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Present and historical accumulation of mercury in Ontario lake sediments

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Present and historical accumulation of mercury in Ontario lake sediments

By

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Thesis submitted to the
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Abstract

Mercury (Hg) is a persistent contaminant present naturally in our environment but, as a result of anthropogenic activity, has now accumulated in lake sediments at concentrations 2.2 times greater than those found in pre-industrial sediments (pre-1850) (Chapter 2). However, present spatial patterns of mercury accumulation do not match patterns in natural mercury accumulation (Chapter 4). Once spatially uniform across south-central Ontario, mercury concentrations in present-day lake sediment display strong spatial correlation. Further, the broad scale spatial patterns (>500 km) which correlate with mean annual precipitation (MAP) found to significantly predict pre-industrial sediment Hg, has now been replaced with finer scale spatial patterns (<120km). Rather than one significant spatial scale explaining sediment Hg, as during the pre-industrial era ($p = 0.01$), present sediment Hg are predicted by more than one spatial scale ($p < 0.001$, $p < 0.001$) both of which are highly correlated with lake pH. While MAP and lake pH explain much variance in mercury accumulation, their significance is spatially dependent. In addition to differences in spatial trends, models which suggest that pre-industrial sediment Hg was in steady state with watershed accumulation do not apply to present day Hg accumulation (Chapter 2). Instead, Hg enrichment in lake sediment decreased as a function of drainage ratio ($R^2 = 0.458$, $p = 0.0001$), suggesting that Hg export from watersheds may be lagging behind atmospheric Hg deposition. The enrichment of Hg since the pre-industrial era is also influenced by the amount of open water ($r = 0.91$, $p = 0.035$), mining activity ($r = 0.94$, $p = 0.019$) and organic deposits within surficial geology ($r = -0.91$, $p = 0.034$) which lead to local hot and cold spots (Chapter 4). There is a close link between the present-day sediment Hg concentrations and that in dorsal muscle of smallmouth bass (*Micropterus dolomieul*) ($r = 0.92$, $p = 0.0002$) (Chapter 3). However, the discrepancies that do exist between these two components are determined by landcover, longitude, and dissolved organic carbon.

An examination of methylmercury in two catchments revealed that the concentration of methylmercury in stream water from ten watersheds is predicted from a time sensitive (lagged regression) interaction among sulfate ($t_{partial} = 9.60$, $p < 0.001$), dissolved organic carbon ($t_{partial} = 7.06$, $p < 0.001$), and temperature ($t_{partial} = 4.44$, $p < 0.001$) (Appendix A). The error of which decreases exponentially with increasing wetland size ($R^2 = 0.838$, $p = 0.0105$). The difference between methylmercury inflow and outflow ($MeHg_{Net}$) within these two catchments (a dystrophic and an oligotrophic lake) was seasonally dependent (Chapter 5). However, seasonal accumulation and loss of methylmercury was significantly larger in magnitude within the dystrophic lake. Further, a net production of methylmercury was found in the dystrophic lake alone (1.9 ± 0.3 mg·d^{-1}). This study examines Hg contamination in a relatively pristine, remote environment which like other regions, has been challenged by contaminants originating from far distances.

Résumé

Le mercure (Hg) est un contaminant persistant, qui se retrouve naturellement dans nos écosystèmes. Cependant, les taux de mercure retrouvés dans les sédiments contemporains excèdent par 2.2 fois les taux de mercure mesurés dans les sédiments préindustriels (avant 1850), ce qui suggère une augmentation de mercure résultant d'activités anthropogéniques (Chapitre 2). Cependant, les modèles courants d'accumulation spatiale pour le mercure ne sont pas représentatifs des modèles de l'accumulation naturelle du mercure (Chapitre 4). Bien que les taux de mercure dans les lacs du centre-sud de l'Ontario étaient stables durant l'ère préindustrielle, de grandes corrélations spatiales furent observées dans les lacs actuels compris dans cette étude. De plus, les patrons spatiaux à grande échelle (>500 Km), corrélant avec la précipitation annuelle moyenne (PAM), qui ont pu prédire les concentrations de mercure dans les sédiments préindustriels, furent remplacés par des modèles à superficie réduite (<120km). Une seule échelle spatiale fut nécessaire pour prédire le Hg dans les sédiments préindustriels ($p = 0.01$), tandis que les taux de Hg dans les sédiments actuels peuvent être predis selon plus d'une échelle spatiale, dont deux ($p < 0.001$, $p < 0.001$) qui sont hautement corrélées avec le pH des lacs. Bien que la PAM et que le pH des lacs ont pu expliquer la majorité de la variation dans l'accumulation de Hg dans les sédiments, leur importance fut spatialement dépendante. En surplus des différences entre les tendances spatiales, les modèles suggérant que l'accumulation de Hg dans les sédiments préindustriels était proportionnelle à l'accumulation de sédiments dans le bassin versant ne s'applique plus à l'accumulation de Hg dans les sédiments actuels (Chapitre 2). Au lieu, l'enrichissement dans les sédiments des lacs actuels diminue en fonction du taux de drainage du lac ($R^2= 0.458$, $p = 0.0001$), suggérant ainsi que le Hg atmosphérique se dépose à des taux plus élevés que la perte de Hg du bassin versant. Le taux d'enrichissement de Hg depuis l'ère industrielle est également influencé par la superficie d'eau ouverte ($r = 0.91$, $p = 0.035$), par l'activité minière, ($r = 0.94$, $p = 0.019$) ainsi que par les dépôts organiques dans la géologie superficielle ($r = -0.91$, $p = 0.034$) menant aux régions locales abondantes ou aux pertes de Hg (chapitre 4). Il existe un lien étroit entre la concentration de Hg dans les sédiments actuels et la concentration de Hg dans le muscle dorsal de l'achigan à petite bouche (*Micropterus dolomieul*) ($r = 0.92$, $p = 0.0002$) (Chapitre 3). Cependant, les différences qui existent entre ces deux facteurs peuvent être déterminées par la superficie du basin versant, par la longitude ainsi que par le taux de carbone organique dissout.

Une analyse du méthyle mercure dans deux lacs de versement a démontré que la concentration de méthyle mercure dans l'eau de dix bassins versants peut être prédite par une interaction (sensible au temps) parmi les sulfates ($t_{partial} = 9.60$, $p < 0.001$), le carbone organique dissout ($t_{partial} = 7.06$, $p < 0.001$), ainsi que la température ($t_{partial} = 4.44$, $p < 0.001$) (Annexe A). L'erreur diminue exponentiellement avec l'augmentation de la taille du marécage ($R^2 = 0.838$, $p = 0.0105$). La différence entre l'apport et la perte de méthyle mercure ($MeHg_{Net}$) dans ces deux lacs (un dystrophique et un autre oligotrophique) fut dépendante de la saison (Chapitre 5). Cependant, l'accumulation saisonnière ainsi que la perte de méthyle mercure étaient significativement plus grandes dans le lac dystrophique. De plus, une production net de méthyle mercure fut seulement retrouvée dans le lac dystrophique (1.9 ± 0.3 mg•d^{-1}). Cette étude porte sur la contamination de Hg dans des lacs relativement isolés et propres, qui comme plusieurs autres lacs, ont subit les conséquences de l'accumulation de contaminants provenant de distances lointaines.

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Contributions by co-authors

There were several key people involved in the construction of each study of this thesis that I would like to acknowledge by manuscript. All statistical analysis including experimental design was performed by myself. The first manuscript of the series was "Factors influencing the achievement of steady state in mercury contamination among lakes and catchments of south-central Ontario". The sampling protocol of this study was a formulation from John Smol of PEARL at Queen's University, Roberto Quilan, Ron Hall, and Jules Blais. Sediment was analyzed for mercury and organic matter by myself, Heather Broadbent, and Trevor Arneson. The second manuscript entitled "Mercury concentrations in smallmouth bass (*Micropterus dolomieu*) in south-central Ontario lakes in relation to lake sediment" was a compilation of data gathered for the first manuscript, as well as a mercury data in smallmouth bass from FISHBASE, a database compiled by Health Canada and the Ontario Ministry of the Environment. "Regional examination of the influence of space, morphometry, and geology on Hg enrichment across Ontario" was based on data compiled for the first manuscript, and I gathered information for landuse, geology and hydrology from a GIS database "Ontario Flow Assessment Techniques" compiled by the Ministry of Natural Resources and the Ontario Ministry of the Environment. The last two manuscripts; "Mass balance approach to methylmercury dynamics in a dystrophic and clear water lake" and "Factors influencing the link between sulfate and methylmercury from ten wetlands" samples were gathered by Ron Ingram. Samples were analyzed for methylmercury content by Tamar Bodek, Kethy Sosso-Kolle, and myself. Financial support was provided by NSERC and the Ontario Ministry of the Environments "Best in Science Fund". David Lean generously donated the measurement of methylmercury in over 600 samples. Andrew Paterson, David Lean and Jules Blais were essential in editing early drafts of each manuscript. Projects involving FISHBASE and regional mercury examination were overseen by Greg Mierle of the Ontario Ministry of the Environment. Two separate investigations by Tamar Bodek "The influence of the spring freshet on MeHg export (M.Sc. Thesis)" and Kethy Sosso-Kolle evaluated "features of the drainage basin on MeHg export (M.Sc. Thesis)" were run concurrently and provided methylmercury data for chapter 5 and appendix A.

Table of Contents

List of Figures

List of Tables

Glossary

AIC	Akaike's information criterion
DOC	Dissolved organic carbon
DMHg	Dimethyl mercury
EF	Enrichment Factor (defined as: $[Hg]_{present\text{-}day\ sediment}$/ $[Hg]_{pre\text{-}industrial\ sediment}$)
Hg	Mercury
Hg^0	Elemental mercury
Hg^{2+}	Inorganic mercury
Hg(II)	Inorganic mercury
LOI	Loss on Ignition
MeHg	Methyl mercury
MMHg	Monomethyl mercury
OM	Organic Matter; all debris with carbon skeleton and is combustible
OMOE	Ontario Ministry of the Environment
THg	Total Hg; including Hg2+, Hg0, and MMHg
TOC	Total organic carbon
SPM	Suspended particulate matter (aka suspended sediment)
GWR	Geographically weighted regression
MAR	Mean annual runoff

Chapter 1

Introduction

The biogeochemical cycle of mercury

The global contamination of surface waters with mercury (Hg) has achieved peak levels in the past several decades. The use of mercury in industrial processes and incorporation into commercial products in our past has increased mercury contamination in all parts of the globe, from the Arctic to the Antarctic (Fitzgerald et al. 2005). Recent studies have observed toxicological effects in aquatic biota at environmentally relevant concentrations (Basu et al. 2005b, Evers et al. 2005, Scheuhammer et al. 2007). Environmental exposures to mercury, primarily dietary consumption, can lead to numerous health effects most notably on the central nervous system (Tchounwou et al. 2003). However, due to its chemical nature, exposure pathways are difficult to assess. In northern boreal forests, like those in the present study, complex patterns of Hg deposition from multiple sources (Lindberg et al. 2007, Bookman et al. 2008) and re-emission from a geologically diverse landscape (Lindberg et al. 1998) create regional hot and cold spots of contamination.

The complexity of Hg contamination has led to early proposals that Hg concentrations in aquatic biota must be attributed to fault lines in the Precambrian Shield (Rasmussen 1993, Friske and Coker 1995). Spatial heterogeneity in Hg contamination led researchers to believe local or site specific influences were the dominant source of Hg to watersheds. While bedrock deposits such as shale have the potential to contribute significant amounts of Hg to the surrounding environment with average concentrations of 42, 129, and 513 ppb for Palaeozoic, Archean, and Aphebian shales, high Hg content in rock occurs only sporadically in Ontario (Cameron and

Jonasson 1972). In general, data show that most rocks from the Precambrian Shield are very low in Hg (Kettles and Shilts 1994), and thus do not participate to any significant degree in the dynamics of Hg cycle (O'Driscoll et al. 2006). More pertinent in the next decade are the large Hg pools associated with organic matter in soils and sediments (Southworth et al. 2000, Meili et al. 2003), which portray the legacy of anthropogenic Hg emission in remote watersheds across Ontario. Despite declining atmospheric Hg concentrations surrounding urban centers of Ontario (Temme et al. 2007) and across northeastern US (Butler et al. 2008), high Hg storage in soil and sediment may delay the Hg decline in surface waters, and yet supply elevated Hg to aquatic biota for many years (Meili et al. 2003). However, atmospheric concentrations (Vanarsdale et al. 2005, Temme et al. 2007) and deposition of Hg (Appendix D; Mercury Deposition Network 2008) in remote areas of Ontario have changed little during the last decade.

Mercury is dispersed across remote areas by atmospheric transport, in which 95 % of Hg exists as elemental Hg (Hg^0) in the gaseous phase (Schroeder and Munthe 1998). Mercury present as Hg^0 has an atmospheric residence time of approximately 1 year (Schroeder and Munthe 1998, Lin and Pehkonen 1999), enabling long range transport (Fitzgerald et al. 1998). In comparison, other Hg forms such as those sorbed to particles may only exhibit an atmospheric residence time of several days (Schroeder and Munthe, 1998). As a result, particulate Hg will be deposited in close proximity to the emission source, and atmospheric Hg deposition rates will vary regionally depending on the composition of atmospheric Hg (Vanarsdale et al. 2005, Parsons et al. 2007, Vijayaraghavan et al. 2007). Schroeder and Munthe (1998) partitioned atmospheric Hg into three forms based upon unique behaviors: elemental mercury Hg^0, gaseous divalent inorganic mercury compounds Hg^{2+}-X (primarily $HgCl_2$), and particulate phase mercury. While Hg^0 is capable of being carried tens of thousands of kilometres from the site of

emission, Hg(II) as a gas will be deposited within a few tens to a few hundreds of kilometres. Particulate phase Hg will be deposited at distances intermediate to the others depending upon the physico-chemical properties of the vector (diameter/mass). The transformation between particulate, reactive divalent species, and elemental Hg may occur rapidly and is largely dependent upon environmental conditions (Lin and Pehkonen 1999), such as ozone ($Hg^0 \rightarrow Hg^{2+}$; (Schroeder and Munthe 1998) or SO_3 concentrations ($Hg^{2+} \rightarrow Hg^0$; (Van Loon et al. 2001)). The atmospheric deposition of mercury may occur through dry deposition (primarily as reactive gaseous mercury(Lindberg and Stratton 1998, Selin et al. 2007)) or wet deposition the flux of which depends on precipitation volume (Sorensen et al. 1994).

Due to the adsorptive properties of organic fractions in soil (Skyllberg et al. 2006, Pant and Allen 2007), the terrestrial ecosystem may prolong the Hg release of atmospheric deposited mercury to surface waters. Hg adsorbed to soils may be released by chemical and physical weathering, increased acidification (Bloom et al. 1999) or erosion especially in regions with high watershed runoff (Allan et al. 2001, Shanley et al. 2005). Other anthropogenic activities which include logging (O'Driscoll et al. 2004), agricultural activities (Engstrom et al. 2007) and emission of sulfate and nitrate from industrial processes that result in acidification may also increase Hg mobilization. Over time Hg stored in watersheds may traverse through the drainage basin and into surface waters. Spatially dependent landscape features such as topography may naturally enhance the appearance and magnitude of local hot spots of Hg contamination (Parsons et al. 2007). High Hg export has been noted in regions of rocky terrain where there is minimal opportunity for physical retention (Allan et al. 2001) and regions dominated by wetland, where Hg is chemically reduced and bound to dissolved organic carbon (Meili et al. 1991, Mierle and

Ingram 1991, Drexel et al. 2002). Such regions which exhibit little retention of Hg will likely respond rapidly to changes in atmospheric deposition.

Whether watershed-lake systems are at steady state will affect future trends in Hg exposures to fish and wildlife. If watersheds are accumulating atmospheric Hg, they may provide elevated Hg loads to surface waters over the next century or two. If deposition were to decline, the Hg concentration in aquatic biota would decline slowly, and changes would not occur in proportion to the change in deposition. In this scenario, the time required to return to background Hg concentrations would depend on whether the watershed or direct deposition was the dominant source of Hg. Munthe et al. (2007) have shown that a change in the loading of inorganic mercury does not necessarily result in an immediate increase or decrease in fish MeHg. Nevertheless, eliminating current anthropogenic emissions and thereby deposition of Hg could only reduce the contamination of sport fish by removing the direct atmospheric deposition to surface waters and the supply of new Hg into existing terrestrial pools.

Methylmercury

Methylmercury (MeHg) is a potent toxicant, which is bioaccumulated and biomagnified through the aquatic food chain, placing consumers of predatory fish at risk regardless of species, location or economic position (Mergler et al. 2007). While anthropogenic emission of Hg, as well as atmospheric transport largely occur as inorganic species of Hg (Hg^0), it is the organic fractions of Hg (primarily MeHg) which bioaccumalate (Evers et al. 2005). Field studies have demonstrated that environmentally realistic concentrations of MeHg may result in such toxic effects as reproductive impairment in fish, mammals, and birds (Scheuhammer et al. 2007). The toxic effects of MeHg accumulation in biota may be buffered in time from the loading of Hg, largely due to the extent to which ecosystem-specific variables favor methylation of Hg (Downs et al.

1998, Munthe et al. 2007). Methylmercury may be directly deposited to the watershed (Hammerschmidt et al. 2007) or more importantly transformed from inorganic species of Hg within the watershed (Watras and Morrison 2008). The transformation may be biotic (Benoit et al. 2003) or abiotic (Weber 1993) and is generally the net result of methylation and demethylation processes, regardless of location in the watershed (Miskimmin et al. 1992).

The legacy of mercury pollution in Ontario using lake sediments

A large portion of the Hg entering a lake may ultimately end up in the sediments (Lockhart et al. 1998, Boyle 2001), however, the magnitude of Hg precipitated out of the water column depends upon the source of Hg (Watras and Morrison 2008). For this reason, paleolimnological techniques are often used to reconstruct long-term trends in Hg contamination (Kamman and Engstrom 2002, Fitzgerald et al. 2005, Perry et al. 2005). Our results have shown that in lakes typical of south-central Ontario, surface sediment concentrations range from 0.11 to 0.48 $\mu g \cdot g^{-1}$. Such Hg concentrations reflect the strong tendency of Hg to adsorb to particulate matter and therefore to accumulate in the sediment (Hurley et al. 1991). In fact, partition coefficients between sediment-water phases, although variable within a single lake, generally range from 104 to 106 (mg sorbed Hg per kg sediment/mg dissolved Hg per litre) (Hurley et al. 1991).

Sediment profiles as accurate measures of mercury deposition

Temporal reconstructions are often performed using lake sediment profiles, this includes temporal reconstructions of Hg contamination. As sediment accumulates at the lake bottom, Hg is buried, creating a long term record of deposition (Appendix C). However, whether or not Hg profiles are a true representation of changes in deposition remains a contentious issue (Lockhart et al. 2000, El Bilali et al. 2002). Studies have shown that in some lacustrine and fluvial

sediments there is an upward flux of Hg that may confound the relationship between actual conditions and those in historical records (El Bilali et al. 2002, Telmer and Desjardins 2004). Nevertheless, profiles of Hg deposition in lake sediments in areas removed from proximal industrial sources around the globe exhibit similar patterns (Engstrom and Swain 1997, Landers et al. 1998, Bindler et al. 2001). Studies attempting to quantify the magnitude of this flux have estimated that only 2-10 % of the Hg deposited to sediments is redistributed under conditions of low sedimentation (Gobeil and Cossa 1993). Further, despite the decomposition of organic carbon Hg remains sequestered within lake sediment (Rydberg et al. 2008). Studies making comparisons of Hg release and sediment profiles verify that redistribution can be considered negligible (Lockhart et al. 2000).

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Local sources of mercury

Atmospheric emission of Hg from anthropogenic sources has steadily fallen over the past 30 years according to the National Pollutant Release Inventory (NPRI, Environment Canada). However, this observation does not exclude the possibility of indirect emission from automobile exhaust or household practices nor the emission of Hg from outside Canada which provides a major portion of Hg deposited into northern boreal forests. In Canada, during peak emission, over 100 tonnes per year of Hg and Hg compounds (CAS: NA-10) was emitted to the atmosphere and substantially more (up to 600 tonnes) was released to the water. This estimate includes only those sources which exceed a certain level in concentration (including all sewage treatment plants), thus requiring registration with the NPRI. The NPRI does not include emissions from vehicles, households or certain commercial sectors such as car repair shops and fuel marketing stations. In the late nineties it was estimated that anthropogenic emissions to the

atmosphere only range from 4.5 to 12 tons per year of which combustion of fossil fuels constitutes 20% of the total (Sang and Lourie 1997, Innanen 1998). Nationwide the three largest contributors were the primary base metals sector (77%) followed by coal combustion (10%) and then municipal waste incineration (8 %) (Environment Canada, 1996). In Ontario, during 2006, a total of 955 kg of Hg was directly released into the environment, 90% into the atmosphere, the remaining 10% has potential to volatilize to the atmosphere. This emission is a significant decrease when compared with Hg emission in 2000, where a total of 1724 kg was released, 92% into the air. In contrast, during that same period, total disposal of Hg had increased 450% to 26160 kg. The fate of this buried mercury is unknown as often re-emission of anthropogenic mercury is often considered as natural in origin.

Global emissions of mercury

The dominant source of Hg loading to any given watershed is dependent on its distance to point source emission. The certainty of source attribution is greater both very near and very far from major point sources (Lindberg et al. 2007). However, most studies of ambient Hg exposure lie in regions subject to local and global sources of Hg and therefore attributing a source is done with less certainty. Bookman et al. (2008) in a study of sediment Hg accumulation in lakes in an urban/suburban setting of central New York, USA, attributed 80% of the total atmospheric Hg deposition to local and regional emission sources. Selin and Jacob (2008) estimate that North American anthropogenic emissions contribute from 20 to 50 % of total Hg deposition in the US, increasing in regions of industrial activity (mainly the upper mid-west). The global pool of Hg has increased by three times the amount that would be found pre-industrially, this is considered to be the dominant source of Hg loading in remote ecosystems. Combustion of fossil fuels is the dominant emission source to the global pool, composing as much as two-thirds of the total

anthropogenic Hg emission (approximately 2190 tonnes) in 2000. Asian countries contributed about 54% to the global Hg emission from anthropogenic sources, with China alone contributing 28 %, followed by Africa (18%) and Europe (11%) (Pacyna et al. 2006).

Although anthropogenic activity constitutes the major contribution of contaminant Hg in the environment, the role of natural events in Hg emission is noted in glacial and sediment cores globally. It has been estimated that natural sources accounted for 13 % of the total Hg emission in Ontario (Innanen 1998). Natural emissions have been estimated to contribute $1/3^{rd}$ of Hg to the global pool with emission of previously deposited anthropogenic and direct emissions each contributing $1/3^{rd}$ (Lindberg et al. 2007). However, this may vary seasonally, according to recent estimates using a natural Hg emission model coupled with the US EPA's SMOKE/CMAQ modeling system (Gbor et al. 2007) the ratio of natural to anthropogenic emissions varied from 0.7 in January to 3.2 in July across North America. Their model explained between 48 to 64 % of the variance in atmospheric concentration but decreased by 15 to 40% when natural emissions were omitted. Since these values vary regionally, we must establish baseline mercury concentrations. However, the complex Hg cycle of deposition and revolatilization points to the question of what constitutes natural emission.

Research objectives

The general objective of this study was to examine the present state of mercury contamination, using present-day sediment mercury concentrations and mercury enrichment, in the remote regions of northern boreal forests and relate this to Hg bioaccumulation in smallmouth bass that reside therein. I attempt to improve predictive models of Hg accumulation in lakes by examining assumptions that lakes are in steady state with surrounding watersheds for Hg, and how this may

vary regionally. In order to accomplish this general objective we grouped the analysis into the following specific objectives:

1. To determine whether or not watersheds in south-central and eastern Ontario are in steady state with respect to Hg deposition and export. A model is developed to test whether Hg (standardized for organic matter) accumulation in lake sediment is a linear product of drainage ratio ($watershed_{area}/lake_{area}$; A_d/A_o), a scenario possible if there is no net retention of Hg in the watershed. Futher, I determine how this retention has changed since pre-industrial times (Chapter 2);
2. To evaluate the significance of acidification on the retention of Hg in Ontario's watersheds as inferred from accumulation in lake sediment. I use present-day and pre-industrial (reconstructed from diatom assemblages) lake pH to test whether lake acidity influences the accumulation of Hg in lake sediment in addition to models using drainage ratio developed under objective 1 (Chapter 2);
3. To determine if Hg concentrations in present-day sediments correlate with Hg in aquatic biota. Further, I examine whether land use, geology, and hydrology act to mediate Hg loading to surface waters and/or determine the partitioning of Hg between sediment or smallmouth bass (Chapter 3);
4. To test whether Hg enrichment ($[Hg_{present\text{-}day}]/[Hg_{pre\text{-}industrial}]$) in lake sediments is uniformly distributed across space and whether key variables (mean annual precipitation and lake pH) are universal. The spatial correlation of Hg enrichment in lake sediment is evaluated by comparing and contrasting against the spatial correlations in $Hg_{present\text{-}day}$ and $Hg_{pre\text{-}industrial}$. I test whether key variables exhibit the same influence (slope of

relationship) within our study area by testing the difference between geographically weighted and uniform coefficients (Chapter 4);

5. To examine the temporal pattern of methylmercury input to and export from a dystrophic and an oligotrophic lake and to test whether they differ significantly in the average net flux ($MeHg_{Net}$) or seasonal amplitude in $MeHg_{Net}$. In addition, I identify physico-chemical parameters which significantly influence the residual flux after removing seasonal trend in $MeHg_{Net}$ (Chapter 5).

By addressing these objectives I will provide novel insight into the fate of mercury across a region of diverse hydrology, geology and land use. I test several assumptions of mercury contamination using empirical models which have large implications to forecasting mercury contamination. I use lake sediments in my analysis since they provide a temporal, as well as a spatial component to data analysis. This study is broken down into several distinct concepts concerning mercury cycling, and the relevant methods can be found in each chapter along with descriptions of study sites and data analysis.

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Chapter 2

Factors influencing the achievement of steady state in mercury contamination among lakes and catchments of south-central Ontario

Abstract

Mercury (Hg) concentrations in recent (0.5-1 cm) and pre-industrial (>30 cm) sediments were examined across lakes in south-central and eastern Ontario (45.53° N 82.41° W to 44.15° N 76.25° W) to determine whether Hg exported from watersheds is at steady state with atmospheric deposition. An examination of headwater lakes revealed that Hg enrichment was not uniform among watersheds, but that the enrichment factor (EF = $[Hg]_{present\text{-}day}/[Hg]_{pre\text{-}industrial}$; standardized for organic matter) decreased as a function of drainage ratio (A_d/A_o; $watershed_{area}/lake_{area}$). Furthermore, the model fit was improved after accounting for differences in sulfate concentrations and pH among lakes EF = (A_d/A_o)^-15.96-0.07(SO_4^{2-})-$(3.55(pH)_{>8.3})$ ($R^2 = 0.458$, $p = 0.0001$)]. Hg concentrations in pre-industrial sediments of headwater lakes showed a positive linear relationship with drainage ratio (partial $t = 4.83$, $p<0.0001$, $n = 66$) that was strengthened following an adjustment for mean annual runoff (MAR) [$Hg_{pre\text{-}industrial} = 0.011 \pm 0.002 (A_d/A_o) + 0.0008 \pm 0.0003$(MAR) ($R^2 = 0.108$, $F_{1,66} = 8.01$, $p = 0.006$)]. Our results suggest that Hg export from watersheds may be currently lagging behind atmospheric mercury deposition, in which case Hg export would increase into the future, even as mercury deposition from the atmosphere stabilizes.

Introduction

Mercury (Hg) is globally distributed because it is ubiquitous in surficial geology at varying concentrations and it has a long atmospheric residence time (Mason et al. 1994, Fitzgerald et al.

1998). Although natural emissions contribute to the pool of atmospheric Hg and its subsequent deposition, the contamination of surface waters has increased dramatically in the past century due to anthropogenic sources (Fitzgerald et al. 1998, Hermanson 1998, Schuster et al. 2002). Lake sediment studies in North America report increases in mercury deposition of 2 to 3 times the historical background (Swain et al. 1992, Engstrom and Swain 1997, Schuster et al. 2002), although regional differences in Hg enrichment exist due to variability in site-specific geology and geographical variation in the distribution of industrial emissions. Such increases have been confirmed by glacial ice cores (Schuster et al. 2002). The increase in industrial activity, and subsequent global release and contamination by Hg over the past century, has left a legacy of largely unknown repercussions for aquatic ecosystems. Present levels of mercury contamination in many north-temperate lakes exceed guidelines for the protection of wildlife, and the human consumption of sport fish (Basu et al. 2005b, Scheuhammer et al. 2008).

Despite regulatory controls that have reduced industrial emissions (Sang and Lourie 1997, Innanen 1998, Trip et al. 2004), atmospheric Hg concentrations have not diminished significantly over the last decade in remote areas (Trip et al. 2004, Vanarsdale et al. 2005). Temme et al. (2007) found that the largest decline in atmospheric concentrations in Canada (CAMNet) over the last decade were in close proximity to large urban areas [17% Pointe Petre (near Toronto), 13% St. Anicet (Montreal)]. Atmospheric Hg concentrations in their study were often coincided with Hg deposition at co-located or nearby NADP-MDN stations. Across the US, Butler et al. (2008) found that atmospheric Hg deposition decreased in the Northeast by 1.70 +/- 0.51% per year since 1998, although no decrease was found for the Southeast. In part, this may be explained by complex patterns of deposition and re-emission of Hg from the Earth's

surface to the atmosphere that may impede a return to pre-industrial conditions in rural areas (Lee et al. 1998, Lindberg et al. 1998, Gustin et al. 2004).

In aquatic ecosystems, an additional barrier to ecosystem recovery from Hg contamination may be that terrestrial environments are not in steady state with surface waters (Swain et al. 1992, Meili et al. 2003). Under a steady-state model, the amount of mercury entering aquatic ecosystems increases proportionately with watershed size and the drainage ratio (A_d/A_o). Meili (1995), however, reported non-linear correlations between mercury enrichment and drainage ratios in Swedish lake ecosystems. A higher relative enrichment was recorded in sediments of lakes with small watersheds (4-6 fold versus 2-3 fold in lakes with large watersheds), suggesting that steady-state had not been achieved (Meili 1995). Thus, in this example, terrestrial export may lag behind declines in atmospheric deposition due to the storage and accumulation of Hg in watersheds (Lindqvist et al. 1991, Meili 1995, Meili et al. 2003, Perry et al. 2005). Consequently, it may take years to decades before significant declines in mercury release to surface waters are realized.

Over time, the relationship between Hg export and watershed characteristics may be further complicated by regional stressors such as acid deposition. Experimental studies have shown that Hg export is largely dependent upon pH. Following liming, Parkman and Munthe (1998) reported a 67% decline in Hg export relative to a reference catchment. Similarly, in a study of 25 boreal lakes in Sweden, Meili (1991) measured Hg concentrations that were twice as high in acidic lakes (pH 5) than in circumneutral lakes. Both studies attributed their findings to increased leaching of Hg-loaded DOC from soils at lower pH. However, increased concentrations of volatile Hg species in high pH lakes may, in part, have contributed to this observation (Vandal et al. 1991). Volatilization estimates as high as 45 % of dissolved Hg have

been made during experimental isotope additions to the epilimnion of Lake 658 (ELA) (Southworth et al. 2007), although volatization of ambient Hg is likely lower, and has been reported at 14% of the atmospheric flux (Vandal et al. 1991).

In many regions, direct measurements of mercury deposition are unavailable, or have only been recorded in detail during the last decade (Vanarsdale et al. 2005). However, Hg exhibits a high affinity for organic matter and a large fraction of Hg entering surface waters is delivered to lake sediments (Boyle 2001). Sediment studies of mercury deposition in remote areas around the globe show similar increases since the pre-industrial era, despite variability in catchment and basin characteristics (Engstrom and Swain 1997, Landers et al. 1998, Bindler et al. 2001). Furthermore, although mercury in lake sediments is potentially susceptible to post-depositional processes (e.g., diagenesis and oxidation/reduction) that may confound the relationship between actual conditions and those in historical records (El Bilali et al. 2002, Telmer and Desjardins 2004), it has been estimated that only 2-10 % of the Hg deposited to sediments is redistributed even under low sedimentation rates (Gobeil and Cossa 1993). Furthermore, three case studies of known mercury deposition to sediments suggest that under moderate sedimentation rates redistribution may be considered negligible in comparison to mercury loading (Lockhart et al. 2000).

The primary objective of this study is to determine whether or not watersheds in south-central and eastern Ontario are in steady state with respect to Hg deposition and export. Specifically, we examine the relationship between A_d/A_o and mercury concentrations in present-day and pre-industrial sediment samples of headwater lakes in south-central and eastern Ontario. Predictive models are constructed to assess the degree to which A_d/A_o influences mercury concentrations in lake sediments, independent of regional differences in hydrology or the

geographic distance between sites. We test the null hypothesis that Hg retention in watersheds has not changed significantly over time by comparing separate models generated with present-day and pre-industrial sediment Hg concentrations. This hypothesis would be supported if present-day and pre-industrial sediment Hg concentrations show similar, proportional increases with A_d/A_o. If present-day and pre-industrial Hg concentrations increase proportionally with drainage ratio, it would suggest that Hg retention in watersheds has not changed during this period.

Secondly, we test the hypothesis that anthropogenic acidification may have altered the relationship between A_d/A_o and sediment Hg concentrations. The watersheds in this study span a geological gradient of buffering capacity (i.e. lakes on and off the Precambrian Shield), thus providing a natural test of this hypothesis. We examined the relationship between Hg enrichment in lake sediments since pre-industrial times, measured lakewater pH and DOC, in headwater lakes for which monitoring data were available. Based on the current understanding of acidity and Hg export we expect that in watersheds that are sensitive to anthropogenic acidification, Hg export will have increased over time, resulting in larger increases in sediment mercury concentrations vs drainage ratio since the pre-industrial era.

Methods

Study sites

Mercury concentrations were measured in pre-industrial and present-day lake sediments from approximately 202 lakes in Ontario, Canada although modelling was restricted to 68 headwater systems to reduce confounding variation in lake chemistry and biology associated with lake order (Table 2.1, Appendix F; Quinlan et al. 2003). The lakes span gradients of hydrological and geological characteristics, and cross the major geological boundary separating the Canadian

Precambrian Shield (granitic geology) from the limestone-based Trenton and Beekmantown formations in eastern Ontario (Chapman and Putnam 1996) (Figure 2.1). The majority of the study lakes lie upon the Grenville Province which is characterized by rugged topography and is underlain with generally shallow tills and soils, with localized areas of thicker clay, sand, and gravel deposits (Jeffries and Schieder 1983). Lakes on the southern border of the Canadian Shield, including lakes on the Bruce Peninsula and south of Georgian Bay, lie upon the sedimentary rocks of the Western St. Lawrence Lowlands, and include regions of agricultural activity (i.e., pockets of forest surrounded by cultivated land with deeper glacial till). Lakes within Killarney Park are surrounded by quartzite ridges which provide little to no buffering capacity to acidic precipitation. These lakes are generally acidic, and largely influenced by the local geology (Snucins et al. 2001). Most of the study lakes lie within the Great Lakes – St. Lawrence Forest Region (Rowe 1977) and land coverage is dominated by mixed forest, mainly coniferous, followed by dense deciduous forest and sparse deciduous forest (refer to Hall and Smol 1996). Much of the study area, in particular southern Ontario, is subjected to acid deposition from long-range sources according to the Canadian acid deposition science assessment (2004). Morphometric (watershed area, lake area, slope of basin, and length of tributaries) and hydrological data (mean annual: precipitation, runoff, evaporation, and snowfall) were delineated for watersheds using digital elevation models (DEM) to determine watershed boundaries. GIS layers (i.e. hydrology, landcover) were compiled using Ontario Flow Assessment Techniques, a GIS based application produced by the Ontario Ministry of Natural Resources (Chang 2002). Since the DEM contain vector information, lake order was established by observing upstream lakes.

Field and laboratory methods

Lake sediments were collected using Lucite™ Glew gravity corers (Glew 1989) in replicate at the deepest point of each lake between 2001 and 2003. Sediment cores were sectioned on the lake shore using a Glew (1988) extruder, into Whirlpak© bags and stored in coolers for transport back to the lab. Samples were refrigerated at the Paleoecological Environmental Assessment and Research Laboratory at Queen's University at 4°C in the dark until analysis.

In this study, two sediment sections were examined in each core: the top 0.5 to 1.0 cm (present-day lake conditions), and a 0.5 to 1.0 cm interval taken at a minimum core depth of 30 cm. Although the precise date of the bottom sample from each lake is not known, dating of lake sediments using ^{210}Pb from many south-central Ontario lakes, in this study and support by others, indicates the pre-industrial time period is typically reached at a sediment depth of 15 to 20 cm (Evans 1986, Clerk et al. 2000). Paleoenvironmental reconstructions from other Precambrian Shield regions indicate similar results (e.g., Adirondacks: Charles (1985), Cumming (1992), Norton and Kahl (1991), Sudbury: Dixit et al (2002), as do results from near surface and deep sediments in 30 lakes from various regions of our study area.

Mercury concentrations were determined using solid phase thermal desorption atomic fluorescence spectroscopy (SP-3D, Nippon Instruments Corp., Osaka, Japan). Sediments were dried at 60°C and ground to a fine powder with a mortar and pestle, and approximately 30 mg of the powder was embedded in activated alumina powder and placed into a ceramic holder. The elemental Hg released from this process was trapped by gold amalgamation. Subsequently, the Hg was thermally-desorbed and then detected by absorption at 253.7 nm. Certified reference material (MESS-3, NIST 1603) was used to calibrate the response.

The variability in mercury concentrations was quantified for duplicate samples, several samples

within a single core (0.5-1cm) and for adjacent cores from the lake bottom prior to developing models. The relative standard error in mercury concentrations for analytical duplicates was 2.6 %, while the error among adjacent cores was 5.9 %.

Unless otherwise stated, mercury concentrations presented in this study were expressed relative to sediment organic matter content as determined through mass loss on ignition. Organic matter content was determined using the difference in sediment weight after sequential heating regimes (Heiri et al. 2001). Organic matter content was inferred from the mass loss on ignition between freeze-dried sediment and following combustion at 550°C.

Data used for water chemistry were gathered from Ontario Ministry of the Environment (OMOE) long-term lake monitoring databases, as well as Hall and Smol (1996), Reavie and Smol (2001), and Dixit et al. (2002). Lake water sampling (Locke and Scott 1986) and chemical analyses (Ontario Ministry of Environment 1983; Janhurst (1998)) were performed by OMOE. In most instances, water chemistry from south-central Ontario lakes represents multiple measurements of volume-weighted whole-lake composites. Some lakes were sampled on a biweekly basis, others monthly, or bimonthly during the ice-free seasons. Water from lakes in eastern Ontario and on the Bruce Peninsula were collected as surface or epilimnetic composites in the spring and late summer only. For more details regarding sediment and chemical sampling procedures, please see Hall and Smol (1996), Reavie and Smol (2001), and Dixit et al. (2002).

Data analysis

In this study we constructed models from Hg concentrations measured in profundal sediment cores. Prior to constructing these models, we assessed sources of variation in our analyses using ANOVA. Variation was quantified at various levels of analysis, including: 1) Hg concentrations

in profundal sediments within and among lakes, and 2) the precision of Hg concentrations from replicate samples.

Statistical analysis was performed in S-Plus version 6.2 (with additional modules) and in Sigma Stat version 3.0. Differences between sediment mercury concentrations, as well as water chemistry (e.g., lake pH) among geological regions were tested using an ANOVA on ranks. Non-parametric multiple comparisons were performed using a Holm-Sidak test. Where no statistical difference was established among the geological regions (i.e., sites on and off the Precambrian Shield) using ANOVA, data were pooled for subsequent analyses. Otherwise data were grouped according to geological region.

Spatial analysis was performed to assess the degree of autocorrelation among lake sediments due to the geographic distance among sites. Semivariograms were constructed assuming there would be local sources of variation in sediment mercury concentrations standardized for organic matter. This was achieved by setting a maximum radius for estimating variance of 10 euclidean distances from the lake location. For the purposes of this study, we chose to use an isotropic variogram, which assumes a symmetrical change in variation with distance from a prediction point (Deutsch and Journel 1992). The semivariance is equal to the sum of square differences divided by 2nh, where h is the distance between lakes and n(h) is the number of paired lakes at each distance of h. Spatial analysis was conducted using the GSTAT module in SPlus (Pebesma 2001).

Following an examination of variance in Hg concentrations as a function of distance using semivariograms, models were constructed using drainage ratio (A_d/A_o) as a predictor of pre-industrial and present-day Hg concentrations ($ng \cdot g^{-1}$ C_{org}), where C_{org} is the organic matter

content of the sediment samples. Linear models were tested for parametric assumptions and corrected for runoff by including mean annual runoff (MAR) in the models. Where spatial autocorrelation was apparent among sediment mercury concentrations, we included a cubic spline model of latitude and longitude. The significance of each model parameter was examined using the residual sum of squares difference. In the case of confounding factors (e.g., MAR), partial residuals were used to access the importance and form of the relationship among independent and dependent variables using SPlus (Larsen and McCleary 1972). The hypotheses were tested after removing the proportion of variance in sedimentary Hg concentrations attributable to confounding variables (i.e., pH and sulfate concentration), as we were interested only in the relationship between drainage ratio and Hg concentrations for the first hypothesis and pH for the second hypothesis, and not the interaction among predictor variables. To reduce the influence of other possible factors that may be correlated with landscape position (Quinlan et al. 2003), we restricted tests of our hypotheses to data from headwater lakes. In testing the second hypothesis, several lakes (n=12) were missing data for sulfate monitoring and so the data set was reduced to 54 lakes.

Results

Lake sediments are spatially heterogeneous mixtures of mineral and organic matter. These characteristics may vary both in their location within a lake (Evans 1986), and vertically within sediment cores (El Bilali et al. 2002). Furthermore, mercury concentrations may vary considerably between littoral and profundal sediments (Evans 1986). However, our assessment of sources of variation in Hg concentrations indicate that most of the variation occurred among lakes ($F=170.28$, $p<0.001$), with non-significant variability among cores within lakes ($F=1.317$, $p=0.25$) (Table 2.2). Our examination of within-lake replication only considers cores from the

deepest basin of each lake, and makes no attempt at estimating whole lake burdens for mercury. Prior research suggests that within-lake variability can be minimized by considering profundal sediments alone (Landers et al. 1998). Non-standardized Hg concentrations were examined for differences between bedrock classes (i.e., on and off the Precambrian Shield), and time period (i.e., pre-industrial and present-day). A 2-way ANOVA indicated a significant interaction in Hg concentrations between bedrock class and time period ($F=15.58$, $p = 0.0001$). Therefore, separate 1-way ANOVA's were conducted for lakes on and off the Precambrian Shield. Surface sediments had significantly higher Hg_{total} concentrations on Precambrian Shield bedrock ($F=34.48$, $p<0.0001$) than on calcareous bedrock. Pre-industrial, Precambrian Shield sediments also had higher Hg_{total} concentrations than sediments of lakes off the Shield, but the relative difference was lower than for present-day sediments ($F=4.51$, $p=0.035$). Our results support previous findings (Friske and Coker 1995) that mean mercury concentration in present-day and pre-industrial sediments is dependent, at least in part, upon geology.

Sediment chronology (i.e. present-day and pre-industrial sediment) was verified for a subset of our study lakes spanning a diverse geology using ^{210}Pb dating. The sampled cores were divided into eight regions (Table 2.3) and the mean ± standard deviation age of present-day sediments (0.5 – 1 cm) and pre-industrial sediments (30-35 cm) was inferred. The inferred age of present-day sediments was 3.4 ± 2.7 years across 30 sediment cores while the inferred age at 30 – 31 cm was greater than 150 years with one exception. On average, the pre-industrial era (1850) was inferred to lie at a depth of 19.3 ± 6.2 cm (n=30, eight regions) below the sediment-water interface, supporting prior observations that 30 cm + captures pre 20^{th} century horizons (Evans 1986, Dixit et al. 2002, Quinlan et al. 2003). Mean sedimentation rate was also determined from ^{210}Pb cores for the present and pre-industrial era. The mean sedimentation rate

over the last 50 years averaged from eight lakes was 0.0154 ± 0.0017 $g \cdot cm^{-2} \cdot a^{-1}$ and during the pre-industrial era for intensively-studied lakes in central Ontario; 0.0109 ± 0.0013 $g \cdot cm^{-2} \cdot a^{-1}$ (Table 2.4).

Mercury concentrations were significantly correlated with organic matter content in surface ($r = 0.31$, $p < 0.0001$) and pre-industrial sediments ($r = 0.29$, $p = 0.003$) according to Spearman rank correlation. Therefore, patterns of Hg concentrations were explored after standardizing for organic matter content. As found in unstandardized data, present-day sediments have significantly higher Hg on the shield ($F=10.60$, $p =0.0015$) than off the shield. However, following standardization, the difference in Hg content of pre-industrial sediments between geological classes was no longer significant ($F=0.317$, $p=0.575$) (Table 2.5). These results suggest that the Hg content per unit organic carbon was similar on and off Shield in pre-industrial times, but the Hg content per unit organic carbon in Shield lakes has increased during the industrial period relative to non-Shield lakes. This difference might arise from changes to Hg input in Shield lakes, or to changes in the decomposition of organic matter relative to the release of Hg in aquatic ecosystems on the Precambrian Shield.

Mercury concentrations in present-day sediments showed a weak but significant correlation with pre-industrial mercury concentrations ($r = 0.222$, $p = 0.003$, $n = 172$, Figure 2.2). However, this correlation was no longer significant once mercury concentrations were standardized for organic matter content ($r = 0.105$, $p = 0.275$). This result suggests that part of the change in the Hg content of present-day sediments is due to changes in the ratio of Hg to organic matter.

An index that portrays the post-industrial increase in mercury concentrations is the sediment Hg enrichment factor (EF) which is $[Hg_{Present\text{-}day}]/[Hg_{Historical}]$. The sediment Hg enrichment factor approximates the ratio of present-day to pre-industrial fluxes to sediments, if we assume sedimentation rate has remained constant through time. The EF was unaffected by the placement of sites on or off the Precambrian Shield (On Shield; 0.6 – 4.8 (5^{th} – 95^{th} percentile), median = 2.3, n = 135; Off Shield; 0.5 – 5.1, median = 2.0, n = 67; p = 0.213).

Semivariance increased with geographical distance in standardized, present-day $Hg_{om\ corr}$ concentrations, a phenomenon that was not observed in pre-industrial sediments (Figure 2.3). This suggests that either the sources of Hg, or processes affecting the export, retention, sedimentation or evasion of Hg from catchments, have changed in a spatially-dependent manner over the last century. The lack of spatial structure in pre-industrial $Hg_{om\ corr}$ concentrations indicates that either the spatial structure is larger than the bounds of our analyses, or the variance between lakes did not change as a function of distance.

By examining the drainage ratios of the study lakes, we can infer whether the watershed retention of mercury has changed since pre-industrial times (Swain et al. 1992, Engstrom and Swain 1997). The drainage ratio explained a small but significant portion of pre-industrial Hg concentrations in sediments ($R^2 = 0.108$, $F_{1,66} = 8.01$, $p = 0.006$). There was no improvement to this model when samples were separated based on their location on and off the Precambrian Shield. However, when we included water load [expressed as mean annual runoff ($mm \cdot yr^{-1}$) (MAR)] in the model, the variance explained was significantly improved for pre-industrial sediments ($R^2 = 0.313$, $F_{2,54} = 12.28$, $p < 0.0001$, Figure 2.4, A). Conversely, a model including drainage ratio and MAR failed to explain a significant portion of the variability in Hg concentrations in present-day sediments (Figure 2.4, C).

Spatial analyses indicated an increase in variance of Hg concentrations with distance between lakes (Figure 2.3), so the above models were corrected using a cubic polynomial of x and y coordinates (Figure 2.4, B, D). The prediction of mercury concentrations in pre-industrial sediments did not improve dramatically after accounting for spatial autocorrelation (Figure 2.4, B). This was expected given that variance in pre-industrial Hg concentrations did not exhibit a strong trend with distance between lakes. Present-day Hg concentrations, however, displayed a tendency for higher variance with increasing geographic distance (Figure 2.3), and model fit was much improved after adjusting for spatial structure ($R^2 = 0.472$, $F_{1,66} = 59.05$, $p < 0.0001$, Figure 2.4, D). Drainage ratio, however, (partial $t = 0.665$, $p = 0.508$) remained unrelated to Hg concentrations in present-day sediments, after correcting for spatial variance and MAR. Furthermore, although MAR was also spatially correlated (data not shown), results from a partial regression analysis indicate that MAR and A_d/A_o only shared 8 % of explained variance with a cubic polynomial for the prediction of pre-industrial $Hg_{om\ corr}$, and <1 % in the prediction of present-day $Hg_{om\ corr}$. No spatial correlation was observed for A_d/A_o.

The Hg EF represents the relative increase due to anthropogenic activity. Presuming that sedimentation rates have not changed substantially, EF should account for variability in factors that influence the export rate of Hg among basins (e.g., surficial geology, depth of till, vegetation, slope of watershed). However, since the pre-industrial era, external factors such as sulfate deposition and subsequent catchment acidification may also have altered Hg export from lake watersheds (Miller and Akagi 1979, Hurley et al. 1995), and its accumulation in lake sediments (Vaidya and Howell 2002). Catchment acidification may have other indirect effects, such as lowering of dissolved organic carbon export (Ravichandran 2004, Wu et al. 2005) which could lead to reduced organic complexation and lower storage (Driscoll et al. 1995), as well as

higher Hg volatilization (Ravichandran 2004). Studies have suggested that in drainage lakes, dissolved organic carbon may buffer the response to depositional changes by increasing the residence time of Hg in the water column (Watras et al. 1995b). However, dissolved organic carbon concentrations in the study lakes were unable to explain any additional variability between drainage ratio and EF between the two time periods.

In contrast to the steady state model used to predict pre-industrial $Hg_{om\ corr}$, MAR did not contribute to the explained variance in EF, and was removed from the model. However, adjusting the EF model for lake pH increased the amount of explained variance ($F_{2,48} = 10.39$, $p < 0.001$), as did sulfate concentrations. EF did not increase in a linear fashion with drainage ratio, suggesting a deviation from steady state conditions. Rather, an inverse relationship was observed and subsequently modeled (Table 2.6).

The impacts of anthropogenic acidification on lake pH varies on and off the Precambrian Shield. Monitoring data indicated that lakes located on the Precambrian Shield had significantly lower pH than lakes off the Shield ($H = 21.915$, $p < 0.001$). However, pH values inferred from diatom assemblages preserved in lake sediments (Hall and Smol 1996, Reavie and Smol 2001) suggest that this was not the case in pre-industrial times. A re-analysis of their findings indicate that the difference in pre-industrial pH for lakes on and off the Precambrian Shield was not significantly different ($t = 1.420$, $p = 0.171$), with a mean decline in pH of 0.51 and 0.29 since pre-industrial times for lakes on granitic bedrock and calcareous limestone, respectively. Conversely, present-day lake pH inferred from sediment fossils (i.e. diatoms) is significantly different between lakes on and off the Shield ($t = 2.522$ $p = 0.020$) (Holm-Sidak multiple comparison test). Similar patterns across regions, and through time, were observed for Hg

concentrations (Table 2). After removing the variance explained by A_d/A_o and sulfate, the partial residuals in Hg concentration declined at pH values above 8.3 (Figure 2.5).

Finally, after removing the variance attributable to lake pH and sulfate concentration, we found that EF was strongly dependent upon drainage ratio (Figure 2.6). An inverse first order polynomial was the model most suited to describe the partial fit of EF (Table 2.7). A downward curvilinear trend is expected only if the relative importance of terrestrial export was larger in the past than it is presently. Mercury enrichment appeared to reach a lower limit for drainage ratios >10. (Adjusted $R^2 = 0.458$, $F_{3,33} = 9.282$, $p = 0.0001$).

Discussion

The primary objective of our study was to determine whether watersheds are at steady state with respect to Hg inputs and outputs. We hypothesized that if sedimentary Hg concentrations are a reflection of surface water concentrations, and if the net Hg export per area was independent of watershed size, Hg concentrations would display a consistent, linear increase with drainage ratio. Despite possible effects from sediment dilution, which may lower concentrations in lakes surrounded by larger watersheds, a significant linear relationship was found between A_d/A_o and Hg ($ng \cdot mg^{-1}$ OM) in pre-industrial sediments prior to adjusting for mean annual runoff (MAR). A recent study of a seepage lake and a drainage lake ($A_d/A_o = 2$) suggested that as fluvial loading increases more Hg is lost from the water column through sedimentation (Watras and Morrison 2008). Watras and Morrison (2008) also found that fluvial inputs were lost more rapidly than direct pluvial inputs. While the increase in suspended matter from fluvial inputs likely increased sedimentation in drainage lakes, A_d/A_o remained the most important predictor of Hg ($ng \cdot mg^{-1}$ OM) after adjusting for MAR.

The prediction of Hg concentrations in pre-industrial sediments using drainage ratio was significantly improved by accounting for differences in MAR among watersheds, suggesting that sites with higher runoff may experience more erosion, or may indicate basins that are more water saturated (i.e., anoxic conditions). The relationship between runoff and Hg export is well established (Allan et al. 2001, Shanley et al. 2005). For example, Shanley et al. (2005) found that stream discharge was the best predictor of Hg export, accounting for 20 % of the variance, including interaction with other variables. This estimate is similar to that found in this study, where MAR explained 20 % of variance in pre-industrial Hg sediment concentration excluding drainage ratio. An increase in MAR would increase the lateral flow and should limit the adhesion of Hg to mineral soils (Watras and Morrison 2008). Other studies have suggested that Hg fluxes to pre-industrial sediments are largely controlled by watershed morphometry (Lindqvist et al. 1991, Swain et al. 1992, Meili et al. 2003), and surrounding geological deposits (Friske and Coker 1995, Landers et al. 1998), although we found no difference in mercury concentrations between lakes situated on or off the Precambrian Shield in this time period.

Mercury concentrations in present-day sediments showed no relationship to drainage ratio, suggesting that watersheds are presently not in steady-state with respect to Hg deposition and export. In part, this may be because mercury concentrations in surficial sediments have been affected by anthropogenic disturbances that have altered mercury export from watersheds (e.g., acid deposition). For example, mercury concentrations displayed a different relationship with measured lake acidity above and below pH 8.3. Inorganic mercury may form oxyhydroxides at high pH (Lodenius and Autio 1989), and HgOOH may display a high affinity for charged particulate matter in soil, thus increasing the likelihood that it will be retained in the catchment at pH > 8 (Miller and Akagi 1979). In contrast, Hg-loaded complexes may be leached from the soil

under acidic conditions; these complexes are primarily coloured substances (Mierle and Ingram 1991). In addition to reduced export, volatile species of mercury are formed at high pH which has in some studies proven to be as high as 14 % of that directly deposited from the atmosphere under ambient conditions (Vandal et al. 1991), and 45 % with experimental additions (Southworth et al. 2007).

Despite the lack of relationship with present-day sediment Hg concentrations, drainage ratio exhibited a strong relationship with EF. Mercury enrichment was highest in watersheds with low drainage ratios, and reached a plateau as catchment areas increased in proportion to lake area. Following the removal of the variance in mercury concentrations that could be explained by pH and sulfate, the form of the relationship between A_d/A_o and mercury enrichment was determined. The increased mercury enrichment at low drainage ratios could only be established if the proportion of mercury entering lakes from terrestrial sources was larger in the past than at present. Thus, our results suggest that more mercury is being retained within watersheds presently than in the past (i.e., large pools of mercury are being accumulated in catchments). The lack of relationship between mercury concentrations and drainage ratio in the present era may indicate that watershed systems are achieving a new steady state between terrestrial runoff and atmospheric deposition. Several other studies have reported that present-day watershed export remains elevated in comparison to observed changes in atmospheric deposition (Kamman and Engstrom 2002, Meili et al. 2003, Perry et al. 2005). As suggested in our study, Perry et al. (2005) implied that watershed Hg supplies to the lake are in excess of modern wet plus dry Hg deposition, and speculated that the timing of watershed export to atmospheric declines may be controlled by watershed, as well as lake storage.

We expect that lakes with proportionally smaller catchments will reach steady state at a faster rate than those with larger catchments. Our results suggest that lakes with low A_d/A_o ratios are responding to immediate changes in atmospheric deposition. The adsorption of mercury by soil particles may have sufficiently slowed the migration of mercury through catchments, thus delaying the full effect of anthropogenic activity on mercury in Ontario's surface waters to future decades. Mercury in pre-industrial sediments was found to be largely correlated to the drainage ratios of watersheds in Ontario. The increase in mercury concentration with drainage ratio was similar among watersheds regardless of variance in other factors. This analysis indicates that during the pre-industrial era, the proportion of mercury entering lake sediments from terrestrial versus atmospheric sources was similar amongst lakes. However, when we examined the enrichment of mercury from pre-industrial to present-day sediments, we observed a non-linear, inverse correlation with drainage ratio. The decrease in Hg enrichment as a function of drainage ratio supports the concept that Hg flux in watersheds is not at steady state with respect to deposition

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Figure Legend

Figure 2.1 Location of study lakes in central and eastern Ontario, Canada (45.53° N 82.41°W to 44.15N 76.25 W). Sediment was collected from 202 lakes using a modified KB corer. Top (present-day) and bottom (pre-industrial) sediment slices were analyzed for total mercury content.

Figure 2.2 Total mercury concentrations ($ng \cdot g^{-1}$ dry weight) in near surface/present-day (0.5-1 cm depth) versus deep/pre-industrial (>30 cm) sediment of lakes in south-central and eastern Ontario. The dashed line represents a one to one relationship.

Figure 2.3 Semivariogram of mercury concentrations in historical (•) and present-day (•) sediments as a function of distance. Semivariance was calculated using the GSTAT extension in SPLUS. The plot assumes a symmetrical change in variance with distance from the prediction point (lake location). Present-day sediments were collected at a depth of 0.5 to 1 cm and historical sediments were collected at depths greater than 35 cm from the sediment-water interface.

Figure 2.4 Observed and predicted mercury concentrations in historical (>30cm depth, a,b) and present-day (0.5-1 cm, c,d) sediments of 54 headwater lakes standardized for organic matter content. Standardized mercury concentrations were predicted before (a,c) and after (b,d) correcting for autocorrelation using a second order regression model, where x = latitude and y = longitude. $Hg_{Historical} = 0.011 \pm 0.002 (A_d/A_o) + 0.0008 \pm 0.0003(MAR)$, $Hg_{Present\text{-}day} = 0.0029 \pm 0.0043(A_d/A_o) + 0.0005 \pm 0.0006(MAR)$.

Figure 2.5 Partial residuals in mercury enrichment from deep core (>35 cm depth) to near surface sediments (0.5 - 1 cm) in 54 headwater lakes as a function of pH after removing the

variance attributable to drainage ratio and sulfate concentrations. Hg EF = (A_d/A_o)^-15.96-0.07(SO_4^{2-})-(3.55$(pH)_{>8.3}$).

Figure 2.6 Increase in mercury concentration from deep core (>30 cm depth) sediments to surface sediments (0.5-1 cm) in 54 headwater lakes of south-central Ontario presented before ○ and after ● correcting for both pH and sulfate concentration as a function of drainage ratio Hg EF = (A_d/A_o)^-15.96-0.07(SO_4^{2-})-(3.55$(pH)_{>8.3}$). The mean increase in mercury concentration over the study area is 2.46 ± 1.64 (– – –).

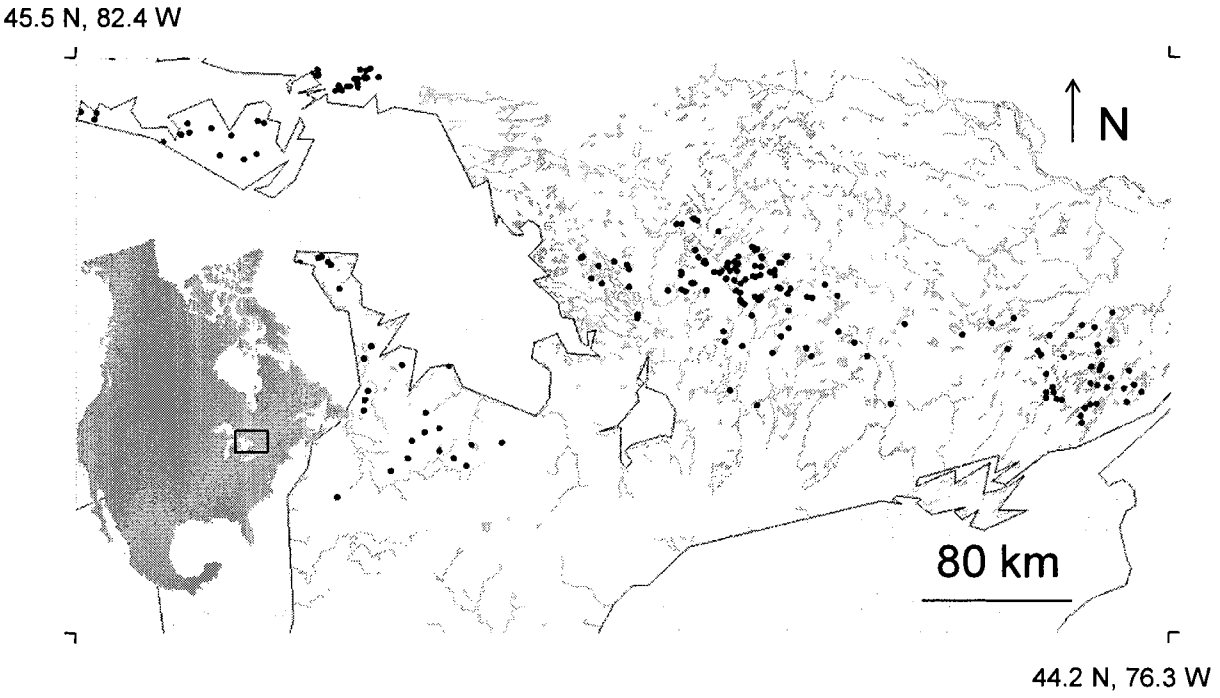

Figure 2.1: Location of study lakes in central and eastern Ontario, Canada (45.53° N 82.41°W to 44.15N 76.25 W). Sediment was collected from 202 lakes using a modified KB corer. Top (present-day) and bottom (pre-industrial) sediment slices were analyzed for total mercury content.

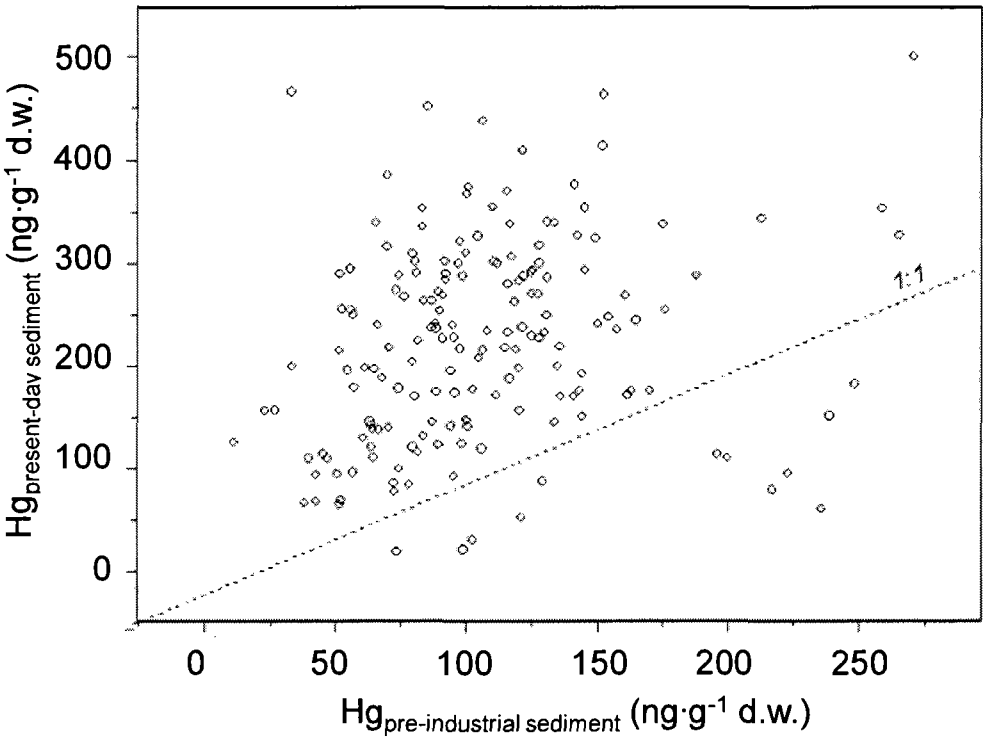

Figure 2.2: Total mercury concentrations (ng·g^{-1} dry weight) in near surface/present-day (0.5-1 cm depth) versus deep/pre-industrial (>30 cm) sediment of lakes in south-central and eastern Ontario. The dashed line represents a one to one relationship.

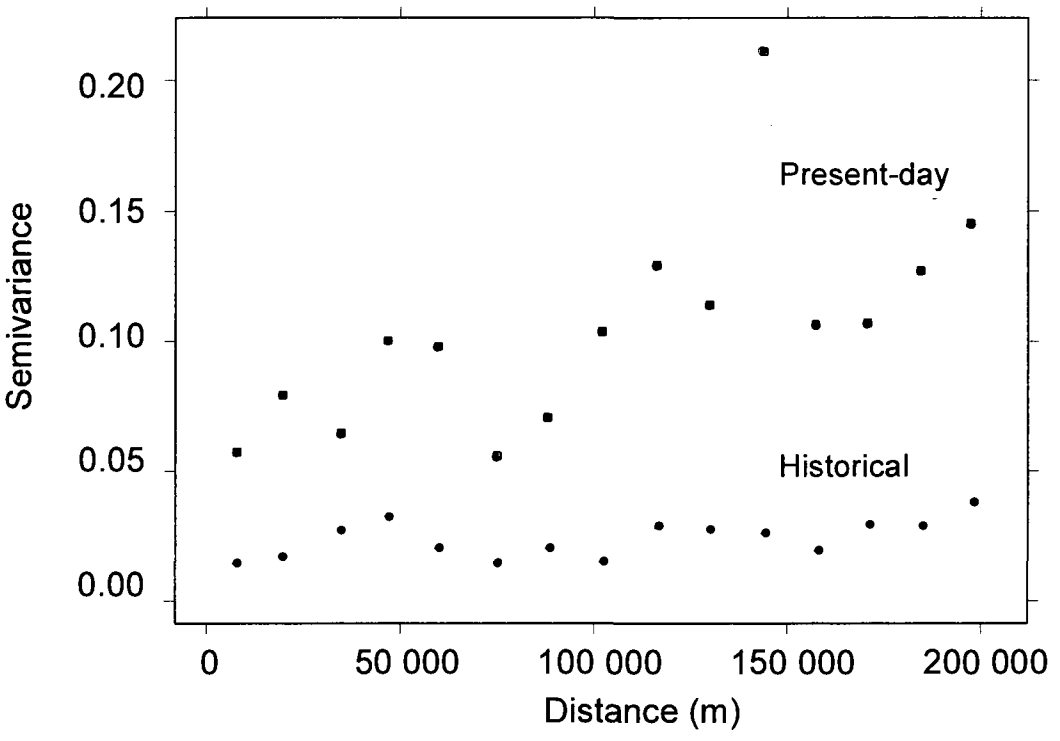

Figure 2.3: Semivariogram of mercury concentrations in historical (•) and present-day (•) sediments as a function of distance. Semivariance was calculated using the GSTAT extension in SPLUS. The plot assumes a symmetrical change in variance with distance from the prediction point (lake location). Present-day sediments were collected at a depth of 0.5 to 1 cm and historical sediments were collected at depths greater than 35 cm from the sediment-water interface.

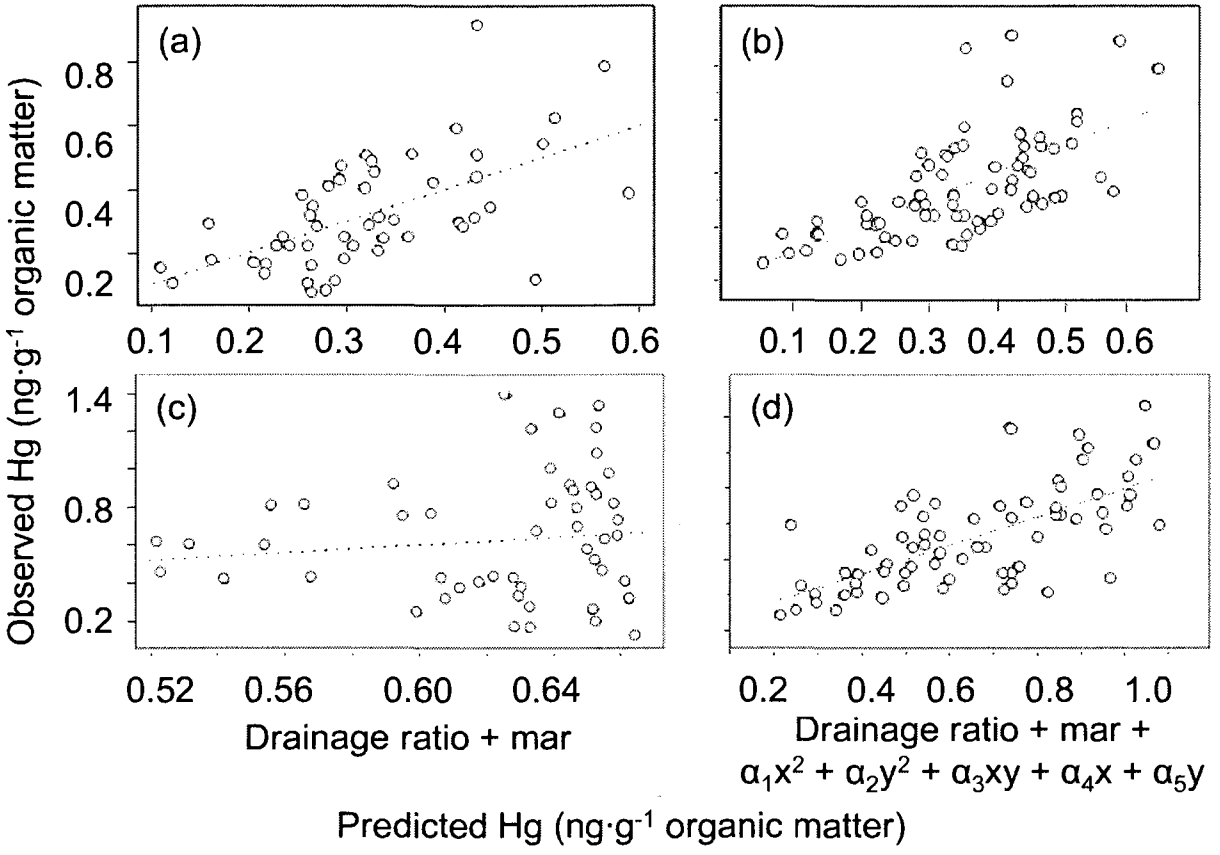

Figure 2.4: Observed and predicted mercury concentrations in historical (>30cm depth, a,b) and present-day (0.5-1 cm, c,d) sediments of 54 headwater lakes standardized for organic matter content. Standardized mercury concentrations were predicted before (a,c) and after (b,d) correcting for autocorrelation using a second order regression model, where x = latitude and y = longitude. $Hg_{Historical} = 0.011 \pm 0.002 (A_d/A_o) + 0.0008 \pm 0.0003(MAR)$, $Hg_{Present\text{-}day} = 0.0029 \pm 0.0043(A_d/A_o) + 0.0005 \pm 0.0006(MAR)$.

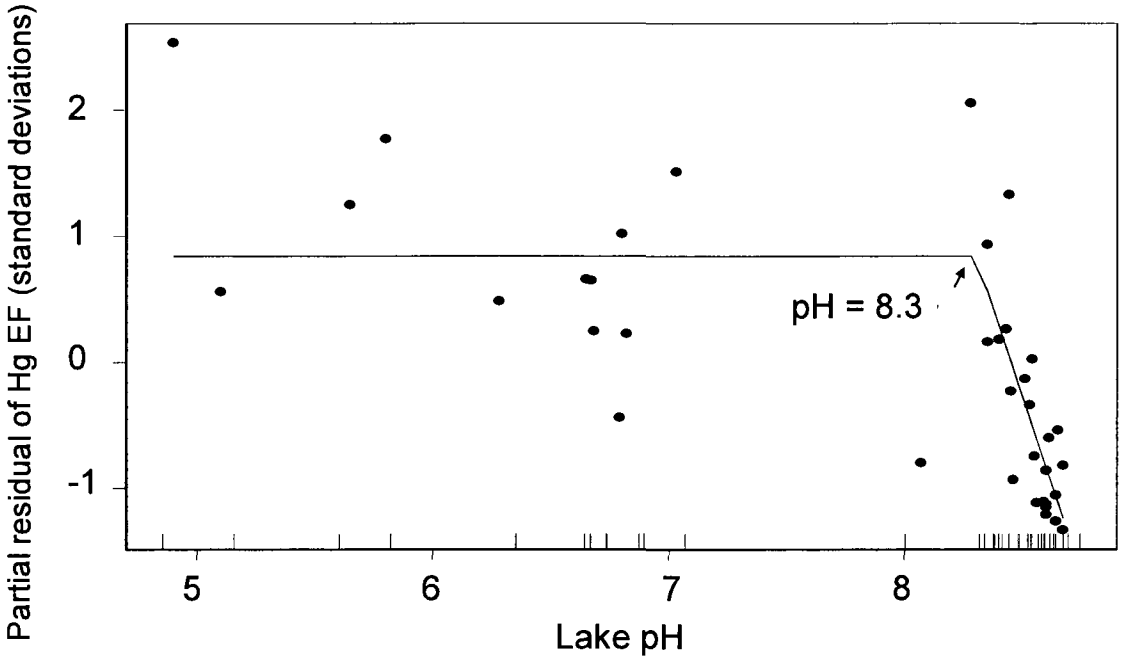

Figure 2.5: Partial residuals in mercury enrichment from deep core (>35 cm depth) to near surface sediments (0.5 - 1 cm) in 54 headwater lakes as a function of pH after removing the variance attributable to drainage ratio and sulfate concentrations. Hg EF = (A_d/A_o)^-15.96-0.07(SO_4^{2-})-$(3.55(pH)_{>8.3})$

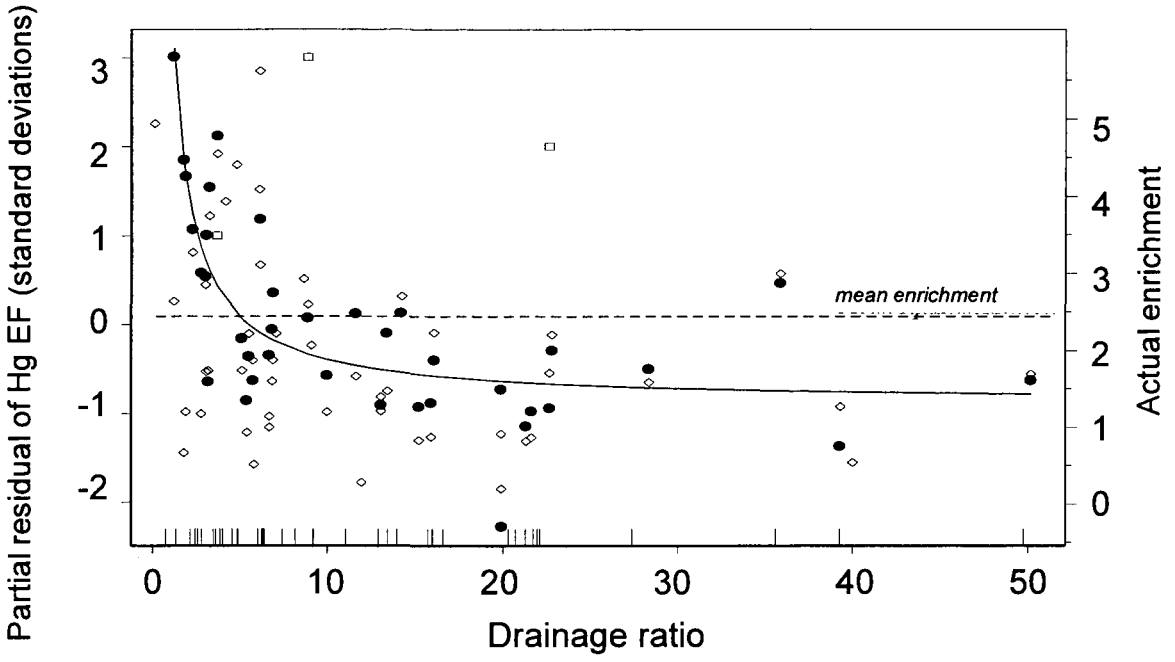

Figure 2.6: Increase in mercury concentration from deep core (>30 cm depth) sediments to surface sediments (0.5-1 cm) in 54 headwater lakes of south-central Ontario presented before ○ and after ● correcting for both pH and sulfate concentration as a function of drainage ratio Hg EF = (A_d/A_o)^-15.96-0.07(SO_4^{2-})-(3.55$(pH)_{>8.3}$). The mean increase in mercury concentration over the study area is 2.46 ± 1.64 (– – –).

Table 2.1: Physical and chemical properties of the 68 headwater lakes used in this study. Hydrology was interpolated among meteorological stations using GIS. Lakewater pH and DOC concentrations represents samples collected during the ice-free and averaged over several years.

Lake	Latitude	Longitude	Watershed km²	Lake area km²	Ad/Ao	Runoff (mm·yr⁻¹)	Precipitation (mm·yr⁻¹)	pH	DOC	Hg_{total} (μg·g⁻¹ om) Present-day	Pre-industrial	Increase	RSE	# of Cores
Acid	46.03	-81.44	4.4	0.2	23	506	774			1.08	0.63	1.7		1
Arran	44.50	-81.24	24	4	7	471	860	8.6	9.7	0.15	0.08	1.9	8.8	2
Bass	44.72	-80.99	6	1	12	471	895	8.6	3.1	0.40	0.24	1.7		1
Bass	45.12	-79.71	5	1	6	493	933	6.3	4.4	0.91	0.41	2.2		1
Beaver	44.77	-78.27	80	2	40	321	823	6.4	4.9	0.97	1.78	0.5	4.7	2
Bell	46.13	-81.23	19	1	23	439	933	8.5	5.5	0.75	0.34	2.2		1
Berford	44.81	-81.19	21	4	5	476	824	8.5	5.8	0.15	0.16	1.0	0.3	2
Brewster	44.34	-80.31	2	0	7	431	809	8.8	6.2	0.24	0.24	1.0	34.8	2
Bruce	45.18	-79.66	3	1	3	495	936	6.8	4.0	0.66	0.38	1.7		1
Cameron	45.23	-81.55	9	2	6	500	764	8.5	5.8	0.56	0.18	3.1	1.9	2
Carlyle	46.05	-81.29	9.0	1.6	6	502	744			0.88	0.47	1.9		1
Chub	45.21	-78.98	3	0	9	495	930	5.6	4.9	0.78	0.30	2.6		1
Collins	44.35	-76.45	37	3	11			7.3	6.0	0.36	0.12	2.9	2.2	3
Crosson	45.09	-79.03	6	1	10	485	939	5.6	4.5	0.81	0.31	2.6		1
Crowe	44.48	-77.72	1444	876	2			7.3	5.1	0.88	0.32	2.7	7.6	3
Crystal	44.75	-78.49	41	4	9	326	836	7.7	5.5	0.60	0.29	2.0	4.5	2
Dankert	44.21	-81.06	1	0	6	471	889	9.1	13.8	0.32	0.07	4.3	5.0	2
David	46.13	-81.28	15.1	4.1	4	503	754			1.32	0.29	4.6		1
Dog	44.43	-76.35	62	5	13			8.2	5.0	0.55	0.49	1.1	3.1	3
Eagle	45.13	-78.51	40	7	6			7.9	4.4	0.82	0.23	3.6	14.7	3
East Bass	45.87	-81.93	25	3	10	517	754	8.5	5.4	0.30	0.25	1.2	22.2	2
Eugenia	44.33	-80.52	138	6	21	444	838	8.7	4.8	0.42	0.51	0.8		1
Farren	44.77	-76.49	12	2	7	354	712	8.2	4.0	0.40	0.18	2.3		1
Gillies	45.28	-81.32	13	2	6			8.6	5.1	0.66	0.24	2.7	48.9	2
Gould	44.59	-81.21	10	2	5	425	796	8.2	3.4	0.75	0.17	4.3	3.4	2
Gravenhurst	44.93	-79.40	11	2	6			7.2	3.9	1.43	0.56	2.6		1
Grippen	44.50	-76.16	20	191	0	456	728	8.1	5.0	0.89	0.18	4.9	4.3	3
Haliburton	45.18	-78.42	144	10	14	468	871	7.0	3.5	1.38	0.51	2.7		1
Hammel	45.19	-79.47	13	2	9	495	938	7.2	4.9	0.87	0.49	1.8		1
Harp	45.38	-79.13	5	1	8	504	906	6.4	3.7	0.84	0.51	1.7		1
Hines	44.42	-80.74	1	0	10	448	887	8.5	4.7	0.36	0.11	3.2	7.8	2
Inverary	44.38	-76.46	10	1	13	504	807	7.5	6.5	0.51	0.42	1.2	9.1	3
Irish	44.27	-80.64	3	0	13	443	935	9.0	5.5	0.31	0.21	1.5	3.3	3
Ishmael	46.11	-81.60	11.7	0.7	16	509	780			0.96	0.43	2.2		1
Kagawong	45.84	-82.28	105	55	2	513	760	8.6	3.8	0.48	0.40	1.2		1
Kennisis	45.24	-78.59	134	14	9	489	902	6.3	2.8	1.29	0.46	2.8		1
Kerr	45.91	-83.08	3	0	15	503	785	8.6	11.4	0.25	0.30	0.8		1
Knowlton	44.47	-76.61	11	2	6	422	811	8.2	3.9	0.90	0.16	5.6	3.1	3
L. Clear	45.40	-79.00	4	0	39			6.8	2.8	0.51	0.40	1.3	3.5	3
L. Kennisis	45.25	-78.58	67	2	29	477	873	6.1	3.7	0.37	0.79	0.5		1
Leggat	44.70	-76.72	12	2	6	327	777	7.6	3.6	0.45	0.11	4.3	3.2	2
Lily	45.88	-83.09	6	2	3	503	785	8.8	7.3	0.19	0.11	1.8	0.6	2
Limerick	44.86	-77.61	181	7	24	389	757	7.9	4.3	0.80	0.29	2.8	4.6	2
Long	45.02	-78.39	8	3	3	475	878	8.8	11.6	0.27	0.23	1.2	2.3	2
Lorne	45.78	-82.61	27	1	22	507	747	8.8	10.2	0.47	0.54	0.9	4.7	1
Loughborough	44.44	-76.39	58	7	8	480	795	7.5	3.6	0.67	0.25	2.7		1
Low	46.10	-81.57	9.7	0.3	29	508	773			1.59	0.34	4.7		1
Manitou	45.72	-81.98	130	106	1	515	752	8.5	2.9	0.66	0.25	2.6	4.7	2
Mc Cullough	44.35	-80.92	32	1	50	451	917	8.5	3.8	0.39	0.23	1.7	1.1	2
Mindemoya	45.72	-82.22	64	36	2	513	752	8.6	3.2	0.32	0.48	0.7	1.2	2
Muskoka Bay	44.95	-79.40	11	2	5			7.1	3.9	0.31	0.75	0.4		1
Nameless	45.82	-82.44	10	1	16	511	750	8.7	3.6	0.81	0.92	0.9	0.2	2
Newboro	44.62	-76.30	375	18	20			8.0	4.8	0.30	0.20	1.5		1
Partridge	46.09	-81.29	0.4	0.1	3	502	744			1.20	0.32	3.7		1
Pike	44.80	-76.33	60	3	19	372	711	8.4	5.5	0.58	0.30	1.9	6.2	2
Pike	45.88	-81.97	32	2	15	516	754	8.5	6.0	0.39	0.31	1.3	2.6	2
Redstone	45.16	-78.55	190	11	17	480	885	6.5	3.0	1.21	0.59	2.0		1
Salmon	44.83	-78.44	7	2	4	339	840	7.8	3.7	0.59	0.15	3.8	8.4	3
Silver	44.08	-81.41	11	1	20	522	814	8.9	6.1	0.11	0.12	0.9	1.5	3
Skootamatta	44.80	-77.22	132	8	16	374	754	6.5	5.1	0.79	0.44	1.8	0.3	3
Solitaire	45.40	-79.01	3	1	2	511	910	6.7	2.1	0.72	0.22	3.3		1
Soyer's	45.01	-78.61	47	3	14	478	881	7.0	5.5	1.02	0.51	2.0		1
Stone's	45.81	-82.50	15	1	28	510	750	8.4	5.2	0.62	0.39	1.6	1.6	2
Tallan	44.84	-78.05	4	0	9	388	815	7.8	5.4	0.41	0.14	3.0	1.5	3
Three Mile	45.17	-79.45	127	6	20			7.1	6.4	1.06	0.90	1.2		1
Tobacco	45.87	-82.45	15	2	7	511	750	8.7	3.9	0.64	0.40	1.6		1
Walker	45.37	-79.09	2	1	3	507	909	6.7	3.4	0.97	0.34	2.8		1
West Bass	45.91	-83.18	1	0	7	503	793	9.1	10.1	0.25	0.22	1.1	10.8	3
Wilcox	44.23	-80.56	1	0	5	456	914	8.4	5.8	0.40	0.23	1.8	1.4	3
Williams	44.40	-80.83	7	1	13	463	924	8.4	2.9	0.42	0.30	1.4		1

Table 2.2: ANOVA in mercury concentrations among various stages of measurement. Lake represents the variation among study lakes, sediment stratum represents the variation between present-day and pre-industrial sediment, and replicate cores represents the variation in sediment mercury concentrations among separate cores at the same depth.

Attribute	Df	Sum of Sq	Mean Sq	F - value	p
Lake	66	275000	4170	5.61	<0.0001
Sediment stratum	1	126000	126000	170.28	<0.0001
Replicate Cores	1	979	980	1.3173	0.2544
Lake:Depth	65	190000	2920	3.931	<0.0001
Residuals	82	60900	744		

Table 2.3: Average age and standard deviation in years of sediment collected within the surficial (0.5 – 1 cm) and deep core (30 – 31 cm) stratums inferred from ^{210}Pb dating. The number of lakes within each region is represents by n.

Region	n	Age $_{(0\text{-}1\ cm)}$ mean(SD)	Age $_{(30\text{-}31\ cm)}$	Depth at 1850 (cm)
Dorset A lake	6	3.7 (1.6)	all >150	17.7 (2.8)
Lake of the Woods	2	2.5 (1.6)	all >150	23.5 (6.4)
Southeastern Ontario	4	3.0 (1.8)	>150, one at 1935	24.0 (12.1)
Muskoka	5	1.4 (0.4)	all >150	20.0 (3.0)
Bruce Peninsula	3	1.6 (2.8)	all >150	18.0 (7.0)
Manitoulin Island	1	1	all >150	26.0 (NA)
Sudbury	4	5.6 (3.6)	all >150	11.5 (3.1)
Wawa	5	5.8 (4.1)	all >150	20.8 (2.4)
Overall	30	3.4 (2.7)		19.3(6.2)

Table 2.4: Sedimentation rates inferred from ^{210}Pb dating in the last 50 years and in the pre-industrial era from eight lakes within the study area. N represents the number of cores dated at each stratum within the study lakes.

Location		Mean Sedimentation rate				Absolute difference in deposition
		Last 50 years		1850 - 1900		
Lake	Region	($g \cdot cm^{-2} \cdot yr^{-1}$)	n	($g \cdot cm^{-2} \cdot yr^{-1}$)	n	
Crosson	SC Ontario	0.0082 ± 0.0006	7	0.0043 ± 0.0011	2	0.0039
Dickie	SC Ontario	0.0227 ± 0.0017	10	0.0071 ± 0.0010	2	0.0156
Harp	SC Ontario	0.0202 ± 0.0037	33	0.0076 ± 0.0013	9	0.0126
Plastic	SC Ontario	0.0097 ± 0.0007	25	0.0197 ± 0.0016	31	-0.0100
Red Chalk Main	SC Ontario	0.0134 ± 0.0021	37	0.0062 ± 0.0012	11	0.0072
Heney	SC Ontario	0.0124 ± 0.0014	31	0.0044 ± 0.0014	9	0.0080
Bigstone Bay	NW Ontario	0.0188 ± 0.0022	11	0.0208 ± 0.0016	2	-0.0020
PP-1	NW Ontario	0.0176 ± 0.0015	36	0.0172 ± 0.0010	3	0.0004
Overall		0.0154 ± 0.0017		0.0109 ± 0.0013		0.0040

Table 2.5: Mercury concentrations expressed as dry weight sediment extracted from surficial (0.5 -1 cm) and deep core (>30 cm) sediment within lakes upon granitic and limestone deposits.

		Mercury (ng/g d.w.)	
Location	Sediment	Within Region	Within Strata
Shield	Surficial	176 ± 5	241 ± 7
	Deep Core		111 ± 7*
Offshield	Surficial	144 ± 7	189 ± 10
	Deep Core		99 ± 10*

**Values are not significantly different from each other at the 95% confidence level*

Errors represent 1 standard deviation from the mean concentration

Table 2.6: Coefficients and the significance of the partial fit of each parameter in the prediction of mercury enrichment ([Hgtotal] present-day/[Hgtotal] historical).

Parameter	Value	Standard Error	t-value	p-value
Intercept	3.26	0.43	7.52	<0.0001
$A_d/(A_o^{\wedge n})$	15.96	6.53	2.44	0.020
$n \times pH_{(\geq 8.3)}$	-3.55	0.89	-4.01	<0.001
$n \times SO_4^{2-}$	-0.07	0.04	-1.68	0.1030

**pH was fit using a piece-wise linear regression were the break point was determined by best fit. The break point was established at pH 8.3.*

Table 2.7: Residual sum of squares and degrees of freedom for several models in the prediction of mercury enrichment ($[Hg_{total}]_{present\text{-}day}/[Hg_{total}]_{historical}$).

Model	Df	RSS
Drainage Ratio	48	68.45
Drainage Ratio + pH	46	47.16
Drainage Ratio(polynomial) + pH +SO_4^{2-}	33	17.28
Drainage Ratio(logarithmic) + pH +SO_4^{2-}	33	16.99

Chapter 3

The relation between mercury concentrations in smallmouth bass *(Micropterus dolomieu)* and lake sediment in south-central Ontario.

Abstract

This study incorporates landscape features and sediment mercury Hg concentrations to determine the most influential factors for Hg concentrations in the dorsal muscle of smallmouth bass (Hg_{Bass}) in Ontario. Hg concentrations in smallmouth bass (*Micropterus dolomieul*) were analyzed in lakes across a diverse landscape in Ontario and were found to be related to both present-day ($Hg_{Sediment}$) ($r = 0.92$, $p = 0.0002$) and pre-industrial lake sediment ($r = 0.76$, $p = 0.0107$) Hg concentrations in headwater systems. Land cover and geology were delineated for each watershed using GIS. Land cover was grouped by the proportion of coniferous and deciduous vegetation and density, anthropogenic disturbances such as; development, mine tailings, croplands, harvesting and burn sites were included before data reduction. Two artificial gradients were constructed to test the significance of watershed characteristics on the fate of Hg: component 1) lakes exhibiting low to high ($[Hg]_{Bass}$ and $[Hg]_{Sediment}$) and a second; component 2) from high $[Hg]_{Bass}$ low $[Hg]_{Sediment}$ to low $[Hg]_{Bass}$ high $[Hg]_{Sediment}$. Physico-chemical properties which enhanced Hg accumulation in both fish and sediment were; lake pH ($component_1$ score = -0.77), longitude (0.52), and the ratio of aluminum to dissolved organic carbon (DOC) (0.22). Properties which favored Hg accumulation in either smallmouth bass or lake sediment were; land cover ($component_2$ score = 0.72), longitude (0.58), and dissolved organic carbon (0.43). Land cover was more influential than geology and landscape features became more important when examining lakes regardless of order. Overall, lake pH and longitude were the dominant factors

in Hg distribution (combined components 1 and 2) explaining 53 % and 27 % of Hg variance, respectively in Ontario lakes.

Introduction

Widespread mercury (Hg) contamination of surface waters has reached levels known to cause harm in fish eating animals even in remote regions in the Northern Hemisphere (Basu et al. 2005b, Evers et al. 2005, Scheuhammer et al. 2007). Biota that inhabit higher trophic levels are especially at risk due to the bioaccumulative properties of organic Hg species. Aquatic biota residing in lakes of close proximity and therefore receiving similar atmospheric depositional Hg loads may exhibit significantly different Hg accumulation (Wiener et al. 2006, Munthe et al. 2007). This variability reflects the influence of ecosystem processes on the bioavailability of Hg to resident biota (Driscoll et al. 1995, Downs et al. 1998, Wiener et al. 2006).

Increasing or decreasing the Hg load to surface waters will result in a response from resident biota. However, the timing and magnitude of this response is dependent upon various ecosystem properties (Munthe et al. 2007). While the timing is largely a factor of drainage ratio, land cover and use (Munthe et al. 2007); the magnitude is a measure of the ability of an ecosystem to translate a given Hg load into MeHg concentrations. The ability to transform inorganic Hg into MeHg is largely the result of hydrology, water quality (dissolved sulfate, dissolved organic carbon, pH, and nutrients), trophic structure and temperature (Hammerschmidt and Fitzgerald 2006, Wiener et al. 2006, Munthe et al. 2007). However, regardless of the numerous processes influencing the timing and magnitude of mercury methylation there is no reason to expect that changes in inorganic Hg loading would not affect MeHg concentrations in ecosystems. In a survey of monitoring data within most of 25 states of the US, two-thirds of the

variation in largemouth bass MeHg concentrations was accounted for by wet atmospheric Hg flux (Hammerschmidt and Fitzgerald 2006).

Smallmouth bass (*Micropterus dolomieu*) is a carnivorous, cool water fish, common to temperate inland lakes of North America, and is a common subject for Hg contamination studies (McMurtry et al. 1989, Rasmussen et al. 1998). While biodilution may alter contaminant – fish size relationships, bioenergetic models suggest that Hg concentrations in smallmouth bass are more responsive to dietary Hg intake than to growth rate (Stafford and Haines 2001). Biodilution or the decreased concentration of chemicals in tissue due to a faster increase in tissue volume than chemical accumulation has been observed in multiple species of fish. To reduce the variability in fish Hg concentrations due to size, fish can be standardized to a certain length. Smallmouth bass is considered an intermediate trophic level species with a diet generally comprised of crayfish, insects and smaller fish. Although, Hg concentrations in some intermediate trophic level species such as smallmouth bass become similar to top-level predators at older ages (Neumann and Ward 1999), different factors influence Hg concentrations among the species (McMurtry et al. 1989).

The primary method of delivery for mercury to fresh water ecosystems is through atmospheric deposition (Hines and Brezonik 2007, Bookman et al. 2008, Watras and Morrison 2008) . Thus most Hg found in fish (Hammerschmidt and Fitzgerald 2006, Harris et al. 2007, Munthe et al. 2007) and most Hg precipitated into lake sediments has arrived from atmospheric sources (Perry et al. 2005). Since Hg exhibits a high affinity for organic matter and a large fraction of Hg entering surface waters is delivered to lake sediments (Boyle 2001) lake sediments can be used to reconstruct mercury loading. Despite variability in catchment and basin characteristics (Engstrom and Swain 1997, Landers et al. 1998, Bindler et al. 2001), sediment

studies of mercury deposition in remote areas around the globe show similar increases since the pre-industrial era. Further, in a repeated series of freeze cores collected over several years from lake sediment, there was no apparent loss of total mercury despite a 20-25% loss of carbon (Rydberg et al. 2008).

With the aid of a geographic information system, we assess the influence of land cover, geology and hydrology on the Hg concentration in dorsal muscle of smallmouth bass (Hg_{Bass}) and present-day lake sediment ($Hg_{Sediment}$) across a broad range of lakes. Hg_{Bass} was standardized to a length of 31 cm to reduce the influence of size on Hg concentrations. Using ordinal methods [redundancy analysis, Canoco v4.5 (ter Braak and Šmilauer 2002)], we discriminate between $Hg_{Sediment}$ and Hg_{Bass}. Our main objective is to test whether landscape features (topography, land cover, and surficial and quaternary geology) affect Hg concentrations in both sediment and fish equally or act to favor Hg accumulation in one or the other. We achieve this objective by creating two artificial gradients in our data; one from low to high concentrations of Hg in both $Hg_{Sediment}$ and Hg_{Bass} and a second from high $Hg_{Sediment}$; low Hg_{Bass} to high Hg_{Bass} low $Hg_{Sediment}$. A subset of headwater lakes was selected from the dataset and the influence of the parameters on $Hg_{Sediment}$ and Hg_{Bass} were reassessed. We would expect that in a more diverse set of catchments (i.e. regardless of lake order), land cover and geology should become more important in determining the fate of Hg. Increased Hg evasion from lake surfaces, decreased quantity of labile carbon from UV degradation, and selective sedimentation of certain fractions of DOC should collectively act to increase the variance from headwater lakes to lakes regardless of lake order.

Methods

Study Lakes

The majority of the study lakes (Figure 3.1) lie upon the Grenville Province which is characterized by rugged topography and is underlain with generally shallow tills and soils, with localized areas of thicker clay, sand, and gravel deposits (Jeffries and Schieder 1983). Land cover is primarily mixed forest, consisting of mainly coniferous, dense deciduous and sparse deciduous forest (Hall and Smol 1996). The study area is subject to acid deposition from long-range sources CADSA (2004). Morphometric (watershed area, lake area, slope of basin, and length of tributaries) and hydrological data (mean annual: precipitation, runoff, evaporation, and snowfall) were delineated for watersheds using digital elevation models (DEM) to determine watershed boundaries. GIS layers (i.e. hydrology, land cover) were compiled using Ontario Flow Assessment Techniques, a GIS based application produced by the Ontario Ministry of Natural Resources (Chang 2002). The base map of land cover was assembled from the Ministry of Natural Resources' Land Information Ontario/ Natural Resource Values Information System. Since the DEM contain vector information, lake order was established by observing upstream lakes. Geological information was drawn from 1:50,000 scale maps, although some data were collected on a smaller scale.

Sample Collection

Data used for water chemistry (Table 3.1) were gathered from Ontario Ministry of the Environment (OMOE) long-term lake monitoring databases, as well as previous studies (Hall and Smol 1996, Reavie and Smol 2001, Dixit et al. 2002). Lake water sampling (Locke and Scott 1986) and chemical analyses (Ontario Ministry of Environment 1983; Janhurst (1998)) were performed by OMOE. In most instances, water chemistry from south-central Ontario lakes represents multiple measurements of volume-weighted whole-lake composites. Some lakes

were sampled on a biweekly basis, others monthly, or bimonthly during the ice-free seasons. Water from lakes in eastern Ontario and on the Bruce Peninsula were collected as surface or epilimnetic composites in the spring and late summer only. Details regarding sediment and chemical sampling procedures have been published previously (Hall and Smol 1996, Reavie and Smol 2001, Dixit et al. 2002).

Field and laboratory methods

Lake sediments were collected using Lucite™ Glew gravity corers (Glew 1989) in replicate at the deepest point of each lake between 2001 and 2003. Sediment cores were sectioned on the lake shore using a Glew (1988) extruder, into Whirlpak© bags and stored in coolers for transport back to the lab. Samples were refrigerated at the Paleoecological Environmental Assessment and Research Laboratory at Queen's University at 4°C in the dark until analysis.

In this study, two sediment sections were examined in each core: the top 0.5 to 1.0 cm (present-day lake sediment) referred to as $Hg_{Sediment}$ in this study, and a 0.5 to 1.0 cm interval taken at a minimum core depth of 30 cm (pre-industrial lake sediment). Although the precise date of the bottom sample from each lake is not known, dating of lake sediments using ^{210}Pb from many south-central Ontario lakes indicates the pre-industrial time (pre-1850) period is typically reached at a sediment depth of 19.3 ± 6.2 cm (Evans 1986, Clerk et al. 2000, Mills et al. 2009). In a previous study of 30 lakes in which we evaluated the age and sedimentation rate of lake sediment from various regions within our study area we determined that the 0.5 to 1.0 cm stratum represented approximately 3.4 ± 2.7 years of age (Mills et al. 2009).

Mercury concentrations of sediment samples were determined using high temperature combustion followed by atomic absorption detection (SP-3D, Nippon Instruments Corp., Osaka,

Japan). Sediments were freeze dried and then ground to a fine powder using a mortar and pestle. Approximately 30 mg of the sample was covered with activated alumina powder and placed into a ceramic holder. A catalyst converted the Hg to elemental Hg which was trapped by gold amalgamation then thermally desorbed and detected by atomic absorption at 253.7 nm. Certified reference material (MESS-3, NIST 1603) was used to calibrate the response. The variability in Hg concentrations was quantified for duplicate samples, several samples within a single core (0.5-1cm) and for adjacent cores from the lake bottom prior to developing models. The relative standard error in Hg concentrations for analytical duplicates was 2.6 %, while difference between adjacent cores was 5.9 %.

Smallmouth bass were collected from inland lakes in Ontario by the Ontario Ministry of Natural Resources and Ontario Ministry of the Environment to monitor the concentration of toxic chemicals in sport fish. The fish were collected using seine nets then selected to represent a gradient of sizes. Thirty-one of these lakes were used in the present study as they overlap with a survey of Hg in lake sediment, 11 of the lakes were headwater systems (no upstream lake). Mercury concentrations were determined by cold vapour atomic fluorescence absorption following acid digestion. Log Hg concentrations (wet weight of dorsal muscle) were regressed against the centered log fish length for each lake using methods in McMurtry et al. (1989). Fish muscle, is commonly examined since most of the Hg found in muscle is in the neurotoxic MeHg form (Bloom 1992) and fish muscle is the major route of human exposure to MeHg. Mercury concentrations from individual fish were discarded if they fell outside the 99 % confidence interval of their populations log Hg vs log length regression, in all ten individuals were discarded. The relationship was then used to predict the concentration of Hg at a standardized length of 31 cm, chosen to represent fish still growing but having reached sexual maturity.

Data Analysis

The association between Hg in present-day and pre-industrial lake sediments, and in dorsal muscle of smallmouth bass of 31 lakes, as well as a subset of 11 headwater systems was examined. Pearson's correlation coefficient was used since Hg concentrations were normally distributed according to the Kolmogorov–Smirnov test. This relationship was examined in headwaters, and separately considering all lakes regardless of landscape position within our study region (Sigma Stat 3.0). Data were assessed for heteroscedacity and linearity prior to further analysis.

Principal components were extracted from GIS layers of an Ontario Ministry of Natural Resources database (OFAT) which included the areal size (km^2) of each classification in land cover, and geology (surficial and quaternary) as noted in Table 3.2. Site scores from the orthogonal axes were used in a redundancy analysis (RDA) to indicate which factors may discriminate the differences between lakes that contain relatively high Hg_{Bass} compared to $Hg_{Sediment}$ and was performed using Canoco 4.5. Two artificial gradients were created the first representing a gradient of low to high Hg_{Bass} and $Hg_{Sediment}$ and a second gradient from high Hg_{Bass}, low $Hg_{Sediment}$ to low Hg_{Bass}, high $Hg_{Sediment}$. Hg accumulation in lake sediment may is a good proxy for secular trends of Hg loading to lakes but gives little indication of the methylation potential of a lake. The second gradient tested in the RDA makes a relative comparison revealing the tendency of Hg to partition between smallmouth bass and lake sediment and therefore assess the methylating potential. Through this analysis we determined if there are characteristics which make biota in certain lakes especially susceptible to Hg contamination. Prior to running the analysis, variables were centered and standardized by their mean and standard deviation, respectively. Forward selection was performed due to the high number of

predictor variables, and the analysis was constrained by keeping variance inflation factors (VIF) below 5. To determine the unique variance which each variable could explain in Hg concentrations (Hg_{Bass} and $Hg_{Sediment}$), Monte Carlo permutations (n = 1000) were conducted. Monte Carlo permutations iteratively delete and insert each variable in various combinations of the remaining variables to establish their significance, in this case explaining variance in Hg_{Bass} and $Hg_{Sediment}$. Variables deemed as important predictors from the RDA were included in a backward stepwise regression (threshold $F > 4$) and selected based upon Akaike's information criterion. Hg_{total} in present-day sediments was forced into the model. Transformation was conducted when necessary according to Levene's test of homogeneity of variance.

Results

Mercury concentrations in the dorsal muscle of smallmouth bass were regressed against the log centered length of fish in 31 lakes of this study, in order to standardize the results among the fish from different lakes. In all lakes, fish shorter and longer than 31 cm were collected. At a standardized length of 31 cm, predicted Hg concentrations in 32 % of the lakes exceeded 0.5 $\mu g \cdot g^{-1}$; the human advisory action level of the World Health Organization (WHO). Figure 3.2 represents the distribution of Hg concentrations in the dorsal muscle of smallmouth bass standardized for 31 cm length in south central Ontario lakes.

Mercury concentrations in the sediments of these lakes varied considerably with an average of 246 ± 113 $ng \cdot g^{-1}$ d.w. sediment. Mean Hg concentration in smallmouth bass was 0.41 ± 0.18 $\mu g \cdot g^{-1}$ wet weight. The relative standard deviation of both concentrations was 46 %. While this may seem high, the study area transects a diverse geology with peak sediment Hg concentrations reaching 500 $ng \cdot g^{-1}$ d.w.. This concentrations is much higher than the 95th percentile for sediment Hg concentrations in Ontario, even for shale deposits (305 $ng \cdot g^{-1}$ (Friske

and Coker 1995). The 95th percentile in our study was 375 ng·g^{-1} with a factor of 3.7 from 5th to 95th percentile, compared to a 9 fold increase across Ontario (Friske and Coker 1995).

Sediment Hg concentrations were found to be significantly correlated with fish Hg concentrations as found in previous studies (McMurtry et al. 1989, Levinton and Pochron 2008). In fact, Hg concentrations in bass were significantly correlated with both present-day and pre-industrial sediment Hg concentrations when all lakes were considered regardless of landscape position. Although, this relationship may be regional since no relationship was found among muscle tissue mercury concentrations of Yellow perch (*Perca flavescens*) or hypolimnetic MeHg and sediment Hg in 47 New Hampshire and Vermont lakes (Kamman et al. 2004). Nevertheless, when we examined the headwater lakes alone, the correlation dramatically increased for present-day sediments (0.5-1cm depth) from $r = 0.37$ to 0.92; $p = 0.012$ to 0.0002 (Figure 3.3). The correlation between pre-industrial sediments and Hg concentrations in smallmouth bass did not increase significantly when we examined headwaters alone.

To evaluate the influence of watershed attributes on fish and sediment Hg concentrations, we first had to reduce the number of parameters used in the redundancy analysis. We reduced the number of parameters by first extracting orthogonal axes from information gathered using GIS layers and then by forward selection procedure. From GIS databases we extracted the principal components of land cover and both surficial and quaternary geology for each watershed of our study lakes after centering the areal coverage by study site and attribute (Table 3.2). The first two PCs for land cover, surficial, and quaternary geology were able to explain 42.7, 45.1, and 54.3 % of the variance in these categories, respectively (Table 3.3).

Redundancy analysis was performed on remote lakes in south-central Ontario (n=31) and on a subset of headwater lakes (n=11) (Figure 3.4). Two artificial gradients were created the first gradient (ordinal axis) represented a gradient of low Hg_{Bass}, low $Hg_{Sediment}$ to high Hg_{Bass}, high $Hg_{Sediment}$ and a second axis a gradient from high Hg_{Bass}, low $Hg_{Sediment}$ to low Hg_{Bass}, high $Hg_{Sediment}$. For headwater lakes, these two ordinal axes captured 97% of the variance in the overall distribution of Hg_{Bass} and $Hg_{Sediment}$. 87% of the variance in Hg_{Bass} and $Hg_{Sediment}$ was explained in the first ordinal axis and the remaining 10% was explained in the second (Table 3.4). Considering both axes, less variance in Hg_{Bass} and $Hg_{Sediment}$ was explained (78 %) when examining lakes regardless of lake order.

Two artificial gradients in Hg_{Bass} and $Hg_{Sediment}$ were created to examine which physico-chemical parameters influence the distribution of Hg in surface waters. The magnitude of the vector representing each parameter is an index of the influence on either of the two gradients. On the first ordinal axis negative values represent low Hg_{Bass}, low $Hg_{Sediment}$ and positive values represent high Hg_{Bass}, high $Hg_{Sediment}$. Lake pH: -0.77 dominated this gradient followed by, longitude (UTM): 0.52, and Al/DOC: 0.22. As in headwater lakes, pH (-0.59) dominated the first ordinal axis regardless of lake order, followed by runoff potential (-0.53) and watershed slope (0.44). Runoff potential is an index (0-100%, 100% complete runoff) created by the US soil conservation society which considers topography, land cover, and soil type. An inverse correlation between DOC and watershed slope was found in this study: DOC = 5.22 – 0.216 x Slope of watershed ($R^2 = 0.52$, n = 53, $p < 0.001$), likely an indication of increased peatland area in watersheds of shallow slope. However, despite high DOC content, which in previous studies has been deemed the primary vector of Hg watershed export (Meili et al. 1991, Mierle and Ingram 1991), total Hg concentrations in present-day lake sediments increased with watershed

slope (R^2 = 0.47, n =53, p<0.001). In headwaters, the second ordinal axis (high Hg_{Bass}, low $Hg_{Sediment}$ to low Hg_{Bass}, high $Hg_{Sediment}$) was dominated by landcover PC1: 0.72, longitude: 0.58, and DOC: 0.43. Likewise, the most significant factors on the second ordinal axis of all lakes were the same: DOC: 0.40, land cover PC1: 0.39, and longitude: 0.35. All three factors acted to increase the proportion of Hg precipitated to lake sediment and/or prevented Hg accumulation by smallmouth bass.

Lake pH and longitude far exceeded other variables in explaining overall distribution of Hg concentrations in our study lakes (i.e. considering both ordinal axes). Accordingly, lake pH was the only variable to explain additional variance in smallmouth bass Hg concentrations above present-day lake sediments $Hg_{Bass} = 1.13 + 0.0006 \times Hg_{Sediment} - 0.115 \times pH$; $R^2 = 0.96$, n = 10, p<0.0001, (Figure 3.5) in headwater lakes. Lake pH ranged from 4.6 to 9.9 with a mean value of 7.7. There was no significant interaction between pH and sediment Hg. Neither the inclusion of dissolved organic carbon, nor any other physico-chemical parameter (listed in Table 3.4) was able to explain any additional variance in Hg_{Bass}. Performing the same analysis on all lakes we found that pH was less important than for headwater lakes alone. Selecting the best model on the basis of AIC we found that watershed area, inverse drainage ratio, runoff potential and lake pH were best able to explain $Hg_{Bass} = 1.454 - 0.107 \times pH - 0.00595 \times$ runoff potential $+ 0.474 \times$ Ao/Ad $- 0.000224 \times$ watershed km^2; $R^2_{adj} = 0.49$, n=31, p=0.007, AIC = -10.9 for all lakes.

Partial regression analysis was performed to determine spatial artefacts in Hg_{Bass} and whether these could be the result of spatially correlated predictor variables. For headwater systems, $Hg_{Sediment}$ and pH were significant and so included along with a 2nd order polynomial of latitude and longitude. As a result, the prediction of Hg_{Bass} increased to $R^2_{adj} = 0.98$, n=11, p=0.005, a 2.1 % increase from excluding a spatial trend. 5.8% of this variance was explained

by space alone, with the majority of the variance coming from $Hg_{Sediment}$ and lake pH which were spatially correlated 78.6%. The remaining variance was explained by the pure effect of $Hg_{Sediment}$ and lake pH. Disregarding lake order, the pure effects of significant predictor variables explained 23.6 % of the variance in Hg_{Bass}, while an additional 28.4 % was spatially correlated with a 2^{nd} order polynomial.

Discussion

The lakes included in this study represent a broad spectrum of water quality characteristics, land cover and geology. Our objective was to determine which parameters best discriminate between Hg concentrations in smallmouth bass (Hg_{Bass}) and those in lake sediment ($Hg_{Sediment}$) within such a lake set. By simultaneous investigation of Hg_{Bass} and $Hg_{Sediment}$ we can make inferences concerning the relative concentration in either compartment. In other words, sites that have high Hg_{Bass} levels do not necessarily represent sites that most efficiently transform Hg load to bioavailable forms of Hg. Rather, sites which have high Hg_{Bass} for a given level of $Hg_{Sediment}$ are most conducive to this transformation. We assumed that variables which increase both Hg_{Bass} and $Hg_{Sediment}$ reflect an increased Hg load and variables which partition between Hg_{Bass} and $Hg_{Sediment}$ reflect the bioavailability of Hg. We conducted the analysis on lakes of all order and then isolated headwater lakes. Although correlated, Hg_{Bass} and $Hg_{Sediment}$ were less significantly correlated in higher order lakes. Headwater lakes were analyzed as a subset to minimize confounding chemical inputs from upstream sources (Hall et al. 1999, Soranno et al. 1999). Hg evasion to the atmosphere, which depends on exposure to UV radiation among other variables (primarily pH and DOC) becomes increasingly important the longer Hg is in the water column (Amyot et al. 1997, O'Driscoll et al. 2003). Further, the precipitation of select fractions of Hg in upstream lakes may increase the variance between Hg_{Bass} and $Hg_{Sediment}$ in higher order lakes.

Such processes can under certain circumstances be significant, such as the volatilization of Hg in high pH lakes (Vandal et al. 1991). Evasional flux has been shown to be as high as 45% of the Hg load after experimental addition (Southworth et al. 2007).

Lake sediment in our study appeared to be relatively contaminated compared to other regions (Friske and Coker 1995). Furthermore, the range between the lower and upper percentiles was less than half of the sediment Hg concentrations observed in previous studies. This may have been a result of sampling in a relatively contaminated area where sediment Hg load has increased. High fish muscle Hg concentrations have been found in the region during previous studies (Rasmussen 1993) which were attributed to geological sources. Although, undoubtedly the majority of Hg delivered to our study lakes arrived through atmospheric deposition, similar to numerous other studies (Engstrom et al. 2007, Parsons et al. 2007, Watras and Morrison 2008). To place the level of Hg contamination in context, thirty-two percent of the study lakes contained standardized Hg values in smallmouth bass in excess of values (0.5 $\mu g \cdot g^{-1}$) known to cause physiological impairment (Wiener and Spry 1996). The spatial correlation and appearance of longitude in the ordinal analysis as a factor which increased with Hg_{Bass} and $Hg_{Sediment}$ could be a result of broad scale geology or anthropogenic deposition. Among headwater systems 78.6 % of the variance in Hg_{Bass} was spatially correlated with pH and $Hg_{Sediment}$. Hydrology and geology were included in the forward selection of variables and so this spatial correlation suggests some additional unaccounted variables as would be provided by anthropogenic activity.

Including lakes which receive flow from upstream lakes did not seem to significantly alter the parameters primarily responsible for the Hg concentrations in smallmouth bass and sediment. An RDA was performed (Figure 3.4) on Hg concentrations in a standardized length of

smallmouth bass and on surficial sediments in lakes of all order and headwater systems alone. We interpret the first axis to be an index of Hg loading to the lake, while the second we interpret as an index of the relative biological Hg accumulation. Results from RDA indicated that in both sets of lakes factors most influential to both gradients in Hg distribution were similar. Mercury loading to our study lakes was largely associated with lake pH explaining the majority of variance in Hg concentrations in sediment (20%; headwater and 53%; all lakes). According to partial regression analysis, much of the variance in $Hg_{Sediment}$ was spatially autocorrelated. Low pH conditions increase the mobility of Hg from the watershed (Lodenius and Autio 1989, Schuster et al. 2008) and decrease the evasion of Hg to the atmosphere (Vandal et al. 1991). Although mercury methylation is generally more rapid at lower pH (Benoit et al. 2003) and many studies have found lake acidity to increase fish muscle Hg (Scheuhammer and Blancher 1994, Haines et al. 1995), pH was not the dominant factor discriminating between $Hg_{Sediment}$ and Hg_{Bass} in our study. Previous studies have noted that acid deposition increases the accumulation of Hg in fish if deposited on to the lake (Richardson et al. 1995).

Mercury distribution between present-day lake sediment and the dorsal muscle tissue of smallmouth bass was influenced by DOC, longitude and $landcover_{PC1}$. Previous studies have observed increased fish-Hg with increased DOC (age 3 to 5 perch; (Driscoll et al. 1995, Watras et al. 1995b). DOC is intimately linked to the transport of Hg from the watershed (Mierle and Ingram 1991), the net methylating/demethylating of the catchment (Watras et al. 1995b, Benoit et al. 2003), and the bioavailability of Hg to aquatic biota (Driscoll et al. 1995). It is therefore difficult to depict a general role of DOC in determining fish-Hg concentrations. While previous studies suggest that Hg availability is diminished at high DOC concentrations (Driscoll et al. 1995), we observed that DOC acts to favor the sedimentation of Hg even at relatively low

concentrations. Dissolved organic carbon concentrations in our study lakes were relatively low (2.3-6.2 mg $C \cdot L^{-1}$, median = 4.1 mg $C \cdot L^{-1}$) in comparison to lakes studied by Driscoll et al. (1995) (2.0 - 20 mg $C \cdot L^{-1}$), nevertheless DOC only displayed significance on RDA_2. Hg loading to surface water is enhanced in the presence of DOC (Mierle and Ingram 1991), and probably most importantly, DOC may be acting as a proxy to peatland area in the watershed which would be a dominant source of MeHg in most of these lakes.

Land $cover_{PC1}$ appeared to represent a gradient of forest cover going from cropland and pastures to dense coniferous and deciduous forests and explained 5% of unique variance in Hg distribution among lakes regardless of order and when isolating headwater systems. Land $cover_{PC2}$ explained an additional 4 % of variance in Hg distribution in the former with little covariance with PC1. Together, these two variables represented 42.7 % of the original land cover information collected using GIS (PC1; 23.4, PC2; 19.3). Similar to results found by Soneston (2003) fish-Hg concentrations were highest in boreal forest lakes (classified as dense coniferous and deciduous forests in this study, represented by Land $cover_{PC1}$). Highly arable lands (croplands/pastures) contained relatively low levels of fish-Hg compared to lake sediments. Organic-rich topsoil of arable lands have been shown to contain higher concentrations of Hg than forest soils (Sonesten 2003), and this could reflect a higher retention in arable soils. Further, the higher ion concentration in lake water observed in association with arable catchments could aid in the precipitation of Hg complexes.

Geology has been shown to alter the concentration of methylmercury in wetlands due to the association between biological activity and lithology (Siciliano et al. 2003). In our study we found that quaternary geology played little role in the distribution of Hg in our study lakes, despite the principal components capturing 53.4 % of the variance in the original GIS database.

Surficial geology did have a minimal but significant effect on Hg distribution on the full lake set, likely due to the covariation between lithology and land cover.

This study considered the sedimentation and/or uptake of Hg by aquatic biota under a wide range of physico-chemical variables. Although pH remains to be a master variable affecting Hg concentrations in fish, DOC was the variable which most influenced the relationship between $Hg_{Sediment}$ and Hg_{Bass}.

Conclusion

We have conducted a study which puts physico-chemical parameters of watersheds into context for determining the distribution of Hg in sediment and smallmouth bass. GIS was utilized to gather a large amount of information describing the land cover, geology and hydrology of surface waters. This study complements the mechanistic approaches of previous studies by examining known variables of importance across a diverse landscape. Furthermore, we have provided insight into whether various parameters are simply acting to increase Hg concentrations in the aquatic ecosystem or acting to enhance the uptake of Hg by aquatic biota.

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Figure Legend

Figure 3.1: Location of study lakes in central and eastern Ontario, Canada (45.53° N 82.41°W to 44.15N 76.25 W). Smallmouth bass and sediment were collected and analyzed for total mercury content.

Figure 3.2: Frequency distribution for the population means of mercury concentrations in the dorsal muscle of smallmouth bass ($\mu g \cdot g^{-1}$ w.w.) standardized for 31 cm length in 31 headwater lakes of south-central Ontario. Standardized concentrations were predicted from the log Hg = centered log length relationship. The dashed line represents the World Health Organization's and Health Canada's guideline for safe consumption.

Figure 3.3: Mercury concentrations in smallmouth bass plotted against mercury concentrations in present-day (•; 0.5-1cm depth) and pre-industrial (○; >30 cm depth) sediment in south-central Ontario lakes a) regardless of landscape position and in b) headwaters.

Figure 3.4: Biplot of physico-chemical properties of lakes in our study region including mercury concentrations in the dorsal muscle of smallmouth bass (predicted for 31 cm length) and surficial sediments (0.5-1cm). Data were centered and standardized prior to analysis (Canoco 4.5). Analysis was performed on a) lakes regardless of lake order (n=31) and b) headwater lakes (n=11).

Figure 3.5: Results from a multiple linear regression of mercury concentrations in the dorsal muscle of smallmouth bass (standardized for 31 cm length) in a) lakes regardless of lake order (n=31) and b) headwater lakes (n=11) from south-central Ontario. Mercury concentrations in smallmouth bass were predicted from pH and sediment mercury concentrations; $Hg_{Bass} = 1.13 + 0.0006 \times Hg_{Sediment} - 0.115 \times pH$ for headwaters and

Hg_{Bass} = 1.454 - (0.107 x pH) - (0.00595 x runoff potential) + (0.474 x Ao/Ad) - (0.000224 x watershed km^2) for all lakes. The dashed lines represent the 95% confidence interval.

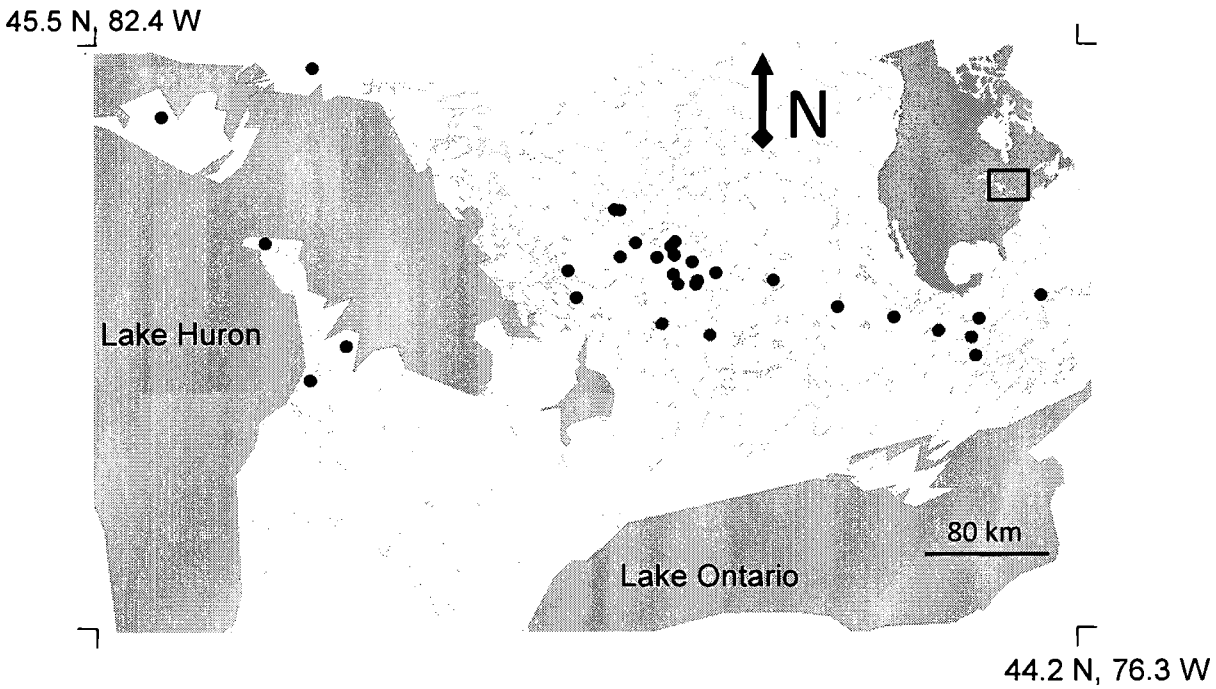
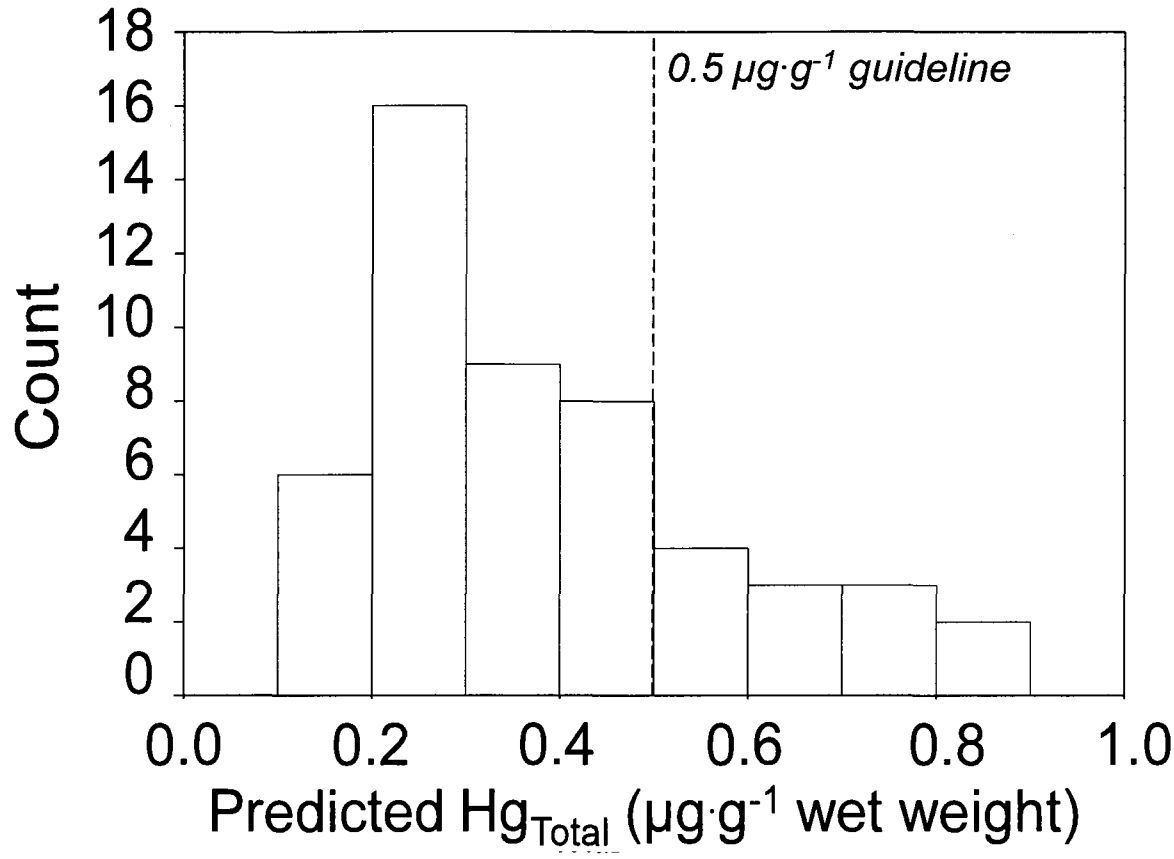


Figure 3.1: Location of study lakes in central and eastern Ontario, Canada (45.53° N 82.41°W to 44.15N 76.25 W). Smallmouth bass and sediment were collected and analyzed for total mercury content.



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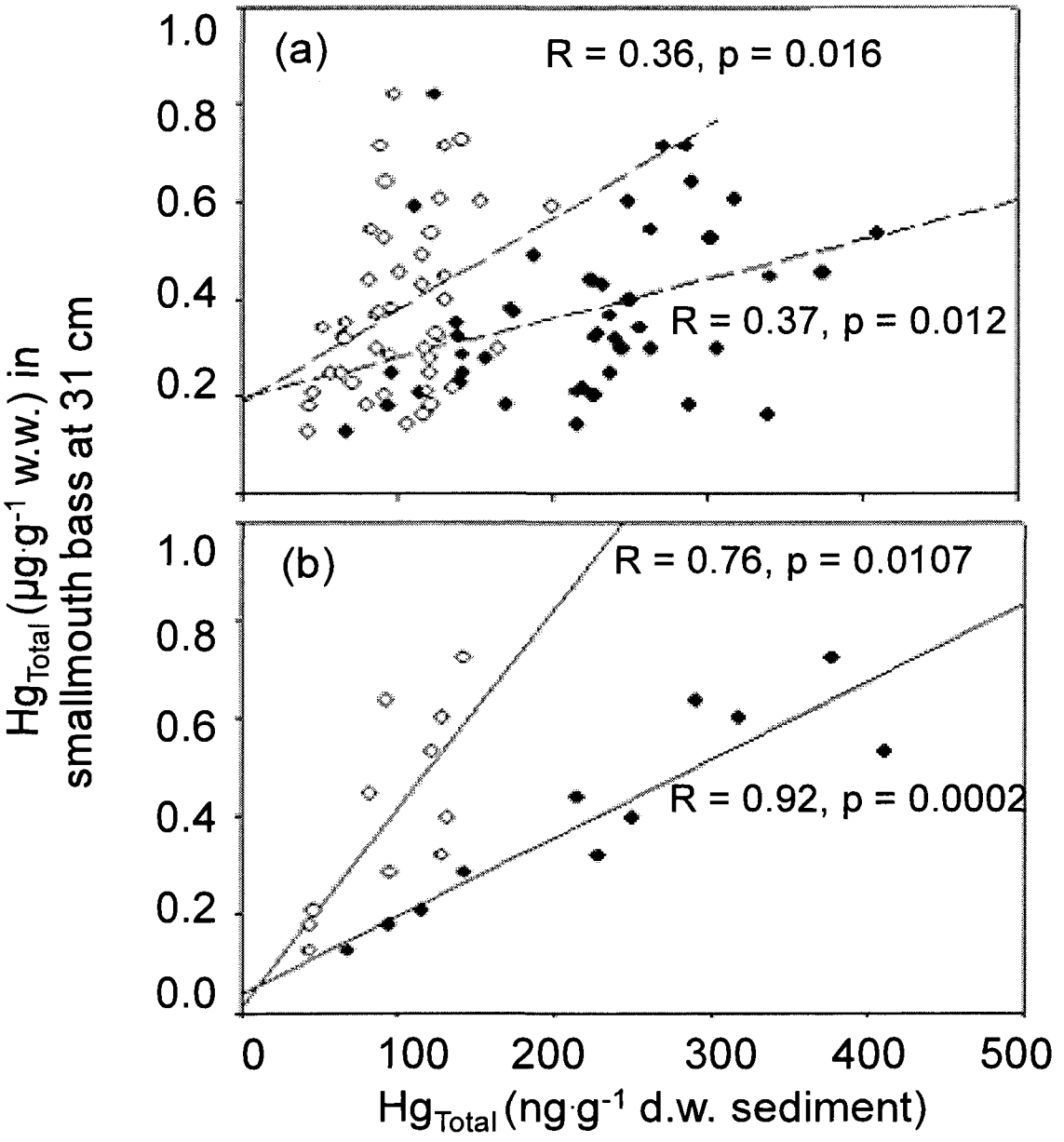

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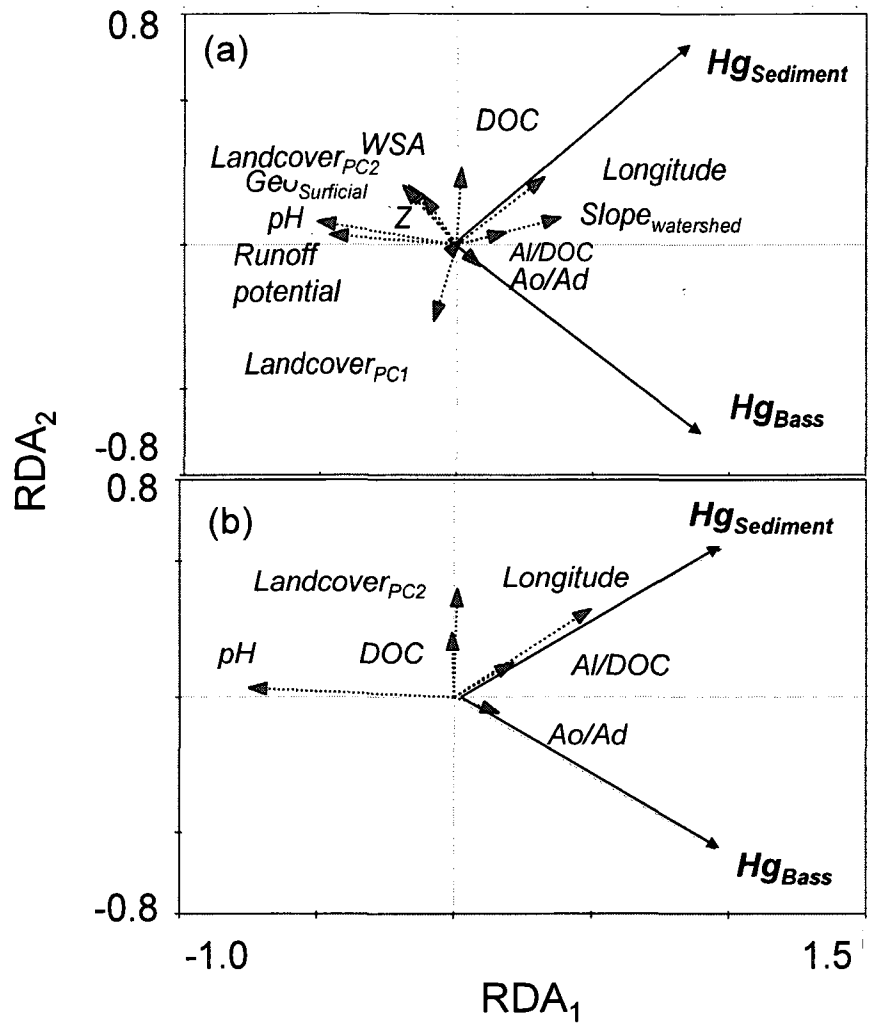

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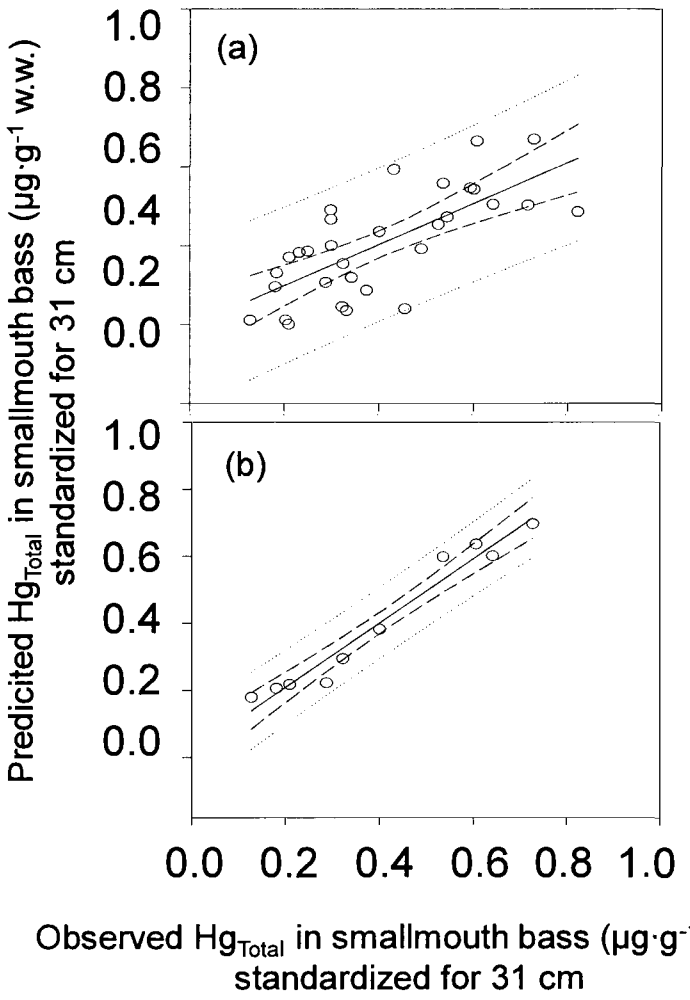

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Table 3.1: Physico-chemical properties of south-central Ontario lakes included this study along with mercury concentrations in smallmouth bass and lake sediment.

				Area (km^2)		Wetland	Max	Slope of	Runoff	pH	DOC	$Hg_{Sediment}$ ($ng \cdot g^{-1}$ OM)		#	Hg_{Fish} ($\mu g \cdot g^{-1}$)		
Lake	Ad/Ao	Latitude	Longitude	Watershed	Lake	(%)	Depth (m)	Watershed	Index		($mg \cdot L^{-1}$)	Present-day	Pre-industrial	Fish	Mean	SD	at 31 cm
Bass	12	44.72	-80.99	5	1	1	15	3	60	8.6	3.1	0.40	0.24	15	0.42	1.44	0.13
Cameron	6	45.23	-81.55	9	2	7	15	2	56	8.5	5.8	0.56	0.18	18	0.17	1.28	0.18
Chub	9	45.21	-78.98	3	0	1	27	9	39	5.6	4.9	0.78	0.30	19	0.74	1.24	0.73
Crystal	9	44.75	-78.49	41	4	5	33	4	38	7.8	5.5	0.60	0.29	9	0.39	1.32	0.40
Gilmour Bay (	4	44.78	-77.95	3	1	2	25	5	59	7.5	4.6	0.45	0.87	8	0.65	1.35	0.44
Harp	8	45.38	-79.13	5	1	2	38	12	49	6.4	3.7	0.84	0.51	10	0.52	1.60	0.60
Kagawong	2	45.84	-82.28	105	55	0	33	2	76	8.6	3.8	0.48	0.40	31	0.28	1.25	0.29
Limerick	24	44.86	-77.61	181	7	1	29	7	45	8.0	4.3	0.80	0.29	18	0.26	1.44	0.34
Muskoka Bay	5	44.95	-79.40	11	2	2	14	5	59	7.1	3.9	0.31	0.75	34	0.56	1.63	0.59
Newboro	20	44.62	-76.30	375	18	2	24	5	59	8.4	4.8	0.30	0.20	7	0.43	1.77	0.38
Pike	19	44.80	-76.33	32	2	0	33	5	70	8.5	5.5	0.58	0.30	11	0.20	1.20	0.22
Skootamatta	16	44.80	-77.22	132	8	2	25	4	45	6.9	5.1	0.79	0.44	9	0.53	2.24	0.30
Three Mile	20	45.17	-79.45	127	6	2	5	5	59	7.1	6.4	1.06	0.90	7	0.22	1.20	0.25
Walker	3	45.37	-79.09	2	1	2	17	9	57	6.7	3.4	0.97	0.34	13	0.52	1.25	0.54

A_d/A_o represents the drainage ratio and is the watershed area/lake area.

Runoff Index was determined using methods of the US Soil Conservation Service.

DOC represents the concentration of dissolved organic carbon.

OM represents the amount of organic matter present in lake sediment as determined by loss on ignition.

SD represents one standard deviation.

Table 3.2: Scores for the first (PCA_1) and second principal component (PCA_2) of attributes classifying landcover, surficial and quaternary geology from 31 south-central Ontario watersheds.

Landcover			Geology					
			Surficial			Quaternary		
	PCA_1	PCA_2		PCA_1	PCA_2		PCA_1	PCA_2
Dense Deciduous Forest	0.42	-0.47	*Escarpment*	0.00	0.00	*gravel and sand* $_{proglacial\ river\ and\ deltaic\ deposits}$	-0.24	0.01
Dense Coniferous Forest	0.77	-0.37	*Esker*	0.00	0.00	*gravel and sand* $_{minor\ till/esker/kame/moraine/ice\text{-}marginal/delta}$	0.01	0.01
Coniferous Plantation	0.60	-0.42	*Lacustrine Deposit*	0.99	0.14	*peat, muck and marl*	0.43	-0.15
Mixed Forest Mainly Deciduous	0.77	0.11	*Organic*	0.00	-0.42	*sand, gravelly sand and gravel* $_{nearshore\ and\ beach\ deposits}$	0.81	-0.37
Mixed Forest Mainly Coniferous	0.66	0.40	*B and A* $_{weak}$	0.01	-0.22	*sandy silt to silt matrix* $_{moderately\ stony,\ strongly\ calcareous}$	0.90	-0.36
Sparse Coniferous Forest	0.32	0.64	*Ground Morain* $_{weak}$	0.36	-0.58	*silt and clay, minor sand* $_{basin\ and\ quiet\ water\ deposits}$	0.83	0.28
Sparse Deciduous Forest	0.24	0.54	*Lime Shale* $_{weak}$	0.99	0.14	*undiffer carbonate/clastic sedimentary* $_{exposed\ at\ surface}$	0.31	0.93
Settlement and Developed Land	0.28	0.09	*Outwash deposit* $_{weak}$	-0.05	-0.39	*undiffer igneous/metamorphic rock* $_{exposed\ at\ surface}$	-0.33	0.31
Mine Tailings	0.04	0.69	*Bedrock*	-0.06	-0.52	*undiffer sandy silt to silt matrix* $_{clasts/high\ carbonate}$	0.29	0.94
Pasture and Abandoned Fields	-0.10	-0.43	*Lime Shale* $_{moderate}$	0.99	0.14			
Cropland	-0.40	-0.46	*Ground Morain* $_{moderate}$	-0.24	0.74			
Recent Cut	0.32	0.10	*Outwash deposit* $_{moderate}$	-0.13	0.50			
Recent Burns	0.60	-0.42						

Table 3.3: The variance explained by the first (PCA_1) and second principal component (PCA_2) of attributes classifying landcover, surficial and quaternary geology from 31 south-central Ontario watersheds.

Attribute	Division	Axis	Eigen values	Cumulative % of Variance
Landcover		PCA_1	23.4	23.4
		PCA_2	19.2	42.7
Geology	Surficial	PCA_1	28.4	28.4
		PCA_2	16.7	45.1
	Quaternary	PCA_1	29.9	29.9
		PCA_2	24.4	54.3

Table 3.4: Results of a redundancy analysis of mercury concentrations in smallmouth bass and present-day lake sediment (0.5-1cm depth) in south-central Ontario lakes (n = 31). The data were subset for headwater lakes (n = 11) and re-analyzed. Two axes were calculated from a redundancy analysis (RDA_1 and RDA_2) for each dataset, and data were centered and standardized prior to analysis. VIF represents the variance inflation factor for each variable.

	All Lakes				Headwaters			
	RDA_1	RDA_2	VIF	Unique variance explained	RDA_1	RDA_2	VIF	Unique variance explained
Longitude	0.37	0.35	1.62	0.10	0.52	0.58	1.63	0.27
Watershed (km^2)	-0.20	0.30	2.89	0.04				
Drainage $Ratio^{-1}$	0.10	-0.11	1.74	0.01	0.17	-0.10	1.63	0.03
Depthmean (m)	0.02	0.03	1.64	0.00				
Watershedslope (%)	0.44	0.14	1.78	0.11				
Runoff Potential (%)	-0.53	0.05	1.68	0.16				
pH	-0.59	0.12	2.23	0.20	-0.77	0.06	1.20	0.53
DOC ($mg \cdot L^{-1}$)	0.02	0.40	2.25	0.03	-0.01	0.43	2.55	0.02
Al/DOC	0.21	0.06	2.49	0.03	0.22	0.23	1.83	0.05
$Geology_{SurficialPC1}$	-0.14	0.26	13.00	0.02				
$Landcover_{PC1}$	-0.10	-0.39	12.85	0.05	0.01	0.72	1.60	0.05
$Landcover_{PC2}$	-0.23	0.31	1.87	0.04				

	Species-environment R	Eigen values	Cumulative % of Eigenvalues	Sum of eigenvalues
Headwater	0.99	0.88	87.5	0.97
	0.97	0.10	97.1	
All Lakes	0.94	0.58	57.6	0.78
	0.77	0.20	77.7	

1

Chapter 4

Regional examination of the influence of space, morphometry, and geology on Hg enrichment across Ontario

Abstract

Atmospherically deposited mercury (Hg) originates from global, regional and local sources. In this study we dissect spatial patterns of mercury concentrations in a northern boreal forest. Total mercury content was analyzed in 171 lakes from pre-industrial (>30 cm depth) and present-day sediments (0.5-1 cm). Non-stationality (local hot spots or cold spots) of mercury enrichment was determined using local tests of autocorrelation. Numerous spots were evident, although in most cases, the maximum correlation among sites was not the nearest neighbor, indicating a strong influence of watershed characteristics on mercury enrichment. Site-level influence on mercury enrichment in the study area was dominated by the area of open water ($r = 0.91$, $p = 0.035$), mine tailings ($r = 0.94$, $p = 0.019$), and organic deposits in surficial geology of the watershed ($r = -0.91$, $p = 0.034$). Despite an increased R^2 value from 0.20 ($p = 0.005$) to 0.60 ($p = 0.013$) by using local coefficients (geographically weighted regression, or GWR), rather than global coefficients (ordinary least squares), an ANOVA indicated little improvement between models due to the number of parameters in GWR ($F = 1.44$). A broad spatial pattern observed only in pre-industrial Hg sediment concentrations was best explained by mean annual precipitation (shared variance = 3.5%), while finer spatial patterns only observed in present-day Hg concentrations and sediment Hg enrichment were best explained by pH (average shared variance = 10.8 %).

Introduction

A large fraction of mercury contamination in lakes and streams of non-industrialized regions of the United States, and Canada is derived from atmospheric deposition (Fitzgerald et al. 1998, Givelet et al. 2003, Lindberg et al. 2007). The global atmospheric pool of mercury has created a nearly uniform enrichment of mercury contamination since pre-industrial times. However, overlaying mercury deposition from a global pool (or of far origin) are local or regional sources of mercury. Such localized sources may lead to regional patterns in mercury deposition due to the emission of atmospherically short-lived species of mercury. In addition, regional gradients in atmospheric oxidants (Lamborg et al. 2002), sulfate deposition (Vanarsdale et al. 2005) and precipitation volume may further contribute to distinct regional patterns of mercury. Further, acid deposition may have an indirect affect on the export of mercury from watersheds as declines in sulfate concentrations have been linked with increasing concentrations of dissolved organic carbon (Monteith et al. 2007).

Regional surveys of environmental mercury contamination with a focus on patterns of deposition (Vanarsdale et al. 2005), atmospheric concentration (Temme et al. 2007), or concentration in lake sediments (Landers et al. 1998, Parsons et al. 2007, Bookman et al. 2008), often note clusters of increased mercury load. The patterns of mercury contamination are generally partitioned among global, regional and local effects. Global effects can be large-scale mercury emissions, both from industrial processes (e.g. gold rush ca 1850-84, modern industrialization) and natural events (e.g. the eruption of Mt St. Helens)(Schuster et al. 2002).

The scale and magnitude of regional patterns in sediment mercury concentrations will largely depend on the proximity to emission sources (Lindberg et al. 2007). Likewise, the time required for the recovery of surface waters from peak mercury contamination depends upon the

existence of near-field emission sources (Parsons et al. 2007, Bookman et al. 2008). The largest recent declines in total gaseous mercury (TGM) concentrations observed by the Canadian Atmospheric Mercury Measurement Network (CAMNet) were close to the urban areas of Toronto and Montreal, where concentrations between 1995 and 2005 fell by 17% at Point Petre, and 13% at St. Anicet, respectively (Temme et al. 2007). In their study region, TGM concentrations were found to correspond to mercury concentrations in precipitation, both declining by similar amounts across the region. The quantity of mercury in precipitation is primarily determined by equilibrium between dissolved Hg (II) in the aqueous phase (0.5% of total) and gaseous Hg0 in the atmosphere, plus an additional fraction of scavenged particulate mercury (26%) (Poissant and Pilote 1998). Thus, the quantity of mercury in precipitation is largely dependent upon atmospheric oxidants (Lamborg et al. 2002). Precipitation acts to collect mercury (primarily Hg II) as it falls to earth and as such is a vector of atmospheric mercury deposition often dominating other processes. In a 3 year survey conducted in Minnesota, Michigan and North Dakota, Sorensen et al. (1994) found precipitation volume was the dominant factor which influenced the magnitude of atmospheric mercury deposition. This resulted in regions of increased precipitation corresponding with increased atmospheric mercury deposition. Likewise, Vanarsdale et al. (2005) found several sub-regional clusters of mercury deposition gathered data from 13 National Atmospheric Deposition Program Mercury Monitor Network (NADP/MDN) monitoring stations (1996-2002).

Regional trends of increased or decreased atmospheric mercury deposition dominate the loading of Hg to lakes in close proximity to urban settings (Engstrom et al. 2007, Bookman et al. 2008). At remote locations, watershed characteristics may result in local hot or cold spots as a result of increased mobility of atmospherically deposited Hg, which can be observed in lake

sediment. Influential watershed characteristics can include the type of vegetation, watershed morphometry (drainage ratio, slope of watershed), near shore wetlands, and mineral composition (Hurley et al. 1995, Vaidya and Howell 2002, Engstrom et al. 2007). In a study of lake sediment from 26 Michigan lakes, Parsons et al. (2007) found that episodic sediment mercury loading events were superimposed upon regional patterns of atmospheric Hg deposition in which geographically proximal lakes exhibited similar profiles of Hg loading. Watershed disturbances such as agriculture activity can result in substantial increases in sediment Hg loading due increased erosional inputs of soil-bound Hg (Engstrom et al. 2007). Regional patterns of Hg in lake sediment are a result of regional atmospheric deposition and local or watershed level factors from the drainage basin. Such factors may alter the retention of mercury in the terrestrial ecosystem and ultimately determine the response time of mercury in surface waters to changes in atmospheric deposition.

Previous results suggest that the peak era [circa 1990 in Northern Hemisphere (Slemr and Scheel 1998, Lindberg et al. 2007)] of atmospheric mercury deposition may not yet have fully manifested itself in surface waters across Ontario (Mills et al. 2009) and elsewhere around the globe (Meili et al. 2003). However, despite several local declines in North America and Europe, Hg deposition has been relatively constant. Mercury retention in watersheds, specifically in soil, is likely dependent upon morphometric, hydrological, and land cover of the terrestrial ecosystem (Zhang et al. 2008). The objectives of this study were, through the aid of GIS, to conduct a thorough examination of the spatial distribution of sediment mercury enrichment since the pre-industrial era, and determine the distances over which sediment Hg enrichment in contiguous sites appears to be related. GIS technology was used to gather land cover data, geology and hydrology for each watershed. We test the hypothesis that more than one spatial scale will

explain a significant amount of variance in sediment mercury concentrations and mercury enrichment in sediments. Specifically, we test whether autocorrelation occurs in sediment mercury concentrations at several distances, suggesting the presence of multiple sources; local and regional. Further, we will evaluate the influence of lake water pH and precipitation on each of the spatial scales deemed as significant. The hypothesis that the relationship between sediment Hg enrichment and key parameters is regionally variable is tested by geographically weighting regression coefficients. The inverse drainage ratio (lake area / watershed area) was incorporated into the model to account for differences in watershed mercury retention.

Methods

Study sites

Mercury concentrations were measured in pre-industrial and present-day lake sediments from 171 lakes in Ontario, Canada. The majority of the study lakes lie upon the Grenville Province of the Canadian Precambrian Shield which is characterized by rugged topography and is underlain with generally shallow tills and soils, with localized areas of thicker clay, sand, and gravel deposits (Jeffries and Schieder 1983). Lakes on the southern border of the Canadian Shield, including lakes on the Bruce Peninsula and south of Georgian Bay, lie upon the sedimentary rocks of the Western St. Lawrence Lowlands, and include regions of agricultural activity, and deeper glacial till. GIS layers (i.e. hydrology, landcover, geology) were compiled using Ontario Flow Assessment Techniques, a GIS-platform produced by the Ontario Ministry of Natural Resources (Chang 2002). Since the DEM contained vector information, lake order could be established by observing upstream lakes. For a more detailed description of the study area, refer to (Mills et al. 2009, Chapter 2).

GIS databases

The data for land cover, hydrology, and geology were collected from OFAT databases. The data were originally compiled from the Ontario land cover data base (25x25m resolution; MNR, 1997) the Soil Landscape of Canada (1:1,000,000; Agriculture and AgriFood Canada (1996)), the Ontario Land Inventory (1:1,000,000; MNR, 1997), Surficial Geology of Ontario (1:1,000,000; Perera et al. (1996)), Quaternary Geology of Ontario (1:1,000,000; MNDM (1997)). Hydrology data were created from the Canadian Daily Climate Data CD (Environment Canada (2001)). For details on collection methods please refer to Chang (2002) and sources therein. Land cover was further divided into 16 classes, which we condensed into five categories (forested, agricultural, wetland, open water, and mine tailings) and a miscellaneous heading, containing categories such as fire impacted. Classifications were chosen if they represented more than 3 % of the average coverage for all sites. In some cases classifications were combined (example, many forest divisions into "forested"). Surficial geology was extracted by 12 categories and quaternary geology by 10 categories. The areas occupied by the different classifications were apportioned to each watershed using watershed boundaries determined through digital elevation models.

Field and laboratory methods

Lake sediments were collected using Lucite Glew gravity corers (Glew 1989) in replicate at the deepest point of each lake. Sediment cores were sectioned on the lake shore using a Glew (1988) extruder, into Whirlpak© bags and stored in coolers for transport back to the lab. Samples were refrigerated at the Paleoecological Environmental Assessment and Research Laboratory at Queen's University at 4°C in the dark until analysis. In this study, two sediment sections were examined in each core: the top 0.5 to 1.0 cm (present-day lake conditions), and a 0.5 to 1.0 cm

interval taken at a minimum core depth of 30 cm, shown previously to represent the pre-industrial time period (Mills et al. 2009).

Mercury concentrations were determined using solid phase thermal desorption atomic fluorescence spectroscopy (SP-3D, Nippon Instruments Corp., Osaka, Japan). Sediments were freeze dried and ground to a fine powder with a mortar and pestle, and approximately 30 mg of the powder was embedded in activated alumina powder and placed into a ceramic holder. The elemental Hg released from this process was trapped by gold amalgamation. Subsequently, the Hg was thermally-desorbed and then detected by absorption at 253.7 nm. Certified reference material (MESS-3, NIST 1603) was used to calibrate the response and test for instrumental drift.

Data used for water chemistry were gathered from Ontario Ministry of the Environment long-term lake monitoring databases, as well as Hall and Smol (1996), Reavie and Smol (2001), and Dixit et al. (2002). Lake water sampling followed procedures in Locke and Scott (1986).

Data analysis

Spatial Autocorrelation Analysis

To test our hypotheses that multiple spatial scales are significantly influencing the concentration of mercury in lake sediments, we chose to first evaluate the autocorrelation in present-day and pre-industrial sediments and the mercury enrichment between the two time periods. The best resolution that was appropriate based upon the sampling design of the data set was 98 km, this distance represents the minimum distance needed to connect all locations to their nearest neighbour. This analysis cannot model spatial structures larger than the boundaries of the sampled region, nor structures smaller than the truncation distance of 98 km. Therefore, processes occurring at less than the truncation distance radius among lakes will not be perceived by tests of autocorrelation.

Global spatial autocorrelation - Geographic locations (decimal degrees of Lat/Long) were fed into the program Spatial Analysis for Macroecologists (SAM 2008; Rangel et al. (2006)). The magnitude of the autocorrelation coefficient was indicated by Moran's I, which in the absence of autocorrelation, is equal to zero. Should variance increase with distance, the presence of negative autocorrelation would result in values of $I < 0$. Values of $I > 0$ indicate that contiguous sites are more similar to one another than would be expected by chance. Through running an analysis of global autocorrelation we can establish whether there is significant autocorrelation in mercury concentrations. However, we cannot test whether more than one spatial scale is influencing mercury concentrations based upon a global analysis of autocorrelation. Thus, in addition, we chose to use principle coordinates of neighbor matrices which evaluated the significance of several principal components relating the geodesic locations of each lake.

Principal coordinates of neighbor matrices (PCNM) - PCNM was performed on sediment mercury concentrations and mercury enrichment to test whether multiple spatial scales could be attributed to spatial autocorrelation. The analysis achieves a spectral decomposition of spatial relationships (Borcard et al. 2004). One advantage of PCNM method is that we can test whether precipitation and/or lake pH is related to the spatial gradients in mercury concentrations and the distance over which this gradient is observed. Dependent variables were first checked for linear trends prior to PCNM. A total of 10 PC variables were calculated which in total accounted for 58.8 % of the variance in mercury concentrations. Additional variables contributed less than 0.1 % of the variance in mercury concentrations and were therefore removed before further analysis. Should point sources which significantly contaminate surface waters in our study lakes on a fine scale (<98 km) exist, such locations would show up as spatial outliers which were identified using SAM (2008).

CLUSTER ANALYSIS

Cluster analysis was used to determine whether land cover or geology is influencing the enrichment of sediment mercury concentrations since pre-industrial times. We combined sites into relatively homogeneous groups based upon location and sediment mercury enrichment. The number of clusters was established by examing the decrease in mean error sum of squares (MESS) of the groups as the number of clusters increased. A noticeable drop in MESS was observed at n = 5 clusters. To form the groups, sites equal distances from one another were selected randomly and additional sites were partitioned into the various groups until we had five clusters remaining based on K-means. The mean site characteristics (land cover/geology) of each cluster was then correlated with the median mercury enrichment of the group to identify the trends in land cover.

GEOGRAPHICALLY WEIGHTED REGRESSION

To test our final hypothesis that allowing the coefficients of precipitation and lake pH to vary geographically should increase the explained variance, we performed a geographically weighted regression (GWR). Specifically, we test the hypothesis that the slope of the relationship between mean annual precipitation (MAP), lake pH and sediment mercury enrichment is similar across our study area. Our study area encompassed a very diverse landscape, providing a reasonable test of such a hypothesis. In GWR spatial drift from average relationships is measured directly and can improve our ability to predict the magnitude and significance of lake pH and MAP on mercury enrichment. The coefficients of MAP and lake pH were calibrated by comparison to 15 to 22.5 % of neighbouring watersheds (Brunsdon et al. 1996). Results were compared to an ordinary least squares regression, which assumes equal coefficients for independent variables

across the study area using an ANOVA to test the significance of weighting variables for location.

Results

Pre-industrial mercury concentrations were weakly, but significantly correlated with present-day concentrations ($r = 0.320$, $p < 0.0001$, $n = 108$). The median present-day mercury concentrations were 216.8 ± 103 ng·g^{-1} d.w. and after correcting for organic matter were 0.6 ± 0.3 μg·g_{OM}^{-1}, pre-industrial mercury concentrations were 99.9 ± 46.8 ng·g^{-1} d.w. and 0.4 ± 0.7 μg·g_{OM}^{-1}, respectively (Figure 4.1). The relative standard deviation of mercury concentrations was 47 % in both periods before correcting for organic carbon. After standardizing for organic carbon, the relative standard deviation increased to 54 and 186 % for present-day and pre-industrial concentrations, respectively.

There is a subset of lakes in which pre-industrial mercury concentrations are higher than expected given the organic content, thus skewing the normality of the distribution. Only present-day sediment mercury concentrations uncorrected for organic content were normally distributed (K-S p value = 0.35). Such a distribution would suggest that there may be hot spots of mercury contamination within pre-industrial sediments of the study area. To determine whether there may be local regions of enrichment "hot spots" we plotted the enrichment over the study area. Data were interpolated in Surfer 7.0 by using a kriging method. Mercury enrichment is highly localized (Figure 4.2), suggesting that enrichment may be controlled by watershed level effects as reported in previous studies conducted in other regions (Perry et al. 2005, Parsons et al. 2007). The average enrichment in our study area is 2.3.

The existence of local hot or cold spots can be confirmed by spatial outliers. For example, Low and Anstruther lakes had exceptionally high present-day mercury concentrations (1.14, 1.59 μg·g OM^{-1}). Furthermore, Low Lake exhibited a high degree of enrichment (EF = 4.7), as did Nellie and Farren lakes (EF =4.6, 5.6). With the exception of Nellie these lakes had circumneutral pH (Nellie; EF = 4.9, pH = 8.0 ±0.59). Sturgeon, Balsam, Bobs, Charleston and Otty lakes were high in background concentrations ($[Hg]_{pre\text{-}industrial}$ = 3.14, 2.99, 2.94, 2.85, 2.53 μg·g OM^{-1}). In general, lakes with exceptionally high pre-industrial mercury concentrations appeared to have large lake surface areas (26.5 ± 21.4 km^2).

Next, we wished to determine the spatial distances over which mercury concentrations were related, or in other words, over what distances significant autocorrelation was observed. Pre-industrial mercury concentrations exhibited spatial autocorrelation over larger distances than present-day concentrations (Figure 4.3). The autocorrelation in pre-industrial mercury concentrations increased at short distances indicating that the closest lakes are not the most similar. The peak correlation occurred at 50 km indicating that site characteristics played a significant role in background mercury concentrations. Beyond 50 km, Moran's I suggests that variance in pre-industrial mercury concentrations increases more uniformly over distance than present-day concentrations.

Significant correlation was found in pre-industrial mercury concentrations up to a distance of 400 km. As opposed to background mercury concentrations, autocorrelation in present-day mercury concentrations exhibited more structure. At short distances <100 km mercury concentrations were positively correlated (I > 0.3 at 20 km). Beyond a 100 km radius, the variance quickly rose (I<-0.3 at 120 km) suggesting that the processes which control present-day sediment mercury concentrations operate on a shorter distance than during the pre-industrial

period (Figure 4.3). Since significant autocorrelation was present in sediment mercury concentrations we continued our analysis by testing whether more than one spatial scale may be significant by using principle coordinates of neighbor matrices.

Previous studies have suggested that atmospheric mercury deposition occurs on several spatial scales (Parsons et al. 2007, Bookman et al. 2008). In addition, regional gradients may exist in land use which may act to enhance such regional patterns of sediment Hg enrichment (Engstrom et al. 2007). To test for the presence of multiple spatial scales in our study area we extracted the principal coordinates of neighbor matrices. This allowed us to evaluate the magnitude and spatial scale of patterns in sediment mercury concentrations. Ten principal coordinates (PCs) were extracted from the locations of the study lakes and 53 % of the variance in site location was explained in the first four coordinates. Present-day mercury concentrations were significantly predicted by two PC ($R^2 = 0.39$, $p<0.001$) suggesting multiple spatial scales of mercury deposition (Table 4.1) supporting our prediction. The second and fourth PCs each explained 20 % of the variance in present-day mercury concentrations ($R^2 = 0.20$, $p<0.001$) the spatial pattern which they represent may be seen in Figure 4.4. Contrary to present-day sediments, only one spatial scale was significant in predicting pre-industrial mercury concentrations and mercury enrichment. The fourth PC was common to present-day concentrations and mercury enrichment, and the first PC was unique to pre-industrial mercury concentrations. From examination of spatial patterns of the significant PCs it is clear that they represent processes occurring at various scales. The first PC exhibits a broad scale pattern slowly increasing in variance up to 500 km (Figure 4.4). The second and fourth PC exhibit increases in variance over short distances which may indicate localized influences of contamination. The broad scale spatial pattern exhibited by the first PC shared variance with

mean annual precipitation (MAP) (3.5 %) in explaining pre-industrial mercury concentrations. MAP was unrelated to the first and fourth PC which represented finer scale spatial patterns. The finer scale spatial patterns of the first and fourth PC were significantly associated with lake pH. In fact, 19 % of the variance in present-day sediment mercury concentrations and 3.8 % of the variance in mercury enrichment was shared between lake pH and the fourth PC. In addition, lake pH shared 9.3 % of the variance in present-day mercury concentrations with the second PC. From PCNM analysis we have determined that multiple spatial scales are significant for present-day mercury concentrations alone. MAP is significantly related to broad spatial scales and lake pH is significantly related to finer spatial scales which predicted present-day mercury concentrations and mercury enrichment. This analysis does not reveal whether the slope of the relationship between lake pH, MAP and mercury concentrations may vary over our study region. Therefore, to test our final hypothesis we conducted a geographically weighted regression.

Geographically weighted regression (Brunsdon et al. 1996) was performed on mercury enrichment using drainage ratio (Mills et al. 2009), pH and precipitation. As the study area has regional differences in MAP and bedrock composition, which would alter buffering capacity, we hypothesed *a priori* that the influence of pH and precipitation would vary spatially. Figure 4.5 indicates the significance of pH and precipitation across the study area. From separate analysis we knew that the inverse drainage ratio was not spatially correlated. The output from the model was interpolated among sites using a kriging method (Surfer 7.0). Allowing coefficients to change among location increased the R^2 from 0.21; $p = 0.005$ (ordinary least squares) to 0.609; $p = 0.013$ (geographically weighted regression) and reduced the residual sum of squares from 88.16 to 44.6; $F = 1.44$. Although there was a large difference in the explained variance, due to the large number of parameters in GWR the increase was minor compared to OLS ($F = 1.44$).

Therefore, although more variance in mercury enrichment could be explained by varying the coefficients of lake pH and MAP we would not reject our null hypothesis based on the fact that the model did not significantly increase the predictive ability. An advantaged of using a GWR is that OLS can potentially misidentify true relationships in spatially correlated data.

From the spatial outliers and sharp increases in variance (Figure 4.3), it is apparent that watershed characteristics may play a large role in sediment mercury concentrations and enrichment. To understand how land cover and geology may influence the extent of sediment mercury enrichment we first clustered the mercury enrichment factors using SAM (2008). Five clusters were isolated and the median mercury enrichment factor calculated for each (Median Hg EF/N/total error SSq); 0.44/30/0.068, 1.6/36/0.84, 2.59/22/0.945, 3.13/11/0.032, 4.64/9/0.072. Mean total error sum of squares was 0.06. Mean watershed properties were plotted for each cluster (Figure 4.6). Correlating the average coverage for each cluster with the median mercury enrichment revealed that the portion of watershed covered by mine tailings and by open water significantly enhanced the increase in mercury concentrations since the pre-industrial period (Table 4.2). Further, the percent of organic deposits in surficial geology significantly decreased the mercury enrichment in our study lakes. The difference in median mercury enrichment factors for the clusters appeared unrelated to quaternary geology at least in our study lakes.

Discussion

Mercury contamination affects even the most remote ecosystems through long range atmospheric transport (Fitzgerald et al. 1998, Schroeder and Munthe 1998, Gbor et al. 2007). However, regional and local emission sources (Bookman et al. 2008), regional differences in atmospheric chemistry (Lamborg et al. 2002) and land use (Engstrom et al. 2007) are superimposed on this global enrichment, which may lead to localized hot spots of contamination. Local environmental

conditions and climate may result in a highly structured pattern of mercury deposition. Other studies have observed strong links between atmospheric mercury deposition quantity of precipitation and the concentration of acid anions in precipitation (Vanarsdale et al. 2005). Once deposited to the surface watershed, other factors may enhance or impede the transport of mercury to surface waters.

In this study we have examined the spatial patterns of mercury enrichment across south-central Ontario, Canada. Spatial autocorrelation was present in pre-industrial and present-day mercury concentrations using Moran's I. The magnitude of the autocorrelation was larger and occurred within shorter distances in present-day than in pre-industrial mercury concentrations. This suggests that processes which influence present-day mercury concentrations do so in a more localized pattern than pre-industrial concentrations. The uniform dissipation of autocorrelation in pre-industrial sediments indicates that historically, mercury concentrations in sediments were not subject to local differences in either the atmospheric deposition of mercury nor interaction with the watershed.

From previous studies we knew that depositional patterns should occur at several spatial scales as this has been noted in other regions such as Michigan and the Upper Midwest, US (Landers et al. 1998, Parsons et al. 2007, Vijayaraghavan et al. 2007). PCNM analysis suggested that there were multiple scales of autocorrelation in present-day mercury concentrations. Mercury concentrations in pre-industrial sediment were significantly predicted by a single broad scale pattern extending to a 500 km radius, an area more than four times larger than that of mercury enrichment. Cohen et al. (2004) determined using NOAA HYSPLIT-4 model that the atmospheric deposition of mercury in the Great Lakes area can be influenced from sources up to 2000 km away, although this was superimposed by significant local sources by incineration and

coal combustion. With a radius of 120 km, the patterns of autocorrelation in our study area are likely derived from localized sources of mercury.

Environmental conditions play a large role in the depositional load and transport of mercury through the ecosystem. Among the key conditions, a previous study identified mean annual precipitation, lake pH, and drainage ratio as the strongest predictors of sediment mercury enrichment which corresponds well with other research from various regions (Sorensen et al. 1994, Poissant and Pilote 1998, Vanarsdale et al. 2005). Drainage ratio may influence the lag period between mercury deposited to the catchment and runoff to surface water (Meili et al. 2003, Perry et al. 2005). In the present study, we were able to attribute these environmental conditions to a spatial scale. Lake pH seemed to influence mercury enrichment on a shorter scale than precipitation. However, the finer structure exhibited by lake pH is likely influenced by the buffering capacity of watersheds. The significance of MAP and lake pH was not constant across the study area as indicated by GWR, nearly 40 % more variation in mercury enrichment was explained when the coefficients were allowed to vary regionally.

Spatial outliers in our study area are evidence that there were site specific processes influencing mercury concentrations in the sediment. Likewise, Parsons et al. (2007) noted that in a survey of Michigan lakes, regional atmospheric deposition patterns overlap episodic events occurring within each watershed. The percentage of open water and mine tailings in the watershed significantly increased mercury enrichment in the sediment. There are 38 areas of mine tailings in the study area, covering an average of 3% of the watersheds in which they are deposited, up to a maximum of 40 %. Surprisingly, the relative amount of open water and amount of organic deposits were almost as significant. There are various reasons why the percentage of open water would increase mercury enrichment including no lag period between

deposition and accumulation in lake sediment. Organic matter, especially reduced sulfur groups in the soil of watersheds is well known to retain mercury (Skyllberg et al. 2006, Pant and Allen 2007). Organic soils, classified previously by Agriculture and AgriFood Canada (1996) were present in 11 of the watersheds examined in this study. This study has shown that the presence of organic soils in the watershed can have significant effects on the fate of mercury in our environment even under coarse examination.

Conclusion

This study represents one of the largest surveys of sediment mercury concentrations in North America. Combined with data collected through long term monitoring efforts and geological information collated from GIS layers we were able to depict the spatial relationships in mercury concentrations presently and pre-industrially as well as the enrichment between the two time periods. As found in other regions of North America and Europe mercury enrichment was found to be a product of site specific attributes and broad scale patterns (mean annual precipitation and lake acidity).

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Figure Legend

Figure 4.1: Mercury concentrations in freeze-dried sediments collected from the profundal zone of 171 lakes in southern and central Ontario. Sediments sections were selected from near surface (0.5-1cm) and deep within the sediment (>35cm).

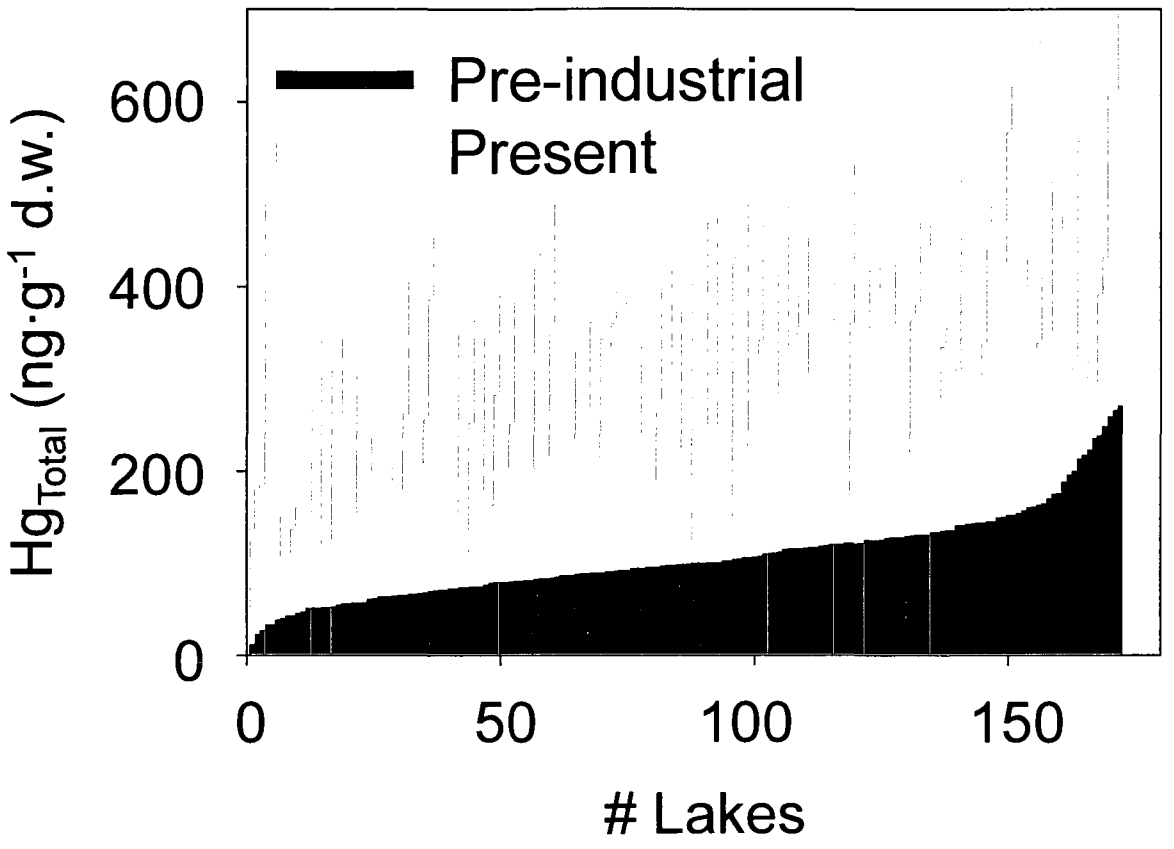
Figure 4.2: Enrichment of mercury concentrations ($ng \cdot g^{-1}$ organic matter) from pre-industrial (>30 cm) to present-day sediment (0.5-1cm) in 171 south-central Ontario lakes. Data were interpolated by kriging (Surfer 7.0).

Figure 4.3: Global correlogram of mercury concentrations standardized for organic matter in present-day (0.5 – 1 cm) and pre-industrial (>30 cm) sediments and the enrichment factor. Moran Index calculated at various distances across surface waters of south central Ontario. Significant distances ($p < 0.05$) are indicated by an asterisk (*).

Figure 4.4: Correlogram of significant principal coordinates used in the prediction of sediment mercury concentrations,.

Figure 4.5: Results from geologically weighted regression of mercury enrichment in lake sediment of south-central Ontario lakes. Local adjusted R^2 values are in the top panel, while the significance (p-value) of mean annual precipitation (middle) and lake pH (bottom) are in the lower panels.

Figure 4.6: Average coverage by land cover, surficial geology and quaternary geology in watersheds for 5 spatial clusters of mercury enrichment in south-central Ontario lake sediment. The mean mercury enrichment for each cluster is on the left. Attributes significantly correlated with mercury enrichment are offset within the pie charts.



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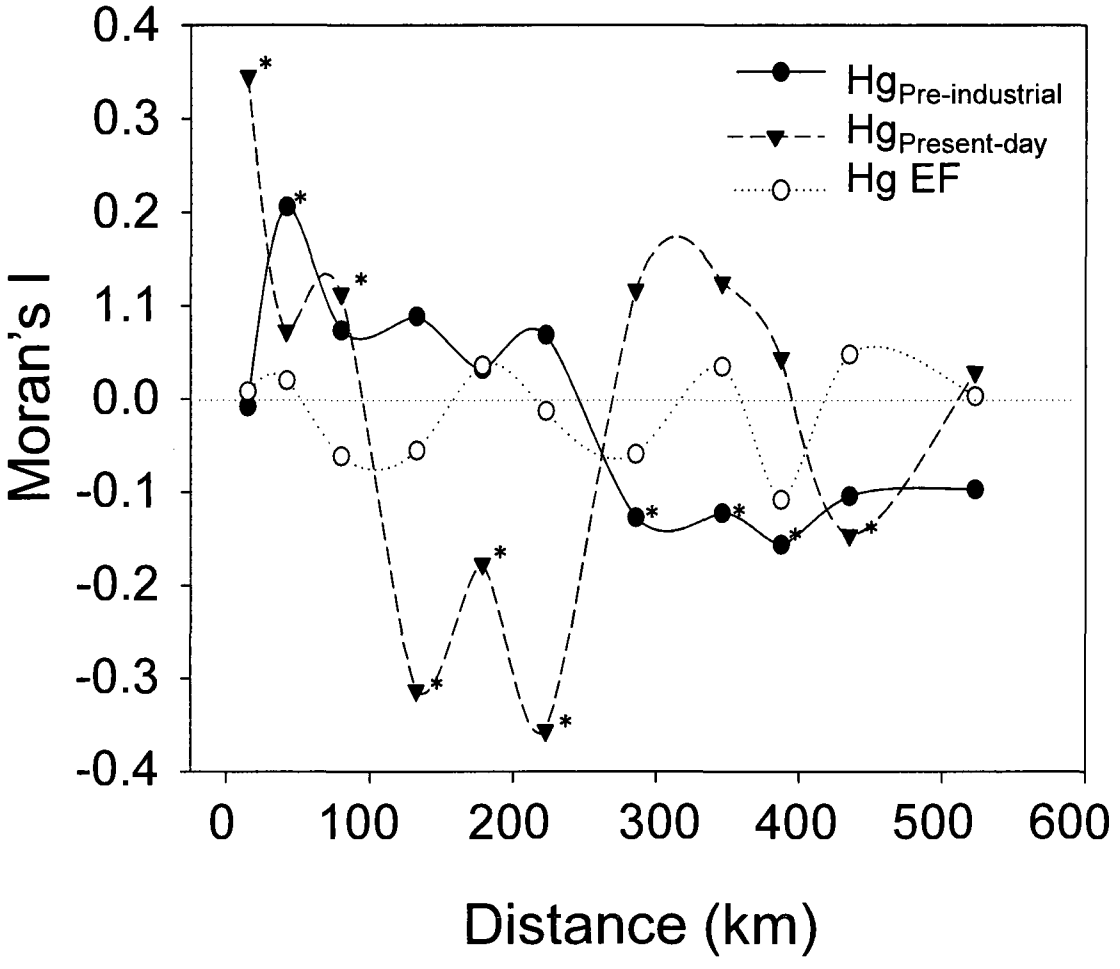

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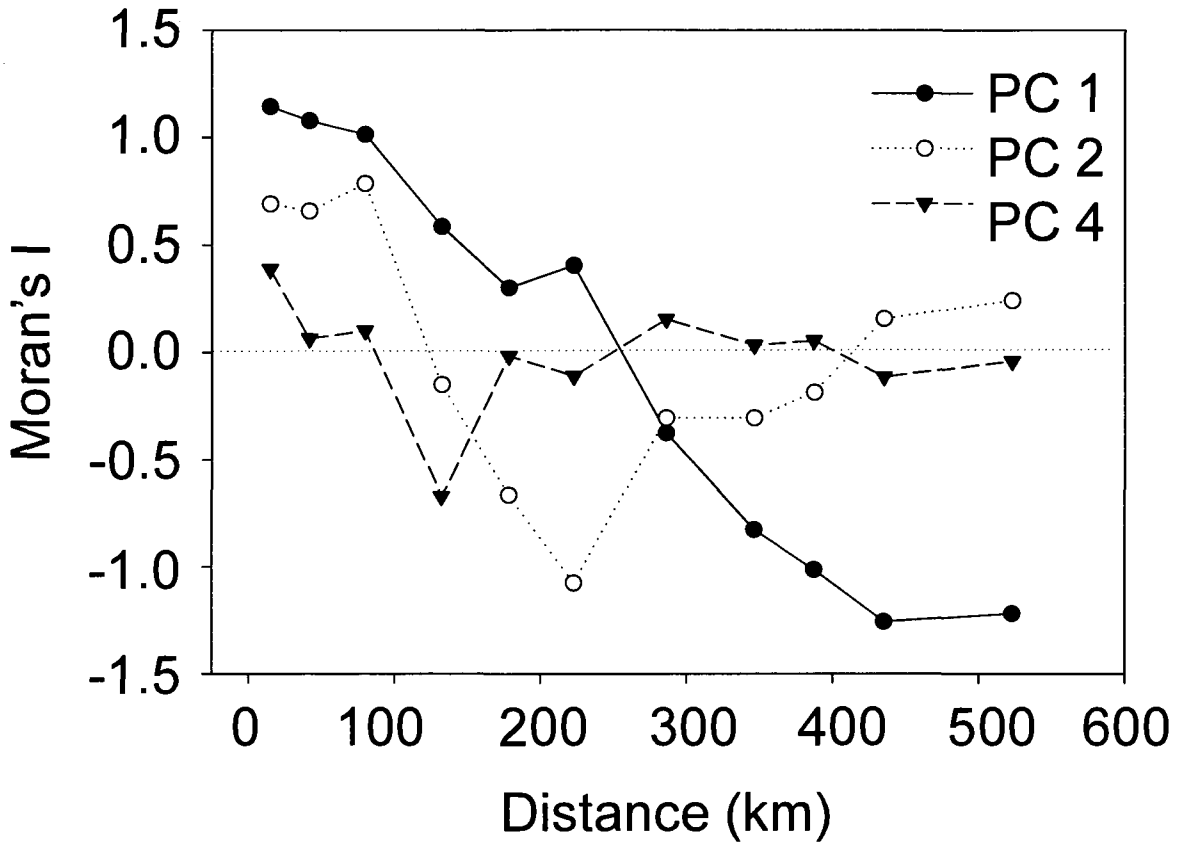

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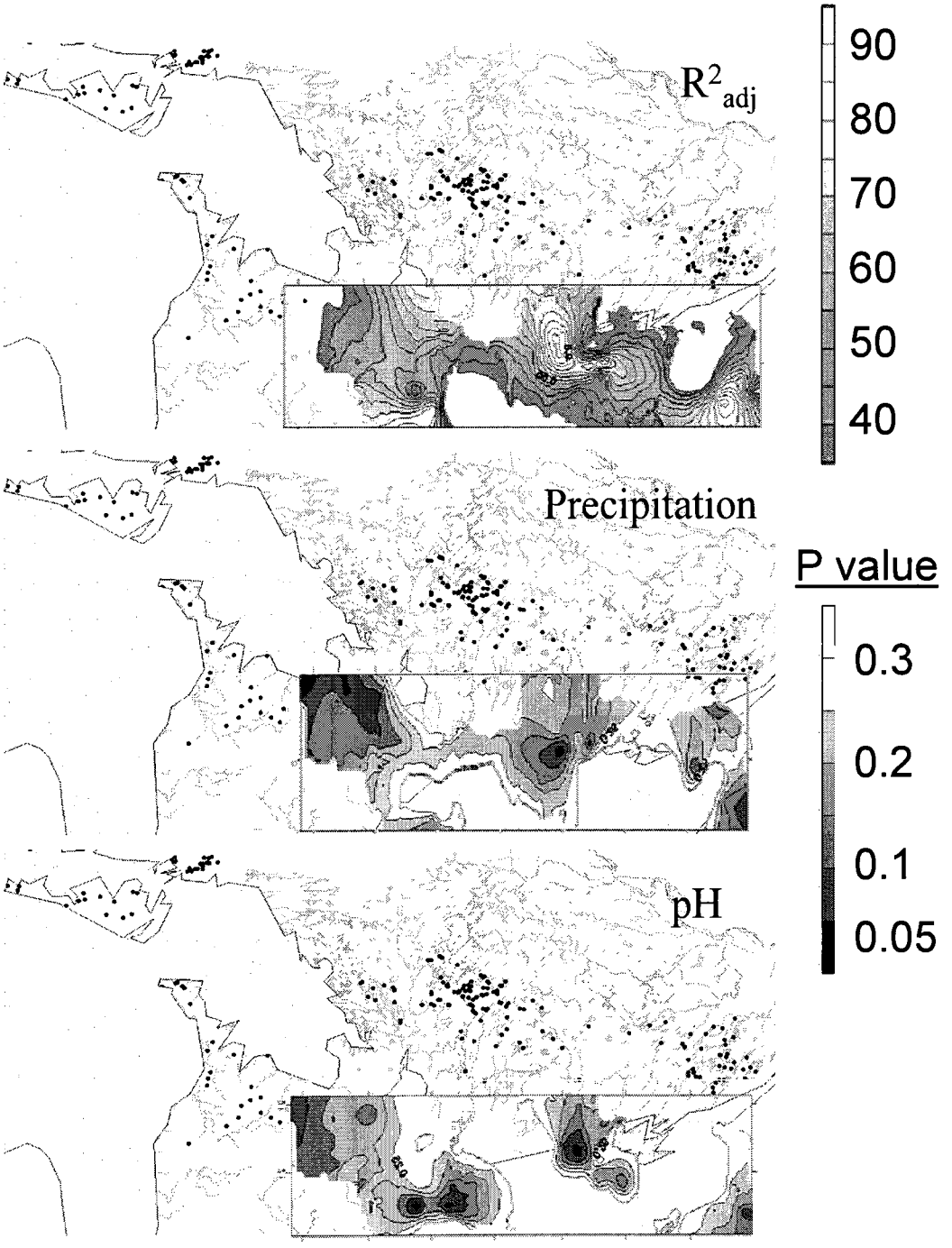

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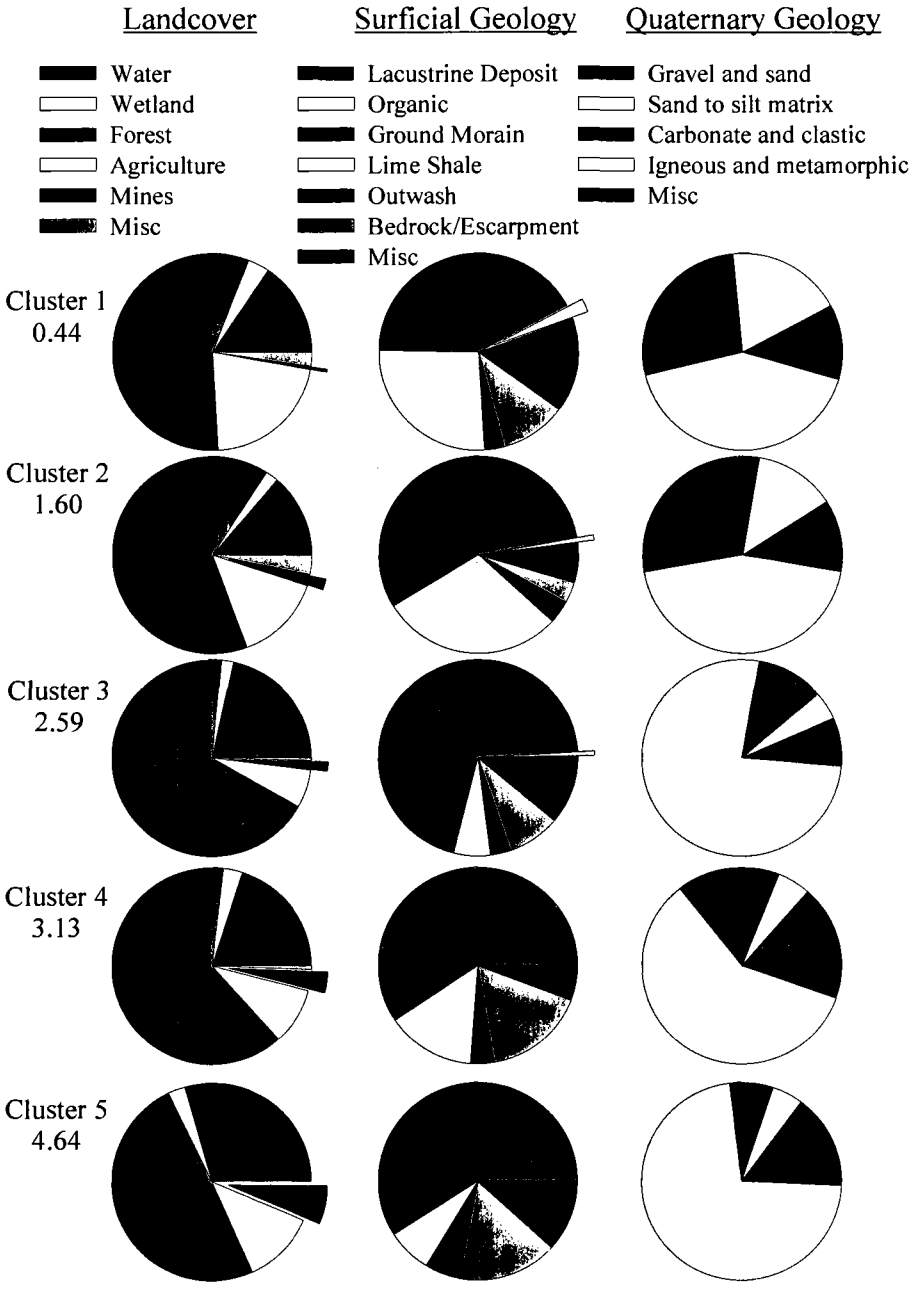

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Table 4.1: First ten principal coordinates of distance and the significance of each coordinate in predicting present-day and pre-industrial sediments and the enrichment factor. Truncation distance was set to 125 km.

		Principal Coordinate (*Eigenvalue*)													
		1	2	3	4	5	6	7	8	9	10	Selected Filters	R^2	p value	AIC
Sediment Stratum		*23.7*	*14.8*	*12.0*	*3.5*	*1.8*	*1.3*	*0.9*	*0.6*	*0.2*	*0.0*				
Present-day	Moran's I	1.2	0.7	0.7	0.4	0.4	0.1	0.2	-0.1	-0.1	-0.1				
	R^2	<.001	0.2	0.1	0.2	0.0	<.001	0.0	0.0	0.0	0.0	2,4	0.39	<.001	-6.6
	p	0.91	**<.001**	0.04	**<.001**	0.35	0.87	0.42	0.24	0.71	0.13				
Pre-industrial	Moran's I	1.2	0.7	0.7	0.4	0.4	0.1	0.2	-0.1	-0.1	-0.1				
	R^2	0.1	0.0	0.0	<.001	0.0	0.0	0.0	<.001	0.0	0.0	1	0.09	0.01	182.1
	p	**0.01**	0.69	0.06	0.80	0.30	0.27	0.49	0.89	0.45	0.28				
Enrichment	Moran's I	1.2	0.7	0.7	0.4	0.4	0.1	0.2	-0.1	-0.1	-0.1				
	R^2	0.0	<.001	0.0	0.1	<.001	0.0	0.0	0.0	0.0	0.0	4	0.08	0.02	262.5
	p	0.32	0.97	0.63	**0.02**	0.87	0.36	0.50	0.41	0.47	0.11				

Table 4.2: Correlation coefficients of mean watershed attributes with mercury enrichment in lake sediment.

Attribute	Classification	r	p-value
Quaternary	*Carbonate and clastic sediment*	-0.86	0.062
	Gravel and sand proglacial and deltaic	0.77	0.127
	Igneous and metamorphic	0.79	0.110
	Sand to silt matrix, some clay	-0.88	0.052
Surficial	*Bedrock/Escarpment*	0.62	0.262
	Ground Morain	0.61	0.272
	Lacustrine Deposit	-0.86	0.061
	Lime Shale	-0.79	0.112
	Organic	**-0.91**	**0.034**
	Outwash	0.83	0.085
Landcover	*Agriculture*	-0.65	0.232
	Forested	-0.37	0.546
	Mined	**0.94**	**0.019**
	Open Water	**0.91**	**0.035**
	Wetland	-0.18	0.767

Chapter 5

Temporal analysis of net methylmercury flow to and from a dystrophic and a clear water lake

Abstract

The concentration of methylmercury (MeHg) in aquatic ecosystems is the net result of the highly dynamic abiotic and biotic processes of mercury methylation and demethylation. In this study, we conduct a detailed examination of the net flux of methylmercury ($MeHg_{Net} = MeHg_{Watershed} - MeHg_{Lake\ outflow}$) across a three year time frame in both a dystrophic lake and an oligotrophic lake. A significant portion of $MeHg_{Net}$ variance in both lakes could be attributed to a seasonal pattern: $y_0 + a \times \sin(2 \times \pi \times day/b+c)^2$ (11.4 %, $p=0.009$; oligotrophic, and 27.0 %, $p<0.0001$; dystrophic) which in both cases, was most correlated with air temperature. Over a two year time frame, the dystrophic lake appeared to be a net source of methylmercury ($MeHg_{Net} = -1.9 \pm 0.3$ mg $MeHg \cdot d^{-1}$) while the oligotrophic lake appeared to be a net sink ($MeHg_{Net} = 0.4 \pm 0.2$ mg $MeHg \cdot d^{-1}$), suggesting that there was net methylation in the dystrophic lake and net demethylation in the oligotrophic lake. Higher MeHg loading to the lakes occurred during the summer season. Between seasons there was a difference in $MeHg_{Net}$ of 1.1 ± 0.3 mg $MeHg \cdot d^{-1}$ and 3.1 ± 0.6 mg $MeHg \cdot d^{-1}$. Seasonal patterns of $MeHg_{Net}$ in the oligotrophic lake lagged behind the dystrophic lake by 39 days. The short term variation was dominated by precipitation ($t = 2.73$, $p = 0.008$; days, $t = 2.53$, $p = 0.017$; oli) with no lag period between precipitation and $MeHg_{Net}$.

Introduction

Mercury (Hg) contamination is widespread even in the most remote environments (Evers et al. 2005). Released into the atmosphere from natural and anthropogenic sources, Hg may travel long distances as elemental mercury (Hg^0) before re-depositing on the earth's surface primarily in oxidized forms (Schroeder and Munthe 1998). Once deposited, divalent mercury is methylated through biotic and abiotic processes which result in the formation of methyl mercury (MeHg) (Weber 1993, Benoit et al. 2003). MeHg may then bioaccumulate through the food web where top predators are susceptible to toxicological effects (Basu et al. 2005a, Basu et al. 2005b, Scheulhammer et al. 2007).

Although reactive Hg species (largely ionic Hg II) in aerosols may be methylated prior to deposition (Hammerschmidt et al. 2007), methylmercury originates largely from processes occurring after atmospheric deposition, and atmospheric deposition of MeHg is not considered to be an important source of MeHg in remote lakes (e.g., 9 % of total input to a small bog lake in Wisconsin (Hines and Brezonik 2007)). However, in urban and/or heavily polluted regions, atmospheric deposition may represent an important source of MeHg to aquatic ecosytems (Hultberg et al. 1995). Post depositional methylation occurs primarily within surface waters at the oxicline and in wetlands (Rudd 1995, Benoit et al. 2003, Eckley et al. 2005). As a result, drainage lakes or lakes with a larger degree of wetland coverage often have higher concentrations of MeHg, and higher accumulations of Hg in fish (Driscoll et al. 1995). Further, in-lake methylation, which depends on allochthonous sources of labile carbon and nutrients, can be up to four to seven fold greater than loading from the wetland (Watras and Morrison 2008). Since watershed level properties are the main influence of methylation (Benoit et al. 2003), MeHg accumulation in fish can vary greatly even in regions receiving similar atmospheric

loadings (Spry and Wiener 1991, Wiener et al. 2006, Munthe et al. 2007). Specifically, these properties include sulfate/sulfide, dissolved oxygen, salinity, nutrients, pH, dissolved organic carbon and temperature (Weber 1993, Benoit et al. 2003). Such properties act to enhance the abiotic and perhaps more importantly biotic methylation of inorganic mercury. Biotic methylation of mercury in the water column and wetlands of boreal forest lakes is predominantly performed by sulfate reducing bacteria (Benoit et al. 2003). The rate of methylation is dependent upon concentrations of sulfate and is maximized when, in addition, there is also a supply of labile organic carbon (Mitchell et al. 2008a). Mitchell et al. (2008b) found rates of methylation more than doubled when organic carbon was added in addition to a supply of sulfate.

There are predictable patterns in the sources and sinks of MeHg within watersheds that over the long term can explain the variation in export among sites (St. Louis et al. 1996). The percentage of the watershed that is wetland area, wetland type (peat, bog or fen) and the annual water yield are known to influence the flux of MeHg into surface waters (Stlouis et al. 1994, 1996, Siciliano et al. 2003, Shanley et al. 2005). Indeed, Shanley et al. (2005) found that percent wetlands alone explained 19% of the variance in MeHg in streams at low-flow, and it was the only significant predictor for MeHg in lakes (7% of the variance). The inclusion of stream discharge in their model resulted in an additional 8% of variance in MeHg being explained, from $R^2 = 0.25$ to 0.33 for lakes across northeastern USA. In the aquatic environment the factors controlling net MeHg processes can be more dynamic as thermal and redox boundaries are established and dispersed physico-chemical conditions of the lake are altered (Benoit et al. 2003, Eckley et al. 2005). These conditions may act on varying temporal scales, from daily (UV radiation (Sellers et al. 1996, Hines and Brezonik 2007)), to seasonal (temperature, DOC

(Miskimmin et al. 1992)), or decadal (pH) time periods. It is therefore important to examine long term, as well as short term variation in the net flux of MeHg.

In this study we measured the flux of MeHg from the inflows and outflows of two lakes in central Ontario, Canada. Flux was measured from each lake on a weekly time step from March 2005 to April 2007. One lake is moderately-coloured (i.e, dystrophic), while the other is a clear, oligotrophic lake, as such we can expect differences in UV penetration, heating and cooling periods and different methylation rates (Miskimmin et al. 1992, Watras et al. 1995b). The importance of DOC in the methylation and transport of MeHg in surface waters has been established, whether DOC also influences seasonal differences in MeHg flux has not been determined.

The primary objective of this study is to test the hypothesis that there are significant differences in the seasonality of net MeHg flux between a moderately coloured and clear water lake. The difference between MeHg flux out of each lake and the sum of MeHg flux into each lake will be deemed the net flux ($MeHg_{Net}$). Specifically, we intend to determine whether an oligotrophic lake and a dystrophic lake exhibit similar patterns in net flux over the course of a three year study, and whether any consistent seasonal variation occurred among years using several indices of seasonal trends. We will use the amplitude, phase and mean annual flux as indices to assess seasonal differences in the rise and fall of $MeHg_{Net}$. We would expect the amplitude and mean annual flux to be higher in the dystrophic lake as previous mesocosm studies have shown that a supply of organic carbon will increase methylation, if present with a sufficient amount of sulfate. Phase will indicate the average date at which increased in-lake methylation is observed and should occur earilier in the season within the dystrophic lake, concurrent with water temperature. Our second objective will be to determine whether seasonal

or point in time events contribute more variability in $MeHg_{Net}$ and, in addition, which physico-chemical parameters are most highly correlated with each source of variation. Point in time events will be defined as the residual difference among $MeHg_{Net}$ which was measured on a weekly interval and the seasonal trend. We test the null hypothesis that point in time events and seasonal trends contribute equally to the variation in net MeHg flux.

Experimental Details

Study Site

The study area included two lake basins in the Muskoka-Haliburton region of south-central Ontario (45°23', 79°08' and 45°09', 79°05'). Harp and Dickie lakes are two small (71.4 and 93.6 ha, respectively) headwater lakes located approximately 26 km apart from each other. Their watersheds are underlain by granitic bedrock and covered with thin (< 1 m) to occasionally deeper till (> 5 m). Harp Lake (A_d/A_o = 7.6) is a relatively deep (max depth = 37.5 m, mean depth 13.3m) oligotrophic and slightly acidic soft water lake (pH = 6.6, conductivity = 36.5 μS•cm-1). Although thermally stratified during the summer the hypolimnion remains oxic.

Dickie Lake (A_d/A_o = 5.3) is moderately shallow (max depth = 12m, mean depth = 5m) dystrophic and acidic lake (DOC = 5.9, pH = 6.0). Dickie is a much shallower basin with an average watershed slope of 6 % compared to 12 % at Harp. The shallow slope of the subcatchments gives rise to larger proportions of wetland coverage, largely present as peatland (% Peat; Dickie = 14, Harp = 6.5) (Figure 5.1). Some wetlands in the region have open water marshes. For the purposes of this study we will refer to all wetland areas as peat. The estimated average runoff curve number using methods from the US Soil Conservation Service is 33 for Dickie and 49 for Harp which indicates that accounting for the watershed slope, land cover and soil type, for a given amount of precipitation, the amount of runoff will be larger at Harp Lake.

Dickie Lake is stratified seasonally and experiences anoxic conditions in the hypolimnion, although the lake may mix infrequently during the summer months. The surficial geology of each subcatchment within the two basins is in Table 1.

Hydrology

Stream discharge was determined from stage – discharge equations which were a minimum of 95 % accurate in predicting observed water flow. Stage height was logged using continuous stage recordings and calibrated from two-stage V-notch weirs located on each stream. Most streams feeding these lakes are ephemeral with mean annual discharges ranging from approximately 3 to 50 $L \cdot s^{-1}$. A detailed description of methods used in calculating stream discharge can be found in Hutchinson et al. (1994). Dickie Lake contains six tributaries one of which is ungauged (Figure 5.1). Watershed runoff provides 69.7% of the water load to the lake. The gauged streams provide 47 % of the runoff load, and additional inflow from the ungauged stream was estimated from historical discharge ratios with gauged weirs monitored for more than a decade. Considering outflow, inflow, precipitation, and evaporation Dickie Lake is a net sink for water (Hutchinson et al. 1994). Harp Lake contains seven tributaries; one ungauged. Watershed runoff provides 79.8 % of the total water load to the lake and 65 % of the runoff is gauged. Runoff from ungauged watersheds was reconstructed from relationships determined by historical measurements spanning over 12 years with gauged watersheds Similar to Dickie Lake, inflows from the ungauged watershed were estimated from historical discharge ratios. Harp Lake provides a minimal source of water downstream (0.2%).

Climatic data were collected using the average of several weather stations in close proximity to the study lakes: Beatrice (45.08, 79.24; max =30km), Ravencliffe (45.21, 79.16; max=30km), Haliburton (45.02, 78.32; max=60km). Data were gathered from the Environment

Canada website as daily values, averaged and then compiled at a weekly resolution corresponding with a database containing physico-chemical properties for each stream from March 30th 2005 to May 28th 2007.

Sample collection

Samples were collected from a V-notch weir at gauged streams with the exception of Hg samples collected slightly upstream from the guage. Water samples for MeHg analyses were collected in duplicate on a weekly basis starting during spring melt and continuing until stream senescence. All bottles were washed in diluted trace metal nitric acid and triple rinsed in Milli-Q water and 2.5 ml of mixed brominating reagent was added (2 %). Teflon bottles were used to collect Hg_{Total} and MeHg samples using the clean hands/dirty hands method. Bottles were contained in ziplock bags at the time of collection. Methylmercury samples were preserved in 2 % HCl during transportation. Samples were kept cool and in the dark until analysis.

Methylmercury was quantified by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by (Cai et al. 1996). An Ai Cambridge (UK) model GC 94 gas chromatograph equipped with a CTC A200S autosampler, and an optic injector module was coupled to the PSA Merlin Detector via a pyrolysis oven held at 800°C. A fused silica analytical column with dimensions of 15 m x 0.53-mm i.d. (Megabore), coated with a 1.5-μm film thickness of DB-1 (J&W Scientific) was used. The carrier gas and make-up gas flows were 4.0 ml/min of helium and 60 ml/min of argon, respectively. Water samples were passed through sulfhydryl-cotton fibers, which were eluted with acidic KBr and $CuSO_4$, and extracted in methylene chloride. pH, chloride ion concentration and salinity were kept within; 3, <0.4 M and <26 °/o, respectively. This mixture remained in the bottles until time of collection when 500 μL of hydroxylamine hydrochloride was added to remove all free bromine. In cases were relative

difference between duplicates exceeded 5 % of their average, values were compared to adjacent measurement and the outlier was removed.

Data Analysis

Methylmercury concentrations in streams were collected in duplicate on most sampling dates and expressed as an average of the two samples, where available. Concentrations ranged from 0 to 7.53 $ng \cdot L^{-1}$, (median = 0.206 $ng \cdot L^{-1}$, n = 840) and relative standard error ranged from 0 to 25.8%, (median = 2.53 %, n = 564). Since there were subcatchments (one in each watershed) in which MeHg was not measured, we estimated the MeHg concentration from the remaining subcatchments. MeHg was averaged over the course of the study to derive the relationship: MeHg = 5.842E-08 x (peat size ($x10^4 m^2$)) + 0.112, $R^2 = 96.5$ (Figure 5.2).

Stage discharge ($m^3 \cdot s^{-1}$) was calculated using empirical relationships between flow rate and staff height. In turn, MeHg flux was determined by: discharge ($m^3 \cdot s^{-1}$) x MeHg concentration ($ng \cdot m^{-3}$). Errors in staff gauge readings (obstructions) were corrected by comparing flow rates with the remaining gauges within the basin. The net flux ($MeHg_{Net}$) for each lake was determined by subtracting the MeHg flux in lake outflow ($MeHg_{lake}$) from the sum of MeHg fluxes in all tributaries ($MeHg_{Watershed}$) on each sampling date. $MeHg_{Net}$ was modeled using a sinusoidal waveform of: $y = y_0 + \alpha[\sin(2\pi/b \text{ x day} + c)]^2$ where y_0 is the mean value of $MeHg_{Net}$ in each lake from March 30th 2005 to May 28th 2007, α is the amplitude in $MeHg_{Net}$, $2\pi/b$ x day is the frequency, and c is the phase (shifts the equation forward or backwards in time). Terms for which account for variation within the amplitude over time were not significant and therefore removed from the model. Autocorrelation in the residuals was tested using the Durbin-Watson statistic and normality was examined using the Kolmogorov-Smirnov test.

The residual variance between predicted $MeHg_{Net}$ and observed values was visually compared in a correlation matrix against several physico-chemical properties of known relevance; DOC, pH, temperature, precipitation, sulfate. Variables indicating a close association with the residuals were tested using autocovariance and then, if need be, lagged before testing their significance as predictor variables for the residual variance in $MeHg_{Net}$ (SPlus). Correlations were tested for significance using a threshold for autocovariance in SPlus and therefore p values were unavailable in some cases. Correlation coefficients listed without p values in this study are significant at $\alpha = 0.05$.

Results

The water residence time averaged over a twelve year period for Harp and Dickie lakes is 3.39 and 1.93 years, respectively. However, during summer stratification epilimnetic and hypolimnetic waters do not mix and watershed discharge will remain in the epilimnion. During our study period we found that in Harp lake, with a volume of 95.07 $x10^5$ m^3, the average time for discharge in the outflow to respond to watershed discharge was 4 weeks ($r= 0.63$). Significant correlation did not occur until after one week and appeared to be at a plateau from week 5 to week 6. In comparison, discharge from Dickie Lake seemed to respond immediately ($\leq$1 week) to watershed discharge ($r = 0.77$, $p<0.05$, lag = 0) and significant correlation terminated by week 3. The volume of Dickie Lake is 46.65 $x10^5 m^3$. In the Dickie basin there was an immediate response to precipitation during summer months ($r = 0.424$, $p<0.05$) and another after a 7 week lag period ($r = 0.174$, $p<0.05$). In the Harp basin there was a peak correlation between discharge and precipitation at a 6 week lag ($r = 0.226$, $p<0.05$).

As found by St. Louis et al. (1994), peatland surface area was a key factor in the flux of methylmercury. In fact, the mean annual MeHg flux from each subcatchment of this study was

strongly related to the peatland area: MeHg ($mg \cdot d^{-1}$) = $4.54x10^{-3}$ x peat m^2 + 0.55 (R^2 = 90.3, n = 10, p <0.0001) (Figure 5.2). The mean annual MeHg flux from subcatchment Harp 4 exported nearly 5 times the expected MeHg based upon peatland size. However, Harp 4 was also one of the largest catchments studied and MeHg could have been deposited through atmospheric precipitation. Generally, MeHg is considered to compose 2 % of Hg_{Total} in upland catchments (St. Louis et al. 1994). In contrast to MeHg flux, the yield of MeHg ($mg \cdot d^{-1} \cdot m^{-2}_{catchment}$) was not significantly related to peatland area (R^2 = 0.112, n = 10, p= 0.345). This suggests that the relationship between MeHg flux and peatland area may be in part due to other watershed properties such as the increased hydrological load that would be expected from larger catchments. For the time period (spring to summer 2005) in which Hg_{Total} was collected, the fraction of Hg_{Total} represented as MeHg exhibited an exponential relationship with percentage of peat coverage: $MeHg/Hg_{Total}$ % = $2.56e^{0.083 \times \% peat}$, R^2 = 90.0, n = 10, p<0.001. Harp 4 was not an outlier in the relationship between $MeHg/Hg_{Total}$ % and percentage peat.

Despite $MeHg_{Net}$ values that were approximately similar between Harp (oligotrophic) and Dickie (dystrophic) lakes, $MeHg_{Watershed}$ and $MeHg_{Lake}$ were often much higher in dystrophic lake than in the oligotrophic lake (Figure 5.3). Maximum correlation between $MeHg_{Watershed}$ and $MeHg_{Lake}$ occurred with no lag period (or less than the sampling interval of one week) and was stronger within the dystrophic lake r = 0.663 p<0.001, than the oligotrophic lake r = 0.434, p<0.001. This suggests more in-lake processing within the oligotrophic lake. Between the two lakes, there was a stronger correlation of $MeHg_{Lake}$ than $MeHg_{Watershed}$ (r=0.277/r=0.223; respectively, both significant p<0.05) and no relationship in $MeHg_{Net}$ (r = 0.184, p = 0.075) (Figure 5.3). The difference in $MeHg_{Net}$ between the study lakes was due largely to the net loss

of MeHg in the dystrophic lake and a net MeHg loading to the oligotrophic lake during fall 2006 through winter 2007.

The net methylation/demethylation of mercury in lakes is known to be influenced by several physico-chemical properties. These include: concentrations of sulfate and dissolved organic carbon, pH, and temperature (Benoit et al. 2003). In addition, atmospheric deposition may contribute to the MeHg load, as well as deliver sulfate and organic carbon to enhance the methylation of mercury (Watras and Morrison 2008). We examined the correlation these parameters had with; 1) $MeHg_{Watershed}$; 2) $MeHg_{Lake}$; and 3) $MeHg_{Net}$ and the response period (time to maximum correlation) if significant (Table 5.3). $MeHg_{Watershed}$ was weakly correlated with mean daily air temperature from 4 weeks previous to the sampling date: Harp $r = 0.19$ $p>0.05$ and Dickie $r = 0.29$, $p<0.05$. Further, $MeHg_{Watershed}$ had a correlation with total daily precipitation from Dickie tributaries; $r = 0.37$ from 6 weeks previous, although $MeHg_{Watershed}$ from Harp was not correlated with precipitation though it is possible that a correlation occurred at higher temporal resolution than we measured (1 week interval). The second flux we examined; $MeHg_{Lake}$ was not correlated with precipitation, however mean daily air temperature was inversely correlated to this measure with no lag period (Harp $r= -0.24$, $p<0.05$/Dickie $r = -0.37$, $p<0.05$). Lastly, $MeHg_{Net}$ within Dickie Lake was significantly correlated to precipitation and temperature $r = 0.43$, $p<0.05$ (4 week lag) and $r = 0.36$, $p<0.05$, respectively. $MeHg_{Net}$ within Harp Lake was significantly correlated with temperature; $r = 0.28$, $p<0.05$. Significant parameters were used to develop a predictive relationship for $MeHg_{Net}$. For the dystrophic lake; $MeHg_{Net} = -7.7 \pm 1.3 + 0.12 \pm 0.02 \times temperature_{(0\ lag)} - 0.024 \pm 0.008\ precipitation_{(1\ week\ lag)} + 1.3 \pm 0.2\ SO_4^{2-}{}_{(4\ week\ lag)}$; $R^2 = 0.62$ %, $df = 48$, $AIC = 1.9$, $p<0.001$ for all variables.

To test whether the seasonal patterns of in-lake processes differed between the dystrophic lake and the oligotrophic lake, we modeled $MeHg_{Net}$ with a sinusoidal equation (Figure 5.4). Prior to modeling $MeHg_{Net}$, we removed a linear trend of -2.9 $\mu g \cdot d^{-1}$ ($t = -3.01$, $p = 0.003$) from the dystrophic lake so that the mean $MeHg_{Net}$ was similar during the study period. Seasonal fluctuations in $MeHg_{Net}$ in the dystrophic lake were 3 fold greater than in the oligotrophic lake with mid-summer values 3.1 $mg \cdot d^{-1}$ higher than in winter (Table 5.4). The dystrophic lake also had a significant mean $MeHg_{Net}$ of -1.9 $mg \cdot d^{-1}$ during the study period. On the other hand, $MeHg_{Net}$ was not significantly different from zero (0.4 $mg \cdot d^{-1}$) in the oligotrophic lake, despite having a larger direct depositional flux from a larger surface area. The sinusoidal trend was able to explain 27% of the variance in the dystrophic lake while only 11.4 % in the oligotrophic lake. Furthermore, the seasonal pattern in the dystrophic lake was lagged 39 days behind the oligotrophic lake. This shift in $MeHg_{Net}$ between the two lakes was similar to that for stream temperature in the outflow where the dystrophic lake was found to lag behind the oligotrophic lake. The temperature signals did not significantly differ in any other aspect (amplitude, mean temperature, and period). The shift in stream temperature seems to be driven by an early warming period from the oligotrophic lake during the second year. The sinusoidal trend in $MeHg_{Net}$ was correlated to mean air temperature in both the dystrophic and the oligotrophic lake as suggested from cross correlation analysis (above); $r = 0.613$, $p < 0.0001$ and $r = 0.342$, $p < 0.0001$, respectively. The residuals in $MeHg_{Net}$ from the seasonal pattern were positively related to precipitation indicating a flux of MeHg into the lake with deposition (partial $t = 2.73$, $p = 0.008$) and (partial $t = 2.53$, $p = 0.017$).

Discussion

The biogeochemistry of methylmercury (MeHg) cycling in watershed ecosystems is complex and seasonally variable. Methylmercury enters the ecosystem through direct deposition and primarily from watershed sources (Rudd 1995, Watras and Morrison 2008). However, in some instances, autochthonous production may be responsible for the majority of MeHg found in surface waters (Watras et al. 1995a, Hines and Brezonik 2007, Watras and Morrison 2008). Estimates from in situ incubations range between 50 and 100 $pmol \cdot m^{2} \cdot d^{-1}$, nearly double that of atmospheric deposition (Watras et al. 1995a).

MeHg is removed from the water column through photoreduction, oxidation (biotic and abiotic), biological uptake, sedimentation and evasion (although the latter is often negligible). In a small bog lake in the Marcell Experimental Forest in north-central Minnesota, Hines and Brezonik (2007) found that photolysis of MeHg removed approximately 3 times the lake mass of MeHg (20 mg) annually or 0.164 $mg \cdot d^{-1}$ if spread evenly over the course of a year. Likewise, Sellers et al. (1996), estimated photodegradation rates to be double that of all external inputs. In our study lakes, the seasonal difference was 3.1 and 1.1 $mg \cdot d^{-1}$ for the dystrophic and oligotrophic lakes respectively and the mean $MeHg_{Net}$ was 1.9 $mg \cdot d^{-1}$ gained for the dystrophic lake. In general, the evasion of Hg is less from highly coloured lakes and instead mercury methylation is favored Watras et al. (1995), although very high concentrations of dissolved organic carbon may interfere with the availability of Hg for methylation (Miskimmin et al. 1992). However, at high concentrations organic matter will also decrease the photodegradation rate of MeHg (Sellers et al. 1996). Dissolved organic carbon was found to correlate with $MeHg_{Lake}$ in the dystrophic lake (lag = 0), however, not with $MeHg_{Net}$ in either lake, suggesting that MeHg was associated with DOC compounds but this was not a prevalent factor in the net

gain or loss of MeHg. Similar to the correlation between DOC and MeHg, pH solely influenced the $MeHg_{Lake}$ and only in the dystrophic lake. Other studies have found a reduction in pH from 7 to 5 to strongly enhance net methylation rates (Miskimmin et al. 1992). Although the seasonal fluctuation in pH of our study lakes is within this range; dystrophic (4.8 – 6.3), oligotrophic (5.6 – 6.9), lake pH was not the dominant factor of $MeHg_{Net}$.

Previous studies have stressed the importance of sulfate on net methylation (Watras et al. 1995a, Selvendiran et al. 2008, Watras and Morrison 2008). Increased sulfate concentrations increase the activity of sulfate reducing bacteria which are known to methylate mercury. $MeHg_{Net}$ in the dystrophic lake was enhanced in response to increased SO_4^{2-} concentrations 4 weeks prior to the sampling date. This lag period may have been due to a period in which SRB populations were expanding in response to increased energy source or increased temperature.

The variable that explained the largest portion of variation in $MeHg_{Net}$ within both the dystrophic lake and oligotrophic lake was air temperature. $MeHg_{Net}$ responded to temperature immediately ($\leq$ 1 week) and was strongly correlated to the seasonal trend in $MeHg_{Net}$; $r = 0.613$, $p<0.05$ (dystrophic lake) and $r = 0.342$, $p<0.05$ (oligotrophic lake). As a result of the seasonality in $MeHg_{Net}$ biota that reside in the lakes may be more susceptible to bioaccumulation during certain parts of the year. In this study, the seasonal pattern, modeled by a sinusoidal regression, comprised 11.4 % and 27 % of the variance in $MeHg_{Net}$ within the oligotrophic and dystrophic lake, respectively. Similarily, Garcia et al. (2007) found that the seasonal trend was the most important source of variation of MeHg in zooplankton during two years of observation contributing 69% and 59% of the variation within two lakes. Furthermore, the same study reported that MeHg concentrations in zooplankton exhibited positive correlations with temperature, DOC and sulfate concentrations.

The majority of variation in $MeHg_{Net}$ in our study lakes was from short term processes or otherwise unaccounted parameters 88.6 (oligotrophic lake) and 73% (dystrophic lake). This short term variation, determined from the residuals between $MeHg_{Net}$ and the seasonal trend, was significantly correlated with precipitation, increasing the MeHg load. Previously observed concentrations for MeHg in precipitation at the experiment lakes area averaged 0.04 $ng \cdot L^{-1}$. Considering the average precipitation during our study was 2.11 $mm \cdot d^{-1}$, this would have led to an atmospheric flux of 0.79 $mg \cdot d^{-1}$ (dystrophic lake) and 0.60 $mg \cdot d^{-1}$ (oligotrophic lake) deposited directly to the lakes. This means that in the oligotrophic lake, at least 1.0 $mg \cdot d^{-1}$ MeHg was removed, while in the dystrophic lake 1.1 $mg \cdot d^{-1}$ was produced. This is a minimum since lake sediments are generally considered a net source of methymercury (Gilmour et al. 1992, Weber 1993). We would expect little or no MeHg in precipitation deposited to the upland catchment to be delivered to the lake (except during snowcover) since uplands are generally sinks for MeHg in precipitation, either stored in soils or demethylated (Lee et al. 1998).

This study presents a detailed examination of MeHg flux in the tributaries and outflow of a dystrophic and clear water lake in central Ontario, Canada. The lakes shared similar characteristics, but one was of moderate color and the other was clear. Three fluxes were observed and cross correlations where made to known influences of net methylation. Trends in $MeHg_{Net}$ were more predictable within the dystrophic lake and largely explained by sulfate, temperature and precipitation.

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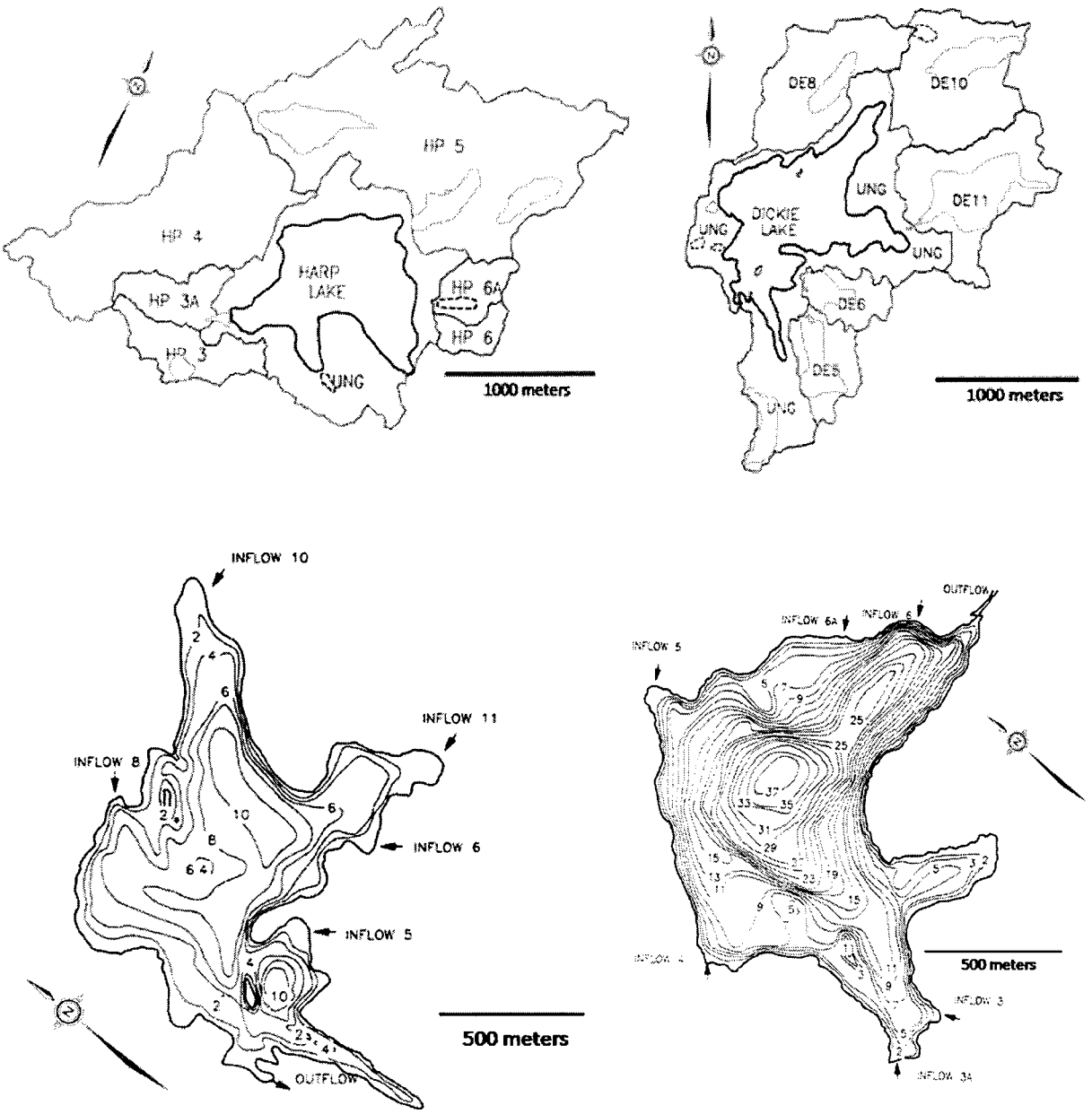
Figure Legend

Figure 5.1: Schematics of the two study basins Harp (left; 45°23', 79°08') and Dickie (right; 45°09', 79°05') in south-central Ontario. The upper panel represents each subcatchment of the watershed and the respective wetlands. The lower panel represents the bathmetric maps of each lake with contour lines representing intervals of 2 m.

Figure 5.2: The average methylmercury flux from ten streams in south-central Ontario measured during a 3 year sampling period as a function of peat size ($x10^4 m^2$). The streams were located within two watersheds (●) Harp and (○) Dickie. The error bars represent one standard deviation.

Figure 5.3: Methylmercury flux ($mg \cdot d^{-1}$) from the sum of all inflows (—●—) and in the lake export (---○---) from a) Harp and b) Dickie lake in south-central Ontario. The study was conducted from March 30th 2005 to May 28th 2007. The bottom panel; (c) represents the difference between the two fluxes ($mg \cdot d^{-1}$) in (—) Dickie Lake and (----) Harp Lake.

Figure 5.4: Net flux of methylmercury ($MeHg_{Net}$ = total input ($MeHg_{Watershed}$) – total output ($MeHg_{Lake}$) ($mg \cdot d^{-1}$) on a weekly time interval from March 2005 to August 2007 in two south-central Ontario lakes; Harp (a) and Dickie (b). Data were fit with a sinusoidal model: $MeHg_{Net} = y_o + a \times \sin(2x\pi x day/b+c)^2$.



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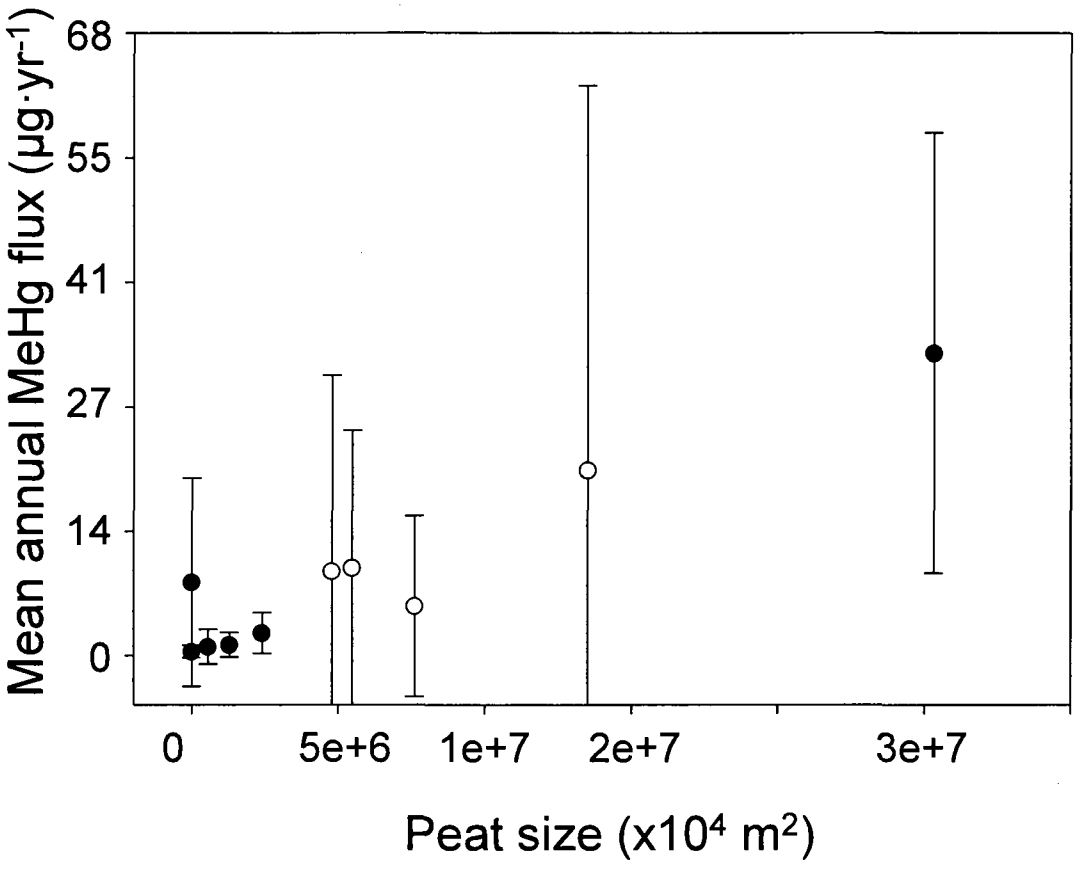

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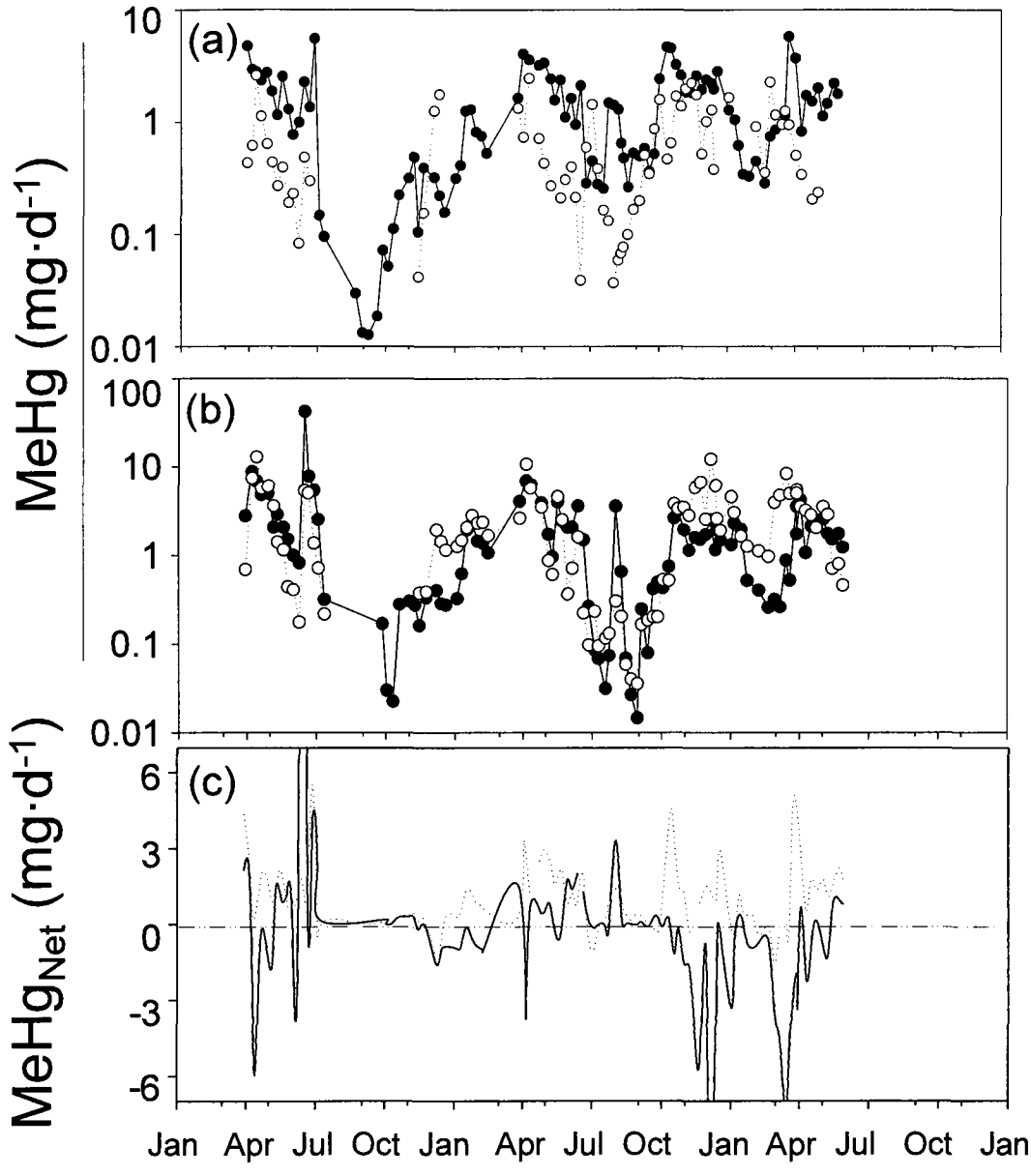

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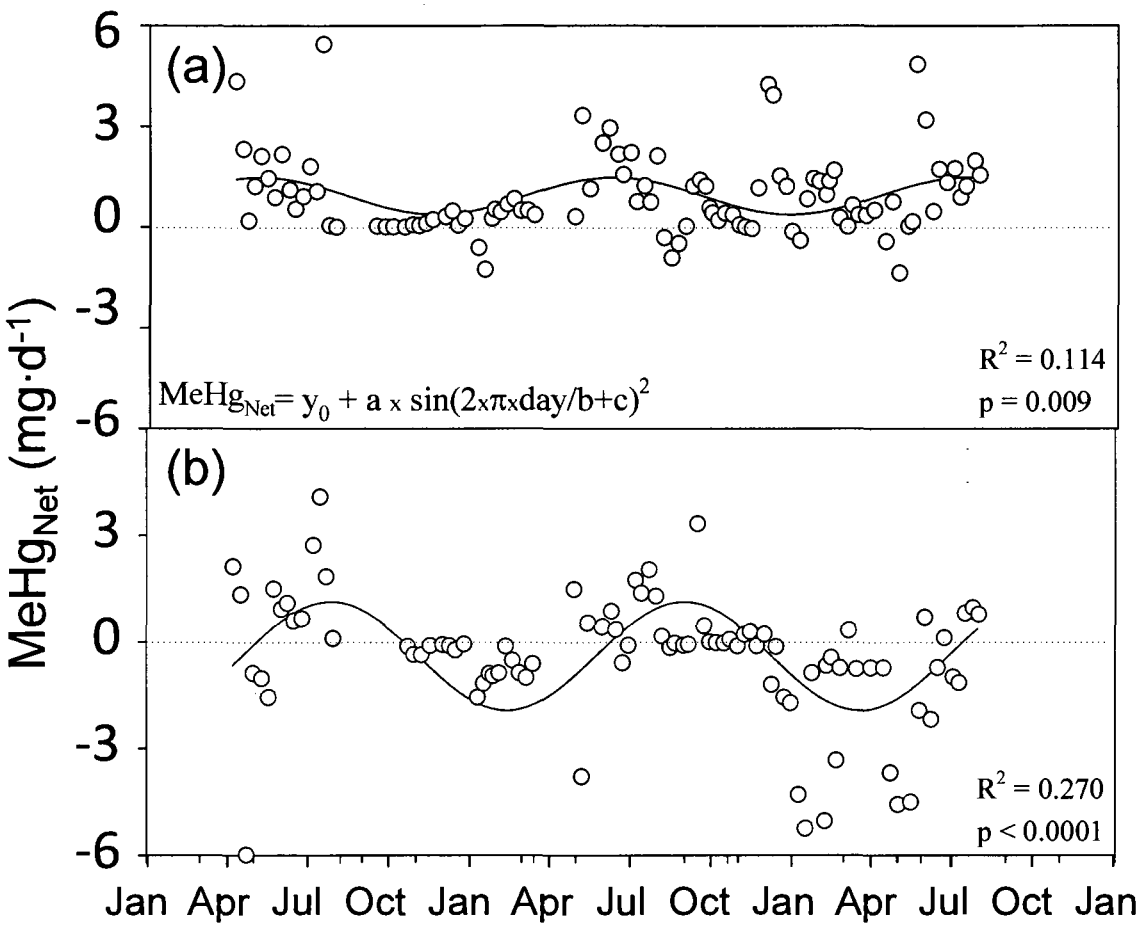

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Table 5.1: Annual water balances for Harp and Dickie lake over a twelve year period (1980-1992). Individual supply and loss terms in $10^3 m^3 yr^{-1}$ and as % of total loss or supply

Basin	Source/Sink	$10^3 m^3 yr^{-1}$	%
Dickie	Precipitation	11356	30.3
	DE 5	1955	5.2
	DE 6	1485	4.0
	DE 8	4435	11.9
	DE 10	4968	13.3
	DE 11	4724	12.6
	Ungauged	8500	22.7
	Outlet	30543	80.5
	Evaporation	7411	19.5
	Lake Storage	-23	-0.1
Harp	Precipitation	8652	20.2
	HP 3	1834	4.3
	HP 3a	3194	7.5
	HP 4	7506	17.6
	HP 5	13682	32.1
	HP 6	700	1.6
	HP 6a	882	2.1
	Ungauged	6151	14.4
	Outlet	34691	85.9
	Evaporation	5604	13.9
	Lake Storage	82	0.2

Table 5.2: Median and range of values in water quality characteristics of the study lakes.

Parameter	Median		Range		Standard Deviation	
	Dickie	Harp	Dickie	Harp	Dickie	Harp
DOC ($mg \cdot L^{-1}$)	5.9	4.4	(2.1-8.3)	(3.5-5.5)	0.8	0.4
pH	6.0	6.6	(3.6-6.3)	(5.6-8.6)	0.5	0.5
Si ($mg \cdot L^{-1}$)	0.8	1.6	(0.1-1.2)	(1.0-1.9)	0.3	0.2
Gran ($mg \cdot L^{-1}$)	1.5	4.3	(-0.1-6.7)	(1.5-6.5)	1.3	1.2
Colour	36.0	18.8	(22.6-52.6)	(15.0-21.8)	6.5	1.7
SO_4^{2-} ($mg \cdot L^{-1}$)	5.4	6.4	(0.1-6.7)	(0.2-9.6)	1.0	1.2
SO_4^{2-}($mg \cdot d^{-1}$)	3.0E+07	2.2E+07	()	()	7.2E+07	6.8E+07
Fe ($\mu g \cdot L^{-1}$)	142.5	41.0	(39-236)	(23.2-103.0)	53.8	20.5
Conductivity	41.5	36.5	(32.2-46.2)	(28.3-38.5)	2.9	2.2
Hg_{Total} ($ng \cdot L^{-1}$)	2.3	1.7	(0.7-3.2)	(1.0-1.9)	0.8	0.3
MeHg ($ng \cdot L^{-1}$)	0.1	0.0	(0.1-0.5)	(0.0-1.0)	0.1	0.1

Table 5.3: Results of cross correlation analysis between physico-chemical properties and methylmercury flux from the watershed ($MeHg_{Watershed}$), from the lake ($MeHg_{Lake}$), and their difference ($MeHg_{Net}$) within a dystrophic and an oligotrophic lake.

	Lag period of significant cross correlations (α=0.05) (weeks)					
	$MeHg_{Watershed}$		$MeHg_{Lake}$		$MeHg_{Net}$	
	Dystrophic	Oligotrophic	Dystrophic	Oligotrophic	Dystrophic	Oligotrophic
Mean daily air temperature	4		0	0	0 (-)	0 (-)
Mean daily precipitation (mm)	6				1 (-)	
Sulfate ($mg \cdot L^{-1}$)	—	—			4	
Dissolved organic carbon ($mg \cdot L^{-1}$)	—	—	0			
pH	—	—	4 (-)			

(-) indicates an inverse correlation

Table 5.4: Results of sinusoidal regression of net methylmercury flux in two south-central Ontario lakes $MeHg_{Net} = y_o + a \times \sin(2x\pi x day/b+c)^2$.

Parameter	Lake	Coefficient	t	p
amplitude - a	Harp	1.1 ± 0.3	3.5	0.001
(mg/d)	Dickie	3.1 ± 0.6	5.5	<0.0001
period - b	Harp	366 ± 35	10.4	<0.0001
(days)	Dickie	365 ± 15	25.1	<0.0001
phase - c	Harp	128 ± 26	8.3	<0.0001
(days)	Dickie	89 ± 11	15.5	<0.0001
Mean flux - y_0	Harp	0.4 ± 0.2	1.8	0.069
(mg/d)	Dickie	-1.9 ± 0.3	-5.9	<0.0001

Chapter 6

Summary and Conclusions

Overview

By examining pre-industrial (pre-1850) and present-day (1996-2003) sediments for a large number of lakes, we were able to observe the spatial, as well as temporal aspects of mercury enrichment ($[Hg_{present\text{-}day}]/[Hg_{pre\text{-}industrial}]$) across south-central Ontario, Canada (Chapters 2-4). Further, we were able to examine the influence of landscape features (topography, hydrology, geology) on sediment and fish mercury concentrations (Chapter 3). The study was conducted on the geological divide of the Precambrian shield and the calcareous deposits to the south from the shores of Georgian Bay to Kingston, Ontario; a region comprised of bedrock ranging from limestone to granitic gneiss, and subject to varying degrees of acid deposition. Due to variation in hydrology, geology and landcover from such a diverse landscape we were able to assess the impact of site specific characteristics on mercury contamination. Few studies of this magnitude have been attempted previously except for a study of Nordic inland lakes where 3000 sites were sampled (Skjelkvale et al. 2001).

In brief, the results presented in this thesis indicate that the contamination of Ontario lakes with mercury is variable but may be predicted with high accuracy after controlling for modifying influences such as; pH and sulfate. While seepage lakes may respond immediately to atmospheric conditions, drainage lakes with larger watersheds may require many decades in order to manifest the changing atmospheric deposition of mercury (Chapter 2). In headwater systems, results indicated that mercury enrichment in lake sediment had an inverse power

relationship with drainage ratio (Chapter 2). Enrichment of Hg in lake sediments was diminished as lake pH rose above 8.3.

$$Hg\ EF = \frac{A_0^{15.56}}{A_d} - 3.55\ x\ pH_{\geq 8.3} - 0.07\ x\ SO_4^{2-}$$

Where Ao is lake area

Ad is watershed area

$pH_{\geq 8.3}$ is a piece wise linear regression with a break point at 8.3

Mercury enrichment in this study region is sporadic and several sites have been identified as spatial outliers. Seepage lakes such as Grippen (Ad/Ao = 0.11) displayed an increase in mercury contamination since the pre-industrial era of 4.9. Other lakes such as Low, Nellie and Farren which were found to be spatial outliers (Chapter 4) would not be considered seepage lakes have mercury enrichment factors (Hg EF) of 4.7, 4.6, and 5.6. However, when examining headwater lakes alone without correction for cultural acidification, all sites in which Hg EF rose above the mean value had a drainage ratio lower than 9. This suggested that surface waters that have low drainage ratios allow for high Hg EF. After correction of such surface waters for pH it was apparent that low drainage ratios were directly associated with elevated Hg EF. Several possibilities have been offered in the literature for the increased sedimentation of mercury to seepage lakes. Watras and Morrison (2008) have mentioned that mercury originating from different sources (i.e. precipitation and watershed) will experience different internal processing within the water column. Mercury entering the water column from runoff will be associated with

dissolved organic carbon, more specifically humic substances (Meili et al. 1991, Mierle and Ingram 1991), and in turn, will be suspended in the water column.

Importance of the study

This study provides the first regional snap shot of mercury enrichment and represents one of the largest sediment mercury inventories in North America. This study comes during a period of reduced emissions and usage of mercury and mercury products in Canada due to the multitude of management initiatives; international, federal legislation (primarily the Canadian Environmental Protection Act 1999), Canada Wide Standards, the Canada-Ontario Agreement, as well as provincial legislation which regulate the emission of mercury. The numerous regulations established have cut the direct emission of mercury to the atmosphere dramatically. Nevertheless, mercury continues to be directly and indirectly emitted to the environment through the release from landfill sites, the scrapping of automobile switches, not to mention the remaining countries in which mercury is still in commercial use. Furthermore, anthropogenic mercury is remitted to the atmosphere from large accumulated pools in soils calling into question the meaning of "natural emission". The legacy of mercury deposition is all around, in the watersheds and aquatic ecosystems we rely on for socio-economic benefit.

This study examines mercury contamination in Ontario and whether the environment has fully manifested anthropogenic mercury emissions. Specifically, the assumption that watersheds are in steady state conditions with respect to Hg deposition and export was tested. The strong spatial patterns exhibited in present-day sediment mercury concentrations and mercury enrichment both of which starkly differ from patterns in pre-industrial mercury concentrations suggests that anthropogenic influence is the dominant process contributing to current mercury contamination. Modeling of mercury enrichment which we speculate to be largely a reflection of

anthropogenic activities, suggests that it would be incorrect to assume steady state conditions. Organic matter in soils is retarding the movement of mercury from watersheds to lakes and may impede the peak enrichment of Hg in Ontario's lakes.

Support for initial hypotheses

In the second chapter we tested the null hypothesis that Hg retention in watersheds has not changed significantly over time by comparing separate models generated with present-day and pre-industrial sediment Hg concentrations. We found that Hg EF, an index of mercury enrichment between pre-industrial and present-day mercury sediment concentrations, displayed an inverse power function with A_d/A_o. Thus the null hypothesis was refuted suggesting that Hg retention in watersheds has changed during this period. Subsequent to this hypothesis, we tested the hypothesis that anthropogenic acidification has altered the relationship between A_d/A_o and sediment Hg concentrations. Examining the relationship between Hg enrichment in lake sediments and lakewater pH, we found that lake pH $\geq$ 8.3 exhibited an inhibitory affect on Hg EF.

In the third chapter we tested whether landscape features (topography, land cover, and surficial and quaternary geology) were increasing Hg concentrations in both sediment and fish equally or whether they acted to favor Hg accumulation in either compartment. Hg concentrations in dorsal muscle of a standardized length of smallmouth bass were used as an index of accumulation. We proposed that as a more diverse set of catchments are included in analysis, land cover and geology should become more important in determining the fate of Hg. While the first principle component of land cover was significant in headwater systems (5 % of variance in RDA), a second principle component of land cover (4 %) and surficial geology (2 %) became significant when we observed lakes disregarding lake order. Land cover, which

represented a gradient of forest to arable lands acted to favor Hg accumulation in lake sediment. Spatial correlation increased when examining a more diverse set of lakes.

In the forth chapter we proposed the hypothesis that the enrichment of mercury is uniformly distributed across our study area. Given that our study region, similar to any other, is subject to mercury deposition from a multitude of sources, we predicted that there would be significant spatial structure in mercury enrichment and surficial mercury concentrations. Further, we predicted that allowing coefficients in a regression model to be weighted spatially (geographically weighted regression; GWR) would enhance the accuracy of the model. In doing so, we test whether key variables exert the same influence (slope of relationship) within our study area (Chapter 4). We refuted the null hypothesis that mercury enrichment in lake sediments was uniform by finding significant spatial structure through an analysis of global autocorrelation and through principal coordinates of neighbor matrices using Moran's I as an index of spatial structure. Secondly, although the GWR explained more variance than ordinary least squares (OLS) regression, no significant difference was found in the accuracy of the two models based upon AIC.

In the fifth chapter, I examined the net flux of methylmercury ($MeHg_{Net}$) between the sum of all tributaries ($MeHg_{Watershed}$) and lake outflow ($MeHg_{Lake}$) and contrasted the results between an oligotrophic lake and a dystrophic lake to test the hypothesis that the two lakes differ in mean $MeHg_{Net}$ and magnitude of seasonal $MeHg_{Net}$ fluctuations. In order to do this we had to first refute the null hypothesis that point in time events contribute equally to the variation in net $MeHg_{Net}$ flux as do seasonal patterns. This was refuted by showing that seasonal patterns were significant and could be predicted by a sinusoidal regression of $MeHg_{Net}$ in both the dystrophic

and the oligotrophic lakes. If point in time events contributed equally to the variation in $MeHg_{Net}$, a periodic trend would not have been significant.

Contribution to original knowledge

This study found that 32 % of lakes had smallmouth bass at a standardized length of 31 cm which exceeded the threshold of toxicological response (0.5 $\mu g \cdot g^{-1}$) set by the World Health Organization. This threshold happens also to represent the consumption guideline for sportfish in Ontario. Despite this, little is known of the regional influences on mercury contamination in surface waters or how aquatic ecosystems respond to changes in anthropogenic activity on a broad scale. Numerous studies have conducted chronographic evaluations of mercury contamination to specific lakes (Lockhart et al. 2000), glaciers (Schuster et al. 2002), or bogs (Givelet et al. 2003). Large efforts have been put forth to understand how isolated areas have responded to mercury deposition. Due to such efforts we know that, in general, sediment profiles may be used as a reliable indicator of mercury deposition and remobilization of mercury from lake sediments are of minor significance when compared to sediment deposition (Gobeil and Cossa 1993, Lockhart et al. 2000). Considering this fact, we have conducted the largest evaluation of sediment mercury enrichment in North America to date (Geological Survey of Canada considered deep sediments alone under the National Geochemical Reconnaissance program (Friske and Coker 1995)) to track changes in mercury deposition through time. In doing so, we have shed light on how mercury contamination in lake sediments is influenced by landscape features, the variability due to watershed level and regional effects, and how this is manifested in the resident aquatic biota.

In this study I have shown that the assumption of steady state conditions in Hg deposition and export does not hold in Ontario watersheds. These watersheds are typical of temperate

boreal watersheds around the globe and so these findings may have large implications for the future of mercury contamination of aquatic ecosystems. This was done by testing the relationship between drainage ratio and mercury enrichment. In addition to this model, I have shown that mercury enrichment also depends upon pH and sulfate.

Recommendations for Future Research

Examination of Hg resuspension

While spatial patterns and physico-chemical properties are the dominant factors influencing mercury concentrations in lake sediment, there will be a fraction which as a result of remobilization, is transferred from pre-industrial to present-day sediment. This fraction is inversely related to the redox potential and is related to the profile of charged particles which may bind to mercury (i.e. sulfides, thiols). Certain watersheds in our study area have been subjected to dramatic land use and land cover alteration since pre-industrial times. It would be useful to profile mercury in lake sediment of such lakes and examine the correlation to control lakes with similar attributes to determine whether time signals correspond with changes in watershed properties we have discovered to be relevant.

Temporal analysis of mercury in smallmouth bass

In this study we observed that mercury concentrations in smallmouth bass correspond well with present-day sediment. Presumably, the increase in either compartment is a reflection of increased mercury loading to surface waters. In order to verify the hypothesis that Ontario's watersheds are slowly achieving new steady state conditions we can expand the number of headwater lakes sampled for smallmouth bass. If the relationship between mercury concentrations in fish and drainage ratio remains as an inverse power function we have more evidence for our hypothesis. Further, analyzing mercury concentrations in fish over time could

provide independent verification of profiles observed in lake sediment without confounding factors such as sediment remobilization.

Physiological effects of mercury contamination on smallmouth bass

Testing for total mercury content in smallmouth bass gives us a broad endpoint for the contamination of our freshwater resources and a measure in which to set consumption regulations. However, what this does not tell us is the magnitude of the effect mercury concentrations have on wildlife. The question of how do mercury concentrations affect wildlife can only be answered by examining physiological endpoints or molecular markers of the chemical insult. In addition, by examining molecular markers of mercury contamination we could determine whether increased contamination directly corresponds to increased stress on aquatic biota.

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Appendix A

Factors influencing the correlation between sulfate and methylmercury from ten wetlands

Abstract

This study presents a detailed examination of the association between sulfate and MeHg in catchments of varying wetland coverage under environmental conditions. The concentration of methylmercury (MeHg) was measured in ten forested wetlands weekly for two years along with sulfate and dissolved organic carbon (DOC) in order to examine the correlation between sulfate and MeHg. Sulfate exhibited an inverse correlation with MeHg which was dependent upon temperature (partial $t = 4.95$, $p<0.0001$) and DOC (partial $t = 4.44$, $p<0.0001$). DOC also had a unique influence on MeHg concentration as did stream discharge. Cross correlation analysis indicated that MeHg was correlated with DOC an average 5 weeks prior to the sampling date and were correlated to sulfate concentrations with no lag period. After correcting for autocorrelation, MeHg concentrations were predicted from: Log MeHg = -0.55 ± 0.06 [SO_4^{2-}] + 0.001 [DOC] + 0.001 ± 0.003 [SO_4^{2-} x DOC] - 0.02 ± 0.01 Discharge + 0.014 ± 0.003 (SO_4^{2-} x temperature) - 0.455, AIC=-3.28, n = 365. The strength of this relationship was dependent upon wetland size; Error (standard deviations) = 0.996+1.32 x e^(-5.6e-5 x wetland size ($x10^4 m^2$)), $R^2 = 0.838$, p = 0.0105.

Introduction

The widespread contamination of remote lakes with mercury (Hg) has increased significantly since pre-industrial times (Swain et al. 1992, Hudson et al. 1995, Fitzgerald et al. 1998). As a result, wildlife and aquatic biota occasionally contain Hg concentrations known to have

toxicological effects. This contamination occurs through the assimilation of organic species of Hg, primarily MeHg (Driscoll et al. 1994), through dietary uptake. Toxicological effects at low MeHg concentrations have been observed in aquatic biota, e.g. alteration of gonadal somatic index and oxidative stress.

While atmospheric deposition of MeHg may be significant in heavily polluted regions (Hultberg et al. 1995) through the methylation of reactive Hg species in atmosphere, in remote areas MeHg deposition is relatively low (9 % of total input to a small bog lake (Hines and Brezonik 2007)). In remote regions, post depositional methylation in wetlands (Stlouis et al. 1994, Rudd 1995, Rencz et al. 2003) and lakes (Watras et al. 1995a, Eckley et al. 2005) are the dominant sources of MeHg in the water column. Thus, drainage lakes with high wetland coverage generally result in high Hg accumulation in fish (Driscoll et al. 1995).

Methylation of inorganic mercury in wetlands occurs through abiotic and biotic processes. Reactive mercury species may react with organic substrates to produce MeHg abiotically, however, net methylation is largely attributed to biotic processing by sulfate reducing bacteria (SRB) and recently to iron reducing bacteria (Fleming et al. 2006). SRB mediate the conversion of ionic mercury (HgII) to MeHg as a detoxification mechanism (Gilmour et al. 1998, Benoit et al. 2003, Jeremiason et al. 2006). As a terminal electron acceptor to SRB, SO_4^{2-} may enhance this activity, transforming SO_4^{2-} to HSO_4^- in the process (Compeau and Bartha 1985).

Mercury methylation in wetlands is influenced by many physical (temperature, redox potential) and chemical conditions (pH, nutrient supply). Consequently, Hg methylation in wetlands is variable between seasons and among wetlands (StLouis et al. 1996). Studies have shown that methylation "hot spots" may occur, typically coinciding with high sulfate and a labile

source of carbon in anaerobic zones, which often occur at the upland-wetland interface (Mitchell et al. 2008b). Once formed, the export of MeHg to lakes may depend on water flow and the presence of dissolved organic carbon which act as transport vectors of MeHg (Shanley et al. 2005).

We wished to test the strength of the sulfate-MeHg relationship among wetlands of various type and size. Specifically, our first objective was to examine the spatial and temporal variation in MeHg which was performed by conducting a nested ANOVA decomposing the variance into basin, subcatchment and season. We hypothesize that wetland size and season will be the dominant source of variation and that two separate basins that receive similar depositional loads but differ in geology will not explain a significant amount of variation in MeHg. Our second objective was to examine the link between MMHg and sulfate in ten catchments of varying wetland coverage ranging from no wetland to over 25 % coverage. The relationship between sulfate and MeHg should improve as a direct response to wetland size. Wetlands are waterlogged soils that have low oxygen concentrations and are favorable for growth of bacteria such as SRB, which methylate mercury. Hence, the proportion of wetland in the watershed is correlated to MeHg concentrations and furthermore the strength of this relationship should increase with wetland size. In addition to the second objective; whether sulfate would provide a unique explanation in MeHg concentrations excluding physico-chemical attributes that influence MeHg concentrations. We expect that the link between sulfate and MeHg will be dependent upon DOC. Besides being the transportation vector for MeHg, DOC may also act as an electron donor for SRB, further enhancing methylation (Mitchell et al. 2008a).

Experimental Details

Study Site

The study area included two lake basins in the Muskoka-Haliburton region of south-central Ontario (45°23', 79°08' and 45°09', 79°05'). Harp and Dickie lakes are two small (71.4 and 93.6 ha, respectively) headwater lakes. Their watersheds are underlain by granitic bedrock and covered with thin to occasionally deep till. Dickie is a much shallower basin with an average watershed slope of 6 % compared to 12 % at Harp. The shallow slope of the Dickie subcatchments gives rise to larger proportions of wetland coverage (Figure A.1). The surficial geology of each subcatchment within the two basins can be seen in table A.1.

Hydrology

Stream discharge was determined from stage – discharge equations with a minimum of 95 % explained variance. Stage height was logged using continuous stage recordings and calibrated from two-stage weirs located on each stream. Most streams feeding these lakes are ephemeral with mean annual discharges ranging from approximately 3 to 50 $L \cdot s^{-1}$. Detailed methods can be found in Hutchinson et al. (1994). Dickie lake contains six tributaries one of which is ungauged (A.1). Watershed runoff provides 69.7% of the water load to the lake. The gauged streams provide 47 % of the runoff load, and additional inflow from the ungauged stream was estimated from historical discharge ratios with gauged weirs monitored for more than a decade. Considering outflow, inflow, precipitation, and evaporation the lake is a net sink for water (Hutchinson et al. 1994). Harp Lake contains seven tributaries; one ungauged. Watershed runoff provides 79.8 % of the water load to the lake 65 % of which is gauged. Similar to Dickie lake, inflows from the ungauged watershed were estimated from historical discharge ratios. Harp lake provides a minimal source of water downstream (0.2%).

Sample collection

Samples were collected on a weekly basis starting during spring melt and continuing until stream senescence. All bottles are washed in diluted trace metal nitric acid and triple rinsed in Milli-Q water. Teflon bottles were used to collect Hg_{total} and MeHg samples. Bottles were contained in ziplock bags at the time of collection. Methylmercury samples were preserved in 2 % HCl during transportation. Samples were kept cool and in the dark until analysis. Samples were collected from a V-notch weir at gauged streams with the exception of Hg samples collected slightly upstream from the guage. Wet deposition was collected at Harp and Dickie into polyethylene bags using wet-only collectors. Bags were collected approximately once a week for chemical analysis by OMOE staff.

Instrumentation

METHYLMERCURY

Methylmercury (MeHg) was quantified by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as in Cai et al. (1996). An Ai Cambridge (UK) model GC 94 gas chromatograph equipped with a CTC A200S autosampler, and an optic injector module was coupled to the PSA Merlin Detector via a pyrolysis oven held at 800°C. A fused silica analytical column with dimensions of 15 m x 0.53-mm i.d. (Megabore), coated with a 1.5-µm film thickness of DB-1 (J&W Scientific) was used. The carrier gas and make-up gas flows were 4.0 ml/min of helium and 60 ml/min of argon, respectively. Water samples were passed through sulfydryl-cotton fibers. Samples were eluted with acidic KBr and $CuSO_4$ and extracted in methylene chloride. pH, chloride ion concentration and salinity must be within the domain of 3, <0.4 M and <26 °/o, respectively. Samples were collected manner similar to Hg_{total} except that 2.5 ml of mixed brominating reagent was added (2 %). This mixture remained in the bottles

until they were used. Prior to using these bottles, 500 µl of hydroxylamine hydrochloride was added to remove all free bromine. The average relative standard error in methylmercury concentrations was 6.3 %, n =72. High variance was treated as with Hg_{total} concentrations.

SULFATE

A PRIC-1 workstation consisting of a Dionex QIC analyzer and a Varian Integrator was used for sulfate determinations. Data from the analyzer was processed in a Dionex DX120 with ChromPerfect software. Water samples (0.014 mL) were eluted using 0.005 M Na_2CO_3 and 0.001 M $NaHCO_3$ at 1.5 mL/minute through an AS14 Dionex column. Standard solutions consisted of sodium sulfate, Na_2SO_4, anhydrous, analytical grade and a certified reference material BMOOS-01 purchased from Environment Canada, National Water Research Institute (NWRI), Burlington, Ontario (certified value: $SO_4 = 5.5 \pm 0.40$ mg/L). Within the limits of calibration (0 to 20 mg/L) the mean standard deviation is 0.0539.

DISSOLVED ORGANIC CARBON

To estimate DOC, water samples were acidified and flushed with nitrogen to remove dissolved inorganic carbon (DIC), followed by wet acid/persulfate photo-oxidation to decompose organic carbon to DIC, followed by carbon dioxide determination using phenylthalein by colorimetry.

Data Analysis

Spatial and temporal variation was quantified among our study sites using a nested ANOVA. Sub-catchments and lake basins were used to represent spatial attributes and season (spring/summer and fall/winter separated for the two study years) was used to account for drying and rewetting of the wetlands. Since MeHg concentrations were not normally distributed we used a rank ANOVA nested within basin (Harp and Dickie) and subcatchment (HP: 3, 3a, 4, 5, 6,

6a and DE: 5, 6, 8, and 10). Once the spatial and temporal variation in MeHg was determined we examined the link between sulfate and MeHg using a mixed effects regression accounting for autocorrelation. Prior to the regression, cross correlations of MeHg with sulfate, DOC, and temperature was performed in SPlus 6.2 to determine the lag period of maximum correlation and adjusted if required before incorporation into the regression. Autocorrelation was accounted for by using an autoregressive model of the first order. Between streams effects (i.e. random effects) were tested for normality and the significance of parameters was evaluated by minimizing Akaike information criterion (AIC). Once the best model (as defined by AIC) was derived excluding SO_4^{2-}, SO_4^{2-} was added and the model was re-evaluated.

Results

Mercury

Total mercury and MeHg concentrations were measured in samples collected from ten streams on a weekly time interval. Total Hg was measured during the spring/summer of the first year while MeHg was measured over a two year period with the exception of no-flow periods. Total Hg flux ranged from 1.2 to 256.5 $\mu g \cdot m^{-2}_{catchment} \cdot yr^{-1}$. Generally, the export of mercury from the catchments was highest during the spring and decreased later in the summer with the exception of the large precipitation event in June. Excluding precipitation events the largest export of mercury was 396 $\mu g \cdot m^{-2} \cdot day^{-1}$ and occurred from Harp 3a during the spring. The export of mercury from the sub-catchments correlated positively with color, and negatively with pH as observed by Mierle and Ingram (1991) at the same study sites. Table A.2 shows the mean and standard deviation of fluxes of total mercury and methylmercury pooled across all the streams examined. Detailed examination of Hg_{total} in the same study region can be found in Mierle and Ingram (1991).

Methylmercury

MeHg concentrations were highly correlated with Hg_{total} in all streams. The fraction of Hg_{total} present as MeHg averaged from each catchment over the study period was related to the area of peat coverage in the sub-catchment according to the equation $MeHg/Hg_{Total} = 2.173 \times e^{(0.09 \times \% \text{ peat})}$, $R^2 = 0.850$, $p<0.001$, $n = 10$), regardless of peatland size. The flux of MeHg was not related to peat coverage but rather to the peat size.

Examining the influence that both peat area and coverage had on MeHg concentrations, we performed a nested ANOVA to determine whether spatial or temporal characteristics were dominating our catchments. Spatial characteristics were the sub-catchments of each basin and temporal characteristics were classified by season. Previous results indicated that seasonal trends including such as the rise and fall of water level; which influences the redox potential, the temperature (which influences biological activity), and detrital matter (which provides labile carbon source), may influence MeHg concentrations. Indeed, results indicated that sub-catchments responded differently between seasons ($F_{8,687} = 2.07$, $p = 0.036$) (Table A.3).

Once we had established that the basin had little effect on MeHg concentration, we moved on to our second objective which was to examine the relationship between MeHg and sulfate. Figure A.2 represents MeHg concentrations in each stream as a function of sulfate concentration on a log scale. The strength of the association was tested through cross correlation and results between MeHg concentrations, sulfate and dissolved organic carbon are presented in table A.4. Sulfate concentrations increased with discharge during the spring and decreased with discharge in the fall, displaying a linear relationship with discharge during low flow. In most instances, sulfate concentrations reached maximum levels following summer drought as

observed in previous studies (Devito and Hill 1999, Eimers and Dillon 2002). To reduce the possibility that the relationship between sulfate and MeHg was the result of covariation with another process, we tested that sulfate significantly predicted MeHg after accounting for all other parameters. A best subsets multiple regression approach was used to determine the best model for the prediction of MeHg; discharge, conductivity, iron, stream temperature, pH, dissolved organic carbon, gran alkalinity, and reactive silica were included in the model (AIC = 80.85, n = 248). When sulfate was added to the model, it contributed a significant amount of variance in MeHg (partial $t_{224} = 2.148$, $p = 0.033$).

Methylation of mercury in wetlands has been shown to be a function of both sulfate and labile fractions of DOC (Mitchell et al. 2008b, Mitchell et al. 2008a). Unlike interactions between MeHg and sulfate, the lag between MeHg and DOC was often higher than 2 weeks (Table A.4) and there was more variation in the lag period. The correlation strength appeared to be related to the extent of peat land, similar to observations between MeHg and sulfate concentrations. This can be expected as previous research has noted the variation that can exist between different types of wetlands (StLouis et al. 1996) and due to the microtopography within a wetland (Mitchell et al. 2008b). As a consequence, we must treat each study site as having a unique relationship between sulfate and MeHg. We can test the validity of this approach and the relationships through mixed model regression.

After adjusting significant parameters to the appropriate lag period and testing for interactions between these variables, we predicted MeHg concentrations. As previously conducted upon the correlation structure, models were compared using the likelihood ratio. MeHg concentrations were predicted using the equation: Log MeHg = -0.55 ± 0.06 $[SO_4^{2-}]$ + 0.001 [DOC] + 0.001 ± 0.003 $[SO_4^{2-}$ x DOC] - 0.02 ± 0.01 Discharge + 0.014 ± 0.003 (SO_4^{2-} x

temperature) - 0.455; AIC=-3.28, n = 365 across 10 streams. We corrected for the presence of autocorrelation (Φ – 0.932) using a continuous arima model which allowed for irregular sampling intervals present in our dataset in a few instances.

In most instances the model was able to accurately predict the observed MeHg concentrations, however the model was unsuccessful at Harp 3a and 4 (Figure A.3). These watersheds have the lowest proportion of peat land among both lake basins (2.9 and 0%). Temperature enhanced the affect of sulfate ($t = 4.95$, $p<0.0001$) on MeHg concentrations as did DOC ($t = 4.44$, $p<0.0001$, Table A.5). Figure A.3 represents observed and predicted the variation in MeHg concentrations as a function of sulfate after accounting for correlated structure and an interaction with DOC. MeHg concentrations exhibited the largest increase per gram of sulfate in sub-catchment Harp 5, the site containing the largest peat land of the study. While only 13 % of the watershed at Harp 5 is peat land, the size is nearly 60 % larger than the next largest peat land (Dickie 11).

The strength of the relationship between MeHg, sulfate, DOC, discharge, and temperature was dependent upon peat land size. The variability in this relationship decreased exponentially with peat land size (Figure A.4) with the exception of the two sub-catchments that contained negligible peat land coverage (Figure A.4) (standard deviation = 0.832 and 0.829). The variability of this relationship was unrelated to the portion of peat land coverage (%); $R^2 = 0.316$, $p = 0.147$, $n = 8$. In other words, our ability to reliably predict MeHg is not influenced by the ratio of uplands to peat lands in a sub-catchment, but rather by the size of peat land.

Discussion

The methylation and export of mercury from terrestrial ecosystems is dependent upon many factors including temperature, hydrology, and chemical parameters (Rudd 1995, StLouis et al. 1996, Mitchell et al. 2008a). As a result, great variation can exist in methylation activity; among wetland types (StLouis et al. 1996) and even within a single wetland (Mitchell et al. 2008b). Hot spots of methylation have been attributed to the availability of sulfate and sources of labile organic carbon (Mitchell et al. 2008b). Sulfate stimulates increased SRB activity, which in turn methylate mercury. In an attenuation study, Jeremiason et al. (2006) observed that MeHg porewater concentrations increased to 1.63 ± 0.27 ng·L^{-1} two weeks following treatment with four times the ambient sulfate load, a 3-fold increase in MeHg. The presence of labile organic carbon can also stimulate bacterial activity through the donation of electrons. Due to the seepage of labile organic carbon sources of uplands, the upland – wetland interface is a key region for mercury methylation. In this study, we measured MeHg concentrations weekly over two years to examine the relationship between MeHg and SO_4^{2-} and how this mechanism may vary in catchments of different wetland size and types. Indeed, increased MeHg concentrations in wetland stream waters coincided with a decrease in SO_4^{2-}, which suggested dissimilatory SO_4^{2-} reduction. Negative correlations between sulfate and methylmercury were observed in all streams except Harp 3a and 4 (Figure A.6) the two catchments with the least wetland coverage. Despite having little relation with sulfate, MeHg concentrations in stream water from these two catchments displayed little variation in between modeled and observed values. This may likely have occurred due to the little variation in actual MeHg concentrations.

The association between sulfate and MeHg was influenced by several other variables; dissolved organic carbon and temperature. Both DOC and temperature significantly altered the relation between sulfate and MeHg by increasing the MeHg concentration. DOC is a vector for

Hg_{Total} and MeHg from terrestrial sources towards surface waters. Thiol groups particularly found in humic substances form a tight association with MeHg pulling MeHg into the dissolved phase (Driscoll et al. 1995, Allan and Heyes 1998). Our results support this mechanism as DOC contributed significantly to the prediction of MeHg concentrations. As a biological process, the dissimulatory reduction of SO_4^{2-} is sensitive to temperature (Benoit et al. 2003) as we observed in this study.

Conclusion

This study examined the relationship between MeHg and sulfate among catchments of various wetland types and sizes. In doing so, we have shown that the mechanism is dependent upon wetland size rather than ratio of wetlands to uplands. Further, we have shown that the relationship between sulfate and MeHg is altered by the presence of DOC and is dependent upon temperature. We have shown that the sulfate – MeHg relationship is universal and is the best correlate of MeHg concentrations in stream water.

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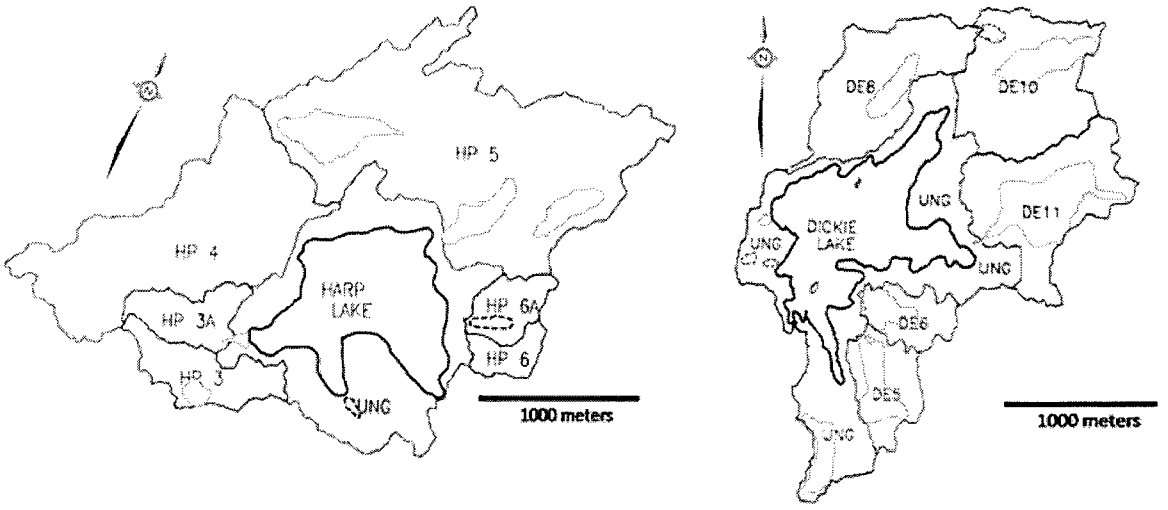
Figure Legend

Figure A.1: Schematics of the two study basins Harp (left; 45°23', 79°08') and Dickie (right; 45°09', 79°05'). Both lakes are in south-central Ontario. Wetlands have been designated with a dashed line.

Figure A.2: Methylmercury concentrations as a function of sulfate concentration on a log-log scale in ten streams of south-central Ontario sampled weekly over a two year period. Each point represents the average of two measurements. Streams are denoted a) Harp 6a b) Harp 4 c) Harp 5 d) Harp 6 e) Dickie 8 f) Harp 3 g) Harp 3a h) Dickie 10 i) Dickie 5 j) Dickie 8.

Figure A.3: Methylmercury concentrations in ten south-central Ontario streams of various wetland coverage as a function of predicted concentrations: Log MeHg = -0.55 ± 0.06 $[SO_4^{2-}]$ + 0.001 [DOC] + 0.001 ± 0.003 $[SO_4^{2-}$ x DOC] - 0.02 ± 0.01 Discharge + 0.014 ± 0.003 (SO_4^{2-} x temperature) - 0.455.a) Harp 6 b) Harp 6a c) Harp 3 d) Harp 3a e) Harp 4 f) Harp 5 g) Dickie 10 h) Dickie 5 i) Dickie 6 j) Dickie 8.

Figure A.4: Standard deviation between predicted and observed MeHg concentrations in ten streams as a function of peat size. The graph represents streams with (○) and without (●) a significant peat area (<1%). The deviation is dependent upon the peat size R^2 = 0.838, p = 0.0105; Deviation = 0.996+1.32 x $e^{(-5.6e-5 \text{ x peat size})}$.



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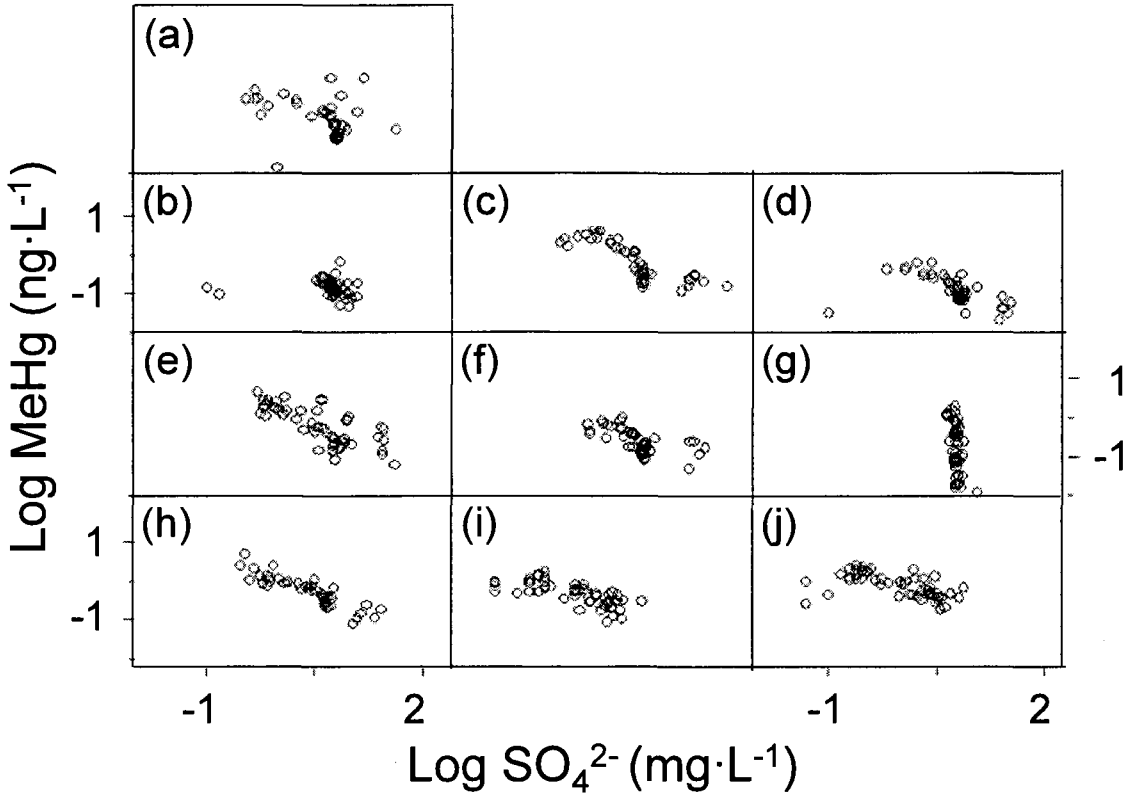

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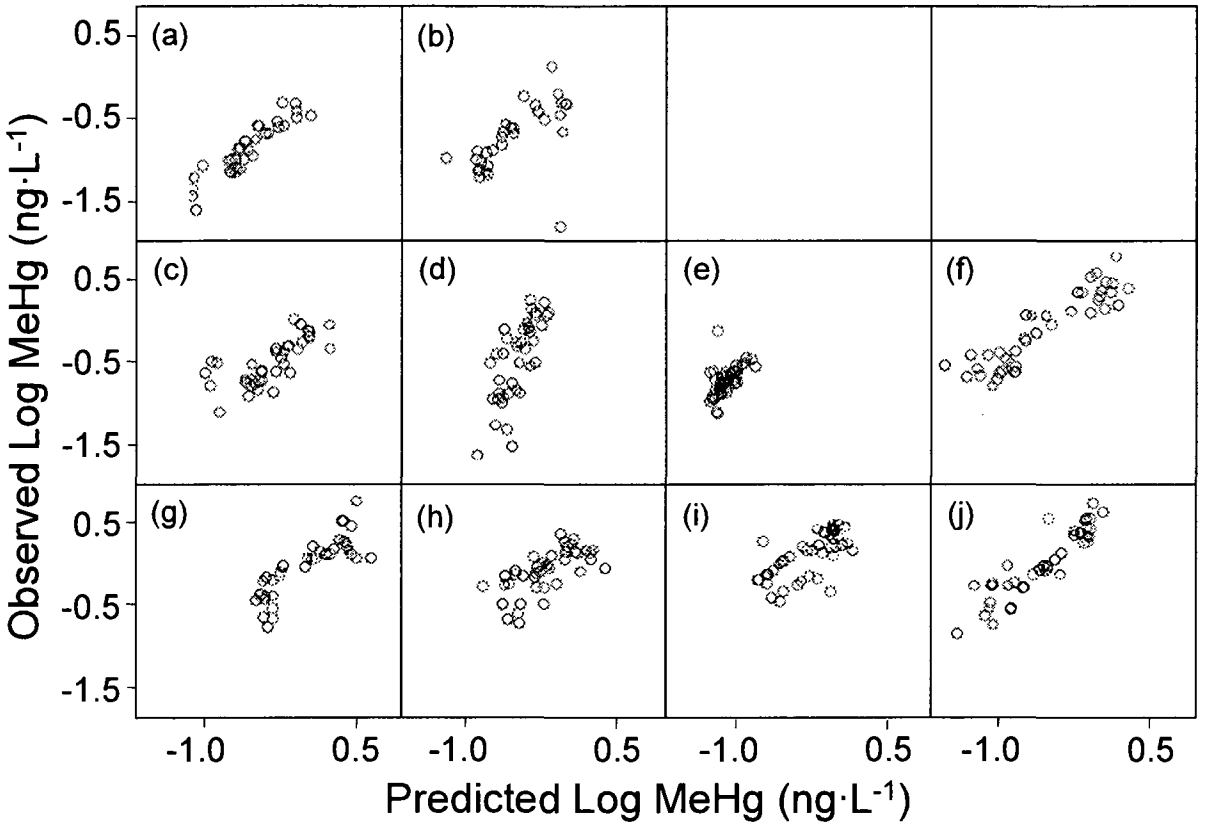

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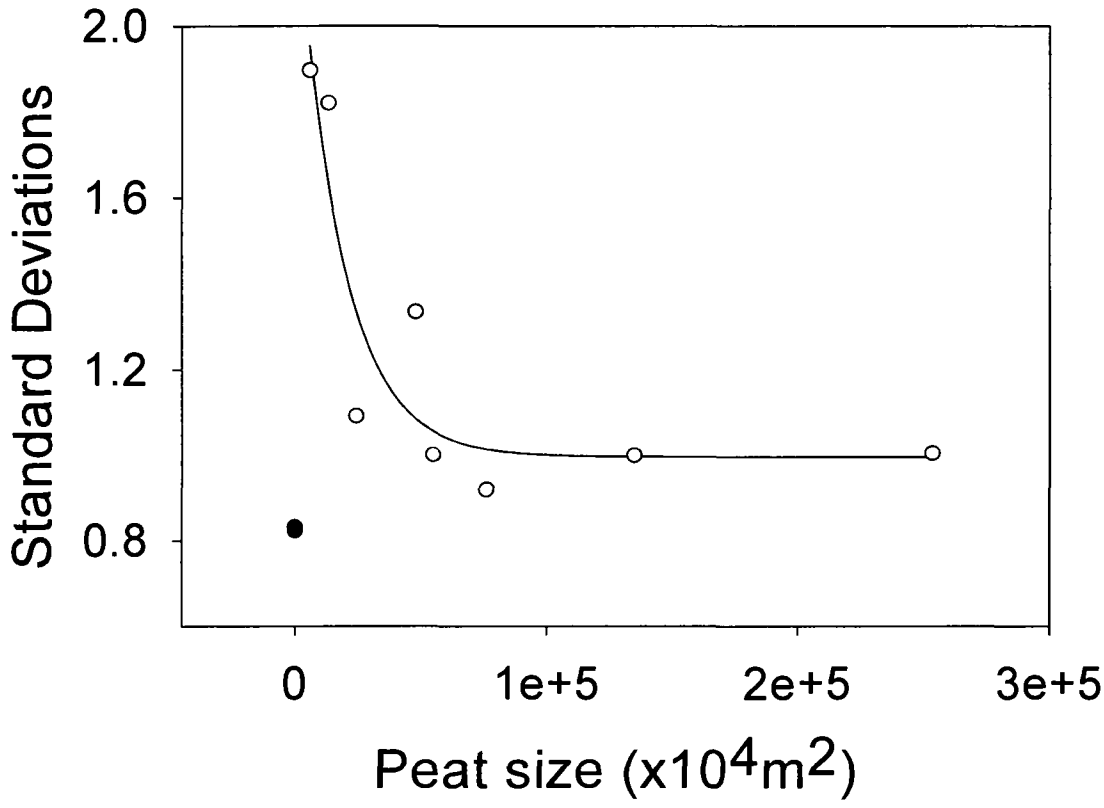

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Table A.1: Surficial geology of tributaries within Harp and Dickie watersheds.

		Area Gauged	Bedrock (% of area gauged)				Surficial Deposits (% of area gauged)					
		(104m2)	Migmatite	Biotite/Horneblende/Gneiss	Diorite	Amphibolite/Schist	Minor Till	Thin Till/Rock Ridges	Peat	Bedrock	Sand	Pond
Harp	1			100			38.5	54.6	6.9			
	3	260000		93		7	79.5	11.2	9.3			
	3a	196500		42.6		57.4	97.1		2.9			
	4	1190900		13.2		86.8	56.1	32.8	0	0.9	7.5	2.7
	5	1905300		100			34.5	48.8	13.3		3.6	
	6	99700		100			45.2	54.8	0			
	6a	152800		33.3	66.7		6.6	84.9	8.5			
	Misc			90.3	1.4	8.4	69.5	23.4	0.6	0.3	6.2	
	Total			68.5	3.1	28.4	49.5	38.5	6.3	0.3	4.3	0.8
Dickie	3		100					82.5	16.2	1.4		
	5	299800	100					74.6	25.4			
	6	218000	100					78	22			
	8	669600	100				13.7	78.1	8.2			
	10	788900	100					82.9	17.1			
	11	762700	100					79.1	20.9			
	Misc		100				11.2	87.1	1.7			
	Total		100				4.7	81.4	13.9			

Table A.2: Concentration and yield of total and methylmercury from ten streams in south-central Ontario over two years.

Station	Hg_{Total} ($ng \cdot L^{-1}$)	MeHg ($ng \cdot L^{-1}$)	MeHg ($\mu g \cdot m^{-2} \cdot yr$) Peat	Hg ($\mu g \cdot m^{-2} \cdot yr$) Catchment	MeHg ($\mu g \cdot m^{-2} \cdot yr$) Catchment
DEOF	2.2 (0.8)	0.1 (0.1)	NA	NA	NA
DE10	8.0 (3.1)	0.7 (0.7)	3.4 (2.4)	5.7 (9.4)	0.6 (0.4)
DE5	3.0 (0.9)	0.5 (0.2)	3.9 (5.5)	3.5 (8.8)	1.0 (1.4)
DE6	5.7 (1.8)	0.8 (0.5)	9.8 (18.5)	5.3 (11.7)	2.1 (4.0)
DE8	10.6 (3.9)	0.5 (0.5)	4.5 (7.0)	5.7 (12)	0.4 (0.6)
HPOF	1.6 (0.3)	0.04 (0.02)	NA	NA	NA
HP3	6.3 (2.8)	0.3 (0.2)	1.8 (1.4)	5.1 (4.7)	0.2 (0.1)
HP3A	2.6 (0.5)	0.2 (0.3)	4.0 (7.9)	1.2 (1.4)	0.2 (0.3)
HP4	3.8 (1.3)	0.1 (0.02)	No peat	232.2 (304.5)	10.6 (10.1)
HP5	5.5 (1.4)	1.7 (2.6)	—	—	—
HP6	5.9 (1.8)	0.1 (0.1)	No peat	256.5 (250.3)	11.5 (10.5)
HP6A	6.1 (2.1)	0.2 (0.1)	1.1 (0.6)	2.9 (4.0)	0.1 (0.1)

Table A.3: Results of an ANOVA on rank transformed MeHg concentrations in 10 different streams nested among basin, subcatchment, and season. Data were collected on a weekly time interval over two years.

Parameter	Df	F	p value
Basin (Harp/Dickie)	1	2.77	0.097
Season (spring/fall)	1	0.34	0.557
Subcatchment within Basin	8	1.47	0.165
Basin across Season	1	0.57	0.449
(Subcatchment within Basin) across Season	8	2.07	0.036

Table A.4: Results of cross correlation analysis between methylmercury concentrations and dissolved organic carbon and sulfate from ten catchments in south-central Ontario. The lag of maximum correlation is in brackets.

		Maximum Correlation of MeHg and lag	
Basin	Station	Dissolved organic carbon ($mg \cdot L^{-1}$)	Sulfate ($mg \cdot L^{-1}$)
Harp	HP3	0.565 (0)	0.646 (0)
	HP3A	NS	0.517 (0)
	HP4	NS	NS
	HP5	0.628 (0)	0.894 (0)
	HP6	0.686 (0)	0.498 (0)
	HP6A	0.721 (3)	0.346 (2)
Dickie	DE5	0.504 (5)	0.749 (1)
	DE6	0.595 (5)	0.615 (1)
	DE8	0.678 (3)	0.721 (0)
	DE10	0.616 (3)	0.945 (0)

All values presented are significant at $\alpha = 0.05$

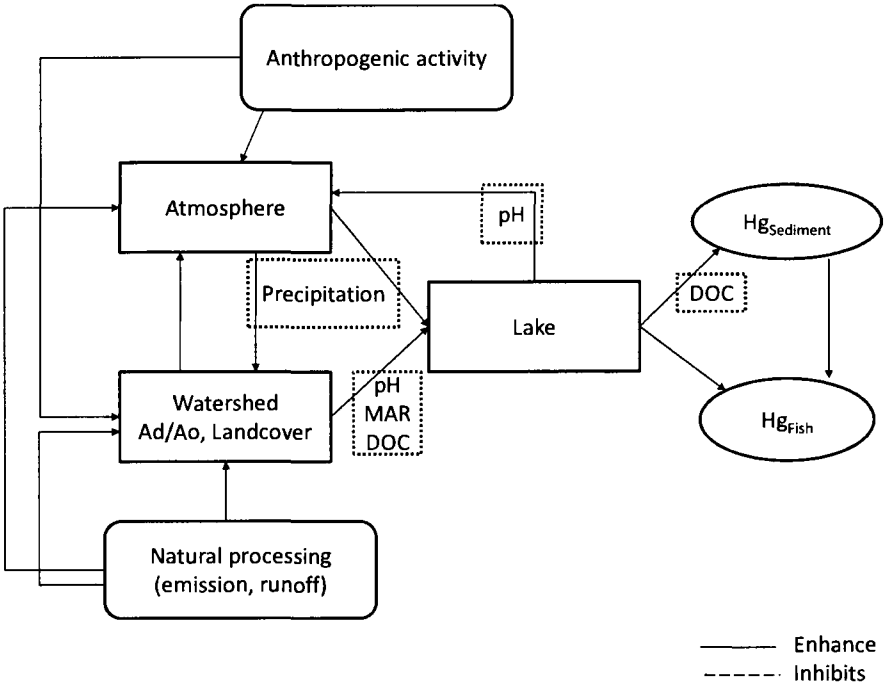
Table A.5: Results of a mixed effects model on the concentration of methylmercury in ten streams

Parameter	Coefficient	Std.Error	DF	t-value	p-value
Intercept	-0.455	0.067	365	-6.79	<.0001
SO_4^{2-} ($mg \cdot L^{-1}$)	-0.549	0.057	365	-9.60	<.0001
DOC ($mg \cdot L^{-1}$)	0.001	0.000	365	7.06	<.0001
SO_4^{2-} x DOC	0.001	0.000	365	4.95	<.0001
Discharge	-0.024	0.011	365	-2.15	0.0319
SO_4^{2-} x Temperature	0.014	0.003	365	4.44	<.0001

The coefficients represent the results of the fixed effects. Results were adjusted for autocorrelation and for colour between streams.

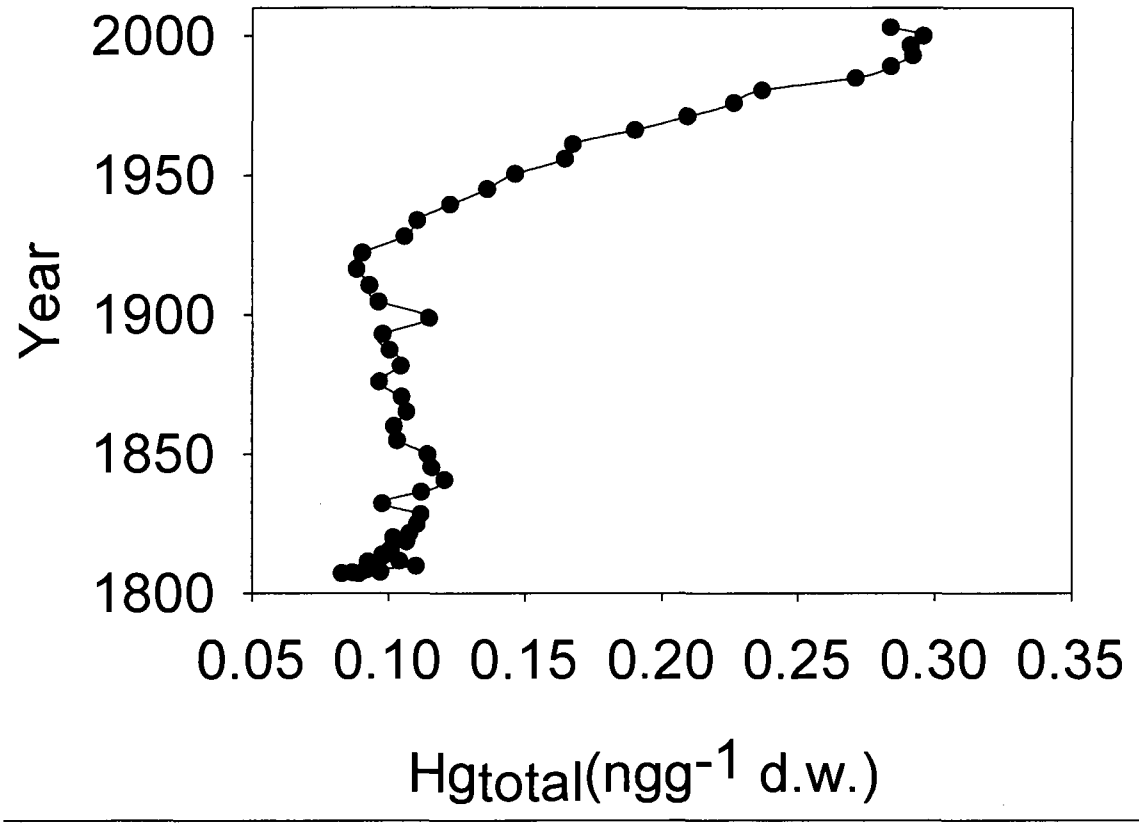
Appendix B

Schematic of major findings



Appendix C

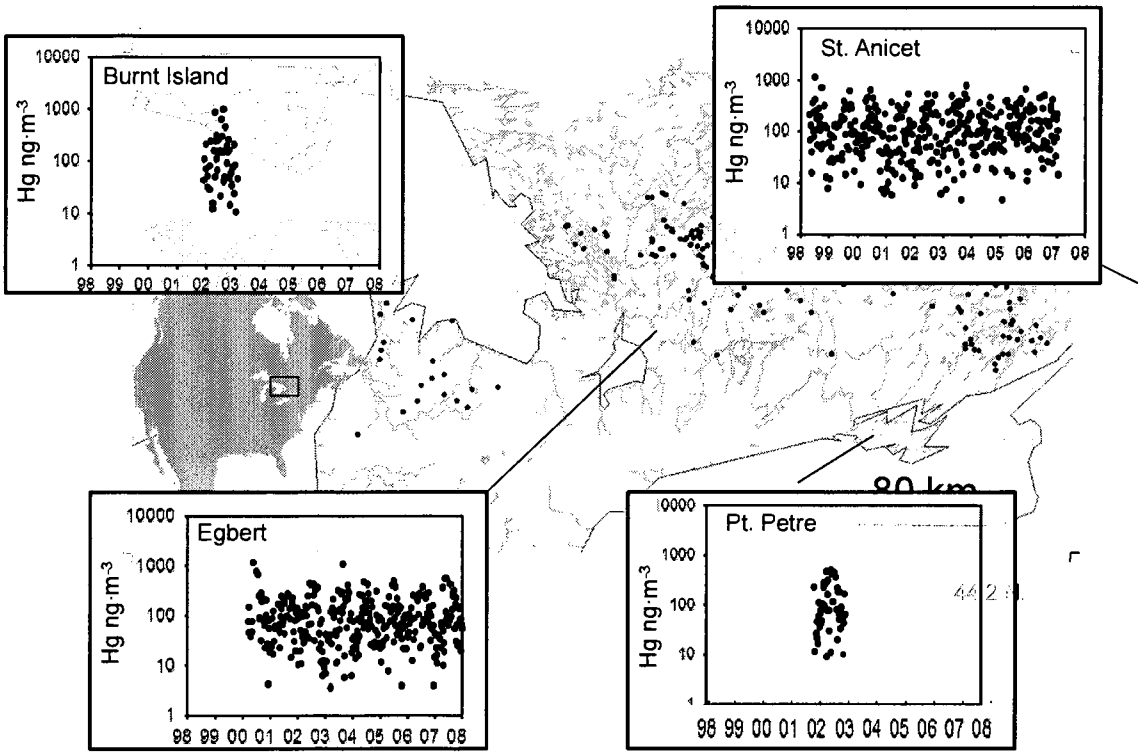
Profile of mercury concentration in plastic lake as a function of year



Average concentration of total mercury as a function of sediment age from two cores collected from Plastic lake in south-central Ontario. Age was determined from ^{210}Pb gamma spectroscopy.

Appendix D

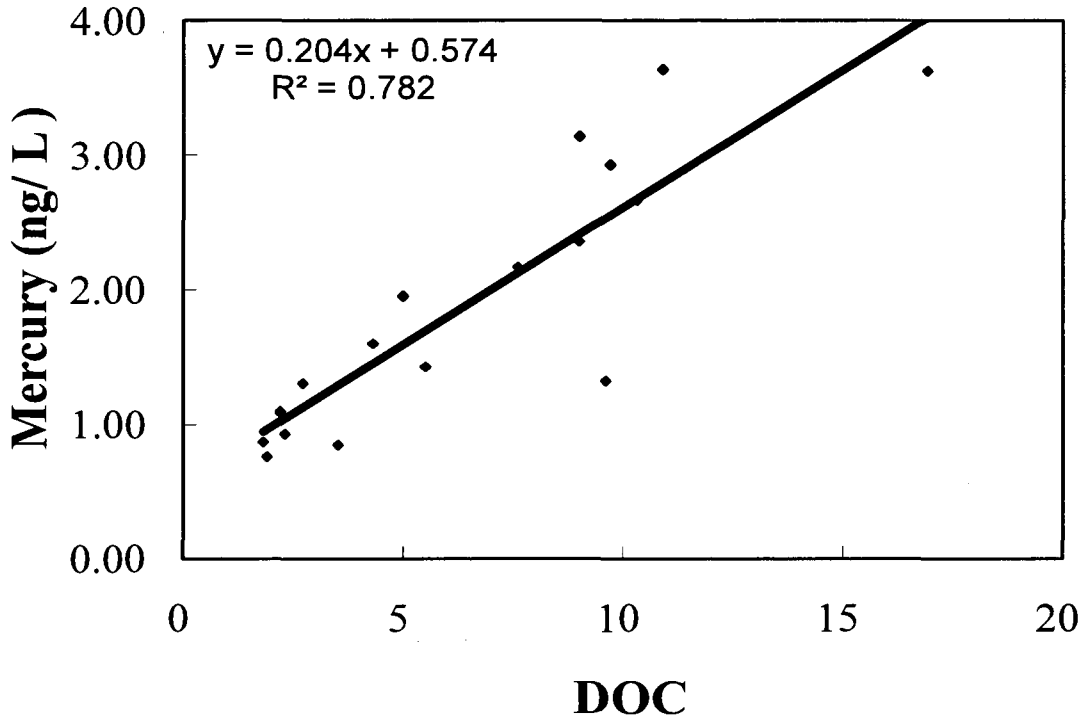
Mercury deposition in Ontario since 1998



Mercury deposition ($ng \cdot m^{-3}$) measured at Egbert, St. Anicet, Pt. Petre, and Burnt Island from the Mercury Deposition Network from 1998 to present. Data was gathered from the Mercury Deposition Network website, National Atmospheric Deposition Program.

Appendix E

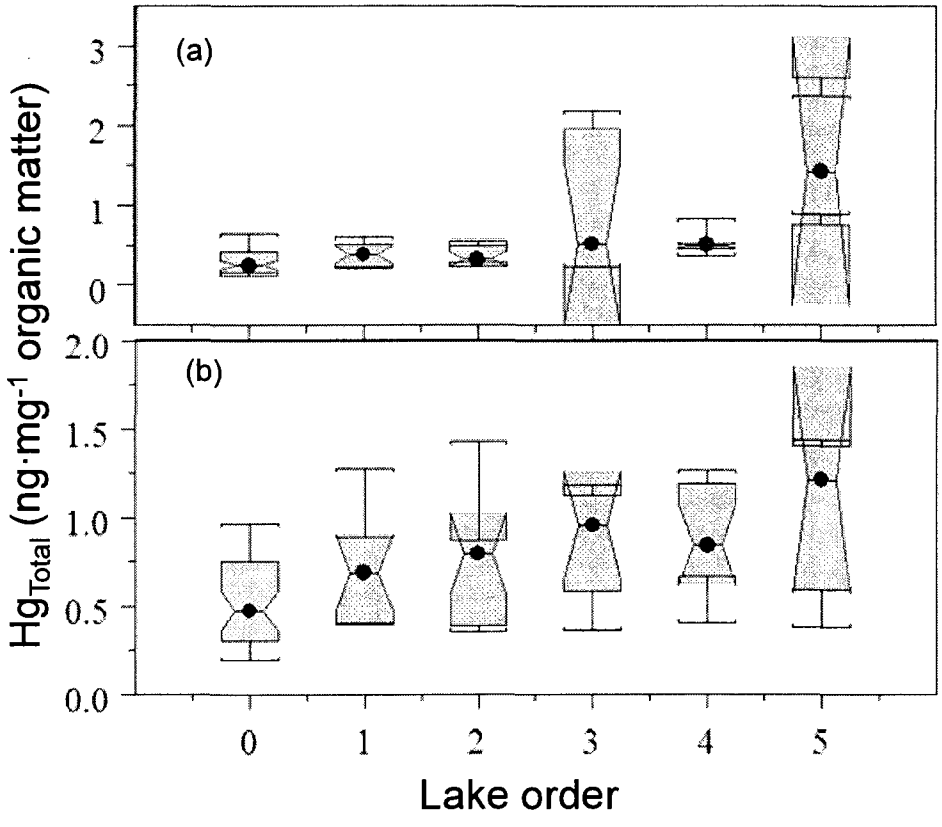
Mercury and dissolved organic carbon concentrations in headwater lakes



Relationship between mercury and DOC in head water lakes of the Muskoka-Haliburton area of Ontario. Data are from McQueen (unpublished).

Appendix F

Distribution of total mercury concentration by lake order



Total mercury concentrations standardized by organic matter content in (a) pre-industrial (>30 cm depth) and (b) present-day (0.5-1.0 cm) lake sediments as a function of lake order as was determined by GIS mapping.