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Hermes: A Modelling Tool for Predicting Mercury Concentrations and Fluxes in Lakes

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HERMES: A MODELLING TOOL FOR PREDICTING MERCURY CONCENTRATIONS AND FLUXES IN LAKES.

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Abstract

A general multimedia mass balance model was developed for Big Dam West, Kejimkujik Park, Nova Scotia to predict mercury (Hg) flux and fate in lakes. This model can be used as a screening-level tool by researchers with little to no modeling experience. The model requires no recalibration when applied to other lakes and few input variables (i.e., concentration of Hg in air and inflow water, lake and inflow water suspended particulate matter (SPM), lake temperature, mean depth, surface area, volume, precipitation rate, sedimentation and resuspension rate) need to be changed for any given location.

Limits of this model termed "Hg Environmental Ratios Multimedia Ecosystem Sources" (HERMES) model were tested through reapplication and verification on Harp and Dickie Lake, along with Lake Ontario. The HERMES model predicts that small lakes with short water residence times and larger lakes with longer residence times are dominated by water inflow Hg concentration and atmospheric Hg concentration, respectively. For Lake Ontario, air concentrations of mercury appear to be most important. These results contrast with the currently held belief that the Niagara River is the main source of Hg to the lake.

To improve model applicability to lakes with limited datasets, as was the case for many of the lakes used in this thesis, estimation methods were developed or adapted from the literature to estimate the most sensitive model input variables (i.e., water inflow Hg concentration, SPM, sediment resuspension rate, water inflow rate) when measured values are missing. Methyl mercury (MeHg) is the bioavailable form that accumulates through food webs, so estimation methods were developed or found to estimate the relative amount of methylated Hg in water inflow, water, and sediment as well.

Error contributions to the model from estimation methods were tested through model application to thirty-five lakes in Ontario using three estimation methods (i.e., SPM, resuspension rate, water inflow Hg). The added value of SPM and resuspension rate estimates were assessed through comparisons with fixed values. A comparison between measured and predicted values for these lakes using these estimation methods revealed no significant difference for sediments.

The HERMES model was used to derive water inflow Hg concentration values from measured sediment Hg. Regression of the derived water inflow Hg values against watershed and lake variables resulted in the following equation: log water inflow Hg concentration = (0.165 x log watershed area (km^2)) + (0.102 x dissolved organic carbon (mg L^{-1})) – (0.342 x log water inflow rate (m^3 h^{-1})) + 0.000778 x direct runoff (mm yr^{-1})) + (0.0154 x mean lake depth (m)) + 0.492 (r^2 = 0.68, $p < 0.0001$). A comparison between the water inflow Hg concentration estimation method (i.e., equation) derived in this study and average measured values for sixteen lakes located in different parts of the world (e.g., Antarctica, Russia, Canada) showed a deviation of only 15.7±18.0%, and was within reported ranges (n = 6). This was found to be a significant ($p < 0.05$) improvement over the previous estimation method for water inflow Hg concentration.

Résumé

Dans cette thèse, un modèle général multimédia de bilan massique a été développé pour prévoir le flux et le sort du mercure (Hg) dans les lacs ruraux et urbains. Pour être employé comme a criblage-niveau outil par des chercheurs et spécialistes en modélisation, le modèle n'exige aucun ré-étalonnage quand appliqué à d'autres lacs et ne requiert que peu de changements aux variables d'entrée (e.g. concentration de Hg dans l'air et le débit entrant, les matières en suspension dans le lac (SPM) et le débit entrant, volume, profondeur, température, superficie, taux de précipitations, le taux de re-suspension et sédimentation des sédiments).

Les limites de ce modèle appelé "Hg Environmental Ratios Multimedia Ecosystem Sources" (HERMES) indiqué que les petits lacs pour lesquels le temps de résidence de l'eau est court, ainsi que les grands lacs avec de plus longs temps de résidence sont dominés par concentration de Hg dans le débit entrant et par la concentration de Hg atmosphérique, respectivement. Pour le lac Ontario, la concentration de Hg atmosphérique est importante. Ces résultats diffèrent de la croyance selon laquelle la rivière Niagara est la source principale de mercure dans ce lac.

Pour améliorer l'applicabilité de ce modèle aux autres lacs avec des ensembles de données limités, ce qui était le cas pour plusieurs des lacs étudiés dans cette thèse, des méthodes d'évaluation ont été développées ou trouvées dans la littérature pour estimer les variables d'entrée les plus sensibles (e.g. la concentration Hg dans le débit entrant, le taux de matières en suspension, le taux de re-suspension des sédiments et le débit entrant) quand les valeurs mesurées sont absentes. Comme le mercure méthylique (MeHg) est la forme bio-disponible du mercure qui s'accumule dans la chaîne alimentaire, des méthodes d'évaluation ont aussi été développées ou trouvées pour estimer la quantité relative de mercure méthylique dans le débit entrant, les lacs, et les sédiments.

Les contributions d'erreur au modèle à partir de méthodes d'estimation ont été testés sur 35 lacs de l'Ontario en utilisant trois méthodes d'estimation (i.e. SPM, taux de re-suspension des sédiments et la concentration Hg dans le débit entrant). L'estimation de la valeur ajoutée du SPM et taux de re-suspension des sédiments étaient évaluées par comparaison avec les valeurs fixes. Une comparaison entre les concentrations mesurées et prévues, n'a indiqué aucune différence significative pour des sédiments.

Le modèle HERMES a été utilisé pour dériver la concentration de Hg dans l'eau à partir de valeurs mesurées de Hg dans les sédiments. Une régression de la concentration du Hg dans le débit entrant en fonction de variables de lacs et de bassins versants ont donné lieu a l'équation suivante : logarithme de la concentration du Hg dans le débit entrant = (0.165 x log du la superficie du bassin versant (km^2)) + (0.102 x carbone organique dissous ($mg\ L^{-1}$)) – (0.342 x log du débit entrant ($m^3\ h^{-1}$)) + (0.000778 x ruissellement direct ($mm\ an^{-1}$)) + (0.0154 x profondeur moyenne du lac (m)) + 0.492 ($r^2 = 0.68$, $p < 0.0001$). Une comparaison entre la méthode d'estimation de la concentration de Hg dans le débit entrant (i.e. l'équation) dérivée de cette étude et les valeurs mesurées moyennes pour 16 lacs situés dans différentes parties du monde (e.g. Antarctique, Russie, Canada) ont démontré une déviation de seulement 15.7±18.0%, et se situait dans les écarts rapportée (n=6). Ceci est considéré comme une amélioration significative ($p < 0.05$) sur les méthodes d'estimation de la concentration de Hg dans le débit entrant retrouvée dans la littérature.

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Contributions from Co-authors

Chapter 2

Don Mackay and Liisa K. Toose-Reid assisted with any modeling-related trouble-shooting. Anton M. Scheuhammer and David R.S. Lean provided funding and support during the write-up of this chapter. Nelson J. O'Driscoll and David R.S. Lean have extensive knowledge about Big Dam West Lake, Kejimkujik Park, Nova Scotia, which turned out to be tremendously useful during model application and verification on this lake.

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Chapter 5

Joseph F. Atkinson created the LOTOX2 Hg submodel and provided the report that contained both the modeled and measured data with which HERMES model output was compared. Joseph V. DePinto was the creator of the original LOTOX2 model. David R. S. Lean provided funding and support during the write-up of this chapter.

Chapter 6

R. Brad Mills, Jules M. Blais, John P. Smol and Andrew M. Paterson provided the lake dataset used in this chapter. David R. S. Lean provided funding and support during the write-up of this chapter.

Appendix 1A and B

These research papers were written with A.M. Scheuhammer, who also provided funding and support. A.M. Scheuhammer and D.E. Bond contributed to field and laboratory sampling and analyses.

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List of Abbreviations

Hg	Mercury
MeHg	Methyl mercury
Me_2Hg	Dimethyl mercury
Hg^0	Elemental mercury
Hg^{2+}	Inorganic mercury
THg-MeHg-Hg^0	Residual mercury (mostly Hg^{2+})
THg	Total mercury
MeHg : Hg^0	Concentration ratio
THg-MeHg-Hg^0 : Hg^0	Concentration ratio

SPM	Suspended particulate matter (i.e., suspended sediment)
DOC	Dissolved organic carbon
TOC	Total organic carbon
Eh	Redox potential

QWASI	Quantitative water air sediment interaction
HERMES	Hg Environmental Ratios Multimedia Ecosystem Sources
D	Transport parameter (advection or diffusion)
K	Partition coefficient
Z	Fugacity capacity
f	Fugacity

LOTOX	Lake Ontario Toxicity
STELLA	Systems Thinking Experiential Learning Laboratory with Animation
R-MCM	Regional Mercury Cycling Model

CHAPTER 1

GENERAL INTRODUCTION

1.0 THESIS RATIONALE

Mercury (Hg) speciation and partitioning mass balance models can be used to rapidly evaluate methyl mercury (MeHg) exposure since they can estimate ecosystem response to changing Hg loads and environmental conditions. Mercury models can be subdivided into: mechanistic and general. Mechanistic models include interconversion and first-order rate constants (i.e., reactions). These models are used for more detailed examinations of Hg species distribution and fate. General models tend to follow a "key" species and use constant ratios to account for the multiple forms. This is a simpler approach with predictions that are comparable to the above-mentioned mechanistic models. All general and mechanistic models constructed so far have been site-specific. In this thesis, a general model is presented that can be applied as a screening level tool to rapidly assess the behavior of Hg in lakes with limited observational data.

1.1 CONTEXT OF RESEARCH

Mercury is widespread, with natural and industrial sources. Communities near rural and urban lakes frequently show signs of physical impairment due to biomagnification of Hg through neighboring aquatic food webs (i.e., primary target is central nervous system) (Pavlogeorgatos and Kikilias, 2002). Data for lakes near rural communities is typically limited, thus making model application difficult since many of the required input variables

for parameterization are frequently absent. Fortunately, environmental models tend to be driven by key input variables related to location (e.g., temperature, atmospheric Hg, precipitation rate) and lake-specific (e.g., water inflow flow rate and Hg concentration, water volume, mean depth, water inflow and water column suspended particulate matter, sedimentation and resuspension rate) information. Identification and the provision of estimation methods (i.e., empirical relationships relating a model input variable to another routinely-measured variable) for these variables are essential for model application to lakes with a limited amount of data. Eventually, the inclusion of additional estimation methods to account for the relative amount of methylated Hg would enable model output (i.e., sediment and water Hg concentration) to serve as input for food web models.

1.1.1 Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model

In Greek mythology, the Roman god Mercury was called Hermes. The well-known symbol for mercury (☿) is even thought to represent Hermes in his winged hat. The general Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model developed and evaluated in this thesis can produce comparable estimates to other more mechanistic Hg models available, even though it uses a different method (i.e., concentration ratios). HERMES was therefore deemed to be a suitable name for the model. For more information regarding the Greek god Hermes (or Roman god Mercury), see http://www.hermograph.com/science/mercury2.htm.

The HERMES modeling framework is based on a published treatment of multi-species chemicals (Toose and Mackay, 2004) and the QWASI (Quantitative Water Air Sediment Interaction) modeling framework (Mackay, 2001) (see Chapter 2.3). Estimation methods (i.e., empirical equations which relate a model input variables to other routinely-measured variables) (Chapter 4) and a sediment emission (i.e., flux) term (Chapter 2.6.2) were added to improve model performance (see Chapter 1.4 for thesis structure). Selection or rejection of estimation methods was based on their relative importance to model performance.

The HERMES steady-state (i.e., non-changing with respect to time) model presented in this paper was written in QBASIC, a DOS programming language, and within an Excel workbook that can be downloaded at no cost from the 'Environmental Toxicology and Chemistry' website as an online appendix for the research paper in Chapter 4 (http://www.setacjournals.org/perlserv/?request=index-html). Details regarding model layout and instructions can be obtained from the website or in Appendix 2.

National (e.g. CARA Hg monitoring network (Environment Canada)), provincial (e.g. Dorset Environmental Research Centre database (see Chapter 6)), and regional (e.g. Kejimkujik Park, NS (see Chapter 2.4); Great Lakes Lakewide Management Plan (LaMP) (see Chapter 5.2.1)) environmental monitoring programs often provide most of the information needed to apply the HERMES model to any given lake (see Chapter 4).

In short, some of the main advantages of HERMES include reduced data requirements, freely available spreadsheet-based model, broadscale applicability, and that it was developed and tested on uncontaminated lakes.

1.1.2 Assumptions and Limits

All models are based on a body of assumptions that lead to both strengths and weaknesses in the tool developed. The two main assumptions in the HERMES model are that the lake is experiencing steady-state conditions and ratios amongst mercury species are constant. Although assumptions increase the broad applicability of the model to other lakes (strength), certain types of information about Hg dynamics in lakes (e.g., temporal fine-scale dynamics (i.e., daily, monthly) or responses to changes in Hg inputs prior to steady-state, interconversion amongst inorganic Hg species, methylation rates) cannot be estimated by applying this particular model. In addition, the model does not estimate biologically relevant Hg (i.e., MeHg) in surface sediments.

1.1.3 Applications

The screening-level modeling tool developed and tested in this thesis has the capacity to assist provincial and state level risk assessors and managers concerned about Hg contamination in systems as a screening level tool where data and resources for monitoring are limited. Model output from applications of the HERMES model beyond the range of data collected in this study or the lake types investigated should be interpreted with necessary caution.

Significant uncertainty remains regarding which Hg processes, sources and / or dynamics (e.g., sediment focusing, remobilization, surface sediment dynamics) are important to which lakes when relating sources of Hg to biologically relevant concentrations in water and sediment that requires further scientific research (empirical work). HERMES could enable the respective mercuric processes to be quantified on a lake-by-lake basis since it is likely that some processes will dominate over others as lake conditions vary.

Models can serve as valuable tools to identify knowledge gaps and guide future Hg research. Experimental research and model development should be conducted simultaneously with models driving experimental research which would result in a better model.

1.2 BACKGROUND INFORMATION

High-risk groups for Hg exposure include those living near point sources (e.g. volcanoes) or those who consume large amounts of fish (Pavlogeorgatos and Kikilias, 2002), groups that are often far removed from industrial sources. Elemental Hg is mainly transported by red blood cells in the human body and accumulates on the cerebral gray matter. Inorganic Hg (mostly Hg^{2+}) compounds accumulate mainly in the liver and kidneys. Organic Hg (mostly MeHg) circulates unchanged in the bloodstream for long periods of time and accumulates in the brain, spleen, heart and hair. Exposure to Hg can result in restlessness, depression, lack of concentration and hand tremors since the primary target is the central nervous system (Pavlogeorgatos and Kikilias, 2002). Pavlogeorgatos and Kikilias (2002) summarize routes

of exposure, allocation, biological action, critical organs and detoxification of elemental, inorganic and organic Hg in the human body.

1.2.1 Mercury in the environment

Mercury is able to travel long distances to remote locations as elemental mercury (Hg^0) due to its low water solubility and relatively high vapour pressure (Chapter 2). It has a residence time of about one year in the atmosphere (Wiener et al., 2003), but through oxidation processes to Hg(II) species it eventually deposits to land and aquatic ecosystems as wet and dry deposition (Lindberg, 1987; Lindberg and Stratton, 1998; Poissant et al., 2004; Selin et al., 2007). Once deposited, a portion of it can be converted to MeHg, the most toxic form that crosses biological membranes and bioaccumulates in foodwebs (Carpi, 1997; Morel, 1998; Wiener et al., 2003; O'Driscoll et al., 2005). Morel et al. (1998) provides a comprehensive review of the entire chemical cycle and bioaccumulation of Hg from global transportation in the atmosphere to methylation and demethylation in lakes.

Mercury is a complex and difficult chemical to model since there are natural and anthropogenic emission sources to consider, multiple chemical forms, several physical states, and a tendency to undergo biological transformations (Pavlogeorgatos and Kikilias, 2002). For example, small lakes removed from industrial sources can show elevated Hg levels in birds (O'Driscoll et al., 2005) with birds near large lakes near industrial sources showing no impairment (Marivin et al., 2004). Referenced in this section are some

characteristics of lakes and their associated watershed that can influence the amount and speciation of Hg in the water column and sediments of lakes.

1.2.1.1 Natural versus anthropogenic sources

Mercury within lakes originates from both industrial emissions and natural sources. Of these, those lakes located near industrial activities (e.g. cinnabar, coal, gold or silver mining) tend to show the highest amounts of sediment and water Hg due to anthropogenic emission sources. In this thesis, I account for industrial Hg sources to lakes through the inclusion of an emission to water (EW) term within HERMES (see Chapter 2).

The model does not directly account for natural sources of Hg, such as from volcanic activity, large-scale forest fires, and mineral deposits, continually released into the environment (Friedli et al., 2003; Pyle and Mather, 2003; Plouffe, 1995). Research conducted in Clyde Forks, Ontario (Appendix 1A) indicates that application of the HERMES model to a lake in close proximity to a naturally elevated mercuric source should not significantly impact model performance.

1.2.1.2 Watershed

Grigal (2002) hypothesized that up to 60% of atmospherically deposited Hg originates from the surrounding watershed (see Chapter 4) since rainfall events release particulate-bound Hg from soils and wetlands, making it available for methylation in the water column or sediments of lakes (Snodgrass et al., 2000). Wetlands are able to mobilize more Hg from the watershed than upland soils by producing more dissolved organic carbon (Peckenham et

al., 2007), and are a source of MeHg to lakes as well (Shanley et al., 2005) (discussed in Chapter 4.3.1.2 and 4.3.2). Export and residence time of total Hg and MeHg from catchments to lakes can also vary with type of wetlands in the watershed since it may take years for watershed to respond to changes in atmospheric deposition (St. Louis et al., 1996).

1.2.1.3 Water column and sediments of lakes

Lake chemistry such as pH, ionic strength, redox potential, dissolved organic matter, dissolved oxygen, sulphide and suspended solids can influence the speciation of Hg once it enters the water column or sediments (Gabriel and Williamson, 2004; Regnell et al., 2001). For example, sulphide is produced as sulphate-reducing bacteria methylate Hg at low dissolved oxygen concentrations and redox potentials (Kerin et al., 2006) and Hg bound to dissolved organic matter or suspended solids will be more bioavailable for methylation and / or demethylation (Morel et al., 1998) (discussed in Chapter 3).

The physical characteristics of a lake such as morphometry and mean depth can influence the amount of Hg in a given area (i.e. erosion and accumulation areas) and speciation in water column and sediments (i.e. deeper lakes tend to have larger oxygen-depleted hypolimnions in the summer) (Hakanson, 2003; 2005; Regnell and Ewald, 1997). Organic carbon availability in lakes for Hg to bind to will also vary with watershed and morphometry (Rasmussen et al., 1989).

1.2.1.4 Sedimentary processes

On average, surface sediments in Ontario have twice (mean = 2.4; range = 0.22 – 10.8 times; n = 168) as much Hg as subsurface sediments (Brad Mills, PhD thesis in progress, University of Ottawa). A number of mechanisms have been put forth over the years to explain these patterns, but uncertainty remains. Sedimentary processes that could be partly responsible are remobilization of Hg from underlying sediments (aka upward flux) (Telmer et al., 2005), focusing of the organic rich sediments (high Hg fraction) (Blais and Kalff, 1995), anthropogenic inputs (Lucotte et al., 1995), or perhaps a simple exchange process is taking place in the top few centimeters (e.g., Boszke et al., 2003). For exchange processes, this would involve the sedimentation of Hg rich material that would decay or be reduced and the Hg would move back into the overlying water column. Over time, lower Hg material would be buried. Other potential mechanisms likely exist in the literature, but it appears as if more work is still required to properly delineate sources. In addition, the relative contribution from each potential mechanism should also vary among lakes and is likely highly variable (i.e., surface sediments are continually enriched compared with subsurface sediments over time, even as sediments are buried). The presence of a transient event in surface sediments would not conflict with the notion that historical archives (subsurface sediment) are representative of previous loadings (see Chapter 2).

1.2.2 Mass balance models

Multimedia mass balance models are generally used to assess how variations in a given media can influence the transport and fate of contaminants in surrounding media on local, regional, national or global scales. Simple regression models ($y = mx + b$) are suitable for

the estimation of a concentration or flux, but provide no information about how variations in one media could influence another. Environmental mass balance models can be further subdivided into different categories (e.g. atmospheric, ecosystem, aquatic, terrestrial, food web, biota) based on function. The HERMES presented in this thesis would be classified as a lake model (local scale). Provided in this section is an overview of some of the other environmental Hg mass balance models that are available.

1.2.2.1 Atmospheric models

These are models that focus on Hg speciation and distribution in the atmosphere. For example, the GEOS-CHEM global 3-D atmospheric Hg model provides estimates for locations throughout the world (Selin et al., 2007). Some other available models include the Acid Deposition and Oxidants Model (ADOM - Germany); Community Multi-Scale Air Quality (CMAQ- USA); Global / Regional Atmospheric Heavy Metals Model (GRAHM – Canada) (Ryaboshapko *et al.*, 2004); and atmospheric mercury speciation and deposition model (Poissant *et al.*, 2004).

1.2.2.2 Ecosystem models

Ecosystem models are those that encompass the whole complex of physical factors that form what we call an environment. For example, a model that describes atmospheric deposition to land, migration to water and uptake through the food web to humans. In order to study an ecosystem, normally two or more environmental models are combined (e.g., atmosphere, terrestrial, lake and food web model) so that the output from one model provides input for another. Examples of ecosystem models would be the Hg Contaminants in Terrestrial and

Aquatic ecosystems (CATS) model that integrates a food web model for Hg with a Hg cycling kinetics model (Hunter et al., 2003) or the ChemCAN model which estimates average concentrations in air, fresh surface water, fish, sediments, soils, vegetation, and marine near-shore waters for 24 regions throughout Canada (Webster et al., 2004).

1.2.2.3 Aquatic models

The intent of these models is to describe the concentration and fluxes of Hg within lakes, rivers, estuaries and oceans. Some examples are: the Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury model (SERAFM – Knightes et al., 2008), RIVMOD (hydrodynamic and sediment transport model) and WASP 5 (water quality model) with MERC 4 subroutine (Wang et al., 2004), Regional Mercury Cycling Model (R-MCM – Tetra Tech Inc., 1996), Fugacity / Aquivalence Quantitative Water Air Sediment Interaction (FA-QWASI) model (Diamond, 1999), Mercury Regional Fate Model (Macleod et al., 2005), and Lake Ontario Toxicity Mercury Sub-Model (LOTOX2 – Atkinson, 2007). These models are designed to predict mercury species distributions, concentrations, and fluxes among abiotic (e.g. FA – QWASI, R – MCM, WASP 5 with MERC 4, ERAFM, RIVMOD), terrestrial (R – MCM), and biotic (R – MCM, WASP 5 with MERC 4, ERAFM, RIVMOD) compartments in aquatic ecosystems using chemical and physical property input data.

1.2.2.4 Terrestrial models

Terrestrial models describe the movement of Hg in the forest canopy, soil or vegetation. For example, there is a soil model (Mackay and Stiver, 1991; Mackay, 2001) and a surface-

vegetation-atmosphere transport (SVAT) resistance model (Bash, 2007) that can be used to evaluate Hg dynamics in a terrestrial environment.

1.2.2.5 Food web models

This group of models encompasses all those that describe the bioaccumulation of contaminants through multiple tiers of a food web. Campfens and Mackay (1997), Burns et al. (1997) and Hope (2003) are some examples of contaminant food web models for lakes and rivers from invertebrate exposure to fish contaminant levels. Barber (2003) contains a review and comparison of fish bioconcentration models.

1.2.2.6 Biota models

These models are organism-specific and enable detailed insights into contaminant distribution within biota. For example, a fish model describes the distribution of Hg within fish organs and tissues. Biota models have been created for a wide range of organisms from invertebrates (Mysis Relicta – Chipps and Bennett, 2002; Patwa et al., 2007) to fish (fish located in southeastern United States - Qian et al., 2001; fish model – Clark et al., 1990) to humans (toxicokinetic model - Carrier et al., 2001; Physiologically Based Pharmacokinetic Model (PBPK) - Cahill et al., 2003).

In general, all mechanistic (e.g. LOTOX2 – Atkinson et al., 2007) and general (e.g. FA-QWASI – Diamond, 1999) models have traditionally been parameterized with available measured data and then remediation strategies for contaminated sites are evaluated (other models referenced in Chapters 2.1 (overview), 5.3, and 6.4.1.2).

1.3 OVERVIEW OF RESEARCH

The research can be divided into three main components: (a) model development; (b) model applications; and (c) field research used to derive the empirical relationships implemented in the model. Experimental data and the HERMES model were also used in combination to derive a better estimate of water (i.e., stream) inflow Hg concentration (Chapter 6).

1.3.1 Overall Objectives and Environmentally Relevant Goals

1. Development and verification of a multimedia Hg model using data from Big Dam West Lake, Kejimkujik Park, Nova Scotia that can be used as a screening tool to assess Hg dynamics in lakes with limited datasets.
2. Identification of sensitive model input variables (i.e., concentration of Hg in air and inflow water, lake and inflow water suspended particulate matter (SPM), lake temperature, mean depth, surface area, volume, precipitation rate, sedimentation and resuspension rate) and provision of estimation methods (including MeHg:THg for foodweb applications) to improve HERMES applicability to lakes with limited datasets.
3. Demonstration of HERMES applicability and model limitations through verification and uncertainty analyses on small (Harp, Dickie) and large (Lake Ontario) lakes, along with a comparison of HERMES model output with a mechanistic model (LOTOX2).

4. Evaluation of model performance using estimation methods, and demonstration of a potential application of HERMES as a research tool, through application to 35 Ontario lakes contained in a dataset compiled by Brad Mills (PhD thesis in prep).

1.3.2 Statement of Hypotheses

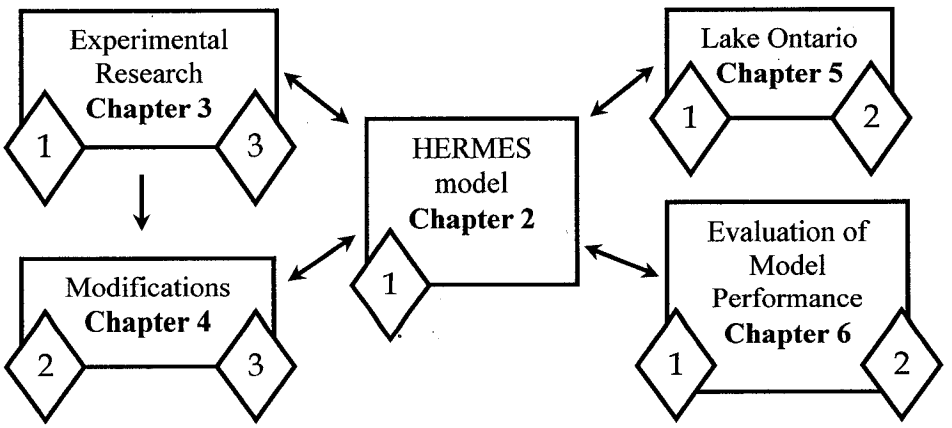
1. Concentration ratios (MeHg : Hg^0, THg-MeHg-Hg^0 : Hg^0) can be used in models to estimate Hg concentrations and fluxes in the environment at steady-state conditions.
2. Models can reliably predict Hg fluxes and concentrations within lakes when few model input variables are adjusted.
3. The relative amount of methylated Hg (MeHg : THg) within lake sediments can be estimated from information on sediment chemical and physical properties.

1.4 STRUCTURE OF THESIS

A general multimedia model (HERMES) was developed that is able to estimate Hg concentrations in lakes (water, sediment, and air) (Chapter 2). Model input driving variables adjusted for model reapplication were concentration of Hg in air and inflow water, lake and inflow water suspended particulate matter (SPM), lake temperature, mean depth, surface area, volume, precipitation rate, sedimentation and resuspension rate. The HERMES model is sensitive to small variations in any of these eleven variables. Experimental research was conducted to assist with model application to other lakes and to produce model estimation methods (Chapter 3) that were included as a model modification (Chapter 4), along with literature estimates. Model limits were evaluated through application to Harp and Dickie

Lake (Chapter 4), along with a large well-studied lake (Chapter 5). Model output was compared with other models (LOTOX2 and STELLA) (Chapter 5) and measured values. Model estimation methods were then evaluated through application to 35 Ontario lakes, testing each estimation method in turn (Chapter 6). Thesis conclusions are presented in Chapter 7 (Figure 1.1).

Figure 1.1: Flowchart of thesis structure and where hypotheses (◇) were tested.



Appendix 2 contains complete instructions for model use. Appendix 3 contains an initial estimation method for surface sediment enrichment in order to convert predicted subsurface sediment Hg (HERMES model output) to measured surface sediment Hg concentration.

1.4.1 Chapter 2: Model development

For modeling purposes we grouped the numerous species of Hg present in the environment into three main forms: methyl mercury (Hg available for bioaccumulation), elemental mercury (Hg^0), and the remainder, which we called residual mercury (THg-MeHg-Hg^0, equal to total mercury (THg) minus MeHg and Hg^0). Hg^0 is the dominant species found in

atmosphere, while THg-MeHg-Hg^0 species (mostly as Hg^{2+}) dominate in water and sediment compartments. Environmental variations among these three Hg species are discussed in Chapter 2, along with details regarding model development and the underlying theory and concepts behind it. Initial model parameterization involved using those that had been previously demonstrated (Macleod et al., 2005; Toose and Mackay, 2004), adjusting model parameters only when change could be justified with literature support.

1.4.2 Chapter 3: Experimental research

Experimental research was conducted to assist with modeling efforts, including: sediment Hg to compare model predictions against; experimentally-derived estimate for sediment Hg; and sediment MeHg : THg estimation method. Furthermore, additional relationships were found between methyl and total Hg and sediment properties for Harp, Dickie and Blue Chalk Lake that could potentially be used in future models. These estimation methods and MeHg : THg ratio were compared with literature values and / or estimates.

1.4.3 Chapter 4: Modifications

Mercury volatilization is an important loss mechanism from lakes that is known to vary with environmental temperature (O'Driscoll et al., 2003a, 2003b; 2005b; Siciliano et al., 2002). An equation was thus inserted into the model so that volatilization rate would be sensitive to changes in the lake temperature (Chapter 4).

The HERMES model modifications consist of estimation methods for three main categories: model input driving variables; MeHg : THg ratio (for food web applications); and alternative estimation methods for sediment and water Hg.

1.4.4 Chapter 5: Lake Ontario

To determine how well the model functions on larger lakes, it was also applied to Lake Ontario (Chapter 5). Model output for Lake Ontario was also evaluated against the more mechanistic (i.e., uses interconversion rates) Lake Ontario Toxicity (LOTOX2) Hg submodel and Systems Thinking Experiential Learning Laboratory with Animation (STELLA) Hg model that were recently developed and tested on Lake Ontario (Atkinson et al., 2007). LOTOX2 is a model that was specifically designed to model contaminants in Lake Ontario, as the name suggests.

1.4.5 Chapter 6: Evaluation of model performance

In order to further evaluate model performance using estimates and a limited amount of data, the model was applied (adjusting only ten variables) to 35 Ontario lakes of varying size (surface area = 0.34 to 14.2 km^2). Six measured values were available for these lakes (i.e., water volume, water inflow rate, surface area, mean depth, precipitation rate) and three were estimated using methods described in Chapter 4 (i.e., water column and inflow suspended particulate matter, resuspension rate and water inflow Hg). Measured sediment Hg was then used to derive an improved estimate for water inflow Hg concentration.

CHAPTER 2

THE DEVELOPMENT AND APPLICATION OF A MASS BALANCE MODEL FOR MERCURY (TOTAL, ELEMENTAL AND METHYL) USING DATA FROM A REMOTE LAKE (BIG DAM WEST, NOVA SCOTIA, CANADA) AND THE MULTI-SPECIES MULTIPLIER METHOD

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Abstract - Big Dam West, located in Kejimkujik Park, Nova Scotia, Canada, is a remote lake with elevated mercury concentrations in fish due in part to low pH and high dissolved organic carbon (DOC) concentrations. These features reflect the poor buffering capacity of peat lands in the flat drainage basin. To address the multiple species of mercury, a model was developed by coupling the "multiplier method" for multi-species chemicals with average concentration ratios to the Quantitative Water Air Sediment Interaction (QWASI) model. Elemental mercury was the "key species" modeled. Total mercury fluxes and concentrations were computed using concentration ratios.

Many of the concentrations and mercury flux processes within the Big Dam West catchment had been previously measured with concentration ratios either computed or taken from the literature when measured data were not available. Measured values for total mercury concentration in each compartment (air, water, sediment) and mercury fluxes (e.g. precipitation, sediment deposition) enable verification of model concentration and flux estimates for total mercury in each environmental compartment. The model was also run with and without the inclusion of upward mercury fluxes from the underlying sediment to determine the significance of this controversial flux.

The mercury QWASI model presented in this paper could be a valuable screening tool, especially for remote lakes, due to its ability to provide reasonable mercury estimates with a limited amount of data (water inflow rate, suspended particulate matter, sediment deposition velocity, and concentration of mercury in atmosphere and inflow water).

Keywords: QWASI, model, lake, air, water, sediment, flux processes, elemental mercury, methyl mercury, total mercury, multiplier method, mass balance

2.1 INTRODUCTION

Mercury emitted from natural and anthropogenic sources is able to travel to remote locations as elemental mercury (Hg^0) due to its low water solubility and relatively high vapour pressure. It has a residence time of about one year in the atmosphere (Wiener *et al.,* 2003), but through oxidation processes it is then deposited to land and aquatic ecosystems as wet and dry deposition. Once deposited in remote locations it is converted to methyl mercury (MeHg), the form that bioaccumulates in foodwebs (O'Driscoll *et al.*, 2005*c*; Carpi, 1997; Lindberg, 1987).

For modeling purposes we grouped the numerous species of mercury (Hg) present in the environment into three main forms: methyl mercury (Hg available for bioaccumulation), elemental mercury (Hg^0), and residual mercury (THg-MeHg-Hg^0) that is equal to total mercury (THg) minus MeHg and Hg^0. Hg^0 is the dominant species found in the atmosphere, while THg-MeHg-Hg^0 species (mostly as Hg^{2+}) dominate in the water and sediment compartments. Due to the ability of MeHg to cross biological membranes and biomagnify through foodwebs, it is considered to be the most toxic species of mercury for biota (Wiener *et al.*, 2003; Bloom, 1992).

Earlier models were used to quantify either mercury atmospheric transport (e.g. Harvard GEOS - CHEM model (Fiore and Jacob, 2003); Acid Deposition and Oxidants Model (ADOM - Germany); Community Multi-Scale Air Quality (CMAQ- USA); Global / Regional Atmospheric Heavy Metals Model (GRAHM – Canada) (Ryaboshapko *et al.*,

2004); atmospheric mercury speciation and deposition (Poissant *et al.,* 2004)) or cycling within lakes and their surrounding watershed (e.g. fugacity / aquivalence QWASI model (FA - QWASI) (Diamond, 1999); RIVMOD (hydrodynamic and sediment transport model), WASP 5 (water quality model), and MERC 4 (a kinetic subroutine for WASP 5) developed by USEPA (see Wang *et al.*, 2004); and the Regional Mercury Cycling Model (R - MCM) (Tetra Tech Inc., 1996)). These models are designed to predict mercury species distributions, concentrations, and fluxes among abiotic (FA – QWASI, R – MCM, USEPA), terrestrial (R – MCM), and biotic (R – MCM, USEPA) compartments in aquatic ecosystems using chemical and physical property input data. A major drawback of the above models is their complexity, as they require interconversion rates among mercury species for which kinetic parameters are not available and they are generally designed for systems with large anthropogenic sources of mercury. Furthermore, none were specifically designed to model mercury in remote environments.

The necessity for mercury models to account for every species and reaction in order to produce reasonable estimations should be reconsidered. What level of complexity is needed? The R – MCM is a complex model that has been reasonably successful at modeling mercury in aquatic environments but it is not readily transferable between lakes because it attempts to account for all major reactions that take place. The US EPA recently assessed the R - MCM as a predictive tool by comparing simulated mercury concentrations with measured mercury concentrations (Ambrose, 2004). It was able to adequately account for the fate and transport processes of mercury in a number of watersheds and water bodies, but could not be directly applied to a new region without

recalibration. Meng *et al.* (2005) developed a series of linear equations to model dissolved organic carbon (DOC), total and methyl mercury in freshwater lakes located within Kejimkujik Park, NS. Channel width, source of water (ground or surface-fed), and pH were used to predict DOC concentration in lakes ($r^2 = 0.69$). DOC was found to be a good predictor of total mercury concentration in the water column ($r^2 = 0.75$). These equations are suitable for estimating water column mercury concentrations when only DOC, or a limited number of physical / chemical parameters are available, but do not provide estimates of overall mercury dynamics or how a lake might respond to change. A major purpose of this paper is to couple and verify the multi-species mercury multiplier method, proposed by Toose and Mackay (2004), to the fugacity - based QWASI model (Figure 2.1, redrawn from Mackay (2001)) for a remote lake experiencing only natural and atmospheric mercury inputs. Big Dam West, a remote lake with elevated mercury concentrations located in Kejimkujik Park, Nova Scotia, was chosen for model verification due to the extensive amount of data available from a recently completed investigation (O'Driscoll et al., 2005*a*).

2.2 DESCRIPTION OF SITE

Kejimkujik National Park is located in central Nova Scotia (44 °N; 65 °W). It is one of Environment Canada's five major ecosystem monitoring sites and covers an area of 381 km^2 with 47 lakes and ponds (Drysdale, 2005). Average annual precipitation is 1.4 m yr^{-1} and average annual temperature is 6.3 °C. Recently a multidisciplinary team of researchers characterized the fate and biogeochemistry of mercury within this region

(O'Driscoll *et al.* 2003*b*) to determine why loons from Kejimkujik National Park contained the highest total mercury blood levels (6 - 7 μg Hg g^{-1}) found in North America (Burgess *et al.*, 1998). Big Dam West Lake (Figure 6.2) was selected for model verification because an extensive data set was compiled for this lake. Although this lake does not receive any direct industrial inputs of mercury, elevated methylmercury levels are found at all trophic levels due to the flat landscape contributing to a high percent of wetlands in the drainage basin and the low pH resulting from the poor buffering capacity of the bedrock.

Big Dam West is an oligotrophic lake with a surface area of 1 km^2, a mean depth of 3.3 m (maximum depth of 6 m), and a watershed area of 40 km^2. It is a seasonally - stratified highly coloured (DOC = 10.5 mg L^{-1}) acidic (pH = 5.0) lake with a flushing rate of 13.1 times yr^{-1} (average residence time = 28 d) (Kerekes and Schwinghamer, 1973). There are three major inflows (Thomas Meadow Brook, Ford Brook and Big Dam East Inlet) to and one major outflow (Still Brook) from the lake. Sediments in this lake contain 9 % organic carbon, a bulk density of 0.05 g dw cm^{-3} ww at the sediment water interface, and sedimentation rates of 45.58 mg^{-1} m^{-2} yr^{-1} (Telmer *et al.*, 2005). Yellow perch (n = 21) obtained from Big Dam West Lake had a mean mercury level of (0.21 ± 0.10 μg g^{-1} ww), comparable to other lakes (n = 24) sampled within Kejimkujik National Park (overall mean of 0.25 ± 0.14 μg g^{-1} (n = 242) for perch) (Drysdale *et al.*, 2005; Hickey *et al.*, 2005). These values are higher than the US national average. Suns and Hitchin (1990) found total mercury residues in yellow perch to range from 0.031 to 0.233 μg g^{-1}; Smith (2006) reported an average total mercury concentration in West Virginia yellow perch of

0.061 μg g^{-1} (ranging <0.0175 to 0.11 μg g^{-1}); and US EPA (2003) estimated a national United States average of 0.052 μg g^{-1} for trophic level 3 fish (i.e., the level occupied by perch).

2.3 MODEL DESCRIPTION

The model presented in this paper utilizes the multiplier method proposed by Toose and Mackay (2004) to model multi-species chemicals that exist with constant (or average) concentration ratios with the Quantitative Water Air Sediment Interaction (QWASI) model that was originally designed for organic chemicals (Mackay *et al.*, 1983; Mackay and Diamond, 1989). The original QWASI contaminant mass balance fate model for lakes can be downloaded from the Canadian Environmental Modelling Centre website (http://www.trentu.ca/cemc). QWASI lake models estimate chemical concentrations and fluxes (emission, intermedia transfer, and advection) for compartments (sediment, water, air), as well as inputs to and outputs from the lake. Figure 2.1, redrawn from original QWASI diagram (see Mackay, 2001), depicts the current model described in this paper.

The fugacity (f) or "escaping tendency" of a chemical is used to describe the rate at which chemicals are transported (D) among compartments or phases (see Table 2.1). Fundamentals of mass balance models that use the fugacity concept such as the one presented in this paper are described in "Environmental Multimedia Models" (Mackay, 2001). Z values or "fugacity capacities" relate chemical concentration (C) to fugacity (f) for any given environmental media using the formula:

$$Z = C / f \quad (1)$$

Partition coefficients (K) are calculated as the concentration (C) of chemical in one media divided by another (e.g. $K_{AW} = C_A$ (air) / C_W (water)). For each mercury species in the model, the Z value for water (Z_W) was set to 1 and all other Z values were deduced from their corresponding partition coefficients (e.g. Z_A (air) = K_{AW} (air-water)). Species-specific D values were then calculated for advection [G (flow rate, m^3/h) x Z] and intermedia transport [A (area, m^2) x Z x k (intermedia transfer rate, m^3/h)] using these species-specific Z values (see Table 2.1 for a list of D values used in model).

Sediment and water transformation rates used in the original QWASI model were set to zero in the model presented here since mercury is conserved in the system and is considered only to exist in three forms (Hg^0, MeHg, and THg-MeHg-Hg^0). The multiplier method assumes that species conversion rates are fast relative to other processes, so that the ratio of species concentrations and fugacities will be relatively constant with respect to time. Nevertheless, variations in the concentration ratios for methyl (MeHg), elemental (Hg^0), and residual (THg-MeHg-Hg^0) mercury do occur in the air, water and sediment with respect to time, but on average remain constant on an annual basis. For example, Hg^0 can range from 2 to 200 pg L^{-1} per day (O'Driscoll *et al.*, 2003b) but remains near 100 pg L^{-1} to establish ratios (see Table 2.2 for values used here and literature values).

Elemental mercury (Hg^0) is the "key species" used in model calculations because it is present in all compartments to at least some extent and it does not readily react to form compounds. The bulk fugacity ratios for THg-MeHg-Hg^0 and MeHg in all compartments were deduced from Hg^0 fugacity and the respective concentration ratio (C_X / C_{Hg0}), where X represents either MeHg or THg-MeHg-Hg^0. Concentration ratios (MeHg : Hg^0 and THg-MeHg-Hg^0 : Hg^0) in all compartments (sediment, water, air) and inflow water are defined from empirical data. Bulk fugacity ratio ($F_{X:Hg0}$) for each compartment are calculated as,

$$F_{X:Hg0} = (C_X / C_{Hg0}) * (Z_{Hg0} / Z_X) \quad (2)$$

R – multipliers (MR) were used to compute the overall D values (D) needed to calculate the fugacity equations (FW (water) and FS (sediment)) listed in Table 2.1.

e.g. Burial (B): $MR_B = 1 + FS_{MeHg:Hg0} * (DB_{MeHg} / DB_{Hg0}) + FS_{THg-MeHg-Hg0:Hg0} * (DB_{THg-MeHg-Hg0} / DB_{Hg0})$ (3)

$$DB = DB_{Hg0} * MR_B \quad (4)$$

All species concentrations and fluxes were calculated by multiplying Hg^0 fugacity (f_{Hg0}) for air, water, or sediment (calculated using equations listed in Table 2.1) by the species respective fugacity ratio. Flux (R) is calculated as f_{Hg0} / D_{Hg0} for Hg^0. Residual and methyl mercury fluxes are calculated as the product of fugacity and D value ratios.

$$R_{X:Hg0} = f_X D_X / f_{Hg0} D_{Hg0} \quad (5)$$

Total mercury concentrations and fluxes were calculated as the sum of individual mercury species.

The model presented in this paper was written in QBASIC, a DOS programming language, and within an Excel workbook. Contact the corresponding author for a copy of either version of the model.

2.4 MERCURY MONITORING DATA FOR STUDY ENVIRONMENT

All of the measured values used in the model and listed in this paper for Big Dam West, unless otherwise noted, originate from O'Driscoll *et al.* (2005*a*).

2.4.1 Emissions

There are no direct mercury emission sources to Big Dam West Lake, other than atmospheric inputs. River inflow has a mean concentration of 4.3 ng L^{-1} (range 4 – 6.2 ng L^{-1}). Other sources of mercury to the water column of a lake may originate from either groundwater (2.0 g yr^{-1}) and / or run - off from the surrounding watershed [caused by periodic rainfall events that remobilize mercury from watershed (atmospheric deposition and / or bedrock)].

Some lakes may have inputs from underlying sediments, due to degassing of methane, erosion, and / or direct flux. Although mobilization of mercury from sediments is controversial, since many researchers believe that the historical profiles faithfully reproduce historical deposition rates. Telmer *et al.* (2005) concluded that mercury in older sediments of Big Dam West Lake could have been remobilized creating the observed upcore - enrichment.

If we assume that the sedimentation rate was actually constant with respect to time, changes in calculated flux (F) at each depth interval with respect to pre-industrial average flux (8.8 $\mu g\ m^{-2}\ yr^{-1}$) could be attributed to an upward flux (F_U) of remobilized mercury (have to assume that contributions from anthropogenic sources are negligible) (e.g. high $F_U = F_{surface} - F_{background}$). Estimates of what low ($F_{background}$, 3.3 $\mu g\ m^{-2}\ yr^{-1}$) and high ($F_{surface}$, 82.4 $\mu g\ m^{-2}\ yr^{-1}$) fluxes from the underlying sediments could have been were calculated in this manner for use as an example in our model (emission from sediment (ES) is equivalent to F_U).

2.4.2 Atmosphere

Elemental mercury (Hg^0) is the dominant form of mercury in the atmosphere (>98 %). Particulate Hg(p) and reactive gaseous mercury are the two main residual forms (THg-MeHg-Hg^0) of mercury present in the atmosphere (<2 %). Methyl mercury (MeHg) only contributes trace amounts that are largely bound to aerosols (Wiener *et al.*, 2003). The average concentration of total gaseous mercury in the atmosphere measured above Big Dam West Lake was 1.52 ng m^{-3} (range 0.51 - 2.9 ng m^{-3}) and the mean concentration of mercury in precipitation was 5.3 ng L^{-1} (range 5-100 ng L^{-1}). Mercury wet deposition rates averaged 6.6 μg m^{-2} yr^{-1} (range 6 - 12 μg m^{-2} yr^{-1}) with a mean concentration of 11.4 ng L^{-1}. All values are within the reported range for other mercury deposition sites in North America.

2.4.3 Water

The residual mercuric species (THg-MeHg-Hg^0) predominate in the water column, often bound to particulate (29.4 % in Big Dam West Lake), colloidal or dissolved compounds. Although abundant in the atmosphere, elemental mercury is typically only 10 % of total mercury in the water column (O'Driscoll *et al.*, 2003*a*; O'Driscoll *et al.*, 2003*b*). The average concentration of total, methyl and elemental mercury measured in the water column of Big Dam West Lake was 5.0 ng L^{-1} (range 1.5 - 6.5 ng L^{-1}), 96.0 pg L^{-1} and 20 pg L^{-1} (range 1 - 200 pg L^{-1}), respectively. Beauchamp *et al.* (2005) used a flux chamber to directly measure water – air Hg^0 flux. Gaseous elemental mercury was found to

volatilize from the lake surface at an average rate of 20 g yr^{-1}, roughly 46 % of the mass deposited by wet deposition. Over the course of one day, this flux can vary from –5 to 18 ng m^{-2} h^{-1} (O'Driscoll *et al.*, 2003*b*).

2.4.4 Sediments

In lakes with high naturally background mercury levels, sediments can constitute 85-95 % of the total amount of mercury in lakes (al-Shahristani and Shihab, 1974). The bulk of this load is trapped within minerals and is not necessarily readily available for either transport or bioaccumulation within these lakes. Telmer *et al.* (2005) measured the total mercury concentration in sediment cores from Big Dam West Lake at 1 cm intervals. Mean mercury sedimentation rate was 95.73 g yr^{-1} for the entire lake (91.2 g m^{-2} yr^{-1}) (O'Driscoll *et al.*, 2005*b*). The total mercury measured in the sediment (and porewaters) of Big Dam West Lake varied from 66.1 ng g^{-1} dw (7 pg g^{-1}) at 5.5 cm to a concentration of 171.2 ng g^{-1} dw (2 pg g^{-1}) at the sediment surface (0.5 cm). These values are low compared to contaminated sites: the Canadian Interim Sediment Quality Guideline (ISQG) for mercury is 0.17 mg kg^{-1} in freshwater environments (CCME, 2002); and United States Effects Range-Low (ERL) for mercury is 0.15 mg kg^{-1} in marine and estuarine sediments (Beckvar *et al.*, 1996).

2.5 MODEL INPUT MERCURY CONCENTRATION RATIOS

The average concentration of total (4.5 ng L^{-1}), methyl (0.148 ng L^{-1}), and elemental (0.076 ng L^{-1}) mercury were calculated from measurements made during June – September 2001 for Big Dam West Lake surface water (O'Driscoll *et al.*, 2003*b*; Beauchamp *et al.*, 2005). These values were used to deduce the concentration ratios for mercury species in water (THg-MeHg-Hg^0 : Hg^0 = 56; MeHg : Hg^0 = 2) for the model. Average methyl (1.40 ng L^{-1}) and elemental (0.100 ng L^{-1}) mercury concentrations were available for Thomas Meadow Brook, as well as the amount of methyl and total mercury export (MeHg / total Hg = 0.33) into Big Dam West (Clair *et al.*, 2005). Water inflow concentration ratios used in the model (THg-MeHg-Hg^0 : Hg^0 = 64; MeHg : Hg^0 = 13) were calculated from this available data. Run-off from the surrounding terrain brought about elevated inflow water methyl mercury levels that were 10 times higher than the lake water. Concentration ratios used for the atmosphere (THg-MeHg-Hg^0 : Hg^0 = 2.8 x 10^{-11}; MeHg : Hg^0 = 0.02) and sediment (THg-MeHg-Hg^0 : Hg^0 = 6.37; MeHg : Hg^0 = 0.31) were adopted from Toose and Mackay (2004) (Table 2.2). An insignificant number (2.8 x 10^{-11}) was used for the atmosphere THg-MeHg-Hg^0 : Hg^0 ratio to avoid divisions by zero that would have resulted in model error. The model assumes that THg-MeHg-Hg^0 species constitute an insignificant amount of the total mercury atmospheric concentration, even though in the environment it can represent up to 2 %.

Due to the inherent reliance of the model on these concentration ratios and their ability to be representative of the aquatic environment, some published values for mercury species

concentrations (in sediment, water, and air) and their corresponding calculated concentration ratios are summarized in Table 2.2. In the literature, it is difficult to obtain an accurate measurement of total residual mercury (THg-MeHg-Hg^0) because not all forms (Hg^0, MeHg, and total Hg) are routinely measured. Since all THg-MeHg-Hg^0 species need to be accounted for in the model, only studies that contained concentrations for MeHg, Hg^0 and total mercury could be included in Table 2.2 and used to deduce the concentration ratios listed (the authors welcome data from other sources that may have been overlooked).

2.6 EVALUATION OF MODEL PERFORMANCE

The steady - state mass balance for total mercury in Big Dam West is depicted in Figure 2.3, along with the individual species (THg-MeHg-Hg^0, Hg^0, MeHg) concentrations and fluxes within / among compartments. Model output concentrations [water column (6.6 ng L^{-1}); sediment solid (59.0 ng g^{-1}); pore water (3.2 pg g^{-1})] and fluxes [volatilization (0.02 kg yr^{-1}); sediment deposition (0.097 kg yr^{-1})] for total mercury were in agreement with available measured background values [water column (4-5 ng L^{-1}); sediment solids (66.1 ng g^{-1}); pore water (2-7 pg g^{-1}); volatilization (0.02 kg yr^{-1}); sediment deposition (0.096 kg yr^{-1})] and O'Driscoll *et al.* (2005*b*) mass balance that was constructed for Big Dam West (Figure 2.4). The diagonal line in Figure 2.4 represents a 1 : 1 relationship, and the model estimate versus measured mercury concentrations and fluxes are all situated close to (30 %) or on this reference line.

2.6.1 Uncertainty Analyses

We recognize that many of the values (including concentration ratios) used in the model will vary from site to site, as well as spatially and temporally within a site. In order to test the overall robustness of the model we performed uncertainty analyses by altering each of these values in turn and examining the effect on model output. Uncertainties in values for model input parameters are expressed in this paper as confidence factors (Cf) that represent the 95 % confidence limits (assumes a log normal distribution, but Macleod *et al.* (2002) did not find the shape of the input distributions to significantly affect the degree of uncertainty associated with output variables) around a median value for each parameter due to uncertainty and variability. The median value and confidence factor for the main input environmental and kinetic model parameters (Table 2.3); or partition coefficients and concentration ratios (Table 2.4) are listed in their respective tables. Confidence factors used in the model for estimates are the recommended defaults that can be used in the absence of measured data (Macleod *et al.*, 2002).

Model input parameters (environmental, chemical, published estimates) will not contribute equally to uncertainties and variability in model output and the model results are sensitive to variations in input parameters to different extents. We used sensitivity analysis to test the effect of changes on model input parameters. A sensitivity (S) analyses tests the effect of change with defined input (I) values on the outputs (O).

$$S = (\Delta O / O) / (\Delta I / I) \quad (4)$$

Uncertainties in the model were assessed in terms of their percent contribution to variance in estimated total mercury concentrations in the water and sediment (Table 2.5). Model input parameters were systematically increased by 1 % while holding all other parameter values constant in order to measure changes in model output (Morgan and Henrion, 1990). The percent contribution to variance in model output for each model input parameter is then calculated from the sensitivity and confidence factor (Macleod *et al.*, 2002).

$$\frac{(\ln Cf_{Ij})^2 S_{Ij}^2}{\sum_{k=1}^{n} (\ln Cf_{Ik})^2 S_{Ik}^2} \qquad (5)$$

The analytical method employed for uncertainty analyses, which does not require detailed parameterization of uncertainties associated with individual inputs, assumes a log normal distribution; whereas the Monte Carlo method does not necessarily make this assumption. Macleod *et al.* (2002) reported no significant bias when output from the analytical method was plotted against results from Monte Carlo method.

Table 2.5 lists all of the major contributors to variance in model output. Variations in any of these environmental parameters (e.g. a 20 % increase in water flow rate, such as during spring floods, results in a 1 % increase in water column mercury concentration) can have a substantial influence on total mercury concentrations in the sediment and water column, as these processes dominate mercury dynamics within Big Dam West. Water inflow rate and mercury concentration were dominant contributors to model variance in the water

and sediment compartments; fraction of water particles, and sediment deposition and resuspension rates were contributors to sediment variance. These parameters govern model performance and it is essential to have good measured data (or estimates) for when applying this model to new systems.

2.6.2 Emission from sediment

The potential for internal loading of mercury from sediments as Hg^0, MeHg, or THg-MeHg-Hg^0 was considered. An emission from sediment term was incorporated into the model to determine if and to what degree the sediment was contributing to the mercury mass balance in Big Dam West. Without the inclusion of any emission from sediment, the model agrees well with measured values. Therefore, an emission from the sediment could only exert a minimal, if any, effect on model output. To determine whether sediment emission would influence the model output, the model was rerun using low (3.3 g yr^{-1}) and high (82.4 g yr^{-1}) fluxes that were calculated (see section 4.1 in this paper) from mercury concentration profiles measured in Big Dam West lake sediment (Telmer *et al.*, 2005). Table 2.6 shows model output without any sediment flux, and with the lower and upper fluxes, as mentioned above. It appears as if emission from sediment may have a minor role with regards to mercury dynamics in the water column of Big Dam West (i.e., <20 % increase). Mercury concentration in the surficial sediment solids and pore waters increases with mercury flux from the deeper underlying sediments, thus accounting for the observed up – core enrichment. These estimated mercury

concentrations and fluxes, even at the highest sediment emission rate, are nevertheless within the ranges reported for this lake.

2.7 DISCUSSION

While most mercury models are constructed for contaminated environments, the mercury lake model developed and verified in this paper provides reasonable estimates of total mercury concentrations and fluxes in a remote lake environment without the need to estimate interconversion rates among species. Even though the underlying sediment was not contributing a significant amount of mercury in Big Dam West Lake, a sediment emission term was included in the model to be used for future applications (e.g. reservoir construction) of the model if needed. Geological parameters other than substrate mercury concentration, such as rock type, have also been thought to contribute to the magnitude of mercury emissions from natural sources (Gustin, 2003).

Variations in concentration ratios were not found to impart changes to model output (Table 2.4). For example: If the air THg-MeHg-Hg^0 / total Hg ratio used in the model had been increased to 2 %, then the concentration of mercury in the water and sediment compartments would have increased by 2 %. O'Driscoll *et al.* (2005*b*) gave a best estimate of error in his mass balance paper for Big Dam West Lake, however it is not a true error as many of his measurements had to be "scaled up". Error is one of the main reasons why models are verified against a number of measured average concentrations and fluxes. If the model was producing estimates that were too high in one compartment,

another compartment or flux could be even further off; but if numerous compartments and/or fluxes agree with measured averages, then the model fits the data.

As a new model that is based on the fugacity principle, as opposed to multiple speciation and partitioning equations, it should be more robust and flexible in its application than most of the other mercury models that are currently available. The FA-QWASI model (Diamond, 1999), which does share some commonalities with the current model, uses the aquivalence (fugacity x activity coefficient) approach. Although the FA-QWASI model does not require the definition of interconversion rates among species, it does apply its concentrations ratios to the Z values, making it not as transparent as the multiplier method (Toose and Mackay, 2004) that was adopted for our model.

2.7.1 Potential Future Model Refinements

2.7.1.1 MeHg : Hg^0 concentration ratio

The simplicity of the mercury model presented in this paper and its reduced need for input data provide considerable benefits; although it is not yet known whether the concentration ratios employed here will translate suitably to other environments, as no two lakes are identical. Future research should focus on developing equations for input into the model that could alter the MeHg : Hg^0 concentration ratio accordingly for new systems, without necessitating the individual measurement of all mercury species in all environmental media (albeit easier than measuring mercury species interconversion

rates). The Mercury Regional Fate Model (Macleod *et al.*, 2005), developed for a contaminated environment (San Fransisco Bay area), utilized different concentration ratios than the ones used in our model. Weech *et al.* (2004) reported a lower % MeHg / total Hg for samples associated with mining wastes compared to uncontaminated upstream sediments. Once accomplished, recalibration of the model to new systems should not be required in order for the methyl mercury output from this model to be suitable as input for foodweb models.

2.7.1.1.1 Water column stratification

Seasonal stratification typically occurs in lakes that exceed a maximum depth of 5 m, although large variations exist in depth of thermocline formation from lake to lake (2 m to more than 20 m) (Horne and Goldman, 1994). This phenomenon, resulting in anaerobic conditions at the sediment surface, is a necessary requirement for methyl mercury formation by sulphate - reducing bacteria (SRB). Siciliano *et al.* (2002) observed a change in Hg^0 with depth, which was found to be somewhat related to stratification in the water column.

2.7.1.1.2 Watershed and lake parameters

A larger watershed, high lake DOC concentration (often related to % wetland area in the drainage basin where mercury methylation is very rapid) and / or low pH (Hg_2S more bioavailable for methylation by SRBs, via diffusive uptake) will promote methylation

within the sediments (Dillon and Molot, 1997; Gilmour and Riedel, 2000; Bjornberg *et al.*, 1988; Benoit *et al.*, 2001). Rasmussen et al. (1989) was able to derive equations to estimate the concentration of DOC in the water column from lake area, drainage ratio and watershed slope using only topographical, hydrological and bathymetric maps. Length of daylight hours (amount of solar radiation), DOC, temperature, and pH can all have an effect on the production and net evasion of elemental mercury from the lake surface (O'Driscoll *et al.*, 2003*b*). Although the annual average remains relatively constant, dissolved Hg^0 concentrations in lakes can change 100 fold in 20 - 60 minutes, with diel changes in solar radiation (O'Driscoll *et al.*, 2003*b*). Each of these lake / watershed characteristics could potentially alter the MeHg / total Hg or MeHg : Hg^0 concentration ratio that should be employed for the water column in the model.

2.7.1.2 Estimates for model input parameters

In order to simplify the data requirements for this model further, equations could be inserted into the model code that would allow the model to estimate sensitive model parameters using other existing information (e.g. [SPM] = ~45 % [POC], where SPM = suspended particulate matter (mg L^{-1}) and POC = particulate organic carbon (mg L^{-1})), particularly if some of the required data was unavailable or missing. For example: suspended particulate matter can also be estimated using either total phosphorus (Lindstrom et al., 1999) or secchi depth (Hakanson, 2006); sediment deposition, resuspension and burial can be estimated using total phosphrous, maximum depth, lake area and pH (Hakanson, 2003). O'Driscoll *et al.* (2003*b*) developed an equation for Big

Dam West (BDW) Lake to estimate Hg^0 based largely on solar radiation (kW m^{-2}) which could be used as a surrogate for Hg^0 in water.

$$Hg^0_{BDW} \text{ (pg } L^{-1}) = 59.2 \text{ x solar radiation}_{(75 \text{ min prior})} + 59.2 \quad (6)$$

Evans (1994) found that the resuspension rate of sediment solids for small deep lakes decreased by an average of 70 mg m^{-2} day^{-1} per meter as lake mean depth increased. For small shallow lakes, Evans (1994) also found that the settling rate of solids (S_R) could be estimated from the lake mean depth (D_M, m).

$$S_R \text{ (g } m^{-2} \text{ day}^{-1}) = 1.04 - (0.07 - D_M) \quad (7)$$

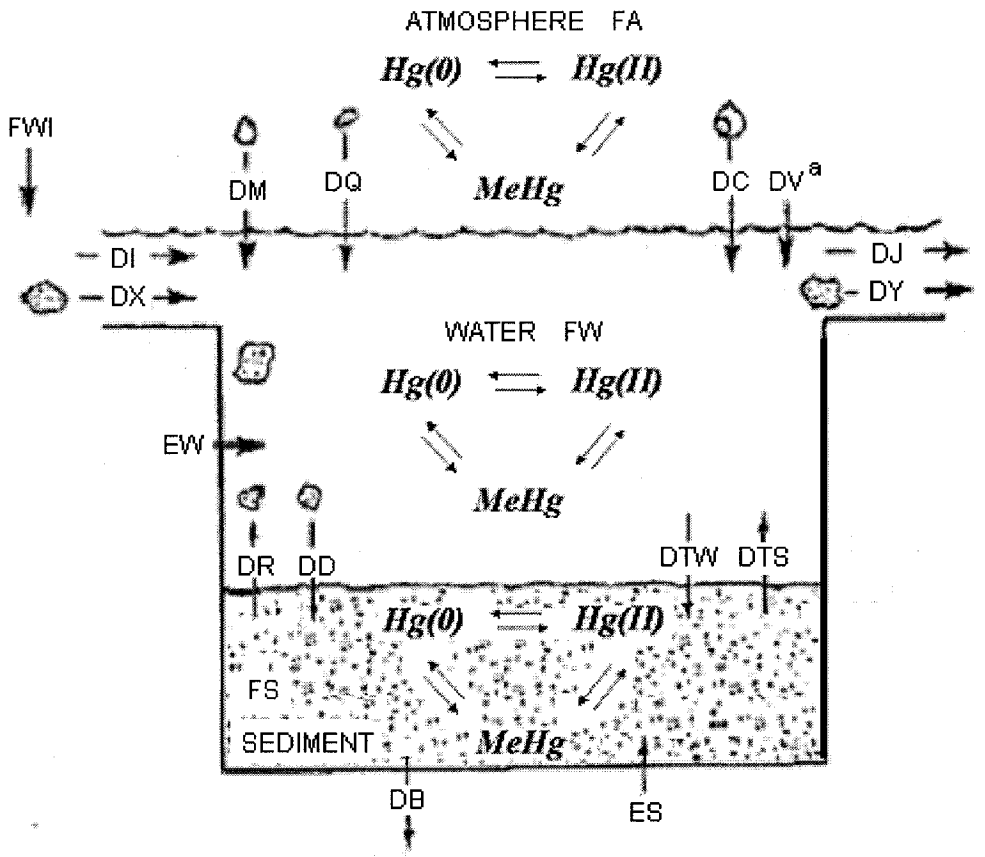
2.8 CONCLUSION

Mercury speciation and partitioning mass balance models assist policymakers to develop cost-efficient measures to mitigate human exposure by improving ecosystem response predictions to changing mercury loads and environmental conditions. For these mercury models to be useful for policymakers or regulatory agencies, they must be able to properly model mercury dynamics at remote locations throughout the environment, and in the vicinity of anthropogenic sources. Indigenous people reside in remote locations far removed from anthropogenic sources of mercury, and yet they often exhibit the highest body burdens due to their high consumption of fish and aquatic mammals.

Mercury cannot be treated or modeled like most other contaminants (e.g. Persistent Organic Pollutants (POPs)), as there is a natural background source to consider. Unless, this distinction among sources can be made, accountability by industries that release mercury into the environment can continually be challenged.

Acknowledgements - I would like to thank Matthew Ethier for his on - going support and encouragement during the construction and write - up of this model. This paper has also benefited from the critical comments of two anonymous reviewers. Their efforts are greatly appreciated.

Figure 2.1: Modified mercury QWASI lake model (redrawn from Mackay, 2001). All D values are defined in Table 2.1. NOTE: Hg(II) represents THg-MeHg-Hg^0.



[a] DV = DVW – DVA

Figure 2.2: Big Dam West Lake, Kejimkujik National Park, NS (Clair *et al.*, 2005).

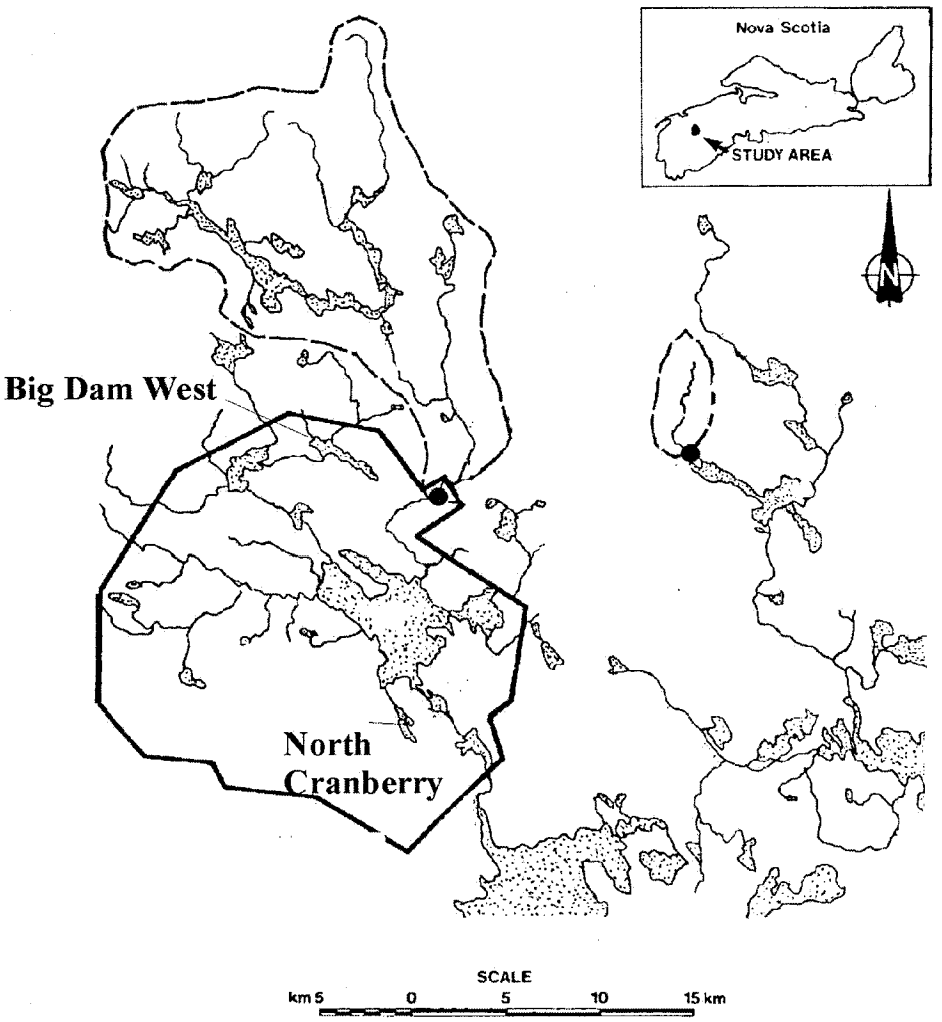


Figure 2.3: A steady-state mass balance for total mercury in Big Dam West.

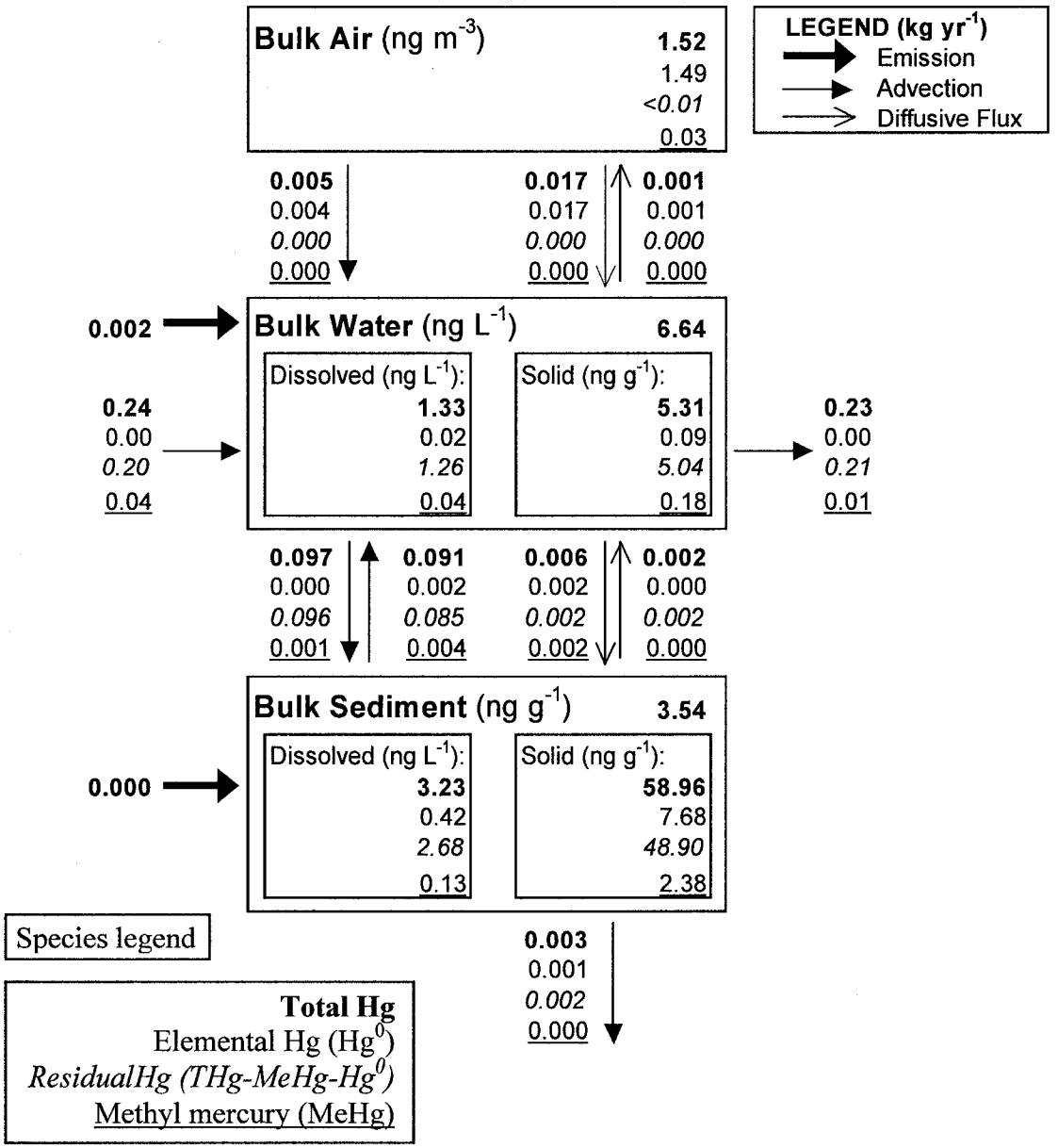


Figure 2.4: Log modeled versus log measured Hg concentration or flux.

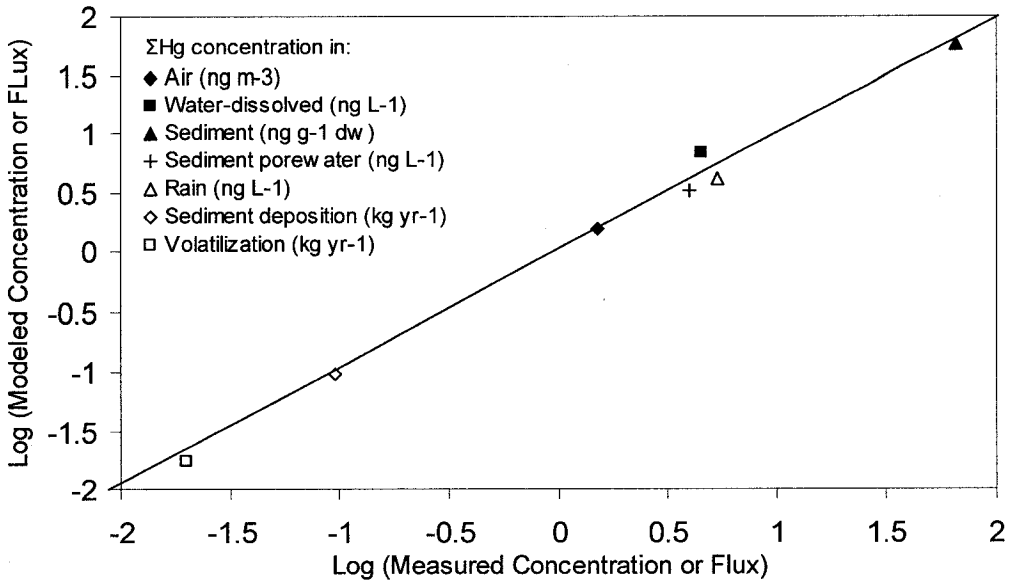


Table 2.1: Equations used to calculate elemental (Hg^0) fugacity in HERMES model.

Air: FA = CA / ZAT

Inflow Water: FWI = CWI / ZWIT

Water: FW = (EW + FWI * (DI + DX) + FA * (DVA + DQ + DC + DM) + ES * ((DTS + DR) / (DTS + DR + DB))) / (((DVW + DJ + DY) + ((DD + DTW) * (DB))) / (DTS + DR + DB))

Sediment: FS = (ES + FW * (DD + DTW)) / (DR + DTS + DB)

Fugacities (Pa)

FA	Fugacity in air
FWI	Fugacity in inflow water
FW	Fugacity in water
FS	Fugacity in sediment

Emissions (mol h^{-1})

EW	Emission to water
ES	Emission from underlying sediment

D values (Intermedia transport parameters; mol h^{-1} Pa)

DI	Water inflow
DX	Suspended sediment inflow
DVW	Volatilization (air-water flux out)
DVA	Absorption (air-water flux in)
DQ	Dry air particle deposition
DC	Wet air particle deposition
DM	Rain dissolution
DTW	Water-sediment diffusion
DTS	Sediment-water diffusion
DR	Sediment resuspension
DB	Sediment burial
DJ	Water outflow
DY	Suspended sediment outflow
DD	Sediment deposition

CA	Hg^0 concentration in air (mol m^{-3})
CWI	Hg^0 concentration in inflow water (mol m^{-3})
ZAT	Fugacity capacity for bulk air (mol m^{-3} Pa)
ZWIT	Fugacity capacity for bulk water (mol m^{-3} Pa)

Table 2.2: Concentration ratios for Hg species (MeHg, Hg^0 and THg-MeHg-Hg^0) in air, water and sediment inferred from measured concentrations of individual species and total Hg, along with ratios employed by other mercury models.

	Measured (ng L^{-1})			Concentration ratios ($Hg^{0\,-1}$)				
	MeHg	Hg^0	total Hg	MeHg	THg-MeHg-Hg^0	NOTES	Country	Reference
Air (gaseous)								
FA - QWASI model				0.01	2.8×10^{-11}			Diamond, 1999
San Francisco Bay				1.0×10^{-6}	0	contaminated	USA	Macleod *et al.*, 2005
				0.02	2.8×10^{-11}			Toose and Mackay, 2004
Europe region		1.745	2.15		1.23	assume MeHg = 0	Europe	Ferrara *et al.*, 2000; Schmolke *et al.*, 1999
USA region		0.0486	3.51		0.014	assume MeHg = 1	USA	Lindberg and Stratton, 1998; Olmez *et al.*, 1998
China region		9.24	9.54		0.032	assume MeHg = 2	China	Fang *et al.*, 2001; Liu *et al.*, 2002
Water (dissolved)								
Lake								
Big Dam West Lake	0.148	0.008	1.5	18.6	169.1	DOC: 6.4 mg L^{-1}	Canada	O'Driscoll *et al.*, 2005*a*
Big Dam East Lake	0.083	0.009	1.4	9.2	145.3	DOC: 3.3 mg L^{-1}	Canada	O'Driscoll *et al.*, 2005*a*
North Cranberry Lake	0.129	0.032	1.5	4.0	41.8	DOC: 4.2 mg L^{-1}	Canada	O'Driscoll *et al.*, 2005*a*
Lake Superior	0.0064	0.02	0.49	0.32	24.18		Canada	Hurley *et al.*, 2000
FA-QWASI model				1.7	30.7	oligotrophic		Diamond, 1999
River								
Lahontan Reservoir	1.01	0.7	23.03	1.4	31.5		USA	Bonzongo *et al.*, 1996
Carson River	0.24	0.035	3.07	6.9	80.9	uncontaminated	USA	Bonzongo *et al.*, 1996
St. Lawrence Estuary	0.043	0.044	0.555	0.9	11.5		Canada	Cossa and Gobeil, 2000
Marine								
San Francisco Bay				3.0	96.0	contaminated	USA	Macleod *et al.*, 2005
Sepetiba Bay	<0.020 - 0.55	0.032 - 0.67	0.12 - 0.67	0.63 - 0.82	1 - 3.75		Brazil	Boszke *et al.*, 2002
Sediment								
FA - QWASI model (solids)				1.0	98.0			Diamond, 1999
FA - QWASI model (pw)				0.3	4.9			Diamond, 1999
San Francisco Bay (solids)				1	588	contaminated	USA	Macleod *et al.*, 2005
St. Lawrence Estuary (pw)	1.706	0.035	~8.643	46.5	205.5		Canada	Cossa and Gobeil, 2000
				0.3	6.4			Toose and Mackay, 2004
Interstitial water (dissolved)								
Sepetiba Bay	0 - 2.46	<2.6	<2.8 - 37.3	1.0	1.1 - 14.3	total Hg estimate	Brazil	Boszke *et al.*, 2002

Table 2.3: Major environmental and kinetic input parameters for Big Dam West Lake with associated 95% confidence factor (Cf).

Big Dam West		**Cf**	**Ref**
Mean environmental temperature	6.3 °C	1.1	a,c
Wet deposition (snow + rain)	1.4 m yr^{-1}	2	a,c
Surface area	1 km^2	1	a,c
Mean water depth	3.3 m	1.15	a,c
Surface sediment depth	0.05 m	3	a
Volume of water	2593000 m^3	1.1	a,c
Bulk density of sediment solids	0.05 g dw cm^{-3} ww (SWI)	1.6	a,c
Organic carbon content	9 % (sediment) and 40 % (water)	1.5	b,c
TSS [d]	12 mg L^{-1}	3	c
Hg emission rate to water (run-off)	0.002 kg yr^{-1}	2	b,c
Hg concentration in inflow water	7 ng L^{-1}	2	a,c
Kinetic Input parameters			
Air side air-water MTC	2 m h^{-1}	3	e
Water side air-water MTC	0.02 m h^{-1}	3	e
Aerosol deposition	10.8 m h^{-1}	3	c
Sediment-water diffusion MTC	0.0002 m h^{-1}	3	e
Sediment deposition	0.1 g m^{-2} day^{-1}	3	c
Sediment resuspension	0.0875 g m^{-2} day^{-1}	3	c
Sediment burial	0.125 g m^{-2} day^{-1}	3	c

[a] from Macleod *et al.* (2005)
[b] from Macleod *et al.* (2002)
[c] estimated / actual value (O'Driscoll *et al.*, 2005)
[d] assumed POC (5.1 mg L^{-1}) was 45 % of TSS
[e] Diamond (1999)
Cf: confidence factor
MTC: mass transfer coefficient

Table 2.4: Partition coefficients (K) and species concentration ratios for Hg in Big Dam West with associated 95% confidence factor (Cf).

	Hg^0			THg-MeHg-Hg^0			MeHg		
Property	**Estimated value**	**Cf**	**Ref**	**Estimated value**	**Cf**	**Ref**	**Estimated value**	**Cf**	**Ref**
Molecular weight (g mol^{-1})	201	1	a	201	1	a	216	1	a
Melting point (°C)	-39	1	a	277	1	a	167	1	a
Partition coefficients									
K air / water	0.32	3	a	1.60E-12	1	a	1.40E-05	3	a
K sediment solids / water	20000	3	a	100000	3	a	5000	3	a
K suspended solids / water	30000	3	a	1000000	3	a	50000	3	a
Concentration ratios	Hg^0 / Hg^0			THg-MeHg-Hg^0 / Hg^0			MeHg / Hg^0		
Air (vapor phase)	1	N/A	a	2.80E-11	1	a	0.02	3	a
Water (dissolved phase)	1	N/A	b	56.2	3	b	2	3	b
Sediment (solid phase)	1	N/A	a	6.37	3	a	0.31	3	a
Water inflow (dissolved phase)	1	N/A	b	64	3	b	13	3	b

Cf: Confidence factor (Macleod *et al.*, 2005)
[a] from Macleod *et al.* (2005)
[b] estimated value obtained from measured data (O'Driscoll *et al.*, 2005)

Table 2.5: Major contributors to variance in modeled total Hg concentrations in sediment and water.

	Major contributors to variance in model output	
Input parameter	**ΣHg concentration in water (%)**	**ΣHg concentration in sediment (%)**
Concentration of Hg in inflow water (ng L^{-1})	**28**	**10**
Water inflow rate (m^3 h^{-1})	**72**	**26**
Fraction of particles in water	**<0.1**	**17**
Sediment deposition velocity (g m^{-2} day^{-1})	**<0.1**	**25**
Sediment resuspension velocity (g m^{-2} day^{-1})	**<0.1**	**22**
Water (THg-MeHg-Hg^0 : Hg^0)	**0.3**	**0.3**
Sediment (THg-MeHg-Hg^0 : Hg^0)	**<0.1**	**0.1**
Total	**100**	**100**

Table 2.6: Variations in model output before (none) and after (low and high) the inclusion of mercury emissions (or flux) from underlying sediments.

	Hg flux from underlying sediments (kg yr^{-1})		
Concentration	**none**	**low (0.0033)**	**high (0.0824)**
Bulk water (ng L^{-1})	6.6	6.7	8.8
Sediment solids (ng g^{-1})	59.0	61.7	127.2
Sediment pore water (ng L^{-1})	3.2	3.4	7.0
Flux			
Sediment deposition (kg yr^{-1})	0.10	0.10	0.13
Volatilization (kg yr^{-1})	0.02	0.02	0.02

CHAPTER 3

THE DEVELOPMENT OF EMPIRICAL EQUATIONS TO PREDICT MERCURY TRENDS IN LAKE SEDIMENTS USING DATA FROM THREE ONTARIO LAKES

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Abstract – Total mercury (THg), methyl mercury (MeHg), total organic carbon (TOC), sediment bulk density (SBD), redox potential (Eh) and percent fines measurements were made along transects from more littoral to pelagic depths in Harp, Dickie, and Blue Chalk lake located near Dorset, Ontario, Canada on the Canadian Shield in order to develop empirical relationships. MeHg was positively correlated with THg in all sediments, the MeHg : THg ratio (0.004 ± 0.004) was comparable to other uncontaminated profundal lake sediments. MeHg, MeHg : THg and TOC decreased with sediment core depth, with THg showing a decrease in Harp Lake. Eh was negatively correlated with sampling depth. MeHg : THg ratio in surface sediments was positively correlated with Eh and negatively correlated with TOC [MeHg : THg = - 0.009 * TOC(%) + 0.001 * Eh(mV) - 1.902, $p=0.026$]; whereas THg was significantly positively correlated with TOC [log THg (ppb) = 0.026 * TOC(%) + 1.400, $p<0.0001$]. TOC explained almost two-thirds of the variability in sediment bulk density (SBD) [SBD (g cm^{-3}) = - 0.202 * $\log_e$ TOC (%) + 2.199, $p<0.0001$]. SBD was significantly correlated with percent fines [SBD = - 0.00655 * fines(%) + 1.650, $p=0.0015$] and sampling depth.

Keywords: sediment, lake, mercury, Hg, methyl mercury, redox potential, organic carbon, sediment bulk density, transect, core

3.1 INTRODUCTION

All lakes, whether deep or shallow, tend to show declining redox potentials in the hypolimnion as summer progresses. Declining redox potentials within the water column and surface sediment of lakes could promote increasing methyl mercury (MeHg) production by anaerobic bacteria (Regnell and Ewald, 1997). Anaerobic bacteria, including the sulphate and iron-reducers, are thought to be responsible for methylating mercury (Hg) using bioavailable Hg^{2+} (Han et al., 2007; Jeremiason et al., 2006; King et al., 2002; Kerin et al., 2006). The MeHg formed is able to biomagnify through foodwebs and toxic effects are observed in biota at higher trophic levels, even in locations far removed from industrial sources (Boudou and Ribeyre, 1997; O'Driscoll et al., 2005a; Rasmussen and Vander Zanden, 2004). MeHg has been found to be both significantly (Regnell and Ewald, 1997) and non-significantly correlated with THg in sediment (Lambertsson and Nilsson, 2006) since numerous mechanisms (e.g., remobilization, focusing, organic carbon content) can influence Hg abundance (see Chapter 1).

Concentrations of MeHg and total mercury (THg) in sediments are known to be highly variable (spatial and temporal), even at remote locations (Rasmussen and Vander Zanden, 2004; French et al., 1999; Lindeberg et al., 2006) and within a lake (Korthals and Winfrey, 1987; Campbell et al., 2003). For example, Mills et al. (submitted) found Hg in the surface sediments of 172 Ontario lakes to range from 19.7 to 501 ng g^{-1} dw (mean: 224 ng g^{-1} dw). Sediments > 25 cm below surface in these lakes had Hg values which ranged from 11.6 to 271 ng g^{-1} dw (mean: 107 ng g^{-1} dw). Boszke et al. (2003) found the

MeHg : THg ratio to vary from 0.0065±0.0034 near the surface to 0.0001 - 0.0005 at greater depths.

Croston et al. (1996) found that temporal and spatial abundance of sediment MeHg reflected variations in redox potential (Eh), Hg availability for methylation, and the nature of bacterial populations. An increase in Eh (- 200 mV to + 50 mV) has been found to result in a decrease in MeHg concentration at the sediment-water interface (DeLaune et al., 2004; Holmes and Lean, 2006). Several other environmental variables have also been reported to show a correlation with THg and / or MeHg in sediments, such as bacterial abundance, acid volatile sulphides, organic matter, Fe, Mn and Al hydroxides, chlorides, and temperature (e.g., Boszke et al., 2003; Roulet et al., 2001; O'Driscoll et al., 2005; Kainz et al., 2003; Drott et al., 2007; Benoit et al., 2003). THg and MeHg have also been found to be positively correlated with organic matter in some sediments, but not in others (e.g. *significantly* (Regnell and Ewald, 1997; Lambertsson and Nilsson, 2006; Regnell et al., 2001 (upper lake); He et al., 2007 (surface sediments), *weakly* (Kamman et al., 2005; Warner et al., 2005; Regnell et al., 2001 (lower lake), and *non-significantly* (Kannan et al., 1998; He et al., 2007 (sediment cores)).

Published studies that examine within-lake variability in MeHg and / or THg concentrations in sediments have largely focused on the reconstruction of historic sedimentary profiles (e.g., Hines et al., 2004; Lockhart et al., 2000). Others have attempted to analyze the horizontal (i.e., transect from littoral to pelagic region of lake) and vertical (i.e., sediment cores) profiles of sediment in remote lakes simultaneously

(e.g., Campbell et al., 2006; He et al., 2007; Kainz et al., 2003). Studies that report a correlation coefficient (r) or significance value ($p < 0.05$) for relationships rarely include information regarding the corresponding equation (or at least the slope of the relationship), information that could potentially be useful for other purposes (i.e., water quality models).

Most of the lakes studied to date have generally been near industrial sources of Hg (e.g., Warner et al., 2005; Marvin et al., 2004; Rose et al., 1997; Kerfoot et al., 2004), although some were from more distant locations (e.g., Wiener et al., 2006; French et al., 1999; Allan et al., 2001). Here we provide data for three relatively pristine lakes receiving only atmospheric inputs to the lake and inputs from streams in the drainage basin. The main objective of this study was to determine whether observations made in three lakes could be used to develop empirical relationships that can then be used for lakes in other regions. The research presented in this study examines horizontal (surface sediment) and vertical (sediment cores) relationships (and corresponding equations) among sediment MeHg, THg, organic content, bulk density, percent fines and Eh as anoxia develops below the thermocline during the summer period. Equations derived in this study were then tested or compared using data from other locations.

3.2 EXPERIMENTAL METHOD

Harp (45°23'N; 79°08'W), Dickie (45°09'N; 79°05'W) and Blue Chalk (45°12'N; 78°56'W) are well-studied lakes near Dorset, Ontario, Canada (Table 3.1) that are

situated on the Canadian Shield. As a result, all of these lakes are low in buffering capacity and calcium content. Blue Chalk (surface area = 52.4 ha; max depth = 23 m) and Dickie (93.6 ha; 12 m) are seasonally stratified with anoxic conditions developing later in the summer (Figure 3.1) with infrequent mixing between periods of stratification in Dickie Lake. Harp Lake (71.4 ha; 37.5 m) does exhibit thermal stratification (~ 4 m, Figure 3.1D), but anaerobic conditions in the water column do not occur in this relatively deep lake (Figure 3.1A). Summer hypolimnetic oxygen (from 1975 - 1995) seldom rose above 1 mg L^{-1} in Dickie Lake, but was consistently over 4 mg L^{-1} in Harp Lake (Quinlan et al., 2005; Eimers et al., 2006).

3.2.1 Sample Collection

Temperature (Figure 3.1 A-C) and dissolved oxygen (Figure 3.1D-F) depth profiles in the water column were measured on-site routinely (bi-weekly: Harp and Dickie Lake; monthly: Blue Chalk Lake) throughout the summer using standard Ontario Ministry of the Environment (MOE) field protocols with a YSI model 58 oxygen / temperature meter (Dorset Environmental Science Centre, Dorset, Ontario; Ingram et al., 2006). Sediment cores (4 or 5) were collected in June and August 2005 with an open-barreled Kajak-Brinkhurst-type gravity corer modified to have an auto suction-seal and a percussion knocker to extend penetration (Dr. Jules Blais, University of Ottawa) from Harp, Dickie, and Blue Chalk Lake. The corer was rinsed with lake water to prevent cross-contamination as cores were sampled along transects from littoral to pelagic region of each lake along the main axis. Lower oxygen levels were anticipated in the more pelagic

August samples. At each site, depth was measured using the rope attached to the sediment corer and the location was recorded using a Garmin portable 12 - channel Global Positioning System (GPS). Variation in lake basin slope (expressed as %) between sediment core sampling locations along each transect was calculated as the difference between sampling depths divided by the distance between samples.

Cores were capped and transported to a lab at the Dorset Environmental Science Centre where duplicate samples from 5 cm slices were taken to a sediment depth of 25 cm. Cores were sectioned under N_2 and placed (with no headspace) in air-tight plastic 50 mL centrifuge tubes. The Eh (mV) was measured on each core with an Orion model 520 meter as it was being extracted by inserting a silver / silver chloride Eh probe into the sediment. Samples were then transported in a cooler to the National Wildlife Research Centre (Environment Canada, Ottawa, Ontario) and freeze-dried.

3.2.2 Laboratory analyses

Sediment bulk density (SBD, g cm^{-3}) was determined by weighing sediment before and after freeze-drying with a water content (WC) conversion described by Jepsen et al. (2001) (i.e., SBD = (SD * WD) / (WD + (SD – WD) * WC), which assumes sediment (SD, 2.6 g cm^{-3}) and water (WD, 1 g cm^{-3}) densities. Percent total organic carbon (TOC, %) was determined using weight loss on ignition method (USGA, 1993) using a muffle furnace set at 440 °C for 12 h. A sodium thiosulfate clean-up was used on extracts of duplicate sediment samples to quench any residual chemical reactions. MeHg was isolated

as bromide derivatives by acidic KBr and $CuSO_4$ with subsequent extraction into a small volume (100 μL) of dichloromethane (Cai et al., 1997). Determination of MeHg was done at the University of Ottawa by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai et al. (1997). Analysis of a MeHg estuarine sediment standard reference material (ERM-CC580, IRMM) was within the reported range (75±4 ppb).

Total Hg was determined at the National Wildlife Research Centre using a high temperature combustion Hg analyzer (AMA-254, Altec, Czech Republic) equipped with an ASS-254 autosampler (Weech et al., 2004). Quality assurance included the use of standard reference materials (LKSD-1, NBS-1646b, LKSD-3) and sample replicates (n = 39). The standard reference materials used were estuarine sediment NBS-1646b [65.2±11.7 ppb (n=3)], lake sediment LKSD-1 [104.9±8.2 ppb (n=46)], and lake sediment LKSD-3 [284.3±18.1 ppb (n=7)]. LKSD-3 was analyzed at the start of each run, and LKSD-1 was analyzed after every 5^{th} sample. Measurements of Hg in all of the SRMs were within 10% of certified values [NBS-1646b = 63±12 ppb (National Bureau of Standards, 1982); LKSD-1 = 110 ppb (Geological Survey of Canada, 1990); LKSD-3 = 290 ppb (Geological Survey of Canada, 1990)]. The relative standard deviation between sediment sample replicates (n=39) averaged ±2.6%.

Dried surface sediment samples were sieved by gently massaging through a 0.64 μm mesh to separate fine (< 63 μm) and coarse (> 63 μm) fractions. Coarse-grained sediments are non-cohesive (i.e., will not stick to each other) and fines (clay and silt) are

cohesive, a separation that has chemical and physical implications for sediment quality (Ongley, 1996).

3.2.3 Statistics

Standard least square regressions were used to examine relationships (r^2) among individual parameters (SBD, TOC, Eh, MeHg, THg, and MeHg / THg (MeHg : THg) ratio). For combined regressions (all sediments), this was repeated for each sediment core interval (e.g., 0-5 cm, 5-10 cm) to address sample independence. Residuals (± range) were reported for data that could not be normalized; if residuals were normal around zero a parametric regression was used. A Spearman's rank correlation coefficient (Rho) was reported when linear regression residuals were not normal. Forward-stepwise multiple regressions were used to determine the significance and relative influence of TOC and Eh on MeHg accumulation in sediments (expressed as MeHg : THg). For all statistical tests, a significance level of $p < 0.05$ was used. The Root Mean Square Error (RMSE) of the slope and intercept was included for all regression equations to provide some indication about the predictive capacity of the empirical relationships described in this study.

A least-squares means analysis of variance (ANOVA) was used to determine if there were significant differences among sampling depths (from more littoral to increasingly pelagic transects), sampling date (June and August) and sediment core depth (surface to 25 cm depth) with regards to THg, MeHg, MeHg : THg ratio and Eh.

Statistical analyses were conducted using JMP® version 4.0.2 (SAS, 2000).

3.3 RESULTS

Methyl Hg (ppb) and MeHg : THg data were normalized by log transformation and THg (ppb) was normalized by a square-root transformation for all ANOVA stats. Transformations used for regression statistics are indicated in the corresponding equation. The SBD, fines (%), and TOC could not be normalized, so a Spearman's Rho significance (non-parametric) was reported if linear regression residuals were not normal.

Figure 3.2 (June) and Figure 3.3 (August) depict horizontal (from more littoral to increasingly pelagic region) and vertical (depth below sediment-water interface) trends in THg, MeHg, TOC, Eh and SBD in Dickie, Harp and Blue Chalk Lake. The MeHg : THg ratio was not significantly ($p > 0.05$) different between June (0.00445, $r^2 = 0.63$) and August (0.00425, $r^2 = 0.50$) (Figure 3.4). No significant differences ($p > 0.05$) were found for THg or MeHg in the study lake sediments between sampling dates. The sediment Eh was significantly higher ($p = 0.0006$) in June than in August. When each lake was examined separately, a significant seasonal difference in Eh was only found for Harp Lake ($p = 0.0002$) sediments (Dickie Lake: $p = 0.079$; Blue Chalk Lake: $p = 0.438$).

3.3.1 MeHg : THg ratio in lake surface sediments

Surface sediment Eh (mV) (log MeHg : THg = 0.001 * Eh - 2.091, r^2 = 0.17, p = 0.035, RMSE = 0.22, n = 26) and TOC (%) (log MeHg : THg = - 0.011 * TOC - 1.937, r^2 = 0.18, p = 0.033 (residuals normal±0.20), RMSE = 0.22, n = 26) were both significantly correlated with MeHg : THg ratio, but not with each other (p = 0.164). The strength of relationship (r^2) with MeHg : THg ratio increased when Eh and TOC were considered together (log MeHg : THg = - 0.009 * TOC + 0.001 * Eh - 1.902, r^2 = 0.27, p = 0.026, RMSE = 0.21, n = 26). Figure 3.5 shows an overall decrease in surface sediment MeHg : THg ratio as redox potential becomes increasingly more negative.

3.3.1.1 Effect of sediment physical properties on Hg abundance

The strength of relationship (r^2) indicates that sediment TOC (%) could explain almost half of the variability in THg (ppb) (log THg = 0.026 * TOC + 1.400, r^2 = 0.48 (0.53-0.73), p < 0.0001 (residuals normal±0.40), RMSE = 0.21 (0.13-0.21)), but less than 10% of the variability in MeHg (ppb) (r^2 = 0.09, p = 0.0007 (residuals normal±0.60)). In addition, it appears as if the relationship between sediment TOC and THg is more linear for sediments with a TOC < 25% (THg = 4.74 * TOC + 1.58, r^2 = 0.53, RMSE = 43.14, n =14).

Strong relationships (high r^2) were found amongst sediment physical properties since SBD (g cm^{-3}) was negatively correlated with TOC (SBD = - 0.0116 * TOC + 1.400, r^2 =

0.63, $p < 0.0001$(residuals not normal), RMSE = 0.06, n = 25) and fines (%) (SBD = - 0.00655 * fines + 1.650, $r^2 = 0.88$, $p = 0.0015$ (residuals not normal), RMSE = 0.05, n = 25) (Figure 3.6).

3.3.2 Mercury trends

3.3.2.1 Sediment cores (depth below sediment-water interface)

Methyl Hg ($p < 0.0001$) and MeHg : THg ($p < 0.0001$) decreased significantly with increasing depth in the core from the sediment surface in all of our study lakes. There was an overall significant decrease in THg ($p = 0.009$) when all lakes were considered together, but only Harp Lake showed a slightly significant decrease ($p = 0.031$) when lakes were considered separately (Dickie Lake: $p = 0.840$; Blue Chalk Lake: $p = 0.175$) (Figure 3.2 and 3.3). No significant difference with depth below sediment surface was found for the Eh ($p = 0.935$) for any of our study lakes.

3.3.2.2 Sampling depth (more littoral to increasingly pelagic transects)

A slightly significant decrease in surface sediment MeHg : THg ratio was found with sampling depth (m) from the more littoral to increasingly pelagic region for all of our study lakes combined (log MeHg : THg = - 2.055 – 0.010 * sampling depth, $r^2 = 0.16$, $p = 0.043$, RMSE = 0.22, n = 26), although a more pronounced difference ($p < 0.05$) was found for THg, MeHg and Eh for Harp, Dickie and Blue Chalk lakes. SBD decreased

significantly with increasing sampling depth (SBD = - 0.00876 * sampling depth + 1.244, $r^2 = 0.24$, p = 0.0126 (residuals not normal), RMSE = 0.16, n = 25). Sediment TOC increased significantly with sampling depth (TOC = 0.49 * sampling depth + 17.5, $r^2 = 0.26$, p = 0.007, RMSE = 8.07, n = 26) (Figure 3.2 and 3.3). The slope of the lake basin between sediment core sampling locations along each transect varied from: Harp = 6.3 - 8.1% (June) and 8.3 - 10.0% (August); Dickie = 1.1 - 1.6% (June) and 1.4 - 2.6% (August); and Blue Chalk = 5.5 - 13.0% (June) and 5.3 - 7.3% (August)).

3.4 DISCUSSION

Harp Lake was the only study lake where a significant difference was found for any of the normalized variables between sampling dates (i.e., redox potential). There was a significant progressive depletion in dissolved oxygen levels in Harp Lake, reaching 2 mg L^{-1} in deepest (> 35 m) area of lake in August that could possibly explain this outcome (Figure 3.1A). Dickie Lake started to show a sharp decrease in dissolved oxygen directly beneath the thermocline (3 - 5 m water depth) in early July, which resulted in near-anoxic conditions below the thermocline during the August sediment-sampling period (Figure 3.1B). A more pronounced difference in redox potential was expected between the June and August sediment samples for Dickie Lake which contrasts to what has been reported by others (e.g., DeLaune et al., 2004). Dissolved oxygen profiles were not measured as frequently in Blue Chalk Lake (Figure 3.1F) compared with Harp (Figure 3.1D) or Dickie Lake (Figure 3.1E), but it is apparent that dissolved oxygen levels are comparable between sampling dates and near-anoxic in the deepest (> 20 m) area of the lake.

No significant difference was found for MeHg, THg or MeHg : THg ratio between sampling dates for sediments collected from our three study lakes. Numerous studies have reported increases in MeHg as anoxia develops during summer stratification in lakes (e.g., DeLaune et al., 2004; Eckley et al., 2005). Regnell and Ewald (1997) found that sediment MeHg levels decreased during summer stratification, and then increased after August.

3.4.1 MeHg : THg ratio

In this study, the MeHg : THg ratio was used as an indicator of the relative amount of methylated Hg in sediments (Kainz and Lucotte, 2006). The relationship between MeHg and THg was linear (0.004±0.004) for the sediments in our study and comparable to uncontaminated profundal sediments from other lakes (Figure 3.7). For example, the measured MeHg : THg ratio was 0.0027 (Chicot) and 0.0050 (Black) in two Louisiana lakes (DeLaune et al., 2004); and 0.0040 in Big Dam West Lake, Nova Scotia (O'Driscoll et al., 2005a). On the other hand, streams and wetland sediments from comparable sites tend to have substantially higher ratios [e.g., 0.032 (Thomas Meadow Brook, Nova Scotia) (O'Driscoll et al., 2005a); 0.017 (Harp Lake inflow streams, Ontario) (Bodek, 2008); < 0.024 (Haihe and Dagu Drainage River, China) (Shi et al., 2005); and 0.022 (mean lake wetland sediment ratio from Lostwood National Wildlife Refuge, North Dakota) (Sando et al., 2007);]. Runoff from wetlands (direct or via streams) could thus elevate the MeHg : THg ratio in littoral surface sediments. For

example, Kainz and Lucotte (2006) found MeHg : THg ratio in littoral sediments to be 39% higher than in profundal sediments from Laforge Lake, Quebec which may partly account for the decrease with sampling depth observed in our study.

The sediment Eh (mV) and TOC (%) were found to be significant predictors of the relative amount of methylated Hg (expressed as MeHg : THg ratio) in surface sediments, individually or combined. Contrary to what was expected, there was a significant increase in the relative amount of methylated Hg with increases in sediment Eh (instead of the expected decrease) (e.g., a 10 mV increase in Eh resulted in a 0.0006 increase in the relative amount of methylated Hg in sediments) (Figure 3.5). This pattern serves as an indicator of a terrestrial and / or watershed source of MeHg (i.e., run-off from the watershed) since the surface sediments with the highest Eh were closest to the shore (Mierle and Ingram, 1991; Peckenham et al., 2007; Siciliano et al., 2005; Allan et al., 2001).

Subsurface sediment MeHg : THg ratio does not appear to be influenced by watershed or terrestrial sources, since the pattern may be indicative of a within lake source (Figure 3.5). An increase in MeHg : THg ratio can be observed as the Eh nears - 118 mV, followed by a subsequent decrease with further decreases in Eh. Bacterial sulfate reduction tends to occur as the Eh in lakes nears - 118 mV and has been implicated in MeHg formation, and its subsequent increase, in sediments (Kerin et al., 2006). Mercury fixed by hydrous ferric or manganese oxides could be released as the Eh drops below – 118 mV due to reductive dissolution which could lead to the observed lower levels in the

pelagic versus littoral sediment (Regnell et al., 2001). The formation of sulphides in sediments would also reduce the availability of Hg for methylation at the lower (> - 118 mV) Ehs through surface sorption, thus reducing bioavailability for microbial transformation (Boszke et al., 2003; Warner et al., 2003).

3.4.1.1 Effect of sediment physical properties on Hg abundance

Sediment TOC (%) explained almost half of the variability in Hg, an outcome that is in agreement with what has been reported for other lakes (e.g., He et al., 2007; Campbell et al., 2003; Sousa et al., 2004). For uncontaminated sediments with a TOC less than 25%, TOC could predict summer sediment THg at other sites reasonably well. For example, TOC only underestimated sediment THg by 16.5% for Resurrection Creek, Alaska (MacFarlane, 2004) and was within range (18.4% above mean) reported for Dipper Harbour – low elevation, Bay of Fundy (Hung and Chmura, 2006) using the equation derived in this study. In addition, He et al. (2007) reported a nearly identical slope for the relationship between THg and TOC (< 25%) (THg (ng g^{-1}) = 4.25 * TOC (%) + 25) to that reported in our study. Methyl Hg was significantly correlated with sediment TOC, but this was likely a result of the strong correlation between MeHg and THg.

SBD, TOC and fines (%, particle mass smaller than 64 μm) were all highly correlated. Sediment TOC explained almost three-quarters of the variability in SBD, since organic matter can retain water (Figure 3.6) (Rawls et al., 2003). For example, sediment with a bulk density greater than 1.2 g cm^{-3} bound organic matter relatively poorly which in turn

caused water content to decrease. Avnimelech et al. (2001) reported an equation correlating SBD with TOC [Bulk density (g cm^{-3}) = 1.776 – 0.363 * Log_e TOC (ppt), r^2=0.70, n=868]. A comparison between the equation reported in this study and theirs, revealed similar correlations between variables (r^2 = 0.72) even though the slope of the Avnimelech et al. (2001) equation was almost 50% greater. The range of TOC used to derive the Avnimelech et al. (2001) SBD equation was roughly < 1 - 17 %, substantially lower than the majority (90%) of our sediments (20 - 35%). Given that the slope of the relationship between these two parameters changes direction as the sediment TOC passes through 20% (see Figure 3.6), it is not surprising that the Avnimelech et al. (2001) equation had a steeper slope. Therefore, the Avnimelech et al. (2001) equation to estimate sediment bulk density from TOC or vice versa would likely be suitable for sediments with very high bulk densities (>1.7 g cm^{-3}) or low TOCs (<15%).

In our study, sediment with a bulk density greater than 1.2 g cm^{-3} and TOC less than 15% was comprised largely of coarse (< 30% fines) material (Figure 3.6). Finer sediments tend to be cohesive, which causes organic carbon and other fine material to bind to particle surface (Jepsen et al., 2001). Brown et al. (1998) and Jepsen et al. (2001) both reported strong correlations among sediment organic carbon, bulk density and particle size that are in agreement with the present study. The coarse littoral sediments were thus not capable of retaining as much water or organic matter as the finer sediments located in the pelagic regions of our study lakes, and they consequently also contained lower Hg concentrations. A comparable pattern was observed by Boszke et al. (2004), since their coarse sediments (higher sand content) did not contain as much Hg per unit mass as their

fines (clay and silt). Therefore, the results of our study and others all indicate that the physical properties of lake sediments (i.e., TOC, SBD, fines) can influence the amount of Hg available for methylation.

3.4.2 Mercury trends

3.4.2.1 Sediment cores (depth below sediment-water interface)

No significant difference in Eh was found with increasing depth below the sediment-water interface, although there was a significant decrease in MeHg to THg ratio. Our results show that the fraction of THg as MeHg is greatest near the sediment-water interface (top 5 cm) in these lakes, regardless of reducing conditions at lower sediment depths. Croston et al. (1996) and Boszke et al. (2003) reported systematic decreases for MeHg : THg ratios from a maximum of < 0.004 and 0.0065$\pm$0.0034, respectively, in surface sediments to zero and 0.0001 - 0.0005, respectively, in deeper sediments, even though Croston et al. (1996) reported maximum MeHg and Hg peaks below 6 cm in half of the sediment cores. This can be explained by the increased activity of methylating bacteria near the sediment-water interface (Boszke et al., 2003). The higher levels of Hg and MeHg at the sediment surface compared to the underlying sediment were likely a function of TOC, given that the Eh did not change significantly with core depth. TOC would increase Hg availability (as shown in our study) and could serve as a substrate for bacterial methylation.

3.4.2.2 Sampling depth (more littoral to increasingly pelagic transects)

Thermocline formation does not appear to influence the relative amount of methylated Hg in sediments from our study lakes, spatially (more littoral to increasingly pelagic regions) or temporally (June and August). He et al. (2007) found a significant correlation in percent MeHg with sediment core depth ($r = 0.58$, $p < 0.01$), but not in surface sediments (spatially) ($r = 0.02$, $p > 0.05$).

The TOC and THg sediment profiles (Figure 3.2 and 3.3) from the more littoral to increasingly pelagic region of our study lakes show progressively enriched surface sediments compared with the underlying sediments. He et al. (2007) found a positive correlation between organic matter content (range: < 10% to ~30%) and methyl ($r = 0.68$, $p < 0.01$) and total ($r = 0.88$, $p < 0.001$) Hg in surface sediments, but not in their sediment core ($p > 0.05$) samples where the organic fraction averaged 29.8 - 32.8%. Kainz et al. (2003) found a significant positive correlation ($r^2 = 0.72$, $p < 0.05$) between MeHg and TOC at the sediment water interface, but not with core depth ($p > 0.1$). Some of the sediment cores Kainz et al. (2003) collected appear to show a relationship between THg and organic matter with core depth at some sites, but not at others, although no statistical correlations were performed. Regnell et al. (2001) found a correlation between organic matter and THg in surface sediments from one of their study lakes (upper lake), but a weak relationship in another (lower lake). The authors suggest that the weak relationship in their lower lake sediments could be due to either the absence of Hg-

polluted material or through the degradation of organic matter that could release bound Hg.

There are three potential reasons for the observed profile along the more littoral to increasingly pelagic transects in our study lakes. The first theory is that the enrichment of Hg in sediment could be attributed to modern contamination. Many researchers insist that historical profiles faithfully reproduce historical deposition rates (Sunderland et al., 2008). Croston et al. (1996) found that sediment Hg profiles reflected historical emissions from the late 1960s and early 1970s, even though the current surficial sediments in their cores were 2.5 - 9 times higher than expected. The surface sediment enrichment pattern found in this study lends support to the notion that sedimentary processes (i.e., focusing and / or remobilization) could be responsible for the discrepancy between the measured and modeled Hg concentrations in surface sediment.

Sediment focusing can create erosional (littoral), transportation and accumulation (pelagic) regions in lakes (Hakanson, 2005; 2003). Evans (1981) measured sediment focusing in lakes near those sampled in our study, observing a shift in sediment organic carbon and texture (i.e., coarse sand to finer materials) at a depth between 9.5 and 12.0 m. In other lakes, this transition region occurs directly beneath the summer epilimnion (Evans, 1981). It appears as if this transition region for our study lakes occurs at water depths of 12 - 13 m (Blue Chalk), 10 - 13 m (Harp), and 5 - 6 m (Dickie). Below this transition region, as the mean slope in the lake basin decreases, there should be a corresponding increase in the accumulation area (~25% increase in accumulation area per

10% decrease in slope) (Blais and Kalff, 1995). Higher threshold current velocities in lakes are required to resuspend sand (20 cm s^{-1}) compared with clay (2 - 3 cm s^{-1}) (Bloesch, 1994). Resuspended sediment should have a higher Hg and organic matter content and percent fines than the sediment that was initially deposited to the lake because the heavier coarse fraction (low percent fines, Hg and TOC) is not as likely to undergo resuspension once deposited. Therefore, those regions that experience the greatest amount of sediment accumulation should have the highest TOC and THg levels which is consistent with sediment profiles measured in our study lakes (Figure 3.2 and 3.3). The slope of basin in Harp, Dickie and Blue Chalk Lake tended to be relatively consistent from the more littoral to increasingly pelagic region. Even though a sediment core collected from Blue Chalk Lake in June was from a region of the lake where the slope differed by more than 2%, there was little variation with depth from surface compared to the other two lakes that had a more (Harp Lake) and less (Dickie) prominent slope. It is thus doubtful that sediment focusing alone could explain the observed sediment profiles with respect to THg, although lead-210 dating can be used to correct for sediment focusing.

The vertical flux or transport of Hg from underlying sediments could be another reason for the observed transect profiles. Gobeil and Cossa (1993) estimated Hg porewater fluxes near sediment surface to be around 1 ng cm^{-2} yr^{-1}, although Hg flux to the sediment surface in contaminated lakes can exceed 1500 ng cm^{-2} yr^{-1} (Lockhart et al., 2000). Telmer et al. (2005) observed an upcore-enrichment trend in sediments from remote lakes (Big Dam East and Big Dam West Lake, Kejimkujik Park, NS) that he thought was due

to the transport of methane containing reduced mercury. This, the authors argued, resulted in Hg remobilization from the older underlying sediments. In all likelihood, sediment focusing and Hg remobilization from underlying sediments were at least partly responsible for the observed sedimentary profiles in this study (porewater profiles should be measured). Other potential possibilities which could be considered are the increases in lake water DOC and the regional climate changes that have taken place in these Dorset lakes over the past few decades (Dorset Environmental Science Centre, Dorset, Ontario).

Equations were derived in this study to facilitate direct comparisons with other values or equations reported in the literature. These empirical relationships can also serve as tools for environmental models since the site-specific data needed to run a model is not always available. For example, some of the equations reported in this study were incorporated into the Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model to provide estimation methods for lakes with missing data (Chapter 4).

Intriguing venues for future research that could improve model performance and uncertainty regarding Hg dynamics include the examination of sedimentary horizontal and vertical profile patterns on a finer scale to increase resolution (e.g., 1 cm slices in sediment cores, collecting six or more cores per transect and / or more transects, or more regular (monthly / seasonal) sediment sampling); lead-210 dating to calculate lake sediment focusing on a finer scale; measurement of pore water Hg, iron and manganese profiles to identify Hg vertical flux patterns and binding in sediments (i.e., peepers); and / or the quantification of methane gas emission rates from sediments (i.e., using peepers and / or $\delta^{13}C$ / $\delta^{2}H$ isotopic profiles).

3.5 CONCLUDING REMARKS

Patterns in sediment properties and Hg from cores collected along littoral to pelagic transects in lakes were examined and then used to formulate empirical relationships that are valid within the range of conditions represented by the study data. Our MeHg and THg results were found to be in agreement with reported ranges for other lakes. Sediment TOC was by far the best estimator of Hg (at least THg) in sediments, as was previously found in other studies (e.g., He et al., 2007). Regnell et al. (2001) analyzed surface sediments from only two stations (shallow and maximum depth) in each study lake. Kainz et al. (2003) collected cores from littoral and pelagic (offshore) sites, but not along a linear transect. He et al. (2007) collected sediment cores in pelagic region of their study lakes, but only surface sediments along linear transects (littoral to pelagic). Due to the importance of in-lake (e.g., sulfate reduction) and terrestrial (e.g., run-off) Hg methylation, as well as the numerous potential sources (e.g., atmospheric, geological, watershed) of Hg, more focus should be placed on the spatial and temporal sediment sample collection methods used for our study.

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Table 3.1: Lake property data (Dorset Environmental Science Centre, Ontario Ministry of the Environment, Dorset, ON).

	Blue	Chalk	Dickie	Harp
Physical properties				
Surface area (ha)		52.4	93.6	71.4
Mean depth (m)		8.5	5.0	13.3
Maximum depth (m)		23.0	12.0	37.0
Water volume ($x10^5$ m^3)		44.7	46.7	95.1
Watershed area (km^2)		1.9	5.0	5.4
Chemical properties				
Dissolved organic carbon (mg/L)		1.8	5.2	3.7
Total phosphorus (µg/L)		5.0	7.5	6.3
Conductivity (µS/cm)		28.4	33.2	37.4
pH		6.7	5.9	6.4

Figure 3.1: Temperature (A-C) and dissolved oxygen (D-F) profiles sampled at various depths throughout the summer of 2004 for Harp (A,D), Dickie (B,E), and Blue Chalk (C,F) lake (Dorset Environmental Science Centre, Ontario Ministry of the Environment, Dorset, ON). * denotes sediment core sampling dates.

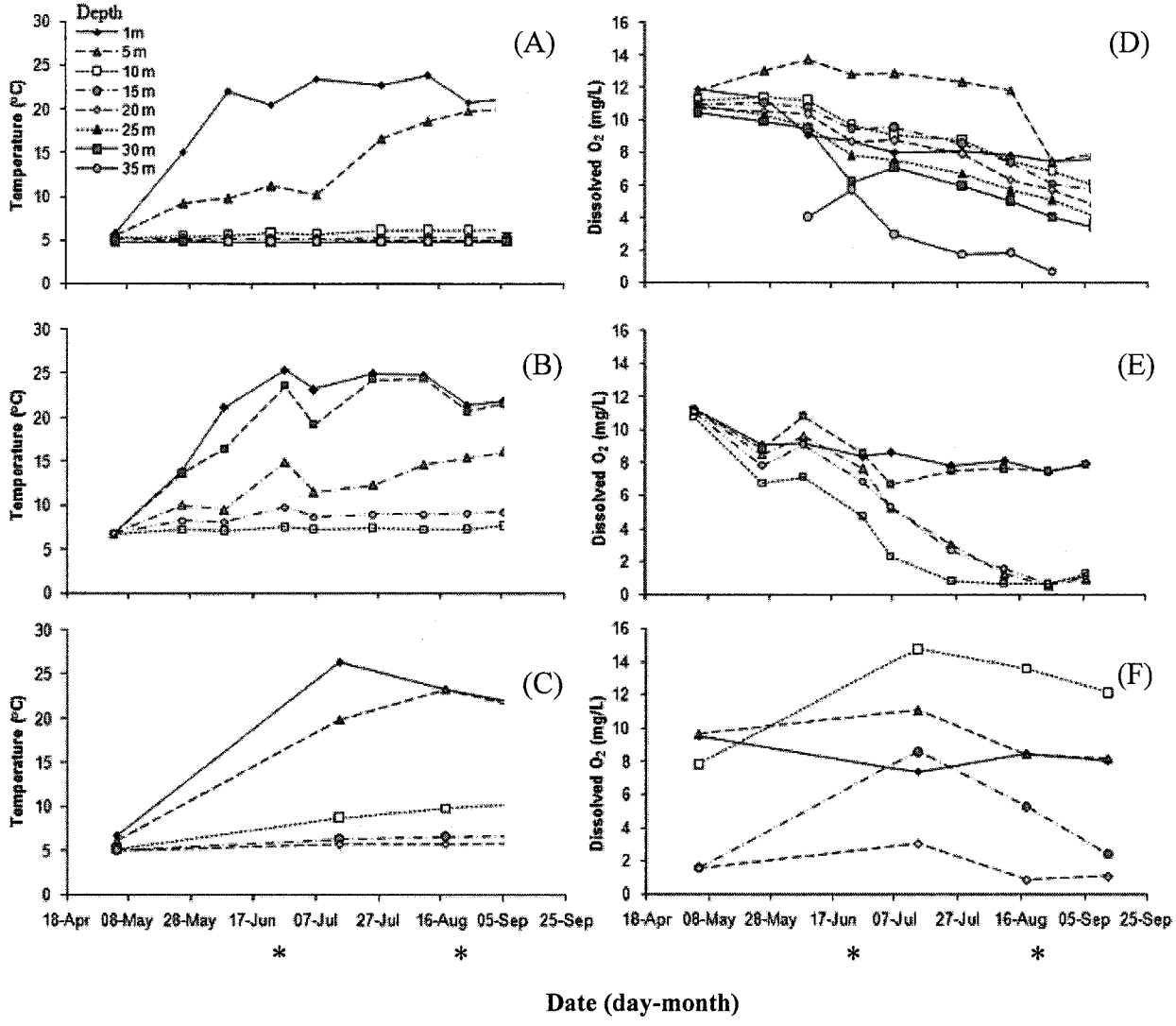


Figure 3.2: THg (ppb), MeHg (ppb), TOC (%), Eh (mV), and SBD (g cm^{-3}) profiles for sediment cores collected along transects from more littoral to pelagic region of Dickie, Harp, and Blue Chalk Lake in June.

June

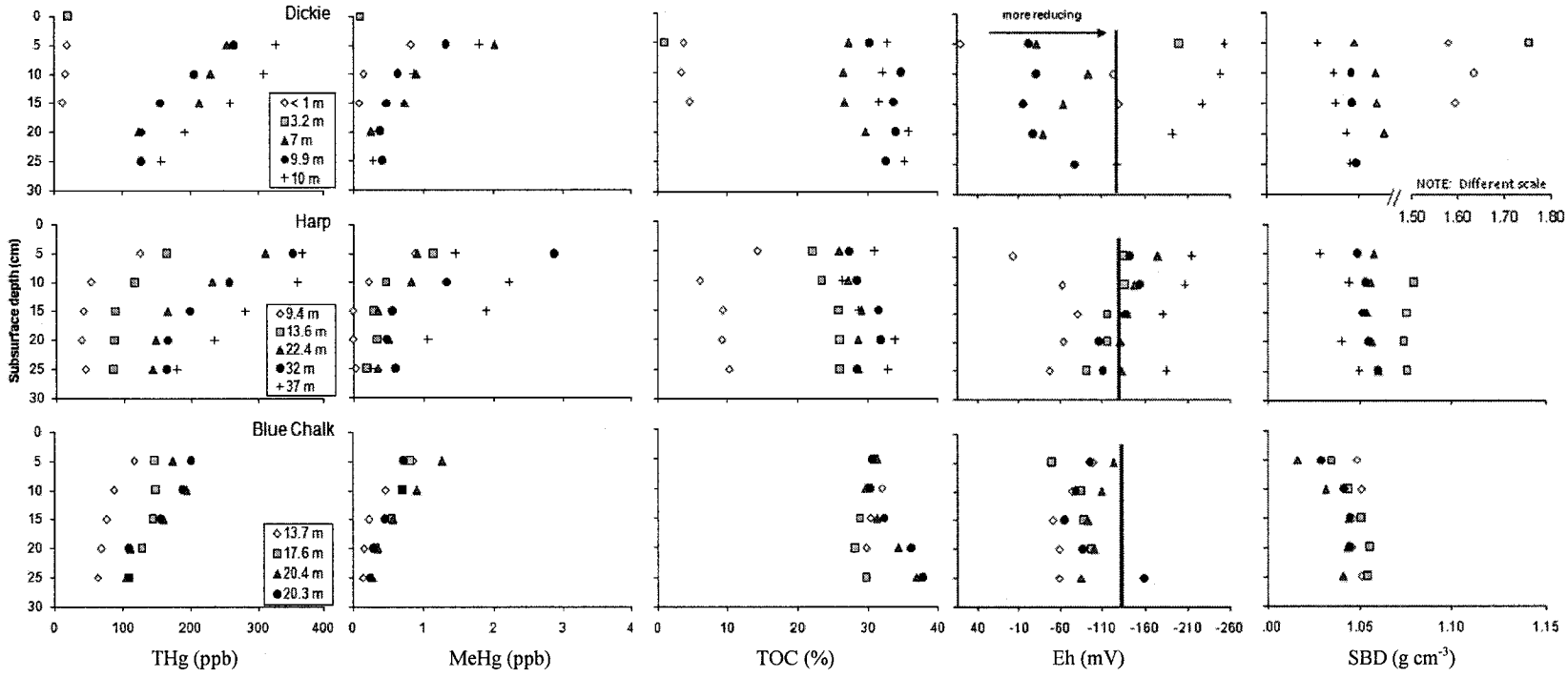


Figure 3.3: THg (ppb), MeHg (ppb), TOC (%), Eh (mV), and SBD (g cm^{-3}) profiles for sediment cores collected along transects from more littoral to pelagic region of Dickie, Harp, and Blue Chalk Lake in August.

August

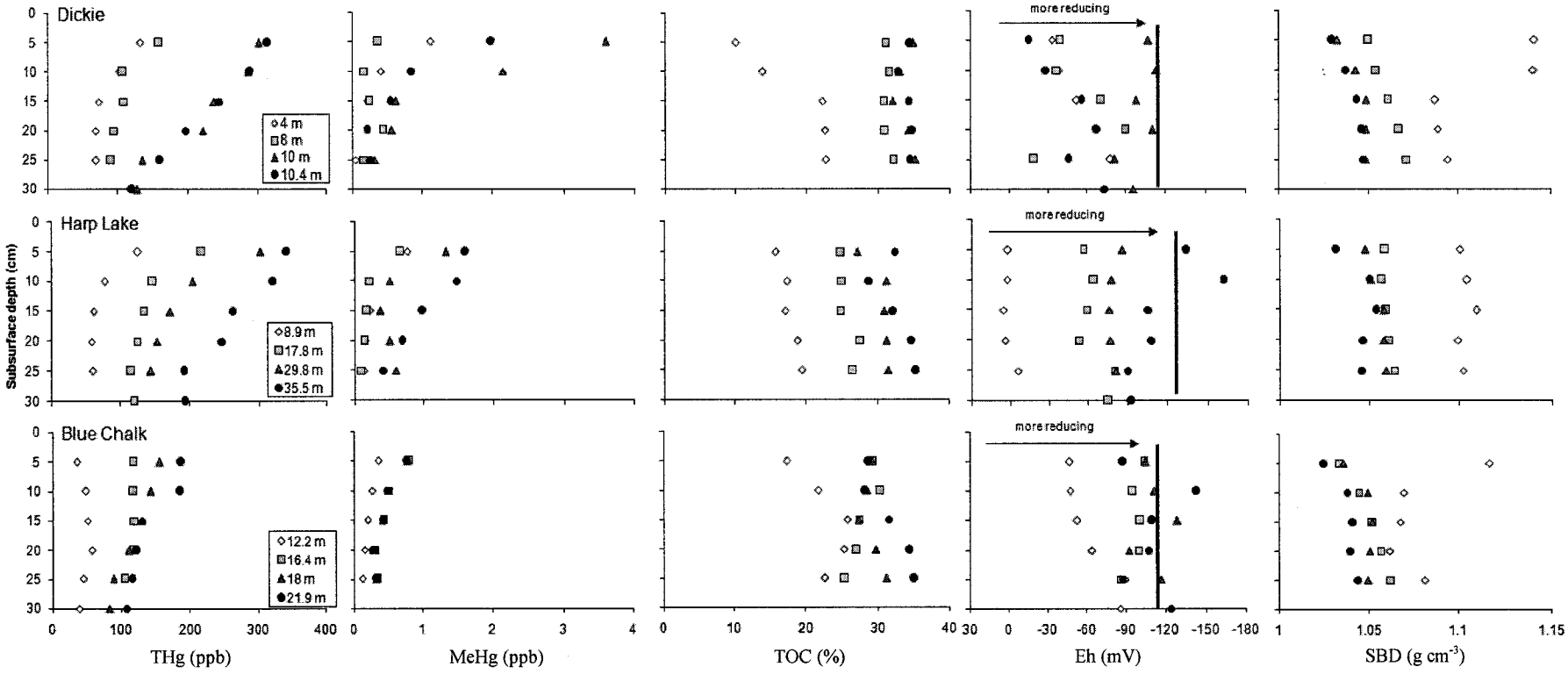


Figure 3.4: Correlation between sediment THg (ppb) and MeHg (ppb) for June (A) and August (B) sampling dates.

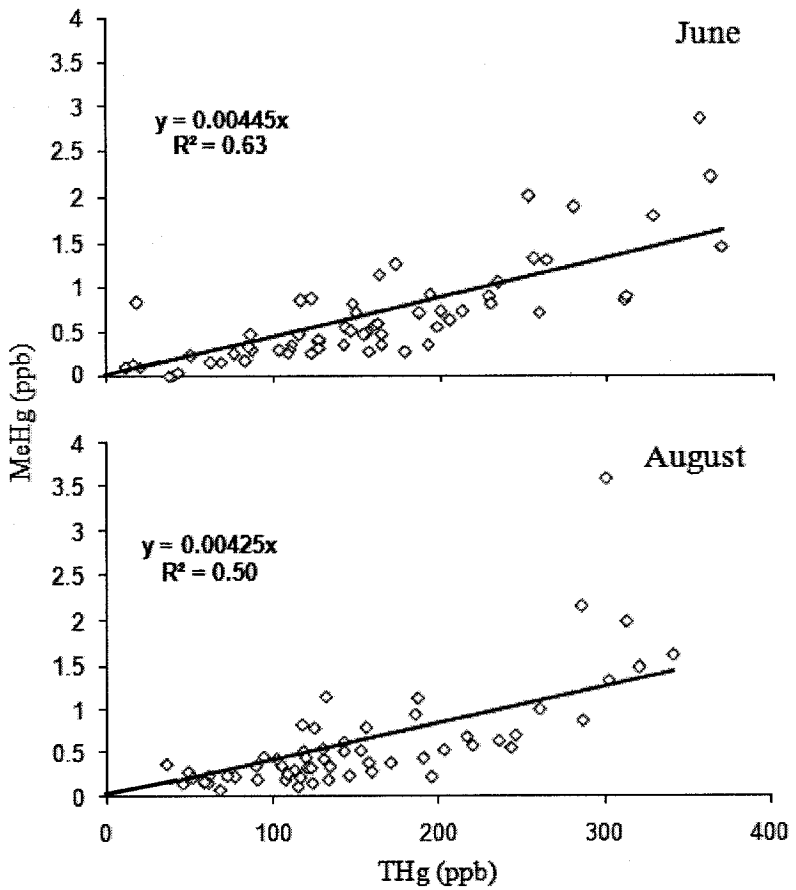


Figure 3.5: Variations in surface (♦) and subsurface (◊) sediment MeHg : THg ratio as a function of Eh (mV).

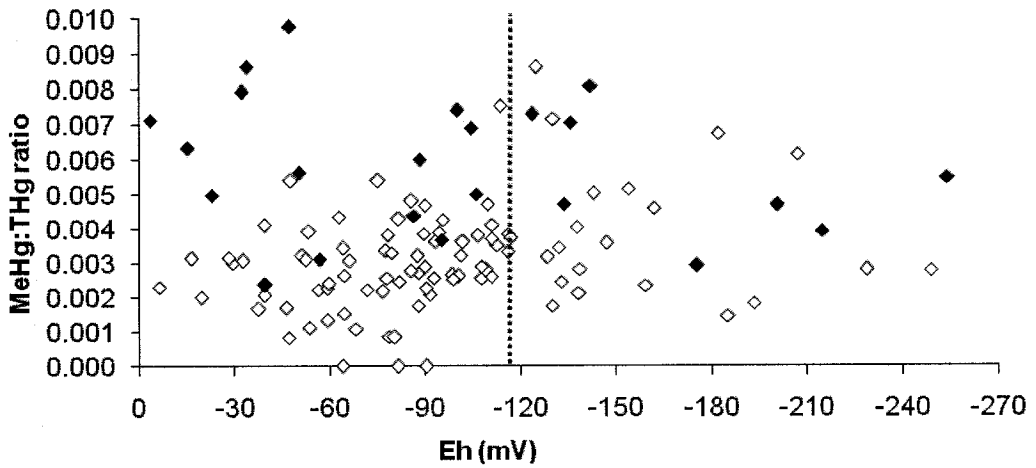


Figure 3.6: Correlations among sediment physical properties [TOC (%, ♦) and surface sediment fines (%, ■)] with respect to sediment bulk density (g cm^{-3}).

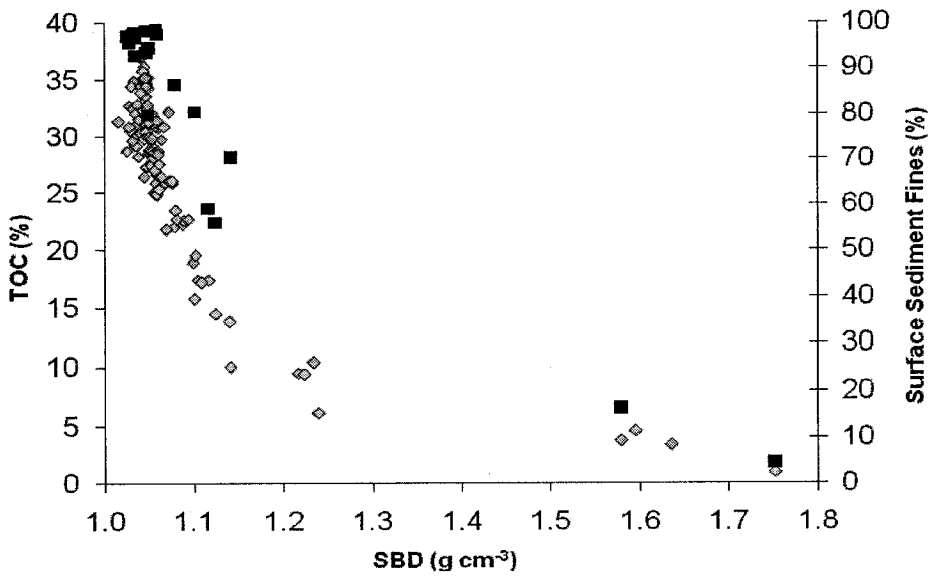
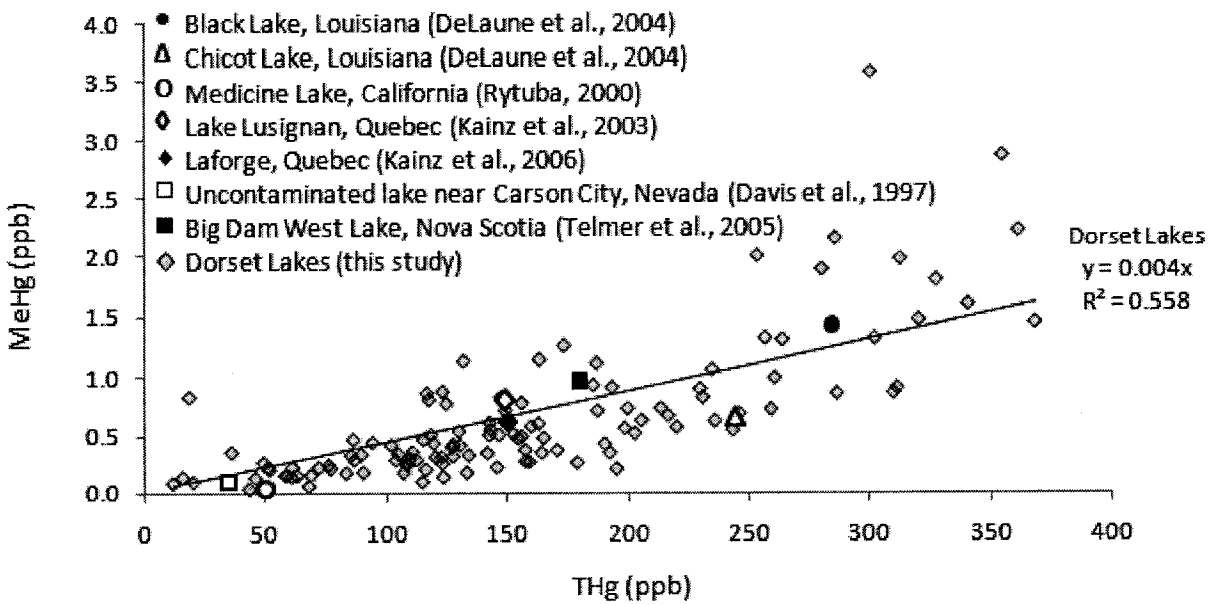


Figure 3.7: MeHg (ppb) versus THg (ppb) for uncontaminated profundal lake sediments (this study and literature values).



CHAPTER 4

PREDICTING MERCURY CONCENTRATIONS AND FLUXES IN THE WATER COLUMN AND SEDIMENT OF LAKES WITH A LIMITED DATASET

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Abstract - The purpose of this study was to evaluate the mercury (Hg) Environmental Ratios Multimedia Ecosystem Sources (HERMES) model on two Ontario lakes (Harp and Dickie) and to include modifications to enable the model to estimate the major model input variables that tend to be missing for lakes with limited datasets. No significant differences were found for either sediment or water mercury (Hg) when the HERMES model was applied to the two Ontario lakes, regardless of whether all available data were altered during application or only the ten variables that tend to cause the most variation in model output (i.e., concentration of Hg in atmosphere, water inflow Hg concentration, water inflow rate, water volume, surface area, mean depth, suspended particulate matter concentration, sedimentation rate of solids in water column, water temperature, and rain rate). Since measured sediment and water Hg values does not currently exist for most lakes removed from industrial activities, empirically-derived linear equations were incorporated into the HERMES model framework in order to provide a method to 'double-check' model output for lakes where this information is unavailable.

Key words: lake, mercury, methyl mercury, model, estimate

4.1 INTRODUCTION

Mercury (Hg) emitted from natural and anthropogenic sources can travel long distances to remote locations as elemental mercury (Hg^0) due to its low water solubility and relatively high vapor pressure. It has a residence time of about one year in the atmosphere (Wiener et al., 2003), but through oxidation processes to Hg^{2+} species it deposits to land and aquatic ecosystems as wet and dry deposition. Once deposited, a portion can be converted to methyl mercury (MeHg), the most toxic form that crosses biological membranes and bioaccumulates in food webs (O'Driscoll et al., 2005; Wiener et al., 2003). Indigenous people are often far removed from anthropogenic sources of Hg, yet these groups often exhibit the highest body burdens due to their consumption of fish and marine mammals.

Mercury speciation and partitioning mass balance models can be used to develop cost-efficient measures to mitigate exposure of humans to MeHg concentrations in fish by improving environmental response estimates to changing Hg loads and conditions. A multimedia mass balance model was developed for Hg using data from Big Dam West, Kejimkujik Park, Nova Scotia and verified for total mercury (THg) (Chapter 2). This Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model combines the multiplier method introduced by Toose and Mackay (2004) for multi-species chemicals with the Quantitative Water Air Sediment Interaction (QWASI) model. Model code is contained within a Microsoft Excel spreadsheet without macros so that calculations could

be more readily understood by non-modelers and adjusted, if needed, as our comprehension of Hg dynamics continues to evolve (see online appendix).

Few models have been developed that can properly represent Hg in remote environments since most were created for systems with large local anthropogenic sources of Hg. Most models also have extensive watershed and lake data input requirements in order to produce estimates. Since most lakes have a limited amount of information available for models, we have attempted to provide simple predictors for the major input variables required. Even though the amount of data the HERMES model requires in order to produce estimates of water and sediment Hg concentrations and fluxes is considerably less than other available Hg models, the results of uncertainty analyses on the HERMES model indicate that this model could provide estimates with even less environmental input data. The model estimates air, water, and sediment fluxes and concentrations for Hg with only ten lake- or location-specific variables (i.e., concentration of Hg in atmosphere, water inflow Hg concentration, water inflow rate, water volume, surface area, mean depth, suspended particulate matter concentration, sedimentation rate of solids in water column, water temperature, and rain rate). Although the HERMES model and the commonly used R-MCM model were both successfully applied to remote Big Dam West Lake (Kejimkujik Park, NS), an extensive dataset was available to facilitate model development. Compilation of this dataset required the efforts of a multi-disciplinary team of twenty scientists studying Hg dynamics in Kejimkujik Park (NS) for over three years (O'Driscoll et al., 2005; Tetra Tech, Inc., 1999). Here we provide simple

estimators of the major model input variables required for model application to lakes where these data are unavailable.

In the present study, the objectives were to evaluate empirically predicted variables against actual measurements in order to test whether the HERMES model can provide estimations of sediment and water Hg concentrations and fluxes within other semi-remote lakes (Harp and Dickie) by adjusting only the most sensitive model variables; and to develop correlations to predict MeHg for food web models. The HERMES model Microsoft Excel workbook, which includes the estimation methods investigated in this study, is available at no cost as an online appendix for this manuscript along with user instructions. Cell locations in the spreadsheets within this workbook are next to the equations discussed in this manuscript.

4.2 SITE DESCRIPTION: HARP AND DICKIE LAKE, DORSET, ONTARIO

The Dorset Environmental Science Centre has monitored a number of lake basins located in south-central Ontario since 1975, providing a long-term continuous environmental monitoring dataset with monthly lake oxygen, temperature, nutrients, major ions, chlorophyll and other water chemistry (Dorset Environmental Science Centre, Ontario, Canada unpublished data). Research and monitoring activities have included trace metal cycling and toxicity, climate related global change, acid precipitation, biological monitoring, and lake nutrient enrichment, among others. The Ontario Ministry of Environment and Ministry of Natural Resources are the two government departments

heading the research at the centre. Harp and Dickie Lake are two of the primary basins studied in the region with Dickie Lake having elevated MeHg concentrations in the water column, sediment, and biota. These lakes are surrounded by forested catchments interspersed with moderate cottage development in a remote region of the Precambian Shield (Hoeniger, 1985). Pioneer settlement was ca. 1850, but there has been no industry and little farming in the past 50 years.

Harp Lake (45°23'N; 79°08'W) is a deep (max depth = 37.5 m) oligotrophic and slightly acidic soft water lake with a surface area of 71.4 ha and a mean depth of 13.3 m. With increasing depth, sediment progresses from a rocky near shore sandy region to a mixture of sand and pebbles at greater depths (Hoeniger, 1985; Molot and Dillon, 1993). Although the lake thermally stratifies during the summer, anoxic conditions do not occur even in the deeper parts of the lake.

Dickie Lake (45°09'N; 79°05'W) seasonally stratifies as well, but is shallower (max depth = 12 m). It is dystrophic and has acidic soft water with a surface area of 93.6 ha and a mean depth of 5.0 m. The sediment is composed of plant litter, sand particles and small stones (Hoeniger, 1985; Molot and Dillon, 1993). Anoxic conditions prevail after the onset of a thermocline in the summer months.

4.3 HERMES MODEL

The HERMES model subdivides Hg into three forms: MeHg, Hg^0, and the remainder, which is referred to as residual mercury and consists of total Hg (THg) minus MeHg and Hg^0 (THg-MeHg-Hg^0). Hg^0 is the dominant species found in the atmosphere, while THg-MeHg-Hg^0 species (mostly as Hg^{2+}) dominate in the water and sediment compartments. MeHg in general constitutes a small percentage (< 1%) of THg in the water and sediment, but at some sites it can be much higher (20-70%). The rationale for including MeHg in the model is that it is the form that biomagnifies in food webs (Rasmussen and Vander Zanden, 2004). To eliminate the need to account for interconversion rates among Hg species, the model merely follows Hg^0 through the lake and the other forms are calculated using compartment-specific concentration ratios. Since Hg species interconversion drives bioavailability, empirical equations need to be added to HERMES so that MeHg : THg ratio can adjust to changing environmental conditions. In each compartment (i.e., air, water, and sediment), THg-MeHg-Hg^0 and MeHg are calculated by multiplying Hg^0 by the corresponding concentration ratio (i.e., THg-MeHg-Hg^0 : Hg^0 or MeHg : Hg^0). THg is then simply the sum of these three forms. Hg^0 was chosen as the "key" species because it does not readily form compounds with other elements and is present to some extent in all environmental media. The underlying assumption in the model is that, on an average yearly basis under steady state conditions, constant concentrations are maintained among the three forms of Hg modeled (i.e., THg-MeHg-Hg^0, MeHg and Hg^0). Although most lakes should be near or at steady-state conditions, some might not be (Harris et al., 2007; Knightes et al., 2008). Ethier et al. (Chapter 2) contains further details about this model, including a detailed account of how it was developed.

The following sections discuss modifications to the model, along with details regarding application to Harp and Dickie Lakes that provides model verification against different datasets. Empirical equations gathered from the literature to estimate the major model input variables and included within the HERMES model framework are also presented in this study. Experimental research conducted to assist with model modifications, reapplication and verification to these lakes is discussed in detail elsewhere (see Chapter 3). In the present manuscript, only details pertaining to how data and equations obtained from this research were incorporated into the HERMES model framework are discussed.

4.3.1 Estimation of major model input variables

Major model input variables are those defined by the modeler during application that can cause the greatest amount of variation in model output for predicted sediment and /or water Hg concentration. Ethier et al. (Chapter 2) performed an sensitivity analysis on Big Dam West Lake, comparable to a Monte Carlo simulations to characterize variance in the data, in order to establish which model input variables had the greatest influence on overall model performance (Table 4.1). Good concentration and flux estimates should be derivable for any new lake as long as accurate estimates for the major model input variables are available. Unlike some other models which require extensive parameterization and calibration for the model to fit measured variables, nothing has been altered in our model except for the lake and location specific variables discussed.

There are a number of general lake characteristics that are available in most databases (Table 4.2). Estimates were needed only for the model input driving variables that are not routinely measured and can be difficult to obtain from the literature (e.g., concentration of Hg in inflow water). Due to their importance to overall model performance, a comprehensive literature review was conducted in order to obtain equations that would enable some of these variables to be estimated from other more readily available data. For example, Hakanson and coworkers have published numerous research papers on property estimation methods, especially with regards to estimating suspended particulate matter (using total phosphorus or secchi depth) in lakes (e.g. Lindstrom, 2000). Estimates of sediment deposition (i.e., sedimentation) and resuspension rates can be obtained from Evans (1994). Each of the equations that were found in the literature was sequentially tested in the model using data from Harp and Dickie Lake.

It is also worthwhile to mention that the model is able to accommodate, as necessary, other direct sources of Hg input such as Hg from local anthropogenic emissions, Hg vertical fluxes from underlying sediments, or terrestrial inputs due to flooding during reservoir creation and changes in water renewal times.

Those equations that were eventually selected for inclusion in the model to enable each of the major model input variables to be measured from other, more commonly measured, environmental data are as follows.

4.3.1.1 Water volume and inflow rate

A mass balance model requires good estimates of lake water volume and flow rates. The following estimates for water volume and inflow rate can be used in the model if some of the inflows into the lake can't be entirely accounted for:

Water Volume (m^3) = Surface Area (m^2) x Mean Depth (m)

['Lake' spreadsheet, CELL L45]

Water Inflow Rate ($m^3\ h^{-1}$) = Water Volume (m^3) x Residence Time (h^{-1})

['Lake' spreadsheet, CELL L47]

Estimating water volume and inflow rates using these equations is commonplace in the literature; equations were obtained from Mackay (2001).

4.3.1.2 Water inflow Hg concentration

Mercury that is deposited in a given watershed should eventually be exported into the lake at relatively constant (annual) and quantifiable rates. Thus, at steady-state conditions it serves as a measure of the concentration of Hg in lake inflow water (derived from Grigal, 2002).

Ln (Concentration of Hg in inflow water ($ng\ L^{-1}$))

= 2.02 – 0.063 x Ln (Watershed (km^2)) ['Lake' spreadsheet, CELL L49]

Although the strength of correlation for the above equation is relatively low ($r^2 = 0.11$), the watersheds used to derive this equation varied over several orders of magnitude which lends some credibility to this estimate (i.e., linear over a wide range). It is unfortunate that higher quality equations to estimate this variable could not be obtained from the literature.

4.3.1.3 Suspended particulate matter

Suspended particulate matter is material that is greater than 47 μm in size that is suspended in the water column of a lake (Oliveira et al., 1999). Given that suspended particulate matter could be derived from several sources (e.g., resuspended, autochthonous, or allochthonous) and vary in composition (e.g., inorganic versus organic), it was decided to include two estimates that use different lake variables.

From Lindstrom et al. (1999) ($r^2 = 0.74$):

Log_{10} (Suspended particulate matter (mg L^{-1}))

=1.56 x Log (Total Phosphorus (μg L^{-1})) – 1.69 ['Lake' spreadsheet, CELL L52]

From Hakanson (2006) ($r^2 = 0.78$; n = 573 lakes):

Log_{10} (Suspended particulate matter (mg L^{-1}))

= ((Log (Secchi depth (m) – 0.769) / -0.698) –1 ['Lake spreadsheet, CELL L53]

4.3.1.4 Sedimentation and resuspension rates

The sedimentation (or deposition) rate of suspended particulate matter can depend on deposition velocity (i.e., sedimentation rate) of particles (a function of size, shape and weight), the type of suspended material, and water decomposition rates (Deckere, 2003). Sedimentation rates have been found to vary from 0.5 to 8.0 m d^{-1} depending on water turbulence (Malmaeus, 2004). Evans (1994) derived an equation to calculate gross sedimentation in lakes from sediment trap data as a function of the mean depth of the lake (up to a maximum mean depth of 13 m) since deeper lakes should experience less water turbulence than shallow lakes ($r^2 = 0.14$; $p < 0.001$; $n = 29$) (i.e., sedimentation rate tends to be higher in shallow lakes).

Gross Sedimentation Rate (g m^{-2} day^{-1}) = 1.04 – (0.07 x Mean Depth (m))

['Lake' spreadsheet, CELL L56]

Wind turbulence and bioturbation, to a lesser extent, are the main processes controlling sediment resuspension in lakes (Deckere, 2003). Thus, it is not surprising that Evans (1994) found resuspension rate to be reduced by 70 mg m^{-2} day^{-1} per m as depth increases for small deep lakes. Sediment resuspension rate is defined, for the purposes of this study, as the amount (expressed as percent) of deposited material that undergoes resuspension within lakes (converted to g m^{-2} day^{-1} in HERMES model). A default resuspension rate of 80 % was used for all shallow (mean depth < 8.5 m) and larger lakes (surface area > 1 km^2 regardless of depth), since this rate should be substantially less than

80% only in small deeper lakes. Blue Chalk Lake, a lake near Harp and Dickie Lake, was used as the baseline from which resuspension rates were calculated for the small deeper lakes since mean depth (8.5 m) and sediment resuspension rate (90 %) were available from Evans (1994).

Resuspension rate (% of deposition) = 90 x (850 - ((Mean Depth (m) - 8.5) x 70)) / 850

['Lake' spreadsheet, CELL L57]

4.3.2 Estimation of MeHg : THg ratio (for use in food web applications)

Methyl Hg formation, and subsequent food chain transfer and accumulation by fish, is influenced by a number of lake-specific factors, including sediment THg concentrations, watershed area, water temperature, and certain water chemistry variables, especially pH / alkalinity, and concentrations of dissolved organic matter and sulfate (Bodaly et al. 1993; Gilmour and Riedel, 2000; St. Louis et al., 1996). For example, a larger watershed, high lake dissolved organic carbon concentration (often related to wetland area, where Hg methylation is very rapid) and / or low pH (HgS more bioavailable for methylation by bacteria, via diffusive uptake) will promote methylation within the sediments (Gilmour and Riedel, 2000; Bjornberg et al., 1988). Few research papers attempt to correlate MeHg, THg, and / or MeHg : THg ratio in environmental media (except biota) with watershed variables, but estimates were found for inflow water, water column and sediment in lakes through experimental research (Chapter 3) and a review of available literature.

Even though the HERMES model uses the MeHg : Hg^0 ratio in model calculations, it is not a value that is ever actually measured and reported in the literature since there was no reason to do so. On the other hand, information on the relative amount of methylated Hg (MeHg : THg) for a number of different systems and environmental media can readily be obtained from available literature (Kainz et al., 2006). In order to adjust the MeHg : THg ratio in the model during application, we assumed that Hg^0 was unaffected by variations in MeHg : THg ratio (i.e., MeHg : THg times fixed Hg^0 : THg equals MeHg : Hg^0 ratio).

A range of MeHg : THg ratios can be expected for different environmental media. Kamman et al. (2005) reported water MeHg : THg averages +/- standard deviations that can be expected for three types of freshwater bodies (River = 0.044$\pm$0.004; Reservoir = 0.029$\pm$0.004; and Lake = 0.018+0.003). Model default values for water column, water inflow, and sediment were borrowed from Harp Lake. The default MeHg : THg ratio used for the water column was 0.030 (Bodek, 2008; Sosso-Kolle, 2008). Since oligotrophic Harp Lake has some reservoir characteristics (i.e., beaver dams and weir), the ratio for water fits with the averages reported by Kamman et al. (2005). In comparison, Dickie is a brown dystrophic lake with a MeHg : THg ratio of 0.050 for the water column. The default MeHg : THg ratio of 0.004 for sediment was used for model application, as no significant difference was found between sampling dates and MeHg was highly correlated to THg in all samples (more littoral to pelagic) collected from these lakes (Chapter 3). Water inflow default value for MeHg : THg ratio was 0.088 (Dickie Lake = 0.140) (Bodek, 2008; Sosso-Kolle, 2008). The default MeHg : THg ratio for air

was assumed (Toose and Mackay, 2004). These defaults for MeHg : THg (used to derive model MeHg : Hg^0 ratio) are sufficient to properly model THg in the environment. Estimated (or even measured) MeHg : THg ratios for the sediment, water, water inflow or even air should only be considered (rather than using default values) if model output is intended for food web applications, since MeHg generally constitutes < 5% THg in lakes.

Seasonal stratification typically occurs in lakes that exceed a maximum depth of 5 m, although large variations exist in depth of thermocline formation from lake to lake [2 m to more than 20 m (especially in clear and transparent southern lakes)] (Horne and Goldman, 1994). This phenomenon, resulting in anaerobic conditions at the sediment surface and lowered redox potentials (-ve), has been suggested to be a requirement for MeHg formation (related to MeHg : THg ratio) in lakes (Croston et al., 1996; DeLaune et al., 2004). On the contrary, Regnell and Ewald (1997) found that sediment MeHg levels decreased during summer stratification in the pelagic region until August before eventually increasing again. Ethier et al. (Chapter 3) found a significant correlation between MeHg : THg ratio and redox potential or total organic carbon, but not with respect to thermocline formation. The redox potential (mV) and total organic carbon (TOC, %) were significantly correlated with MeHg : THg, but not with each other, and could explain more of the variation in sediment MeHg : THg ratio when considered together ($r^2 = 0.27$).

Log_{10} (Sediment MeHg : THg)

= -1.9025 - 0.0086 x TOC (%) + 0.0011 x Redox potential (mV)

['Lake' spreadsheet, CELL P22]

The equation provides an estimate of sediment MeHg : THg ratio (used to adjust MeHg : Hg^0 ratio in model – Hg^0 is held constant). The relative amount of methylated Hg (expressed as MeHg : THg) in sediments is a difficult variable to estimate, as a thorough search of the literature couldn't produce a better estimation method. According to this equation, it can be expected that relative amount of methylated Hg in lake sediments will increase in areas where there is less total organic carbon and a higher redox potential. At first glance, this equation appears to be contrary to what previous research has found, but in could actually merely be a function of Hg bioavailability (i.e., in littoral regions the redox is higher, the TOC is lower, and more MeHg is being formed per unit of Hg available). Since less Hg is available for methylation in littoral sediments, a higher percentage of the available Hg pool will undergo methylation. Runoff from the surrounding watersheds (i.e., direct or via stream inflows) is another possible reason for elevated ratios since wetlands tend to have higher MeHg : THg ratios than lakes (Holmes and Lean, 2006; Kainz et al., 2003). Ethier et al. (Chapter 3) found a significantly higher concentration of MeHg in the profundal compared with the littoral region or their study lakes, but the MeHg : THg ratio was greater in the littoral region.

A method to estimate water MeHg : THg ratio was derived from equations used to predict MeHg ($r^2 = 0.53$) and THg ($r^2 = 0.75$) using dissolved organic carbon (DOC) (Meng et al., 2005). DOC binds Hg, assisting in its transport from neighboring wetlands to the lake and increasing bioavailability for methylation (Peckenhame et al., 2007).

For summer and DOC < 20 mg L^{-1}:

Water MeHg : THg = (-0.4 + 0.128 x DOC (mg L^{-1})) / (0.48 x DOC (mg L^{-1}))

['Lake' spreadsheet, CELL P21]

The amount of wetland in the watershed (%) was used to estimate the water inflow MeHg ($r^2 = 0.24$; $p < 0.0001$; $n = 79$; derived from Shanley et al., 2005) and the watershed area was used to estimate the water inflow THg (Grigal, 2002). Dividing the estimated MeHg by the THg produces the estimated MeHg : THg ratio used in the model.

$$\text{Water Inflow MeHg : THg} = 10^{((\%\ \text{wetland} \times 0.056) - 1.12)} / e^{(2.02 - 0.063 \times \text{Ln (Watershed (km2)))}}$$

['Lake' spreadsheet, CELL P25]

Since the relative amount of methylated Hg tends to be highest in wetland areas, those watersheds with extensive wetlands should have more MeHg per unit of THg available than lakes with little to no surrounding wetland (Shanley et al., 2005). Peckenham et al. (2007) found that wetlands mobilized more Hg from the watershed than uplands by producing more DOC, even though the upland could transport more Hg per unit of DOC.

Methyl Hg and THg data for Harp and Dickie Lake sediment (Chapter 3), along with water inflow and water column ratios (Bodek, 2008; Sosso-Kolle, 2008) were used to confirm MeHg : THg estimates that were obtained or derived from the literature.

4.3.3 Vapour pressure

Elemental Hg is a volatile element, so the vapour pressure is sensitive to changes in environmental temperature. Unfortunately, the vapour pressure in the HERMES model was not sensitive to changes in lake temperature. It was therefore decided to include an equation that would enable the model to adapt to ambient temperature changes. In order to make the vapour pressure of each of the Hg species sensitive to changes in environmental temperature, the Clausius-Clapeyron equation was used.

$$VP_2 = VP_1 \times \exp\left(-\left(\Delta H_{vap} / R\right)\left(1 / T_2 - 1 / T_1\right)\right)$$

['Environment (Input)' spreadsheet, CELL B15-D15]

where VP_2 (Pa) is defined as vapour pressure at environmental temperature (T_2, K); VP_1 is a known vapour pressure related to a given temperature (T_1); ΔH_{vap} is change in heat of vaporization; and R is the gas constant. VP_1 and T_1 for each of the Hg species were obtained from the literature (Environment Canada, 2003). In addition, an equation was included in the model code so that the water solubility of elemental Hg would vary with temperature changes as well (Loux, 2000).

$$\text{Water solubility (mg L}^{-1}) = 8000000 \times 10^{(-122.911 + (4475.3 / T2) + (40.2205 \times \text{Log (T2)}))}$$

['Environment (Input)' spreadsheet, CELL B11]

The model mass transfer coefficients (MTCs, m h^{-1}) for air-side volatilization (2) and water-side volatilization (0.02) originate from Toose and Mackay (2004) ['Environment (Input)' spreadsheet, CELL H32-33]. Loux (2000) reported MTCs for air-side (9) and water-side (0.09) volatilization that were over four times higher than those currently used in the model. It is recommended that the volatilization MTCs reported by Loux (2000) be used for model application to large (>20 km^2) unsheltered (or windy) lakes with minimal ice cover in the winter since these conditions would tend to favor higher volatilization MTCs ['Environment (Input)' spreadsheet, CELL I32-33].

4.4 MODEL APPLICATION AND VERIFICATION

An abundance of data (past and present) exists from on-going research conducted in lakes near Dorset, ON, thus facilitating model reapplication in this region. Included amongst the available data was invaluable information regarding weekly MeHg along with some THg measurements for lake water inflow and outflow for Harp and Dickie Lake, Dorset, ON. These values were used either as model input (e.g. concentration of Hg in water inflow, MeHg : THg ratio for water column (equals lake outflow ratio)), or to verify model output (e.g. water column THg approximates outflow THg). The HERMES lake model was applied and verified against data from these two chemically and physically different lakes in order to check model performance and consistency.

The model output for Harp Lake (sediment solids Hg = 127.8 ng g^{-1}; water dissolved Hg = 1.74 ng L^{-1}) and Dickie Lake (sediment solids Hg = 120.2 ng g^{-1}; water dissolved Hg =

2.17 ng L^{-1}) was comparable to measured concentrations [Harp: deeper (20 - 25 cm) sediment solids Hg = 124.7 $\pm$ 52.2 ng g^{-1} (n = 9) (Chapter 3) and water dissolved Hg = 1.60 $\pm$ 0.31 ng L^{-1} (n = 10) (Bodek, 2008; Sosso-Kolle, 2008); Dickie: deeper (20 - 25 cm) sediment solids Hg = 123.1 $\pm$ 36.7 ng g^{-1} (n = 6) (Chapter 3) and water dissolved Hg = 2.17 $\pm$ 0.77 ng L^{-1} (n = 11) (Bodek, 2008; Sosso-Kolle, 2008)] for these lakes. Model output for sediment solid Hg for these two lakes was comparable to the littoral and deeper (20 - 25 cm) pelagic sediments, and roughly three times less than the surface (0 - 10 cm) sediments in the pelagic region (Harp = 335.7 ng g^{-1}; Dickie = 291.2 ng g^{-1}) (Chapter 3). These results are comparable to the pattern observed with the HERMES model output for Big Dam West, Kejimkujik Park, NS (Chapter 2).

Since no measured data were available for suspended particulates, total phosphorus was used to estimate suspended particulate matter (Harp = 0.463 mg L^{-1}; Dickie = 0.848 mg L^{-1}). Doubling the suspended particulate matter in each lake resulted in a decrease in sediment solid Hg (Harp = 10 %; Dickie = 17 %) and water dissolved Hg (Harp = 10 %; Dickie = 18 %). The resuspension rate was adjusted for Harp Lake (54.4 % resuspension; calculated using estimation method in'Lake' spreadsheet, CELL L57) to account for the high mean depth to surface area (default assumes 80 % resuspension). Estimates for resuspension rate and suspended particulate matter were borrowed from the equations discussed earlier in this paper.

In order to determine whether the model could actually produce good Hg estimates with a limited amount of information, it was put to the test on Harp and Dickie Lake. The only

variables altered from those in the original HERMES model, other than MTCs mentioned above, were: concentration of Hg in air, rain rate, lake temperature, surface area, mean depth, water volume, water inflow rate, suspended particulate matter, along with deposition and resuspension rates (input data listed in Table 4.2). Model output for dissolved THg in water (Harp = 1.99 ng L^{-1}; Dickie = 2.62 ng L^{-1}) and sediment solids (Harp = 132.0 ng g^{-1}; Dickie = 130.0 ng g^{-1}) was close to the measured values [water dissolved Hg (Harp = 1.60 $\pm$ 0.31 ng L^{-1}; Dickie = 2.17 $\pm$ 0.77 ng L^{-1}) and deeper (20-25 cm) sediment Hg (Harp = 124.7 $\pm$ 52.2 ng g^{-1}; Dickie = 123.1 $\pm$ 36.7 ng g^{-1})] for these two lakes. Uncertainty analyses on Harp and Dickie Lake indicated that sedimentary processes and water Hg concentration ratios (THg-MeHg-Hg^0 : Hg^0) are likely more important input variables in lakes with longer water residence times (Table 4.1). Although additional variables could be altered to potentially further improve model performance, this test demonstrates the true strength of the model in its capability to provide reasonable estimates with a limited amount of data.

4.5 DOUBLE-CHECK' FOR MODEL OUTPUT

There are those that perform the experimental research and others who use these results to develop models that produce concentration and flux estimates, and few ever venture across this imaginary line. A 'double-check' for concentration of THg in water and sediment was thus incorporated into the model to enable the model output to be directly compared against empirically derived equations to increase overall confidence in model estimates when reapplied in regions where no Hg data is available.

4.5.1 Concentration of THg in sediment

Total organic carbon (TOC) can explain up to 70 – 94 % of the variability of THg in soils located in environments receiving large Hg inputs from a natural atmospheric inorganic Hg source (volcano or high subsurface till) or from general atmospheric Hg deposition (Tomiyasu et al., 2003). Ethier et al. (Appendix 1B) found a 0.044 $\mu g\ g^{-1}$ increase in soil Hg with every 10 % increase in TOC. A comparable increase was found for sediment Hg in both the Dorset (Chapter 3) and Clyde Forks (Appendix 1A), Ontario lakes (data combined), but only at lower (< 30 %) TOC levels ($r^2 = 0.37$).

Sediment with TOC < 20%: Sediment THg ($\mu g\ g^{-1}$) = 0.0044 x TOC (%) + 16.225

['Lake' spreadsheet, CELL P12]

For locations that have low sediment organic carbon levels (< 20%) and no measured sediment THg, this estimation method may provide a better sediment THg estimate than HERMES since sediment TOC may impact model performance. The influence of TOC on THg dissipates (slope ~ zero) as TOC increases, so model output sediment THg should be close to measured values for TOC > 20%. For example, predicted sediment Hg using this equation for Cameron Lake, Ontario would be 89.6 ng g^{-1} (measured: 93.9 ng g^{-1}) since sediment TOC is 16.6% (data from Mills et al., PhD thesis in progress).

4.5.2 Concentration of THg in water

Meng et al. (2005) developed a series of linear equations to model DOC, THg and MeHg in freshwater lakes located within Kejimkujik Park, NS. DOC was found to be a good predictor of THg concentration in the water column ($r^2 = 0.75$).

Water with DOC < 20 mg L^{-1}: Water THg (ng L^{-1}) = 0.48 x DOC (mg L^{-1})

['Lake' spreadsheet, CELL P13]

The equation is suitable for estimating water column Hg concentrations when only DOC, or a limited number of physical / chemical variables are available, but does not provide any indication or estimate of the overall Hg dynamics or how a given lake might respond to change. For example, predicted lake water column Hg using the equation above would be 1.8 ng L^{-1} for Harp Lake (DOC = 3.7 mg L^{-1}) and 2.5 ng L^{-1} for Dickie Lake (DOC = 5.2 mg L^{-1}) (measured values: Harp = 1.60 $\pm$ 0.31 ng L^{-1}; Dickie = 2.17 $\pm$ 0.77 ng L^{-1}). Even though the equation was included in the model to double-check model output against an empirically derived equation and to improve confidence in overall model performance, it does not replace the value of the model itself.

For researchers who are wary of models, this 'double-check' for the model against empirically derived equations should improve their overall confidence in model performance and thereby increase the likelihood that the HERMES model will be used by a broad and diverse group of scientists.

4.6 DISCUSSION

The HERMES model, along with the modifications discussed in this manuscript, could serve as a valuable tool for conducting risk assessments in remote areas that have limited datasets to work with, especially if the model was incorporated into a Geographical Information system (GIS) platform. A food web model integrated with the HERMES model could also be used to determine what impact these various scenarios would have on fish or humans, using the output from the model discussed in this paper.

Other potential future applications of the model could include contaminated environments (e.g., the Great Lakes), to explore the impacts of various dam construction strategies, to study Hg vertical flux from underlying sediments, or climate change research. There is an emission to water term in the model code that was intentionally included in order to account for direct sources of industrial contamination to the lake, if any exist. Peak and long-term impacts of various dam construction strategies on sediment, water and fish (with food web model) could be explored prior to construction. When new dams are constructed along a river system, the topography of the land, flow rate, distance between dams, and the height of dam wall are known and can be used to calculate the reservoir volume and the amount of flooded land. From this data, the model can be used to calculate expected peak (includes max emission to water from flooded land) and long-term Hg concentrations once the reservoirs have stabilized (without emission from flooded land). Although the topic remains highly controversial, the emission from underlying sediment (ES) term in the model code can be used to account

for either past industrial re-emissions or a potential natural emission from the underlying sediment. The HERMES model is now sensitive to lake temperature variations, thus enabling the model to be used in much colder or warmer climates or to study the impact of climate change on Hg distribution.

The uncertainty analyses conducted on the HERMES model highlights the need for more research on water inflow THg concentration and sediment deposition, resuspension and burial rates (Table 4.1), along with water column concentration ratios (THg-MeHg-Hg^0 / Hg^0). Of all the variables tested in the model, these variables are without a doubt the most important determinants of overall model performance for small lakes. As estimates for these variables improve, a corresponding improvement should be observed in the estimates the model provides. Since suspended particulate matter is an important variable that is not too difficult to measure, it should be included with all the other water chemistry variables (e.g., secchi depth, total phosphorus, DOC) that are routinely measured in lakes.

Further research and model modifications could focus on the incorporation of estimation methods (i.e., equations) to account for transient processes within surface sediments, since the enriched pelagic surface sediments are most likely a combination of focusing and Hg remobilization from underlying sediments. Lars Hakanson (2005) discussed equations that could be used to predict sedimentation, resuspension and burial rates based on lake morphometry characteristics that could improve estimates for these sedimentary processes in the model if the required data is available. Predictive equations relating

volatilization MTCs with lake and location specific variables (e.g., wind velocity and ice cover) would be valuable as well. Presently, the model must fix the relative amount of Hg^0 in order to utilize MeHg : THg ratios from the literature. The inclusion of an equation relating Hg^0 to watershed and / or lake variables could thus improve the realiability of the MeHg : THg estimates within the model since the relative amount of Hg^0 would adapt to changes.

4.7 CONCLUSION

Even though the HERMES model was originally developed for Big Dam West, Nova Scotia, this study demonstrates how readily the model can be applied to lakes in other provinces within Canada. In addition, the inclusion of equations to estimate the major model input variables within the model framework should undoubtedly increase the number of lakes to which the model can readily be applied. As long as the next lake to which the model is applied has physical and chemical characteristics within the range where model performance has been demonstrated, the model should fit the data. Caution needs to be applied during model application if the lake falls outside these ranges.

Studying Hg dynamics in the environment can quickly become overwhelming, thus making it difficult to pinpoint major gaps in our understanding. Multimedia models could serve as a valuable tool to explore all the various aspects of Hg flux and fate in lakes simultaneously. Exploring every aspect of Hg dynamics is worthwhile, but the

main focus should be on those variables that are the most important determinants of Hg fate in the environment.

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Table 4.1: Major contributors to variance in model output.

Input variable	water (%)	sediment (%)
Big Dam West (adapted from Chapter 2)		
Concentration of mercury in air (ng m^{-3})	<0.1	<0.1
Concentration of mercury in inflow water (ng L^{-1})	28	10
Water inflow rate (m^3 h^{-1})	72	26
Suspended particulate matter (mg L^{-1})	<0.1	17
Density of water particles (kg m^{-3})	<0.1	0.1
Sedimentation rate (g m^{-2} day^{-1})	<0.1	25
Sediment burial rate (g m^{-2} day^{-1})	<0.1	<0.1
Sediment resuspension rate (g m^{-2} day^{-1})	<0.1	22
Water (dissolved phase) (THg-MeHg-Hg^0 :Hg^0)	0.3	0.3
Sediment (solid phase) (THg-MeHg-Hg^0 :Hg^0)	<0.1	0.1
Total	**100**	**100**
Harp Lake		
Concentration of mercury in air (ng m^{-3})	<0.1	0.1
Concentration of mercury in inflow water (ng L^{-1})	15.4	32.3
Water inflow rate (m^3 h^{-1})	12.2	25.6
Suspended particulate matter (mg L^{-1})	0.6	1.4
Density of water particles (kg m^{-3})	1.2	4.6
Sedimentation rate (g m^{-2} day^{-1})	44.2	2.1
Sediment burial rate (g m^{-2} day^{-1})	5.4	18.7
Sediment resuspension rate (g m^{-2} day^{-1})	16.3	1.1
Water (dissolved phase) (THg-MeHg-Hg^0 :Hg^0)	4.6	13.5
Sediment (solid phase) (THg-MeHg-Hg^0 :Hg^0)	<0.1	0.5
Total	**100**	**100**
Dickie Lake		
Concentration of mercury in air (ng m^{-3})	0.4	0.7
Concentration of mercury in inflow water (ng L^{-1})	17.0	31.3
Water inflow rate (m^3 h^{-1})	13.0	24.0
Suspended particulate matter (mg L^{-1})	2.5	5.2
Density of water particles (kg m^{-3})	0.9	5.2
Sedimentation rate (g m^{-2} day^{-1})	34.1	0.1
Sediment burial rate (g m^{-2} day^{-1})	1.7	4.5
Sediment resuspension rate (g m^{-2} day^{-1})	19.2	1.2
Water (dissolved phase) (THg-MeHg-Hg^0 :Hg^0)	11.2	26.4
Sediment (solid phase) (THg-MeHg-Hg^0 :Hg^0)	<0.1	1.0
Total	**100**	**100**

Table 4.2: Main location and lake specific input variables for the HERMES lake model (adapted from Chapter 2).

	Dickie Lake	Harp Lake
A General lake characteristics		
Surface area (km^2)	0.93	0.76
Mean depth (m)	5.0	13.3
Water volume (m^3)	4.67×10^6	9.51×10^6
Water temperature (^oC)	11.5	9.4
B Atmospheric values		
Precipitation ($m\ yr^{-1}$)	0.908	0.906
Mercury concentration in air ($ng\ m^{-3}$)	1.52	1.52
C Major model input variables		
Mercury concentration in inflow water ($ng\ L^{-1}$)	6.52	4.72
Water inflow rate ($m^3\ h^{-1}$)	281	310
Suspended particulate matter ($mg\ L^{-1}$)	0.848	0.463
Deposition rate of solids ($g\ m^{-2}\ day^{-1}$)	0.304	0.304
Sediment resuspension rate (% of deposition)	80	54

CHAPTER 5

ESTIMATING MERCURY CONCENTRATIONS AND FLUXES WITHIN THE WATER COLUMN AND SEDIMENT OF LAKE ONTARIO WITH THE GENERAL HERMES MODEL

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Abstract - The general Hg Environmental Ratio Multiple Exposures and Sources (HERMES) model was developed from data from Big Dam West, Nova Scotia and tested on several smaller lakes in Ontario. Here it is applied to one of the Great Lakes of the world (Lake Ontario) in order to evaluate model performance on a much larger lake, which has a drainage basin containing 10 million people. In addition, this model will be compared to the model output from two other mechanistic models (LOTOX2 and STELLA) for this lake. Even though only eleven lake and drainage basin variables (i.e., water temperature, precipitation rate, concentration of Hg in air, surface area, mean depth, water volume, water (stream) inflow rate, concentration of Hg in inflow water, inflow / water suspended particulate matter, and sedimentation rate) were required to run the HERMES model, average predicted model output was significantly correlated to the LOTOX2 and STELLA mechanistic models.

Sensitivity analysis on HERMES model output indicated that the main source of Hg input to Lake Ontario was the atmosphere, compared with the watershed source found for Big Dam West Lake, Kejimkujik Park, Nova Scotia. This contrasts with the view that the Niagara River is the main source of Hg to this lake.

Keywords: model, HERMES, mercury, Hg, lake, Lake Ontario, LOTOX2, STELLA

5.1 INTRODUCTION

Models are essential for the integration of information. They enable large data sets to be synthesized in a systematic way and put into perspective. Data relationships can be examined and queried within a structure that recognizes the processes that occur simultaneously in our environment, regardless of whether they are mechanistic or general in nature. General models serve as screening level tools to guide Hg research prior to sampling or to assess different policy initiatives and mechanistic models allow for a more detailed examination of Hg dynamics.

In elemental form (Hg^0), mercury (Hg) can travel to remote locations throughout the environment and deposit to lakes and watersheds as divalent Hg (Hg^{2+}), subsequently partitioning to solids and / or undergoing bacterial methylation and bioaccumulation through foodwebs (Wiener et al., 2006; Chapter 3). Numerous interconversion rates must therefore be accounted for, especially among the Hg species, in order to fully grasp the chemical speciation dynamics and reaction rates within a model framework. Several models that use interconversion rates to predict Hg dynamics within lakes include the Regional Mercury Cycling Model (R-MCM) (Tetra Tech Inc., 1996) and the Lake Ontario Toxicity (LOTOX2) Hg submodel (Atkinson et al., 2007).

An alternative approach to modelling Hg involves the use of concentration ratios (i.e., speciation coefficients). It is a method that tends to be more useful for screening level applications (e.g., assess which lakes likely contain more Hg than others), compared with

the more mechanistic models mentioned above (i.e., fewer input variables). Examples include the Fugacity / Aquivalence Quantitative Water Air Sediment Interaction (FA-QWASI) model (Diamond, 1999), Mercury Regional Fate Model (Macleod et al., 2005), and more recently the Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model (Chapter 2).

HERMES is a mass balance steady-state model (Chapter 2) that considers the dynamics of the three main Hg forms; Hg^0, methyl mercury (MeHg) and residual mercury (total mercury minus elemental and methyl mercury - THg-MeHg-Hg^0). Residual Hg is primarily composed of inorganic species (i.e., Hg^{2+}). Concentration ratios between MeHg and THg-MeHg-Hg^0 with respect to Hg^0, the ``key`` species modelled, are assumed to be constant on an average annual basis. Originally, this model was developed and verified with data from a well-studied remote lake (Big Dam West) in Kejimkujik Park, NS. Advective and diffusive processes between air, water and sediment, along with inflows and outflows from the system are accounted for as transport parameters (D) in the model. Fluxes are obtained by multiplying these D values by the appropriate fugacity (F). The HERMES model can be downloaded from the 'Environmental Toxicology and Chemistry' website as an online appendix for Ethier et al. (Chapter 4).

Experimental research (Chapter 3) and a review of available literature were collectively used to provide estimation methods for the sensitive model input variables established by Ethier et al. (Chapter 2) that enable model application to remote lakes with limited information (Chapter 4). Model evaluation was performed through application of the model to thirty-

five remote lakes in Ontario (Chapter 6), altering only six model input variables with each application. To improve the estimates used for water inflow Hg, the model was used to backcalculate these values for each of the thirty-five lakes using available measured sediment Hg concentrations once error contributions from the other estimates had been minimised. A multiple regression of backcalculated water inflow Hg against watershed and lake data was used to derive the equation that could be employed to estimate this input variable. An application of this equation to estimate water inflow Hg to sixteen other lakes (Antarctica to Canada) revealed a significant ($p < 0.05$) improvement over the previous literature estimate (Chapter 4) and a good correlation ($p > 0.20$) with mean measured values. Estimates were consistently within reported ranges as well.

The main objective of this study was to further evaluate performance of the HERMES model through application to a large well-studied lake (Lake Ontario) with urban and non-urban areas, as the model has been applied only to small remote lakes thus far. HERMES model output was then compared and contrasted against another recognized mechanistic Hg model that was previously developed for the same lake.

5.2 LAKE ONTARIO

The Great Lakes basin contains five lakes that are crucial to international maritime commerce and hold about 20% of the world`s surface freshwater (Petering and Klump, 2003). Lake Ontario (Figure 5.1) is the furthermost downstream and smallest of the Great Lakes chain, even though it is the 14th largest lake in the world (surface area: 18960 km^2)

and over 1700 times larger (by surface area) than any of the other lakes previously studied (Chapter 6). The general characteristics of Lake Ontario are listed in Table 5.1.

Agricultural and large urban (e.g., Toronto, Hamilton, Buffalo) sectors are situated within the Lake Ontario watershed. The Niagara River, which drains into Lake Ontario, receives effluent discharge from numerous industries (e.g. steel mills, coal fired generating stations, and chloralkali plants (previous source)) and was historically the primary source of Hg to lake sediments. Eventually, water contained within this lake discharges into the St. Lawrence River (US EPA, 2006). Lake Ontario was the most contaminated of the entire Great Lakes with respect to Hg, although in recent years the surface sediment Hg has declined by approximately 25% from 1968 (0.790 μg/g) to 1998 (0.586 μg/g) (Marvin et al., 2007). Based on these declining trends and the relatively short water residence time (6 years), most of the lake (i.e., surface sediment has a longer clearance rate than water column) should be near the steady-state conditions required for HERMES model verification.

Lake selection was based on the abundance of measured Hg values for model verification, estimates from LOTOX2 / STELLA models, and the large surface area and relative homogeneity of sediments (variation does exist between nearshore and offshore) within Lake Ontario (Atkinson et al., 2007).

5.2.1 Mercury monitoring

Lake Ontario is one of the more intensively studied lakes in North America. The major Hg monitoring programs that were developed for this lake include Environment Canada's sediment survey and the Lakewide Management Plan (LaMP) (US EPA, 2006).

Environment Canada routinely collected hundreds of sediment surface and core samples for all the Great Lakes and the St. Lawrence River from 1968 to 2004 in order to examine spatial and temporal trends with respect to Hg. For example, Marvin et al. (2002a; 2002b; 2007) and Thomas (Thomas, 1972) published some of the measured data from this sampling program which includes suspended, surface and subsurface sediment trends within Lake Ontario (Table 5.2).

As part of the Great Lakes Water Quality Agreement (GLWQA), a Lakewide Management Plan (LaMP) was developed for each of the five Great Lakes. The Lake Ontario LaMP is aimed at reducing chemical pollutants entering the lake and addressing factors that impact the lake (US EPA, 2006). The most recent 2006 status report provides updated information regarding atmospheric Hg loadings through the Lake Ontario Atmospheric Deposition Study (LOADS), along with tributary loadings and water column total, reactive and dissolved gaseous Hg (Lai et al., 2007; US EPA, 2006) (Table 5.2).

In short, almost all of the measured data needed to verify HERMES model output originated from either one of these recognized research programs for this well-studied lake.

5.3 MECHANISTIC MODELS

Atkinson et al. (2007) described the development and verification of a coupled Hg modeling framework for Lake Ontario that required interconversion rates (i.e., first-order rate constants) among species in order to model Hg dynamics and chosen as the mechanistic models that the general HERMES model would be compared with.

5.3.1 LOTOX2 Hg submodel

As the name implies, the Lake Ontario Toxicity model (LOTOX1) and the more recent version (LOTOX2) were designed to model chemical fate within Lake Ontario (DePinto et al., 1997; 1999). The main difference between these two model versions is that LOTOX1 considers the Lake Ontario water column as a single segment, compared with the increased spatial resolution of twenty-two water column segments in LOTOX2. Since Hg is a Lake Ontario LaMP priority pollutant, a submodel was created within LOTOX2 so that the model could account for the distribution of Hg in this lake (Atkinson et al., 2007). Given that the LOTOX2 model was designed for PCBs (one species), some chemical structural components of the original model were modified so that the submodel presented here could consider multiple Hg species. Other model components, such as the physical structure and transport terms, remained the same.

The LOTOX2 model differentiates between the epilimnion (fourteen segments) and the hypolimnion (seven segments), with vertical and horizontal fluxes between each segment (Figure 5.1). Fluxes to and from the hypolimnion or nearshore epilimnion to sediment (fourteen segments) are also included. LOTOX2 requires information regarding first-order rate constants since it considers oxidation, reduction, methylation and demethylation reactions which occur among the four species of Hg modelled, namely Hg^0, Hg^{2+}, MeHg and dimethyl mercury (Me_2Hg). In the model, formation of Me_2Hg occurs only within sediment via MeHg transformation and it is lost through volatilization and no Hg^0 is accounted for in sediment segments (Figure 5.2A).

5.3.2 STELLA Hg model

The Systems Thinking Experiential Learning Laboratory with Animation model (STELLA) is a flexible easy-to-use modelling computer package with an intuitive interface that can be employed to model everything from economics to physics, literature to calculus, and chemistry to public policy (ISEE, 2008). Modelling in STELLA consists of construction of a qualitative model, adding parameters, and then exploring model dynamics using four model building blocks (stocks, flows, connectors, and converters) (ISEE, 2008). Atkinson et al. (2007) constructed the Lake Ontario STELLA model in order to confirm coding for the LOTOX2 submodel (Figure 5.2B). STELLA has been successfully employed to model Hg dynamics in other lakes as well (e.g., Lake Champlain, New York (Gao et al., 2006); Spring Lake, Minnesota (Hines and Brezonik, 2007); Willamette Basin, Oregon (Hope, 2006)).

5.3.3 Structural comparison between HERMES (general) and mechanistic models

As expected, model output from the two mechanistic models (LOTOX2 and STELLA) was essentially the same since they were created with nearly identical frameworks (i.e., both used the same fluxes, rates, and Hg species within their model code). The only identifiable difference between the STELLA and LOTOX2 models was the number of segments used [STELLA = 3 (2 water column and 1 sediment); LOTOX2 = 36 (22 water column and 14 sediment)]. This clearly demonstrates that when the model framework and interactions are for the most part duplicated between two models, it does not matter which modelling platform (e.g., LOTOX2 or STELLA) is chosen. For studying the specifics of Hg dynamics in Lake Ontario, LOTOX2 would be the optimum choice since it has been rigorously tested on this lake. STELLA would be the optimum choice for application to other lakes to study the specifics of Hg dynamics compared with LOTOX2, which was designed for and tested on Lake Ontario. The visual programming interface of STELLA also makes it easier for beginners to understand.

Hg^0, Hg^{2+}, MeHg and Me_2Hg are the four Hg forms considered within the mechanistic models developed by Atkinson et al. (2007), who acknowledge that Me_2Hg is not present in any appreciable quantity except in anoxic sediments. Therefore, HERMES, STELLA and LOTOX2 essentially model the same three forms of Hg since THg-MeHg-Hg^0 is almost entirely composed of Hg^{2+} species. The models also consider distribution amongst three environmental media (i.e., air, water, and sediment), even though the mechanistic models further subdivide the water and sediment compartments and require the use of first-order

reaction rate constants. Table 5.3 lists the most noteworthy structural differences and similarities among the three models. Figure 5.2 contains a visual comparison of the prominent structural features of the models, including a legend that defines the terms used.

The STELLA / LOTOX2 Hg submodel defined 40 variables for all thirty-six segments, even though some may not have contributed to model variance. Eleven rate constants were among these variables; inputs that the HERMES model does not require.

5.4 HERMES MODEL APPLICATION

The HERMES model can be downloaded from the 'Environmental Toxicology and Chemistry' web site as a Microsoft Excel workbook online appendix (Chapter 4). A complete description of model design (Chapter 2) and modifications (Chapter 4) are provided elsewhere. Model layout and instructions for use are on the model website. Readers are encouraged to download the model themselves and to substitute data for other lakes.

The eleven variables altered during application were the 1) water temperature, 2) precipitation rate, 3) concentration of Hg in air, 4) surface area, 5) mean depth, 6) water volume, 7) water inflow (i.e., stream) rate, 8) concentration of Hg in inflow water, 9) inflow water suspended particulate matter (SPM) (i.e., suspended sediment), 10) lake water SPM, and 11) sedimentation rate. Even though sediment and SPM percent organic carbon data were available, altering this number provided no additional value to model output. A default

sediment resuspension rate of 80% was used (i.e., amount of sediment deposited that will eventually undergo resuspension - it is not effectively buried). Model output for the HERMES model [Processes (THg, kg yr^{-1}): sediment-water diffusion = 116 and 5.4 (MeHg); sediment deposition = 12.4 (MeHg); volatilization = 416; absorption = 274; wet particle deposition = 233; dry particle deposition = 13.5 *and* Concentrations (THg): water = 1.21 ng L^{-1}, 0.02 (Hg^0), 1.15 (Hg^{2+}), and 0.04 (MeHg); air = 2.59 ng m^{-3}; sediment pore water = 3.49 ng L^{-1}; bulk sediment solids = 71.29 ng g^{-1}] was found to be in good agreement with measured data (no significant difference: $r^2 = 0.99$) (n = 6) [Processes (THg, kg yr^{-1}): volatilization = 410; absorption = 300; wet particle deposition = 238; dry particle deposition = 20 *and* Concentrations (THg): sediment solids = 40-210 ng g^{-1}; air = 2.59 ng m^{-3}] and LOTOX2 model values (no significant difference: $r^2 = 0.98$) (n = 9) [Processes (THg, kg yr^{-1}): sediment-water diffusion = 22-100 and 1-9 (MeHg); sediment deposition = 30 *and* Concentrations (THg): water = 1.05-1.15 ng L^{-1}, 0.02 (Hg^0), 1.0-1.1 (Hg^{2+}), 0.03 (MeHg); sediment pore water = 4.64 ng g^{-1}] (Table 5.4). The US EPA (2006) reported a "not detected / not measurable" for water outflow concentration, but the low model estimate (0.33 kg/yr) was consistent with this result.

An uncertainty / sensitivity analysis was conducted on the eleven major HERMES model input variables using an approach described in Macleod et al. (2002) by increasing each of these variables in turn by 1% and observing the corresponding variation in predicted sediment and water Hg concentrations. For Lake Ontario, it was found that the concentration of Hg in air was the major contributor to variance in model output for both water (64%) and sediment (63%). Precipitation and sedimentation rate explained almost all

of the remaining variance (i.e., > 95% of total model variance). Water inflow rate and concentration of Hg in inflow water contributed no variance (< 0.1%) to model output. Table 5.5A lists the percent contribution to variance for the variables altered during application of the HERMES model to Lake Ontario.

The model does not currently account for sedimentary processes (e.g., Hg remobilization or focusing) that may contribute to surface enrichment other than anthropogenic inputs (i.e., atmospheric contributions). In all likelihood, the model predicts what surface sediment Hg concentration would be in lakes if no other sedimentary processes occurred (i.e., HERMES model predicts sediment Hg that appears to approximate subsurface (20-25 cm depth) values in relatively uncontaminated lakes). Included within the model framework is a sediment emission term that can be used to account for Hg remobilization from underlying sediments (i.e., vertical flux), thus providing a method to account for any surface sediment Hg enrichment owing to remobilization within sediments. A sediment emission of 5800 kg yr^{-1} (0.306 ng m^{-2} yr^{-1}) had to be assumed in order for the model to predict Hg in Lake Ontario surface sediments that is roughly 11% of the predicted Hg sedimentation flux. In addition, the inclusion of this Hg sediment emission within the model caused both the predicted water concentration and volatilization rate to increase ten-fold. This indicates that other origins (e.g., sediment focusing) or processes not accounted for are likely at least partly responsible for the surface sediment enrichment as well.

5.5 DISCUSSION

In this study, the HERMES model was applied to a lake over 1700 times larger than any of the previous thirty-six lakes to which this model has been previously applied (Chapter 2, 4 and 6). As mentioned earlier, only eleven model input variables were altered during application. All other model variables are identical to those used for the initial Hg model development (Chapter 2), except for the mass transfer coefficients for air-side and water-side volatilization as previously mentioned (Chapter 4). For verification, the model was compared against six measured data and nine LOTOX2 model values that included values for total, elemental, divalent and methyl Hg. The HERMES model output was found to be significantly correlated with these other measured or modelled values, suggesting that Lake Ontario should for the most part be near steady-state conditions. Thus, our study concludes that this model should be able to provide reasonable Hg estimates for a wide range of lake sizes within Eastern and Atlantic Canada with a minimal amount of model input variables. Caution should be used during model application to other lakes if there are physical and / or chemical variables beyond the range of lake characteristics where model performance has already been demonstrated (see Chapter 2 and 4)..

The major model input driving variables for Lake Ontario (determined with sensitivity analysis) were the concentration of Hg in air, along with rain and sedimentation rate (Table 5.5A). Altering any one of these variables will result in noticeable changes to predicted water and sediment Hg concentrations. For example, the atmospheric concentration of Hg (2.59 ng m^{-3}) in Lake Ontario is over 70% higher than what has been reported for more

remote locations (i.e., 1.52 ng m^{-3} (O'Driscoll et al., 2005)). If atmospheric emissions of Hg in the vicinity of Lake Ontario were reduced so that the concentration in air reached 1.52 ng m^{-3}, a 41% reduction could be expected for water and sediment Hg concentrations within the lake. Predicted sediment Hg for HERMES model agreed with LOTOX2 sediment Hg predictions (63 ng g^{-1}) and background measured sediment Hg (40 ng g^{-1}) when atmospheric Hg was 2.59 ng m^{-3} and 1.52 ng m^{-3}, respectively. On the other hand, an increase in water inflow rate causes little to no change in model sediment or water Hg concentrations (not a driving variable). For example, if the inflow from the Niagara River were actually 130 ng L^{-1} (Marvin et al., 2007) instead of the 12 ng L^{-1} (value used in all three models) (over 1000% higher), the predicted water and sediment Hg would increase only by 5%. It is also worthwhile to mention that the driving variables for Lake Ontario differed from the original uncertainty analysis conducted on Big Dam West Lake, Kejimkujik Park, NS which found water inflow rate and concentration of Hg in inflow water to be important driving variables (Table 5.5B). Additionally, a proportionate increase in the concentration of Hg in the atmosphere (from 1.52 to 2.59 ng m^{-3}) caused little to no change in sediment or water concentrations for Big Dam West Lake (< 0.1%). The main source of Hg input to Lake Ontario is thus the atmosphere, compared with the watershed source for Big Dam West Lake, which contrasts with the view that the Niagara River is the main source of Hg to this lake. This could be due to the fact that Lake Ontario experiences less ice cover and much higher wind velocities than Big Dam West.

5.5.1 General versus mechanistic Hg models

Output from the HERMES model was found to be in agreement with the LOTOX2 Hg submodel, and thus the STELLA model as well. The advantages of the LOTOX2 compared with the HERMES model are that it accounts for any Me_2Hg formation in sediment, it enables a more detailed examination of reactions amongst Hg species, multiple segments enable visualisation of horizontal and vertical (epilimnion versus hypolimnion) trends, and the dynamic (i.e., changes can be observed with respect to time) model code permit more temporal resolution. In addition, LOTOX2 can evaluate fish concentrations. HERMES is currently a steady-state (i.e., no change with respect to time) model, but it is possible to rewrite the model code so that it can be dynamic in nature as well. The main advantages of the HERMES compared with the LOTOX2 or any other mechanistic model are that it requires far fewer input variables, can readily be transferred to another lake, accounts for vertical flux and / or groundwater inputs, and the relative amount of each species can be adjusted with equations relating Hg and watershed parameters as they surface in the literature. One intriguing venue for further research, that neither model presently addresses, would be the inclusion of an equation that would enable the model to account for variations in surface sediment Hg concentrations.

As for the other general models that have been published, the HERMES stands apart since it verifies sediment estimates against subsurface Hg concentrations, the original model verification was performed on a remote lake, and no attempt has been made to make the

model do what other models have already perfected (i.e., details regarding interconversion rates among species).

In contrast to LOTOX2 and most other mechanistic or general models, HERMES was designed to be used by researchers as a tool to guide their research as well as modellers. The complete model code is written within a Microsoft Excel workbook without any inaccessible formulas or hidden macros and is readily available at no cost either from the corresponding author or as an online appendix for Ethier et al. (Chapter 4) manuscript from the 'Environmental and Toxicology' website. Additionally, methods to estimate any unknown major input variables, to adjust MeHg : THg ratios, or to check model output against other experimentally-derived estimates (for lakes with no measured Hg data) have all been included within the Microsoft Excel workbook alongside the model code.

5.6 OVERALL ASSESSMENT

The HERMES model requires less data for parameterization for a given lake other than what was required for the original model verification, which means that fewer input variables need to be adjusted using measured or estimated values during model application. Subsurface Hg is consistently predicted for every lake to which the model has been applied, regardless of whether the main source of Hg originated from the atmosphere (Lake Ontario) or watershed (Big Dam West Lake). As demonstrated in this paper (i.e., model agreement with LOTOX2 output (with 2.59 ng m^{-3}) or background (with 1.52 ng m^{-3}) sediment Hg depending on atmospheric Hg concentration), differences between modelled and measured

sediment Hg could likely be representative of any increases / decreases between current (i.e., expected model output) and past (i.e., measured subsurface values) Hg loadings. Researchers have proposed sediment focusing and Hg remobilization as alternatives to contamination to account for the observed surface sediment profile in these remote lakes, and these are possibilities that should not be disregarded.

All mercury models at this time need to be calibrated with measured data due to uncertainty in the underlying processes that need to be resolved by the greater research community. Models should be viewed as research tools that can help elucidate these uncertainties and guide the next step in research since research hypotheses could be formulated to address potential reasons for observed model deviations.

Table 5.1: Lake Ontario characteristics (Fuller et al., 1995; Marvin et al., 2007; US EPA, 2006).

Atmosphere		
Air temperature (°C)	8.2	
Precipitation (mm yr^{-1})	813.8	
Wind speed (km h^{-1})	17.2	EAST

Lake	
Surface area (km^2)	18960
Watershed area (km^2)	64030
Mean depth (m)	86
Maximum depth (m)	244
Volume (km^3)	1640
Retention time (yrs)	6

Processes		Measured	Model
Organic carbon (%)	sediment	3	3
	suspended sediment	16-48	40
Sedimentation rate (g m^{-2} yr^{-1})		0.23-4.4	2
Inflow rate (m^3 h^{-1})	calculated from residence time and water volume		31202

Water source (% of total)		
Main inlets	Lake Erie	75
	other tributaries	5
	precipitation	10
	Direct point source discharges	10
Main outlet	St. Lawrence River	93

Table 5.2: Lake Ontario mercury data (Marvin et al., 2007) and model input variables (Atkinson et al., 2007).

Parameter		Measured Hg	Model	Units
Niagra River (loading)		0.13	0.012	$\mu g\ L^{-1}$
Suspended sediment	winter	0.584		$\mu g\ g^{-1}$
	spring-fall	0.2		$\mu g\ g^{-1}$
Surficial sediments	average	0.586		$\mu g\ g^{-1}$
	minimum	0.04		$\mu g\ g^{-1}$
Subsurface sediments	1978-79	0.21		$\mu g\ g^{-1}$
	1963-64	1.9-3.6		$\mu g\ g^{-1}$
Volatilization	Poissant et al. (2000)	478		$kg\ g^{-1}$
		410		$kg\ g^{-1}$
Atmosphere		2.59	2.59	$ng\ m^{-3}$
Atmospheric deposition (wet + RGM)		238		$kg\ yr^{-1}$

Table 5.3: Structural comparison between the HERMES, LOTOX2, and STELLA models.

Feature	HERMES	LOTOX2 and STELLA
Hg concentration in water	yes	yes
Hg concentration in sediment	yes	yes
Advective Hg fluxes	yes	yes
Diffusive Hg fluxes	yes	yes
Reactive Hg rates	no	yes
Atmosphere deposition flux	estimated	defined
Volatilization rate	estimated	defined
Number of segments (total without atmosphere)	2	40
Steady-state	yes	no
Emission to water	yes	yes
Emission to sediment	yes	no
Mercury species modelled	3	4

Estimated: calculated with model
Defined: model input

Table 5.4: Comparison of HERMES model output with measured data and LOTOX2 values.

	Form	HERMES	Measured	LOTOX2	Notes	Reference
Process (kg yr^{-1})						
Sediment-water diffusion	total Hg	116		22-100		Cohen et al. (2006)
	MeHg	5.4		1-9		Cohen et al. (2006)
Sediment deposition	MeHg	12.4		30		Cohen et al. (2006)
Volatilization	total Hg	416	410		as Hg(0)	Lai et al. (2007)
Absorption	total Hg	274	300		as Hg(0)	Lai et al. (2007)
Water outflow	total Hg	0.33	ND		authors did not specify detection level	US EPA (2006)
Wet particle deposition	total Hg	233	238		wet + RGM	Lai et al. (2007)
Dry particle deposition	total Hg	13.5	20			Lai et al. (2007)
Concentration						
Water (ng L^{-1})	total Hg	1.21		1.05-1.15	epilimnion was 97% of total volume	Atkinson et al. (2007)
	Hg(0)	0.02		0.02		Atkinson et al. (2007)
	Hg(II)	1.15		1.0-1.1		Atkinson et al. (2007)
	MeHg	0.04		0.03		Atkinson et al. (2007)
Sediment pore water (ng L^{-1})	total Hg	3.49		4.64	converted from 22 kg in top 2.5 cm surface sediment	Cohen et al. (2006)
Sediment solids (ng g^{-1})	total Hg	71.3	40-210	63	sediment DMHg + Hg(0) (ng L^{-1})	Marvin et al. (2007); Atkinson et al. (2007)
Bulk air (ng m^{-3})	total Hg	2.59	2.59		input variable	Marvin et al. (2007)

Table 5.5: Contribution to variance for the model input variables altered during application.

(A) Lake Ontario (this study)

	Contribution to variance in model output	
Input variable	**ΣHg concentration in water (%)**	**ΣHg concentration in sediment (%)**
Concentration of Hg in air (ng m^{-3})	**63.93**	**62.98**
Rain rate (m yr^{-1})	**17.76**	**17.10**
Concentration of Hg in inflow water (ng L^{-1})	**<0.1**	**<0.1**
Water inflow rate (m^3 h^{-1})	**<0.1**	**<0.1**
Sedimentation rate (g m^{-2} day^{-1})	**17.60**	**15.67**
Suspended particulate matter (mg L^{-1})	**0.26**	**3.81**
Inflow suspended particulate matter (mg L^{-1})	**<0.1**	**<0.1**
Year-round mean temperature (°C)	**0.45**	**0.43**
Total	**100**	**100**

NOTE: surface area, water volume and mean depth are fixed lake variables and were therefore not included in uncertainty analysis.

(B) Big Dam West, Kejimkujik Park, Nova Scotia (Chapter 2).

	Contribution to variance in model output	
Input parameter	**ΣHg concentration in water (%)**	**ΣHg concentration in sediment (%)**
Concentration of Hg in inflow water (ng L^{-1})	**28**	**10**
Water inflow rate (m^3 h^{-1})	**72**	**26**
Fraction of particles in water	**<0.1**	**17**
Sediment deposition velocity (g m^{-2} day^{-1})	**<0.1**	**25**
Sediment resuspension velocity (g m^{-2} day^{-1})	**<0.1**	**22**
Water (THg-MeHg-Hg^0 / Hg^0)	**0.3**	**0.3**
Sediment (THg-MeHg-Hg^0 / Hg^0)	**<0.1**	**0.1**
Total	**100**	**100**

Figure 5.1 : LOTOX2 model segments (Atkinson et al., 2007).

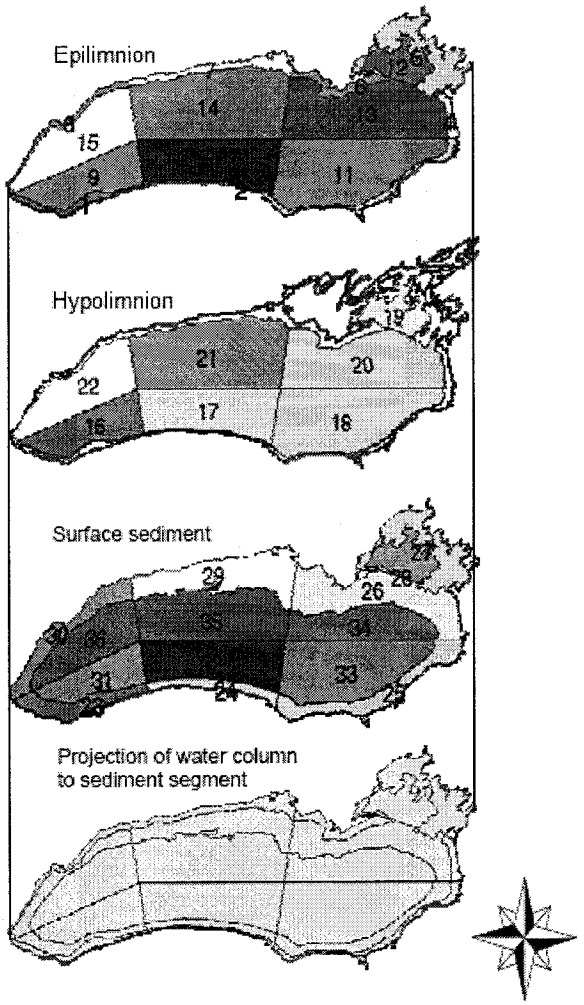
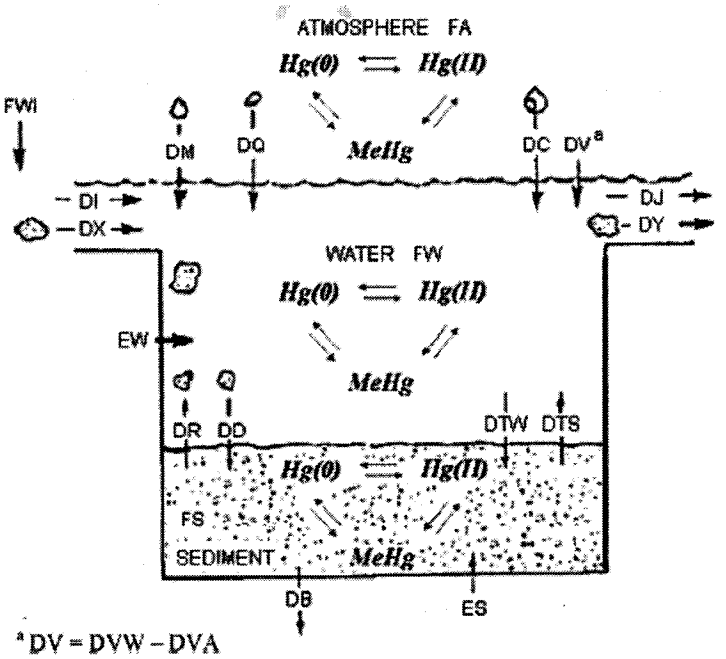
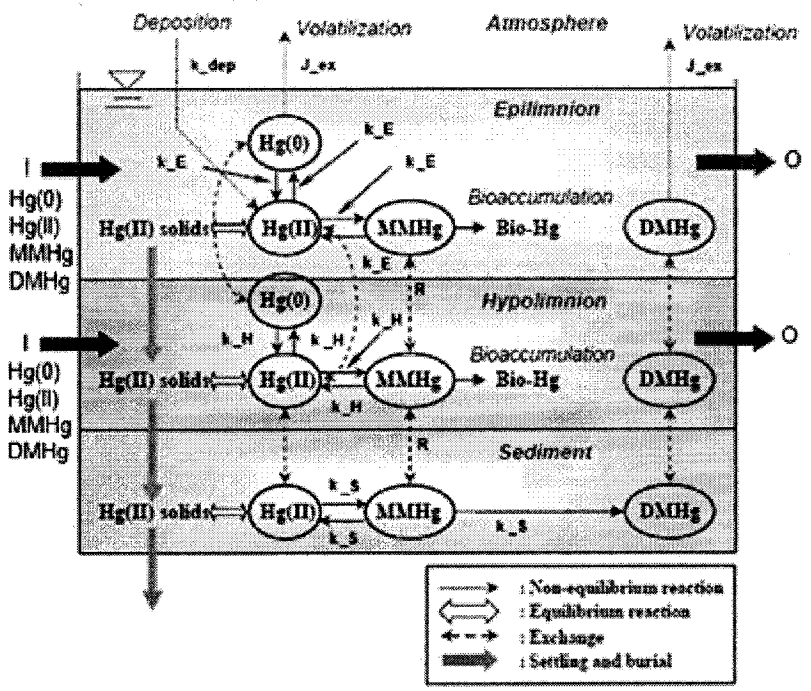


Figure 5.2: Visual comparison of the three Hg lake models. All fluxes are defined in legend.

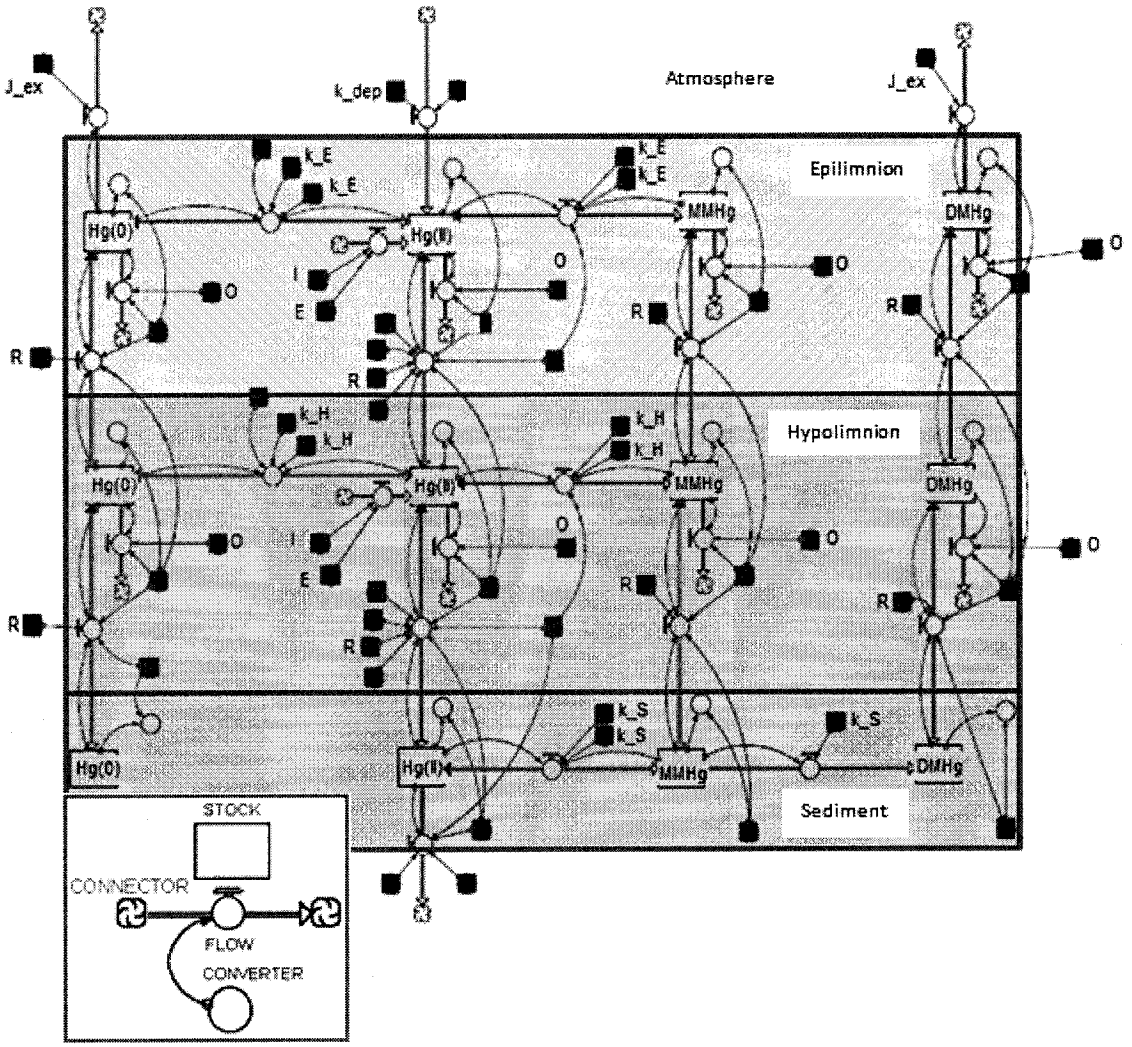
(A) HERMES (Chapter 2)



(B) LOTOX2 (Atkinson et al., 2007; DePinto et al., 2004)



(C) STELLA (Atkinson et al., 2007; ISEE, 2004)



Legend:			
k_H	hypolimnion first order rate constant (e.g., oxidation, reduction, methylation, demethylation)	k_E	epilimnion first order rate constant (e.g., oxidation, reduction, methylation, demethylation)
k_S	sediment first order rate constant (e.g., oxidation, reduction, methylation, demethylation)	k_dep	wet and dry deposition rate from air (DM + DQ + DC)
I	particulate (DX) and water (DI) inflow	J_ex	atmospheric exchange flux (i.e., volatilization (DV))
O	particulate (DY) and water (DJ) outflow	R	bulk dispersion coefficient
Hg(0)	elemental mercury concentration	E	emission to water (EW) or sediment (ES)
Hg(II)	inorganic (or residual) concentration	FA	air fugacity
MMHg	methyl mercury concentration	FWI	inflow water fugacity
MeHg	methyl mercury concentration	FW	water fugacity
DMHg	dimethyl mercury concentration	FS	sediment fugacity
D	advective or diffusive transport parameters (e.g., DR is resuspension; DD is deposition; DTW/DTS is water/sediment diffusion; DB is burial)		

CHAPTER 6

APPLICATION OF HERMES MERCURY MODEL TO THIRTY-FIVE LAKES IN ONTARIO, CANADA

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Abstract - To determine how reliable any model performs it should be tested on a data set other than that used for its development. Here we apply the Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model developed for Big Dam West Lake, Nova Scotia, Canada to thirty-five lakes in Ontario, Canada (2000 km west from where the model was originally developed). Only ten location and lake-specific variables were substituted to characterize the lake and drainage basin features of each lake. These variables included measured values for water inflow rate, precipitation rate, lake temperature, lake volume, surface area, and mean depth which were combined with estimates for water inflow Hg concentration (i.e., streams), water column and inflow suspended particulate matter, and resuspension rate. All of the original underlying variables, such as mass transfer coefficients and concentration ratios, were left unchanged. Model predicted sediment Hg was significantly ($r^2 = 0.51$, $p < 0.05$) correlated with measured values (error < 25%).

The HERMES model was then used to derive water inflow Hg concentration values from measured sediment Hg. Regression of the derived water inflow Hg values against watershed and lake variables resulted in the following equation: log water inflow Hg concentration = (0.165 x log watershed area (km^2)) + (0.102 x dissolved organic carbon ($mg\ L^{-1}$)) – (0.342 x log water inflow rate ($m^3\ h^{-1}$)) + 0.000778 x direct runoff ($mm\ yr^{-1}$)) + (0.0154 x mean lake depth (m)) + 0.492 ($r^2 = 0.68$, $p < 0.0001$).

A comparison between the water inflow Hg concentration estimation method (i.e., equation) derived in this study and average measured values for sixteen lakes located in

different parts of the world (e.g., Antarctica, Russia, Canada) showed a deviation of only 15.7±18.0%, and was within reported ranges (n = 6). This was found to be a significant ($p < 0.05$) improvement over the previous literature estimation method for water inflow Hg concentration.

Keywords: model, error, mercury, estimate, inflow, watershed, lake

6.1 INTRODUCTION

The complex speciation patterns of mercury (Hg) in the environment make model application difficult. To accomplish this task, the Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model uses an approach where elemental mercury (Hg^0) is the "key" species modeled (Toose and Mackay, 2004, Chapter 2). The two other species modeled, methyl mercury (MeHg) and residual Hg (total Hg minus MeHg and Hg^0), are then predicted using constant concentration ratios. HERMES was initially developed and verified for Big Dam West Lake in Kejimkujik Park, Nova Scotia (Chapter 2).

Elemental mercury represents most of the Hg in the atmosphere and is the form involved in long range transport, moving from sites of emission toward more polar regions. When oxidized to Hg^{2+} it is deposited to the earth as wet and dry deposition. However, only after conversion to MeHg does it become biomagnified in food webs.

For Big Dam West, Harp and Dickie Lake, it was determined that the HERMES model input variables that had the largest impact on predicted sediment and water Hg concentrations were suspended particulate matter (water column and inflow), water inflow rate, water inflow Hg concentration, along with sedimentation and resuspension rate. These model input driving variables, expressed as yearly averages, are sensitive to variation in these small sheltered lakes (Table 6.1, Chapter 2 and 4). Model performance

will largely depend on the quality of these sensitive model input driving variables regardless of whether the values were estimated or measured.

In order to increase the utility of the model so that it could be applied to lakes with limited datasets, general estimation methods were gathered from the literature (Chapter 4) for the seven sensitive model input driving variables (Table 6.1). In previous work, the model was successfully applied to Harp and Dickie Lake, Ontario where predicted water and sediment levels were found to be within 10% of measured values (Chapter 4), and Lake Ontario (Chapter 5). A comparison was made of model output for Harp and Dickie Lakes with (a) all measured data and (b) only the six most sensitive and site-specific (i.e., water volume, surface area, mean depth, lake temperature) variables revealed no significant differences (Chapter 4).

The primary objective of the study was to evaluate the limits of the mercury model capabilities when some of the key variables are measured (precipitation rate, lake volume, lake surface area, mean depth, average annual temperature, water inflow rate), and other variables are estimated (water inflow Hg concentration, water column / inflow SPM, sedimentation and resuspension rate) (Table 6.2).

The second objective of this study was to use the HERMES model to improve the estimation method used for water inflow Hg concentration. Water inflow Hg concentration is one of the most sensitive model input driving variables (influencing both sediment and water Hg predictions), and yet it is not routinely measured. The predictive

power of the current literature estimation method used for water inflow Hg concentration is low ($r^2 = 0.11$), even though it is one of the most sensitive model driving input variables (Grigal, 2002).

6.2 METHODS

6.2.1 Site description

The model was applied to thirty-five Ontario lakes located between Minden and Ottawa (Table 6.3), including Harp and Dickie Lake. The watershed area of the lakes ranged from 2 to 927 km^2, the lake surface area from 0.34 to 14.17 km^2, mean depth from 3.9 to 23.5 m, direct runoff rate to the lake from watershed from 3.2 to 5.0 m yr^{-1} and dissolved organic carbon (DOC) ranged from low values of 1.8 to 5.5 mg L^{-1}. The measured subsurface sediment Hg ranged from 57.2 to 223 ng Hg g^{-1} dw.

Information for these lakes was gathered from an Ontario lakes dataset compiled by Mills et al. (PhD thesis in prep) which contains watershed and lake data for 203 lakes in Ontario. One hundred and seventy-five of the lakes in this dataset included the measured subsurface sediment Hg concentrations required to verify model output. The HERMES model does not presently account for the any transient sedimentary processes (e.g., focusing or remobilization) in surface sediments, so predicted sediment Hg tends to approximate measured subsurface (i.e., background) sediment Hg in uncontaminated lakes.

6.2.2 Model input variables

Ten sensitive and site-specific model input variables were adjusted during model application to each of the thirty-five lakes. Measured data were available for six of these model variables (i.e., water volume, surface area, water inflow rate, mean depth, precipitation rate, and lake temperature). Estimation methods were used for the remaining four (i.e., water column / inflow SPM, resuspension rate, and water inflow Hg concentration) (Table 6.2). The settling rate of solids was assumed to be 0.304 g m^{-2} d^{-1} (from Harp and Dickie Lake – Chapter 4) for all lakes since the estimation method for this model input variable was not found to be sufficiently reliable.

Water inflow rates were calculated from residence time (or flushing rate) and water volume which were only available for thirty-five of the lakes that contained sediment Hg concentrations. Therefore, only thirty-five of the 203 lakes in the dataset had all the information required in order to apply and evaluate the HERMES model.

SPM (mg L^{-1}) was not available for all lakes, so estimation method A (Lindstrom et al., 1999) [Log_{10} SPM = 1.56 x Log_{10} (Total Phosphorus (TP, µg L^{-1})) – 1.69; r^2 = 0.74] was used for the initial model tests and compared with the measured values for the five lakes in the dataset that reported an SPM (0.5 mg L^{-1} in four lakes; 1.5 mg L^{-1} in one lake) (see Table 6.2). The same value was used for water column and inflow SPM since TP and measured SPM values were not available for inflow water (i.e., acknowledging that

inflow is likely greater than water column SPM). Resuspension rate (% of deposition) and water inflow Hg (ng L^{-1}) were calculated using mean depth of lake [estimation method B (Evans, 1994): resuspension rate = 90 x (850 – ((mean depth (m) – 8.5) x 70)) / 850, no information available on r^2 or p values] and watershed area [estimation method C (Grigal, 2002): Ln (water inflow Hg) = 2.02 – 0.063 x Ln (watershed area (km^2)), r^2 = 0.11], respectively (see Table 6.2). The resuspension rate of particulates in the larger lakes (mean depth > 9 m) was assumed to be 80% of the sedimentation rate. An estimation method was only needed for the small deeper lakes where the resuspension rate was lower and variable. No estimation methods were found in the literature that would provide a significant relationship to predict water inflow Hg concentration, as the one that was selected had an r^2 of only 0.11 (Grigal, 2002).

6.2.3 Model evaluation

Evaluation of the HERMES model can be subdivided into four main tests: quantification of error in current model estimations (Test 1); influence of variable versus fixed SPM on model error (Test 2); influence of variable versus fixed sediment resuspension rate on model error (Test 3); and derivation of an improved water inflow water Hg concentration estimation method (Test 4). In short, total model error with estimates for SPM, resuspension rate, and water inflow Hg was quantified (Test 1) (Objective 1). Estimation methods used to estimate SPM (Test 2) and resuspension rate (Test 3) were then compared with fixed values to determine whether the use of a variable estimate (equation) reduced or increased model error (Objective 1). Derived water inflow Hg

concentration values (from measured subsurface sediment Hg using HERMES model) were then regressed against available watershed and lake variables to derive a better water inflow Hg concentration estimation method (Objective 2) (Figure 6.1)

Two assumptions that the HERMES model makes that need to be taken into consideration for this paper are: (1) Historical Hg profiles are correct except for some deviation due to surface sediment enrichment in some lakes (but not others) from sediment processes, such as focusing or Hg mobility; and (2) There hasn't been a significant amount of change in sediment Hg since measured subsurface sediment Hg (with which model output is being compared) was initially deposited.

6.2.4 Model error

Measured values for the model input driving variables should contribute less error to model predictions than the estimation methods used in this paper for suspended particulate matter, resuspension rate, and water inflow Hg concentration. Error is an inherent component of any model and it is advisable to attempt to quantify and account for potential sources. Estimation methods with higher correlations (r^2 values) will impart less error to model predictions. A decrease in model performance can be expected as the number of estimates used increases since error is cumulative.

Deviation of the predicted sediment Hg from the measured subsurface Hg concentration was reported as average absolute error $\pm$ SD (Error = 1 – measured / predicted).

6.2.5 Derivation of estimation method for water inflow Hg concentration

In order to obtain a better estimation method for the water inflow Hg concentration input variable, the HERMES model was used to derive water inflow Hg concentration values from measured subsurface sediment Hg. This was done by repeatedly adjusting the water inflow Hg input variable in the model until the predicted sediment Hg matched the measured subsurface sediment Hg.

The Ontario lakes dataset compiled by Mills et al. (PhD thesis in prep) contains numerous watershed and lake variables, some of which were used during model application and many others that were not. A scatterplot matrix was used to identify any watershed and / or lake variables within this dataset that had some degree of correlation with water inflow Hg and these were tested for normality and transformed to improve fit when possible.

A stepwise forward multiple linear regression was then used to determine which of these variables should be included in the estimation method for water inflow Hg concentration and in what order (i.e., watershed and lake variables that were correlated with calculated water inflow Hg values). Variables were included as long as the r^2 continued to increase (more variability explained) and the Akaike's Information Criterion (AIC) decreased. The AIC indicates the best number of variables to include in a model. Once the regression was completed, the residuals were checked for normality.

A 'double-check' of the equation produced to estimate water inflow Hg concentration was carried out by reapplying the model to each of the thirty-five lakes (for the fifth time) using the new estimation method for water inflow Hg concentration. This was done to demonstrate potential for model improvement since no conclusions could be drawn from this circular 'double-check'.

To test the predictive power of the water inflow Hg concentration estimation method (i.e., equation) derived in this study, a literature review was conducted to identify a broad range of lakes (e.g., Antarctica, Poland, Russia, Canada) that contained measured values or ranges for water inflow Hg concentration along with the watershed and lake variables required (i.e., those included in regression model) to apply the water inflow Hg concentration estimation method. When a lake contained more than one DOC measurement, the estimate was calculated using the minimum and maximum values so that variation could be examined. Error for the previous water inflow Hg concentration estimate (equation C, Table 6.2) was then compared with the estimate derived here.

6.2.6 Statistics

Statistical analyses were conducted using JMP (SAS, 2000), including the derivation of the water inflow Hg concentration estimate. Log-transformed normalized data (measured versus predicted sediment Hg; measured versus derived and previous water inflow Hg estimates) were all compared using paired T-tests.

6.3 RESULTS

The HERMES model sediment Hg output was significantly correlated with measured sediment Hg concentration in the thirty-five Ontario lakes using a limited dataset and estimation methods for model input variables. The model estimation method for water inflow Hg concentration derived in this study was able to improve model performance further, with a significant ($p < 0.05$) improvement over previous estimation methods. Predicted water inflow Hg concentration was found to be ±15% of the measured average and within reported ranges for lakes located throughout the world (e.g., Antarctica, Poland, Russia, and Canada).

Details regarding the outcome of each of these tests are discussed in the following sections (Test 1 to 4). Any readers who wish to see model details may download the HERMES model from the 'Environmental Toxicology and Chemistry' website as an online appendix for Chapter 4 manuscript, or by requesting a copy from the corresponding author, and to insert the variables for each lake (Table 6.3).

6.3.1 Quantification of error in current model estimations (Test 1)

The purpose of the first test (Test 1) was to evaluate the performance of the HERMES model when applied to lakes without recalibration using limited datasets and the estimation methods for model input driving variables. In short, this test shows how well

the model predicts subsurface sediment Hg when using a limited dataset without any prior knowledge of measured subsurface sediment Hg concentrations. For lakes that show surface sediment enrichment (e.g., surface 3-5x higher than subsurface sediment Hg), predicted sediment Hg should approximate surface sediment Hg concentrations once transient surface sedimentary processes (e.g., focusing and remobilization) are accounted for. At present, HERMES does not account for these sedimentary processes. The model methods used here must also assume that there have been no major decreases or increases in atmospheric Hg since the subsurface sediment was initially deposited (i.e., deviation between predicted and measured subsurface sediment Hg concentration).

This test of model error involved altering the most sensitive and site-specific model input variables with application to each lake, using estimates for SPM, resuspension rate, and water inflow Hg (Table 6.2). The absolute error (%) for predicted versus measured subsurface sediment Hg using all three estimates was determined to be 31±23% (Figure 6.2a). No significant correlation ($p < 0.05$) was found between measured and estimated subsurface sediment Hg for this initial test ($p = 0.13$, $r^2 = 0.38$, $n = 35$).

Measured versus predicted sediment Hg had a slope of 1.10 ($r^2 = 0.09$) when the intercept was forced through zero (Figure 6.3a), so it was within 10% of the optimal 1:1 relationship. Predicted water column Hg showed a high amount of scatter and no relationship ($r^2 = 0.00$) when plotted against another water column Hg estimate (water column Hg (ng L^{-1}) = 0.48 x DOC (mg L^{-1}), $r^2 = 0.75$) (Meng et al., 2005) (Figure 6.3b).

6.3.2 Influence of variable versus fixed SPM on model error (Test 2)

The next step in model evaluation involved individually testing each of the estimation methods used during model application. SPM estimation method is tested and described here (Test 2). Resuspension rate estimation method is then tested in the following section (Test 3).

Five of the thirty-five lakes had a measured SPM, four were 0.5 mg L^{-1} and one was 1.5 mg L^{-1}. Spring TP (not yearly average) was available from which SPM estimates could be derived (equation A, Table 6.2). No correlation ($p < 0.05$, paired t-test) was found between the estimated and measured values for these five lakes since the lakes with a measured SPM of 0.5 mg L^{-1} had estimates ranging from 0.2 to 1.3 mg L^{-1} and the lake with an SPM of 1.5 mg L^{-1} had an estimate of 0.2 mg L^{-1}. Dillon and Rigler (1974) contain an equation to convert spring TP into an annual average, but this would have compounded estimate error (i.e, estimating one variable (annual TP) in order to estimate another (SPM)). Due to the high variability in the estimate, an SPM of 0.5 mg L^{-1} was therefore assumed in the second test given that the majority of the lakes should be near this value (i.e., all the lakes have low DOC).

Setting the water column and inflow SPM at 0.5 mg L^{-1} was able to reduce the model error to 24±18% (Test 2) and this resulted in a significant correlation ($p < 0.05$) between measured and estimated sediment Hg ($p = 0.02$, $r = 0.51$).

6.3.3 Influence of variable versus fixed sediment resuspension rate on model error (Test 3)

For larger lakes, assuming a resuspension rate of 80% is acceptable (Mackay, 2001). On the other hand, small deeper lakes can have resuspension rates that are considerably lower (Evans, 1994). Twenty-three of the thirty-five lakes chosen were small (< 10 km^2) and twelve were deep (mean > 8.5 m). In order to determine whether the model estimate for resuspension rate (equation B, Table 6.2) was increasing or reducing model error, the model was reapplied to all thirty-five lakes with a fixed resuspension rate of 80%.

Setting the SPM and the resuspension rate (80% of deposited material) caused a slight increase in model error (2%), regardless of whether all lakes were compared (n = 35) or only the small deeper lakes affected by fixing the resuspension rate (n = 23). Therefore, subsequent applications of the model in this study used an SPM of 0.5 mg L^{-1} and a variable resuspension rate for all of the small deeper lakes.

6.3.4 Derivation of estimation method for water inflow Hg concentration (Test 4)

The estimation method used for water inflow Hg concentration was the most probable source of model error given the low strength of correlation and the high contribution to model variance for this estimate. An assumption that most of the remaining variance could be attributed to this estimation method was therefore made in order to conduct the fourth test described here.

Water inflow Hg concentration was calculated from measured sediment Hg using a fixed SPM (0.5 mg L^{-1}) and variable resuspension rate to reduce estimate error, as was determined from the previous three tests described above. Five watershed and lake variables (i.e., watershed area, DOC, water inflow rate, direct runoff, and mean depth), when taken together, were found to be significantly ($r^2 = 0.68$, $p < 0.0001$) correlated with water inflow Hg. The resulting equation was: Log water inflow Hg (ng L^{-1}) = 0.4922 + [0.1647 x log watershed area (km^2)] + [0.1020 x DOC (mg L^{-1})] – [0.3421 x log water inflow rate (m^3 h^{-1})] + [0.000778 x direct runoff (mm yr^{-1})] + [0.0154 x mean lake depth (m)] (equation D, Table 6.4). Few studies exist in the literature that report measured water inflow Hg concentration, along with the above mentioned watershed and lake variables required to use equation D (Table 6.4). Therefore, two additional equations were derived that require fewer watershed and lake input variables (equation E ($r^2 = 0.64$, $p < 0.0001$): watershed area, DOC water inflow rate, mean depth; equation F ($r^2 = 0.44$, $p < 0.0001$): watershed area, water inflow rate) (Table 6.4). Although equation E and F (Table 6.4) have a higher r^2 than the previous estimate (equation C, Table 6.2), their strength of correlation is lower than equation D which uses more watershed and lake variables (Table 6.4).

Measured versus predicted sediment Hg for the thirty-five lakes with the new water inflow Hg equation (D, Table 6.4) had a slope of 0.94 ($r^2 = 0.45$) when the intercept was forced through zero (Figure 6.3c), with a decrease in error range (-36 to 32%) (Figure 6.2b). Although the water inflow Hg concentration estimate used DOC as well (i.e., there

is a circular component), it is noteworthy that a plot of model predicted water column Hg against estimate used by Meng et al. (2005) (Figure 6.3d) had a slope of 0.97 ($r^2 = 0.11$, intercept forced through zero),

The estimate derived in this study (using either equation D, E or F in Table 6.4) was much closer ($p = 0.16$, $r^2 = 0.94$, error: 15.7±18.0%) to measured ranges or literature values for water inflow Hg concentration (ng L^{-1}) ($n = 16$) than the previous (equation C, Table 6.2) estimate ($p = 0.87$, $r^2 = 0.27$, error: 74.0±82.1%) (Table 6.5). For the six studies that reported a range of measured water inflow Hg values, the estimates derived in this study were always within this range (i.e., no error). In addition, when the water inflow Hg estimate was calculated using the minimum and maximum DOC for the three lakes that had a range of reported values, both estimates were within the measured range for water inflow Hg concentration. As expected, there was no significant correlation found between the current (this study) and previous water inflow Hg concentration estimates ($p = 0.83$).

6.4 DISCUSSION

6.4.1 Model evaluation

Model predicted sediment Hg concentration was found to be significantly correlated with subsurface sediment Hg measured values, since the model does not provide estimates of

surface sediment Hg without information regarding Hg lake specific sedimentary processes.

6.4.1.1 SPM estimation method

Measured TP for the thirty-five lakes within the dataset was only measured in the spring, not the yearly average required for the model estimate (equation A, Table 6.2), and could potentially be one reason why no correlation existed between measured and estimated SPM (Test 1). Since SPM (or suspended sediment) can be a difficult variable to measure (Ongley, 1996), it is also possible that the values contained within the dataset were not accurate. Ethier et al. (Chapter 4) describes another method to estimate SPM that uses Secchi depth instead of TP. However, this variable was only available for the five lakes that had a measured value for SPM.

6.4.1.2 Comparison with other Hg models

The Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury (SERAFM) model developed by the U.S. Environmental Protection Agency is comparable to the model evaluated in this study given that both are steady state mass balance Hg models that have been applied to lakes as a single segment. Knightes et al. (2008) applied this SERAFM model to contaminated Steamboat Creek, Nevada and found that after a critical verification, model error was found to range from 12 to 17%.

Knightes and Cyterski (2005) evaluated predictive errors for the commonly used Regional Mercury Cycling Model (R-MCM) developed by Tetra Tech Inc. (1996) on four different lake types. A significant correlation ($p < 0.05$) was found between estimated and observed values for well-mixed medium-sized lakes and small circumneutral stratified oligotrophic lakes. On the other hand, no correlation ($p > 0.65$) existed between estimated and observed values when the R-MCM model was applied to acidic or small stratified eutrophic lakes. The lakes in this study varied from acidic to basic (pH: 5.7 to 8.0); oligotrophic to eutrophic (TP: 2.7 to 23.6 $\mu g\ L^{-1}$; DOC: 1.8 to 5.5 $mg\ L^{-1}$); small to large (surface area: 0.34 to 14.17 km^2); and some of these lakes stratify while others do not.

The atmosphere is often the main source of Hg (direct or via runoff from the watershed) to lakes at remote locations throughout the world, so any estimate error for this variable (i.e., atmospheric Hg concentration) would likely impart a corresponding error to lake models that may use this estimate. Selin et al. (2007) compared measured total gaseous Hg (TGM) with GEOS-CHEM global 3-D atmospheric Hg model estimates for locations throughout the world. Model error for the original application varied from -64.2 to 29.4%, but was reduced to 6.3% for 12 of the 22 sites before the manuscript was published. Therefore, the absolute error established for the HERMES model (24±18%, Test 2) was in agreement with error reported for other models.

French et al. (1999) derived an equation to estimate sediment Hg that requires even fewer variables than the model employed here. The equation uses the ratio of watershed to lake area (WA:LA) to estimate sediment Hg as follows,

$$\text{Sediment Hg } (\mu g\ g^{-1}) = 0.01122\ (\text{WA:LA})^{0.581} \qquad (n = 34;\ r^2 = 0.37;\ p = 0.029)$$

Absolute error for this equation when applied to all thirty-five lakes listed in Table 6.3 was found to be 102.8±92.1%, over four times greater than what was determined for the HERMES model.

4.1.3 Additional source of variation between measured and predicted sediment Hg

Instrumental error for total Hg in the water column is typically ±15%, so two samples can differ by 30% from each other and not be considered different (EPA, 2002). Gottgens et al. (1999) reported a compounded error of ±11% and ±29% (varied with analytical rigor) for sediment Hg analysis. Since measured sediment Hg was used to evaluate model error, model estimates may well have even been within analytical error depending on the degree of rigor employed during sediment analyses.

6.4.2 Derivation of water inflow Hg concentration estimation method

In order to further enhance model performance using limited datasets for future model applications, improving the water inflow Hg concentration estimation method used by the HERMES model is essential as it is not a routinely measured variable.

Although the inclusion of multiple variables to estimate water inflow Hg increases the strength of the relationship, very few datasets will likely contain all the required information. Selection of equation (D-F, Table 6.4) would essentially be based on data availability. Naturally, those equations with the strongest relationship should be used when the required data are available. In order to maximize the number of lakes included in Table 6.5, all three equations listed in Table 6.4 had to be used.

For data that are known to have temporal variability (i.e., DOC, runoff, inflow rate), consistent averages are recommended because these variables can differ among years. For example, it is best not to use a DOC average from one year and an inflow rate from another since lakes can change over time. The lake data required to assemble Table 6.5 were not always available for the same year (or time of year) and this might have contributed to some of the observed deviation between predicted and measured values.

On the other hand, using temporal variables in the equation to estimate water inflow Hg can enable predictions regarding how changes within the watershed (e.g., logging) may impact the concentration of Hg in streams (i.e., water inflow to lake). For the three lakes

in Table 6.5 that had reported ranges for DOC and water inflow Hg concentration, estimates using minimum and maximum DOC fell within the measured range for water inflow Hg. The inclusion of DOC in the estimation method for water inflow Hg concentration should also cause a noticeable improvement in water Hg estimates (see Meng et al., 2005).

6.4.2.1 Comparison with previous water inflow Hg concentration estimate

No significant correlation was neither found nor expected between the water Hg inflow estimates (previous and this study) since there was over a four-fold reduction in estimate error. If the water inflow Hg estimates derived in this study had been compared against measured ranges (instead of averages), it is likely that the derived equation would have been significant since those estimates that did differ were still relatively close (error was only 15.7%). Considerable increases in predictive power can therefore be expected if the HERMES model were to be applied to another dataset, such as the one used here, using the water inflow Hg estimate(s) derived here.

6.4.2.2 Assumptions

Water inflow Hg concentration is a model input driving variable that is not routinely measured, so it is advantageous to be able to use the HERMES model to derive water inflow Hg values from measured data (i.e., sediment Hg). Several attempts were made here to reduce model error from the other estimation methods used (e.g., SPM and

resuspension estimate) prior to the derivation of these water inflow Hg values but it is likely that some error remained. Although the method assumed that all remaining error was attributable to the water inflow Hg concentration estimate, this may not necessarily be the case. Mean depth and runoff rate in equation D (Table 6.4) for example could instead be a reflection of residual estimate error in resuspension rate and suspended particulate matter concentration, respectively.

6.4.3 Future research

Models can serve as a valuable tool to guide Hg research that is often done by scientists who are not modelers. More focus should therefore be placed on designing simple models to help researchers conduct their experiments. In addition, research conducted with the aid of models might in turn be able to enhance model performance by decreasing the number of estimates used within the model.

Routine water chemistry and Hg measurements inflowing streams and rivers could allow for the development of a multiple linear model that could provide reliable estimates of expected variation in water inflow Hg concentration into lakes as conditions fluctuate. If this equation were then applied to other rivers, any remaining discrepancy between estimate and measured values could be attributed to differences in watershed variables.

In addition, further research should focus on improving some of the other estimation methods (e.g., sedimentation rate or water inflow rate) that were not evaluated in the

present study. For example, the sedimentation rate estimation method would likely vary with water current velocity and losses from volatilization are not currently accounted for in water inflow rate estimation method.

6.5 CONCLUSION

Given that only six variables ended up being altered for each lake, it is remarkable that the HERMES model could provide estimates that were significantly correlated with the actual measured sediment values. It is expected that the model estimates would show an even stronger correlation with measured values if the model was retested using a different lake dataset and the water inflow Hg concentration estimation method derived here since this one variable accounts for a large proportion of the model variability in these lakes.

Although the method used here to derive an estimation method for water inflow Hg concentration using model derived values may differ from other strategies found in the literature to produce equations, it clearly demonstrates one of the potential applications of the HERMES model.

Acknowledgements - I would like to thank the Dorset Environmental Research Center for making this study possible through the use of their Ontario lakes dataset.

Table 6.1: Contributors to model variance for sediment and water total Hg concentrations (Chapter 2).

	Major contributors to variance in model output	
Input parameter	**ΣHg concentration in water (%)**	**ΣHg concentration in sediment (%)**
Concentration of Hg in inflow water (ng L^{-1})	**28**	**10**
Water inflow rate (m^3 h^{-1})	**72**	**26**
Fraction of particles in water	**<0.1**	**17**
Sediment deposition velocity (g m^{-2} day^{-1})	**<0.1**	**25**
Sediment resuspension velocity (g m^{-2} day^{-1})	**<0.1**	**22**
Water (THg-MeHg-Hg^0 / Hg^0)	**0.3**	**0.3**
Sediment (THg-MeHg-Hg^0 / Hg^0)	**<0.1**	**0.1**
Total	**100**	**100**

Table 6.2: Model input variable estimate equations that were tested (Chapter 4).

A **Log_{10} (Suspended particulate matter (mg L^{-1})**
= 1.56 x Log (Total Phosphorus (µg L^{-1})) – 1.69
$r^2 = 0.74$ Lindstrom et al. (1999)

B **Resuspension rate (% of deposition)**
= 90 x (850 – ((Mean Depth (m) – 8.5) x 70)) / 850
Evans (1994)

C **Ln (Concentration of mercury in inflow water (ng L^{-1})**
= 2.02 – 0.063 x Ln (Watershed (km^2))
$r^2 = 0.11$ Grigal (2002)

Table 6.3: Thirty-five lakes in Ontario used to evaluate model performance.

Lake	Latitude (dec deg)	Longitude (dec deg)	Watershed area (km^2)	Lake surface area (km^2)	Mean lake depth (m)	Water volume (m^3)	Rain rate ($m\ yr^{-1}$)	Direct runoff ($mm\ yr^{-1}$)	Water inflow rate ($m^3\ h^{-1}$)[a]	Spring TP ($\mu g\ L^{-1}$)	DOC ($mg\ L^{-1}$)	Subsurface sediment Hg ($ng\ g^{-1}$)[b]
Anstruther	44.7251	-78.2407	84	2.57	12.6	80000000	0.826	333	4566.7	10.0	4.2	100.4
Art	45.0554	-78.4476	11	1.26	7.5	9504000	0.890	482	575.3	19.7	4.2	149.3
Beaver	44.7653	-78.2725	80	2.00	7.0	56000000	0.823	321	219.3	14.0	4.9	83.3
Big Hawk	45.1575	-78.7337	261	3.89	18.1	6202500	0.913	488	1115.0	5.0	2.5	111.9
Bitter	45.1662	-78.5999	2	0.43	11.5	4916000	0.913	489	79.1	9.2	2.6	104.4
Blue Chalk	45.1947	-78.9382	2	0.52	8.5	4467000	0.928	493	126.8	5.0	1.8	57.2
Canning	44.9317	-78.6330	287	2.44	6.7	16930000	0.883	475	13085.8	9.0	4.4	129.3
Chub	45.2110	-78.9843	3	0.34	8.9	3043000	0.930	495	186.8	8.3	4.9	141.5
Crosson	45.0870	-79.0328	6	0.57	9.2	5216000	0.939	485	397.0	10.8	4.5	152.3
Crystal	44.7469	-78.4948	41	4.46	11.2	53900000	0.836	326	2203.7	4.0	5.5	130.7
Davis	44.7873	-78.7016	12	0.93	10.8	10002000	0.833	373	587.2	23.6	4.8	145.1
Dickie	45.1434	-79.0949	5	0.94	5.0	4667000	0.908	492	350.5	7.5	5.2	128.0
Drag	45.0540	-78.4375	106	10.03	18.0	180075000	0.888	480	5401.3	5.3	4.1	164.7
Esson	45.0090	-78.2513	21	2.45	10.9	26638000	0.872	475	1075.4	19.2	4.0	114.9
Glamor	44.9517	-78.3810	26	1.94	10.2	19790000	0.886	467	1234.1	16.0	4.7	91.1
Haliburton	45.1780	-78.4230	144	10.14	17.7	179650000	0.871	468	6804.0	7.6	3.5	107.9
Harp	45.3762	-79.1260	5	0.71	13.3	9508000	0.906	504	375.6	6.3	3.7	154.3
Johnson	45.2567	-78.6154	31	1.51	18.4	26960600	0.881	486	1381.6	4.2	2.5	125.5
Kabakwa	45.1094	-78.7959	3	1.15	6.9	7936000	0.906	485	170.2	5.8	3.8	70.2
Kennisis	45.2382	-78.5944	134	14.17	23.5	330009000	0.902	489	7195.7	2.7	2.8	97.7
Kushog North	45.1357	-78.8404	39	1.84	13.4	24691000	0.910	488	2013.3	5.4	3.1	98.3
L. Kennisis	45.2473	-78.5832	67	2.31	15.1	34819000	0.873	477	3443.2	5.1	3.7	223.1
L. Redstone	45.2090	-78.5564	138	2.26	12.8	30084000	0.880	478	6941.2	5.9	3.9	160.5

(cont'd)

McFadden	45.3344	-78.8424	2	0.54	11.5	6267000	0.896	498	118.8	10.3	2.5	94.0
Moose	45.1445	-78.4648	182	2.90	15.8	48140000	0.900	483	8734.9	6.6	3.3	235.8
Mountain	44.9926	-78.7019	927	3.23	8.5	42431000	0.871	460	461.2	5.5	3.0	95.2
Nunikani	45.1889	-78.7439	183	1.16	7.9	9092000	0.905	491	8602.6	4.6	2.5	83.9
Oblong	45.1785	-78.4331	151	0.91	10.0	9554000	0.875	477	7202.0	6.9	3.5	125.2
Percy	45.2075	-78.3868	71	5.96	15.6	65404000	0.860	464	3565.8	6.0	4.7	174.8
Red Pine	45.2117	-78.7126	177	3.65	10.1	36751000	0.904	490	7175.1	4.4	2.6	86.7
Redstone	45.1618	-78.5547	190	11.30	21.9	232925000	0.885	480	9453.9	5.0	3.0	74.4
Salmon	44.8270	-78.4387	7	1.72	11.3	19700000	0.840	339	466.0	4.0	3.7	80.7
Soyer's	45.0134	-78.6087	47	3.33	14.3	47493000	0.881	478	2825.1	6.2	5.5	145.3
Tallan	44.8418	-78.0491	4	0.45	3.9	4460000	0.815	388	231.3	12.0	5.4	88.1
Twelve Mile	45.0021	-78.7027	914	3.50	12.1	36254000	0.892	481	38843.9	4.7	3.3	90.9

a = calculated from water residence time (h^{-1}) and water volume (m^3)

b = more than 25 cm below surface

TP = total phosphorus

DOC = Dissolved Organic Carbon

Hg = mercury

Table 6.4: Equations used to estimate water inflow mercury (ng L^{-1}) from watershed variables (this study).

D Log **water inflow Hg** = 0.4922 + [0.1647 x log **watershed area**] + [0.1020 x **DOC**] – [0.3421 x log **water inflow rate**] + [0.000778 x **direct runoff**] + [0.0154 x **mean lake depth**]

$r^2 = 0.68$; $p < 0.0001$; RMSE = 0.11

E Log **water inflow Hg** = 0.8876 + [0.1425 x log **watershed area**] + [0.0809 x **DOC**] – [0.3177 x log **water inflow rate**] + [0.0153 x **mean lake depth**]

$r^2 = 0.64$; $p < 0.0001$; RMSE = 0.12

F Log **water inflow Hg** = 1.2206 + [0.1130 x log **watershed area**] - [0.2539 x log **water inflow rate**]

$r^2 = 0.44$; $p < 0.0001$; RMSE = 0.14

Units:	Confidence Interval:
Log water inflow Hg (ng L^{-1})	
Log watershed area (km^2)	0.24-1.00
DOC = dissolved organic carbon (mg L^{-1})	0.57-1.00
Log water inflow rate (annual average, m^3 h^{-1})	0.96-1.00
Direct runoff (mm yr^{-1})	0.05-0.97
Mean depth (m)	0.29-1.00

Table 6.5: Comparison of estimated versus measured values for water inflow mercury (ng L^{-1}).

			Water inflow Hg (ng L^{-1})						Watershed variables					
Lake name	Region	Country	Measured (literature)	Predicted	Equation *	Error (%)	Previous estimate	Error (%)	Watershed area (km^2)	Water inflow rate ($m^3 h^{-1}$)	DOC ($mg L^{-1}$)	Mean lake depth (m)	Direct runoff ($mm yr^{-1}$)	Reference
Big Dam West	NS	Canada	4.3	4.5	E	4.6	4.5	5.1	31.2	3878	8.1	2.5		Clair et al., 2005
North Cranberry	NS	Canada	2.5	3.1	E	18.8	5.2	51.8	3.6	347	3.8	1.4		Clair et al., 2005
Lake Ontario	ON	Canada	6	4.3	F	38.8	2.8	117.5	82990.0	31202		86.0		Atkinson et al., 2007
Lake Michigan	MN	USA	7.94	6.1	F	29.2	2.7	194.3	118000.0	9132		85.1		McCarty et al., 2004; Hurley et al., 1998
Spring	MN	USA	17	34.4	E	50.6	6.0	181.9	0.3	4	11.0	2.0		Hines and Brezonik, 2007
Bay of Puck	Baltic	Poland	0.62-2.1	2.7	F	21.8	3.7	43.7	693.5	24212		3.1		Boszke, 2005
Pallette	WI	USA	12.4-19.6	13.7	E	0.0	5.8	240.8	0.7	6	4.6	9.6		Eckley et al., 2005
Pallette	WI	USA	12.4-19.6	15.8	E	0.0	5.8	240.8	0.7	6	5.4	9.6		Eckley et al., 2005
Devils	WI	USA	2.25-9.49	4.9	E	0.0	4.0	0.0	220.0	40982	10.8	4.3		Eckley et al., 2005; Hurley et al., 1995
Devils	WI	USA	2.25-9.49	8.3	E	0.0	4.0	0.0	220.0	40982	13.6	4.3		Eckley et al., 2005; Hurley et al., 1995
Lake 240 (ELA)	WI	USA	8.4-10.5	9.3	D	0.0	5.0	66.6	5.7	69	7.0	6.1	226	Kelly et al., 1995
Lake Champlain	NY	USA	0.5-2.6	1.8	E	0.0	3.0	13.5	21328.0	892487	4.2	19.5		Gao et al., 2006
Lake Champlain	NY	USA	0.5-2.6	2.3	E	0.0	3.0	13.5	21328.0	892487	5.6	19.5		Gao et al., 2006
Amituk	NWT	Canada	0.76	1.7	E	54.3	4.0	80.8	265.0	19080	0.6	19.4		Semkin et al., 2005
Harp	ON	Canada	4.72	5.3	D	11.0	5.1	6.7	5.4	332	3.7	13.3	504	unpublished data
Dickie	ON	Canada	6.52	5.2	D	24.5	5.1	28.3	5.0	281	4.8	5.0	492	unpublished data
Onondaga	NY	USA	4	5.5	F	26.9	3.8	6.5	610.0	1380				Henry et al., 1995
Baikal	Siberia	Russia	0.4-1.7	1.3	F	0.0	2.5	31.5	450000.0	6849315				Meuleman et al., 1995
Lake Hoare	McMurdo	Antartica	0.9	1.1	E	18.3	5.4	83.4	1.8	57000		14.0		Vandal et al., 1998
ELA = Experimental Lakes Area														
* Equations are from Table 4														

Figure 6.1: HERMES model evaluation flowchart.

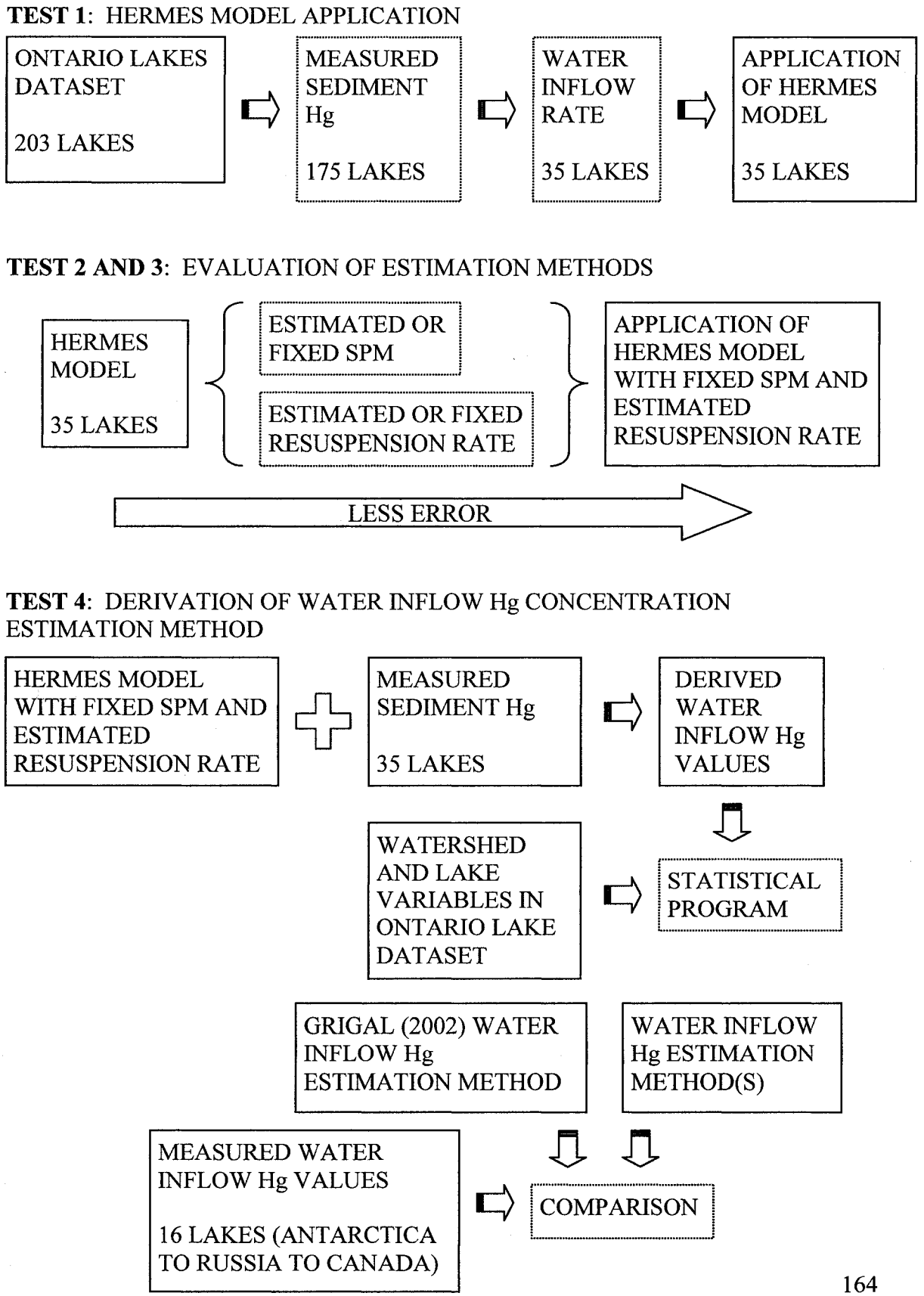


Figure 6.2: Deviation of error from zero for predicted sediment Hg concentration with the previous [A, Grigal (2002)] and derived [B, this paper] water inflow Hg concentration estimates.

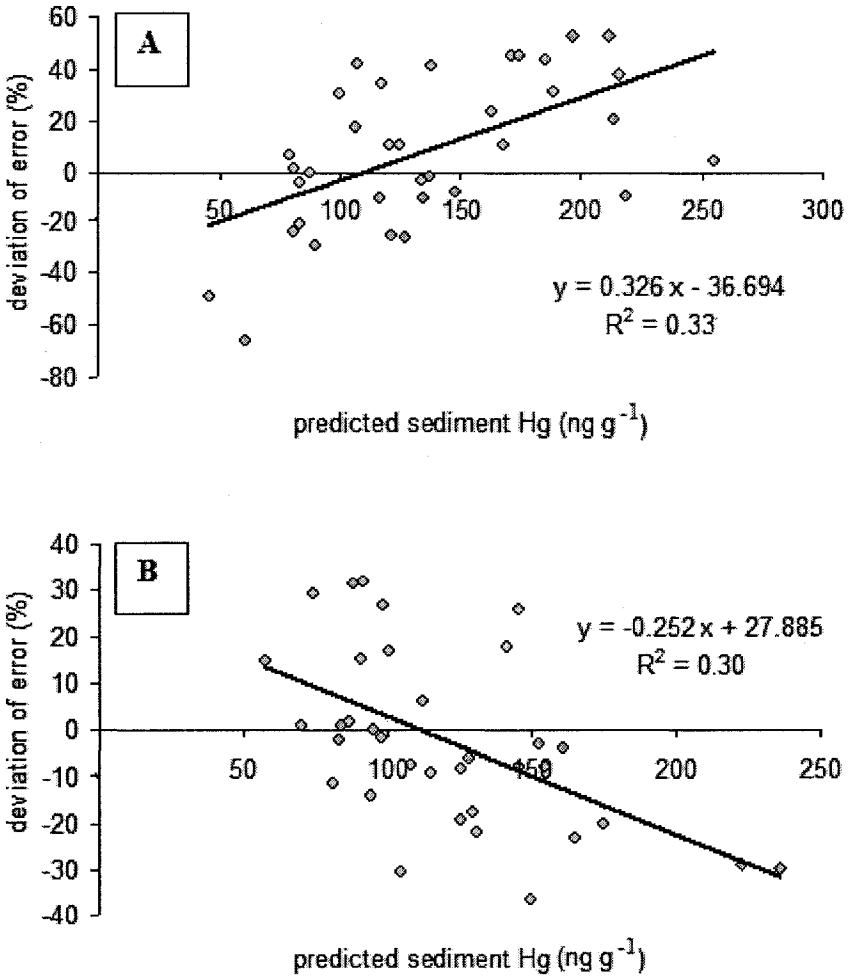
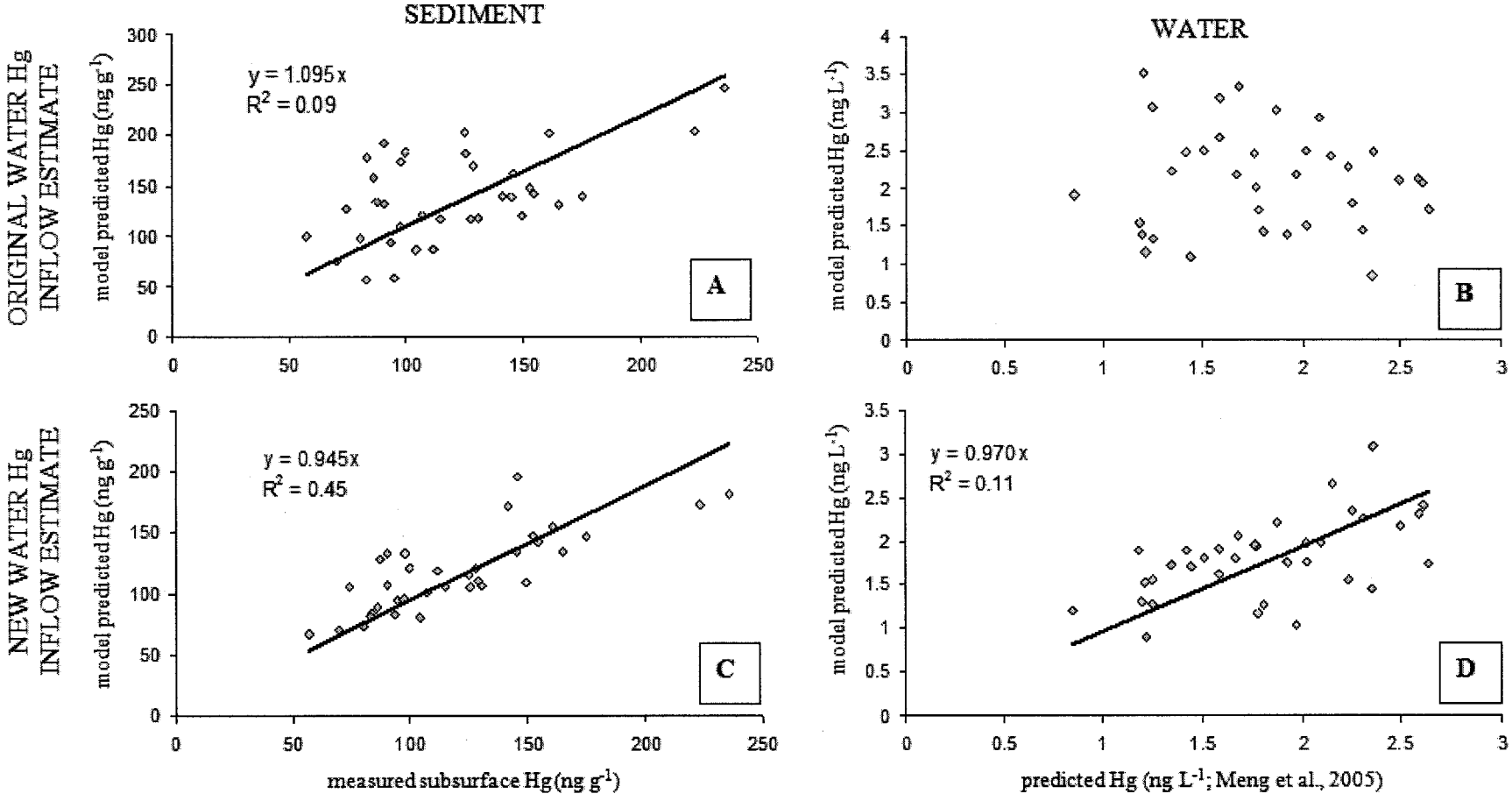


Figure 6.3: Measured versus predicted sediment (a, c) and water (b, d) Hg concentration with the previous (a, b) and derived (c, d) water inflow Hg concentration estimates.



CHAPTER 7

THESIS SUMMARY

7.0 SUMMARY AND CONCLUSIONS

A general Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model developed for Big Dam West, Kejimkujik Park, Nova Scotia was then successfully applied to 36 lakes throughout Ontario, including Harp Lake, Dickie Lake, and Lake Ontario. Application of the model to each lake involved changing very few model input variables ($n \leq 11$) and no further calibration. Some variables were specific to the location (e.g. concentration of Hg in air, precipitation rate), while others were specific to the lake (e.g. suspended particulate matter, sedimentation rate) or surrounding watershed (e.g. water inflow Hg concentration). Model output was found to be in agreement with output from more mechanistic models (i.e. numerous input variables adjusted with extensive calibration).

Experimental research was used to check model predictions for Harp and Dickie Lake, Ontario, and create model estimation methods (e.g., sediment THg and MeHg : THg ratio), along with others found in the available literature (e.g., suspended particulate matter). Estimation methods were included (1) for the lake or watershed model input variables to assist with model application to lakes with limited datasets; (2) as a 'double-check' for model output when measured Hg values are missing; and (3) to adjust MeHg : THg ratios for food web applications. In addition, an estimation method for water inflow Hg concentration that was

derived in this thesis was found to have a significantly higher correlation with measured values than the previous literature estimate.

Sensitivity analyses on model output for Big Dam West, Nova Scotia showed that water inflow Hg concentration was the most important mercuric source for small lakes (surface area < 10 km^2), with only negligible Hg contributions from the atmosphere. On the other hand, larger lakes (e.g., Lake Ontario) appear to show the opposite (i.e., atmospheric Hg important). If indeed true, this could have tremendous repercussions for local industries that have been accused of discharging mercuric wastes directly into Lake Ontario.

Potential reasons why model predictions for sediment Hg concentration tend to approximate subsurface sediment Hg in uncontaminated lakes have been addressed in this thesis (e.g., Chapter 2, 3). If the model is actually predicting surface sediment Hg when transient surface sedimentary processes are not accounted for (e.g., remobilization, focusing), then the next logical step would be to develop an equation to convert these model predictions (which tend to align closely with subsurface sediment Hg in uncontaminated lakes) to measured surface sediment Hg values. An attempt was undertaken with some of the lakes from the 203 lake dataset discussed in Chapter 6 to see whether an equation could be obtained with available data to enable predicted sediment Hg values to approximate measured surface sediment Hg (discussed in Appendix 3). In short, surface sediment Hg could be estimated by multiplying predicted sediment Hg (i.e., approximates subsurface sediment Hg in uncontaminated lakes) with an estimated surface sediment enrichment (surface / subsurface Hg) [log Surface Sediment Enrichment = 2.195 - (1.00299 x log Subsurface Sediment Hg (ng g^{-1})) + (0.000534

x Organic Carbon (surface, mg g^{-1})) + (0.02595 x Slope Watershed (%)) - (0.01065 x Dissolved Inorganic Carbon (mg L^{-1}), $r^2 = 0.64$, n = 53). Measured versus predicted surface sediment Hg was highly correlated ($r^2 = 0.70$, slope = 0.9, n =5) (note that this is an initial approximation since only a few lakes were used - see Appendix 3).

The general HERMES model was designed a screening-level tool for researchers and modellers to study Hg patterns and relationships with other environmental variables for lakes with limited datasets. Fine-scaled examinations would require the use of more mechanistic models that include interconversion and reaction rates among mercuric species, although Knightes and Ambrose (2007) suggested that the greatest change in predictive capability for the R-MCM (mechanistic) model could be gained by parameterizing the more general characteristics (e.g., pH, lake size, trophic status, stratification). HERMES should continue to evolve over time and eventually lend new insights into our understanding of Hg flux and fate in lakes (especially with regards to sediment total and bioavailable (MeHg) Hg fraction).

Future model applications could extend uncertainty analysis to include partition coefficients and fugacity capacities or to show fluxes in sensitivity analysis. Future model applications may also reveal other sensitive model parameters that merit further research.

7.1 SUPPORT FOR INITIAL HYPOTHESES

Hypothesis 1: Concentration ratios (MeHg : Hg^0, THg-MeHg-Hg^0 : Hg^0) can be used to model Hg concentrations and fluxes in the environment at steady-state conditions.

1 An sensitivity analysis on model output for Big Dam West Lake, Nova Scotia indicated that variations in concentration ratios do not result in significant changes to model output, although caution should be taken with THg-MeHg-Hg^0 : Hg^0 water column concentration ratio for some lakes (e.g., Harp and Dickie Lake). Model application to the 35 Ontario lakes provided further support for this conclusion since the same concentration ratios were used for each lake.

2 Experimental research conducted in this thesis showed that there was minimal horizontal and vertical spatial variation in MeHg : THg ratio throughout Harp, Dickie, and Blue Chalk lakes (homogeneous), even though other systems (e.g., St. Lawrence River) have reported substantial spatial variation. NOTE: Homogeneity within environmental media is an assumption of the HERMES model.

3 Environmental MeHg : Hg^0 and THg-MeHg-Hg^0 : Hg^0 ratios were obtained or calculated from the literature to find the expected range in a number of different media (e.g., river, lake, sediment). Few research papers in the literature were found that reported any two of elemental, methyl and total Hg concentrations in order to determine the extent of natural variations in the environment.

4 Model estimation methods for MeHg : THg ratio (i.e. stream (i.e., water inflow), lake, sediment) were obtained from the literature and through experimental research conducted in this thesis (i.e. sediment estimate).

Hypothesis 2: Models can reliably predict Hg fluxes and concentrations within lakes when only the most sensitive model input driving variables are adjusted.

1 The HERMES model was able to provide good predictions of sediment and water total Hg concentration for Harp and Dickie Lake, Ontario when few model variables (i.e., water inflow rate and Hg concentration, water inflow and lake suspended particulate matter, sedimentation rate, resuspension rate, rain rate, lake volume, surface area and mean depth) were adjusted, and without further model calibration. Predicted sediment Hg was then compared against data obtained from experimental research.

Application of the model to Lake Ontario indicated that the model could provide good Hg concentration and flux estimates for large urban lakes, even after adjusting few (n=11) model input variables (i.e., those adjusted for Harp and Dickie Lake plus atmospheric Hg concentration). Model output was found to be comparable to output from more specific models (i.e., use first-order rate constants – LOTOX2, STELLA).

2 No significant difference ($p < 0.05$) between model predictions and measured subsurface sediment Hg concentrations were found when model was applied to the 35 Ontario lakes, adjusting only ten model input variables with each application. The difference between model and measured values was attributed to the reliability of the estimation method used to predict water inflow Hg concentration. Measured

watershed and lake data for these 35 lakes were then used to improve the model estimation method for water inflow Hg concentration.

Hypothesis 3: The relative amount of methylated Hg (MeHg : THg) within lake sediments can be estimated from information on sediment chemical and physical properties.

1 MeHg was found to be highly correlated with THg in lake sediments.

2 Redox potential and TOC explained a significant portion of the MeHg : THg variability in sediments (measure of relative amount of methylated Hg).

3 Sediment THg was highly correlated with TOC, percent fines, and bulk density. The amount of organic matter will therefore influence the availability of Hg for methylation in sediments. In addition, sediment bulk density and percent fines are likely partly responsible for Hg distribution in lakes.

7.2 RECOMMENDATIONS FOR FUTURE RESEARCH

The HERMES model presented in this thesis could serve as a valuable screening level tool for Hg research. Numerous opportunities for future Hg environmental research are possible with the use of this model, a few of which are described in this section.

7.2.1 Food web models

Initial steps were taken in this thesis to improve model predictions for MeHg (i.e., bioavailable fraction). To further evaluate the MeHg : THg ratios and estimation methods (i.e., for water, sediment, water inflow) presented in this thesis, food web models should be constructed that use model predictions for sediment and water MeHg concentrations as input variables.

Future experimental research could involve measurements of Hg and MeHg concentrations in different media, and to subsequently relate MeHg : THg ratios to environmental variables. These relationships could be used to derive better estimation methods for MeHg : THg ratio, enhancing model MeHg predictions (i.e., for use in food web models). For example, if watershed variables and annual average Hg concentration (MeHg and THg) were measured in numerous lakes, MeHg : THg could be correlated with watershed variables. An estimation method (i.e., equation) could then be subsequently inserted into the Hg model so that the model water column MeHg : THg ratio adjusts to variations in the watershed.

As mentioned in the introduction, the model will not be able to properly estimate the biologically relevant Hg until surface sediment Hg can be estimated using subsurface model output and a multiplier that can account for variability in lake and watershed characteristics.

7.2.2 Surface sediment Hg

Although the topic of Hg remobilization within sediments remains unresolved, the emission from underlying sediment (ES) term in the model code can be used to account for either natural or past industrial Hg flux in sediments. In addition, an estimation method could be included in model code to account for sediment focusing so that the relative contribution from remobilzation and / or sediment focusing on surface sediment Hg enrichment patterns can be quantified.

An estimate is currently used in the model for the sediment-water mass transfer coefficient ($0.0002\ m\ h^{-1}$), a variable that influences the predicted amount of Hg in sediments. Measured values could not only improve this parameter, but if values differed among sites (e.g., contaminated versus uncontaminated), an equation could readily be incorporated into the model code to account for this.

7.2.3 Model input variables

Emission to water (EW) is a term that was intentionally included in the model code in order to account for direct sources of industrial contamination to the lake. A potential application of the model could include the evaluation of remedial action plans for contaminated lakes. In addition, the relative contribution from atmospheric, natural and direct industrial sources of Hg could be ascertained. Other mercuric sources could then be identified.

Of all the model input variables, water inflow Hg concentration is one of the most important determinants of overall model performance for small lakes. As estimation methods for this variable improve, a corresponding increase in model predictive ability should therefore be observed. The addition of suspended particulate matter as a routinely measured (or predicted from particulate organic carbon) lake water chemistry variable (e.g., secchi depth, total phosphorus, DOC) would improve model predictions. As the sensitivity analysis for Dickie Lake indicated, variations in water Hg^{2+} / Hg^0 ratios among lakes warrants further investigation. Model could adjust to account for variation when source(s) are found.

Even though the water inflow Hg concentration estimation method developed in Chapter 6 was able to produce good estimates, the equation may contain some residual error from the other sensitive sedimentary processes indicated in the Harp and Dickie Lake uncertainty analyses. Therefore, each variable in the equation should be assessed separately to determine whether their respective contribution relates to water inflow Hg concentration or another sensitive model input variable.

As the HERMES model is applied to more lakes in different areas or continents, potential shortcomings in the model will surface. If indeed this happens, it should be viewed as an opportunity for further research since it indicates that our understanding of the environment and the processes therein is incomplete. The model could serve as a tool to help identify the source(s) of the discrepancy within the lake, which would in turn improve the model. For example, application of the HERMES model to Lake Ontario (Chapter 5) indicated that the air-water and water-air volatilization mass transfer coefficients will likely vary with wind

velocity and percent ice cover (i.e., should add an equation in the model so that these variables are adjusted automatically).

7.2.4 Dam construction and removal

The model could be applied to a river system by dividing the river into a series of relatively homogeneous segments (i.e., models). For example, a hydro dam could divide one segment from another. Outflow from the first segment would be the inflow for the second segment in the series, outflow from the second would then be inflow for the third, and so forth down the stretch of river being modeled.

When new dams are constructed along a river system, the topography of the land, flow rate, distance between dams, and the height of dam wall are known and can be used to calculate the reservoir volume (a model segment) and the amount of flooded land. From this data, the model could be used to calculate expected peak (includes max emission to water from flooded land) and long-term Hg concentrations once the reservoirs have stabilized (without emission from flooded land). Model output, along with a food web model, could then be used to predict expected peak concentrations in local fish populations.

7.2.5 GIS platform

Incorporation of the model into a GIS platform would highlight potential areas of concern since the model can readily be applied to numerous lakes without recalibration. Data from

other modelers and /or researchers could be incorporated into the same platform to enable direct (and visual) comparisons to be made. GIS digital maps of the watershed could also potentially enable the incorporation of mercury transport equations within the model framework that could account for variations such as slope, aspect, elevation, etc…

7.2.6 Climate change

The vapour pressure used in the HERMES model presented in this thesis is sensitive to variations in lake temperature, as is the water solubility. The model thus contains the necessary components to study Hg distribution in lakes from much colder or warmer regions, or to study the impact of climate change on lakes in general.

REFERENCES

Allan C. J., Heyes A., Roulet N. T., St Louis V. and Rudd J. (2001) Spatial and temporal dynamics of mercury in Precambian Shield upland runoff. *Biogeochemistry* **52**, 13-40.

al-Shahristani, H. and Shihab, K.M. (1974) Variation of biological half-life of methylmercury in man. *Arch Environ Health* **28(6)**, 342-344.

Ambrose, R.B. (2004) Impacts of atmospheric deposition and lake and watershed processes on mercury exposures of fish and piscivorous wildlife in New England Lakes. Office of Research and Development, National Exposure Research Laboratory. FY04 Research Abstract, US EPA.

Atkinson, J. F., Jensen, J. N., Brown, S. and DePinto, J. V. (2007) Implementing a long term plan to improve modeling capabilities for toxic chemicals in Lake Ontario: Refinements to LOTOX2 atmospheric deposition processes and mercury submodel. Final Project Report. US EPA Region 2, EPA Agreement No. x-98269900-0

Avnimelech, Y., Ritvo, G., Meijer, L. E. and Kochba, M. (2001) Water content, organic carbon and dry bulk density in flooded sediments. *Aquacul Eng* **25**, 25-33.

Barber, M. (2003) A review and comparison of models for predicting dynamic chemical bioconcentration in fish. *Environ Toxicol Chem* **22(9)**, 1963-1992.

Bash, J.O., Bresnahan, P. and Miller, D.R. (2007) Dynamic surface interface exchanges of mercury: A review and compartmentalized modeling framework. *J Appl Meteorol Climatology* **46(10)**, 1606-1618.

Bash, J.O., Miller, D.R., Meyer, T.H. and Bresnahan, P. (2004) Northeast United States and southeast Canada natural mercury emissions estimated with a surface emission model. *Atmos Environ* **38**, 5683-5692.

Beauchamp, S., Tordon, R., Phinney, L., Abraham, K.,Young, K. and Macintosh, A. (2005) Mercury flux in aquatic and terrestrial ecosystems in Kejimkujik Park. In: O'Driscoll, N.J., Rencz, A.N., Lean, D.R.S., editors. Mercury cycling in a wetland dominated environment: A multidisciplinary study, Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 19-38.

Beckvar, N., Field, J., Salazar, S. and Hoff, R. (1996) Contaminants in aquatic habitats at hazardous waste sites: Mercury. NOAA Technical Memorandum NOS ORCA 100, National Ocean Service, National Oceanic and Atmospheric Administration, Seattle, WA

Benoit, J., Gilmour, C., Heyes, A., Mason, R.P. and Miller, C. (2003) Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems.

In: Chai, Y. and Braids, O.C., editors. Biogeochemistry of environmentally important trace elements, Washington DC: ACS, pp. 262-297.

Benoit, J., Gilmour, C. and Mason, R. (2001) The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of Desulfobulbus propionicus (1pr3). *Environ Sci Technol* **35**, 127-132.

Bjornberg, A., Hakanson, L. and Lundbergh, K. (1998) A theory on the mechanism regulating the bioavailability of mercury in natural waters. *Environ Poll* **49**, 53-61.

Blais J. M. and Kalff J. (1995) The influence of lake morphometry on sediment focusing. *Limnol Oceanogr* **40(3)**, 582-588.

Bloesch J. (1994) A review of methods used to measure sediment resuspension. *Hydrobiologia* **284**, 13-18.

Bloom, N.S. (1992) On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can J Fish Aquat Sci* **49**, 1010-1017.

Bodaly R, Hecky R and Fudge R. (1993) Increases in fish mercury levels in lakes flooded by the Churchill River Diversion, Northern Manitoba. *Can J Fish Aquat Sci* **41**, 682-91.

Bodek, T. (2008) Snow as a source of methyl mercury to temperate aquatic ecosystems. MSc thesis, University of Ottawa, Ottawa, ON.

Bonzongo, J.C., Heim, K.J., Chen, Y., Lyons, W.B., Warwick, J.J., Miller, G.C. and Lechler, P.J. (1996) Mercury pathways in the Carson River-Lahontan Reservoir system, Nevada, USA. *Environ Toxicol Chem* **15(5)**, 677-683.

Boszke, L. (2005) Fluxes and balance of mercury in the inner Bay of Puck, southern Baltic, Poland: an overview. *Oceanologia* **47(3)**, 325-350.

Boszke L., Kowalski A. and Siepak J. (2004) Grain size partitioning of mercury in sediments of the Middle Odra River (Germany / Poland). *Wat Air Soil Poll* **159**, 125-138.

Boszke L., Kowalski A., Glosinska G., Szarek R. and Siepak J. (2003) Environmental factors affecting speciation of mercury in the bottom sediments; An overview. *Pol J Environ Studies* **12(1)**, 5-13.

Boszke, L., Glosinska, G. and Siepak, J. (2002) Some aspects of speciation of mercury in a water environment. *Polish J Environ Studies* **11(4)**, 285-298.

Boudou A. and Ribeyre F. (1997) Mercury in the food web: Accumulation and transfer mechanisms. *Met Ions Biol Syst* **34**, 289-319.

Brown, D. S., Snyder, G. L., Taylor, R. L. (1998) Mercury concentrations in estuarine sediments, Lavaca and Matagorda Bays, Texas, 1992. USGS Water Resources Investigations Report 98-4038.

Burgess, N.M., Evers, D.C. and Kaplan, J.D. (1998) Mercury and reproductive success of common loons breeding in the Maritimes. In: Mercury in Atlantic Canada: A Progress Report, pp. 104-9. Environment Canada-Atlantic Region, Sackville, NB, Canada.

Burns, T.P., Hadden, C.T., Cornaby, B.W. and Mitz, S.V. (1997) A food web model of mercury transfer from stream sediment to predators of fish for ecological risk based clean-up goals. ASTM special tech pub 1317, pp. 7-27.

Cahill, T., Cousins, I. and Mackay, D. (2003) Development and application of a generalized Physiologically Based Pharmacokinetic Model for multiple environmental contaminants. *Environ Toxicol Chem* **22**, 26-34.

Cai Y., Jaffé R., Alli A. and Jones R. (1997) Determination of organic mercury compounds in natural waters by solid phase extraction and capillary gas chromatography with atomic fluorescence detection. *Anal Chim Acta*, **334,** 251-259.

Campbell L., Hecky R., Muggide R., Dixon D., and Ramlal P. (2003) Variation and distribution of total mercury in water, sediment and soil from northern Lake Victoria, East Africa. *Biogeochemistry* **65**, 195-211.

Campfens, J. and Mackay, D. (1997) Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. *Environ Sci Technol* **31**, 577-583.

Carpi, A. (1997) Mercury from combustion sources: A review of the chemical species emitted and their transport in the atmosphere. *Water Air Soil Poll* **98(3-4)**, 241-254.

Carrier, G., Bouchard, M., Brunet, R.C. and Caza, M. (2001) A toxicokinetic model for predicting the tissue distribution and elimination of organic and inorganic mercury following exposure to methyl mercury in animals and humans. II. Application and validation of the model in humans. *Toxicol Appl Pharmacol* **171(1)**, 50-60.

CCME (2002) Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Chen, C., Stemberger, R., Kamman, N., Mayes, B. and Folt, C. (2005) Patterns of Hg bioaccumulation and transfer in aquatic food webs across multi-lake studies in the northeast US. *Ecotoxicology* **14**, 135-147.

Chipps, S.R. and Bennett, D.H. (2002) Evaluation of a Mysis bioenergetics model. *J Plankton Res* **24**, 77-82.

Clair, T.A., Arp, P., Gabriel, C.E., Staicer, C., Brun, G.L., Holmes, J. and Lean, D.R.S. (2005) Surface water mercury budgets from a clear and a brown-water lake in Kejimkujik National Park. In: O'Driscoll, N.J., Rencz, A.N., Lean, D.R.S., editors. Mercury cycling in a wetland dominated ecosystem: A multidisciplinary study, Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 251-263.

Clark, K.E., Gobas, F.A.P.C. and Mackay, D. (1990) Model of chemical uptake and clearance by fish from food and water. *Environ Sci Technol* **24**, 1203-1213.

Cohen, M., Mierle, G., Sunderland, E. and Wang, S. (2006) Progress made development of a multi-compartment mercury model for the Great Lakes region. Presentation for the GLERL Seminar Series. September 14, 2006. Research & Development, International Joint Commission, US. ftp://ftp.glerl.noaa.gov/webcast/2006/sunderland/20060914.pdf

Cossa, D. and Gobeil, C. (2000) Mercury speciation in the Lower St. Lawrence Estuary. *Can J Fish Aquat Sci* **57(Suppl. 1)**, 138-147.

Croston N. J., Bubb J. M. and Lester J. N. (1996) Spatial distribution and seasonal changes in methylmercury concentrations in shallow lakes. *Hydrobiologia* **321**, 35-45.

Davis, A., Bloom, N. S. and Que He, S. S. (1997) The environmental geochemistry and bioaccessibility of mercury in soils and sediments: A review. *Risk Analysis* **17(5)**, 557-569.

Deckere, E. (2003) Faunal influence on sediment stability in intertidal mudflats. University of Groningen, Netherlands. PhD thesis dissertation. ISBN 9036717760. pp. 120 http://irs.ub.rug.nl/ppn/243063490

DeLaune R., Jugsujinda A., Devai I. and Patrick, Jr, W. (2004) Relationship of sediment redox conditions to methyl mercury in surface sediment of Louisiana lakes. *J Environ Sci Health* **A39(8)**, 1925-1933.

DePinto, J. V., Booty, W. and Young, T. C. (1997) A long term plan to improve modeling capabilities for toxic chemicals in Lake Ontario: Progress summary and draft implementation plan. Pre-workshop report submitted to EPA-Region II, Great Lakes Program, University of Buffalo, Buffalo, New York.

DePinto, J. V., Liu, S., Young, T. C. and Booty, W. G. (1999) An update of the Lake Ontario contaminant mass balance modeling project: Application of LOTOX2 to other LaMP chemicals. Proceedings of the Third Annual Lake Ontario Research and Management Workshop, October 27-28, 1999, Toronto, Ontario. H. Domske (ed). Great Lakes Monograph No. 13, Great Lakes Program, University of Buffalo, Buffalo, New York. pp. 33-36.

DePinto, J. V., Freedman, P. L., Dilks, D. M. and Larson, W. M. (2004) Models quantify the Total Maximum Daily Load process. *J Environ Eng* **130(6)**, 703-713.

Devito, K.J., Dillon, P.J. and Lazerte, B.D. (1989) Phosphorus and nitrogen retention in five Precambian shield wetlands. *Biogeochem* **8**, 185-204.

Diamond, M., Ganapathy, M., Peterson, S. and Mach, C. (2000) Mercury dynamics in the Lahontan Reservoir, Nevada: Application of the QWASI Fugacity/Aquivalence multispecies model. *Wat Air Soil Poll* **117(1-4)**, 133-156.

Diamond, M. L. (1999) Development of a fugacity/aquivalence model of mercury dynamics in lakes. *Water Air Soil Poll* **111**, 337-357.

Dillon, P. J. and Molot, L. A. (1997) Dissolved organic and inorganic carbon mass balances in central Ontario lakes. *Biogeochem* **36(1)**, 29-42.

Dillon, P. J., and Rigler, F. H. (1974) The phosphrous-chlorophyll relationship in lakes. *Limnol Oceanogr* **19(5)**, 767-773.

Drott, A., Lambertsson, L., Bjorn, E. and Skyllberg, U. (2007) Importance of dissolved neutral mercury sulfides for methyl mercury production in contaminated sediments. *Environ Sci Technol* **41(7)**, 2270-2276.

Drysdale, C. (2005) Kejimkujik National Park and Historic Site. In: O'Driscoll, N.J., Rencz, A.N., Lean, D.R.S., editors. Mercury cycling in a wetland dominated environment: A multidisciplinary study, Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 1-4.

Environment Canada. (2003) Canadian water quality guidelines for the protection of aquatic life: Inorganic and methylmercury. Environment Canada Report no. 1-7.

Eckley C., Watras C., Hintelmann H., Morrison K., Kent A. and Regnell O. (2005) Mercury methylation in the hypolimnetic waters of lakes with and without connection to wetlands in northern Wisconsin. *Can J Fish Aquat Sci* **62**, 400-411.

Eimers M., Paterson A., Dillon P., Schiff S., Cumming B. and Hall R. (2006) Lake sediment core records of sulphur accumulation and sulphur isotopic composition in central Ontario, Canada lakes. *J Paleolimnol* **35**, 99-109.

EPA. (2002) Total maximum daily load of mercury for Lake Lariat, Calvert County, Maryland. US EPA Region 3, Philadelphia, PA, December 2002, pp. 1-20.

Evans, R. D. (1994) Empirical evidence of the importance of sediment resuspension in lakes. *Hydrobiologia* **284,** 5-12.

Evans, R. D. (1981) Measurements of sediment accumulation and phosphorus retention using lead-210 dating. PhD thesis, McGill University, Canada. AAT 0535887

Fang, F., Wang, Q., Liu, R., Ma, Z. and Hao, Q. (2001) Atmospheric particulate mercury in Changchun City, China. *Atmos Environ* **35**, 4265-4272.

Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E. and Pirrone, N. (2000) Temporal trends in gaseous mercury evasion from the Mediterranean seawaters. *Sci Tot Environ* **259**, 183-190.

Fiore, A.M. and Jacob, D.J. (2003) The GEOS-CHEM chemical mechanism version 5-07-8. Harvard University, Cambridge, MA, USA. Available at http://www.env.leeds.ac.uk/~mat/GEOS-CHEM/geoschem_mech.pdf.

Friedli, H.R., Radke, L.F., Lu, J.Y., Banic, C.M., Leaitch, W.R. and MacPherson, J.I. (2003) Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements. *Atmos Environ* **37**, 523-567.

French K. J., Scruton D. A., Anderson M. R. and Schneider D. C. (1999) Influence of physical and chemical characteristics on mercury in aquatic sediments. *Wat Air Soil Poll* **110**, 347-362.

Fuller, K., Shear, H. and Wittig, J. (1995) The Great Lakes: An environmental atlas and resource book (3rd ed). Environment Canada Ontario Region, Toronto, Ontario and US EPA Great Lakes National Program Office, Chicago, Illinois. EPA http://www.epa.gov/glnpo/atlas/glat-ch1.html

Gabriel, M.C. and Williamson, D.G. (2004) Principal biogeochemical factors affecting the speciation and transport of mercury through the terrestrial environment. *Environmental Geochemistry and Health* **26**, 421-434.

Gao, N., Armatas, N. G., Shanley, J. B., Kamman, N. C., Miller, E. K., Keeler, G. J., Scherbatskoy, T., Holsen, T. M., Young, T., McIlroy, L., Drake, S., Olsen, B. and Cady, C. (2006) Mass balance assessment for mercury in Lake Champlain. *Environ Sci Technol* **40(1)**, 82-89.

Gilmour, C. and Riedel, G. (2000) A survey of size-specific mercury concentrations in game fish from Maryland fresh and estuarine waters. *Arch Environ Contam Toxicol* **39**, 53-59.

Gobeil, C., Macdonald, R.W. and Smith, J.N. (1999) Mercury profiles in sediments of the Arctic ocean basins. *Environ Sci Technol* **22**, 4194-4198.

Gobeil, C. and Cossa, D. (1993) Mercury in sediments and sediment pore water in the Laurentian Trough. *Can J Fish Aquat Sci* **50**, 1794-1800.

Goodwin, B. (2008) Personal email correspondence dated December 11, 2008. Atomic Energy of Canada Limited, Chalk River, Ontario.

Gottgens, J.F., Rood, B.E., Delfino, J.J. and Simmers, B.S. (1999) Uncertainty in paleoecological studies of mercury in sediment cores. *Wat Air Soil Pollut* **110(3-4)**, 313-333.

Grigal, D.F. (2002) Inputs and outputs of mercury from terrestrial watersheds: a review. *Environ Rev* **10**, 1-39.

Gustin, M.S. (2003) Are mercury emissions from geologic sources significant? *Sci Tot Environ* **304**, 153-167.

Hakanson, L. (2006) The relationship between salinity, suspended particulate matter and water clarity in aquatic systems. *Ecol Res* **21**, 75-90.

Hakanson, L. (2005) The importance of lake morphometry for the structure and function of lakes. *Internat Rev Hydrobiol* **90**, 433-461.

Hakanson, L (2003) Quantifying burial, the transport of matter from the lake biosphere to the geosphere. *Internat Rev Hydrobiol* **88(5)**, 539-560.

Han S., Obraztsova A., Pretto P., Choe K., Gieskes J., Deheyn D. and Tebo B. (2007) Biogeochemical factors affecting mercury methylation in sediments of the Venice Lagoon, Italy. *Environ Toxicol Chem* **26(4)**, 655-663.

He T., Lu J., Yang F. and Feng X. (2007) Horizontal and vertical variability of mercury species in pore water and sediments in small lakes in Ontario. *Sci Tot Environ* **386**, 53-64.

Henry, E.A., L.J. Dodge-Murphy, G.N. Bigham, S.M. Klein, and C.C. Gilmour (1995) Total mercury and methylmercury mass balance in an alkaline, hypereutrophic urban lake (Onondaga Lake, NY). *Water Air Soil Poll* **80**, 509–518.

Hickey, M.B., Gibson, J.C., Hill, J.R., Ridal, J.J., Davidson, J., Richardson, G.M., Holmes, J. and Lean, D.R.S. (2005) Influence of lake chemistry on methyl mercury concentrations in lake water and small fish in Ontario and Nova Scotia. In: O'Driscoll, N.J., Rencz, A.N., Lean, D.R.S., editors. Mercury cycling in a wetland dominated environment: A multidisciplinary study, Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 347-365.

Hines, N. A. and Brezonik, P. L. (2007) Mercury inputs and outputs at a small lake in northern Minnesota. *Biogeochemistry* **84(3)**, 265-284.

Hines N., Brezonik P. and Engstrom D. (2004) Sediment and porewater profiles and fluxes of mercury and methylmercury in a small seepage lake in Northern Minnesota. *Environ Sci Technol* **38**, 6610-6617.

Hoeniger, J. (1985) Microbial decomposition of cellulose in acidifying lakes of South-central Ontario. *Appl Environ Microbiol* **50(2)**, 315-322.

Holmes, J. and Lean, D. R. S. (2006) Factors that influence methylmercury flux rates from wetland sediments. *Sci Tot Environ* **368**, 306-319.

Hope, B. K. (2006) An assessment of anthropogenic source impacts on mercury cycling in the Willamette Basin, Oregon, USA. *Sci Tot Environ* **356(1-3)**, 165-191.

Hope, B. (2003) A basin-specific aquatic food web biomagnification model for estimation of mercury target levels. *Environ Toxicol Chem* **22(10)**, 2525-2537.

Horne, A. and Goldman, C. (1994) Limnology (2nd ed). McGraw-Hill, Inc.

Hung, G. A. and Chmura, G. L. (2006) Mercury accumulation in surface sediments of salt marshes of the Bay of Fundy. *Environ Poll* **142(3)**, 418-431.

Hunter, J.G., Burger, J. and Cooper, K.R. (2003) Use of an integrated mercury food web model for ecological risk assessment. *J Environ Sci Health Part A* **38(7)**, 1201-1214.

Hurley, J.P., Back, R.C., Armstrong, D.E., Shafer, M.M. and Rolfhus, K.R. (2000) Watershed influences on transport, fate, and bioavailability of Hg in Lake Superior (abstract). EPA Report R827629.

Hurley, J.P., Cowell, S.E., Shafer, M.M. and Hughes, P.E. (1998) Tributary loading of mercury to Lake Michigan: Importance of Seasonal events and phase partitioning. *Sci Tot Environ* **213(1-3)**, 129-137.

Hurley, J. P., Benoit, J. M., Babiarz, C. I., Shafer, M. M., Andren, A. W., Sullivan, J. R., Hammond, R. and Webb, D. A. (1995) Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environ Sci Technol* **29**, 1867-1875.

ISEE. (2008) Systems Thinking Experiential Learning Laboratory with Animation mercury model (STELLA). ISEE systems (formerly High Performance Systems), Lebanon, NH, USA.

Jepsen, R., Roberts, J., Lucero, A. and Chapin, M. (2001) Canaveral ODMDS dredged material erosion rate analysis. EPA Region 4 report. Sandia National Laboratories, USA.

Jeremiason J., Engstrom D., Swain E., Nater E., Johnson B., Almendinger J., Monson B. and Kolka R. (2006) Sulfate addition increases methylmercury production in an experimental wetland. *Environ Sci Technol* **40**, 3800-3806.

Kainz, M. and Lucotte, M. (2006) Mercury concentration in lake sediments - revisiting the predictive power of catchment morphometry and organic matter composition. *Wat Air Soil Poll* **170**, 173-189.

Kainz M., Lucotte M. and Parrish C.C. (2003) Relationships between organic matter composition and methyl mercury content of offshore and carbon-rich littoral sediments in an oligotrophic lake. *Can J Fish Aquat Sci* **60**, 888-896.

Kamman N., Chalmers A., Clair T., Major A., Moore R., Norton S. and Shanley J. (2005) Factors influencing mercury in freshwater surface sediments of Northeastern North America. *Ecotoxicology* **14**, 101-111.

Kannan K., Smith, Jr, R. G., Lee R. F., Windom H. L., Heitmuller P. T., Macauley J. M. and Summers J. K. (1998) Distribution of total mercury and methyl mercury in water, sediment, and fish from South Florida estuaries. *Arch Environ Contam Toxicol* **34**, 109-118.

Kelly C.A., Rudd J.W.M., St.Louis V.L. and Heyes A. (1995) Is total mercury concentration a good predictor of methyl mercury concentration in aquatic systems. *Water Air Soil Poll* **80**, 715-724.

Kereks, J. and Schwinghamer, P. (1973) Aquatic resource inventory, Kejimkujik National Park, N.S. Hydrographic maps, area and volume curves. Maitland Bridge (NS): Parks Canada, Canadian Wildlife Service Eastern Region, Dartmouth (NS).

Kerfoot W., Harting S., Jeong J., Robbins J. and Rossman R. (2004) Local, regional, and global implications of elemental mercury in metal (Copper, Silver, Gold, and Zinc) ores: Insights from Lake Superior sediments. *J Great Lakes Res* **30(Suppl 1)**, 162-184.

Kerin E. J., Gilmour C. C., Roden E., Suzuki M. T., Coates J. D. and Mason R. P. (2006) Mercury methylation by dissimilatory iron-reducing bacteria. *Appl Environ Microbiol* **72(12)**, 7919-7921.

King J., Harmon S., Fu T. and Gladden J. (2002) Mercury removal, methylmercury formation, and sulfate-reducing bacteria profiles in wetland mecocosms. *Chemosphere* **46**, 859-870.

Knightes, C.D. (2008) Development and test application of a screening-level mercury fate model and tool for evaluating wildlife exposure risk for surface waters with mercury-contaminated sediments (SERAFM). *Environ Model Software* **23**, 495-510.

Knightes, C.D. and Ambrose Jr., R.B. (2007) Evaluating regional predictive capacity of a process-based mercury exposure model, regional-mercury cycling model, applied to 91 Vermont and New Hampshire lakes and ponds, USA. *Environ Toxicol Chem* **26(4)**, 807-815.

Knightes, C.D. and Cyterski, M. (2005) Evaluating predictive error of a complex environmental model using a general linear model and least square means. *Ecol Model* **186**, 366-374.

Korthals E. and Winfrey M. (1987) Seasonal and spatial variations in mercury methylation and demethylation in an oligotrophic lake. *Appl Environ Microbiol* **53**(10), 2397-2404.

Lai, S., Holsen, T., M., Han, Y., Hopke, P. P., Yi, S., Blanchard, P., Pagano, J. J. and Milligan, M. (2007) Estimation of mercury loadings to Lake Ontario: Results from the Lake Ontario atmospheric deposition study (LOADS). *Atmos Environ* **41**, 8205-8218.

Lambertsson L. and Nilsson M. (2006) Organic material: The primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. *Environ. Sci. Technol.* **40**, 1822-1829.

Lindeberg C., Bindler R., Renberg I., Emteryd O., Karlsson E. and Anderson N. (2006) Natural fluctuations of mercury and lead in Greenland lake sediments. *Environ Sci Technol* **40**, 90-95.

Lindberg, S.E. and Stratton, W.J. (1998) Atmospheric mercury speciation: Concentrations and behavior of reactive gaseous mercury in ambient air. *Environ Sci Technol* **32**, 49-57.

Lindberg, S.E. (1987) Emission and deposition of atmospheric mercury vapor. In: Hutchinson, T.C., Meema, K.M. Lead, mercury, cadmium and arsenic in the environment: John Wiley & Sons Ltd., pp. 89-106.

Lindstrom, M., Hakanson, L., Abrahamsson, O. and Johansson, H. (1999) An empirical model for prediction of lake water suspended particulate matter. *Ecol Model* **121**, 185-198.

Lindstrom, M. (2000) Predictive modeling of heavy metals in urban lakes. Comprehensive summaries of Uppsala dissertations from the Faculty of Science and Technology 584. Dissertation for PhD in Sedimentology, Acta Universitatis Upsaliensis, Uppsala.

Liu, S., Nadim, F., Perkins, C., Carley, R.J., Hoag, G.E., Lin, Y. and Chen, L., (2002) Atmospheric mercury monitoring survey in Beijing, China. *Chemosphere* **48**, 97-107.

Lockhart W. L., Macdonald R. W., Outridge P. M., Wilkinson P., DeLaronde J. B. and Rudd J. W. M. (2000) Tests of the fidelity of lake sediment core records of mercury deposition to known histories of mercury contamination. *Sci Tot Environ.* **260**(1), 171-180.

Loux, N. (2000) Diel temperature effects on the exchange of elemental mercury between the atmosphere and underlying waters. *Environ Toxicol Chem* **19(4)**, 1191-1198.

Lucotte, M., Mucci, A., Hillaire-Marcel, C., Pichet, P., Grondin, A. 1995. Anthropogenic mercury enrichment in remote lakes of northern Quebec (Canada). *Wat Air Soil Poll* **80(1-4)**, 467-476.

MacFarlane, B. (2004) Mercury concentrations in water and sediment in Resurrection Creek, Alaska. Final report. USDA Forest Service, Chugach National Forest, Anchorage, Alaska.

Mackay, D. (2001) Multimedia environmental models: The fugacity approach (2nd edition). Lewis Publishers, London.

Mackay, D. and Stiver, W. (1991) Predictability and environmental chemistry. Chapter 8, pp. 281-297.

Mackay, D. and Diamond, M.L. (1989) Application of the QWASI (Quantitative Water Air Sediment Interaction) Fugacity Model to the Dynamics of Organic and Inorganic Chemicals in Lakes. *Chemosphere* **18**, 1343-1365.

Mackay, D., Joy, M. and Paterson, S. (1983) A Quantitative Water, Air, Sediment Interaction (QWASI) Fugacity Model for Describing The Fate of Chemicals in Lakes. *Chemosphere* **12**, 981-997.

Macleod, M., KcKone, T.E., Mackay, D. (2005) Mass balance for mercury in the San Franscisco Bay area. *Environ Sci Technol* **39**, 6721-6729.

Macleod, M., Fraser, A.J. and Mackay, D. (2002) Evaluating and expressing the propagation of uncertainty in chemical fate and bioaccumulation model. *Environ Toxicol Chem* **21**, 700-709.

Malmaeus, J. (2004) Variation in the Settling Velocity of Suspended Particulate Matter in Shallow Lakes, with Special Implications for Mass Balance Modelling. *Internat Rev Hydrobiol* **89(4)**, 426-438.

Marvin, C., Charlton, M., Milne, J., Thiessen, L., Schachtschneider, J., Sardella, G. and Sverko, E. (2007) Metals associated with suspended sediments in Lakes Erie and Ontario, 2000-2002. *Environ Monit Assess* **130**, 149-161.

Marvin C., Painter S. and Rossman R. (2004) Spatial and temporal patterns in mercury contamination in sediments of the Laurentian Great Lakes. *Environ Res* **95**, 351-362.

Marvin, C. H., Charlton, M. N., Reiner, E. J., Kolic, T., Macpherson, K., Stern, G. A., Brakevelt, E., Estenik, J. F., Theiessen, L. and Painter, S. (2002a). Surficial sediment contamination in lakes Erie and Ontario: A comparative analysis. *Journal of Great Lakes Research* **28(3)**, 437–450.

Marvin, C. H., Charlton, M. N., Stern, G. A., Brakevelt, E., Reiner, E. J. and Painter, S. (2002b). Spatial and temporal trends in sediment contamination in Lake Ontario. *Journal of Great Lakes Research* **79(2)**, 317–331.

McCarty, H.B., Miller, K., Brent, R.N. and Schofield, J. (2004) Results of the Lake Michigan mass balance study: Mercury data report. Great Lakes National Program Office (G-17J), US Environmental Protection Agency, Chicago, IL. EPA 905 R-01-012.

Meng, F., Arp, P., Sangster, A., Brun, G.L., Rencz, A.N., Hall, G.E., Holmes, J., Lean, D.R.S. and Clair, T.A. (2005) Modeling dissolved organic carbon, total and methyl mercury in Kejimkujik freshwaters. In: O'Driscoll, N., Rencz, A., Lean, D., editors. Mercury cycling in a wetland dominated environment: A multidisciplinary study, Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 267-284.

Meuleman, C., Leermakers, M. and Baeyens, W. (1995) Mercury speciation in Lake Baikal. *Water Air Soil Pollut* **80**, 539–551.

Mierle G. and Ingram R. (1991) The role of humic substances in the mobilization of mercury from watersheds. *Wat Air Soil Poll* **56**, 349-357.

Mills, R.B., Paterson, A.M., Blais, J.M., Lean, D.R.S., Smol, J.P. and Mierle, G. xxxx. Factors influencing the achievement of steady state in mercury contamination among lakes and catchments of south-central Ontario. Submitted to Can J Fish Aquat Sci.

Molot, L. and Dillon, P. (1993) Nitrogen mass balances and denitrification rates in central Ontario lakes. *Biogeochemistry* **20**, 195-212.

Morel, F.M.M., Kraepiel, A.M.L. and Amyot, M. (1998) The chemical cycle and bioaccumulation of mercury. *Annu Rev Ecol Syst* **29**, 543-566.

Morgan, M.G. and Henrion, M. (1990) Uncertainty. A guide to dealing with uncertainty in quantitative risk and policy analysis. Cambridge University Press, New York.

O'Driscoll N. J., Rencz A. N. and Lean D. R. S. (2005a) Mercury cycling in a wetland dominated environment: A multidisciplinary study. Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC).

O'Driscoll, N.J., Beauchamp, S.T., Clair. T.A., Rencz, A.N., Telmer, K.H., Siciliano, S.D. and Lean, D.R.S. (2005b) Mercury mass balance for Big Dam West Lake, Kejimkujik Park: the role of volatilization. In: O'Driscoll, N..J, Rencz, A.N., Lean, D.R.S., editors. Mercury cycling in a wetland dominated environment: A multidisciplinary study, Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 303-319.

O'Driscoll, N., Rencz, A., Lean, D. (2005c) The biogeochemistry and fate of mercury in natural environments. In: Sigel, A., Sigel, H., and Sigel, R.K.O., editors. Metal Ions in Biological Systems (Volume 43). Marcel Dekker, Inc., New York.

O'Driscoll, N.J., Siciliano, S.D. and Lean, D.R.S. (2003a) Continuous analysis of dissolved gaseous mercury in freshwater lakes. *Science Total Environ* **304**, 285-294.

O'Driscoll, N.J., Beauchamp, S.T., Siciliano, S.D., Rencz, A.N. and Lean, D.R.S. (2003b) Continuous analysis of dissolved gaseous mercury (DGM) and mercury flux in two freshwater lakes in Kejimkujik Park, Nova Scotia: Evaluating mercury flux models with quantitative data. *Environ Sci Technol* **37**, 2226-2235.

Oliveira, A., Rodrigues, A., Jouanneau, J.M., Weber, O., Alveirinho-Dias, J.M. and Vitorino, J. (1999) Suspended particulate matter distribution and composition on the northern Portuguese margin. *Bol Inst Esp Oceanogr* **15(1-4)**, 101-109.

Olmez, I., Ames, M.R. and Gullu, G. (1998) Canadian and U.S. sources impacting the mercury levels in fine atmospheric particulate material across New York state. *Environ Sci Technol* **32**, 3048-3054.

Ongley, E. (1996) Sediment measurements. In: Bartram, J. and Ballance, R. *editors*. Water quality monitoring – A practical guide to the design and implementation of freshwater quality studies and monitoring programmes. UNEP/WHO.

Patwa, Z., Christensen, R., Lasenby, D.C., Webster, E. and Mackay, D. (2007) An exploration of the role of mysids in benthic-pelagic coupling and biomagnification using a dynamic bioaccumulation model. *Environ Toxicol Chem* **26(6)**, 186-194.

Pavlogeorgatos, G. and Kikilias, V. (2002) The importance of mercury determination and speciation to the health of the general population. *Global Nest: the Int J* **4(2-3)**, 107-125.

Peckenham J. M., Kahl J. S., Nelson S. J., Johnson K. B. and Haines T.A. (2007) Landscape controls on mercury in streamwater at Acadia National Park, USA. *Environ Monit Assess* **126**, 97-104.

Petering, D. H. and Klump, V. (2003) Importance of the Great Lakes. *Environmental Health Perspectives* **111(3)**, A142.

Plouffe, A. (1995) Glacial dispersal of mercury from bedrock mineralization along Pinchi Fault, north central British Columbia. *Water Air Soil Poll* **80**, 1109-1112.

Poissant, L., Pilote, M., Xu, X. and Zhang, H. (2004) Atmospheric mercury speciation and deposition in the Bay St. Francois wetlands. *J Geophys Res* **109**, D11301.

Poissant, L., Amyot, M., Pilote, M. and Lean, D. (2000) Mercury water-air exchange over the Upper St. Lawrence River and Lake Ontario. *Environ Sci Technol* **34(15)**, 3069-3078.

Pyle, D.M. and Mather, T.A. (2003) The importance of volcanic emissions for the global atmospheric mercury cycle. *Atmos Environ* **37**, 5115-5124.

Qian, S.S., Warren-Hicks, W., Keating, J.I.M., Moore, D.R.J. and Teed, R.S. (2001) A predictive model of mercury fish tissue concentrations for the southeastern United States. *Environ Sci Technol* **35(5)**, 941-947.

Quinlan R., Paterson A. M., Smol J. P., Douglas M. S. V. and Clark B. J. (2005) Comparing different methods of calculating volume-weighted hypolimnetic oxygen (VWHO) in lakes. *Aquat. Sci.* **67**, 97-103.

Rasmussen J. and Vander Zanden M. (2004) The variation of lake food webs across the landscape and it effect on contaminant dynamics. In Food Webs at the Landscape Level (eds. G. Polis, M. Power, G. Huxel). University of Chicago Press, Chicago, pp. 169-182.

Rasmussen, J.B., Godbout, L. and Schallenberg, M. (1989) The humic content of lake water and its relationship to watershed and lake morphometry. *Limnol Oceanogr* **34(7)**, 1336-1343.

Rawls W. J., Pachepsky Y. A., Ritchie J. C., Sobecki T. M. and Bloodworth H. (2003) Effect of soil organic carbon on soil water retention. *Geoderma* **116**, 61-76.

Regnell, O., Hammar, T., Helgee, A., and Troedsson, B. (2001) Effects of anoxia and sulfide on concentrations of total and methyl mercury in sediment and water in two Hg-polluted lakes. *Can J Fish Aquat Sci* **58**, 506–517.

Regnell O. and Ewald G. (1997) Factors controlling temporal variation in methyl mercury levels in sediment and water in a seasonally stratified lake. *Limnol Oceanogr* **42(8)**, 1784-1795.

Rose J., Hutcheson M., Rowan West C., Pancorbo O., Hulme K., Cooperman A., DeCesare G., Maietta R. and Screpetis A. (1997) Fish mercury distribution in Massachusetts lakes. Massachusetts Department of Environmental Protection (MA DEP), 42 pp. http://www.mass.gov/dep/images/fish_hg.pdf

Roulet, M., Guimaraes, J. and Lucotte, M. (2001) Methylmercury production and accumulation in sediments and soils of an Amazonian floodplain – effect of seasonal inundation. *Wat Air Soil Poll* **128**, 41-60.

Ryaboshapko, A., Artz, R., Bullock, R., Christensen, J., Cohen, M., Dastoor, A., Davignon, D., Draxler, R., Ilyin, I., Munthe, J., Pacyna, J., Petersen, G., Syrakov, D., Travnikov, O. (2004) Intercomparison study of numerical models for long-range atmospheric transport of mercury. Progress Report. Stage III: Comparison of modeling results with long-term observations and comparison of calculated items of regional balances. EMEP. Meteorological Synthesizing Centre – East, Moscow, Russia.

Rytuba, J. J. (2000) Mercury and methylmercury concentration in sediment cores and surface water from Medicine Lake, California, USGS. In Bathymetric, geophysical and geologic sample data from Medicine Lake, Siskiyou County, northern California (eds. Childs, J. R., Lowenstern, J. B., Phillips, R. L., Hart, P., Rytuba, J. J., Barron, J. A., Starratt, S. W., Spaulding, S.) USGS 00-043.

Sando, S. K., Krabbenhoft, D. P., Johnson, K. M., Lundgren R. F., and Emerson, D. G. (2007) Mercury and methylmercury in water and bottom sediments of wetlands at Lostwood National Wildlife Refuge, North Dakota, 2003-2004: US Geological Survey Scientific Investigations Report 2007-5219, 66 pp.

SAS (2000) JMP. Version 4.0.2. SAS Institute, Inc., Cary, NC, USA.

Schmolke, S.R., Schroeder, W.H., Kock, H.H., Schneeberger, D., Munthe, J. and Ebinghaus, R. (1999) Simultaneous measurements of total gaseous mercury at four sites on a 800km transect: spatial distribution and short-time variability of total gaseous mercury over central Europe. *Atmos Environ* **33**, 1725-1733.

Selin, N.E., Jacob, D.J., Park, R.J., Yantosca, R.M., Strode, S., Jaegle, L. and Jaffe, D. (2007) Chemical cycling and deposition of atmospheric mercury: Global constraints from observations. *J Geophys Res* **112**, D02308, pp. 1-14.

Semkin, R.G., Mierle, G. and Neureuther, R.J. (2005) Hydrochemistry and mercury cycling in a High Arctic watershed. *Sci Tot Environ* **342(1-3)**, 199-221.

Shanley, J.B., Kamman, N.C., Clair, T.A. and Chalmers, A. (2005) Physical controls on total and methylmercury concentrations in streams and lakes of the Northeastern USA. *Ecotoxicology* **14**, 125-134.

Shi, J., Liang, L., Jiang, G. and Jin, X. (2005) The speciation and bioavailability of mercury in sediments of Haihe River, China. *Environ International* **31**, 357-365.

Siciliano S. D., Sangster A., Daughney C. J., O'Driscoll N. J. and Lean D. R. S. (2005) Geological dependence of MeHg concentrations in wetlands of Kejimkujik National Park. In Mercury cycling in a wetland dominated environment: A multidisciplinary study (eds. N. J. O'Driscoll, A. N. Rencz and D. R. S. Lean). Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 197-227.

Siciliano, S.D., O'Driscoll, N.J. and Lean, D.R.S. (2002) Dissolved gaseous mercury profiles in freshwaters. In: Cai, Y., Braids, O., editors. Biogeochemistry of environmentally important trace elements. ACS symposium series #835.

Smith, B.J. (2006) Exposure to mercury in West Virginia. Public Health Report. West Virginia Department of Health and Human Resources, Charleston, West Virginia.

Sosso-Kolle, K. (2008) Influences of geochemical features of the watershed on methylmercury export in streams: Spatial and temporal trends. M.Sc. thesis, University of Ottawa, Ottawa, Ontario.

Sousa, W. P., Carvalho, C. E. V., Carvalho, C. C. V. and Suzuki, M. S. (2004) Mercury and organic carbon distribution in six lakes from the North of Rio de Janeiro State. *Brazil Arch Biol Technol* **47(1)**, 139-145.

St. Louis, V., Rudd, J., Kelly, C., Beaty, K., Flett, R. and Roulet, N. (1996) Production and loss of methlymercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ Sci Technol* **30**, 2719-29.

Sunderland, E.M., Cohen, M.D., Selin, N.E. and Chmura, G.L. (2008) Reconciling models and measurements to assess trends in atmospheric mercury deposition. *Environ Poll* **156(2)**, 526-535.

Suns, K. and Hitchin, G. (1990) Interrelationships between mercury levels in yearling yellow perch, fish condition and water quality. *Water Air Soil Poll* **50**, 255–265.

Telmer K. H., DesJardins M. J. and Ferguson P. (2005) Mercury cycling in lake sediments and porewaters on modern to Holocene times scales. In Mercury cycling in a wetland dominated environment: A multidisciplinary study (eds. N. J. O'Driscoll, A. N. Rencz and D. R. S. Lean). Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC), pp. 69-114.

Tetra Tech Inc. (1999) Total maximum daily load and implementation plan for mercury: Arivaca Lake, Arizona. Arizona Department of Environmental Quality. U.S. Environmental Protection Agency, Region 9. Tetra Tech, Inc.

Tetra Tech Inc. (1996) Regional Mercury Cycling Model: A model for mercury cycling in lakes (R MCM Version 1.0b Beta). Tetra Tech Inc., Lafayette, CA.

Thomas, R.L. (1972) The distribution of mercury in the sediments of Lake Ontario. Canadian *Journal of Earth Sciences* **9**, 636–651.

Tomiyasu, T., Okada, M., Imura, R. and Sakamoto, H. (2003) Vertical variations in the concentration of mercury in soils around Sakurajima Volcano, Southern Kyushu, Japan. *Sci Total Environ* **304(1-3)**, 221-30.

Toose, L. and Mackay, D. (2004) Adaptation of fugacity models to treat speciating chemicals with constant species concentration ratios. *Environ Sci Tech* **38**, 4619-4626.
US EPA (2006) Lake Ontario Lakewide Management Plan 2006. US EPA Region 2 http://epa.gov/greatlakes/lakeont/2006/index.html

Upton, G. and Cook, I. (2004) Central limit theorem. A Dictionary of Statistics. Oxford University Press.

US EPA (2003) US EPA National listing of fish and wildlife advisory (NLFWA) fish tissue database. National fish and wildlife contamination program, U.S. Environmental Protection Agency (US EPA), Washington D.C.

USGA (1993) Standard test method for organic matter content of putting green and sports turf root zone mixes. United States Golf Association. ASTM F 1647-02a.

Vandal, G.M., R.P. Mason, D.M. McKnight and W. Fitzgerald. (1998) Mercury speciation and distribution in a polar desert lake (Lake Hoare, Antarctica) and two glacial meltwater streams. *Sci Tot Environ* **213(1-3)**, 229-237.

Wang, Q., Kim, D., Dionysiou, D.D, Sorial, G.A. and Timberlake, D. (2004) Sources and remediation for mercury contamination in aquatic systems – a literature review. *Environ Poll* **131**, 323-336.

Warner K., Bonzongo J., Roden E., Ward G., Green A., Chaubey I., Lyons W. and Arrington D. (2005) Effect of watershed parameters on mercury distribution in different environmental compartments in the Mobile Alabama River Basin, USA. *Sci Tot Environ* **347**, 187-207.

Warner K. A., Roden E. E. and Bonzongo J. (2003) Microbial mercury transformation in anoxic freshwater sediments under iron-reducing and other electron-accepting conditions. *Environ Sci Technol* **37**, 2159-2165.

Webster, E., Mackay, D., Di Guardo, A., Kane, D. and Woodfine, D. (2004) Regional differences in chemical fate model outcome. *Chemosphere* **55**, 1361-1376.

Weech, S., Scheuhammer, A., Elliott, J. and Cheng, K. (2004) Mercury in fish from Pinchi Lake region, British Columbia, Canada. *Environ Poll* **131**, 275-86.

Wiener J., Knights B., Sandheinrich M., Jeremiason J., Brigham M., Engstrom D., Woodruff L., Cannon W. and Balogh S. (2006) Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. *Environ Sci Technol* **40**, 6261-6268.

Wiener, J., Krabbenhoft, D., Heinz, G., Scheuhamer, A. (2003) Ecotoxicology of Mercury. In: Hoffman, D., Rattner, B., Burton, G., Cairns, J., editors. Handbook of Ecotoxicology (2nd ed), Lewis Publishers, Florida, pp. 409-463.

Correlates of Mercury in Fish from Lakes near Clyde Forks, Ontario, Canada

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Ethier, A.L.M., Scheuhammer, A.M., Bond, D.E. 2008. Correlates of mercury in fish from lakes near Clyde Forks, Ontario, Canada. Environ Pollution 154(1): 89-97.

Abstract
Subsurface soils near Clyde Forks, Ontario, Canada, can have naturally high concentrations of mercury (Hg) from local geological sources. To investigate Hg in local aquatic food webs, Hg was measured in fish dorsal muscle (mainly yellow perch [YP] and pumpkinseed sunfish [PS]) and sediments from 10 regional lakes. Water chemistry, along with fork length, weight, and stable isotopes ($\delta^{15}N$, $\delta^{13}C$, $\delta^{34}S$) in fish were also measured. No lake sediments had elevated Hg, and average Hg concentrations in fish were not sufficiently high (< 1 µg/g dw) to be of concern for fish-eating wildlife. Variance in fish Hg was best explained by lake variables (e.g., pH for YP) and dietary carbon source ($\delta^{13}C$). PS with more pelagic had higher $\delta^{34}S$ and Hg than those with more littoral feeding habits. Potential biological linkages between fish Hg and $\delta^{34}S$, a parameter that may be related to the lake sulphate-reducing bacteria activity, requires further investigation.

Capsule: Fish from lakes near a localized geological Hg source do not have elevated Hg concentrations.

Keywords: mercury, fish, sediment, sulfur isotopes, nitrogen isotopes, carbon isotopes

1. Introduction

Methylmercury (MeHg) is a persistent, bioaccumulative, and highly toxic form of mercury (Hg) that biomagnifies through aquatic foodchains. A major source of MeHg in aquatic systems is the methylation of inorganic Hg by sulfate-reducing bacteria (Regnell et al., 2001). Bacterial production of MeHg, and subsequent food chain transfer and accumulation by fish, is influenced by a number of lake-specific factors, including sediment Hg concentrations, watershed area, water temperature, and certain parameters of water chemistry, especially pH/alkalinity, and concentrations of dissolved organic matter (DOC) and sulfate (Bodaly et al. 1993; Chen et al., 2005; Gilmour and Riedel, 2000; Regnell et al., 2001; St. Louis et al., 1996; Weech et al., 2004). A major route of exposure to MeHg in humans and predatory wildlife is the consumption of fish that contain significant amounts of MeHg (Scheuhammer et al., 2007; USEPA, 1997).

There are numerous anthropogenic sources of inorganic Hg, the most important of which include coal combustion, municipal waste incineration, the use of Hg-amalgamation in gold mining, and waste from chloralkali production (Ikingura et al., 2006). Hg is also emitted to the environment from natural sources, such as from volcanic activity, large-scale forest / grass fires, and dispersal into soils and sediments near cinnabar (HgS) deposits (Friedli et al., 2003; Pyle & Mather, 2003; Plouffe, 1995).

A number of studies have examined Hg accumulation in biota in ecosystems contaminated by industrial sources of Hg (eg – Akagi et al., 1995: Barr, 1986; Weech et al. 2004), but studies examining the food-chain transfer and accumulation of Hg in aquatic environments near natural geologic Hg occurrences in the absence of mining activity are scarce. One purpose of the present study was to determine if elevated subsurface soil Hg

from a local geologic source was reflected in elevated Hg concentrations of surface sediments and small fish in nearby lakes. In addition to sediment Hg concentrations, various other parameters known to potentially influence fish Hg concentrations such as fish size (fork length and weight), relative trophic level, as indicated by $\delta^{15}N$ (Atwell et al., 1998; Weech et al., 2004), dietary carbon source, as indicated by $\delta^{13}C$ (Power et al. 2002), lake depth, lake surface area, and water chemistry [DOC, pH, SO_4, total phosphorus (TP), and total nitrogen (TN)] were also assessed. We also examined $\delta^{34}S$ in fish muscle as a possible correlate of fish Hg concentrations, since sulphur (S) is known to fractionate in the environment through the action of sulphate-reducing (SRB) (Brunner & Bernasconi, 2005; Kaplan & Rittenburg, 1964), and these bacteria are also responsible for much of the in-lake production of MeHg, the main form of Hg accumulated in fish.

2. Materials and Methods

Locations of study lakes, in relation to the estimated pattern of Hg concentrations in deep subsurface soils (till), are shown in Figure 1. Lakes were chosen because they were located at various distances from sites where Natural Resources Canada (NRCan) reported elevated Hg concentrations in till (up to 900 – 1000 μg/kg - Jonasson and Boyle, 1972; Kettles & Schilts, 1995). Silver Lake was the most distant of our study lakes, and is situated in an area having geologically low (<100 μg/kg) concentrations of Hg in till. Surface sediment (July and October 2002), fish (August 1999), and water (August 1999 and October 2002) were sampled from ten lakes (Robertson, Joe's, Flower Round, Silver, Little Green, Malcolm, Pine, Crotch, Lavant Long, and Widow), with the exception that we were

unable to collect sediment samples from Widow Lake.

Samples of profundal surface sediment (3-4 samples per lake) were collected from a small boat using an Eckman dredge and stored frozen in polyethylene bags prior to analysis. Sampling locations were spaced along the approximate centre line of the lake and were spatially recorded using a Garmin portable 12-channel Global Positioning System (GPS).

Individuals of the most abundant fish species [primarily pumpkinseed sunfish (*Lepomus gibbosus*) (PS) and yellow perch (*Perca flavescens*) (YP) with fork lengths <14 cm] were collected using baited minnow traps and by angling from boats. Fish were killed using tricaine methanesulfonate (MS-222, Sigma) added to water (100 μg/ml), and stored frozen prior to processing at the National Wildlife Centre (NWRC), Ottawa, Ontario. A total of 139 pumpkinseed sunfish (PS) and 67 yellow perch (YP) were collected from 9 lakes. We attempted to collect at least 15 individual fish from each study lake. There was only one lake (Little Green Lake) where neither PS nor YP were collected, as Little Green Lake had a different assemblage of fish species than other lakes in the area. Rock bass (*Ambioplites rupestris*; RB) and small mouth bass (*Micropterus dolomieui*; SMB) were the dominant species collected from Little Green Lake.

Water samples were collected (~40 cm below the surface, one sample per lake) at the approximate geographical centre of each lake in clean, acid-washed glass containers. Analysis of pH, DOC, SO_4^{2-}, TP, and TN was performed at the Great Lakes Forestry Centre in Sault Ste. Marie, Ontario. Additional lake information (maximum lake depth, lake area) was obtained from Mississippi Valley Conservation State of the Lake Environment Reports (MVC, 2000*a*; 2000*b*; 2000*c*; 2000*d*; 2002*a*; 2002*b*; 2002*c*).

2.1. Mercury Analyses

Total Hg concentrations in freeze dried dorsal muscle from these fishes and sediment samples were determined using continuous flow cold vapour atomic absorption spectrophotometry, or a dedicated Hg analyzer (AMA-254, Altec, Czech Republic) equipped with an ASS-254 autosampler using the method described previously (Scheuhammer and Bond, 1991; Weech et al., 2004). A Student's *t*-test on recovery of Hg in over 68 analyses of certified Standard Reference Materials (SRMs) using these two related analytical methods showed no statistical difference ($P = 0.99$).

Quality-assurance (QA) procedures included the analyses of replicate samples of fish and sediment to estimate analytical precision and of Standard Reference Materials (SRMs) [Fish Hg: DOLT-2 and DORM-2 (Dogfish liver and muscle, respectively, National Research Council Canada, NRCC), RM 1566 (Oyster Tissue, National Bureau of Standards, NBS) and Fish 279 (Hg Quality Assurance Program, MQAP); Sediment Hg: Estuarine Sediment 1646 (NBS) and Samples 1 to 4 (Northern Contaminants Program Interlaboratory Study NCP-II-1 Analysis of trace metals in sediments) (National Water Research Insitute, NWRI)] to estimate accuracy.

For determination of fish Hg by the AMA-254, recoveries averaged 99.7 ± 2.0% (n=12) for SRMs and 133.7 ± 2.5% (n =7) for the MQAP samples. For CVTAAS analyses, recovery averaged 97.7 ± 3.3% for SRMs and 99.3 ± 2.8% for the MQAP samples. For determination of sediment Hg by the AMA-254, recovery averaged 109.2 ± 15.1% (n=41) for SRMs. Precision for the AMA-254, as measured by same day replicate analyses, was 4.8 ± 3.9% RSD (n=11). Precision for CVTAAS, as measured by duplicate sample

analyses, was 7.3 ± 7.0% RSD (n=11).

2.2 Stable Isotope ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) Analyses

Duplicate samples of freeze-dried dorsal muscle (1.0 mg [for $\delta^{13}C$ and $\delta^{15}N$] or 1.8 mg [for $\delta^{34}S$]) from 89 pumpkinseed sunfish (PS) and 40 yellow perch (YP) were sealed into 5 x 9 mm tin capsules (Costech Analytical Technologies, Inc., Valencia, CA, USA) and analyzed for stable C, N, and S isotopes. Stable carbon and nitrogen isotope analyses were performed at the University of California, Davis by continuous-flow isotope-ratio mass spectrometry (CFIRMS) interfaced with a high-temperature (1000°C) elemental analyzer (ANCA-GSL, PDZEuropa). Samples were combusted to N_2 and CO_2 gases at 1000°C and separated on a Carbonsieve G column (Supelco, Bellefonte, PA, USA) before introduction into an isotope ratio mass spectrometer (IRMS). Sample isotope ratios were compared to those of standard gases injected directly into the IRMS before and after the sample peaks, and $\delta^{15}N$ and $\delta^{13}C$ values were calculated. The international reference standards used were carbonate rock from the Pee Dee Belemnite (PDB) formation for $\delta^{13}C$ (Craig, 1957), and atmospheric nitrogen gas (AIR) for $\delta^{15}N$ (Mariotti, 1983). Standards were assigned δ – values of 0.0‰ by convention. For $^{13}C_{PDB}$, the gas was calibrated against Hydrocarbon Oil – NBS 22 (NIST 8539); for $^{15}N_{AIR}$, the gas was calibrated against International Atomic Energy Agency N1 (NIST 8547). Ammonium sulphate ($\delta^{15}N$ = 1.33‰) and sucrose ($\delta^{13}C$ = -23.83‰) were used as check standards; these were analyzed before and after each set of samples, as well as after every twelfth sample, to determine accuracy of $\delta^{15}N$ and $\delta^{13}C$ measurements. Mean values ± SD for repeat analyses of check standards were 1.33 ± 0.09‰ for $\delta^{15}N$, and -23.83 ± 0.02‰ for $\delta^{13}C$ (n = 13).

Stable S analyses were performed at the University of Waterloo with the TracerMass / Roboprep system (Europa-UK). The international reference standard used for S was Canyon Diablo meteorite (δ –value of 0.0‰ by convention). Organic sulphur materials (Bovine Liver, NIST-SRM-1577; and Mussel, NIST-SRM-2977) were analyzed throughout the run as check standards (SD $\pm$ 0.5‰) and used to correct any machine drift, along with replicates that were added after every fifteenth sample (5.9 $\pm$ 4.3%; n=3). Since all our study lakes were located in the same area with comparable food webs, lake dimensions and water chemistry, no baseline correction was applied to our isotope data.

2.3 Statistics

Statistical analyses were conducted using SAS (SAS, 2002) or JMP (SAS, 2000). Fish Hg concentrations were normalized using the square-root transformation (residuals = 0 $\pm$ 0.15), and a least-squares means analysis of covariance (ANCOVA) with fork length as a covariate was used to determine if there were significant differences among study lakes and/or between YP and PS, with regard to fish Hg concentrations. Tukey's tests were then used to determine which lakes were significantly higher than others.

Subsequently, for each species, a general linear model (GLM) was run to determine which variables were best correlated with fish Hg. Initially, all continuous fish-related variables (weight, fork length, $\delta^{15}N$, $\delta^{13}C$, $\delta^{34}S$) plus the single categorical variable "Lake" were entered into the model. Subsequent iterations of the GLM were run by manually removing, in a stepwise manner, the non-significant variable with the least explanatory power, re-running the model, and repeating this procedure until only significant ($p < 0.05$) variables remained. The fish variables remaining in the model were then regressed

(forward stepwise regression) against square root fish Hg concentrations.

Because "Lake" was always a significant variable in the GLM, lake-specific least squares mean fish Hg concentrations, corrected for significant fish-related variables, were then used in a forward stepwise multiple regression against a selection of lake-specific variables (lake area, lake depth, sediment Hg, pH, SO_4, DOC, total phosphorus [TP], total nitrogen [TN]) to determine if any of these lake parameters explained a significant amount of remaining variance in fish Hg concentrations after biological variables had been accounted for.

A Mann-Whitney U test was used to determine whether there was a significant difference in fish $\delta^{34}S$ (and/or Hg) between the littoral and pelagic zones of across all of our study lakes. For the purposes of the present study, fish with $\delta^{13}C > -26‰$ were classed as "littoral", and fish with $\delta^{13}C < -26‰$ were classed as "pelagic" (adapted from Vander Zanden and Rasmussen, 1999).

All concentration data are expressed on a dry weight basis ± standard deviation, unless otherwise specified.

3. Results

Our study lakes were 60 – 870 ha in area, and generally mesotrophic (TP: 0.01 – 0.04 µg/ml; TN: 0.3 – 0.8 µg/ml) with a relatively narrow range in pH (7.4 – 9.2). Numbers of fish (YP and PS) sampled from each lake, fish and sediment Hg concentrations, along with other selected fish and water chemistry parameters from each lake are summarized in Table 1. Neither sediments nor fish were enriched in Hg in the lakes closest to reported mineral sources of Hg (Lavant Long Lake, and Little Green Lake)

(Fig. 2). Although PS from Lavant Long Lake did have significantly different (higher) Hg levels than PS from other lakes ($p<0.05$, Tukey's), PS Hg levels were substantially lower than those associated with reproductive or other impairments in fish-eating wildlife.

Although RB had the highest average fish Hg concentrations (~0.9 μg/g) of the 4 species sampled, RB and SMB were found only in Little Green Lake, therefore our statistical analyses focused on YP and PS which were sampled from a number of different lakes. Overall, YP from the present study averaged 11.5 ± 3.3 cm in fork length, with 0.63 ± 0.23 μg/g Hg in their dorsal muscle tissue; PS averaged 10.2 ± 3.6 cm with 0.36 ± 0.17 μg/g Hg.

There were significant differences (one-way ANCOVA with fork length as covariate, $P < 0.05$) in fish Hg concentrations between YP and PS across all our study lakes. In lakes where they co-occurred, YP tended to have significantly higher Hg concentrations than PS with the exception of Joe's Lake where there was no significant difference between YP and PS (Table 1).

3.1 Correlates of Fish Hg

Overall, fork length was significantly related to fish Hg in YP ($r = 0.43$; $p < 0.05$), but not in PS ($r = 0.08$, $p > 0.05$). However, results of the GLM stepwise elimination of non-significant parameters indicated that neither fork length nor weight significantly influenced fish Hg in either YP or PS, once variables with greater importance (primarily $\delta^{13}C$) were entered into the model.

For YP, only $\delta^{13}C$ and Lake had a significant effect ($p < 0.05$) on fish Hg in the final iteration of the GLM, although $\delta^{34}S$ was almost significant ($p=0.0726$) and thus was

retained with $\delta^{13}C$ in the regression analysis. In a regression of fish Hg against $\delta^{13}C$ and $\delta^{34}S$ using a forward stepwise approach, $\delta^{13}C$ explained 27% of the variation in fish Hg ($p = 0.0005$) and $\delta^{34}S$ did not explain a significant amount of additional variance (3%, $p = 0.182$). The resulting equation was: Square root [YP Hg (μg/g)] = $-0.046\ \delta^{13}C - 0.484$. Since the GLM also indicated a significant effect of Lake on YP Hg concentrations, lake-specific least squares mean YP Hg values corrected for the effects of $\delta^{13}C$ were generated and regressed against selected lake variables (lake area, lake depth, sediment Hg, pH, SO_4, DOC, TP, TN) using a forward stepwise approach. The first variable entering into the model was pH which alone explained 75% of the remaining variance in fish Hg ($p = 0.012$). The second variable entering the model was TN, which together with pH explained 97% of the remaining variation in YP Hg. No other lake variable was significant ($p>0.05$). The resulting equation was: Square root [YP Hg (μg/g)] = $4.4 - 0.52$ pH + 0.87 TN (ppm)]. Thus a combination of biological variables (primarily dietary carbon source, as indicated by $\delta^{13}C$), together with certain lake variables (especially pH) explained the majority of the variance in YP Hg concentrations.

For PS, only $\delta^{13}C$, $\delta^{15}N$, and Lake had a significant influence ($p < 0.05$) on fish Hg in the final iteration of the GLM. In a regression of fish Hg against $\delta^{13}C$ and $\delta^{15}N$ using a forward stepwise approach, $\delta^{13}C$ explained 32% of the variation in fish Hg ($p < 0.0001$); inclusion of $\delta^{15}N$ with $\delta^{13}C$ did not explain a significant amount of additional variance (2%, $p = 0.09$). The resulting equation was: Square root [PS Hg (μg/g)] = $-0.034\ \delta^{13}C - 0.277$. Since the GLM also indicated a significant effect of Lake on PS Hg concentrations, lake-specific least squares mean PS Hg values corrected for the effects of $\delta^{13}C$ were generated and regressed against selected lake variables (lake area, lake depth, sediment Hg, pH, SO_4,

DOC, TP, TN) using a forward stepwise approach. However, no lake variables met the significance level ($p<0.15$) for entry into the model.

3.2 $\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$

There was a significant negative relationship between $\delta^{15}N$ and $\delta^{13}C$ for both YP ($r = -0.47$, $p<0.01$) and PS ($r = -0.36$, $p<0.01$). Based on their range of $\delta^{15}N$ values, YP and PS occupied a similar trophic position; however, PS exhibited a wider range of $\delta^{13}C$ than YP, possibly indicating both littoral and pelagic feeding in this species, whereas YP were primarily pelagic feeders. PS with the more enriched (littoral) ^{13}C values also tended to have more depleted ^{15}N values (Figure 3).

There was considerable variability in fish $\delta^{34}S$ across our study lakes. Fish (both species) had average $\delta^{34}S$ values ranging from <2 ‰ (Joe's Lake) to >8 ‰ (Silver Lake). For PS, there was a significant positive relationship between $\delta^{15}N$ and $\delta^{34}S$ ($r = 0.63$, $P < 0.01$) and a significant negative relationship between $\delta^{13}C$ and $\delta^{34}S$ ($r = -0.43$, $P < 0.01$) (Figure 4). YP also showed a significant positive relationship between $\delta^{15}N$ and $\delta^{34}S$, though the association was poorer than in PS ($r = 0.34$; $P < 0.05$). A regression of PS $\delta^{34}S$ against $\delta^{15}N$ revealed that $\delta^{15}N$ explained about 40% of the variance in fish $\delta^{34}S$ ($P < 0.01$). The resulting equation was: Fish $\delta^{34}S(‰) = 1.26\ \delta^{15}N(‰) - 7.3$.

We divided all PS from all lakes into 2 groups, based on estimated pelagic vs. littoral feeding habits, as defined by their $\delta^{13}C$ values (France, 1995; Vander Zanden and Rasmussen, 1999). We considered fish with $\delta^{13}C < -26$ as primarily pelagic, and $\delta^{13}C > -26$ as primarily littoral; Figure 3. A significant ($P < 0.05$) between-group difference in both $\delta^{34}S$ and fish Hg was found. PS with more pelagic feeding habits tended to have both

higher Hg and greater ^{34}S enrichment than fish with more littoral feeding habits (Pelagic: $\delta^{34}S = 5.2 \pm 2.2‰$, and fish Hg = 0.42 ± 0.13 μg/g; Littoral: $\delta^{34}S = 3.2 \pm 1.8‰$, and fish Hg = 0.28 ± 0.12 μg/g). The majority of YP had $\delta^{13}C < -26$ (pelagic), thus a similar $\delta^{34}S$ comparison between pelagic and littoral fish were not practical for this species.

4. Discussion

An initial goal of the present study was to determine if elevated Hg concentrations in surficial sediments and aquatic biota (fish) were characteristic of lakes in close proximity to a reported local geological source of Hg in southeastern Ontario, Canada (Jonasson and Boyle, 1972). However, little evidence of elevated environmental Hg was observed. Surface sediments from lakes close to reported geological sources of Hg did not have higher Hg concentrations than more distant lakes. Surficial sediment Hg concentrations of all our study lakes (65-195 μg/kg) were well within the normal range reported previously for various lakes throughout Ontario (5 - 305 μg/kg) (Friske and Coker, 1995). Similarly, small fish from our study lakes did not have Hg concentrations sufficiently high (>1 μg/g) to be of potential concern for piscivorous wildlife, although numerous other lakes in Ontario contain small fish of various species (including YP) with average Hg concentrations high enough to be of concern for piscivorous wildlife (Scheuhammer & Blancher 1994).

Small- to medium-sized YP and PS from lakes in the Clyde Forks area had mean Hg concentrations typical of or lower than those in the same species from a number of other lakes that we have studied in Ontario. For example, Hg in <20 cm YP sampled from over 20 lakes across south-central Ontario averaged between about 0.2 and 2 μg/g Hg,

depending on the lake, with an overall mean of 0.76 ± 0.51 μg/g Hg (averaging individual fish-Hg data from Atchison, 1995; Scheuhammer & Graham, 1999; Scheuhammer et al., 1998). Small (~9 cm) YP from a number of lakes in Nova Scotia and New Brunswick, Canada, had substantially higher average Hg concentrations (~1.7 μg/g, converted from wet wt by assuming 80% water content) (Burgess & Hobson, 2006) than the slightly larger (mean 11.5 cm) YP from the current study. Thus, proximity of lakes to a localized geological source of Hg may not invariably result in elevated Hg concentrations in fish; nor were surface sediments obviously enriched with Hg in any of our study lakes. However, for PS, there was some indication that proximity to geological Hg sources might be important. After controlling for the effects of significant fish-related variables (primarily $\delta^{13}C$), PS from Lavant Long Lake, the lake closest to reported Hg occurrences in till, had significantly higher Hg concentrations than PS from other lakes. None of the physical or chemical lake variables tested (lake depth, lake area, sediment Hg, pH, DOC, SO_4, TP, TN) explained the significant among-lake difference in PS Hg; thus, some other lake-related factor not quantified in the present study must be the source of these lake differences.

Higher fish-Hg concentrations are often associated with waters with lower alkalinity, pH, and/or productivity (Burgess & Hobson, 2006; Chen et al., 2005; Munthe et al., 2007; Wiener et al., 2003). All of our study lakes had relatively high pH values (circumneutral to alkaline), conditions generally not associated with elevated Hg accumulation in fish relative to more acidic lakes; however, pH was a significant lake variable correlated with Hg in YP in the present study. Scheuhammer & Blancher (1994) reported lake pH and fork length to be among the best correlates of Hg concentrations in small perch from a large number of Ontario lakes; Greenfield et al. (2001) likewise found

that, for 43 northern Wisconsin lakes, of a number of parameters including biological traits such as fish trophic position and body condition, spatial traits such as lake hydrologic position and surrounding wetland abundance, and chemical traits such as pH and water color, the strongest predictor of perch Hg concentrations was lake pH.

4.1 $\delta^{15}N$, $\delta^{13}C$, $\delta^{34}S$, sulphate reducing bacteria, and fish Hg

Differences in feeding habits and/or trophic position are known to significantly influence Hg concentrations in fish; for example, there can be a 3 - 5-fold increase in MeHg between trophic levels (AMAP, 2005; Jackson, 1991; Power et al., 2002; Weech et al. 2004). Small YP and PS generally feed at a similar trophic level (3.0 - 4.0), (Vander Zanden et al., 1997) with diets consisting mainly of phytoplankton and zooplankton (juveniles), switching to benthic macroinvertebrates and some smaller fish as adults, especially for YP which become more piscivorous as they grow (Scott and Crossman, 1973). In the present study, average YP Hg concentrations were almost 2-fold higher than PS Hg concentrations, yet YP were not significantly enriched in ^{15}N when compared with PS (mean $\delta^{15}N = 9.3$ and 9.0, respectively; $P > 0.05$). It is doubtful that differences in trophic position between YP and PS can explain the observed differences in Hg concentrations in these 2 co-occurring fish species. However, PS had significantly higher mean $\delta^{13}C$ values than YP (mean -25.4 and -27.2, respectively; $P < 0.01$), which we interpret to possibly indicate a more littoral feeding strategy by PS; the base of the littoral food web tends to be enriched in ^{13}C (less negative $\delta^{13}C$) relative to the base of the pelagic food web in small freshwater lakes (France 1995). Thus higher Hg concentrations in YP may in part be related to a more pelagic feeding strategy in this species. Macrozooplankton

from pelagic zones frequently have higher MeHg concentrations than from littoral zones (Kainz et al., 2002).

Although numerous studies have reported on C and N isotope fractionation in food webs, fewer have examined S isotope fractionation in aquatic organisms (McCutchan et al., 2003). In the present study, we observed highly significant positive correlations between fish $\delta^{34}S$ and $\delta^{15}N$, especially for PS. It is generally thought that there is little or no fractionation of S isotopes with increasing trophic level (Krouse et al., 1991; Fry, 1988). Assuming a maximum 1-2‰ increase in ^{34}S with each trophic level ($\delta^{15}N$ = 3.14‰ per trophic level), the resulting relationship ($\delta^{15}N$ versus $\delta^{34}S$) should have a slope of 0.32 - 0.64. However, the regression of PS $\delta^{15}N$ versus $\delta^{34}S$ from the present study yielded a slope of 1.26, approximately double the expected maximum if fish ^{34}S enrichment were due solely to trophic fractionation. An additional influence may come from lake SO_4; ^{34}S enrichment in both PS and YP was greatest in the lake with the highest dissolved SO_4 concentration (9.0 μg/ml). Considerable fractionation of S isotopes can occur in lakes with SO_4 concentrations >4.0 μg/ml (Canfield, 2001; Thode, 1991) due to the dissimilatory reduction of SO_4 by SO_4-reducing bacteria (SRB), with lake water becoming enriched in ^{34}S relative to rain water (rainwater $\delta^{34}S$ = 2.2–4.2‰ for remote lakes on the Canadian Shield; Nriagu & Coker, 1978). In turn, lake SO_4 is also related to MeHg production by SRB. In freshwater (and estuarine) environments, a major source of Hg in fish muscle is MeHg created by SRB at near-anoxic (O_2 < 1 mg/L; redox potential ≤ -118 mV) conditions in surficial lake sediments and water column, and subsequently transferred to higher trophic levels mainly through diet (Axelrad et al., 2007; Regnell et al., 2001; King et al., 2001). Increasing lake SO_4 concentrations can be associated with both increased SRB activity and

elevated Hg concentrations in fish (Munthe et al., 2007). Thus, there may be significant biological linkages between bacterial SO_4 reduction, MeHg production, and consequent S fractionation and MeHg accumulation in fish. A further indication of such a linkage is our observation that when PS were divided into 2 groups based on higher or lower $\delta^{13}C$ values, significant differences were found in both $\delta^{34}S$ values and Hg concentrations.

Another potential source of ^{34}S enrichment in aquatic biota is anthropogenic pollution. For example, biota had enriched ^{34}S signatures downstream from a pulp mill compared with upstream sites (Wayland & Hobson, 2004). However, our study lakes were relatively remote from urban, industrial, or large-scale agricultural activity, thus it is unlikely that any of these activities can explain the observed variance in fish $\delta^{34}S$ in the present study.

4.2 Dam formation

There are no known local industrial sources of Hg in the Clyde Forks region. The main potential man-made influence on fish Hg concentrations in the region comes from the Crotch Lake, Barrett Chute and Mountain Chute dams, which together flooded over 1000 km^2 during reservoir creation. Crotch Lake is a true reservoir, and a few of our other study lakes (Pine, Malcolm, Widow) had small dams (<270 km^2 flooded). Reservoir formation is a known source of MeHg production and input to lakes and aquatic biota (Jackson, 1988; Louchouarn et al., 1993; Bodaly et al., 1984; Jackson, 1991). However, the dams in our study area, including Crotch Lake dam (ca. 1926), were all built over 30 years ago, and we judge that sufficient time has probably passed for fish Hg concentrations to have substantially declined following putative elevations subsequent to dam formation. This

interpretation is supported by the observation that YP collected from Crotch Lake did not have higher-than-average Hg concentrations compared with other nearby study lakes (Table 1).

5. Conclusions

In the present study, the presence of localized geological Hg sources had no clear influence on Hg concentrations in surface sediments, perch, or sunfish collected from nearby lakes. Fish in all study lakes had Hg concentrations equal to or lower than average for these species collected from other parts of the province, and lower than those reported to cause reproductive or other impairment in piscivorous wildlife such as common loons (*Gavia immer*). It may be that high Hg tills in the study area are sporadically distributed, and do not contribute greatly to the average Hg concentrations in lake sediments and fish. Similarly, Rasmussen et al. (2005) reported that elevated soil and air Hg in this area are restricted to a localized zone of linear bedrock shear, and decline rapidly within meters of the shear zone. In addition, all of our study lakes were circumneutral-to-alkaline, chemical conditions that tend to be associated with lower MeHg production and accumulation by fish compared with lower alkalinity/acidic conditions.

The best correlates of Hg in PS and YP in our study lakes were biological traits such as dietary carbon source ($\delta^{13}C$), which may reflect an influence of different feeding strategies on Hg accumulation. Lake variables known to influence the production and food chain transfer of MeHg (e.g. - lake pH, especially for YP) also played a role in explaining some of the variation in fish Hg. An indirect link between Hg and $\delta^{34}S$ in PS, mediated through differences in dietary carbon source ($\delta^{13}C$) was also observed. Because

environmental fractionation of S isotopes can result from the activity of SRB, which are also responsible for a large proportion of the Hg methylation activity in lake water and surface sediment, we suggest that relationships between SRB, $\delta^{34}S$, and the food chain transfer of MeHg to fish and wildlife warrant further investigation.

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References

Akagi, H., Malm, O., and Kinjo, Y. 1995. Methylmercury pollution in the Amazon, Brazil. Sci. Total Environ. 175, 85–95.

AMAP, 2005. AMAP Assessment 2002: Heavy metals in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, 265 pp.

Atchison, C.M., 1995. Mercury exposure in common loons (*Gavia immer*) breeding in Ontario. MSc Thesis, Trent University, Peterborough, Ontario, 82 pp.

Atwell, L., Hobson, K.A., Welch, H.E., 1998. Biomagnification and bioaccumulation of mercury in an arctic marine food web: Insights from stable nitrogen isotope analysis. Can. J. Fish. Aquat. Sci. 55, 1114-1121.

Axelrad, D.M., Atkeson, T.D., Lange, T., Pollman, C.D., Gilmour, C.C., Orem, W.H., Mendelssohn, I.A., Frederick, P.C., Krabbenhoft, D.P., Aiken, G.R., Rumbold, D.G., Scheidt, D.J., Kalla, P.I., 2007. Chapter 3B: Mercury Monitoring, Research and Environmental Assessment. In: *2007 South Florida Environmental Report – Volume I,* South Florida Water Management District, West Palm Beach, FL.

Barr, J.F., 1986. Population dynamics of the Common loon (*Gavia immer*) associated with mercury-contaminated waters in northwestern Ontario. Can. Wildl. Serv. Occas. Pap. No. 56, Ottawa, Canada, 25pp.

Bodaly, R.A., Rudd, J.W.M., Fudge, R.J.P., Kelly, C.A., 1993. Mercury concentrations in fish related to size of remote Canadian Shield lakes. Can. J. Fish Aquat. Sci. 50, 980-87.

Bodaly, R., Hecky, R., Fudge, R., 1984. Increases in fish mercury levels in lakes flooded by the Churchill River Diversion, Northern Manitoba. Can. J. Fish Aquat. Sci. 41, 682-91.

Brunner, B., Bernasconi, S.M., 2005. A revised isotope fractionation model for dissimilatory sulfate reduction in sulfate reducing bacteria. Geochim. Cosmochim. Acta 69, 4759-71.

Burgess, N.M., Hobson, K.A., 2006. Bioaccumulation of mercury in yellow perch (*Perca flavescens*) and common loons (*Gavia immer*) in relation to lake chemistry in Atlantic Canada. Hydrobiologia 567, 275-282.

Canfield, D., 2001. Isotope fractionation by natural populations of sulfate-reducing bacteria. Geochim. Cosmochim. Acta. 65, 1117-24.

Chen, C., Stemberger, R., Kamman, N., Mayes, B., Folt, C., 2005. Patterns of Hg bioaccumulation and transfer in aquatic food webs across multi-lake studies in the northeast US. Ecotoxicology 14, 135-147.

Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acta 12, 133-149.

France, R., 1995. Differentiation between littoral and pelagic food webs in lakes using stable carbon isotopes. Limnol. Oceanogr. 40, 1310-1313.

Friedli, H.R., Radke, L.F., Lu, J.Y, Banic, C.M., Leaitch, W.R., MacPherson, J.I., 2003. Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements. Atmos. Environ. 37, 523-567.

Friske, P., Coker, W., 1995. The importance of geological controls on the natural distribution of mercury in lake and stream sediments across Canada. Water Air Soil Pollut. 80, 1047-51.

Fry, B., 1988. Food web structure on Georges Bank from stable C, N, and S isotopic compositions. Limnol. Oceanogr. 33, 1182-1190.

Gilmour, C., Riedel, G., 2000. A survey of size-specific mercury concentrations in game fish from Maryland fresh and estuarine waters. Arch. Environ. Contam. Toxicol. 39, 53-59.

Greenfield, B., Hrabik, T., Harvey, C., Carpenter, S., 2001. Predicting mercury levels in fish: use of water chemistry, trophic ecology, and spatial traits. Can. J. Fish Aquat. Sci. 58, 1419-29.

Ikingura, J., Akagi, H., Mujumba, J., Messo, C., 2006. Environmental assessment of mercury dispersion, transformation and bioavailability in the Lake Victoria Goldfields, Tanzania. J. Environ. Manag. 81, 167-173.

Jackson, T., 1988. The mercury problem in recently formed reservoirs of Northern Manitoba (Canada): Effects of impoundment and other factors on the production of methyl mercury by microorganisms in sediments. Can. J. Fish Aquat. Sci. 45, 97-121.

Jackson, T., 1991. Biological and environmental control of mercury accumulation in lakes and reservoirs of Northern Manitoba, Canada. Can. J. Fish Aquat. Sci. 48, 2449-70.

Jonasson, I., Boyle, R., 1972. Geochemistry of mercury and origins of natural contamination of the environment. Can. Mining Metallur. Bull. 65, 32-39.

Kainz, M., Lucotte, M., and Parrish, C.C. 2002. Methyl mercury in zooplankton – the role of size, habitat, and food quality. Can. J. Fish. Aquat. Sci. 59, 1606-1615.

Kaplan, I., Rittenberg, S., 1964. Microbiological fractionation of S isotopes. Gen. Microbiol. 34, 195-212.

Kettles, I., Shilts, W., 1995. Geochemistry of surficial sediments, southeastern Ontario: Geological Survey of Canada, Open File 3175, 16 map sheets, Ottawa, Canada.

King, J., Harmon, S., Fu, T., Gladden, J., 2002. Mercury removal, methylmercury formation, and sulfate-reducing bacteria profiles in wetland mesocosms. Chemosphere. 46. 859-70.

Krouse, H.R., Stewart, J.W.B., Grinenko, V.A., 1991. Pedosphere and biosphere. In: Krouse, H.R., Grinenko, V.A. (Eds.), Stable Isotopes. Natural and Anthropogenic Sulphur in the Environment. SCOPE, Vol. 43, John Wiley and Sons Ltd., Chichester, UK, pp 267–306.

Louchouarn, P., Lucotte, M., Mucci, A., Pichet, P., 1993. Geochemistry of mercury in two hydroelectric reservoirs in Quebec, Canada. Can. J. Fish Aquat. Sci. 50, 269-81.

Mariotti, A., 1983. Atmospheric nitrogen is a reliable standard for natural ^{15}N abundance measurements. Nature 303, 685-687.

McCutchan, J.H.Jr., Lewis, W.M.Jr., Kendall, C., and McGrath, C.C., 2003. Variation in trophic shift for stable isotope ratios of carbon, nitrogen, and sulfur. Oikos 102, 378-390.

Munthe, J., Bodaly, R.A., Branfireun, B.A., Driscott, C.T., Gilmour, C.C., Harris, R., Horvat, M., Lucotte, M., Maim, O., 2007. Recovery of mercury-contaminated fisheries. Ambio 36, 33-44.

MVC, 2000*a*. State of the Lake Environment Report (December 2000): Crotch Lake. Watershed Watch. Mississippi Valley Conservation (http://www.mvc.ca).

MVC, 2000*b*. State of the Lake Environment Report (December 2000): Malcolm Lake. Watershed Watch. Mississippi Valley Conservation, (http://www.mvc.ca).

MVC, 2000*c*. State of the Lake Environment Report (December 2000): Pine Lake. Watershed Watch. Mississippi Valley Conservation, (http://www.mvc.ca).

MVC, 2000*d*. State of the Lake Environment Report (December 2000): Silver Lake. Watershed Watch. Mississippi Valley Conservation, (http://www.mvc.ca).

MVC, 2002*a*. State of the Lake Environment Report (December 2002): Flower Round Lake. Watershed Watch. Mississippi Valley Conservation, (http://www.mvc.ca).

MVC, 2002*b*. State of the Lake Environment Report (December 2002): Joe's Lake. Watershed Watch. Mississippi Valley Conservation, (http://www.mvc.ca).

MVC, 2002*c*. State of the Lake Environment Report (December 2002): Robertson Lake. Watershed Watch. Mississippi Valley Conservation, (http://www.mvc.ca).

Nriagu, J., Coker, R.D., 1978. Isotopic composition of sulphur in atmospheric precipitation around Sudbury, Ontario. Nature 274, 883-885.

Plouffe, A., 1995. Glacial dispersal of mercury from bedrock mineralization along Pinchi Fault, north central British Columbia. Water Air Soil Pollut. 80, 1109-1112.

Power, M., Klein, G., Guiguer, K., Kwan, M., 2002. Mercury accumulation in the fish community of a sub-Arctic lake in relation to trophic position and carbon sources. J. Appl. Ecol. 39, 819-30.

Pyle, D.M., Mather, T.A., 2003. The importance of volcanic emissions for the global atmospheric mercury cycle. Atmos. Environ. 37, 5115-5124.

Rassmussen, P.E., Edwards, G., Schroeder, W., Ausma, S., Steffen, A., Kemp, J., Hubble-Fitzgerald, C., Bilali, L.E., and Dias, G. 2005. Measurement of gaseous mercury fluxes in the terrestrial environment. In: Parsons, M.B., Percival, J.B. (Eds.), Mercury: Sources, Measurement, Cycles, and Effects. Mineralogical Association of Canada Short Course Series, vol 34, Ottawa, Canada, pp. 123-138.

Regnell, O., Hammar, T., Helgee, A., Troedsson, B., 2001. Effects of anoxia and sulfide on concentrations of total and methyl mercury in sediment and water in two Hg-polluted lakes. Can. J. Fish Aquat. Sci. 58, 506-17.

Reuther, R., 1994. Mercury accumulation in sediment and fish from rivers affected by alluvial gold mining in the Brazilian Madeira River basin, Amazon. Environ. Monitor. Assessment. 32, 239-258.

SAS, 2002. Stats done with SAS 9.1 TS level 1M3 XP Pro platform
SAS Institute Inc., Cary, NC, USA.

SAS, 2000. JMP. Version 4.0.2. SAS Institute, Inc., Cary, NC, USA.

Scheuhammer, A., Blancher, P., 1994. Potential risk to common loons (*Gavia immer*) from methylmercury exposure in acidified lakes. Hydrobiologia 279/280, 445-455.

Scheuhammer, A., Bond, D., 1991. Factors affecting the determination of total mercury in biological samples by continuous-flow cold vapour atomic absorption spectrophotometry. Biol. Trace Elem. Res. 31, 119-29.

Scheuhammer, A., Graham, J., 1999. The bioaccumulation of mercury in aquatic organisms from two similar lakes with differing pH. Ecotoxicology 8, 49-56.

Scheuhammer, A.M., Atchison, C.M., Wong, A.H.K., Evers, D.C., 1998. Mercury exposure in breeding common loons (*Gavia immer*) in central Ontario, Canada. Environ. Toxicol. Chem. 17, 191-196.

Scheuhammer, A.M., Meyer, M.W., Sandheinrich, M.B., Murray, M.W., 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. Ambio 36,

12-18.

Scott, W., Crossman, E., 1973. Freshwater Fishes of Canada. Fisheries Research Board of Canada Bulletin 184, Ottawa, Canada, 966 pp,

St. Louis, V., Rudd, J., Kelly, C., Beaty, K., Flett, R., Roulet, N., 1996. Production and loss of methlymercury and loss of total mercury from boreal forest catchments containing different types of wetlands. Environ. Sci. Technol. 30, 2719-29.

Thode, H.G., 1991. Sulphur isotopes in nature and the environment: An overview. In: Krouse, H.R., Grinenko, V.A. (Eds.), Stable Isotopes. Natural and Anthropogenic Sulphur in the Environment. SCOPE, Vol. 43, John Wiley and Sons Ltd., Chichester, UK, pp. 1-26.

USEPA, 1997. Mercury Study Report to Congress, Vol. VII: Characterization of human health and wildlife risks from mercury exposure in the United States. EPA-452/R97-009. Office of Air Quality Planning and Standards, and Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC.

Vander Zanden, M., Rasmussen, J., 1999. Primary consumer $\delta^{13}C$ and $\delta^{15}N$ and the trophic position of aquatic consumers. Ecology 80, 1395-1404.

Vander Zanden, M., Cabana, G., Rasumssen, J., 1997. Comparing trophic position of freshwater fish calculated using stable nitrogen isotope ratios $\delta^{15}N$ and literature dietary data. Can. J. Fish. Aquat. Sci. 54, 1142-1158.

Wayland, M., Hobson, K., 2004. Stable carbon, nitrogen, and sulfur isotope ratios in riparian food webs on rivers receiving sewage and pulp-mill effluents. Can. J. Zool. 79, 5-15.

Weech, S., Scheuhammer, A., Elliott, J., Cheng, K., 2004. Mercury in fish from Pinchi Lake region, British Columbia, Canada. Environ. Pollut. 131, 275-86.

Wescott, K., Kaiff, J., 1996. Environmental factors affecting methyl mercury accumulation in zooplankton. Can. J. Fish Aquat. Sci. 53, 2221-28.

Wiener, J., Krabbenhoft, D., Heinz, G., Scheuhammer, A., 2003. Ecotoxicology of mercury. In: *Handbook of Ecotoxicology (second edition)*, D.J. Hoffman, B.A. Rattner, G.A. Burton, & J. Cairns, eds. Lewis Publishers, CRC Press, Boca Raton. pp. 409-4.

Appendix 1A

Table 1. Summary of study lake locations, sizes, and water chemistry and mean Hg concentrations in lake sediments and fish (μg/g dw).

										Mean concentration of Hg (ug/g) ±SD (n)						Mean stable isotope (‰) +SD (n)									
Lake name	Latitude (dd)[a]	Longitude (dd)	Lake Area (ha)	Lake Depth (m)[b]	pH	SO4 ppm	DOC ppm	TP ppb	TN ppm	Sediment		PS[c]		YP[d]		$\delta^{13}C$ (PS)		$\delta^{13}C$ (YP)		$\delta^{15}N$ (PS)		$\delta^{15}N$ (YP)		$\delta^{34}S$ (PS)		$\delta^{34}S$ (YP)	
Joe's Lake	45.1327	-76.6416	63.7	4.3	9.17	4.11	9.74	285	0.687	0.19	±0.01 (3)	0.24	±0.14 (14)	0.62	±0.33 (3)	-26.69	±0.69(6)	-26.30	±0.09(2)	6.81	±0.89(6)	6.54	±0.04(2)	0.95	±0.35(5)	0.96	±0.22(2)
Flower Round Lake	45.1684	-76.6908	98.3	12.8	7.91	6.47	7.07	399	0.537	0.17	±0.10 (3)	0.38	±0.09 (16)	0.68	±0.11 (10)	-26.66	±1.24(13)	-29.21	±1.43(7)	9.55	±0.50(13)	10.25	±0.71(7)	3.51	±0.66(12)	3.30	±0.66(7)
Silver Lake	44.8308	-76.5896	248.2	24.4	8.25	9.02	6.06	175	0.864	0.19	±0.13 (4)	0.41	±0.10 (39)	0.56	±0.10 (16)	-27.09	±1.02(26)	-27.42	±0.98(8)	10.10	±0.58(26)	9.50	±0.50(8)	7.12	±0.94(24)	8.06	±0.28(7)
Robertson Lake	45.0611	-76.6553	72.4	30.5	8.06	6.53	3.72	94	0.515	0.09	±0.04 (3)	0.29	±0.13 (21)	0.35	±0.00 (1)	-24.58	±0.78(17)	-25.15	±0.00 (1)	9.26	±0.74(17)	8.86	±0.00 (1)	2.10	±0.79(16)	4.24	±0.00 (1)
Lavant Long Lake	45.1348	-76.7382	91.3	9.1	7.99	8.07	5.91	141	0.436	0.18	±0.03 (3)	0.47	±0.17 (13)			-23.83	±1.81(10)			7.68	±0.45(10)			1.96	±1.22(10)		
Malcolm Lake	44.9135	-76.8693	214.9	4.6	8.11	5.26	5.88	75	0.563	0.06	±0.00 (3)	0.23	±0.08 (18)	0.46	±0.29 (3)	-22.88	±1.05(15)	-21.92	±0.00 (1)	8.25	±0.46(15)	7.06	±0.00 (1)	3.78	±1.05(15)	3.04	±0.00 (1)
Pine Lake	44.9000	-76.8811	194.5	17.7	7.41	4.71	6.95	64	0.403	0.17	±0.11 (3)			0.84	±0.26 (15)			-26.63	±2.12(12)			8.99	±0.64(12)			5.50	±0.41(9)
Little Green Lake	45.1420	-76.6083	32.7	21.0	8.39	9.90	5.60	26		0.18	±0.02 (4)																
Crotch Lake	44.8700	-76.8061	867.0	31.1	7.55	5.18	7.29	92	0.357	0.14	±0.07 (3)			0.63	±0.15 (16)			-27.10	±0.52(13)			9.57	±0.78(13)			4.74	±0.58(13)
Widow Lake	45.1450	-76.6861	95.0	6.1	8.04	6.28	7.53	142	0.547			0.45	±0.28 (17)	0.52	±0.16 (3)												

[a] dd = decimal degrees

[b] Maximum lake depth (m)

[c] PS = Pumpkinseed sunfish

[d] YP = Yellow perch

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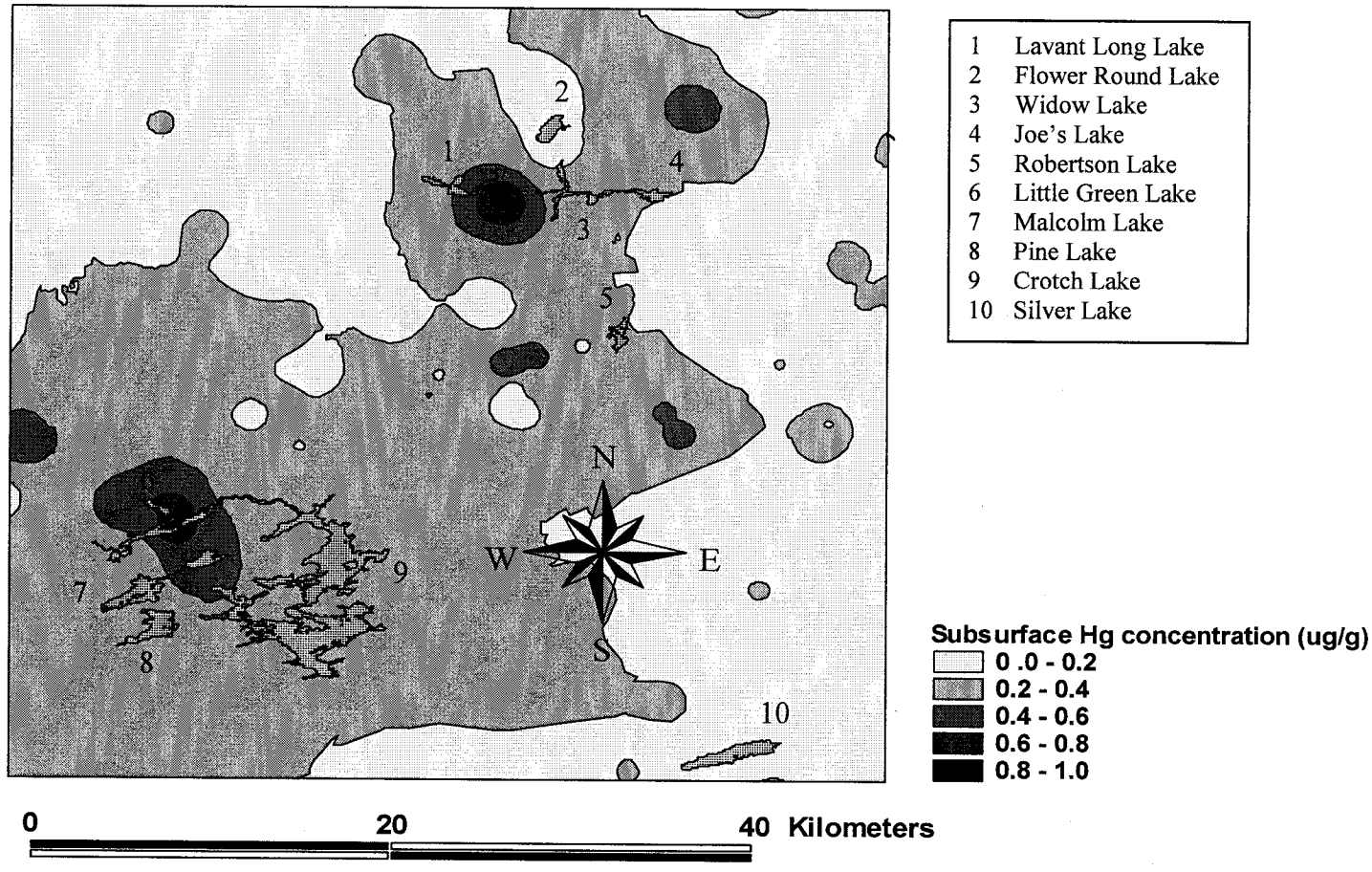

1 Lavant Long Lake
2 Flower Round Lake
3 Widow Lake
4 Joe's Lake
5 Robertson Lake
6 Little Green Lake
7 Malcolm Lake
8 Pine Lake
9 Crotch Lake
10 Silver Lake
N
W
E
S
Subsurface Hg concentration (ug/g)
0 .0 - 0.2
0.2 - 0.4
0.4 - 0.6
0.6 - 0.8
0.8 - 1.0
0
20
40 Kilometers

Figure 1

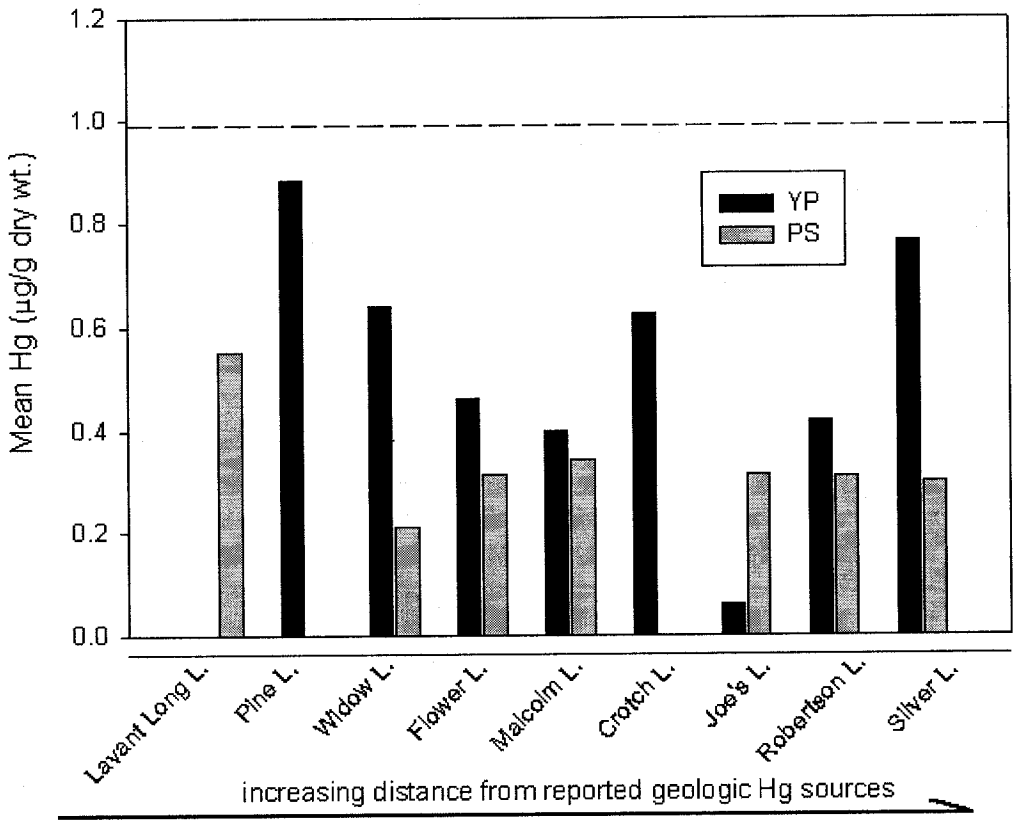


Figure 2

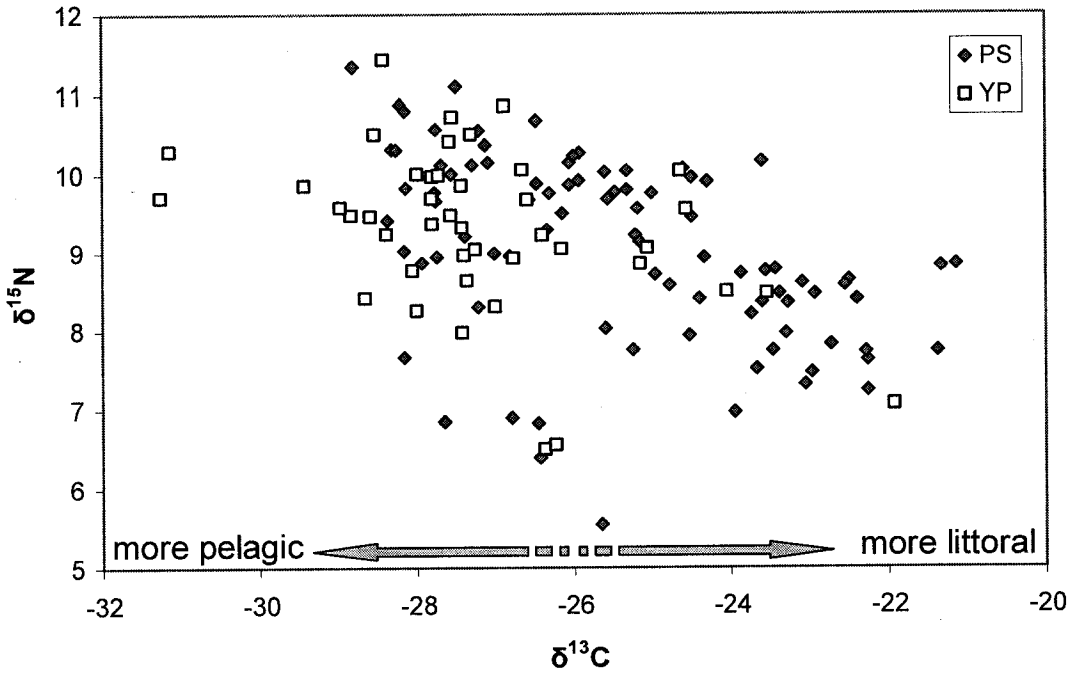
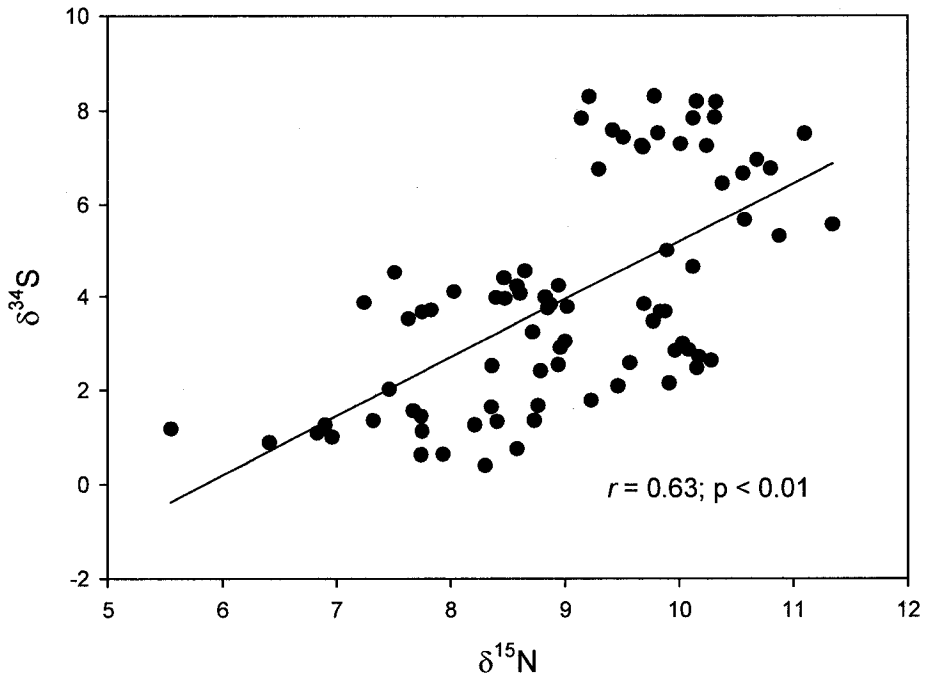


Figure 3


10
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6
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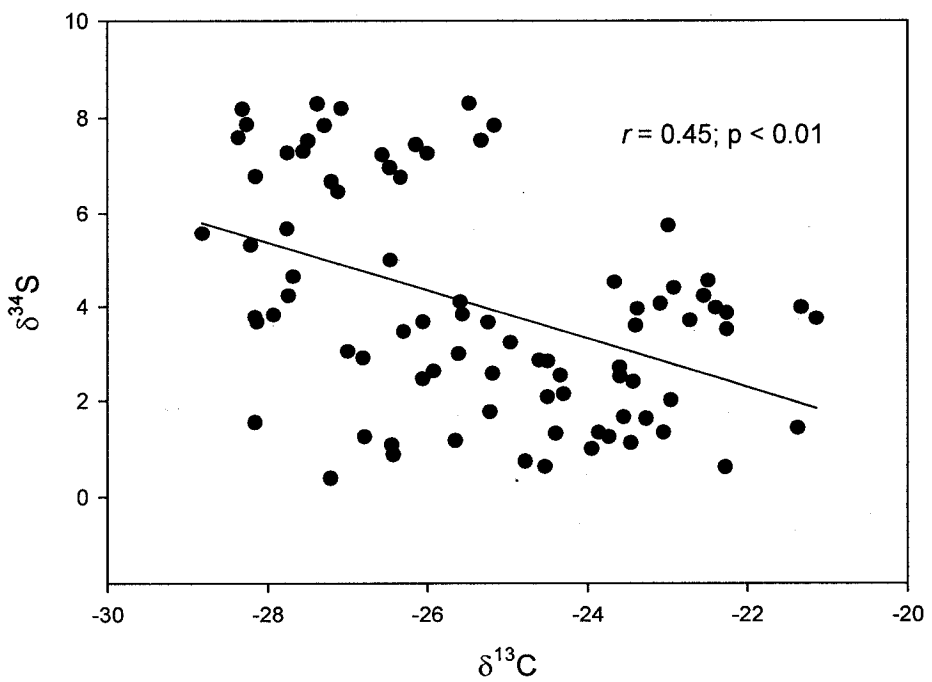
-2
5
6
7
8
9
10
11
12
δ34S
δ15N
r = 0.63; p < 0.01


10
8
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-30
-28
-26
-24
-22
-20
δ34S
δ13C
r = 0.45; p < 0.01

Figure 4

Mercury in Soils and Lake Sediments from the Clyde Forks Area, Ontario, Canada

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Abstract

Soil and sediment samples were collected near Clyde Forks, Ontario where localized areas of high Hg from geological sources have been identified in previous surveys. Samples were measured for total Hg, % sand/fines, and % organic matter (OM). Surface soil (0.09 μg/g dw) and surficial lake sediment (0.14 μg/g dw) Hg was generally low, typical of rural soils and sediments in eastern Canada. Although a few locations had elevated (> 0.3 μg/g) surface soil Hg, levels declined rapidly to background horizontally (<3 m) and with depth (<3 cm). Surface soil Hg was highly correlated with OM (explained >70% of the variability); Hg increased ~ 0.04 – 0.06 μg/g with every 10% increase in OM. The sediment fines (< 63 μm) generally contained higher concentrations of Hg than the coarse fractions. Sediment OM was variable (2% - 87%), but no significant correlation was observed between sediment Hg and %OM.

Capsule: Soil Hg was highly variable (horizontally and with depth) and strongly correlated with organic matter; sediment Hg was generally contained in fines.

Keywords: mercury; soil; sediment; organic matter

1. Introduction

There are numerous anthropogenic sources of inorganic Hg to the environment, the most important of which include coal combustion, municipal waste incineration, the use of Hg-amalgamation in gold mining, and waste from chloralkali production. Hg is also emitted to the environment from natural sources, such as from volcanic activity, large-scale forest/grass fires, and dissolution from soils and sediments near cinnabar (HgS) deposits (Schroeder et. al., 2005; Weech et al. 2004).

Typically, deep subsurface rural soils across most of eastern Ontario, Canada contain < 0.2 μg/g; however some locations such as near Clyde Forks, Ontario, are known to have elevated Hg concentrations (> 0.3 μg/g) from natural mineral sources (Coker et al. 1995; Jonasson & Boyle, 1972; Kettles, 1992; Kettles and Shilts 1995). Rytuba (2002) suggested that the flux of Hg to the environment from mineralized areas and mine sites reflects both local and global contributions of Hg, but the local source typically predominates in mineralized areas. The main objectives of the present study were to examine soils and sediments near a local geologic Hg occurrence in order to: 1) compare Hg concentrations in surface versus subsurface soils; 2) determine if Hg concentrations were correlated with soil or sediment organic matter (OM) and/or sediment grain size; and 3) examine horizontal and vertical variations in soil Hg concentrations. Results of a related study dealing with correlates of Hg in fish from lakes in this same study area are reported elsewhere (Ethier et al., 2007).

2. Materials and Methods

The study area, in relation to the pattern of Hg concentrations in deep subsurface

soils (till) as reported by the Geological Survey of Canada (GSC), is shown in Figure 1. All soil and sediment samples except those collected near or within Silver Lake were chosen because of their proximity to local mineral deposits where Hg concentrations in till can be >0.9 μg/g (Coker et al. 1995; Jonasson & Boyle, 1972). Soil and sediment samples collected near or within Silver Lake served as a control because it is situated in an area having lower (< 0.1 μg/g) concentrations of Hg in surrounding till.

Samples of surface (top 10 cm) sediment (3 - 4 samples per lake) were collected from a small boat using an Eckman dredge and stored frozen in polyethylene bags prior to analysis. Sampling locations were spaced along the approximate centre line of each lake and were spatially recorded using a Garmin portable 12-channel Global Positioning System (GPS). Georeferenced surface soil samples (78) were collected in close proximity to two sites with elevated till-Hg concentrations, as well as near Silver Lake (control site), and randomly near other previous GSC sampling points throughout the study area (Figure 1). All surface soil samples (200 - 300 g per sample) were collected from rural forested areas > 25 m from roads and buildings and stored in clean polyethylene bags after removal of loose vegetation and surface debris.

Soil core samples (7) were collected with a soil corer (45.7 cm depth) at the same latitude / longitude as some of the subsurface samples previously collected by GSC (Figure 1) and at a few other locations where we observed high Hg concentration in surface soil. Cores were subdivided vertically into at least nine slices (2.5 and / or 5 cm intervals); each slice was analyzed for total Hg concentration. A muffle furnace was used to determine the percent OM in the soil and sediment samples, calculated as the difference between the dry and ashed sample divided by the dry sample weight. This method is useful for estimating

soil OM overt a range of < 1 – 45 %, with a sensitivity of 0.2 – 0.5 % (US Fish & Wildlife Service, 2007).

Occasionally, earthworms and wood pieces of various sizes were encountered within soil samples, and these were also freeze-dried, weighed, and analyzed for total Hg.

Sediment samples were freeze-dried, dry sieved (63 μm), weighed, and the fine (clay / silt; < 63 μm) and coarse (sand; > 63 μm) fractions were analyzed for total Hg concentration.

2.1. Mercury Analyses

Total Hg concentrations in freeze dried surface soil, sediment, soil cores, earthworm and wood fragment samples were determined at National Wildlife Research Centre, Ottawa, Canada, using a dedicated Hg analyzer (AMA-254, Altec, Czech Republic) equipped with an ASS-254 autosampler as described previously (Weech et al., 2004).

Quality-assurance (QA) included analyses of replicate samples at a rate of 20% (soil samples), or 30% (sediment samples) to estimate analytical precision; and Standard Reference Materials (SRMs) [Estuarine Sediment 1646 (NBS) and Samples 1 to 4 from Northern Contaminants Program Interlaboratory Study NCP-II-1 Analysis of trace metals in sediments (National Water Research Insitute, NWRI) to estimate accuracy.

Recovery of Hg from SRMs was within 10 % of certified values, and averaged 105.7±9.3 % (soil) and 109.2±15.1 % (sediment). Precision, as measured by same day replicates, was 5.8±5.1 % (soil) and 10.8±8.7 % (sediment) relative standard deviation (RSD). Between day precision was 5.0±3.5 % (soil) and 5.2±4.1 % (sediment) RSD.

2.2. Statistics

Simple linear regressions were used to determine the relatedness of: % clay/silt in sediment and sediment Hg concentrations; % OM content and soil (or sediment) Hg concentration; and to compare subsurface Hg (from published GSC data) with surface soil Hg concentrations collected from the same locations. A paired T-test was used to determine whether there was a significant difference in subsurface and surface soil Hg concentrations, with and without correction for the OM content of the soil.

The Hg concentrations of georeferenced surface soil samples nearest the Hg occurrences identified by GSC (Coker et al. 1995; Kettles and Shilts 1995) were analyzed with the Inverse Distance Weight (IDW) function in ArcView® GIS (version 3.2) in order to visualize changes in surface soil Hg concentrations along transects with increasing distance from an elevated Hg occurrence.

Statistical analyses were conducted using SAS® (2001) and Microsoft® Excel (2002).

3. Results

There was a significant difference ($p < 0.05$) between subsurface (0.36 ± 0.14 µg/g) and surface soil (0.10 ± 0.09 µg/g) Hg concentrations (n=20). This difference remained even after a correction was applied to account for variations in the OM content of the surface soil. In a few locations, surface soil Hg concentrations were elevated, but elevated levels returned to background concentrations within 5 cm vertically (Figure 2); and within a few meters horizontally (Figure 3). Mean surface soil Hg concentrations for samples collected near Silver Lake (control location) (0.08 ± 0.07 µg/g; $n = 6$) were comparable to surface

samples taken near geological Hg occurrences at Lavant Long Lake (0.07 $\pm$ 0.09 µg/g; n = 19) and Little Green Lake (0.10 $\pm$ 0.09 µg/g; n = 26) (Figure 4).

A weak but statistically significant correlation was found between total Hg in sediment and % fines in sediment ($r = 0.398$, $p<0.05$) (Fig. 5A). Although a paired t-test of Hg in fines versus Hg in coarse fraction failed to reveal a significant difference ($p < 0.05$), the ratio of Hg in fines:Hg in coarse tended to be above 1 in most cases (Fig. 5B). Organic matter in sediment samples varied widely, from about 2% to 87%; however, there was no significant relationship between sediment Hg and %OM in sediments ($r = -0.05$, $p>0.05$).

In soil samples, %OM was strongly correlated with soil Hg concentration both within soil cores and among surface soil samples. In soil cores, %OM and Hg concentrations were both highest in the top layers of the core (Fig. 2). Percent OM explained a large portion of the variability in soil Hg concentrations ($R^2 = 0.94$ and 0.71 for soil cores and surface samples, respectively). Linear regression relationships indicated that every 10% increase in OM was associated with an approximate increase of 0.065 µg/g Hg within soil cores; and 0.044 µg/g Hg in surface soils.

Earthworms (n=3) collected from surface soil contained an average of 1.54 µg/g dry wt Hg, approximately 24-times the Hg concentration of the surrounding soil in which they were found. Concentrations of Hg in one large and several small wood pieces taken from within a soil core ranged from ~0.2 µg/g to ~0.8 µg/g. The larger wood piece had lower (~49 %) and the smaller wood pieces had higher (~140 %) Hg concentrations than the soils in which they were found.

4. Discussion

The average Hg concentrations of our surface soil (0.09 μg/g) and surface sediment (0.14 μg/g) samples were comparable to the average natural background values cited in the literature (0.07 [range: 0.02 - 0.15] μg/g for North American soils; and 0.12 [range 0.035 - 0.222] μg/g for lake sediments in Ontario) (OECD, 1995; Friske and Coker, 1995). Also, mean surface soil samples collected near Silver Lake, which was intended to be the control site for our study, had mean Hg levels that were comparable to those taken near locations of previously reported Hg occurrences (near Lavant Long Lake and Little Green Lake). Furthermore, surface soils collected throughout the Clyde Forks area had significantly lower concentrations of Hg ($p < 0.05$) than the subsurface soils (tills) formerly analyzed by the GSC (Kettles and Shilts, 1995). In locations where we encountered elevated Hg concentrations in surface soil, these elevated levels were extremely localized, falling rapidly to background values both vertically and horizontally through the soil. Together, these observations indicate that the Hg occurrences in the underlying geology of our study area appear to be having only minimal influence on Hg concentrations in surface soils and sediments. Similarly, Hg levels in aquatic biota appear not to be influenced by proximity to these Hg occurrences (Ethier et al., 2007). The most prevalent rock types found in the Clyde Forks area are shale, sandstone, and marble, along with mafic and felsic intrusives, minerals that have variable Hg contents ranging from 0 - 2.8 μg/g (Kettles, 1992; Trip et al., 2000).

In contrast to the apparent lack of influence of subsurface Hg occurrences, total Hg concentrations in our surface soil samples were very closely correlated with %OM both within soil cores and among surface soil samples, with OM explaining 70% - 94% of the variability in soil Hg concentrations. Similar strong correlations between soil Hg and OM

have been reported in other environments such as those receiving Hg inputs from a natural atmospheric inorganic Hg source (volcano) (Tomiyasu et al., 2003), and from general atmospheric Hg deposition (Campbell et al., 2003; Wiener et al. 2006). A few of our soil cores exhibited some deviation at lower depths from the profile expected if the soil Hg concentration was entirely dependent on the amount of OM in the soil. Slight increases in Hg concentrations at lower depths in a few of our core samples may indicate the beginning influence of deeper mineralized tills, some of which have elevated Hg concentrations in our study area (Coker et al. 1995; Kettles and Shilts 1995). The OM content of our soil samples was never > 5 % below a depth of 5cm (Figure 2).

The GSC subsurface samples collected in the past were georeferenced at a resolution of approximately $\pm$ 100 m (NRCan, 1996), in contrast with current GPS that allows for a resolution of $\pm$ 10 m. Thus, we have only limited confidence that our surface sampling locations corresponded precisely with the older GSC sampling sites. Nevertheless, the concentrations of Hg in our surface soil samples were too low to have been generally influenced by mineralized Hg sources (such as cinnabar). Variations in surface soil Hg appear to be mainly due to variations in OM content; a minor part of the variability may be due to the localized presence of minerals with elevated Hg concentrations.

Earthworms recovered from surface soil in the Clyde Forks area had an average Hg concentration that was 24-times higher than the surrounding soil. This observation is consistent with Cocking et al. (1994) who reported that at soil Hg concentrations < 0.4 μg/g, concentrations in earthworms were greater than those in soil. Although we measured only total Hg in soil and worm samples, previous reports indicate that most (> 80 %) of the

Hg in earthworms is inorganic, rather than methylmercury (Bull et al. 1977). The unintentional inclusion of soil invertebrates in soil Hg analyses could potentially affect soil Hg concentration estimates.

Sediments previously collected from lakes in and around our study area were found to contain, on average, 68 % sand, 26 % silt, and 7 % clay (calculated from metadata in Kettles and Shilts,1995). In the present study, more Hg (~76 %) was associated with the fines (< 63 μm) compared to coarse fractions of surface sediments. A gradual increase in Hg concentration with decreasing grain size was also observed by Boszke et al. (2004) for river bed sediments. A variable amount of the mass of our sediment samples was composed of OM, Organic matter in sediments can range from coarse to very fine particles, however we did not assess the distribution of OM in fines versus coarse fractions. However, it may be that much of the sediment Hg was associated with OM particles in the fines fraction (<63 μm) because this fraction would have a much greater surface area:mass ratio than the course fraction, with more potential organic binding sites for Hg. A similar trend of increasing Hg concentration with increasing surface area:mass ratio was apparent for the wood pieces we retrieved and analyzed from our soil samples. Hg concentrations averaged almost 3-fold higher in the smaller (higher surface area:mass) compared with the larger (lower surface area:mass) pieces. In addition, that the smaller pieces (with greater overall surface area: mass ratio) had higher Hg concentrations than the larger pieces, indicates that much of the Hg associated with the wood chips may be adsorbed onto the surface of the wood, rather than biologically incorporated into the living tissue. Grigal (2003) reported that Hg concentrations in wood of living trees are generally very low (<0.02 μg/g), whereas Hg in some of the wood pieces we analyzed was much higher (>0.2

μg/g). Hg tends to be higher in foliage than in wood of living trees; and Hg in foliage originates primarily from the atmosphere (Grigal, 2003).

5. Conclusions

Surface soil Hg concentrations in the Clyde Forks, Ontario area were variable, but on the whole were comparable to other rural sites removed from urban/industrial influences. Occasionally elevated (> 0.3 μg/g) concentrations were extremely localized, and concentrations rapidly fell to background levels both in a horizontal and vertical direction through the soil. Surface soil Hg concentrations were highly correlated with the OM content of the soil. Grain size had a moderate influence on Hg concentrations in surface sediments, as more Hg was bound to the fines (< 63 μm) than was present in sand.

The high amount of variability the we observed in surface soil Hg concentrations in the Clyde Forks area, as well as the low precision of the latitudes and longitudes (± 100 m) of former GSC sampling sites, indicates that the subsurface soil maps created by GSC may not show enough detail to provide an accurate representation of the local pattern of subsurface (or surface) Hg concentrations in this area. The use of modern GPS with higher resolution (± 10 m) and more frequent sampling of the subsurface and surface soils in the area warrants further consideration.

Acknowledgements

Financial support for this research project was provided by the Metals In The Environment – Research Network (MITE-RN) and Environment Canada. The authors thank Ewa Neugebauer, Angela Clark, Heather Jones, Nancy Wong, Rene Silke, and April White for their valuable assistance during sample collection and laboratory analyses.

References

Boszke, L., Kowalski, A., Siepak, J., 2004. Grain size portioning of mercury in sediments of the Middle Odra River (Germany/Poland). Water Air Soil Poll 159, 125-138.

Bull, K.R., Roberts, R.D., Inskip, M.J., Goodman, G.T. 1977. Mercury concentrations in soil, grass, earthworms and small mammals near an industrial emission source. Environ. Pollut. 12: 135-140

Campbell, L., Hecky, R., Muggide, R., Dixon, D., Ramlal, P., 2003. Variation and distribution of total Hg in water, sediment and soil from northern Lake Victoria, East Africa. Biogeochemistry 65, 195-211.

Cocking, D, King, M.L., Ritchie, L., Hayes, R. 1994. Earthworm bioaccumulation of mercury from contaminated flood plain soils. In: Mercury Pollution: Integration and Synthesis, Watras, C.J., and Huckabee, J.W., eds. Lewis Publishers, Boca Raton, FL., pp. 381-395.

Coker, W.B., Kettles, I.M., Shilts, W.W. 1995. Comparison of mercury concentrations in modern lake sediments and glacial drift in the Canadian Shield in the region of Ottawa/Kingston to Georgian Bay, Ontario, Canada. Water Air Soil Pollut. 80, 1025-1029.

Ethier, A., Scheuhammer, A., Bond, D., 2007. Correlates of mercury in fish from lakes in the Clyde Forks Region, Ontario, Canada. Environ Pollut, *submitted for publication.*

Friske, P., Coker, W., 1995. The importance of geological controls on the natural distribution of mercury in lake and stream sediments across Canada. Water Air Soil Pollut. 80, 1047-1051.

Grigal, D.F. 2003. Mercury sequestration in forests and peatlands: A review. J. Environ. Qual. 32, 393-405.

Jackson, T., 1991. Biological and environmental control of mercury accumulation in lakes and reservoirs of Northern Manitoba, Canada. Can J Fish Aquat Sci 48, 2449-2470.

Jonasson, I., Boyle, R., 1972. Geochemistry of mercury and origins of natural contamination of the environment. Can Mining Metallurg (CIM) Bulletin, January 1972, pp. 32-39.

Kettles, I., Shilts, W., 1995. Geochemical and lithological composition of surficial sediments, southeastern Ontario. Geological Survey of Canada, Open File 3175, Ottawa, Canada.

Kettles, I., 1992. Glacial geology and glacial sediment geochemistry in the Clyde Forks-Westport area of Ontario. Geological Survey of Canada, Open File 2274, Ottawa, Canada.

NRCan, 1996. Canadian Topographic Maps – NTS Metadata (031F02 and 031C15). Centre for Topographic Information, Natural Resources Canada (NRCan), Ottawa, ON. http://maps.nrcan.gc.ca

OECD, 1995. Mercury background and national experience with reducing risk: Risk Reduction Monograph No. 4. OECD Environment Monograph Series No. 103, OECD/GD(94)98. Organisation for Economic Co-operation and Development, Paris.

Rytuba J. Chapter J: Mercury geoenvironmental models. *In*: Seal R, Foley N. (eds) Progress on geoenvironmental models for selected mineral deposit types. USGS Report 02-195, 2002. http://pubs.usgs.gov/of/2002/of02-195/OF02-195J.pdf

SAS, 2001. SAS. Version 4.01. SAS Institute, Inc., Cary, NC.

Schroeder, W., Beauchamp, S., Edwards, G., Poissant, L., Rasmussen, P., Tordon, R., Dias, G., Kemp, J., Van Heyst, B., Banic, C., 2005. Gaseous mercury emissions from natural sources in Canadian landscapes. J Geophys Res 110, D18302.

Smith, C., 1996. Mercury: Forms, Fates & Effects. Chapter 2. Mercury in Massachusetts: An Evaluation of Sources, Emissions, Impacts and Controls. Massachusetts Department of Environmental Protection (MA DEP).

Tomiyasu, T., Okada, M., Imura, R., Sakamoto, H., 2003. Vertical variations in the concentration of mercury in soils around Sakurajima Volcano, Southern Kyushu, Japan. Sci Total Environ 304(1-3), 221-30.

Trip, L., Chevalier, P., Smith, J., 2000. The status of mercury in Canada. A Background Report to the Commission for Environmental Cooperation (2nd), North American Task Force on Mercury, Environment Canada.
http://www.cec.org/files/PDF/POLLUTANTS/Hgcan-e3.pdf

US Fish & Wildlife Service, 2007. Soil OM: Loss-on-ignition. Method code 011, Laboratory and Environmental Testing, Inc. Laboratory Methods, US Fish & Wildlife Service Analytical Control Facility (Division of Environmental Quality). Accessed February 13, 2007. http://www.fws.gov/chemistry/methods_let_lab.htm#MethodCode011

Weech, S., Scheuhammer, A., Elliott, J., Cheng, K., 2004. Mercury in fish from the Pinchi Lake region, British Columbia, Canada. Environ Poll 131, 275-86.

Wiener, J.G., Knights, B.C., Sandheinrich, M.B., Jeremiason, J.D., Brigham, M.E., Engstrom, D.R., Woodruff, L.G., Cannon, W.F., and Balough, S.J. 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. Environ. Sci. Technol. 40, 6261-6268.

Figures

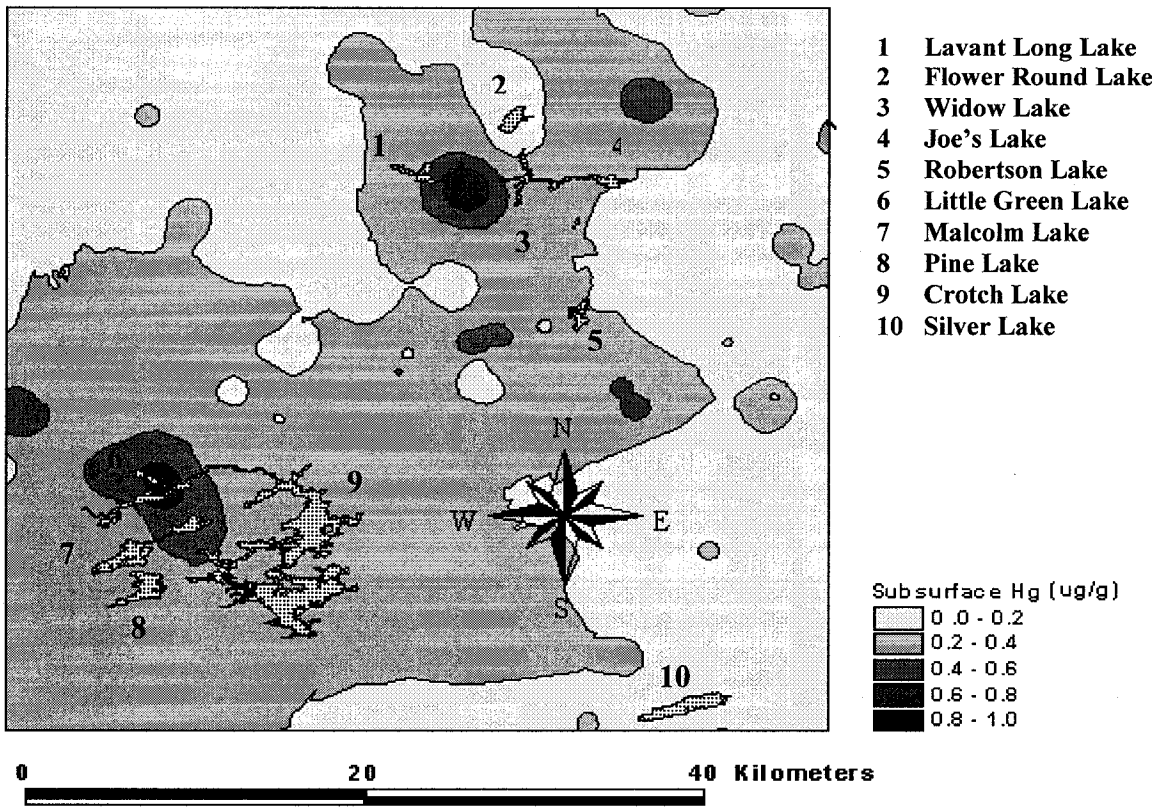

1 Lavant Long Lake
2 Flower Round Lake
3 Widow Lake
4 Joe's Lake
5 Robertson Lake
6 Little Green Lake
7 Malcolm Lake
8 Pine Lake
9 Crotch Lake
10 Silver Lake
N
W
E
S
Subsurface Hg (ug/g)
0.0 - 0.2
0.2 - 0.4
0.4 - 0.6
0.6 - 0.8
0.8 - 1.0
0
20
40 Kilometers

Figure 1

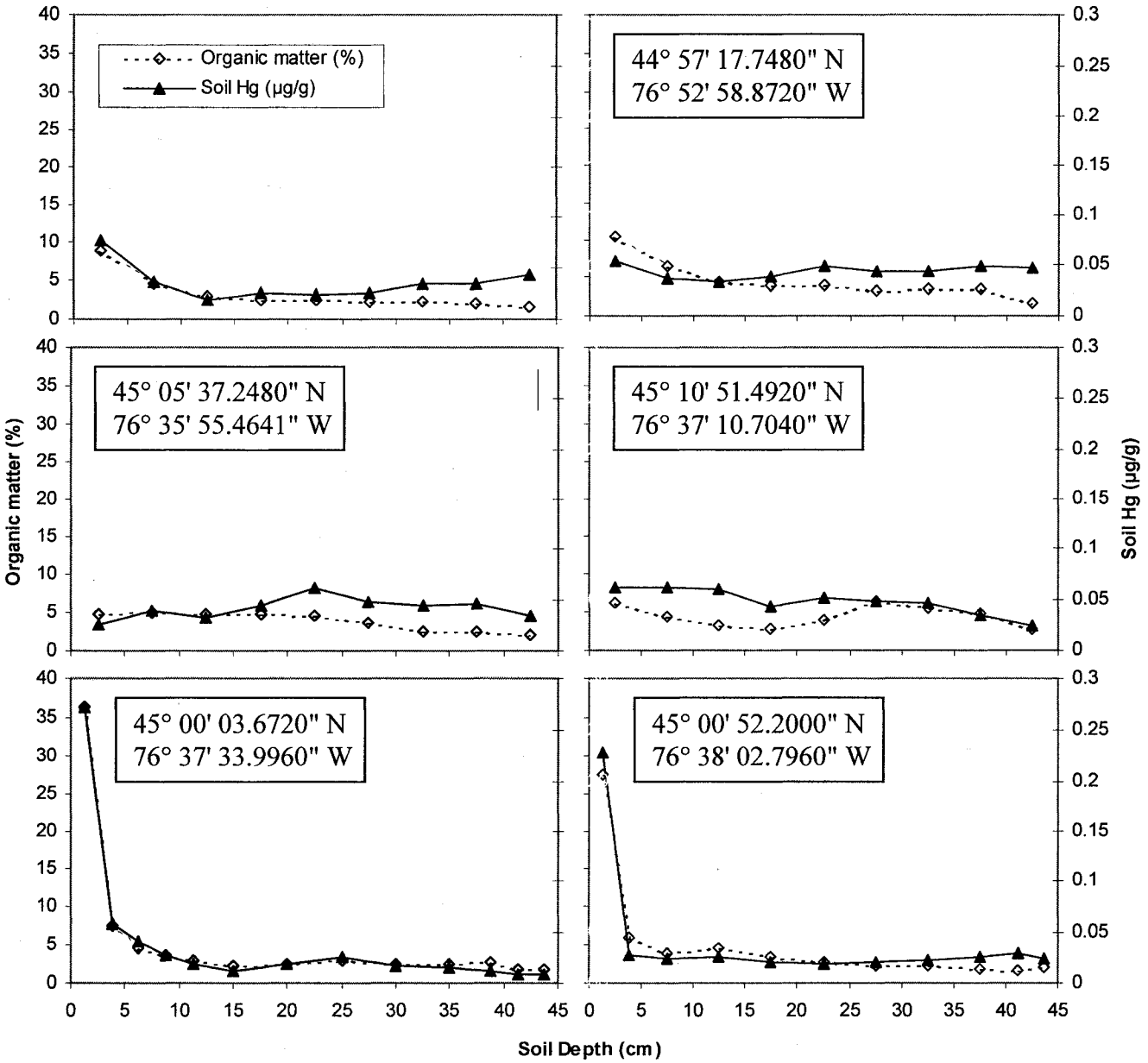

Organic matter (%)
Soil Hg (µg/g)
44° 57' 17.7480" N
76° 52' 58.8720" W
45° 05' 37.2480" N
76° 35' 55.4641" W
45° 10' 51.4920" N
76° 37' 10.7040" W
45° 00' 03.6720" N
76° 37' 33.9960" W
45° 00' 52.2000" N
76° 38' 02.7960" W
Organic matter (%)
Soil Hg (µg/g)
Soil Depth (cm)

Figure 2

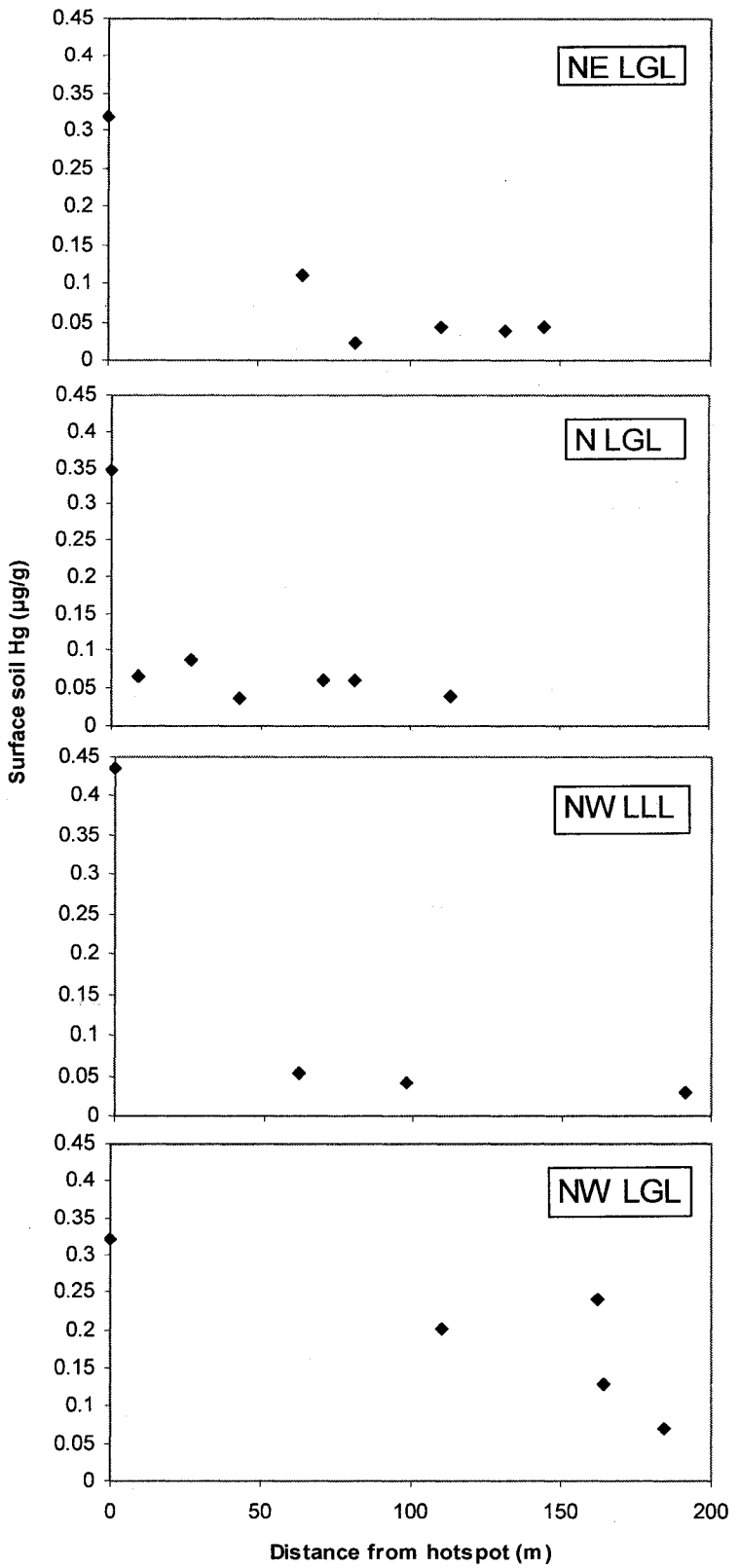

NE LGL
N LGL
NW LLL
NW LGL
Surface soil Hg (µg/g)
Distance from hotspot (m)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
50
100
150
200

Figure 3

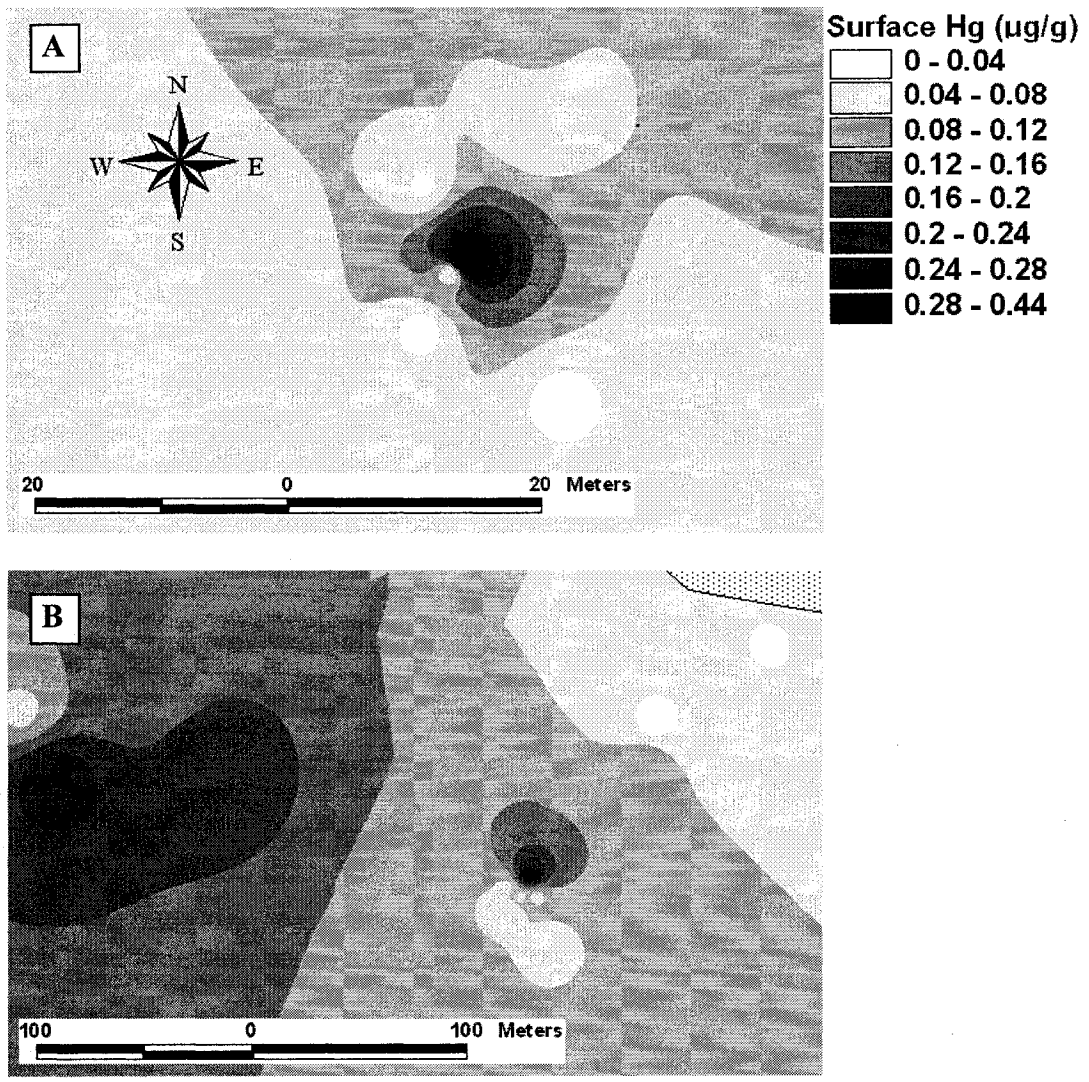

A
N
W
E
S
20
0
20 Meters
Surface Hg (ug/g)
0 - 0.04
0.04 - 0.08
0.08 - 0.12
0.12 - 0.16
0.16 - 0.2
0.2 - 0.24
0.24 - 0.28
0.28 - 0.44
B
100
0
100 Meters

Figure 4

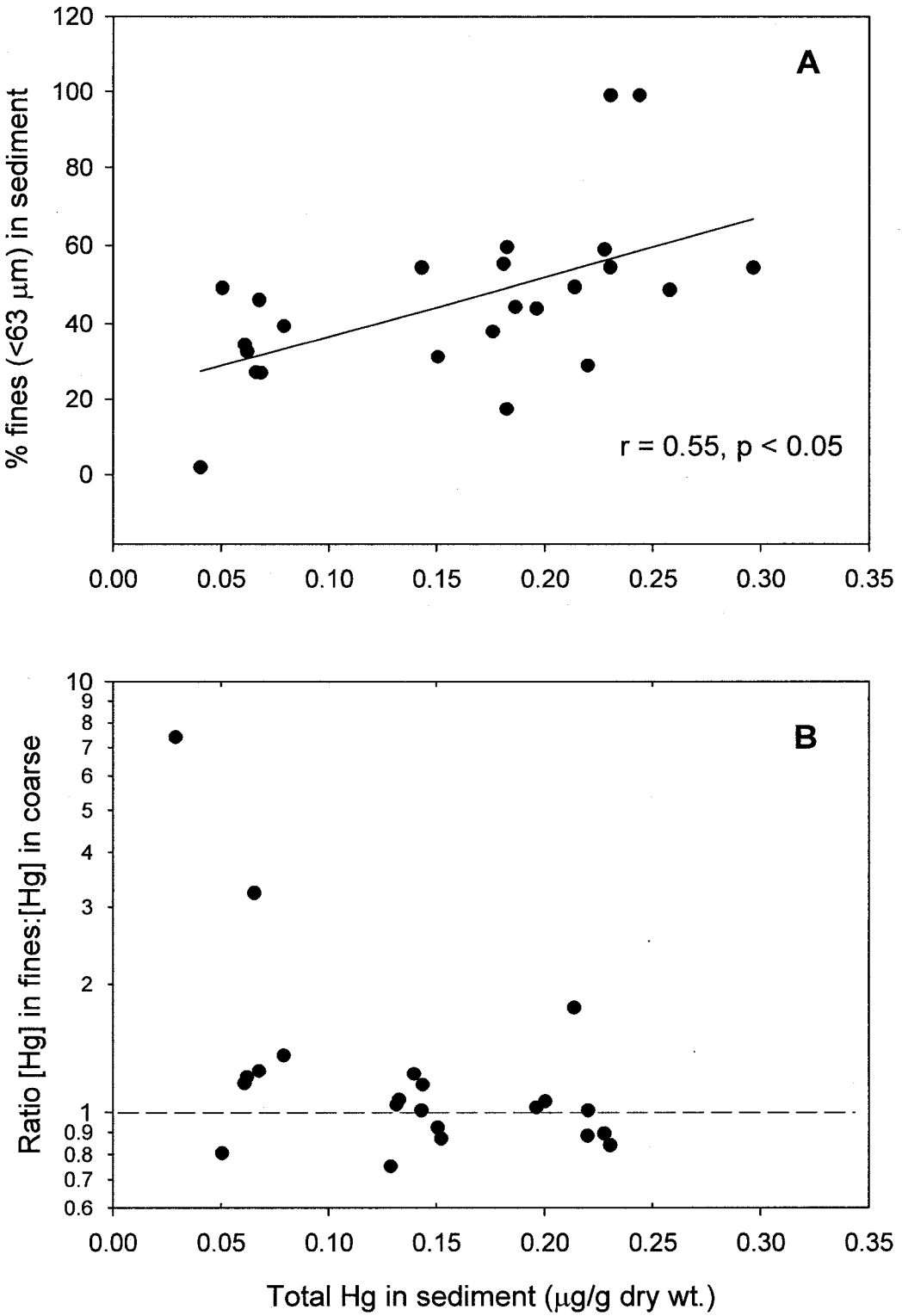

A
% fines (<63 μm) in sediment
120
100
80
60
40
20
0
r = 0.55, p < 0.05
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
B
Ratio [Hg] in fines:[Hg] in coarse
10
9
8
7
6
5
4
3
2
1
0.9
0.8
0.7
0.6
Total Hg in sediment (μg/g dry wt.)

Figure 5

HERMES MODEL (MICROSOFT EXCEL WORKBOOK)

Model layout and user instructions

The HERMES model Excel workbook is subdivided into five spreadsheets, appropriately called 'Lake', 'Environment (Input)', 'Model Set-up', 'Model Output', and 'Diagram'. Each spreadsheet serves a specific purpose that is described here. Figure 1-5 can be used as a reference when reading the instructions here but the reader is invited to download the model, and input or change data to view outcome for different lakes. The model on the web will differ slightly as further improvements are included.

'Lake' spreadsheet (Figure 1)

BASIC module (CELLS A10-E28)

The model requires five input variables for which no estimates are provided (CELLS C12-C16), although they are relatively easy to obtain for any given lake (i.e., concentration of Hg in air, precipitation rate, lake temperature, surface area, and mean depth). Contained within this module are eight other input variables (CELLS C19-C27) for which estimates are provided and can be used as needed (see BASIC ESTIMATION module on 'Lake' spreadsheet). The emission to water (C19) and from sediment (C20) terms should both read 'none' unless the lake is receiving industrial or groundwater inputs (emission to water) or when estimating surface sediment Hg concentrations (emission from sediment). Suspended particulate matter (SPM, C24) (aka suspended sediment) is the concentration of non-dissolved matter in the water column that can be approximated by dividing the particulate organic carbon (POC) concentration by 0.44. The value for lake SPM (C24) can be used for inflow SPM (C25) if value is not known. Settling or sedimentation rate of solids (C26) (aka deposition rate) is the rate at which suspended particulate matter is descending towards the sediment surface. Default values listed in CELLS E12-E27 are for Harp Lake, ON.

See Ethier et al. (Chapter 2) for a description of the uncertainty analyses used to reduce the number of model input variables.

COMPLETE module (CELLS A30-I32)

This module provides more model variables to be adjusted during application to a new lake when an extensive dataset is available. In order to run the COMPLETE module, refer to instructions listed in CELLS A30 – I32. Simply put, all of the input variables listed in BASIC module should be set to 'none'. Any of the model variables in the 'Environment (Input)' spreadsheet that do not interfere with model calculations (colored purple) can then be adjusted accordingly (e.g., main residual species might change (Hg_2OH versus Hg_2Cl) if model were to be applied to an estuary or ocean rather than a lake), but there is little need to do so for most of these variables (i.e., molecular weight of elemental Hg (Hg^0) will remain the same regardless of which lake is being modeled).

BASIC ESTIMATION module (CELLS A42-M59)

No modifications to this module are required for the model to function properly. Contained within this section are the estimation methods described in the attached manuscript for the major model input variables. Measured data should be used when available, but this section will be tremendously valuable for lakes where this data is absent. Once a major model input variable has been estimated in this module, the number should be inserted into the respective location within the BASIC module (CELLS C19-C27).

EXTRA module (CELLS G10-Q28, K29-Q32)

This module was two functions: (1) to compare model output with other Hg estimates when no measured sediment or water Hg data is available; and (2) to provide estimates that can be used to change the modeled sediment, water and inflow water MeHg / total Hg ratios (for foodweb applications).

Objective 1
Experimental research conducted in Clyde Forks (Appendix 1B) and Dorset (Chapter 3), ON was used to develop sediment Hg estimation method as part of first objective (CELLS G12-P13). Estimation methods for water and sediment Hg are described in the attached manuscript. If you enter the lake variable for water mercury concentration (CELL I12) or sediment mercury concentration (CELL I13) an estimate will appear in CELL P12 and CELL P13, respectively. Be sure to pay attention to the criterion for these estimates that are mentioned in CELL L12 and L13.

Objective 2
The second objective of this module relates to (CELLS G21-P25) estimation methods used for water, sediment, and water inflow MeHg / total Hg ratios are discussed in the manuscript. Although the model uses the MeHg / Hg^0 ratio for calculations, these ratios are never reported in the literature. On the other hand, the MeHg / total Hg ratio can be obtained from numerous research papers. The model thus assumes that Hg^0 was constant (annual average) and unaffected by variations in the relative amount of MeHg among lakes. An equation will be put into the model at a later date to enable adjustments of the Hg^0 concentration as well. To adjust the model MeHg / total Hg ratio, either enter a measured ratio (CELL P21-P25, leave as 'none' if using default) or enter watershed variable(s) required to estimate a given ratio (CELLS N21-N25) and then copy this estimate (CELLS P21-P25) over into CELLS I21-I25 to alter the ratio used in the model. Model defaults (CELLS G21-G25) and the relative average ratios (±standard deviation) for a lake, river and reservoir (CELLS N29-P31) are also provided.

'Environment (Input)' spreadsheet (Figure 2)

All the model input variables (major and minor), along with some initial calculations, are in this spreadsheet. Every model input variable can be viewed, but only alter variables as described for COMPLETE module in 'Lake' spreadsheet. There are a number of venues for future research contained within this spreadsheet since the model still has to rely on estimates in many cases.

'Model Set-up' spreadsheet (Figure 3)

DO NOT TOUCH OR ALTER ANYTHING (except concentration ratios if needed) since the underlying model code is contained on this page. Air (CELLS B24-B25), water (CELLS B29-B30), sediment (CELLS B34-B35), and water inflow (CELLS B39-B40) concentration ratios can be altered only if the method used to calculate these ratios is fully understood.

Partition coefficients (K), fugacity capacities (Z), transport parameters (D), and multipliers (R) are listed in CELLS G3-I12, B5-D11, G16-I29, and G33-I46 respectively for each of the Hg forms modeled. Partition coefficients are the ratio of concentration (C) in one media with respect to another (e.g., C air (A) / C water (W) = KAW). Fugacity (f) is the escaping tendency of a chemical in units of pressure (Pa). Fugacity capacities are used in the model to relate fugacity to concentration (e.g., CW x ZW = fW). Transport parameters are used to describe advective and diffusive processes between compartments. The multipliers are used to relate Hg^0 to total Hg, so that all three forms can be modeled. Therefore, these multipliers are a function of the concentration ratios listed in CELLS B24-B41.

'Model Output' spreadsheet (Figure 4)

Once all of the basic input variables have been changed, all of the model output (i.e., predictions) can be found in this spreadsheet. First check if model inputs equal model outputs. To do this, CELLS G5-H5 should read 'MODEL BALANCES', otherwise it will read 'ERROR IN MODEL' which indicates that a term or calculation in the model code needs to be corrected. A potential source for 'ERROR IN MODEL' could result if sedimentation rate does not equal resuspension plus burial rate.

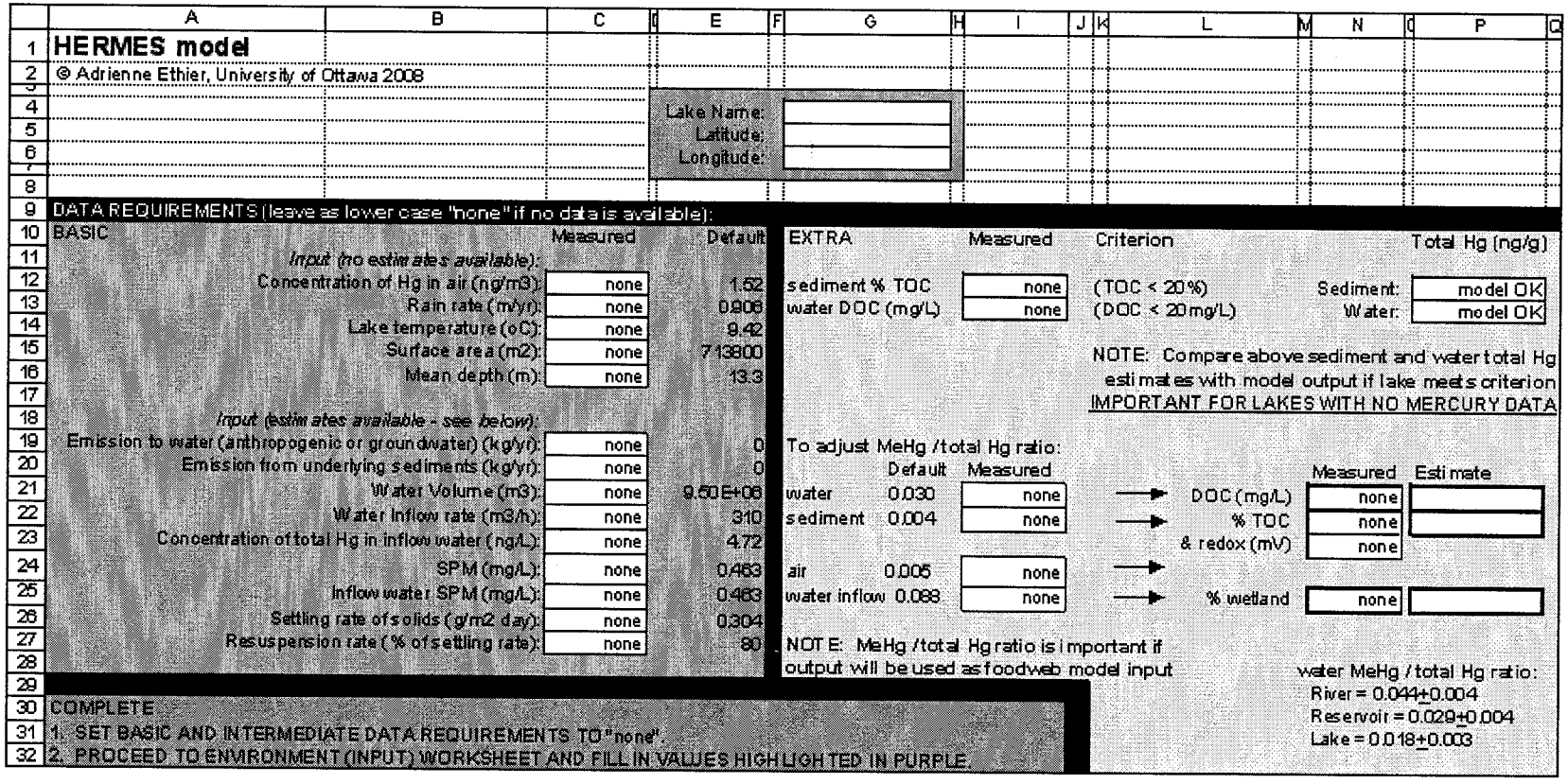
In this spreadsheet are all the individual fluxes or processes (CELLS B29-B44) and concentrations (CELLS B13-B20) that the model calculates for total Hg, along with the respective contribution from each of the three forms modeled (i.e., Hg^0, methyl, and residual). Bulk concentrations (CELLS B23-B25) consider dissolved and particulate forms together. There is no need to alter anything on this spreadsheet, especially not CELLS B3-D9 (model code).

'Diagram' spreadsheet (Figure 5)

This spreadsheet provides a visual representation of model output, showing the concentration of total, methyl (MeHg), elemental (Hg^0) and residual (shown as Hg^{2+}) Hg in each compartment (i.e., air, water and sediment). The diagram also shows total fluxes (i.e., emission, advection (in/out), upward/downward fluxes) among these compartments; refer to 'Model Output' spreadsheet for individual fluxes.

DOWNLOAD THE CHAPTER 4 HERMES MODEL ONLINE APPENDIX AND EXPLORE CAPABILITIES ON OTHER LAKES. QUESTIONS? CONTACT ethiera@aecl.ca GOOD LUCK AND HAVE FUN!

Figure A2.1: 'Lake' spreadsheet from HERMES model MS Excel workbook.



HERMES model

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Lake Name:
Latitude:
Longitude:

DATA REQUIREMENTS (leave as lower case "none" if no data is available):

BASIC	Measured	Default
Input (no estimates available):		
Concentration of Hg in air (ng/m3):	none	1.52
Rain rate (m/yr):	none	0.906
Lake temperature (oC):	none	9.42
Surface area (m2):	none	713800
Mean depth (m):	none	13.3
Input (estimates available - see below):		
Emission to water (anthropogenic or groundwater) (kg/yr):	none	0
Emission from underlying sediments (kg/yr):	none	0
Water Volume (m3):	none	9.50E+06
Water inflow rate (m3/h):	none	310
Concentration of total Hg in inflow water (ng/L):	none	4.72
SPM (mg/L):	none	0.463
Inflow water SPM (mg/L):	none	0.463
Settling rate of solids (g/m2 day):	none	0.304
Resuspension rate (% of settling rate):	none	80

EXTRA	Measured	Criterion	Total Hg (ng/g)	
sediment % TOC	none	(TOC < 20 %)	Sediment:	model OK
water DOC (mg/L)	none	(DOC < 20 mg/L)	Water:	model OK

NOTE: Compare above sediment and water total Hg estimates with model output if lake meets criterion
IMPORTANT FOR LAKES WITH NO MERCURY DATA

To adjust MeHg /total Hg ratio:

	Default	Measured		Measured	Estimate
water	0.030	none	→ DOC (mg/L)	none	
sediment	0.004	none	→ % TOC	none	
			& redox (mV)	none	
air	0.005	none	→		
water inflow	0.088	none	→ % wetland	none	

NOTE: MeHg /total Hg ratio is important if output will be used as foodweb model input

water MeHg / total Hg ratio:
River = 0.044±0.004
Reservoir = 0.029±0.004
Lake = 0.018±0.003

COMPLETE
1. SET BASIC AND INTERMEDIATE DATA REQUIREMENTS TO "none".
2. PROCEED TO ENVIRONMENT (INPUT) WORKSHEET AND FILL IN VALUES HIGHLIGHTED IN PURPLE.

(cont'd)

	A	B	C	E	G	I	L
34	NOTES:						
35	WATER INFLOW RATE --> NEED TOTAL OF ALL SOURCES, OTHERWISE USE ESTIMATE						
36	MUST HAVE INPUT FOR BASIC MODEL REQUIREMENTS - INTERMEDIATE AND ADVANCED DATA ARE OPTIONAL						
37	BASIC MODEL - INPUT INTRODUCES HIGH AMOUNT OF VARIABILITY TO MODEL OUTPUT						
38	INTERMEDIATE MODEL - LITERATURE AND EXPERIMENTAL RESULTS HAVE FOUND THESES INPUT TO						
39	INTRODUCE VARIABILITY IN EXTREME ENVIRONMENTS						
40	ADVANCED MODEL - FOR USERS WHO WANT TO MAKE USE OF MORE EXTENSIVE DATA SETS						
41							
42	BASIC ESTIMATIONS						Calculation
43	Emission to water (direct run-off) (kg/yr) =	leave at 0 kg/yr unless there is an industry dumping Hg directly into lake					
44	Emission from underlying sediments (kg/yr) =	leave at 0 kg/yr unless anthropogenic / natural Hg is being remobilized in sediments					
45	Water Volume (m3) =	Surface Area (m2) * 1E6 * Mean Depth (m)				=	#VALUE!
46	Residence Time (yr) =						
47	Water Inflow Rate (m3/h) =	Water Volume (m3) * Residence Time (h-1)				=	#VALUE!
48	Watershed Area (km2) =	5.42					
49	Concentration of total Hg in inflow water (ng/L) =	e(2.02 - 0.063 * ln(Watershed (km2)))				=	5.06
50	Total Phosphorus (ug/L) =	7.4					
51	OR Secchi Depth (m) =	3.8					
52	SPM (mg/L) =	10E (1.55 x log(total phosphorus (ug/L)) - 1.69)				=	0.463
53		= 10E (((log Dsecchi (m) - 0.769) / - 0.698) -1)				=	0.867
54		NOTE: select one method to estimate SPM (not both) and use in model "BASIC"					
55		data requirement for lake and / or inflow water SPM (mg/L)					
56	Settling rate of solids (g/m2 day) =	1.04 - (0.07 * Mean depth(m))			(max mean depth = 13 m)	=	0.109
57	Resuspension rate (% of deposition) =	reduced by 70mg/m2 day per m as depth increases				=	54.4
58		NOTE: estimate for small lakes (surface area=~1km2) with a mean depth >8.5m.					
59		Default assumes resuspension is 80% of deposition (settling rate).					

Figure A2.2: 'Environment (Input)' spreadsheet from HERMES model MS Excel workbook.

	A	B	C	D	E	F	G	H
1	**Chemical Properties of Mercury Species**		NOTE: Only alter purple cells (where needed) when applying to new lake.					
2			NOTE: Yellow cells change in response to 'BASIC DATA REQUIREMENTS' on 'Lake' worksheet.					
3	Temperature of lake (oC)	9.42	9.42					
4	Temperature of lake (K)	282.42						
5								
6		Elemental Hg	Inorganic	Organic				
7		Hg0	Hg2+	MeHg				
8	Molecular weight (g/mol)	200.59	271.5	215.73				
9	Log Kow	0.623	-0.301	2.255	Schroeder and Munthe (1998)			
10	Melting point (oC)	-38.87	277	167				
11	Water solubility (mg/L)	0.02598	66194.7	10547	Hg0 equation from: Loux, N. 2000. Diel temperature effects on the exc			
12	Water solubility (mol/m3)	1.30E-04	2.44E+02	4.89E+01				
13	Kow	4.20E+00	5.00E-01	1.80E+02				
14	Melting point (K)	2.34E+02	5.50E+02	4.40E+02				
15	Vapour pressure (Pa)	0.06128	8.32E-03	1.63E+00	derived from Clausius-Clapeyron equation: VP2 = VP1 x exp(-(ΔHvap/			
16	Subcooled liquid vapor pressure (Pa)	6.13E-02	5.18E+00	7.20E+01		for residual and organic Hg; Hg0 from Loux, N. 2000. Diel t		
17	Fugacity ratio	1.00E+00	1.61E-03	2.26E-02				
18	Henry's Law constant (Pa*m3/mol)	4.73E+02	3.41E-05	3.33E-02				
19	Overall MTC (water side)	1.91E-02	2.91E-08	2.84E-05				
20								
21	**Chemical Inputs of Mercury (total)**			Unit conversion				
22	Emission to water (kg/yr)	0	0	0	mol/h			
23	Emission from underlying sediments (kg/yr)	0	0	0	mol/h			
24	Inflow water concentration (ng/L)	4.72	4.72	2.3531E-08	mol/m3			
25	Inflow water rate (m3/h)	310	310					
26	Concentration of chemical in air (ng/m3)	1.52	1.52	7.5776E-12	mol/m3			
27	Outflow water rate (m3/h)	310						
28	Particle Inflow rate (m3/h)	5.98E-05						
29	Particle Outflow rate (m3/h)	5.98E-05						
30								

(cont'd)

	A	B	C	D	E	F	G	H
31	**Lake Physical Properties**			Unit conversion			**Mass Transfer Coefficients (MTC) (m/h)**	
32	Water surface area (m2)	713800	713800				Volatilization (air side)	2
33	Water volume (m3)	9.50E+06	9500000				Volatilization (water side)	0.02
34	Mean water depth (m)	13.32	13.3				Sediment-water diffusion	0.0002
35	Sediment active layer depth (m)	0.05						
36	Rain rate (m/yr)	0.906	0.906	73.8245205	m3/h		Scavenging ratio (air per rain)	200000
37	Deposition rate of solids (g/m2*day)	0.304	0.304	0.0037673	m3/h			
38	Resuspension rate of solids (g/m2*day)	0.165	0.165	0.0020503	m3/h		Sediment surface area (m2)	713800
39	Burial rate of solids (g/m2*day)	0.139	0.139	0.0017170	m3/h		Sediment active volume (m3)	35690
40	Total suspended solids in water (mg/L)	0.463	0.463				Volume of sediment pore water (m3)	32477.9
41	Total suspended solids in inflow water (mg/L)	0.463	0.463				Volume of sediment solids (m3)	3212.1
42	Concentration of particles in air (ug/m3)	40						
43	Aerosol dry deposition velocity (m/h)	10.8						
44	Volume fraction particles in surface sediment	0.09					**Volume fraction**	
45	Density of particles in water (kg/m3)	2400					Water particles	1.93E-07
46	Density of sediment particles (kg/m3)	2400					Inflow water particles	1.93E-07
47	Density of aerosol particles (kg/m3)	1500					Atmosphere particles	2.67E-11
48	Fraction OC in water column particles	0.47	suspended material has roughly 15% higher OC					
49	Fraction OC in sediment solids (SS)	0.32	than sediment solids: Hakanson (2005)				**Aerosol deposition rates (m3/h)**	
50	Fraction OC in resuspended SS	0.32					Wet particle	0.000394
51	Fraction OC in inflow suspended SS	0.47					Dry particle	0.000206
52							Total aerosol	0.000599

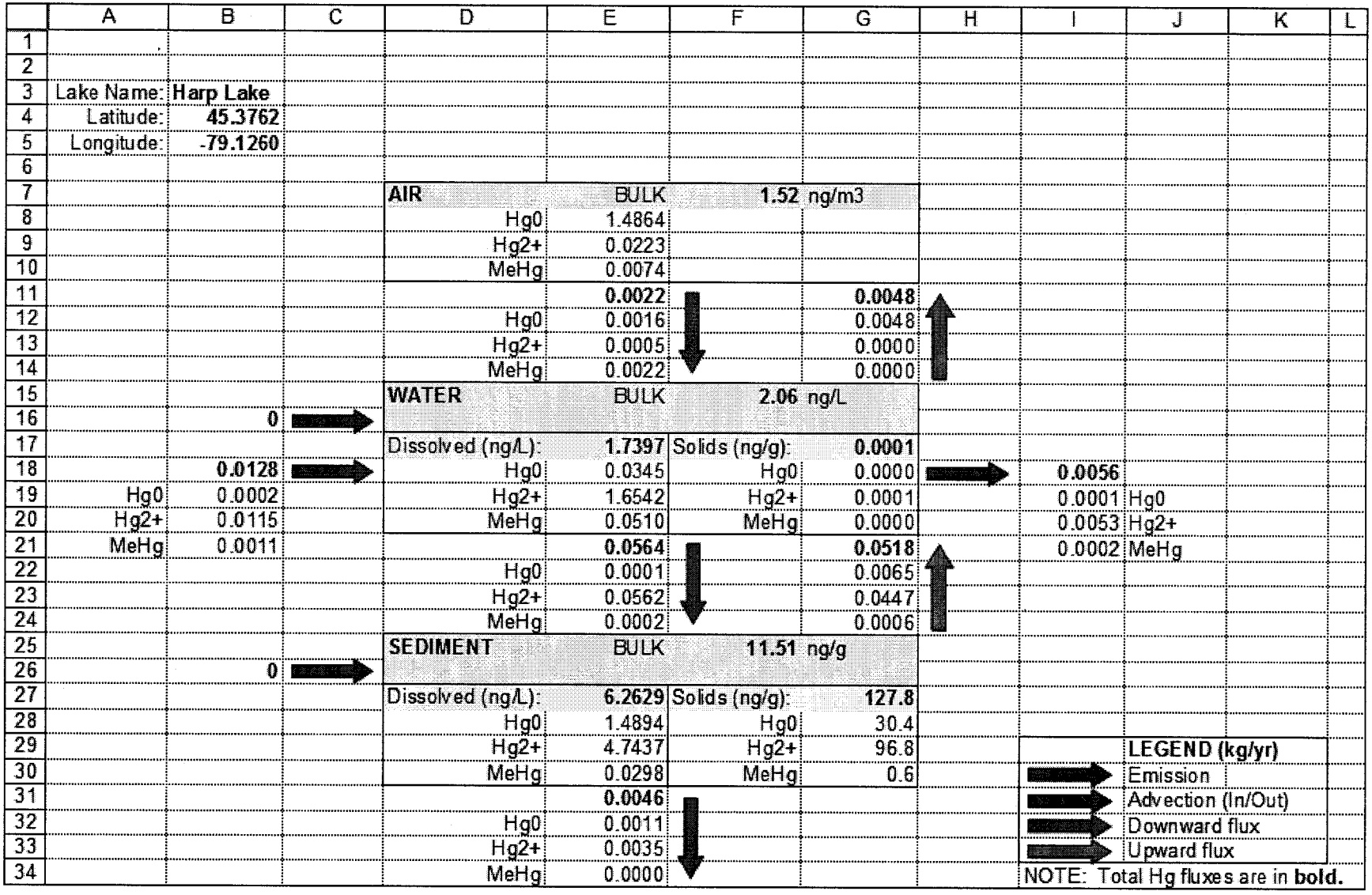
Figure A2.3: 'Model Set-up' spreadsheet from HERMES model MS Excel workbook.

	A	B	C	D	E	F	G	H	I	J
1	Gas constant (R)	8.314				Partition coefficients				
2							Elemental (Hg0)	Inorganic (Hg2+)	Organic (MeHg)	
3	Z values					KAW	0.202	1.45415E-08	1.4197E-05	
4		Elemental (Hg0)	Inorganic (Hg2+)	Organic (MeHg)		KOC	1.679035936	0.200013814	71.95483661	
5	ZW	1	1	1		PKPW	0.78914689	0.094006493	33.8187732	
6	ZA	0.202	1.454E-08	1.4197E-05		KPW	30000	1000000	50000	
7	ZQ	1.973E+07	1.685E-02	1.183E+00		PKSW	0.5372915	0.06400442	23.02554771	
8	ZP	3.00E+04	1.00E+06	5.00E+04		KSW	20000	100000	5000	
9	ZPI	3.00E+04	1.00E+06	5.00E+04		PKRW	0.5372915	0.06400442	23.02554771	
10	ZS	2.00E+04	1.00E+05	5.00E+03		KRW	30000	1000000	50000	
11	ZR	3.00E+04	1.00E+06	5.00E+04		KQW	9.791E+07	1158441.856	83305.75587	
12						KPA	1.4886E+05	6.8769E+13	3.5219E+09	
13										
14	Bulk Z values					D values				
15		Elemental (Hg0)	Inorganic (Hg2+)	Organic (MeHg)			Elemental (Hg0)	Inorganic (Hg2+)	Organic (MeHg)	NET (used
16	ZAT	0.202055049	1.45419E-08	1.4197E-05		DB	34.33984497	171.6992248	8.584961242	1.444E+02
17	ZST	1800.91	9000.91	450.91		DR	61.50856588	2050.285529	102.5142765	1.376E+03
18	ZWT	1.005787307	1.192916474	1.00964564		DT	142.76	142.76	142.76	6.131E+03
19	ZWIT	1.005787306	1.192916437	1.009645639						2.451E+02
20						DD	113.0183333	3767.277778	188.3638889	1.529E+05
21	Ratios					DV	13601.10393	0.020759404	20.23891991	1.363E+04
22		Concentration	MeHg/THg adj.	Bulk Fugacity						1.937E+04
23	Air					DJ	310	310	310	1.331E+04
24	Hg2+/Hg0	1.50E-02	1.50E-02	2.084E+05		DY	1.794125	59.80416667	2.990208333	2.427E+03
25	MeHg/Hg0	0.005	0.005	7.116E+01		DM	73.82452055	73.82452055	73.82452055	3.170E+03
26	TOTAL	1.02E+00	1.02E+00			DC	7769.028144	6.63258E-06	0.000465663	7.770E+03
27						DQ	4056.3588	3.463E-06	0.000243131	4.057E+03
28	Water					DI	310	310	310	1.898E+04
29	Hg2+/Hg0	48	48	4.047E+01		DX	1.794125	59.80416667	2.990208333	3.248E+03
30	MeHg/Hg0	1.48	1.480	1.474E+00						
31	TOTAL	50.48	50.48			R-multipliers				
32							Elemental (Hg0)	Inorganic (Hg2+)	Organic (MeHg)	TOTAL
33	Sediment					MRB	2.377E-01	7.575E-01	4.748E-03	4.206E+00
34	Hg2+/Hg0	3.185	3.185	6.373E-01		MRR	4.469E-02	9.494E-01	5.950E-03	2.238E+01
35	MeHg/Hg0	0.02	0.020	7.988E-02		MRTW	2.329E-02	9.424E-01	3.433E-02	4.294E+01
36	TOTAL	4.205	4.205			MRTS	5.824E-01	3.711E-01	4.652E-02	1.717E+00
37						MRD	7.394E-04	9.974E-01	1.817E-03	1.352E+03
38	Water Inflow					MRW	9.977E-01	6.163E-05	2.189E-03	1.002E+00
39	Hg2+/Hg0	64	64	5.396E+01		MRVA	7.022E-01	2.234E-01	7.436E-02	1.424E+00
40	MeHg/Hg0	6.3	6.300	6.2759		MRJ	2.329E-02	9.424E-01	3.433E-02	4.294E+01
41	TOTAL	71.3	71.3			MRY	7.394E-04	9.974E-01	1.817E-03	1.352E+03
42						MRM	2.329E-02	9.424E-01	3.433E-02	4.294E+01
43						MRC	9.998E-01	1.779E-04	4.264E-06	1.000E+00
44						MRQ	9.998E-01	1.779E-04	4.264E-06	1.000E+00
45						MRI	1.633E-02	8.812E-01	1.025E-01	6.124E+01
46						MRX	5.524E-04	9.937E-01	5.778E-03	1.810E+03

Figure A2.4: 'Model Output' spreadsheet from HERMES model MS Excel workbook.

	A	B	C	D	E	F	G	H
1	**Inflow and air fugacities**						mol/h	kg/yr
2		Elemental (Hg0)	Inorganic (Hg2+)	Organic (MeHg)		Total Input	5.81E-06	1.02E-02
3	FA	3.67675E-11	7.663E-06	2.616E-09		Total Output	5.81E-06	1.02E-02
4	FWI	3.28123E-10	1.771E-08	2.05928E-09				
5							MODEL BALANCES	
6	**Water and sediment fugacities**							
7		Elemental (Hg0)	Inorganic (Hg2+)	Organic (MeHg)				
8	FW	2.01956E-10	8.17322E-09	2.97752E-10				
9	FS	1.81828E-08	1.15871E-08	1.45242E-09				
10								
11					Species concentrations (national units)			
12	**Concentrations**	**total Hg (mol/m3)**	Unit conversion (national units)		Hg0	Hg2+	MeHg	
13	Air (gaseous)	7.56E-12	1.52E+00	ng/m3	1.49E+00	2.23E-02	7.43E-03	
14	Aerosol particles	1.93E-14	2.59E-09	ng/g	2.54E-09	3.81E-11	1.27E-11	
15	Water	8.67E-09	1.74E+00	ng/L	3.45E-02	1.65E+00	5.10E-02	
16	Water particles	1.58E-09	1.32E-04	ng/g	2.62E-06	1.26E-04	3.87E-06	
17	Inflow water	2.35E-08	4.72E+00	ng/L	6.62E-02	4.24E+00	4.17E-01	
18	Sediment solids	1.53E-03	1.28E+02	ng/g	3.04E+01	9.68E+01	6.08E-01	
19	Sediment pore water	3.12E-08	6.26E+00	ng/L	1.49E+00	4.74E+00	2.98E-02	
20	Rain	7.67E-06	1.54E+03	ng/L	1.51E+03	2.26E+01	7.54E+00	
21								
22	**Bulk Concentrations**							
23	Air	7.58E-12	1.52E+00	ng/m3	1.49E+00	2.24E-02	7.45E-03	
24	Water	1.03E-08	2.06E+00	ng/L	4.07E-02	1.96E+00	6.03E-02	
25	Sediment	1.38E-04	1.15E+01	ng/g	2.74E+00	8.72E+00	5.47E-02	
26								
27				Species process rates (kg/yr)				
28	**Process rates**	**mol/h**	**kg/yr**	**Hg0**	**Hg2+**	**MeHg**		
29	Emission to water	0.00	0.00					
30	Emission to sediment	0.00	0.00					
31	Burial	2.63E-06	4.61E-03	0.00110	0.00350	0.00002		
32	Sediment resuspension	2.50E-05	4.40E-02	0.00197	0.04174	0.00026		
33	Sediment-water diffusion	4.46E-06	7.83E-03	0.00456	0.00291	0.00036		
34	Water-sediment diffusion	1.24E-06	2.18E-03	0.00005	0.00205	0.00007		
35	Sediment deposition	3.09E-05	5.42E-02	0.00004	0.05410	0.00010		
36	Volatilization	2.75E-06	4.84E-03	0.00483	0.00000	0.00001		
37	Absorption	7.12E-07	1.25E-03	0.00088	0.00028	0.00009		
38	Water outflow	2.69E-06	4.72E-03	0.00011	0.00445	0.00016		
39	Water particle outflow	4.90E-07	8.61E-04	0.00000	0.00086	0.00000		
40	Rain dissolution	1.17E-07	2.05E-04	0.00000	0.00019	0.00001		
41	Wet particle deposition	2.86E-07	5.02E-04	0.00050	0.00000	0.00000		
42	Dry particle deposition	1.49E-07	2.62E-04	0.00026	0.00000	0.00000		
43	Water inflow	6.23E-06	1.09E-02	0.00018	0.00964	0.00112		
44	Water particle inflow	1.07E-06	1.87E-03	0.00000	0.00186	0.00001		

Figure A2.5: 'Diagram' spreadsheet from HERMES model MS Excel workbook.



	A	B	C	D	E	F	G	H	I	J	K	L
1												
2												
3	Lake Name:	**Harp Lake**										
4	Latitude:	**45.3762**										
5	Longitude:	**-79.1260**										
6												
7				**AIR**	BULK		**1.52** ng/m3					
8				Hg0	1.4864							
9				Hg2+	0.0223							
10				MeHg	0.0074							
11					**0.0022**		**0.0048**					
12				Hg0	0.0016		0.0048					
13				Hg2+	0.0005		0.0000					
14				MeHg	0.0022		0.0000					
15				**WATER**	BULK		**2.06** ng/L					
16		**0**	→									
17				Dissolved (ng/L):	**1.7397**	Solids (ng/g):	**0.0001**					
18		**0.0128**	→	Hg0	0.0345	Hg0	0.0000	→	**0.0056**			
19	Hg0	0.0002		Hg2+	1.6542	Hg2+	0.0001		0.0001	Hg0		
20	Hg2+	0.0115		MeHg	0.0510	MeHg	0.0000		0.0053	Hg2+		
21	MeHg	0.0011			**0.0564**		**0.0518**		0.0002	MeHg		
22				Hg0	0.0001		0.0065					
23				Hg2+	0.0562		0.0447					
24				MeHg	0.0002		0.0006					
25				**SEDIMENT**	BULK		**11.51** ng/g					
26		**0**	→									
27				Dissolved (ng/L):	**6.2629**	Solids (ng/g):	**127.8**					
28				Hg0	1.4894	Hg0	30.4					
29				Hg2+	4.7437	Hg2+	96.8			**LEGEND (kg/yr)**		
30				MeHg	0.0298	MeHg	0.6		→	Emission		
31					**0.0046**				→	Advection (In/Out)		
32				Hg0	0.0011				→	Downward flux		
33				Hg2+	0.0035				→	Upward flux		
34				MeHg	0.0000				NOTE: Total Hg fluxes are in **bold.**			

ESTIMATION METHOD FOR SURFACE SEDIMENT Hg

Adrienne L.M. Ethier

1. INTRODUCTION

The issue regarding surface sediment mercury (Hg) enrichment might remain unresolved, but how can a model consistently predict subsurface sediment Hg concentrations while all other fluxes and concentrations (including sediment pore water) agree with measured values.

The Hg Environmental Ratios Multimedia Ecosystem Sources (HERMES) model developed and discussed in this thesis predicts sediment Hg that is consistent with measured subsurface concentrations. Chapter 3 discusses several possible reasons for the observed sediment Hg profiles, including anthropogenic inputs, focusing, and remobilization from underlying sediment. Chapter 1 and 5 use the emission from sediment term (ES) in the model to estimate the amount of Hg remobilized on a yearly basis, assuming that a vertical flux from underlying sediments was solely responsible for surface sediment enrichment (not likely). The model does account for current anthropogenic inputs (atmospheric or watershed) in model calculations, but it does not currently account for any surface sedimentary processes that could lead to surface enrichment (e.g., remobilization or focusing).

The objective of this paper was to introduce an estimation method that could perhaps be used in future model applications to convert predicted subsurface to surface sediment Hg concentration until the issue regarding sources of surface enrichment in sediments is resolved.

2. METHODS

Lake information was gathered from a dataset compiled by Mills et al. (PhD thesis in prep and paper submitted) which contains watershed and lake data for 203 lakes in Ontario located between Mindon and Ottawa. The watershed area of the lakes ranged from 0.1 to 4764 km^2, the lake surface area from 0.03 to 876 km^2, mean depth from 0.6 to 31.6 m, surface sediment organic matter concentration from 74.6 to 711.2 mg g^{-1}, and dissolved inorganic carbon (DIC) ranged from 2.2 to 64.2 mg L^{-1}. The measured surface and subsurface sediment Hg ranged from 19.7 to 500.6 ng Hg g^{-1} dw and 11.6 to 270.8 ng Hg g^{-1} dw, respectively.

Surface sediment enrichment was calculated by dividing measured surface by subsurface sediment Hg concentration. A scatterplot matrix was then used to look for watershed and lake variables within the 203 lakes dataset that might be correlated with this surface sediment enrichment.

A stepwise forward multiple linear regression was used to determine which of these variables should be included in the estimation method for surface sediment enrichment and in what order. Variables were included as long as the r^2 continued to increase (more variability explained) and the Akaike's Information Criterion (AIC) decreased. The AIC indicates the best number of variables to include in a model. Once the regression was completed, the residuals were checked for normality.

An initial comparison between measured and predicted surface sediment Hg was done for lakes which contain the required watershed and lake variables for model application, along with the estimation method for surface enrichment. Predicted surface sediment Hg concentration was calculated by multiplying surface sediment enrichment (calculated with estimation method derived in this study) with the subsurface sediment Hg predicted with the HERMES model.

Statistical analyses were conducted using JMP (SAS, 2000).

3. RESULTS

An estimation method for surface sediment enrichment (SSE) was obtained [Log SSE = 2.195 - (1.003 x log Subsurface sediment Hg (ng g^{-1})) + (0.000534 x Surface sediment organic matter (mg g^{-1})) + (0.0260 x slope watershed (%)) - (0.0107 x Spring dissolved inorganic carbon (mg L^{-1})), (r^2 = 0.70; n = 53; RMSE = 0.092)]. Model predicted subsurface sediment Hg can be converted to surface sediment Hg concentration by multiplying estimated surface sediment enrichment by predicted subsurface Hg concentration.

Fifty-three of the initial 203 lakes used in this paper contained all of the watershed and lake variables required to use the surface sediment enrichment estimation method derived in this paper (Table 1). Chapter 6 used thirty-five lakes from this 203 lake dataset to evaluate model performance. Anstruther, Beaver, Crystal, Salmon and Tallan Lake (n = 5) were the

only lakes that had all of the watershed and lake variables required for model application and the surface sediment enrichment estimation method. For these lakes, predicted versus measured surface sediment Hg values were found to be highly correlated ($r^2 = 0.70$, slope = 0.9, intercept = 0; RMSE = 0.040).

4. DISCUSSION

The HERMES model was able to provide reasonable surface sediment Hg predictions using surface sediment enrichment estimation method derived in this paper and predicted subsurface sediment Hg concentrations (output from HERMES model). This evaluation considered five lakes which were part of the fifty-three lakes used to derive the estimation method for surface sediment enrichment, so this can only be considered an initial examination.

The surface sediment enrichment estimation method considers four watershed and lake variables (i.e., slope of watershed, surface sediment organic matter, subsurface sediment Hg, and spring dissolved inorganic carbon). Previously, slope of watershed was shown by Blais and Kalff (1995) to be correlated with sediment focusing in lakes. Organic matter was shown in Chapter 3 to be highly correlated with sediment Hg concentration. As discussed in Chapter 3, degradation of organic matter could lead to Hg remobilization from underlying sediments. Sediment focusing could also increase with increases in organic matter since bound Hg will be more prone to resuspension in lakes. The scatterplot matrix produced in this study showed that both surface and subsurface sediment Hg were correlated with surface sediment enrichment. The estimation method for surface sediment enrichment

supports the notion that sedimentary processes (i.e., focusing and remobilization) are likely responsible for measured sediment Hg profiles, but not the relative influence of each process.

Future research should focus on the development of estimation methods for Hg focusing and remobilization within sediments. In this manner, the relative contribution of each process to measured sediment Hg profiles can be properly addressed.

5. CONCLUSION

An estimation method to convert model predicted subsurface to surface sediment Hg concentration using surface enrichment is presented here. Further evaluation of the estimation method may be required, but it should provide reasonable approximations of surface sediment Hg concentration with the HERMES model until issues regarding the relative contribution of sedimentary processes are clarified or resolved.

ACKNOWLEDGEMENTS – I must acknowledge the person who continually pestered me until I caved and developed this estimation method. Thanks David.

REFERENCES – see reference list for thesis

Table A3.1: Fifty-three lakes used in this study.

							HERMES Model		
Lake	Slope of watershed (%)	Spring DIC (mg L^{-1})	Surface sediment Hg (ng g^{-1})	Subsurface sediment Hg (ng g^{-1})	Surface sediment enrichment	Surface organic matter (mg g^{-1})	Predicted subsurface sediment Hg concentration	Estimated surface sediment enrichment	Predicted surface sediment Hg concentration
Anstruther	6	2.2	367.8	100.4	3.5	321.9	121.0	2.6	312.0
Arran	4	34.2	68.9	52.3	1.3	447.0			
Balsam	7	12.4	170.5	80.3	2.1	237.9			
Bass	3	44.4	67.4	42.8	1.6	166.5			
Beaver	7	2.6	354.1	83.3	4.3	365.0	81.4	4.3	346.0
Bell	3	47.4	291.9	125.1	2.3	387.5			
Berford	1	31.6	52.2	121.3	0.4	340.2			
Big Clear	8	24.2	227.1	128.0	1.8	431.2			
Big Gull	4	5.8	335.7	83.1	4.0	386.0			
Blue	5	64.2	21.6	98.9	0.2	75.3			
Brewster	2	34.0	114.5	196.1	0.6	478.0			
Charleston	3	23.8	216.8	97.7	2.2	273.8			
Christie	5	14.2	156.8	120.4	1.3	349.2			
Crystal	4	19.4	249.6	130.7	1.9	418.8	107.0	1.9	206.2
Dankert	3	28.0	197.0	65.0	3.0	620.4			
East Bass	1	41.8	92.8	95.4	1.0	307.9			
Eugenia	3	48.1	77.8	72.7	1.1	187.2			
Farren	6	21.4	148.7	99.9	1.5	368.5			
Gananoque	4	29.2	140.0	70.8	2.0	404.1			
Gould	7	17.4	236.4	88.5	2.7	316.7			
Grippen	4	19.1	294.9	55.9	5.3	332.3			
Hines Lake	3	45.0	123.5	89.6	1.4	345.9			
Inverary	5	31.4	99.4	74.4	1.3	195.3			
Irish	3	20.2	175.6	170.1	1.0	557.9			
Kagawong	2	28.7	142.3	94.4	1.5	295.5			
Kerr	3	38.4	170.6	135.8	1.3	689.5			
Leggat	3	6.2	250.2	56.9	4.4	551.6			
Lily (West)	1	30.6	116.5	81.5	1.4	601.0			
Limerick	7	23.6	256.1	52.6	4.9	321.8			
Long	9	24.8	176.3	143.0	1.2	655.6			
Lorne	1	33.8	170.1	140.8	1.2	365.2			
Lower Beverley	3	31.8	145.6	87.0	1.7	333.8			
Manitou	2	27.0	198.0	61.4	3.2	298.5			
Mc Cullough	3	53.3	141.5	100.5	1.4	359.6			
Mc Gill	6	41.1	279.9	115.9	2.4	708.9			
Mindemoya	2	26.4	84.3	78.5	1.1	266.2			
Nameless	2	31.6	182.5	248.6	0.7	226.3			
Otty	3	24.0	174.8	88.6	2.0	503.5			
Pike	5	14.0	219.5	135.6	1.6	377.0			
Pike	4	31.4	151.0	144.1	1.0	385.3			
Red Horse	3	30.6	142.7	63.8	2.2	395.7			
Salmon	4	18.6	301.7	80.7	3.7	514.1	72.7	3.3	236.4
Sharbot	7	20.6	374.1	100.9	3.7	472.0			
Silver	2	35.2	64.7	51.7	1.3	601.5			
Skootamatta	4	2.8	306.0	117.2	2.6	388.1			
Stone's	4	37.2	79.6	217.2	0.4	128.3			
Tallan	6	23.4	241.0	88.1	2.7	583.6	129.0	2.0	253.7
Tobacco	3	31.6	147.2	100.1	1.5	228.3			
West Bass	3	24.8	176.2	163.0	1.1	711.2			
Wilcox	3	42.1	171.7	111.2	1.5	433.2			
Williams	3	47.6	31.2	102.7	0.3	74.6			

DIC: Dissolved Inorganic Carbon