Assessment of Mercury Loadings from Tributaries to the St. Lawrence River (Cornwall) Area of Concern

DRAFT Report

Report in support of the St. Lawrence River (Cornwall) Remedial Action Plan

ST. LAWRENCE RIVER RESTORATION COUNCIL

St. Lawrence River Institute of Environmental Sciences
University of Ottawa

uOttawa

November, 2009

Assessment of Mercury Loadings from Tributaries to the St. Lawrence River (Cornwall) Area of Concern

Report prepared for the Raisin Region Conservation Authority, Cornwall, ON and the Ontario Ministry of the Environment, Eastern Region, Kingston, ON in support of the St. Lawrence River (Cornwall) Remedial Action Plan

Prepared by Jeff Ridal, Crystal Veenstra, St. Lawrence River Institute of Environmental Sciences, Cornwall, ON and David Lean, Emmanuel Yumvihoze, University of Ottawa, Ottawa, ON

November 19, 2009

EXECUTIVE SUMMARY

Mercury (Hg) contamination of sediments and fish are key beneficial use impairments in the St. Lawrence River (Cornwall) AOC. While there have been past and ongoing studies to evaluate the atmospheric, upstream and sediment sources of Hg to Lake St. Francis portion of the St. Lawrence River, contributions from tributaries remain poorly characterized.

The purpose of the project is to determine Hg concentrations in the main tributaries within the AOC and provide preliminary estimates of the loadings of Hg from tributaries. This information can be used to evaluate their contributions to elevated levels observed in fish such as walleye within the AOC.

Hg samples were taken as part of a tributary sampling program from eight major tributaries that drain in the St. Lawrence River (Finney, Fraser, Gunn, Pattingale, Raisin, Sutherland, Westley and Wood). Samples were taken monthly from July through October 2008 and in April and June 2009.

The following results were obtained:

- Annual geometric means of total Hg levels in the tributaries ranged 0.693 ng/L for the Raisin River to 1.62 ng/L for Fraser Creek. Methyl Hg levels ranged from 0.13 ng/L for the Raisin River to 0.25 ng/L for Fraser Creek. These values are 2-8 times greater than values observed in uncontaminated zones of the St. Lawrence River
- The percent of methyl Hg of total Hg ranged 19-27% which is higher than the 5-10% range normally found in most uncontaminated freshwater systems
- Loadings of total Hg and methyl Hg are on the order of 280 and 50 ng/yr, respectively. Three tributaries (Raisin, Sutherland and Fraser) provide approximately 85% of the Hg loadings
- Using a bioaccumulation factor of 1.3×10^6 derived from Hg data for eastern Ontario freshwaters, concentrations in small yellow perch residing in the tributaries are predicted to range from 0.19-0.33 mg/kg. These values are similar to the most stringent Hg fish consumption guideline of 0.26 mg/kg set by the province of Ontario for sensitive consumers. Therefore, small yellow perch and similar prey could contribute to elevated levels of Hg in large piscivores in the AOC that frequently forage in the tributaries or at tributary mouths.

Recommendations include:

- Further characterization of concurrent mercury and flow data to improve the loading estimates
- Additional measurements in tributary headwaters and along the course of the watershed to characterize source of Hg to these tributaries
- Characterization of wetland conditions (disturbed vs. undisturbed) in headwater wetlands
- Direct measurement of Hg concentrations in small forage fish from these small tributaries
- Over the longer term develop a Hg mass balance model for Lake St. Francis that would characterize the main loadings and identify the significance of tributary loadings.

Table of Contents

Introduction 1
Methods 1
Results and Discussion 2
    Tributary Water Quality Characteristics 2
    THg Concentrations 2
    MeHg Concentrations 3
    Percent MeHg 3
    Tributary Loadings of Hg to the St. Lawrence River 3
    Comparisons to Mercury Loadings to the St. Lawrence from other Sources 5
    Relationship to Fish Tissue Concentrations 5
Conclusions and Recommendations 6
References 7
APPENDIX 1 24

Table of Figures

Figure 1. Comparison of mercury concentrations in walleye from Lake St. Francis and Lake St. Lawrence. 14
Figure 2. Map of Tributaries and sampling points. 15
Figure 3. Mean total mercury (THg) in tributaries. 16
Figure 4. Seasonal variation of total mercury (THg) in the monitored tributaries..... 17
Figure 5: Mean values of methylmercury (MeHg) in monitored tributaries. 18
Figure 6. Variations in MeHg concentrations in the tributaries 19
Figure 7. Dependence of MeHg concentrations on temperature 20
Figure 8. Mean percent methyl mercury (%MeHg) of total mercury..... 21
Figure 9. Relationship (R^2) between MeHg and THg with season. 22
Figure 10. Proportions of total mercury (THg) and methyl mercury (MeHg) loads 23

Assessment of Mercury Inputs from Lake St Francis Tributaries

Introduction

Mercury (Hg) contamination of sediments and fish are key beneficial use impairments in the St. Lawrence River (Cornwall) AOC. For instance, levels of Hg in walleye, despite a long-term decline remain above acceptable fish consumption levels and are elevated above similar fish collected upstream of the AOC (Figure 1). Most of the Hg in fish is found as methyl mercury (MeHg) which is the most toxic form of Hg that can cross the brain and placental membranes and is a well-known health risk (Harada 1995).

Sources of Hg to freshwater environments include inputs from industrial and municipal discharges, atmospheric deposition, resuspension and diffusion from sediments, and inputs from tributaries (Environment Canada 2003). There have been past and ongoing studies to evaluate the atmospheric, upstream and sediment sources of Hg to the AOC (Ridal et al., 2009 and references therein), but the contributions from tributaries remain poorly characterized. High concentrations of total Hg (THg) and MeHg have been previously reported for the Raisin River water some 20 times that of levels in St. Lawrence River water into which it drains (Maharaj 2008).

The purpose of the project is to provide a preliminary estimate of the loadings of Hg from tributaries draining into Lake St. Francis (the section of the river which bounds the AOC) and to evaluate the contributions to elevated levels observed in some fish.

When coupled with discharge rate data collected in the tributary outlet sampling program, it is possible to calculate and evaluate the relative inputs of Hg from tributaries to Lake St. Francis. This project will provide useful information towards a more comprehensive assessment of Hg sources to Lake St. Francis fish.

Methods

Hg samples were taken as part of a tributary sampling program from eight major tributaries that drain into the north (Ontario) section of Lake St. Francis (Figure 2). Lake St. Francis is a lake-like section of the St. Lawrence River bounded by the Moses-Saunders dam at the west and the Beauharnois dam at the east. Major tributaries that were not sampled include the Delisle and Beaudette Rivers which drain in the Quebec section of the River, Grey's Creek at Cornwall (which was not past of the routine monitoring program), and the main tributaries on the South Shore of Lake St. Francis.

Samples were taken monthly from July through October 2008 and in April and June 2009. Duplicate samples were taken directly into 1-L pre-cleaned polyethylene bottles using a "clean hands - dirty hands" technique and stored cold in dedicated coolers while in the field.

Additional field measurements included temperature, specific conductivity, dissolved oxygen, water height and velocity. Samples were also taken for suspended solids, turbidity, total

phosphorus, total dissolved phosphorus, chlorophyll a, E. coli bacteria and nitrates and nitrites (RRCA 2009). Hg samples were preserved with concentrated HCl (5 mls/L) and shipped on ice to the University of Ottawa Hg laboratory for analysis of THg and MeHg using established ultra-trace techniques (Ridal et al., 2009). Results were analyzed using MiniTab ® statistical software. All Hg concentration data were log transformed to normalize the distribution of the data and to reduce heteroscadescity, with the exception of the Fraser Creek results where log transformation did not improve normality.

Results and Discussion

Tributary Water Quality Characteristics

Overall, the tributaries are alkaline with median pH values ranging 8.3-8.8. They have relatively high conductivity (439-700 uS/cm), and low median suspended solids values (1-15 mg/L, Table 1). They are eutrophic systems with median TP values ranging from 0.050-0.173 mg/L and median nitrate values ranging 0.18-3.75 mg /L. While median dissolved oxygen values ranged 54-120%, low oxygen conditions can be found in some tributaries during low flow conditions in late summer Water temperatures during sampling ranged 0.5-24^{o}C.

THg Concentrations

Annual geometric mean THg values ranged from a low of 0.69 ng/L for the Raisin River to a high of 1.62 ng/L for Fraser Creek. These values are 2 to 4-fold higher than summertime mean concentrations collected from uncontaminated embayments in the St. Lawrence River near Cornwall (Ridal et al, 2009). In order of increasing values the pattern was: Raisin, Gunn, Finney, Sutherland, Westley's, Wood, Fraser, and Pattingale (Figure 3). Concentrations in the individual tributary samples varied about a factor of four between low and high concentrations with a range for the entire dataset between 0.34 and 4.39 ng/L. The range in values for Lake St. Francis tributaries are similar to concentrations recently measured in the Yamaska and St. Francois rivers, both of which drain agricultural watersheds and discharge to the St. Lawrence River at Lake St. Pierre (Caron and Lucotte, 2008). THg in filtered samples averaged 1.14 ng/L and particulate-bound THg averaged 1.16 ng/L for a combined average of 2.30 ng/L.

No strong seasonal patterns are evident for THg concentrations in the tributaries although in general there is a decline in concentrations in the fall (Figure 4). There was no notable correlation between THg values and specific conductivity, TSS, temperature or % wetland for the combined dataset. Dissolved organic carbon which often correlates with Hg concentrations was not measured.

Tributary THg values are much lower than the Provincial Water Quality of Objective of 200 ng/L and the Canadian Water Quality Guideline for the Protection of Aquatic Life is 26 ng/L. The authors of the Guideline acknowledge that the 26 ng/L aquatic life criterion, while protecting the health of the fish themselves, may not prevent the unacceptable bioaccumulation of Hg in fish tissue, which would adversely affect the health of humans consuming the fish (Environment Canada 2003).

MeHg Concentrations

Annual geometric mean MeHg values ranged from a low value of 0.13 ng/L for the Raisin River to a high of 0.25 ng/L for Fraser Creek (Figure 5). These values are 4-8 fold higher that summertime mean concentrations in St. Lawrence River water collected from uncontaminated embayments near Cornwall (Ridal et al, 2009). In order of increasing MeHg concentrations, the following pattern was observed: Raisin, Gunn, Wood, Finney, Westley's, Sutherland, Pattingale and Fraser. Concentrations in individual samples ranged from a low of 0.020 ng/L to a value as high as 3.78 ng/L although most values were below 1.2 ng/L.

Seasonally, greatest concentrations were observed in spring and early summer with minimum values generally found in the fall (Figure 6). No significant correlations were observed between MeHg and specific conductivity, TSS and total phosphorus. MeHg concentrations are weakly correlated with temperature ($p<0.001$, $r^2=0.4$, Figure 7).

It is estimated, based on conservative assumptions, that MeHg concentrations below 0.007 ng $Hg \cdot L^{-1}$ may be required to protect all wildlife species in Canada while concentrations above 0.2 ng $Hg \cdot L^{-1}$ may pose a risk to wildlife species (CCME 2003). MeHg concentrations in water between these limits may be hazardous to some wildlife depending on their feeding habits (preferred prey items), trophic level and bioaccumulation factors of prey items (Environment Canada 2003).

Percent MeHg

The %MeHg to THg is considered an indication of the net MeHg production within a site. The % MeHg varied ranged from 19%-29% (Figure 8). Typically, these %MeHg values are relatively high as MeHg typically represents less than 10% of the total Hg in surface waters, whereas values up to 30% are generally associated with perturbed systems such as newly formed reservoirs (CCME 2003).

There is an interesting seasonal trend to the strength of the correlation between MeHg and THg. (Figure 9). The strength of the relationship between MeHg and THg strengthens from spring to summer (r^2 increases from 0.61 to 0.76) but falls apart in late fall ($r^2=0.0001$). Water temperatures at the time of the November sampling (average 1.0 ^oC) were much lower than at other sample times (i.e. average water temperature 7.5^oC at the time of the April sampling event). Since MeHg formation is bacterially driven and dependent on temperature (Figure 7), the rate of MeHg production is lowest in the winter months.

Tributary Loadings of Hg to the St. Lawrence River

While the Hg data collected in this investigation comprise only six collections, they represent collections made in spring, summer and fall when the major of runoff is expected to occur. One sampling event occurred in early spring (April) that coincided with the spring freshet. The averages of these values are therefore are expected to be a reasonable representation of the annual variations in Hg concentrations and provide a starting point for estimating tributary loads of Hg to Lake St. Francis.

Staff gauges and water velocity measurements were undertaken so that the discharge rates of the individual tributaries could be estimated. Unfortunately, flow rates for most tributaries were very low at the sampling sites and discharges rates could not be calculated during most of the sampling dates. An alternative approach to estimate the Hg loading and the relative importance of each of the tributaries has been used recently to determine TP loading (AECOM 2009). This approach uses the watershed area for each tributary, a constant runoff value and annual mean concentration data to estimate the mass loadings for each tributary.

An examination of gauged rivers in the Raisin Region provided the following runoff coefficients based on the available long term data (personal communication, Phil Barnes, Source Water Planning Engineer, RRCA, 2010):

Raisin River	0.40 m/yr
Beaudette River	0.45 m/yr
Delisle River	0.39 m/yr

Therefore, a mean value of 0.41 m/yr was used to calculate mass loadings from the Raisin Region tributaries.

Using this simple approach, the annual total Hg loading to Lake St Francis is calculated to be 277 g/yr with an estimated uncertainty range of 210-386 g/yr based on propagation of the uncertainties for the Hg data (Table 2). The annual precipitation amount measured at Cornwall during the sampling period was 822 mm which is less approximately 20% less than the long term mean of 1002 mm/yr for Cornwall area (Environment Canada 2009). The bulk of the Hg export (85%) is associated with the Raisin River (60%), Sutherland Creek (14%) and Fraser Creek (11%) while the other tributaries individually account for <5% of the remainder loadings (Figure 10).

The annual total MeHg loading is calculated to be 50 g/yr with an uncertainty range of 40-66 g/yr based on propagation of the error in MeHg data (Table 3). The bulk of the loading (86%) is from three tributaries: the Raisin River accounts for 64% of the loading, Sutherland Creek contributes 12% and Fraser Creek 10% of the total. The other tributaries, while they may contain higher concentrations, individually contribute 5% or less of the loadings (Figure 10).

The three main tributaries have the largest watersheds and therefore the greatest discharge amounts but also contain the largest fraction of wetland at 15% (Fraser), 10% (Raisin) and 3% (Sutherland) (Table 4). A correlation between THg concentration and % wetland for each tributary was however not significant. Research undertaken in the Raisin River indicates that headwater wetlands, particularly bogs, are an important source of THg and MeHg and DOC to the River (Maharaj 2008). Bogs contain peat, which accumulate pollutant metals from long-term atmospheric deposition; these include Al, Cr, Ni, Cu, Zn, Cd, Hg and Pb (Shotyk 1992). The greatest impact appears to be when the wetlands are disturbed for instance when water levels are altered. Metals can be released from peat by drying and rewetting conditions. Drying causes oxidation of sulphur compounds and production of sulphuric acid which lowers porewater pH and, with rewetting, mobilizes metals (Tipping et al, 2003). It is estimated that 12% of the Fraser wetland is composed of bog and may account for the higher than expected concentrations of MeHg and THg from this tributary.

Comparisons to Mercury Loadings to the St. Lawrence from other Sources

A recent inventory of Hg sources has not been done for Lake St. Francis. However, it is interesting to compare these values with historical Hg loadings from point sources at Cornwall (summarized in Dreier 2000). Loadings of THg in 1989-1990 from all Cornwall point sources (Domtar, ICI Canada, ICI Conpack, Cornwall Chemicals, Courtaulds, and the Cornwall Water Pollution Control Plant) was 148 g/day (54.0 kg/yr). There were also sizable air emissions from the ICI Canada chlor-alkali plant with an average value for 1993 of 434 g/day. For comparison, the total upstream loadings to the north channel at Cornwall of 104 g/day (38.0 kg/day) with a river-wide estimate 304 g/day (111 kg/yr) (Quémerais et al., 1999).

Present day loadings from Cornwall point sources have been significantly reduced because of the closure of all major industrial sources. Current loadings from sources upstream of Cornwall are expected to be similar to the mid-90s, as current concentrations of THg and MeHg in main channel St. Lawrence River water are similar to those measured by Quémerais et al., (1999) (Ridal et al., 2010). Despite the large loading values calculated from upstream sources, much of the THg loading is associated with the main current which discharges through the main channel of Lake St. Francis. Tributary loadings, on the other hand, influence near shore and wetland areas and have the potential to impact near shore fish communities.

Relationship to Fish Tissue Concentrations

Generally, the Hg criteria for fish consumption are set as tissue concentrations guidelines and not as water quality criteria.

In some cases in the United States where waterborne loadings appear to be the main source of 0Hg to fish and where limits on loadings are to be set, the US-EPA has identified a water quality objective based on bioaccumulation factors (BAF). For instance, a THg limit of 2.8 ng/L has been set for the Savannah River in Georgia (USEPA 2001). This value relates to a concentration that is expected to be protective for fish consumption (limit of 0.23 mg/kg) using a methyl/total Hg ratio of 3.8% and a bioaccumulation factor (BAF) for MeHg in sportsfish (model fish is a largemouth bass of 315 millimeters in length) of 4×10^6 where:

$$BAF = C_{MeHg_{fish}} / C_{MeHg_{water}} \quad (1)$$

BAF values are site specific and depend among other things on the chemical properties of the water body (e.g. pH, alkalinity, DOC). A recent survey of Eastern Ontario lakes and rivers has been carried out where fish Hg concentrations were determined along with the concentrations of THg, MeHg and other chemical properties (Hickey et al. 2005). These lakes do not contain known Hg sources or contaminated sediments. Based on a subset of the data with chemical properties similar to the Lake St. Francis tributaries, an average BAF value of 1.3×10^6 is derived for juvenile (10 cm) yellow perch (Appendix 1).

This BAF values from regional data can be used to estimate the MeHg values of small fish that habitat these tributaries and that may serve as a prey for larger fish like walleye. The Raisin River, for instance, is an important walleye spawning run. Based on the BAF, the predicted Hg values range from 0.19 mg/kg in the Raisin River to 0.33 mg/kg in Fraser Creek (Table 5). This

range of values is very similar to the most stringent Ontario fish consumption advisory of 0.26 mg/kg for sensitive human populations such as children, pregnant women, and frequent fish consumers (Ontario Ministry of the Environment 2007). This range of predicted fish concentrations is consistent with Hg concentrations in yellow perch (mean length 16.0 cm) collected from various tributaries and wetlands areas from around Lake St Francis (including south shore) ranged between 0.07-0.34 mg/kg with mean value of 0.16 mg/kg (Larivière 2001).

A typical food chain multiplier between a non-piscivorous fish such as small perch and a large piscivorous predator like walleye is about 3 (Grapentine et al. 2003). This multiplier results in predicted concentrations ranging 0.6 to 1.0 mg/kg for walleye regularly consuming prey within these tributaries. This range matches the range of Hg concentrations measured walleye from Lake St. Francis. The Hg concentration for a standard 50 cm walleye is 0.6 mg/kg with a range between 0.2 and 1.8 mg/kg based on a regression analysis of recent MOE sport fish monitoring data for Lake St. Francis (Figure 1). It is therefore possible that tributaries that discharge into the St. Lawrence contribute to elevated Hg concentrations in Lake St Francis sport fish.

Conclusions and Recommendations

The following conclusions are made:

- Mean annual concentrations of THg and MeHg ranged from 0.69-1.62 ng/L and 0.13-0.25 ng/L respectively in AOC tributaries, which are 4-8 times higher than background St. Lawrence River concentrations
- Tributaries are a source of THg and MeHg to the St. Lawrence River with three tributaries (Raisin, Sutherland and Fraser) providing approximately 85% of the loadings which on the order of 280 and 50 g/yr, respectively.
- It is estimated that MeHg in small (10 cm) yellow perch residing in these tributaries would range between 0.19-0.33 mg/kg, in some instances exceed the MOE's fish consumption criterion for sensitive populations.
- Small yellow perch and similar prey could contribute to elevated levels of Hg in large piscivores that frequently forage in tributaries or at tributary mouths.

Recommendations:

- Undertake further characterization of concurrent mercury and flow data to improve the loading estimates
- Include measurements for Greys Creek, Delisle and Beaudette rivers and, preferably, south shore tributaries to fully characterize tributary loadings to Lake St. Francis.
- Conduct additional measurements in tributary headwaters and along the course of the watershed to characterize source of Hg to these tributaries
- Characterize wetland conditions (disturbed vs. undisturbed) in headwater wetlands
- Undertake direct measurements of Hg concentrations in small forage fish from these small tributaries
- Over the longer term, develop a Hg mass balance model for Lake St. Francis that would characterize the main loadings and identify the significance of tributary loadings.

References

AECOM. 2009. Evaluation of remedial action plan tributary nutrient delisting criteria for the St. Lawrence River, Cornwall, Area of Concern. Report prepared for the Ontario Ministry of the Environment, Project Number 111293. 57 pp.

Caron,S. and M. Lucotte, 2008. Regional and seasonal inputs of mercury in Lake St. Pierre (St. Lawrence River), a major commercial and sports fisheries in Canada. *Water, Air and Soil Pullution*. 195:85-97.

CCME. 2003. Canadian Environmental Quality Guidelines for the Protection of Aquatic Life. Mercury: Inorganic and Methylmercury. Accessed at: http://www.ceqg-rcqe.ccme.ca/download/en/191/

Dreier. S.I. 2000. Cornwall, Ontario waterfront sediment review of environmental studies from 1970 to 1999. Ontario Ministry of the Environment, Eastern Region and Environment Canada, Environmental Conservation Branch, Restoration Programs Division. ISBN 0-7778-9545-5

Environment Canada. 2003. Canadian water quality guidelines for the protection of aquatic life: inorganic mercury and methylmercury. Scientific Supporting Document. Ecosystem Health: Science-based Solutions Report No. 1-7. National Guidelines and Standards Office, Water Policy and Coordination Directorate, Environment, Canada. Ottawa. 107 pp.

Environment Canada. Accessed at http://www.climate.weatheroffice.ec.gc.ca

Grapentine, L., D Milani, & S. Mackay, 2003. Assessment of the potential for mercury biomagnification from sediment in the St. Lawrence River (Cornwall) Area of Concern. Environment Canada Publication, National Water Research Institute, Burlington, Ontario, Canada.

Harada, M. 1995. Minamata disease: Methylmercury poisoning in Japan caused byenvironmental pollution. Critical Reviews in Toxicology, 25:1–24.

Hickey, M.B.C., J.C. Gibson, J.R. Hill, J.J. Ridal, J. Davidson, G.M. Richardson, J. Holmes, D.R.S. Lean. 2005. The influence of lake chemistry on methyl mercury concentrations in lake water and small fish in Ontario and Nova Scotia. Chapter 15 in: Mercury Cycling in a Wetland-Dominated Ecosystem: A Multidiciplinary Study. N. O'Driscoll ed. SETAC Press, Pensacola, Florida.

Larivière, Emilie. 2001. Mercury in yellow perch (Perca Flavescens) from Lake St. Francis and surrounding tributaries of the St. Lawrence River. M.Sc. thesis, University of Ottawa, Ottawa, Ontario. 125 pp.

Maharaj, S. 2008. Factors contributing to elevated levels of methyl and total mercury related to alteration in wetland conditions and agricultural activity (the Raisin River Watershed). M.Sc. thesis, University of Ottawa, Ottawa, ON.

Ontario Ministry of the Environment. 2007. Guide to eating Ontario sport fish 2007-2008 – Twenty-fourth edition, revised. Queen's Printer for Ontario, Canada.

Quémerais,B., D. Cossa, B. Rondeau, T.T. Pham, P. Gagnon and B. Fortin. 1999. Sources and fluxes of mercury in the St. Lawrence River. *Environmental Science and Technology*. 33, 840-849.

Ridal, J.J., L.E. Yanch, A.R. Fowlie, N.R. Razavi, T.M. Delongchamp, E.S. Choy, M. Fathi, P.V. Hodson, L.M. Campbell, J.M. Blais, M.B.C. Hickey, E.Yumvihoze, D.R.S. Lean. 2009. Potential causes of enhanced transfer of mercury to St. Lawrence River biota: implications for sediment management strategies at Cornwall, Ontario, Canada. *Hydrobiologia* (published on line) DOI 10.1007/s10750-009-9951-1.

Shotyk, W. H. Wayne Nesbitt, Fyfe and William S. 1992. Natural and anthropogenic enrichments of trace metals in peat profiles. *International Journal of Coal Geology*, 20, 49-84.

Tipping, E., E.J. Smith, A.J. Lawlor, S. Hughes, and P.A. Stevens. 2003. Predicting the release of metals from ombrotrophic peat due to drought-induced acidification. *Environmental Pollution* 123. 239–253

USEPA. 2001. TOTAL MAXIMUM DAILY LOAD (TMDL) for total mercury in fish tissue residue in the middle & lower savannah river (Ga) watershed. 76 pp. Accessed at: http://www.epa.gov/Region4/mercury/TMDLs.htm

Table 1. Summary of water quality characteristics measured during the study. Shown are number of observations (N), median values, and range.

Measure	Site	N	Median	Minimum	Maximum
Temperature (^{o}C)	Finney	12	10.4	0.7	19.3
	Fraser	12	13.1	0.9	19.6
	Gunn	12	10.3	0.9	19.6
	Pattingale	10	13.5	3.0	15.6
	Raisin	12	14.5	1.0	23.8
	Sutherland	12	10.1	0.6	20.6
	Westley's	10	11.2	0.5	20.8
	Wood	12	11.0	0.7	21.0
Specific conductivity (uS/cm)	Finney	12	600	553	769
	Fraser	12	439	418	539
	Gunn	12	700	485	2309
	Pattingale	10	526	497	690
	Raisin	12	481	407	543
	Sutherland	12	592	530	711
	Westley's	10	533	281	605
	Wood	12	549	477	868
pH	Finney	12	8.48	7.80	9.30
	Fraser	12	8.33	7.80	8.99
	Gunn	12	8.31	7.90	8.85
	Pattingale	10	8.45	8.13	9.06
	Raisin	12	8.83	8.30	9.15
	Sutherland	12	8.52	7.87	9.03
	Westley's	10	8.67	8.07	9.05
	Wood	12	8.54	7.70	10.20
DO (%)	Finney	12	83	16	145
	Fraser	12	71	7	118
	Gunn	12	88	42	126
	Pattingale	10	120	8	148
	Raisin	12	96	47	132
	Sutherland	12	98	37	147
	Westley's	10	123	47	139
	Wood	12	54	13	125
TSS (mg/L)	Finney	12	6	<1	22
	Fraser	12	3	1	5
	Gunn	12	7	<1	34
	Pattingale	10	8	5	66
	Raisin	12	1	<1	5
	Sutherland	12	15	11	26
	Westley's	10	10	1	19
	Wood	12	7	2	54

Table 1 (Continued). Summary of water quality characteristics measured during the study. Shown are number of observations (N), median values, and range.

Measure	Site	N	Median	Minimum	Maximum
TP (mg/L)	Finney	12	0.134	0.053	0.224
	Fraser	12	0.050	0.040	0.083
	Gunn	12	0.067	0.041	0.114
	Pattingale	10	0.173	0.120	0.440
	Raisin	12	0.054	0.032	0.077
	Sutherland	12	0.072	0.057	0.092
	Westley's	10	0.050	0.185	0.328
	Wood	12	0.053	0.056	0.107
Nitrates (as N mg/L)	Finney	12	1.24	0.014	4.74
	Fraser	12	0.18	0.005	0.60
	Gunn	12	3.44	0.008	6.54
	Pattingale	10	3.75	0.040	5.63
	Raisin	12	0.45	0.004	1.51
	Sutherland	12	1.45	0.006	3.84
	Westley's	10	2.98	0.024	5.99
	Wood	12	1.52	0.050	5.12

Table 2. Geometric mean annual total mercury (THg) and methyl mercury (MeHg) concentrations, 95% confidence intervals, watershed areas, areal and annual loads from monitored tributaries. The uncertainty in the annual load is propagated from the 95% confidence limits of THg measurements and does not take into account other factors.

THg

Tributary	Mean THg (ng/L)	Lower 95% C.I. (ng/L)	Upper 95% C.I. (ng/L)	Watershed Area (ha)	Areal Load (g/ha/yr)	Annual Load (g/year)
Finney	0.889	0.691	1.14	3191	0.00364	12
Fraser	1.618	1.19	2.05	4621	0.00663	31
Gunn	0.853	0.654	1.11	1039	0.00350	4
Pattingale	1.659	1.23	2.24	900	0.00680	6
Raisin	0.693	0.419	1.15	57982	0.00284	165
Sutherland	1.175	0.841	1.64	7922	0.00482	38
Westley	1.143	0.762	1.72	1588	0.00469	7
Wood	1.123	0.703	1.79	3086	0.00461	14
				Total Load		277
				Uncertainty		210 - 386

MeHg

Tributary	Mean MeHg (ng/L)	Lower 95% CI (ng/L)	Upper 95% C.I. (ng/L)	Watershed Area (ha)	Areal Load (g/ha/yr)	Annual Load (g/year)
Finney	0.177	0.086	0.363	3191	0.000724	2
Fraser	0.253	0.170	0.377	4621	0.001038	5
Gunn	0.148	0.098	0.222	1039	0.000606	0.5
Pattingale	0.191	0.087	0.415	900	0.000781	1
Raisin	0.134	0.095	0.190	57982	0.000550	32
Sutherland	0.187	0.075	0.465	7922	0.000765	6
Westley	0.185	0.067	0.504	1588	0.000756	1
Wood	0.176	0.128	0.242	3086	0.000720	2
				Total Load		50
				Uncertainty		40 - 66

Table 3. Land Use Designations in the Tributary Watersheds (from AECOM 2009).

Watershed	% Wetland	% Forested	% Agriculture
Finney	0	21	79
Fraser	15	43	42
Gunn	0	21	79
Pattingale	1	10	89
Raisin	10	40	50
Sutherland	3	23	74

Table 4. Predicted MeHg concentrations in 10 cm perch residing in each tributary based on BAF value for uncontaminated Eastern Ontario lakes and rivers (Appendix 1).

Tributary	Mean MeHg (ng/L)	BAF	Predicted Fish Concentration (mg/kg)
Finney	0.177	1.3×10^6	0.23
Fraser	0.253	1.3×10^6	0.33
Gunn	0.148	1.3×10^6	0.19
Pattingale	0.191	1.3×10^6	0.25
Raisin	0.134	1.3×10^6	0.18
Sutherland	0.187	1.3×10^6	0.24
Westley	0.185	1.3×10^6	0.24
Wood	0.176	1.3×10^6	0.23

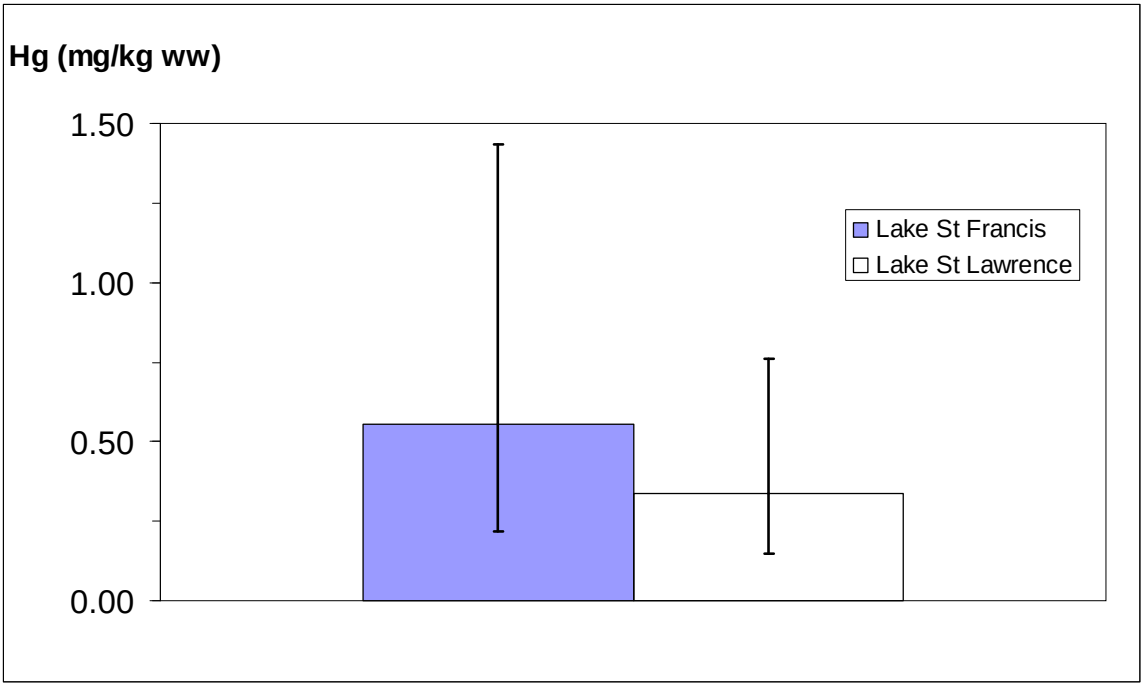


Figure 1**.** Mercury concentrations (and 95% prediction intervals) in 50 cm length walleye from Lake St. Francis and Lake St. Lawrence (above the dam) collected in 2002.

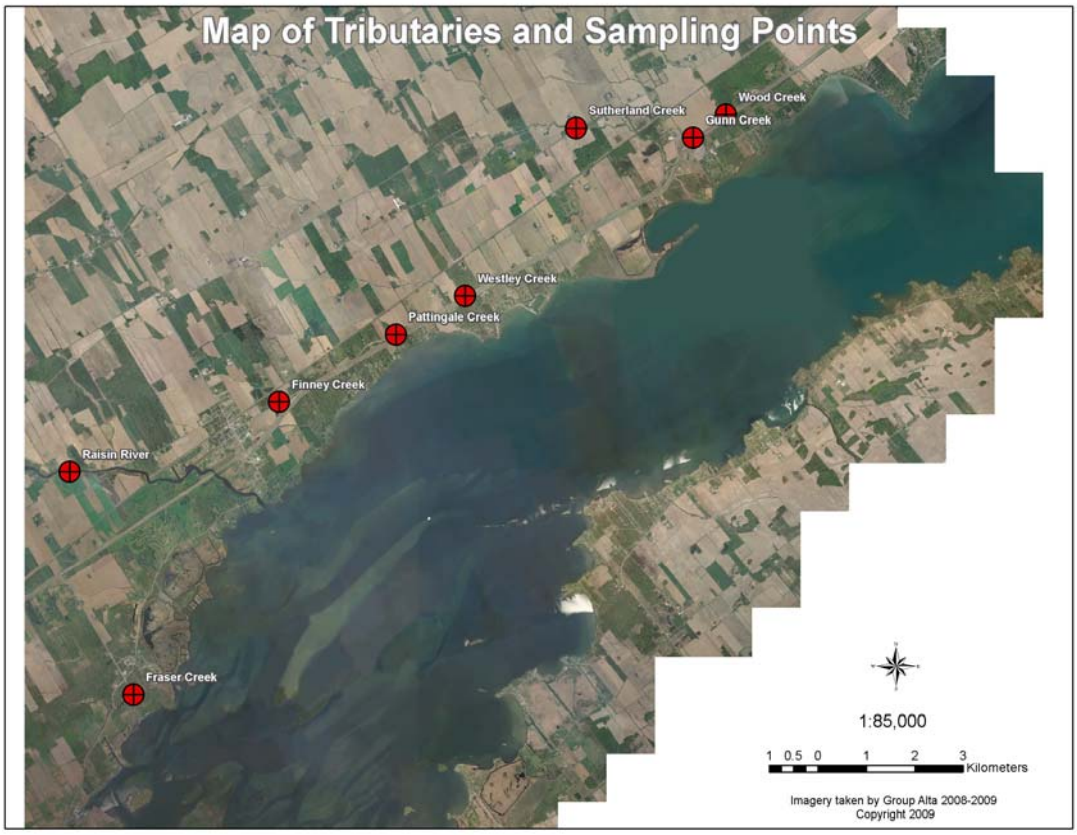


Figure 2. Map of Tributaries and sampling points.

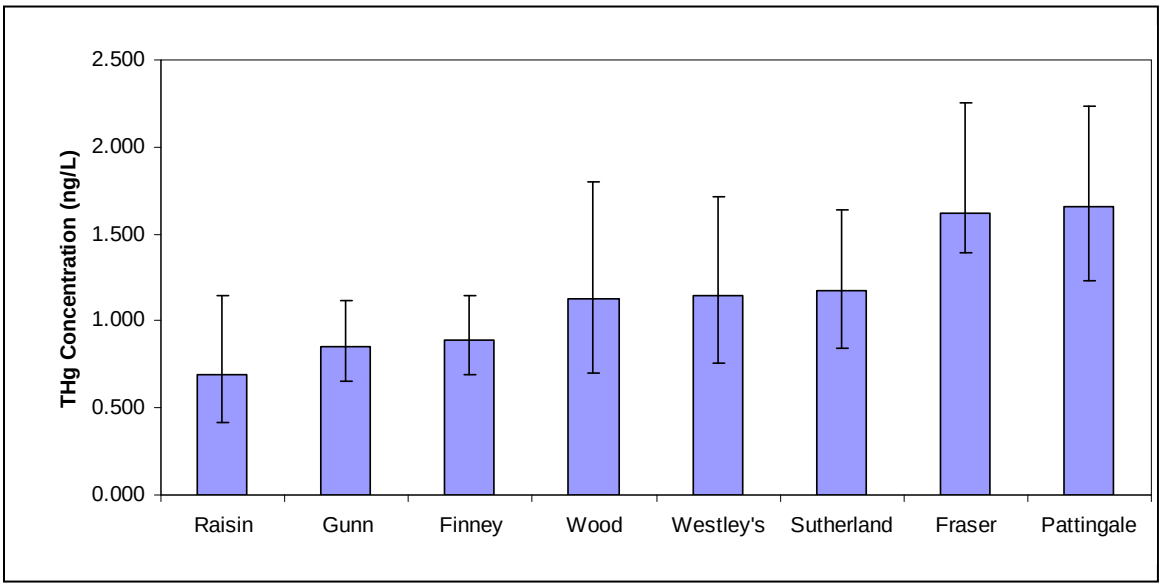


Figure 3. Mean total mercury (THg) data measured in samples collected from tributaries. All data show geometric mean and 95% confidence intervals of the mean except for Fraser Creek data which are arithmetic means. A total of 12 samples were taken on 6 sampling dates for all tributaries except Pattingale and Westley's which had 10 samples.

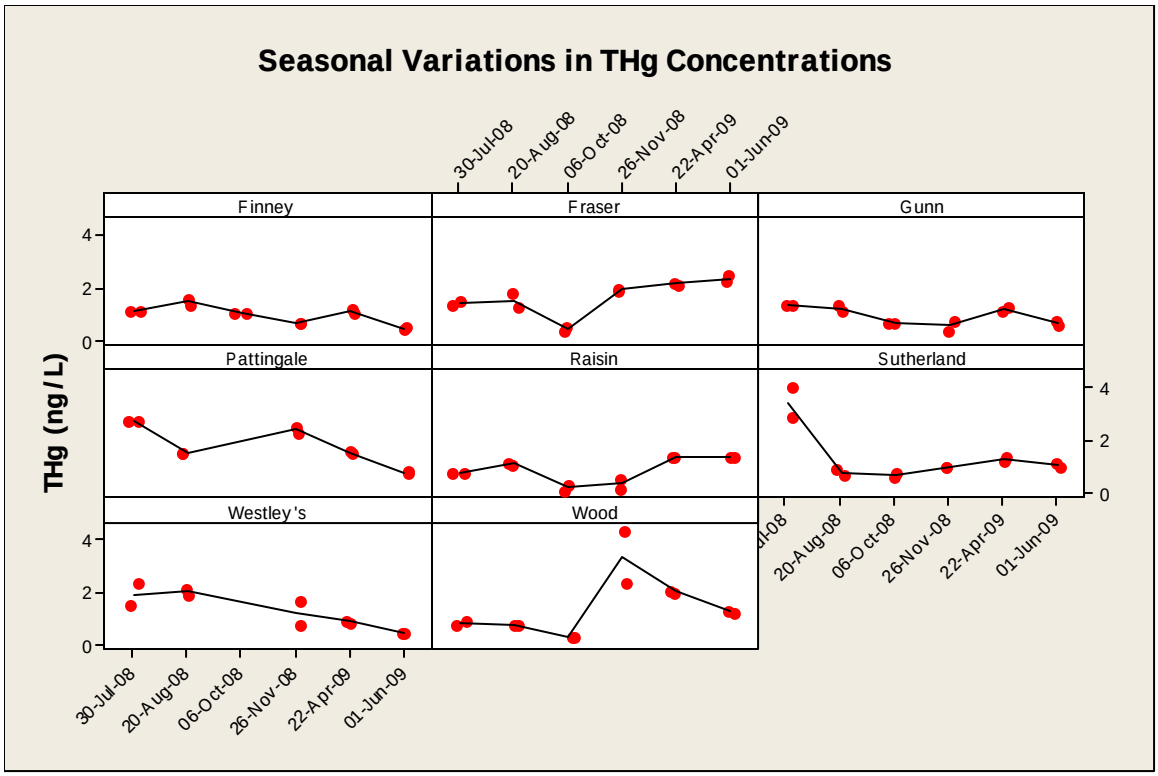


Figure 4. Seasonal variation of total mercury (THg) in the monitored tributaries.

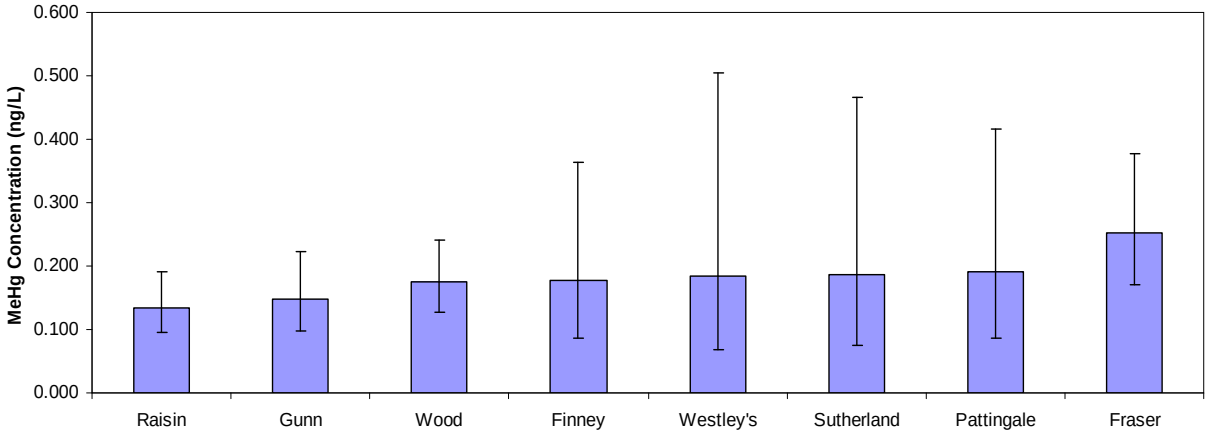


Figure 5: Mean values of methylmercury (MeHg) in monitored tributaries. All data show geometric mean and 95% confidence intervals of the mean except for Fraser Creek data which are arithmetic means. A total of 12 samples were taken on 6 sampling dates for all tributaries except Pattingale and Westley's which had 10 samples.

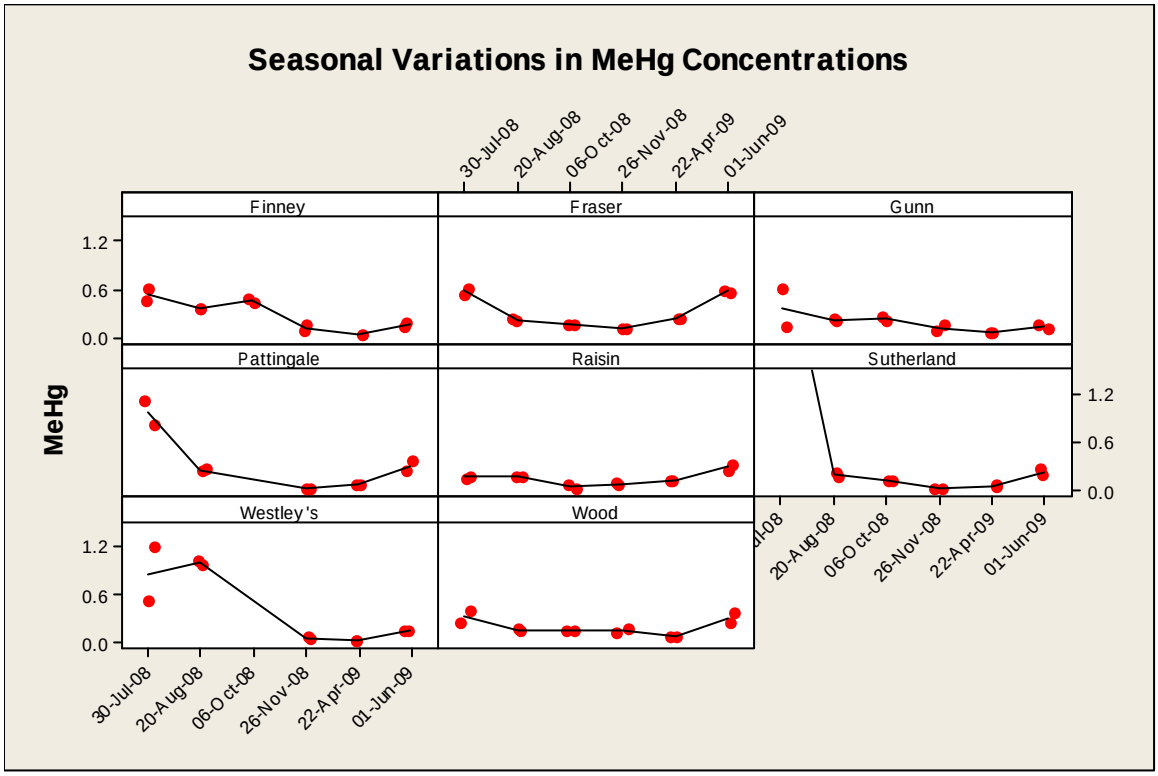


Figure 6. Variations in MeHg concentrations in the tributaries over the sampling period.

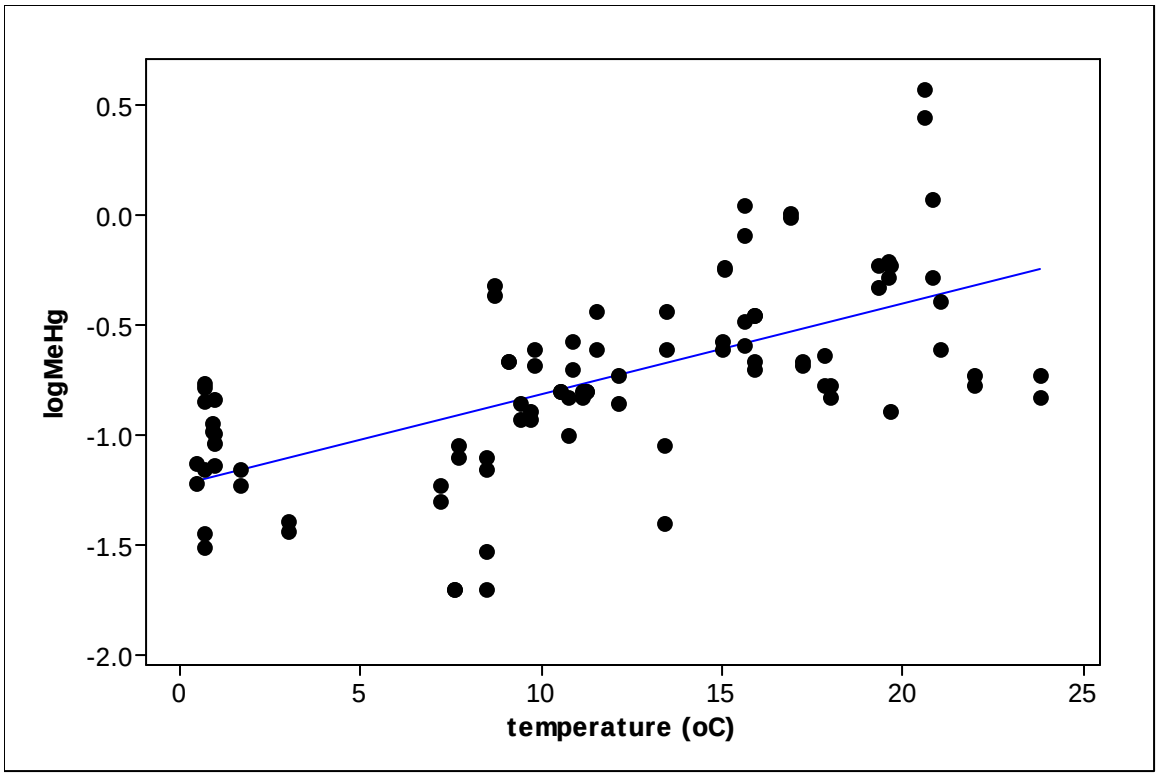


Figure 7. Dependence of MeHg concentrations on temperature (data for all tributaries).

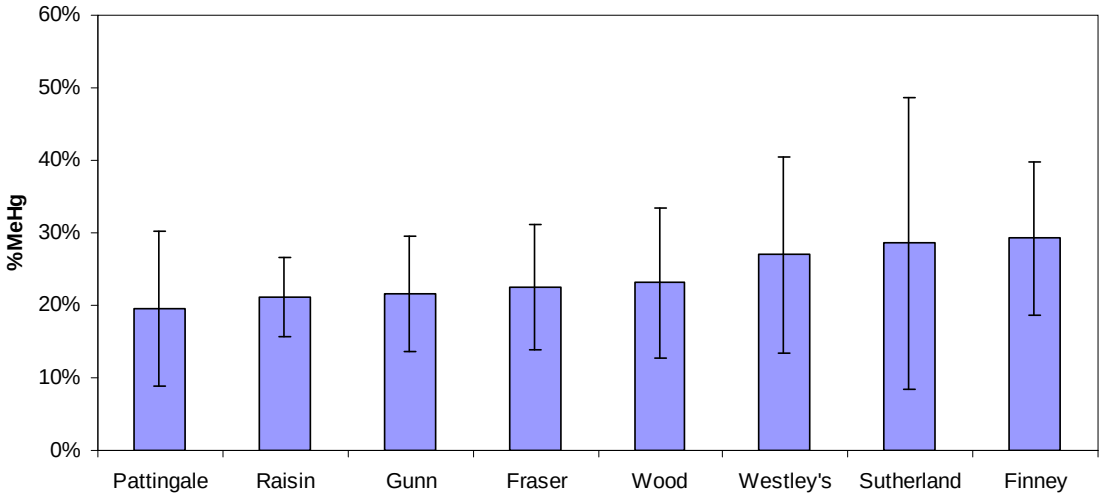


Figure 8. Mean percent methyl mercury (%MeHg) of total mercury for individual tributaries (n=12 for all sites except for Westley and Pattingale where n=10).

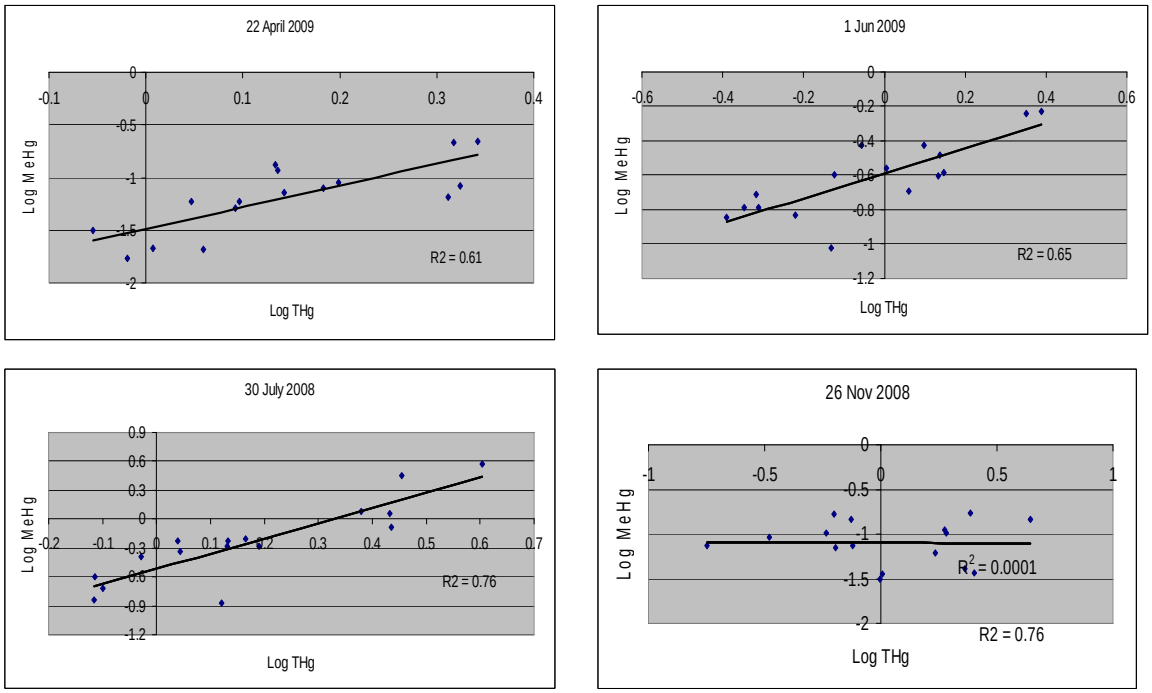
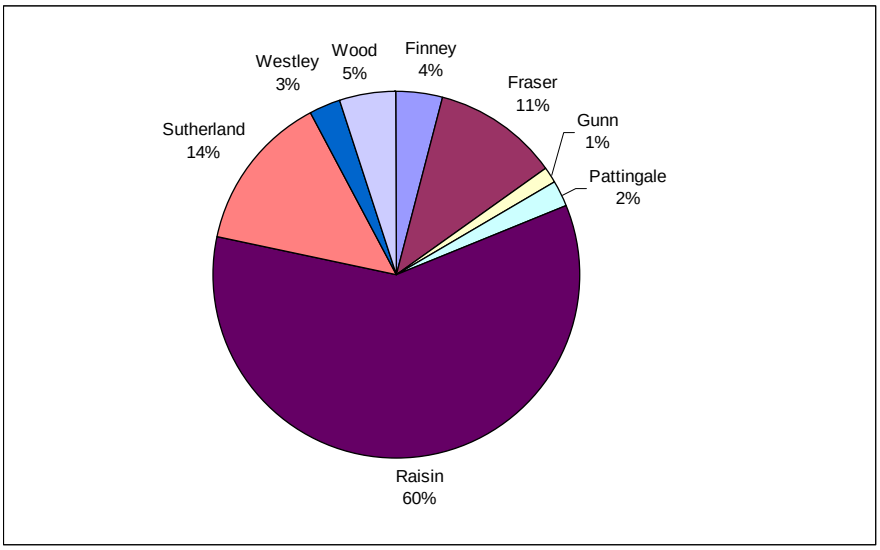


Figure 9. Relationship (R^2) between MeHg and THg with season. The relationship improves from spring to summer but fall apart in late fall.

THg



MeHg

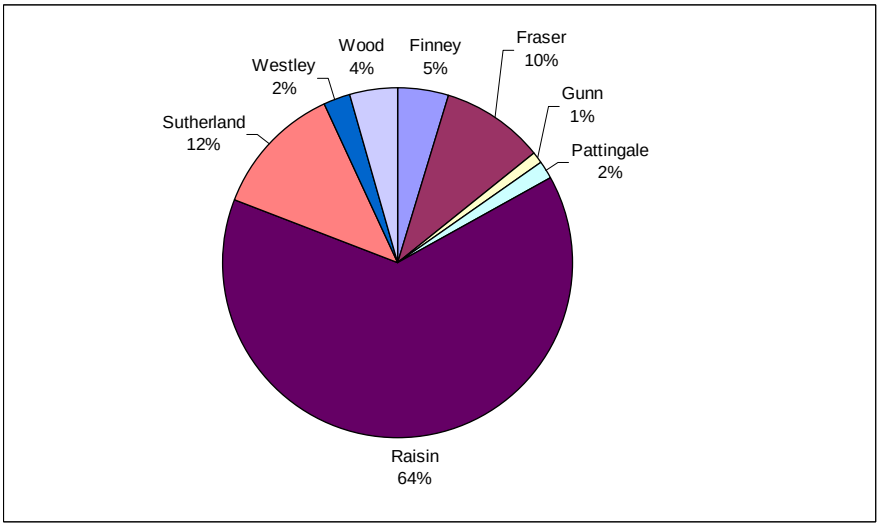


Figure 10. Proportions of total mercury (THg) and methyl mercury (MeHg) loads contributed by each tributary.

APPENDIX 1

Water chemistry characteristics, mercury concentrations in small yellow perch and bioaccumulation factors for selected Eastern Ontario lakes and rivers (data from Hickey et al. 2005).

Appendix 1: Water chemistry characteristics, mercury concentrations in yellow perch and bioaccumulation factors for Eastern Ontario lakes and rivers.

LAKE	LAT	LONG	pH	DOC (mg C/L)	ALK. (mg/L)	SP. COND. (uS/cm)	TP (ug/L)	TOTAL Hg (ng/L)	MeHg (ng/L)	MeHg (%)	Yellow Perch N	Length (cm)	Fish [Hg] (ng/g)	BAF
BEAVER	44.500N	77.033W	8.0	7.6	62	157	12.3	1.1	0.029	3	6	10	48	1.7E+06
BELLAMYS	44.717N	76.033W	9.1	9.9	125	274	13.8	0.7	0.058	8	6	10	64	1.1E+06
ELOIDA	44.667N	75.967W	8.9	8.5	127	282	13.0	1.1	0.094	9	4	9	95	1.0E+06
GRAHAM	44.450N	76.150W	8.6	7.8	78	190	18.0	0.8	0.070	9	8	10	75	1.1E+06
LIME	44.400N	77.117W	8.5	5.2	192	361	13.0	0.8	0.048	6	11	11	120	2.5E+06
LOCH GARRY	45.250N	76.700W	8.7	11.5	99	209	20.1	1.0	0.071	8	10	14	102	1.4E+06
NORWAY	45.333N	76.717W	8.9	8.6	110	225	6.6	0.6	0.034	6	9	10	58	1.7E+06
ODESSA	44.317N	76.683W	9.1	13.1	87	277	41.1	1.1	0.180	17	10	12	81	4.5E+05
OPINICON	44.567N	76.317W	8.5	6.8	90	219	19.4	0.9	0.054	6	3	10	49	9.0E+05
SAND	44.567N	76.267W	8.8	7.0	75	191	19.4	1.0	0.045	5	7	7	15	3.3E+05
TROY	44.517N	76.267W	9.2	6.5	76	224	26.6	1.0	0.020	2	4	9	44	2.2E+06
											average	10	68	1.3E+06