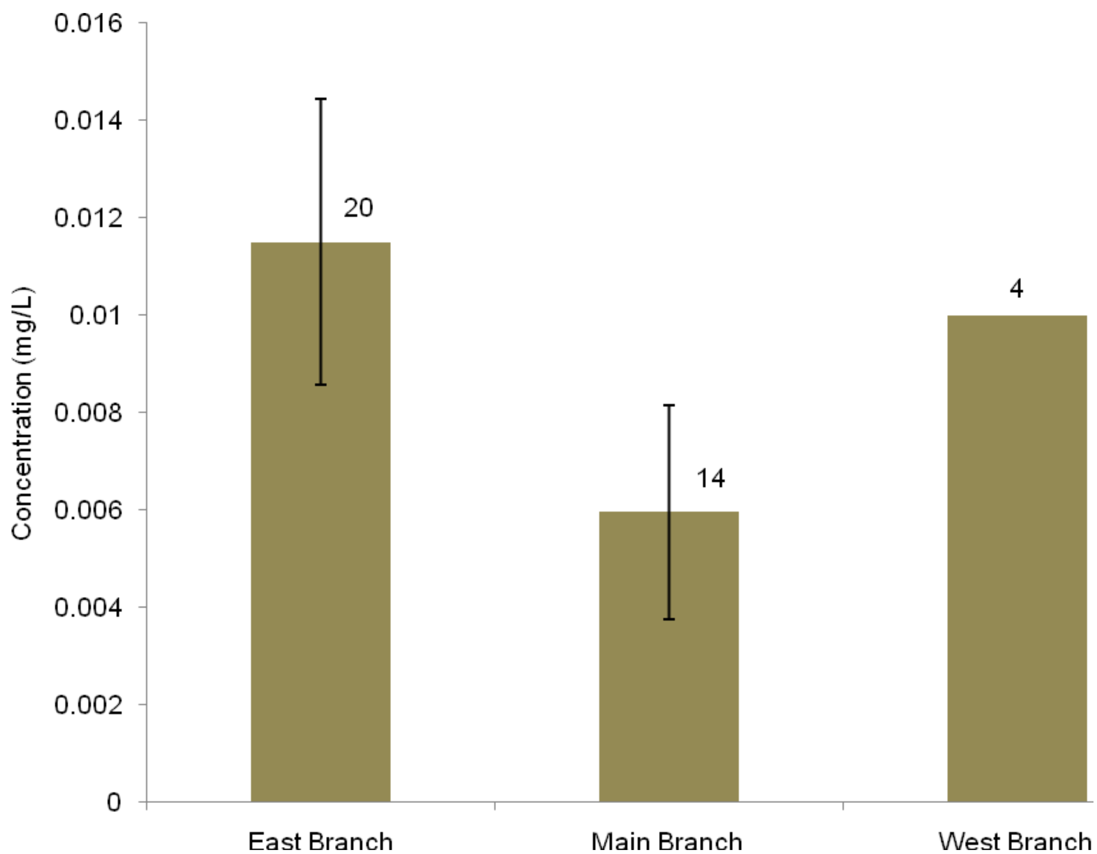


Figure 33: Mean zinc concentrations of three branches of St. Mary's River. Error bars represent 95% confidence intervals of mean estimate; error bars too small to be visible for West Branch. Values represent sample size used to calculate means.

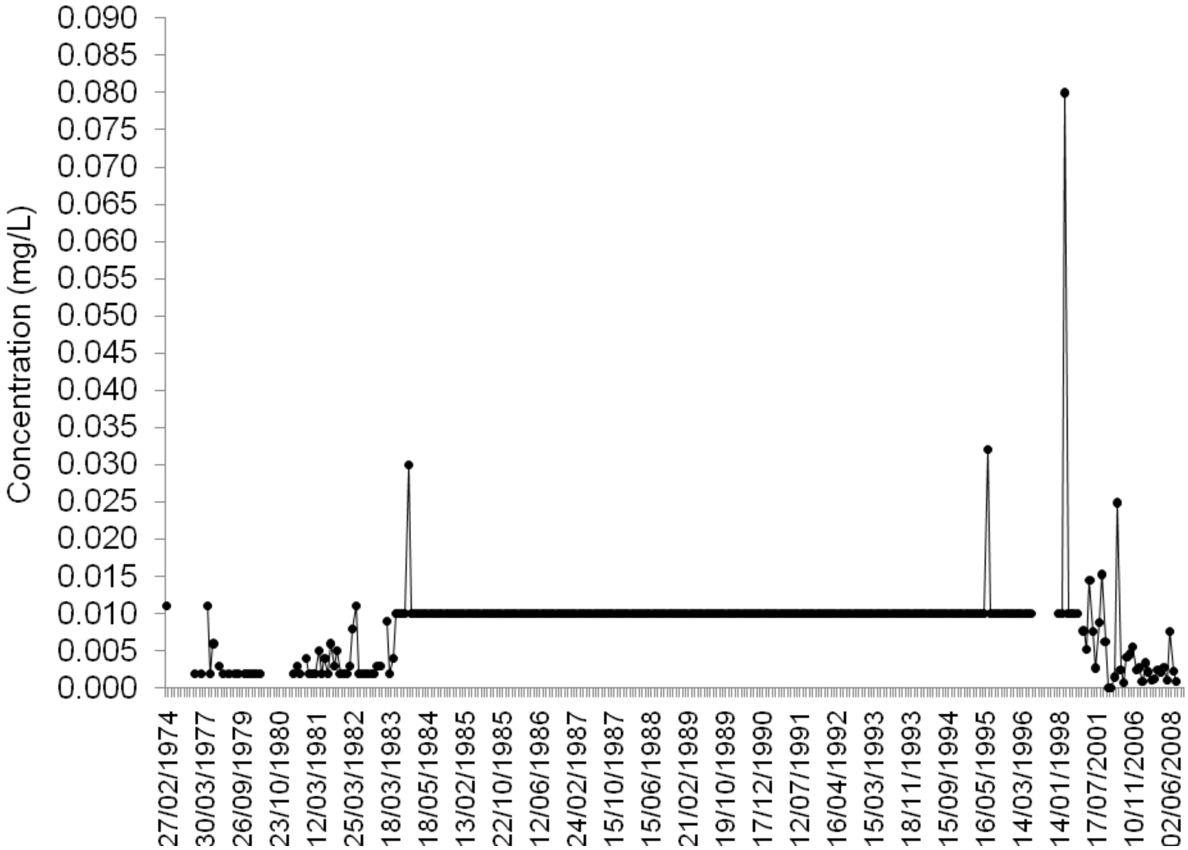


Figure 34: Zinc concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed line indicating CCME Water Quality Guideline not shown on this figure as it is 0.3 mg/L which is an order of magnitude greater than the data displayed.

The CCME zinc guideline for the protection of aquatic life is 0.3 mg/L and the Health Canada Drinking Water objective is ≤5.0 mg/L. Zinc concentrations have not exceeded either CCME or Health Canada guidelines over 330 measurements. The maximum zinc concentration (0.08 mg/L) is an order-of-magnitude less than the CCME guideline and two orders-of-magnitude less than the Health Canada limit.

There is no evidence that zinc is of concern in the St. Mary’s River as this element has been extensively sampled, concentrations are low, and they have not exceeded Health Canada or CCME aquatic life guidelines.

<u>Low Priority Metals</u>

Nine metals were classified as “low priority” for analyses as they do not have CCME guidelines and this was interpreted as these elements not being of sufficient concern to require guideline development to date. These elements are antimony, barium, beryllium, cobalt, magnesium, manganese, strontium, thallium, and vanadium. Three of these (antimony, barium, manganese) have Health Canada drinking water limits. Summary statistics for these nine elements are provided in Table 8. This analysis will be limited to comparing the three elements to their respective Health Canada drinking water guidelines and a detailed analysis of magnesium and manganese, each of which have large sample sizes.

(i) Antimony (Sb)

Of 36 measurements (9 from Dalziel, 1994; 27 from Environment Canada), two (5.4%) exceeded the Health Canada MAC of 0.006 mg/L (August 25, 2008; October 15, 2008). This low frequency of exceedance and lack of CCME guidelines initially suggest that antimony is likely not an element of concern in the St. Mary`s River. However, the apparent high toxicity of this element (Health Canada MAC of 0.006 mg/L which is roughly equivalent to that of cadmium, and is a lower limit than all previously considered metals except mercury) causes concern that the lack of historical data may be missing an important water quality parameter. Due to the small historical sample size and uncertainty around this potentially toxic metal, antimony should continue to be monitored (*Recommendation #6*).

(ii) Barium (Ba)

Of 39 measurements (10 from Dalziel, 1994; 29 from Environment Canada), only one (2.6%) exceeded the Health Canada MAC of 1.0 mg/L (February 21, 2008), and this value is questionable as it is 9.0 mg/L while the next greatest value is 0.1 mg/L. This raises the doubt as the whether the value of 9.0 mg/L might be a typographical error. This low frequency of exceedance and lack of CCME guidelines suggest that barium is likely not an element of concern in the St. Mary`s River. As barium does not possess high toxicity, as evidenced by the high Health Canada limit of 1.0 mg/L, further sampling of this metal is not warranted.

(iii)Magnesium (Mg)

Analysis of magnesium is confined to the Environment Canada data (N=298 measurements); this element was not reported by Hart Buckland–Nicks or Dalziel. Apart from the maximum value of 2.4 mg/L (September 18, 1974), values have ranged between 0.3 and 1.23 mg/L (Figure 35), with 95% of all measurements being ≤0.8 mg/L. There is no evidence of long-term increases or decreases in magnesium concentration over time (linear regression slope = 0.000005, $p = 0.132$; $r^2 = 0.008$). Magnesium concentrations were also reported by Green et al. (1986). They showed mean concentrations at Stillwater (1966-1985) of 0.63 mg/L (SD=0.15; N=123) and range of 0.30-1.7 mg/L. There is no significant difference in mean magnesium concentrations at Stillwater (based on 95% confidence intervals) between the period 1966-1985 and 1974-2008 indicating no change over time.

The low and quite constant concentration over time suggests that this background level of magnesium is consistent and likely not of concern. Unfortunately, without criteria of some form (e.g., CCME and Health Canada) interpretation of these results is difficult.

Table 8: Summary statistics of "Low Priority" metals distribution in the St. Mary's River. Data from Hart Buckland-Nicks (1995), Dalziel (1994), and Environment Canada (Stillwater).

| | Mean (SD); N | Range | Median | $10^{th}$-$90^{th}$ percentile |
|---|---|---|---|---|
| **Antimony (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.0004 (0.0006); 9 | 0.00003 - 0.0021 | 0.00014 | 0.00007 - 0.0007 |
| Main Branch at Stillwater | 0.0080 (0.0266); 27 | 0.0001 - 0.1000 | 0.0001 | 0.0001 - 0.0002 |
| **Barium (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.006 (0.002); 10 | 0.004 - 0.010 | 0.006 | 0.004 - 0.008 |
| Main Branch at Stillwater | 0.325 (1.668); 29 | 0.005 – 9.000 | 0.009 | 0.006 - 0.032 |
| **Beryllium (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.00003 (0.00002); 11 | 0.00001 - 0.00009 | 0.00003 | 0.00001 - 0.00006 |
| Main Branch at Stillwater | 0.0001 (0); 27 | 0.0001 - 0.0001 | 0.0001 | 0.0001 - 0.0001 |
| **Cobalt (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.00007 (0.00005); 11 | 0.00002 - 0.00022 | 0.00007 | 0.00002 - 0.00011 |
| Main Branch at Stillwater | 0.0002 (0.0005); 29 | 0.0001 - 0.003 | 0.0001 | 0.0001 - 0.0002 |
| **Magnesium (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.668 (0.111); 10 | 0.484 - 0.842 | 0.678 | 0.532 - 0.778 |
| Main Branch at Stillwater | 0.634 (0.157); 298 | 0.300 - 2.400 | 0.615 | 0.480 - 0.760 |
| **Manganese (mg/L)** | | | | |
| East Branch | 0.086 (0.221); 20 | 0.010 – 1.020 | 0.040 | 0.010 – 0.060 |
| Main Branch | 0.043 (0.015); 14 | 0.014 – 0.070 | 0.045 | 0.025 – 0.059 |
| West Branch | 0.060 (0.031); 14 | 0.030 – 0.130 | 0.050 | 0.030 – 0.105 |
| Main Branch at Stillwater | 0.046 (0.025); 281 | 0.010 – 0.246 | 0.040 | 0.020 - 0.070 |
| **Strontium (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.009 (0.002); 11 | 0.005 - 0.011 | 0.010 | 0.007 - 0.011 |
| Main Branch at Stillwater | 0.268 (1.345); 27 | 0.006 – 7.00 | 0.009 | 0.007 - 0.012 |

Table 8 (Cont'd): Summary statistics of "Low Priority" metals distribution in the St. Mary's River.

| | Mean (SD); N | Range | Median | $10^{th}$-$90^{th}$ percentile |
|---|---|---|---|---|
| **Thallium (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.00001 (0.000001); 8 | 0.00001 - 0.00003 | 0.000009 | 0.000 - 0.00001 |
| Main Branch at Stillwater | 0.0001 (0); 4 | 0.0001 - 0.0001 | 0.0001 | 0.0001 - 0.0001 |
| **Vanadium (mg/L)** | | | | |
| Ford Pool & DNR picnic site | 0.0001 (0.00004); 9 | 0.00006 - 0.0002 | 0.0001 | 0.00008 - 0.0002 |
| Main Branch at Stillwater | 0.0002 (0); 27 | 0.0001 - 0.0005 | 0.0002 | 0.0001 - 0.0003 |

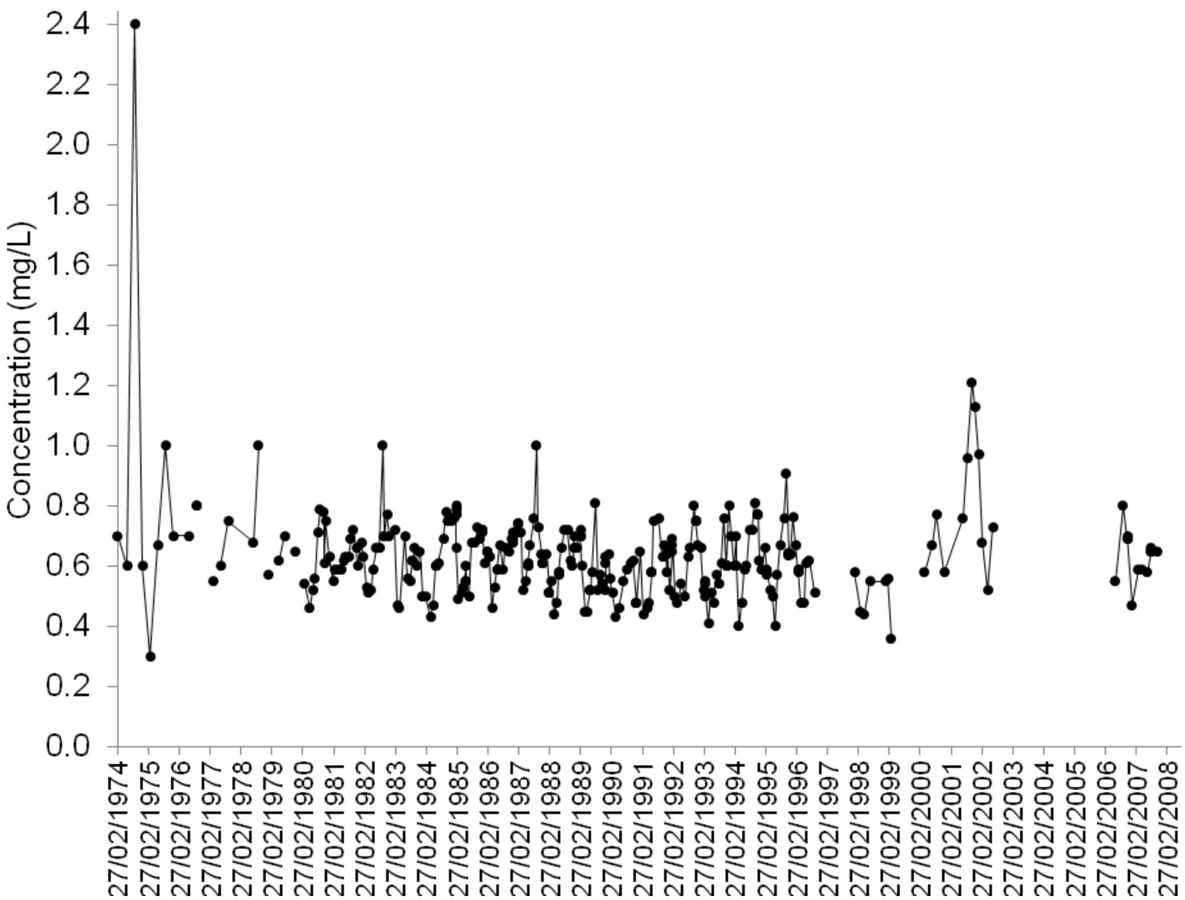


Figure 35: Magnesium concentration over time (1974-2008) measured at Stillwater by Environment Canada.

(iv) Manganese (Mn)

Manganese concentrations in the St. Mary's River have been reported by Hart Buckland-Nicks (1995; N=38), Dalziel (1994; N=10), and Environment Canada at Stillwater (N=282). There is no significant difference in manganese concentration among branches (ANOVA = 0.685), with mean concentrations by branch ranging between 0.043 and 0.086 mg/L (overall mean 0.065; Table 8). Manganese concentrations over time at Stillwater have been variable, with the central 80th percentile of the distribution (i.e., $10^{th}$-$90^{th}$ percentiles) between 0.02 and 0.07 mg/L (Table 8; Figure 36). Over the period of sampling at Stillwater by Environment Canada there is weak indication of long term increase (linear regression slope = 0.0000024, $p << 0.001$; $r^2 = 0.062$). The regression is statistically significant but the slope is very low and the amount of variation explained also very low suggesting little confidence be placed in it. Green et al. (1986) reported mean manganese values at Stillwater (1966-1985) of 0.039 mg/L (SD=0.024; N=108) and range of 0.006 to 0.160 mg/L. There is no significant difference in mean manganese concentrations at Stillwater (based on 95% confidence intervals) between the period 1966-1985 and 1974-2008 indicating no change over time.

Manganese in the St. Mary`s River appears to be elevated relative to the Health Canada Drinking Water Aesthetic Objective of ≤0.05 mg/L, with 76 of 282 (26.9%) measurements in excess of 0.05 mg/L (Figure 36). These exceedances have occurred relatively regularly over time suggesting that manganese is naturally elevated in the water, likely due to bedrock geology and depressed pH. Note, however, the Health Canada is an aesthetic objective, not based on health concerns related to manganese. Where only aesthetic objectives are specified by Health Canada, the values are below those considered to constitute a health hazard.

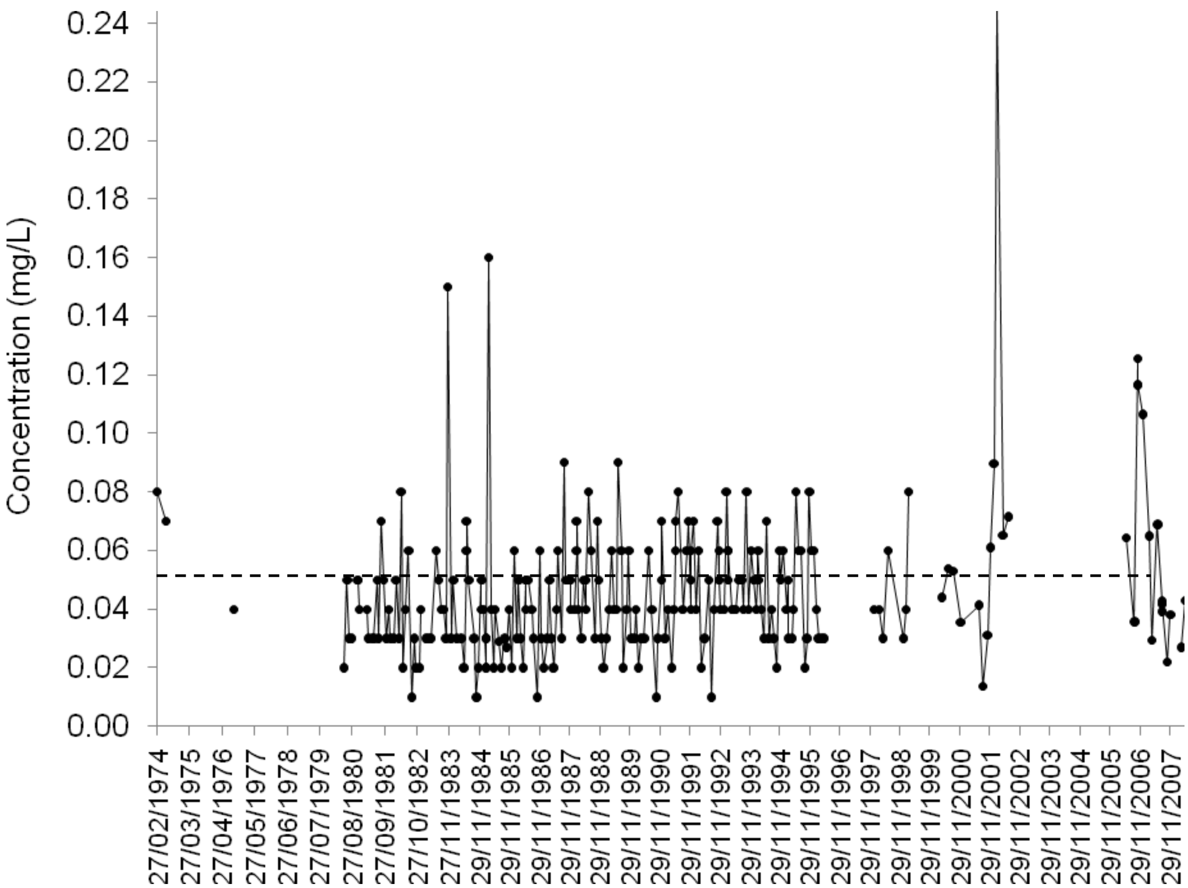


Figure 36: Manganese concentration over time (1974-2008) measured at Stillwater by Environment Canada. Dashed line indicates Health Canada Drinking Water Aesthetic Objective.

<u>Excluded metals</u>

Seven metals were excluded from these analyses due to small sample sizes (<20 measurements) preventing meaningful analyses. These excluded metals were boron (Bo), magnesium (Mg; extractable), rubidium (Ru), selenium (Se), thorium (Th), tin (Sn), and uranium (U).

### *5.1.5 Discussion (River Water)*

Physical Parameters

In general, water temperatures within the West Branch, St. Mary's River are slightly elevated relative to the East and Main Branches. This is likely due, at least in part, to river morphology of the West Branch, which is largely overwidened and so the water flows as long shallow runs and riffles. This stands in contrast to the East and Main Branches where there is greater frequency of deep water as deep runs and pools, as these channels have remained largely intact and functioning properly. The shallow water of the West Branch has greater surface area exposed to the air and so heats more rapidly in response to air temperature.

Though there is little evidence of consistent, directional heating or cooling in terms of mean monthly summer temperatures between 1991-92 and 2008-10, there is evidence of increasing frequency of maximum temperatures for the East and Main Branches, but not the West Branch. This increase may potentially be problematic for organisms adapted to cold water, as these maxima may exceed thermal tolerances. This is less of an issue for mobile taxa (e.g., fish) than for sessile organisms (e.g., molluscs), as there are cold water refugia for mobile organisms to retreat to during these temperature extremes. On the West Branch, MacMillan et al. (2005) identified Indian Man, Clark and Chisholm Brooks as being cool water[13], and the lower West Branch, MacLeod Lake Brook and Nelson River as being warm water areas. They list 11 other West Branch streams (Sutherland, McDonald, Glencross, Barren, Mitchell, Kelly, Beaver, Archibald Mill, MacDonald Mill, Cross, and Long John Brooks) classified as intermediate temperature. In addition to this identification of cool versus warm water streams, in 2008 the SMRA conducted a survey for cold water areas during high air temperatures. Those results are provided in Figure 37, and these locations are likely to be ecologically very important during high temperature events in the summer.

Turbidity has been, unfortunately, measured in two incompatible units (JTU and NTU) which limits inferences to be drawn. However, this analysis suggests that there is some indication of slight decrease in turbidity over time, that turbidity tends to be highest in November, December, March and April (generally months of high streamflow), and during low flow there is little suspended matter in the water. Excessively high levels of turbidity can be harmful to stream biota as it indicates a high concentration of suspended material. This material then can scour aquatic organisms, damaging body surfaces, eyes, gills, and respiratory structures. Aquatic ecosystems are adapted to occasional and transient increases in turbidity which, provided it is not excessive, does not damage the biota. Based on this, the levels of turbidity observed in the St. Mary`s are not expected to be problematic for biota. High levels of turbidity can also complicate, and make more expensive, the treatment of water for distribution as drinking water. The levels observed here are unlikely to significantly affect drinking water treatment as they are neither excessively high nor frequent.

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[13] MacMillan et al. (2005) define cool water as mean summer temperature <16.5$^{\circ}$C, warm water systems as mean summer temperature >18.9$^{\circ}$C, and intermediate between the two temperatures.

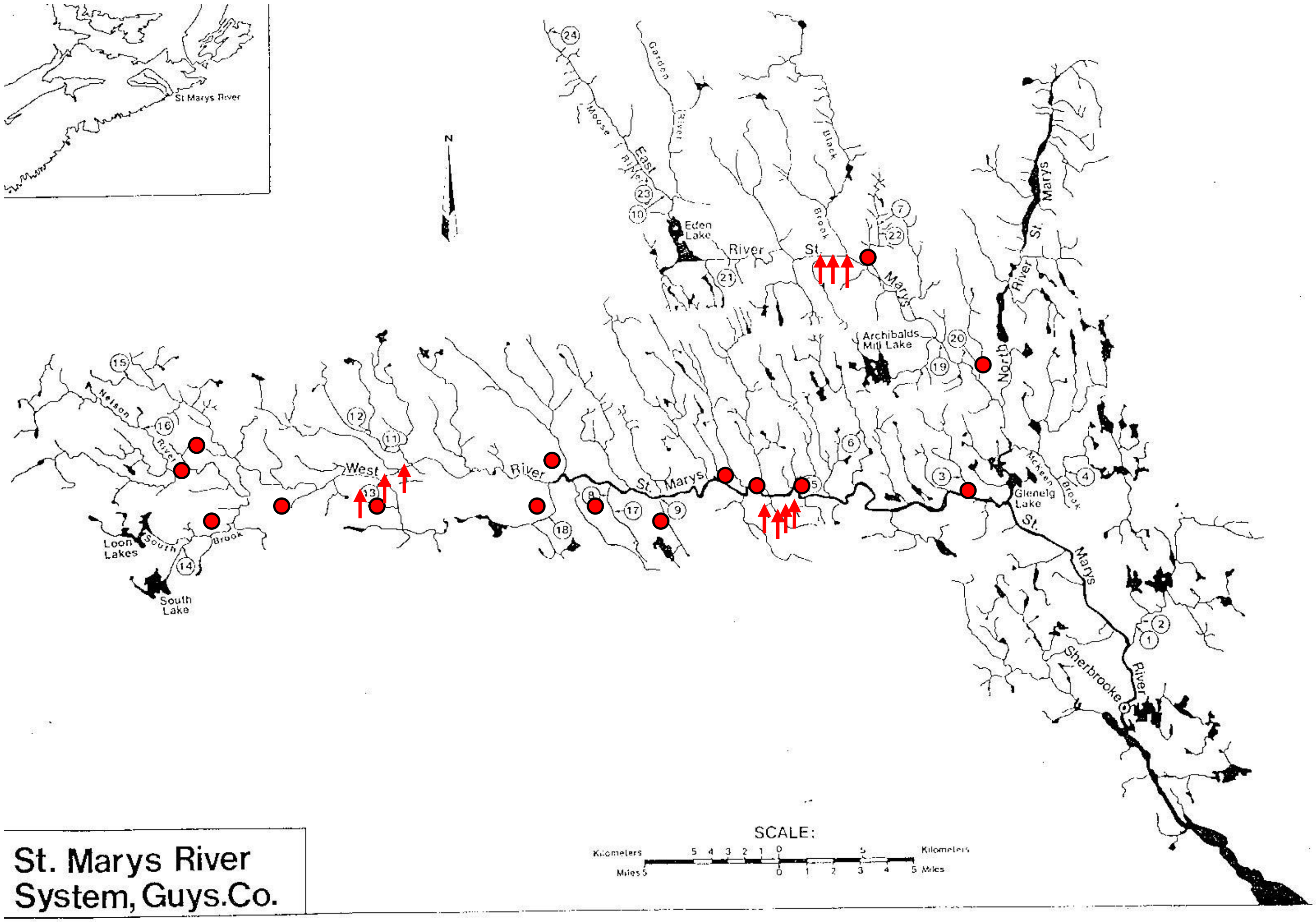


Figure 37: Locations of cold water areas in the St. Mary's River. Red circles are cool water streams (bridge crossings by Highways 347 & 348) identified during stream temperature survey where water temperature at least 5$^{o}$C cooler than air temperature when air >22$^{o}$C. Red arrows are cold water areas in the mainstem due either to incoming cold tributaries or springs.

The low turbidity at low flows, implying little suspended matter, is interesting in the context of the parameter of colour. Colour differed significantly between the East and West branches. Yet at low flows there is little suspended matter, so the colour difference (darker in the West Branch) must be due to dissolved substances. Given the presence of bogs, peatlands, and wetlands on the West Branch, and lesser abundance on the better-drained soils of the East Branch, the dissolved substances darkening the water of the West Branch are likely derived from these acidic wetlands and so are probably humic acids and tannins. Unfortunately there has not been sampling of humic acids in the East versus West Branches; only on the Main Branch at Stillwater which is not useful in determining differences among branches. The dark colour of the West and Main Branches are consistent with typical Atlantic Coast streams of Nova Scotia, while the clear water of the East Branch is more similar to streams draining into Northumberland Strait.

Chemical Parameters

The pH of Atlantic Shore rivers of Nova Scotia has declined between the 1950s and late 1970s-early 1980s. The source of this acidity causing the decline in pH is from atmospheric deposition (i.e., acid rain originally from industrial sources in the US; Watt 1997) but also the natural organic acids from peatlands and bogs (Gorham et al. 1986, Kerekes et al. 1986, Underwood et al. 1987, Korman et al. 1994). Acidification is exacerbated in Atlantic shore rivers by hardrock geology with little buffering capacity, poor soils, and an abundance of acidic heaths, peatlands and bogs (Watt et al. 1983, Watt 1987, 1997). This is illustrated well in the St. Mary's drainage where the West and Main branches (low pH) drain an area of bogs, peatlands and wetlands, underlain by shale, sandstone, conglomerate, granite, diorite, granodiorite, and siltstones, while the higher pH East Branch drains siltstones, shales, greywacke, volcanic tuff and ash, with few wetlands.

The pH of rivers of Nova Scotia's Atlantic shore has declined between the 1950s and late 1970s-early 1980s by between 0.2 pH units (LaHave River) and 0.8 pH units (Roseway River) with a mean rate of decline of -0.017 pH units/year over this period (Farmer et al. 1980, Watt et al. 1983). Based on the data analyzed here, for the St. Mary's River, there is no obvious evidence of change in pH between 1974 and 2008, and possibly as far back as 1966. One explanation for this apparent lack of decrease over time relative to other rivers is that the Environment Canada data on which the regression is based, are collected downstream of the confluence of the East and West Branches. The better buffered East Branch may mask any decline in the West Branch as the pH is measured after the two branches have mixed. Thus, the East Branch may be responsible for maintaining adequate pH when other rivers suffer from acidification.

Seasonally, pH is higher in winter than in summer. On short time scales, pH varies from week-to-week (±0.02 units) and month-to-month (±0.6-0.8 units). The West Branch appears to be more variable on a week-to-week basis than the East or Main and this may be a reflection of lower buffering capacity and so greater sensitivity to pH alterations from rain, snowmelt, or low water conditions.

Depressed pH has the potential to detrimentally affect multiple aspects of stream ecology (e.g., chemical speciation in water, toxicity of parameters, life history of benthic invertebrates, mortality of fish), but the greatest volume of relevant research and information has concentrated on effects of low pH on Atlantic salmon. Low pH (i.e., acidic water) can affect all freshwater stages of Atlantic salmon. Farmer (2000) lists Atlantic salmon life stage sensitivity to acidification (in decreasing order) as:

Fry > Smolt > Small parr > Large parr >Alevin >Eggs

Fry are the most sensitive salmon stage to low environmental pH (Johnston et al. 1984, Farmer 2000). The estimated $LL_{50}$[14] for fry is pH 5.3 with no survival expected at pH 5.0 or below (Lacroix et al. 1985). Significant mortality (19%-71%) of fry occurred at pH of about 5.0, and pH must be increased to about 5.4 to reduce mortality during the fry stage (Farmer 2000). Of 63 rivers along the Atlantic Shore, salmon are considered extirpated in 14 rivers where mean annual pH <4.7, reduced by 90% in 20 rivers where pH is in the 4.7-5.0 range, reduced by about 10% in 16 rivers in pH range 5.1-5.4, and apparently unaffected in 13 rivers with pH >5.4 (Watt 1987, 1997, Farmer 2000). Thus, a mean pH >5.4 appears to maintain salmon populations, with declining abundance as pH is reduced below that level. Relatively few measurements appear to be potentially problematic for salmon, that is with pH <5.4. Low pH effects on salmon may be expected in some localized areas of the West Branch (e.g., Mitchell, McQuarrie's, Kelly, and Glencross Brooks) and Main Branch (Archibald's Brook, Stillwater) where mean pH ≤5.5, but the small scale nature of this is unlikely to have a depressing effect on the river-wide salmon population.

The East Branch is clearly differentiated from the West and Main branches in terms of alkalinity, hardness, and specific conductance, in addition to pH. Again, this is a function of the different geology and soil conditions. Based on hardness, this water is considered "soft" water and the alkalinity values imply it is sensitive to acidification relative to other rivers, such as those along the Northumberland Shore which are more resistant to acidification.

Dissolved oxygen concentrations are highly variable over time periods of days, weeks and months, and from place to place, dependent upon factors such as amount of decaying organic material (absorbing dissolved oxygen) and primary production (producing oxygen during day via photosynthesis) as well as presence of riffles and rapids oxygenating water from atmospheric gases. Mobile species, such as aquatic invertebrates and fish will move in response to low dissolved oxygen concentrations and seek more well oxygenated environments. Sessile species cannot do this but the impact of low dissolved oxygen, if any is exerted at all, is expected to be highly localized to a few areas and transient in time. Eggs of fish and invertebrates, the most sessile and often most vulnerable stage to low dissolved oxygen tend to be laid in high oxygen environments (e.g., in riffles, among plants) or to be tolerant of low dissolved oxygen concentrations. It is very unlikely that dissolved oxygen is problematic in the St. Mary's River, except possibly for few areas of deep water, without atmospheric oxygenation and with large masses of decaying material. Throughout most of the watershed, however, there is no reason to believe that low dissolved oxygen concentrations are of concern from an ecological perspective.

[14] $LL_{50}$ is the "Lethal Level 50" for a substance which is the level (concentration) at which 50% of the test organisms die by the end of a determined time limit, often 24, 48 or 72 hours.

Nutrients

Nutrient concentrations, particularly phosphorous, are relatively low in the St. Mary's River, but not sufficiently low for the system to be considered oligotrophic. Rather, given the phosphorous levels it might be considered mesotrophic. In aquatic systems phosphorous is more likely to be the limiting nutrient than nitrogen (Wetzel, 1975), thus nitrogen in the St. Mary's is unlikely to be a limiting factor. Wetzel (1975) also points out that aquatic algae and macrophytes typically contain phosphorous and nitrogen in the ratio of 7N:1P (i.e., 7 nitrogen for every phosphorous). The nitrogen:phosphorus ratio from the mean values in Table 6 is 15.0 N:P, suggesting nitrogen is present in sufficient concentration to match the available phosphorous for plant growth. Analysis of 247 paired phosphorous and nitrogen measurements by Environment Canada at Stillwater indicate a mean ratio of 43.6 (SD=46.5) N:P. Only 1.5% of these measurements are of ratio less than 7N:1P. It is most likely that phosphorous is the limiting nutrient in the St. Mary's.

Nitrogen concentrations in the water are lowest in summer and peak in winter, and this is most likely associated with the growing season as plants take up available nitrogen to be used for structural components. With decomposition in autumn, this nitrogen is then re-released into the water, increasing concentrations. There is some indication of increases in phosphorous and nitrogen in the river over time, but this conclusion is weak as the data are very "noisy". Whether this "increase" in nutrients has had any effect on river biota is unknown.

Both phosphorous and nitrogen can be problematic at high concentrations by promoting excessive algal and macrophyte growth (i.e., eutrophication). Additionally, excessively high levels of nitrogen in the form of ammonia can be toxic to invertebrates and fish. The nutrient concentrations measured in the St. Mary's River are not sufficiently high to contribute to either of these problems. Further, because ammonia toxicity decreases with decreasing pH, the relatively low pH throughout the West and Main Branches provide some further protection from ammonia toxicity. However, the small sample size of ammonia, and different form measured (dissolved) versus that reported by CCME (total) limits inferences of ammonia toxicity and threat in the St. Mary's River.

Nutrient concentrations in Atlantic Coast rivers are low compared to other rivers in Nova Scotia or in adjacent provinces (e.g., New Brunswick). This is a naturally occurring condition and only in areas of intense nutrient inputs (e.g., some agricultural practices, sewage outfalls, etc.) are elevated nutrient levels likely to be problematic. This is not so in the St. Mary's. Indeed, prior to this analysis, the concern was that nutrient levels may be depressed and so impacting proper river functioning by limiting production. However, this analysis suggests that though levels are low, they are not sufficiently depressed to generate truly oligotrophic conditions, and the N:P ratio is reasonable to encourage appropriate growth. Thus, nutrient concentrations do not appear to be parameters of concern in the St. Mary's River.

Metals

The 16 metals considered in some depth here may be classified into four general categories:

1. Metals of concern (aluminum)
2. Metals of high toxicity with analytical issues compromising interpretation (cadmium, copper, lead)
3. Metals with insufficient data requiring monitoring in the future (antimony, chromium, mercury, nickel, silver)
4. Metals likely not of concern (arsenic, barium, iron, manganese, magnesium, molybdenum, zinc)

(i) Metals of concern

Aluminum concentrations are elevated in the St. Mary's River, almost always exceeding CCME guidelines for the protection of aquatic life. The high aluminum concentrations are likely a function of the bedrock geology being composed of aluminum-rich rocks and the depressed pH over the last 50 years accelerating the rate of leaching of metals from rock. Aluminum concentrations in Atlantic coast streams have been reported as approximately doubling between 1945-55 and 1980-81 (Watt et al. 1983). In this analysis, no increase over time was found, but this is likely due to any increases having already occurred between 1945-55 and 1974 when Environment Canada sampling, producing the data used here, was initiated. That is, the levels reported here are stable and represent values after the increase noted by Watt et al. The elevated levels in the East Branch are surprising as the pH in this branch is significantly greater than the West and Main branches and so it would be logical that aluminum would be at lower concentrations as it would be less readily leached out of the bedrock. It is not, however, significantly different in this branch, though the small sample sizes among branches must be kept in mind.

These elevated aluminum concentrations are a concern with respect to aquatic life as aluminum is known to have a number of detrimental effects on aquatic biota. In acidic waters, aluminum is generally more toxic over the pH range 4.4 - 5.4, with maximum toxicity around 5.0; toxicity also increases under alkaline conditions (Anonymous, 1992). Aluminum toxicity is affected by a number of variables, including the chemistry of the water, the form(s) of aluminum present, the duration of exposure, whether there was pre-exposure to aluminum, the rate of change in the aluminum concentration, physical factors such as temperature, and the species and life stage exposed (Havas, 1986). Aluminum interferes with respiration, sodium and chloride regulation, and possibly calcium uptake in some species (Havas and Jaworski, 1986). There is quite an extensive body of literature on aluminum toxicity and its environmental effects in the aquatic environment; for good reviews see Havas and Jaworski (1986), Butcher (1988), and Gensemer and Playle (1998). Interestingly, the weight of evidence is that aluminum does not contribute to salmon mortality in low pH rivers (Lacroix and Townsend 1987, Lacroix 1989, Peterson et al. 1989, Lacroix et al. 1990) but rather the mortality is due to acid toxicity (Lacroix 1989, Peterson et al. 1989).

Aluminum very rarely exceeded Health Canada drinking water guidelines. Thus, aluminum may have ecological effects, but is unlikely to affect drinking water quality.

(ii) Metals of high toxicity with analytical issues compromising interpretation

Analysis of data for cadmium, copper, and lead was compromised by analytical issues. Both cadmium and lead had analytical detection limits which were greater than CCME guidelines, and so it was possible to have a concentration less than detection, yet still exceeding the CCME guidelines. The "true" concentrations are unknown and so comparison with an independent standard is not relevant in these cases. Taking this into account, cadmium appears to be present at very low concentrations, and there is no obvious indication of elevated cadmium in the St. Mary's River, despite a large number of samples (N=303). Cadmium is highly toxic as evidenced by the very low values for the guidelines. However, comparison with US EPA and Health Canada guidelines further indicate that cadmium is not elevated to a level of concern in these samples.

Lead may be expected to be elevated in the waters of the St. Mary's given the bedrock geology and that it is sufficiently concentrated to allow mining (e.g., lead mine on West Branch). Lead concentrations have exceeded the Health Canada drinking water MAC on only three occasions, and on two of these (May 5, 1998; May 7, 2002) cadmium was also elevated suggesting a condition of general elevated metals on these two dates. In the great majority of cases, lead concentrations are below Health Canada guidelines indicating no risk to drinking water. Once analytical detection limits were reduced below CCME guidelines (in 2000), 19% of measurements exceeded CCME guideline. These finding suggests that lead concentrations may be elevated sufficiently to affect aquatic life, but not sufficiently to affect use of the river as a drinking water source.

Uncertainties with analytical methods also affect interpretation of copper concentrations. Different analytical detection limits among studies makes comparison among branches problematic as it masks "true" concentration. Differential reporting limits also make comparison over time problematic. In addition, different forms of copper sampled (Total vs Extractable) makes comparison with guidelines difficult. In general though, copper appears to exceed CCME guidelines approximately 10% of the time. Similar to lead, copper appears to be sufficiently elevated to occasionally have effects on aquatic life, but there is no evidence that it is at concentrations to be a risk to drinking water. Elevated copper concentrations occur in the tills of the St. Mary's River, with Stea and Fowler (1979) showing mean concentrations of 58.8 to 134.4 mg/kg, thus elevated levels in the water are not surprising. Copper is known to be quite toxic to aquatic life at low doses and so from an ecological perspective this element is of concern.

(iii)Metals with insufficient data requiring monitoring in the future

Five metals are identified as having been sampled infrequently, yet to be of toxicity sufficient to require dedicated future sampling to determine concentrations. These are chromium (N=38), mercury (N=53), nickel (N=36), silver (N=37), and antimony (N=36). Each of these are quite toxic and it is a significant data gap to not have more complete data sets for each of these. It is recommended (*Recommendations #2,#5,#6, #7*) that future sampling should focus on these five to determine baseline data for their concentrations in various locations within the watershed. In particular, chromium, mercury, silver and antimony are highly toxic. To establish a solid baseline of the concentration of these metals, the sample size should be increased for each element to $N \geq 50$ over the next five years with samples collected throughout the watershed.

(iv) Metals likely not of concern

Seven metals are identified as likely not of concern. These are arsenic, iron, molybdenum, zinc, barium, and magnesium.

Arsenic is present at low concentrations in the St. Mary's River with the great majority of samples being below analytical detection limits. Arsenic is present at relatively high concentrations of the underlying bedrock geology, with Stea and Fowler (1979) showing mean concentrations of 10.6 to 31.7 mg/kg, but does not appear to leaching into the waterway. This element is potentially toxic, as reflected in the low CCME and Health Canada guidelines, but the very infrequent exceedance of these guidelines in the data set of 152 measurements suggest that arsenic is not a parameter to be concerned with in this watershed despite it's potentially high toxicity.

Barium suffers from small sample size, but the lack of exceedance of the Health Canada guidelines and apparent low toxicity of this element suggests that it is not an element of concern.

Iron is a fairly benign metal in terms of environmental or human toxicology and it can frequently be found where groundwater flows into low pH streams (i.e., springs/seeps). At these locations the iron precipitates out of solution upon entering surface water. These isolated, localized area of iron enrichment are common. Similar to aluminum and arsenic, the underlying geology of the St. Mary's is iron-rich, and so elevated levels of iron are not surprising. Due to its common, though isolated occurrences, and low toxicity, it is not considered an element of concern in the St. Mary's River.

At first glance, manganese appears elevated, but that is relative to the Aesthetic Objective of Health Canada. This is not an objective associated with health risk, and so exceedances of it do not, necessarily, pose a risk to health. The Province of British Columbia established a manganese guideline of 0.8 mg/L for water quality. The maximum reported manganese value in the St. Mary's River was 1.02 mg/L (East Branch, April 1999) but that is likely an error as the next greatest value of 328 measurements is 0.246 mg/L which is only one-fourth of the BC guideline. Of all measurements of manganese, 90% are less than 0.11 mg/L, indicating manganese concentrations are very low relative to the BC guideline. Based on this, manganese is not considered an element of concern in the St. Mary's River.

Magnesium is naturally in high concentrations in the rocks underlying the St. Mary's River and so may be expected to be elevated. Stea and Fowler (1979) provide data showing mean concentrations of 8,000 to 9,200 mg/kg magnesium in the tills of the St. Mary's. Lack of guidelines for either environmental protection or drinking water suggests that this is, in general, not a problematic element. Thus, it is concluded that these values for magnesium in the St. Mary's River are not cause for concern.

Molybdenum suffers from a small sample size (N=36), but the observation that the maximum value is an order-of-magnitude lass than the CCME guideline suggests that molybdenum is present at very low levels and not to be considered a risk.

Zinc has been extensively sampled (N=330) yet there are no exceedances of CCME or Health Canada guidelines implying that zinc is not a metal of concern in the St. Mary's River.

### 5.2 LAKES

Four lakes (Moose Lake and Ellen Brown Lake in the headwaters of the West Branch; Black Brook Lake and Eden Lake in upper reaches of East Branch) were sampled by Environment Canada between 1997 and 2000 (Table 9). The number of samples is very low (1 to 3) which limits inferences which may be drawn. However, some notable features do arise from these limited data.

- Alkalinity value for Eden Lake is much higher than all other lakes, but still well within the range shown by river water.
- The colour in Black Brook Lake is very high relative to the other lakes. This stream is named Black Brook due to the inherent colour of the water, derived from wetlands upstream of the lake.
- Black Brook Lake shows some of the lowest pH values, despite lying on the East Branch. Again, this is a reflection of the wetland drainage area upstream of the lake.
- Phosphorous is at concentrations at the low end of the range compared with phosphorus in river water. This may be a function of the time of sampling (generally mid- to late-summer) when phosphorous largely depleted by organisms.
- Aluminum concentrations are elevated in the lakes relative to concentrations seen in the river water.
- Cadmium, copper and manganese concentrations in lake water are less than that observed in river water.
- Lead, magnesium, and zinc concentrations are approximately the same as those seen in river water.

Apart from these observations, little else may be concluded on lake water quality, apart from Lochaber Lake (see below), given the very limited sampling of lakes within this watershed.

Lochaber Lake was subjected to a comprehensive water quality survey in 1994 (Taylor et al., 1995). A summary of their data is presented as Table 10. In their extensive report they concluded that the lake is oligotrophic, very unproductive and phosphorous-limited (i.e., a N:P ratio of 35:1). Of greatest concern was the bacteriological results. They reported the North River, St Mary's (at north end of lake) and Gusset Brook as having elevated nutrient levels on a sporadic basis, and these levels being attributable to livestock and manure storage practices. These streams at the head of the lake were generally unsuitable for swimming and untreated irrigation due to the high bacteriological levels. Within the lake water itself, 6 of 92 bacteriological samples (6.5%) exceeded 100 fecal coliform/100 mL (CCME guideline for protection of agriculture), and three of these exceeded 200/mL. Of 56 samples taken from inflowing streams 24 were >100 fecal coliform/mL and 15 > 200/mL. High values often occurred after heavy rains as material washed into streams from land. As a further assessment of the bacteriological condition of the lake, 100 sanitary sewer systems were surveyed, of which 9 were noted as malfunctioning. Taylor et al. concluded at the time however, that impacts from these properties were likely minimal at that time. Given that it has been 17 years since that survey, it is recommended that further bacteriological water sampling be conducted in Lochaber Lake to compare current conditions with past (*Recommendation #8*).

### 5.3 GROUNDWATER

Groundwater in the St. Mary's River watershed has only been sampled twice. Environment Canada collected five samples from the Sherbooke High School Well between July and December, 1972 and the Nova Scotia Department of Natural Resources collected a single groundwater sample for analysis at a Stillwater well on December 13, 2006. Between these two samples, 52 parameters have been assessed (Table 11). Of these 52, only 22 have Health Canada Drinking Water Guidelines and none of these guidelines were exceeded in any sample. Only the Health Canada guidelines are appropriate for comparison as groundwater is used for drinking water supply. Application of CCME guidelines for protection of aquatic life would be inappropriate here.

Based on this analysis of a very small sample size, there does not appear to be any parameters to be concerned about in the groundwater in this area of the St. Mary's River. A groundwater sampling program is recommended to provide more information on groundwater quality (*Recommendation #9*).

Table 9: Results of water quality sampling of selected lakes within the St. Mary's River watershed by Environment Canada.

| | MOOSE LAKE July 14, 1997 | ELLEN BROWN LAKE July 14, 1997 | BLACK BROOK LAKE July 5, 1998 | BLACK BROOK LAKE October 2, 1998 | BLACK BROOK LAKE October 2, 1998 | EDEN LAKE, September 28, 2000 |
|---|---|---|---|---|---|---|
| **Physical** | | | | | | |
| Alkalinity (mg/L $CaCO_3$) | 1.23 | 2 | 1.42 | 1.22 | 1.21 | 6.73 |
| Colour (Apparent) (Relative units) | 7 | 6 | 80 | 90 | 90 | 8 |
| pH (pH units) | 5.88 | 6.29 | 5.59 | 5.45 | 5.48 | 7.07 |
| Specific conductance (µS/cm) | 18 | 20.9 | 33.3 | 36.4 | 26.5 | 48.5 |
| **Nutrients** | | | | | | |
| Total nitrogen (mg/L) | 0.178 | 0.112 | 0.13 | 0.1 | 0.09 | |
| Dissolved nitrate nitrogen (mg/L) | | | 0.03 | <0.02 | <0.02 | |
| Total phosphorous (mg/L) | 0.0042 | 0.0049 | 0.005 | 0.005 | 0.006 | 0.006 |
| **Major Ions** | | | | | | |
| Calcium (Dissolved) (mg/L) | | | 0.72 | 1.05 | 1.06 | |
| Calcium (Extractable) (mg/L) | 0.52 | 0.91 | | | | |
| Dissolved Inorganic Carbon (mg/L) | 0.8 | 0.8 | | | | |
| Dissolved Organic Carbon (mg/L) | 2 | 1.8 | | | | |
| Total Inorganic Carbon (mg/L) | | | 0.7 | <0.5 | <0.5 | |
| Total Organic Carbon (mg/L) | | | 9.6 | 11.9 | 11.7 | 3 |
| Chloride (Dissolved) (mg/L) | 1.93 | 2.23 | 6.12 | 6.44 | 6.45 | |
| Potassium (Dissolved) (mg/L) | | | 0.28 | 0.23 | 0.23 | |
| Potassium (Extractable) (mg/L) | 0.21 | 0.21 | | | | |
| Silica dioxide (mg/L) | 0.64 | 0.14 | | | | |
| Sodium (Dissolved) (mg/L) | | | 4.27 | 4.53 | 4.48 | |
| Sodium (Extractable) (mg/L) | 1.65 | 1.84 | | | | |
| Sulphate (Dissolved) (mg/L) | 0.8 | 0.2 | 1.62 | 2.05 | 2.03 | |

Table 9 (Cont'd): Results of water quality sampling of selected lakes within the St. Mary's River watershed by Environment Canada.

| | MOOSE LAKE July 14, 1997 | ELLEN BROWN LAKE July 14, 1997 | BLACK BROOK LAKE July 5, 1998 | BLACK BROOK LAKE October 2, 1998 | BLACK BROOK LAKE October 2, 1998 | EDEN LAKE, September 28, 2000 |
|---|---|---|---|---|---|---|
| **Metals** | | | | | | |
| Aluminum (Extractable) (mg/L) | | | 0.26 | 0.38 | 0.37 | |
| Cadmium (Extractable (mg/L) | | | <0.001 | <0.001 | <0.001 | |
| Copper (Extractable) (mg/L) | | | <0.002 | <0.002 | <0.002 | |
| Iron (Extractable) (mg/L) | | | 0.11 | 0.17 | 0.17 | |
| Lead (Extractable) (mg/L) | | | <0.002 | <0.002 | <0.002 | |
| Magnesium (Dissolved) (mg/L) | | | 0.43 | 0.62 | 0.61 | |
| Magnesium (Extractable) (mg/L) | 0.43 | 0.48 | | | | |
| Manganese (Extractable) (mg/L) | | | <0.01 | <0.01 | <0.01 | |
| Zinc (Extractable) (mg/L) | | | <0.01 | <0.01 | <0.01 | |

Table 10: Summary of water quality data from Lochaber Lake (1994). Data from Taylor et al. (1995).

| Water quality variable | Mean (range); sample size |
|---|---|
| **Physical** | |
| Alkalinity (mg/L) | 7.9 (<1.0 - 10.0); 103 |
| Colour (True) (TCU) | 10.7 (<3.0 - 15.0); 103 |
| Dissolved oxygen (mg/L) | 10.2 (7.6 - 14.0); 105 |
| Hardness (mg/L) | 14.8 (9.9 - 17.9); 24 |
| pH (pH units) | 7.0 (6.3 - 7.7); 103 |
| Specific Conductance (μS/cm) | 53.4 (50.0 - 67.7); 103 |
| Transparency (Secchi depth) (m) | 4.0 (2.5 - 5.3); 36 |
| Turbidity (NTU) | 0.6 (0.3 - 3.8); 103 |
| **Nutrients** | |
| Ammonia nitrogen (mg/L) | <0.01 (<0.01 - 0.10); 103 |
| Nitrate + Nitrite nitrogen (mg/L) | 0.135 (<0.070 - 0.210); 103 |
| Ortho-phosphorous (mg/L) | <0.001 (<0.001 - 0.001); 103 |
| Total nitrogen (mg/L) | 0.246 (0.180 - 0.290); 103 |
| Total phosphorous (mg/L) | 0.007 (<0.001 - 0.022); 103 |
| **Biological** | |
| Chlorophyll "a" (mg/L) | 1.6 (0.5 - 2.8); 72 |
| Pheophytin (mg/$m^3$) | 0.9 (0.1 - 1.5); 72 |
| **Bacteriological** | |
| Fecal coliform (#/100 mL) | 96.8 (0 - 3100) |
| **Major Ions** | |
| Calcium (mg/L) | 4.5 (2.3 - 5.5); 24 |
| Chloride (mg/L) | 5.9 (4.2 - 6.8); 24 |
| Potassium (mg/L) | 0.4 (0.3 - 0.4); 24 |
| Silica (mg/L) | 2.2 (<0.5 - 2.5); 23 |
| Sodium (mg/L) | 4.1 (3.6 - 5.0); 24 |
| Sulphate (mg/L) | 6.3 (4.0 - 10.0); 24 |
| Total Organic Carbon (mg/L) | 3.8 (2.0 - 5.6); 103 |

Table 10 (Cont'd): Summary of water quality data from Lochaber Lake (1994).

| Water quality variable | Mean (range); sample size |
|---|---|
| **Metals** | |
| Aluminum (mg/L) | 0.048 (0.030 - 0.086); 13 |
| Antimony (mg/L) | <0.05 (<0.002 - <0.05); 13 |
| Arsenic (mg/L) | <0.002 (<0.002 - <0.002); 3 |
| Barium (mg/L) | 0.010 (<0.005 - 0.012); 13 |
| Beryllium (mg/L) | <0.005 (<0.005 - <0.005); 13 |
| Boron (mg/L) | <0.01 (<0.01 - <0.01); 13 |
| Cadmium (mg/L) | <0.002 (<0.002 - <0.002); 13 |
| Chromium (mg/L) | <0.002 (<0.002 - 0.002); 12 |
| Cobalt (mg/L) | <0.002 (<0.002 - <0.002); 13 |
| Copper (mg/L) | <0.002 (<0.002 - 0.013); 24 |
| Iron (mg/L) | 0.021 (<0.02 - 0.048); 23 |
| Lead (mg/L) | <0.002 (<0.002 - <0.002); 13 |
| Magnesium (mg/L) | 0.9 (0.8 - 1.0); 24 |
| Manganese (mg/L) | 0.015 (<0.010 - 0.027); 23 |
| Nickel (mg/L) | <0.002 (<0.002 - <0.003); 13 |
| Selenium (mg/L) | <0.002 (<0.002 - <0.002); 13 |
| Tin (mg/L) | <0.05 (<0.002 - <0.05); 3 |
| Vanadium (mg/L) | <0.002 (<0.002 - 0.002); 13 |
| Zinc (mg/L) | <0.007 (<0.01 - 0.08); 24 |

Table 11: Summary of groundwater quality data for the St. Mary's River area. Data from Environment Canada (1972) and Nova Scotia Department of Natural Resources (2006).

| | 1972 High School Well | | | | 2006 Stillwater Well | Health Canada Drinking Water Quality Guidelines |
|---|---|---|---|---|---|---|
| | Mean (SD); N | Range | Median | 10th-90th pctle | | |
| **Physical** | | | | | | |
| Alkalinity (mg/L $CaCO_3$) | 54.58 (2.419); 5 | 51.4 - 57.6 | 53.8 | 52.36 - 57.08 | 58 | |
| Colour (True) (TCU) | | | | | <5 | Aesthetic objective < 15 TCU |
| Colour (Apparent) (Relative Units) | 8 (6.708); 5 | 5 - 20 | 5 | 5 - 14 | | |
| Hardness (mg/L $CaCO_3$) | | | | | 58 | |
| pH (pH units) | 6.9 (0.412); 5 | 6.5 - 7.6 | 6.8 | 6.62 - 7.28 | 7.32 | 6.5 - 8.5 |
| Specific Conductance (μS/cm) | 197.4 (20.069); 5 | 176 - 222 | 196 | 177.6 - 218.4 | 140 | |
| Total Organic Carbon (mg/L) | | | | | 2.5 | |
| Turbidity (JTU) | 3.08 (3.818); 5 | 0.5 - 9.1 | 0.6 | 0.5 - 7.34 | | |
| Turbidity (NTU) | | | | | 0.4 | |
| **Nutrients** | | | | | | |
| Nitrogen (Ammonia) (mg/L) | 0.1 (0); 2 | 0.1 - 0.1 | 0.1 | 0.1 - 0.1 | 0.09 | |
| Nitrogen (Nitrate) (mg/L) | | | | | 0.13 | MAC = 45 mg/L |
| Nitrogen (Nitrite) (mg/L) | | | | | <0.01 | |
| Nitrogen (Nitrate & Nitrite) (mg/L) | 0.12 (0.053); 5 | 0.07 - 0.21 | 0.11 | 0.08 - 0.18 | 0.13 | |
| Phosphorous (Orthophosphate) (mg/L) | | | | | <0.01 | |
| Phosphorous (Phosphate) (mg/L) | 0.02 (0.003); 2 | 0.02 - 0.025 | 0.022 | 0.02 - 0.024 | | |
| Phosphorous (total) (mg/L) | | | | | <0.1 | |

Table 11 (Cont'd): Summary of groundwater quality data for the St. Mary's River area.

| | 1972 High School Well | | | | 2006 Stillwater Well | Health Canada Drinking Water Quality Guidelines |
|---|---|---|---|---|---|---|
| | Mean (SD); N | Range | Median | 10th-90th pctle | | |
| **Major ions** | | | | | | |
| Bromide (mg/L) | | | | | <0.5 | |
| Calcium (mg/L) | 21.54 (1.51); 5 | 19.5 - 23.5 | 22 | 19.98 - 22.9 | 19 | |
| Chloride (mg/L) | 27.6 (5.029); 5 | 22 - 33 | 28 | 22.4 - 32.6 | 5 | Aesthetic objective < 250 mg/L |
| Fluoride (mg/L) | 0.12 (0); 2 | 0.12 - 0.12 | 0.12 | 0.12 - 0.12 | <0.1 | MAC = 1.5 mg/L |
| Potassium (mg/L) | 2.6 (0.141); 5 | 2.5 - 2.8 | 2.5 | 2.5 - 2.76 | 1.8 | |
| Silica (Reactive) (mg/L) | 13.25 (0.957); 4 | 12 - 14 | 13.5 | 12.3 - 14 | 12 | |
| Sodium (mg/L) | 11.7 (0.974); 5 | 10.5 - 13 | 12 | 10.7 - 12.6 | 6.8 | Aesthetic objective < 200 mg/L |
| Sulphate (mg/L) | 6.76 (1.059); 5 | 5.2 - 7.8 | 7.1 | 5.6 - 7.68 | 6 | Aesthetic objective < 500 mg/L |
| **Metals** | | | | | | |
| Aluminum (mg/L) | | | | | 0.035 | 0.1 (operational guideline) |
| Antimony (mg/L) | | | | | <0.002 | MAC = 0.006 |
| Arsenic (mg/L) | | | | | <0.002 | MAC = 0.01 |
| Barium (mg/L) | | | | | 0.011 | MAC = 1.0 |
| Beryllium, (mg/L) | | | | | <0.002 | |
| Boron (mg/L) | | | | | 0.008 | MAC = 5.0 |
| Cadmium (mg/L) | 0.001 (0); 2 | 0.001 - 0.001 | 0.001 | 0.001 - 0.001 | <0.0003 | MAC = 0.005 |
| Chromium (mg/L) | | | | | <0.002 | MAC = 0.05 |
| Cobalt (mg/L) | | | | | <0.001 | |
| Copper (mg/L) | 0.01 (0.004); 2 | 0.007 - 0.014 | 0.01 | 0.007 - 0.013 | <0.002 | Operational guideline < 1.0 mg/L |
| Iron (Dissolved) (mg/L) | 0.02 (); 1 | 0.02 - 0.02 | 0.02 | 0.02 - 0.02 | <0.05 | Operational guideline<0.3 mg/L |
| Iron (Extractable) (mg/L) | 0.21 (0.098); 2 | 0.14 - 0.28 | 0.21 | 0.154 - 0.266 | | |
| Lead (Extractable) (mg/L) | 0.003 (0.002); 2 | 0.001 - 0.005 | 0.003 | 0.001 - 0.004 | <0.0005 | MAC <0.01 mg/L |

Table 11 (Cont'd): Summary of groundwater quality data for the St. Mary's River area.

| | 1972 High School Well | | | | 2006 Stillwater Well | Health Canada Drinking Water Quality Guidelines |
|---|---|---|---|---|---|---|
| | Mean (SD); N | Range | Median | 10th-90th pctle | | |
| Magnesium (Dissolved) (mg/L) | 3.6 (0.254); 5 | 3.3 - 4 | 3.6 | 3.38 - 3.84 | 2.2 | |
| Manganese (Dissolved) (mg/L) | 0.01 (0); 2 | 0.01 - 0.01 | 0.01 | 0.01 - 0.01 | 0.037 | Operational guideline < 0.05 mg/L |
| Manganese (Extractable) (mg/L) | 0.71 (0.001); 2 | 0.07 - 0.072 | 0.071 | 0.070 - 0.072 | | |
| Mercury (mg/L) | | | | | <0.00001 | MAC = 0.001 |
| Molybdenum (mg/L) | | | | | <0.002 | |
| Nickel (mg/L) | | | | | <0.002 | |
| Selenium (mg/L) | | | | | <0.002 | MAC = 0.01 |
| Silver (mg/L) | | | | | <0.0005 | |
| Strontium (mg/L) | | | | | 0.064 | |
| Thallium (mg/L) | | | | | <0.0001 | |
| Tin (mg/L) | | | | | <0.002 | |
| Titanium (mg/L) | | | | | <0.002 | |
| Uranium (mg/L) | | | | | 0.0005 | MAC = 0.02 mg/L |
| Vanadium (mg/L) | | | | | <0.002 | |
| Zinc (mg/L) | 0.021 (0.001); 2 | 0.02 - 0.022 | 0.021 | 0.02 - 0.021 | <0.005 | Operational guideline < 5.0 mg/L |

# 6.0 CONCLUSIONS

From this analysis of a variety of data sources going back 35+ years, the following conclusions are made regarding water quality in the St. Mary's River.

- Water quality differs greatly between the East and West Branches due to differing underlying bedrock geology and soils. The East Branch is of higher pH, alkalinity, hardness and specific conductance, and of lower colour values (i.e., clearer) than the West Branch.
- pH is slightly depressed throughout the West and Main Branches but not to an extent to cause widespread impacts to Atlantic salmon. pH effects on salmon may be localized and transient on the West Branch.
- Nutrient concentrations are low throughout the watershed, and phosphorous likely the limiting nutrient.
- Concentrations of the metals aluminum, chromium, copper, lead. mercury, antimony, nickel and silver are of some concern. Aluminum concentrations are established to be elevated, but for the remaining metals, either analytical limitations or small sample sizes limit inferences and conclusions regarding these concentrations. These latter metals need to be sampled and assessed in the future.
- Water temperatures may be problematic to cold water species as summer temperatures reach high values and there is evidence on the Main and East Branches of increasing frequency of warm temperatures. The West Branch is slightly warmer than the East and Main Branches.
- Coliforms may be problematic in Lochaber Lake due to agriculture, livestock and residential development. This parameter should be monitored to ensure lake water uses are still supported.
- Water quality of groundwater, based on very small sample sizes, appears to be well within the Health Canada Drinking Water Guidelines. Future groundwater sampling throughout the watershed is recommended.

# 7.0 RECOMMENDATIONS

The following recommendations are provided in order that they appear in the text, not necessarily order of priority.

**Recommendation #1:** Total ammonia should be sampled within the St. Mary's River for comparison with CCME water quality guidelines for the protection of aquatic life. Sampling should include a minimum of three locations on each branch to provide spatial evaluation and, at a minimum, should occur in summer when pH is lowest and temperature highest, but ideally should be sampled in Spring, Summer and Autumn. This sampling should be done for three consecutive years to provide temporal data. pH and water temperature are to be measured concurrently as ammonia toxicity is pH and temperature dependent.

**Recommendation #2**: Based on this review, there is little evidence that chromium is a parameter of concern in the St. Mary's River though the very small sample size and inconsistent sampling makes this conclusion preliminary. Further sampling of chromium in the future should continue until the sample size is greater than 80 measurements (currently at N=38) and a review of the data conducted then. Sampling should include a minimum of three locations on each branch to provide spatial evaluation.

**Recommendation #3**: Copper, in the form of Total Copper, should be sampled in future water quality surveys within the St. Mary's River in order to allow comparison with CCME guidelines for protection of aquatic life. This parameter should be sampled to a minimum sample size of 80 samples. Sampling should include a minimum of three locations on each branch to provide spatial evaluation.

**Recommendation #4:** There is an absence of historical lead data measured with accuracy (i.e., sufficiently low analytical detection limit) to compare with CCME guidelines. Future sampling should be conducted to measure lead concentrations with a detection limit of 0.001 mg/L until a sample size of 80 is reached. Sampling should include a minimum of three locations on each branch to provide spatial evaluation.

**Recommendation #5**: The small sample size of historical mercury data, and inconsistency between sampled mercury (total) and guideline form (methylmercury) makes conclusions regarding mercury in the St. Mary's River tentative. Sampling should be conducted in the near future for mercury with spatial coverage (i.e., minimum of 30 samples from each of the East Branch and West Branch) to assess methylmercury and total mercury in the water and also fish tissue to determine whether mercury is an issue in the watershed.

**Recommendation #6:** Antimony has a small historical sample size yet has high potential toxicity. Future water quality sampling should include sampling for this metal. Sampling should include a minimum of 30 samples per river branch, and these samples collected from a variety of areas to assess spatial distribution of antimony. Further, Environment Canada should be contacted and requested to sample antimony as part of their regular sampling at Stillwater.

**Recommendation #7:** Nickel and silver each have small historical sample sizes yet have high potential toxicity. Future water quality sampling should include sampling for these metals. Sampling should include a minimum of 30 samples per river branch, and these samples collected from a variety of areas to assess spatial distribution of these metals.

**Recommendation #8:** The water quality survey of Lochaber Lake in 1994 found that fecal coliforms may be problematic. In the intervening 17 years there have been improvements in livestock and manure management, but also the development of many new residences along the lakeshore. A repeat of the bacteriological survey of Taylor et al. (1995), including their lake locations and inlet and outlet streams is recommended during the summer period to compare with historic data. In addition, given the new developments over the past two decades, new sample locations should be determined in addition to the historic ones.

**Recommendation #9:** There is very little groundwater water quality data available for the St. Mary's River. A small-scale groundwater sampling program to assess spatial distribution of water quality should be developed. Such a program should include sampling a minimum of five wells on each branch (total of 15 wells).

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