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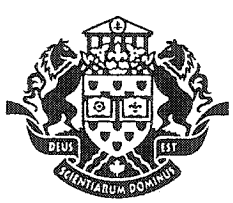

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DISSOLVED GASEOUS MERCURY DYNAMICS AND MERCURY VOLATILIZATION IN FRESHWATER LAKES

NELSON JAMES O'DRISCOLL

Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
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Abstract

This thesis examines the production and distribution of dissolved gaseous mercury (DGM) in freshwater ecosystems and its relationship to mercury volatilization. The importance of volatilization was assessed within a multidisciplinary mercury mass balance for Big Dam West Lake (BDW) Kejimkujik Park, Nova Scotia. The magnitude of volatilization was found to be approximately double the direct wet deposition over lake and wetlands, and 27% of the direct wet deposition to the terrestrial catchment. Over the entire basin area the mass of mercury volatilized is 46% of the mass deposited by wet deposition.

A new method of continuous (5 minute) DGM analysis was developed and tested. The detection limit for DGM was 20 fmol L^{-1} with 99% removal efficiency. Control experiments showed that there was no interference due to methyl mercury, which is present in similar concentrations to DGM. Experiments comparing continuous DGM analysis with discrete DGM analysis showed that the results are not significantly affected by typical variations in water temperature (4-30 $^{\circ}$C), oxidation-reduction potential (135-355 mV), dissolved organic carbon (4.5- 10.5 mg L^{-1}), or pH (3.5- 7.8). The continuous analysis was within 4.5% of the discrete analysis when compared across 12 samples analyzed in triplicate.

Diurnal patterns for dissolved gaseous mercury (DGM) and mercury flux were measured (using this new DGM method and a Teflon flux chamber method) in two lakes with contrasting dissolved organic carbon (DOC) concentrations in Kejimkujik Park, Nova Scotia. Consistently higher DGM concentrations were found in the high DOC lake as compared to the low DOC lake. Cross-correlation analysis indicated that DGM dynamics changed in response to solar radiation with lag-times of 65 and 90 minutes. An examination of current mercury flux models using this quantitative data indicated some good correlations between the data and predicted flux (r ranging from 0.27 to 0.83) but generally poor fit (standard deviation of residuals ranging from 0.97 to 3.38). This research indicates that DOC and wind speed may play important roles in DGM and mercury flux dynamics that have not been adequately accounted for in current predictive models.

The link between DOC concentrations and DGM production was further investigated using tangential ultrafiltration to manipulate DOC concentrations in water samples. In this way, a range of samples with different DOC concentrations was produced for each lake without substantial changes to DOC structure or dissolved ions. This was repeated for four lakes in northern Quebec; two with drainage basins that were extensively logged and two drainage basins were minimally logged. On two separate days for each lake, abiotic water samples of varying DOC concentrations were incubated in clear and dark Teflon bottles on the lake surface with temperature and DGM concentrations measured

at 3.5-hour intervals over the course of 10.5 hours. Levels of DGM increased with increasing cumulative irradiation for all lakes until approximately 4000 kJ m^{-2} (400-750 nm, photosynthetically active radiation (PAR)), when DGM concentration reached a plateau (between 20 and 200pg L^{-1}). Assuming that DGM production was limited by the amount of photo-reducible mercury, reversible first-order reaction kinetics fit the observed data well (r^2 ranging from 0.59 to 0.98). The DGM plateaus were independent of DOC concentrations but differed between lakes. In contrast photo-production efficiency (DGM_{prod}), *i.e.* the amount of DGM produced per unit radiation (fg L^{-1} $(kJ/m^2)^{-1}$) prior to 4000 kJ m^{-2} PAR, was linearly ($P<0.0005$) proportional to DOC concentration. Furthermore, logged lakes had a lower ($P<0.006$) DGM_{prod} per unit DOC than the non-logged lakes. In these four lakes, the rate of DGM production per unit PAR was dependent on the concentration of DOC, with significant differences between lakes presumably due to different DOC structures and dissolved ions.

The distribution of DGM in the water columns of shallow and deep freshwater lakes was investigated in lake Ontario and several small freshwater lakes. When DGM concentrations were expressed on an areal basis, DGM concentrations above the thermocline in Lake Ontario average 1.5 ng m^{-2} and in small freshwater lakes it ranged between 0.1 and 0.8 ng m^{-2}. Further, it was demonstrated that the majority of DGM in large freshwater lakes such as Lake Ontario exists below the thermocline where photochemical oxidation and reduction processes cannot occur. The depth profiles indicate that vertical mixing in the water column may alter the DGM concentration in the upper epilimnion, and that turn over in deep lakes may result in a transfer of large concentrations of DGM from the hypolimnion into the epilimnion. In addition, the results indicate that microbial processes may be an important factor regulating DGM in the water column of freshwater lakes, particularly in the hypolimnion.

Résumé

La production et la distribution du mercure gazeux dissous (DGM) dans des écosystèmes d'eau douce ainsi que son rapport avec la volatilisation du mercure ont été étudiés. L'importance de la volatilisation a été évaluée dans un bilan de masse du mercure multidisciplinaire pour le lac Big Dam West (BDW) dans le parc Kejimkujik, en Nouvelle-Écosse. L'ampleur de la volatilisation s'est avérée approximativement le double du dépôt humide direct au-dessus du lac et des terres humides, et 27% du dépôt humide direct sur le bassin-versant. Au-dessus de la superficie entière du bassin, la masse de mercure volatilisé équivaut à 46% de la masse déposée par dépôt humide.

Une nouvelle méthode d'analyse continue de DGM (5 minute d'intervalle) a été développée et examinée. La limite de détection du DGM était de 20 fmol L^{-1}, avec un rendement d'élimination de 99%. Des expériences de contrôle ont démontré qu'il n'y avait aucune interférence due au methyl-mercure, qui est présent en concentrations semblables au DGM. Des expériences comparant l'analyse continue de DGM à l'analyse discrète de DGM ont démontré que les résultats ne sont pas significativement affectés par des variations typiques de la température de l'eau (de 4 à 30°C), du potentiel d'oxydation-réduction (de 135 à 355 mV), du carbone organique dissous (de 4,5 à 10,5 mg L^{-1}), ou du pH (de 3,5 à 7,8). L'analyse continue était à moins de 4.5% de l'analyse discrète lorsque ces deux méthodes ont été comparées à l'aide de 12 échantillons analysés en triplicat.

Des cycles diurnaux du flux du mercure gazeux dissous (DGM) et du mercure ont été mesurés (en utilisant la nouvelle méthode pour le DGM et une méthode de chambre de flux en Téflon) dans deux lacs ayant des concentrations différentes de carbone organique dissous (DOC) au parc Kejimkujik en Nouvelle-Écosse. Des concentrations uniformément plus élevées de DGM ont été observées dans le lac ayant une concentration élevée de DOC par rapport au lac dont la concentration de DOC était faible. Une analyse de corrélation croisée a indiqué que la dynamique de DGM change selon le rayonnement solaire, avec des temps de réponse de 65 et 90 minutes. Un examen des modèles courants de flux de mercure en employant ces données quantitatives a indiqué de bonnes corrélations entre le flux observé et le flux prédit (r s'étendant de 0,27 à 0,83) mais l'ajustement était généralement faible (écart type des résidus s'étendant de 0,97 à 3,38). Cette recherche indique que la concentration de DOC et la vitesse du vent peuvent jouer des rôles importants dans la dynamique du flux du DGM et du mercure qui ne sont pas pris en compte adéquatement par les modèles de prévision courants.

Le lien entre les concentrations de DOC et la production de DGM a été étudié en utilisant l'ultrafiltration tangentielle permettant de modifier les concentrations de

DOC dans des échantillons d'eau. De cette façon, une gamme d'échantillons ayant différentes concentrations de DOC a été produite pour chaque lac sans changements importants à la structure du DOC ou des ions dissous. Ceci a été répété pour quatre lacs au nord du Québec; deux lacs pour lesquels la coupe forestière est importante dans le bassin-versant et deux lacs pour lesquels la coupe forestière dans le bassin-versant est minimale. Des expériences ont été entreprises à deux occasions dans chaque lac. Durant celles-ci, des échantillons abiotiques d'eau ayant des concentrations variées en DOC ont été incubés à la surface du lac dans des bouteilles de Téflon claires et foncées. La température et les concentrations de DGM ont été mesurées à 3,5 heures d'intervalle pendant une periode de 10,5 heures. Dans tous les lacs, les niveaux de DGM ont augmenté avec l'augmentation de l'irradiation cumulative, jusqu'à environ 4000 kJ m^{-2} (de 400 à 750 nm, rayonnement actif photosynthétique (PAR)), niveau d'irradiation auquel la concentration de DGM atteint un plateau (entre 20 et 200 pg L^{-1}). En supposant que la production de DGM était limitée par la quantité de mercure photo-réductible, la cinétique de réaction réversible de premier ordre ajuste bien les données observées (r^2 s'étendant de 0,59 à 0,98). Les plateaux de DGM étaient indépendants des concentrations de DOC mais différaient entre lacs. À l'opposé, l'efficacité de photo-production (DGM_{prod}), c'est-à-dire la quantité de DGM produit par unité de radiation (fg L^{-1} $(kJ/m^2)^{-1}$) sous 4000 kJ m^{-2} PAR, était linéairement ($P<0,0005$) proportionnelle à la concentration de DOC. De plus, les lacs autour desquels la coupe forestière est importante avaient un DGM_{prod} par unité de DOC inférieur ($P<0,006$) à celui des lacs autour desquels la coupe forestière n'est pas importante. Dans ces quatre lacs, le taux de production de DGM par d'unité de PAR dépendait de la concentration du DOC, avec des différences significatives entre les lacs probablement dues à des structures de DOC et à des ions dissous différents.

La distribution de DGM dans la colonne d'eau de lacs d'eau douce peu profonds et profonds a été étudiée dans le lac Ontario et dans plusieurs petits lacs d'eau douce. Lorsque les concentrations de DGM sont exprimées en terme de superficie, les concentrations de DGM au-dessus de la thermocline sont en moyenne 1,5 ng m^{-2} dans le lac Ontario et elles s'étendent de 0,1 à 0,8 ng m^{-2} dans les petits lacs d'eau douce. De plus, on a démontré que la majorité du DGM dans de grands lacs d'eau douce tels que le lac Ontario se retrouve sous la thermocline, où les processus photochimiques d'oxydation et de réduction ne peuvent pas se produire. Les profils de profondeur indiquent que la concentration de DGM dans la partie supérieure de l'épilimnion peut être altérée par le mélange vertical dans la colonne d'eau, et que le renversement dans les lacs profonds peut résulter en un transfert de grandes concentrations de DGM de l'hypolimnion à l'épilimnion. Également, les résultats indiquent que les processus microbiens peuvent être un facteur important réglant le DGM dans la colonne d'eau des lacs d'eau douce, en particulier dans l'hypolimnion.

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This thesis is dedicated to the women in my life who made me the person I am today: Mary O'Driscoll (grandmother), Agnes O'Driscoll (mother), Claire Wilson O'Driscoll (wife), and Ellen O'Driscoll (daughter).

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List of Abbreviations

AST: Atlantic Standard Time

BDW: Big Dam West Lake

CVAFS: Cold Vapour Atomic Fluorescence Spectroscopy

DGM: Dissolved Gaseous Mercury

DO: Dissolved Oxygen

DOC/TOC: Dissolved Organic Carbon / Total Organic Carbon

GEM: Gaseous Elemental Mercury

GIS: Geographic Information System

GMT: Greenwich Mean Time

HDPE/LDPE: High Density Polyethylene / Low Density Polyethylene

IR: Infra Red

MDN: Mercury Deposition Network

MeHg: Methyl Mercury

NADP: National Atmospheric Deposition Program

ORP: Oxidation-Reduction Potential

PAR: Photo synthetically Active Radiation

QA/QC: Quality Assurance / Quality Control

RSD: Relative Standard Deviation

SOP: Standard Operating Protocol

TADS: Tekran Automated Dual Sampling System

USEPA: United States Environmental Protection Agency

UV: Ultra Violet

Chapter 1

Introduction

1.1. Thesis Rationale

Mercury is an important environmental contaminant that bioaccumulates in food chains and causes severe health effects in aquatic predators and the human populations that consume them. Mercury pollution first received worldwide attention with the Minimata Bay disaster in Japan in 1956, when large numbers of fisherman near the Chisso Chemical Company plant were diagnosed with neurological disorders (Takizawa & Osame, 2001). Since then, it has been shown that environmentally realistic concentrations of mercury decrease the reproductive success of some fish populations (eg. Hammerschmidt *et al.* 2002), and that elevated levels of mercury in fish-eating birds can severely reduce clutch sizes and hatchability as well as increasing hatchling mortality (Wolfe *et al.*, 1998). Human populations particularly at risk for mercury poisoning are those that consume large amounts of fish, such as aboriginal peoples (Wheatley and Paradis, 1995). Effects of mercury exposure in humans include immunotoxicity (Sweet and Zelikoff, 2001) and neurological damage characterized by ataxia, sensory disturbances and changes in the mental state (Chang, 1987).

Elevated levels of mercury in biota are present not only in contaminated sites but also in relatively remote freshwater lakes. For example, Kejimkujik Park in Nova Scotia has no direct anthropogenic inputs of mercury and yet has loons with the highest blood mercury concentrations in North America (Burgess *et al.*, 1998; Evers *et al.*, 1998). Likewise, many fish in other remote lakes have been found to have elevated mercury levels in tissue (Sorensen *et al.*, 1990; Lathrop *et al.*, 1991; Cabana *et al.*, 1994).

The key to understanding mercury dynamics in the environment is a more detailed knowledge of the mercury cycle. Indeed, both the US-EPA and Health Canada have identified the study of mercury cycling in the environment as a top research priority (USEPA, 1997). There are several forms of mercury and a variety of processes implicated in the mercury cycle (Figure 1-1). The three major species of mercury are elemental mercury (Hg^0), inorganic mercury (Hg^{2+}), and methyl mercury (CH_3Hg^+). Elemental mercury is volatile and the main form of mercury found in the atmosphere, while inorganic mercury is the predominant form found in water, bound to various organic and inorganic ligands. Methyl mercury is the form of mercury that bioaccumulates in the food chain. Very low methyl mercury levels in water (< 0.1 ng L^{-1}) can result in concentrations in higher trophic levels that exceed human consumption guidelines (> 0.5 $\mu g\ g^{-1}$ wet weight) (Morel *et al.*, 1998).

One important process in the mercury cycle is the creation of dissolved gaseous mercury (DGM) in freshwater lakes and its loss to the atmosphere by volatilization. DGM is believed to consist primarily of elemental mercury (Hg^0) formed from inorganic mercury through the process of reduction (O'Driscoll *et al.*, 2003b). DGM is the form in which mercury volatilizes from water to air, and volatilization is one of the primary means of mercury removal from an ecosystem.

Mercury volatilization has not been studied in detail in a diversity of ecosystems,

but several researchers have indicated in a general way that it is a significant part of the mercury cycle. For example, Rolfhus and Fitzgerald (2001) found that mercury volatilization from Long Island Sound was equivalent to 35% of total annual mercury inputs to the system, and studies on the Great Lakes show that mercury volatilization is equivalent to as much as 50% of the total mercury inputs (Mason and Sullivan, 1997; Watras *et al.*, 1995). In other studies, Mason *et al.* (1994) and Amyot *et al.* (1994) found that mercury volatilization and wet deposition were close to being in balance. Volatilization has also been shown to be an important factor in the global distribution of mercury, and Mason *et al.* (1994) indicate that mercury volatilization from the ocean surface may account for approximately 30% of the total global mercury emissions to the atmosphere.

The overall result of DGM formation and volatilization is a reduction in the mercury burden of freshwater lakes. A reduction in total mercury may ultimately result in less formation of methyl mercury and therefore in a reduction of mercury poisoning in the food chain (Nriagu, 1994; Morel *et al.*, 1998). A better understanding of the factors that affect DGM formation and its relation to volatilization may help to identify areas at risk for mercury bioaccumulation. This research may also help to increase the accuracy of global distribution models for mercury.

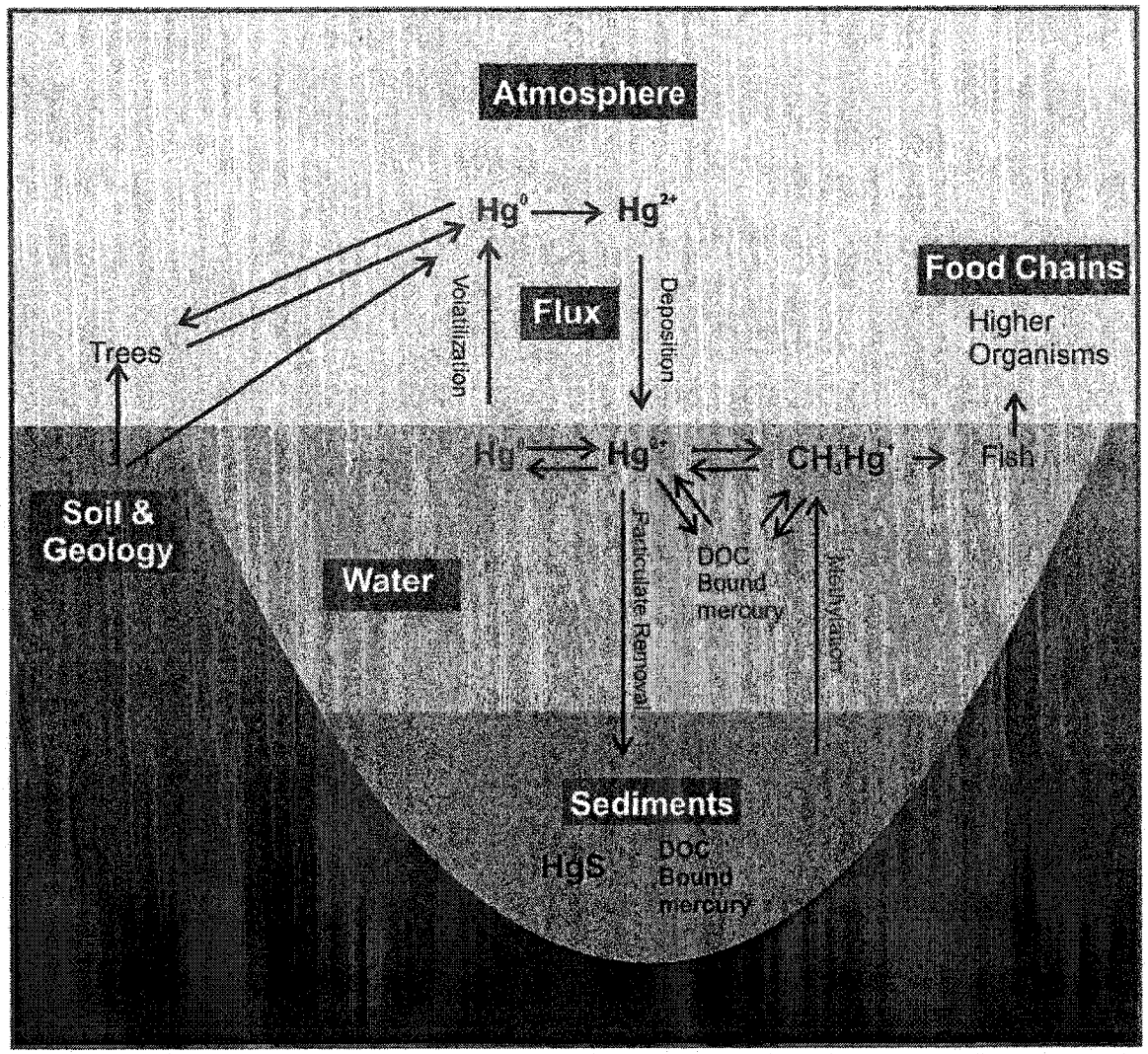

Figure 1-1: Conceptual diagram outlining the major processes within the mercury cycle of freshwater lakes

1.2. A Review of Photo-Reduction and Photo-Oxidation

The processes responsible for the formation of DGM in lakes (reduction) and the conversion of DGM to inorganic mercury (oxidation) are believed to be driven by solar radiation. Photo-reduction of mercury has been observed by many researchers in both saltwater (Amyot *et al*, 1997c; Baeyens and Leermakers, 1998; Costa and Liss, 1999; Lanzillotta and Ferrara, 2001) and freshwaters

(Zhang and Lindberg, 2001; Amyot *et al.*, 1994, 1997a), in temperate lakes and rivers (Vandal *et al.*, 1991; Amyot *et al.*, 1994, 1997a, 2000), Artic lakes (Amyot *et al.*, 1997b), and southern wetlands (Krabbenhoft *et al.*, 1998), yet the mechanisms by which it occurs are not well understood.

Both abiotically- and biotically-mediated mechanisms for photo-reduction have been suggested in the literature. Nriagu (1994) outlined various abiotic mechanisms including homogeneous photolysis, reduction by inorganic particulates and organic molecules, as well as transient reductants. More recently Zhang and Lindberg (2001) have suggested that iron(III) mediated photo-reduction is a significant mechanism in DGM formation.

There are also many photo-produced reductants that may result in the conversion of inorganic mercury to DGM (Figure 1-2). Several researchers (Cooper *et al.*, 1989a; Zepp *et al.*, 1987) suggest that when DOC absorbs solar radiation aqueous electrons are released. It is possible that these electrons are available to reduce mercury. An alternative to reduction by aqueous electrons is direct reduction of mercury by humic substances. While the exact reduction mechanism is not clear, semiquinones (which are present in humic acids) are thought to act as redox intermediates. Allard and Arsenie (1991) determined that reduction by DOC is possible except at very low pH or with high chloride concentrations.

Several researchers have also suggested that bacteria mediate mercury reduction (Barkay *et al.*, 1991; Vandal *et al.*, 1994). Siciliano *et al.* (2002) recently examined the role of microbial reduction and oxidation processes in regulating DGM diel patterns in freshwater lakes (Appendix 1). We showed that photo-chemically produced hydrogen peroxide regulates microbial oxidation processes and may account for the diel patterns observed in DGM data (Appendix 1). Overall, the mechanisms responsible for mercury reduction and the relative contributions of biotic and abiotic processes are still unclear.

Photo-oxidation is the reversal of photo-reduction, that is, the transformation of DGM into inorganic mercury. As with photo-reduction, both abiotic (Zhang and Lindberg, 2001; Lalonde *et al.*, 2001) and biotic (Siciliano *et al.*, 2002) mechanisms for photo-oxidation have been proposed (Figure 1-2). Lalonde *et al.* (2001), who discovered that DGM can be photo-oxidized, claimed that chloride ions stabilize Hg(I) in solution and decrease the Hg(I)/Hg(0) potential such that electron transfer to semiquinones may take place. They determined that photo-oxidation of Hg(0) follows pseudo-first-order kinetics with a rate constant of 0.25 h^{-1} for freshwater and 0.6 h^{-1} for saline waters.

While the relative importance and precise mechanisms of these competing processes are currently unknown, it is likely that the balance of photo-reduction and photo-oxidation controls DGM dynamics in freshwaters. There are many aspects of this part of the mercury cycle that require clarification if we are to quantify the significant flux processes within an entire lake ecosystem. The

influence of mercury reduction and oxidation in mercury evasion (Figure 1-2) is especially critical and is the focus of this thesis.

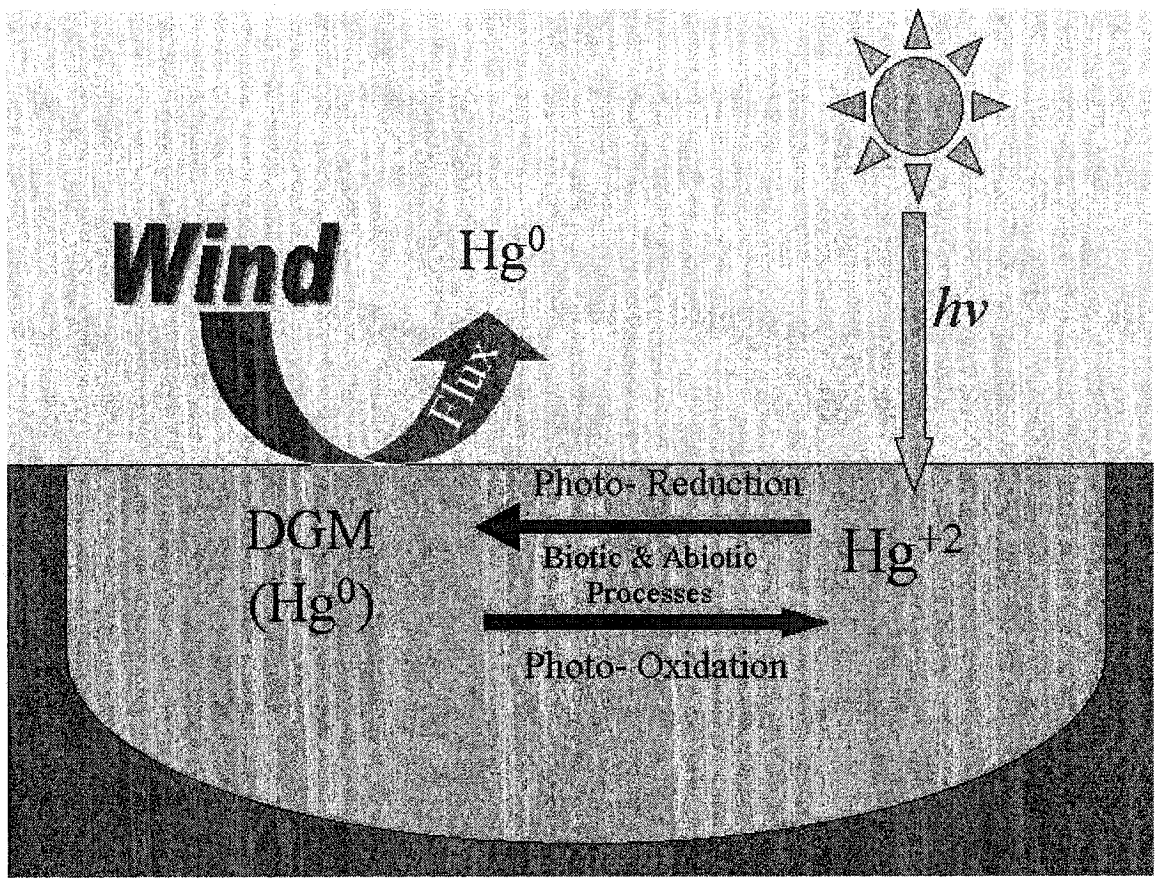

Figure 1-2: Conceptual diagram outlining relationship between solar radiation, DGM formation and mercury volatilization.

1.3. Limitations of Previous DGM Research

As outlined in the previous section, several studies have identified DGM volatilization as a significant portion of the mercury cycle (Mason *et al.*, 1994; Amyot *et al.*, 1994; Watras *et al.*, 1995; Mason and Sullivan, 1997; Rolfhus and Fitzgerald, 2001). While some mercury mass balances have included values for volatilization, most studies to date have been pieced together using disparate

data, literature values and theoretical modeling. None have investigated the importance of mercury volatilization using primary data within a multidisciplinary mass balance model. While volatilization of DGM is thought to be an important process determining the distribution of mercury, very little research has directly measured DGM diurnal dynamics in relation to volatilization.

Partly responsible for this are the difficulties presented in the analysis of DGM. Typically, DGM in freshwater is present at concentrations that are 5 - 20 % that of total mercury (Amyot *et al.*, 2000). While the total amount of mercury present in pristine lake water is in the ng L^{-1} range, the amount that is elemental mercury is much less (20 - 200 pg L^{-1} range). The accurate measurement of such small quantities is difficult, and this has been one of the challenges in performing DGM research. Another difficulty has been the measurement of fast changes in DGM. Analysis times typically range from 20 – 90 minutes (Amyot *et al.*, 2000; Lindberg *et al.*, 2000), while DGM concentrations may change within minutes (O'Driscoll *et al.*, 2003b). In order to see realistic changes in DGM, an analysis method that can measure low pg L^{-1} quantities in a very short time-span is required.

Many researchers have recognized the importance of DGM dynamics and volatilization in theoretical mercury fate models (Rolfhus and Fitzgerald, 2001; Mason and Sullivan, 1997; Watras *et al.*, 1995), particularly with regard to the global cycling of mercury (Mason *et al.*, 1994). While a number of predictive models for mercury volatilization have been proposed, no work to date has

measured DGM and volatilization simultaneously, nor have they measured meteorological variables that may have an important influence on DGM dynamics and mercury flux. Therefore, current theoretical mercury flux models have not been tested or calibrated against quantitative data sets.

There are several factors that are thought to affect DGM formation and distribution within a lake. One such factor is DOC and the role it plays in DGM formation. The relationship between DOC and DGM is not consistent in the published literature, with some authors reporting a positive relationship (O'Driscoll *et al.*, 2003b; Xiao *et al.*, 1995) and some reporting a negative relationship (Amyot *et al.*, 1997a; Watras *et al.*, 1995). Part of the confusion may be due to the confounding effects of DOC structure and dissolved ions on mercury photo-reduction and photo-oxidation processes. To date no study has attempted to control changes in DOC structure and dissolved ions while working with natural freshwater samples. This is likely because it is difficult to alter DOC concentrations without substantially changing the other chemical constituents (cations, anions, nutrients) present in lake water. More information on the complex role that DOC plays in mercury cycling is essential to quantifying the fate of mercury in ecosystems.

Finally, another important factor that has not been adequately explored is the distribution of DGM in the water column. A few researchers have attempted a limited number of depth profiles for DGM, however no clear observations have emerged (Amyot *et al.*, 1994; 1997a; 1997c). The distribution of DGM in both

shallow and deep freshwater lakes has not been examined, nor have areal differences in DGM between the epilimnion and the hypolimnion. An understanding of DGM distribution in the water column is required in order to build whole-lake models for mercury volatilization that incorporate the effects of water column mixing.

1.4. Thesis Organization

This thesis attempts to address the limitations in current DGM and mercury flux research that are outlined in Section 1.3. The following is a statement of the general and specific objectives of the thesis, followed by an overview of chapters 2-6 and the null hypotheses tested in each.

1.4.1. General and Specific Objectives

General Objectives

The general objective of this research is to contribute to a better understanding of mercury flux processes in the following ways:

- Through the examination of mercury volatilization within a mercury mass balance for Big Dam West Lake in Kejimkujik Park, Nova Scotia, using data collected in collaboration with the multidisciplinary research team supported by the Toxic Substances Research Initiative from 1999-2002;

- Through the development of an improved methodology for the

continuous analysis of dissolved gaseous mercury (DGM) in freshwater lakes;

- Through a series of studies focused on factors that affect DGM formation and distribution, and on the relationship between these and mercury volatilization (loss from the ecosystem).

Specific Objectives

- The creation of a mass balance model using quantitative data, to examine the relative importance of mercury volatilization in the Big Dam West Lake ecosystem (Chapter 2);
- The development of a method for the near-continuous analysis of DGM and water chemistry that can be used in remote locations (Chapter 3);
- Examination of the role of DGM in mercury volatilization from lakes, and specifically the quantification of relationships between DGM, water chemistry variables, meteorological variables, and mercury volatilization over a diurnal cycle (Chapter 4);
- Quantification of the relationship between DOC concentration and DGM photo-production in freshwater, and the development of a logical model based on field measurements (Chapter 5);
- Examination of trends in DGM distribution through the water columns of shallow and deep lakes, and the implications for whole-lake modeling of DGM dynamics (Chapter 6).

1.4.2. Thesis Overview and Null Hypotheses

This thesis consists of five papers (chapters 2-6), each one of which tests a series of hypotheses stemming from one of the specific objectives outlined above (Section 1.4.1). It should be noted that since each paper has its own introduction and conclusions, the overall introduction and conclusions of the thesis (Chapters 1 and 7) have been kept intentionally brief to avoid redundancy. An overview of Chapters 2-6 and the hypotheses they test is provided below.

Chapter 2 describes a multidisciplinary mass balance model of mercury cycling developed for Big Dam West Lake in Kejimkujik Park Nova Scotia, and examines the importance of mercury volatilization within this cycle. The following null hypothesis was tested:

$H_0$2-1: DGM production and volatilization to the atmosphere is not a significant loss process in the mercury cycle of Big Dam West Lake over the course of a year.

Chapter 3 details the development, quality assurance/ quality control, and field-testing of a new methodology for the continuous analysis of DGM in-situ. The following null hypotheses were tested:

$H_0$3-1: Continuous measurements of DGM do not calibrate well with discrete DGM measurements.
$H_0$3-2: Methyl mercury does not interfere with DGM measurement.
$H_0$3-3: Temperature, ORP, DOC and pH will not alter continuous DGM measurements in comparison to discrete measurements.

The results of Chapter 3 made it possible to collect the continuous DGM data outlined in Chapter 4 of the thesis. Chapter 4 investigates the relationships between DGM, mercury volatilization, water chemistry and meteorological variables over a diurnal cycle in two freshwater lakes. The data presented here is also used to test some of the existing theoretical models for mercury flux. The following null hypotheses were tested:

$H_0$4-1: Diurnal dynamics of DGM and mercury volatilization are not correlated with solar radiation.

$H_0$4-2: There is no time lag between solar radiation measurements and changes in DGM concentration over a diurnal cycle.

$H_0$4-3: Current mercury flux models accurately predict the relationship between DGM, meteorological variables, and mercury flux.

$H_0$4-4: Water chemistry and meteorological parameters are not useful predictors of DGM dynamics.

The results of Chapter 4 indicated that current mercury flux models do not accurately predict diurnal dynamics. However, these models may be improved by the incorporation of time-shifted solar radiation values and inter-site differences such as DOC concentration. It was also observed that the high-DOC lake consistently had higher concentrations of DGM in the surface water than the low-DOC lake over a diurnal cycle. The effects of DOC on DGM dynamics are not well understood, with conflicting opinions presented in the published literature. It

was therefore decided to examine this in more detail.

Chapter 5 examines the effects of DOC concentration on DGM photo-production in four freshwater lakes in northern Quebec. Two of the lakes are in logged catchments, while two are in catchments where little or no logging has taken place. The following null hypotheses were tested:

$H_0$5-1: Changes in DGM concentration are not related to cumulative solar radiation.

$H_0$5-2: The DGM plateau is not related to changes in DOC concentration.

$H_0$5-3: The initial DGM production rate is not related to changes in DOC concentration.

$H_0$5-4: DGM photo-production cannot be accurately modeled as a reversible reaction based on the photo-reduction of the photo-reducible mercury fraction.

$H_0$5-5: The initial DGM photo-production rate is not different between logged and non-logged freshwater lakes.

The results of chapter 5 indicated that DGM photo-production increases linearly with solar radiation in all lakes to a point (approximately 4000 kJ m^{-2} cumulative PAR), and then it levels to a plateau. The DGM photo-production results were accurately modeled using kinetic equations based on a first order reversible reaction. The DGM plateaus were not related to DOC concentrations, but the initial DGM production rate was significantly related to DOC concentration in each lake. In addition, the logged lakes were found to have lower rates of initial DGM production. This indicates that logging may reduce a lake's ability to

produce DGM and thus result in an increase in a lake's mercury pool. One important caveat for the presented results is that the experiments were performed on surface water. In a whole-lake DGM model, the effects of water column mixing and solar attenuation would have to be taken into account.

Chapter 6 examines the DGM distribution in the water columns of freshwater lakes. An understanding of DGM distribution with depth is essential to creating whole-lake models of mercury volatilization that account for the effects of water column mixing on DGM dynamics. The following null hypotheses were tested:

$H_0$6-1: There are no differences between areal DGM concentrations in small and large lakes.

$H_0$6-2: There are no differences between the areal DGM concentrations above and below the thermocline of large and small lakes.

$H_0$6-3: Microbial oxidation and reduction processes are not important to the distribution of DGM in the water column.

The results in Chapter 6 show that the small freshwater lakes examined had lower areal DGM concentrations than lake Ontario. Furthermore, in large freshwater lakes the majority of DGM exists below the thermocline where photo-induced oxidation and reduction processes cannot occur. This supports the theory that microbial reduction processes may be important in DGM production. This area of study is further examined in a co-authored paper that is included as Appendix 1. The results presented in Appendix 1 indicate that microbial reduction

and hydrogen peroxide induced microbial oxidation may in part explain the diurnal DGM dynamics observed in lakewater. While the relative importance of abiotic and biotic mechanisms is still unclear, the work presented in appendix 1 implies that biotic mechanisms may be critical to modeling DGM dynamics. This thesis is concluded by a brief summary of the major findings in each chapter, the significance and potential impacts of these findings, and recommendations for future research in the area of DGM dynamics.

Chapter 2

MERCURY MASS BALANCE FOR BIG DAM WEST LAKE, KEJIMKUJIK PARK, NOVA SCOTIA: EXAMINING THE ROLE OF VOLATILIZATION

Reproduced in part with permission from: Nelson J. O'Driscoll, Steve D. Siciliano, Steven T. Beauchamp, Andy N. Rencz, Thomas A. Clair, Kevin H. Telmer, and David R.S. Lean. Mercury Cycling in a Wetland Dominated Ecosystem: A Multidisciplinary Study. Chapter 13: Mercury mass balance for Big Dam West Lake, Kejimkujik Park, Nova Scotia: Examining the role of volatilization. SETAC Press. Submitted.

2.1. Introduction

The role of volatilization is an important process as it determines the rate at which mercury is being removed from an ecosystem and returned to the atmosphere (Schroeder and Munthe 1998; Xu *et al.* 1999; Poissant *et al.* 2000). Mercury accumulation and eventually bioaccumulation may increase if more mercury enters than leaves an ecosystem. With few exceptions (Rolfhus and Fitzgerald 2001), no studies have attempted to examine the importance of mercury volatilization within a whole-ecosystem mercury mass balance.

To determine the relative importance of the different mercury flux pathways, a multidisciplinary team was assembled to determine all known mercury flux processes within one lake basin (O'Driscoll *et al.* 2001). The team was comprised of geologists, chemists, biologists, GIS experts, microbiologists, atmospheric scientists, and ecologists with a wide range of knowledge in the area of mercury cycling. We chose Big Dam West Lake in Kejimkujik National Park, NS, as our study site in part because of the amount of previous mercury research that has been conducted and because Kejimkujik Park is one of the long-term acid rain monitoring sites. As such it is one of Canada's main meteorological stations where mercury deposition and air concentrations are measured biweekly. There is also a clear indication that mercury contamination is a serious problem as loons in Kejimkujik Park have been identified as having some of the highest blood mercury concentrations in North America (Burgess *et al.*, 1998). While a large amount of mercury research has been performed in

Kejimkujik, the underlying cause of the mercury bioaccumulation problem was not clear prior to our investigation. This was likely due to the large number of processes that can affect the speciation and transport of mercury through an ecosystem.

Some of the processes that affect mercury accumulation and fate in ecosystems include (i) mercury deposition in atmospheric precipitation, (ii) inputs of methyl mercury from surrounding wetlands (St. Louis *et al.*, 1994; Driscoll *et al.*, 1998), (iii) atmospheric scavenging and incorporation of mercury into vegetation (St. Louis *et al.*, 2001), (v) mercury deposition to sediment, and (iv) mercury volatilization from water, soil and vegetation (Schluter, 2000).

While several researchers have attempted mass balances for mercury in rivers and lakes (Henry *et al.*, 1995; Lee *et al.*, 1998; Driscoll *et al.*, 1998; Quemerais *et al.*, 1999), none have attempted to collect quantitative mercury measurements with a whole-ecosystem approach. Rolfhus and Fitzgerald (2001) examined mercury evasion in a coastal marine system and estimated it was equivalent to 35 % of the total annual mercury inputs to the system. However, the authors used predictive models rather than take direct measurements of mercury volatilization. In many studies volatilization and interaction with vegetation is often not taken into account. The purpose of this study was to examine a complete set of mercury fluxes in order to assess the role of volatilization in the Big Dam West lake basin.

2.2. Site Description

Kejimkujik National park is located in the southwestern Nova Scotia, Canada. The topography is relatively flat with clusters of glacial derived landforms such as drumlins and erratics (Rencz *et al.*, 2003). In general the Kejimkujik lakes and streams are characterized by shallow depths (mean depth ranging from 1.0 to 4.4 m), high dissolved organic carbon (2.6 to 17 mg L^{-1}), low pH (4.2 to 5.5), and high percentage wetlands (1 to 26 % of the drainage basin area) in the catchment basins (Kerekes & Freedman, 1989, Howell, G.D., 1989).

All sampling, unless noted, was from Big Dam West Lake. The major physical and chemical characteristics for Big Dam West Lake (BDW) are displayed in Table 2-1. There are three major inflows that drain a large area of low-lying wetlands (>50% of the total catchment area), and which provide a large source of dissolved organic carbon to the lake. The linkage to the wetlands is largely responsible for the lake's low pH (5.0) and high colour (94 Hazens) (Table 2-1).

Physical Parameter	Big Dam West
Easting Nad83	317825
Northing Nad83	4925517
Lake Elevation (m)	120
Surface Area (hectares)	105.0
Total Catchment Area (km^2)	40.0
Wetland Area (km^2)	20.2
Volume (m^3)	2593000
Mean Depth (m)	2.5
Max Depth (m)	9.5
Shoreline Length (km)	6.1
Flushing Rate (times/yr)	13.1
Deep Marsh (% wshd)	0.29
Bog (% wshd)	1.65
Fen (% wshd)	3.06
Total Wetland (% wshd)	5.04
Water Chemistry	
pH	5.0
Dissolved Oxygen	11.05
Total Organic Carbon (mg L^{-1})	10.5
Color (Hazens)	94
Alkalinity (mg L^{-1})	0.07
Specific Conductance (uS cm^{-1})	30.1
Total Hg - unfiltered (ng L^{-1})	5.01
Cl (mg L^{-1})	4.84
SO_4 (mg L^{-1})	1.69
Total N_2 (mg L^{-1})	0.111
Na (mg L^{-1})	3.52
K (mg L^{-1})	0.307
Ca (mg L^{-1})	0.641
Mg (mg L^{-1})	0.364
Al (mg L^{-1})	0.198
Fe (mg L^{-1})	0.165

Table 2-1: Major physical and chemical characteristics of Big Dam West Lake

2.3 Methods

Various methods were used to obtain the data from different media presented in this paper. The following is a summary of the major sampling and analytical methods used to derive data for the presented mass balance.

2.3.1 Lakewater & Inflow/Outflow Sampling and Analysis

Water samples were collected from the major inlets (Thomas Meadow Brook, Ford Brook, BDE inlet), outlets (Still Brook), and the center of the lake for total mercury analysis. Total mercury samples were collected in 500 mL Teflon bottles. The bottles were pre-cleaned in the laboratory through several stages: washing with Contrad70 detergent / purified water, soaking for one week with reagent grade HNO_3, , followed by a purified water rinse, soaking for one more week with Seastar high purity HNO_3, final rinsing with copious amounts of polished high purity water (>10 Mohms), and filling to the top with high purity water and stored until use in individual Ziplock bags with a pair of latex surgical gloves for manipulation of samples. After sampling the bottles were returned to the bags for shipping.

Total mercury samples were digested in the presence of bromine monochloride (BrCl) and UV irradiation. All samples were then pre-reduced with hydroxylamine hydrochloride and reduced to elemental form with $SnCl_2$. The Hg^0 is purged from

the sample with nitrogen onto a gold-coated wire trap, and desorbed by heating and purging the trap with a stream of argon into the atomic fluorescence detector (CV-AFS). The method detection limit is 0.2 ng L^{-1}.

2.3.2 Total Mercury in Precipitation

Precipitation samples used for mercury analysis were collected using an Aerochem Metrics Model 301 automatic sensing wet/dry precipitation collector with Teflon coated lid supports and gasket pads to prevent evaporative sample loss. The sampler was equipped with a 128 cm sampling orifice and a borosilicate glass sampling train leading to a 1 L borosilicate glass bottle housed in a temperature controlled enclosure. The sampler was located at the CAPMON research site near the entrance of Kejimkujik Park (~ 8km South East of BDW Lake). Precipitation amounts were measured using a Belfort Model B-5-780 recording rain gauge results of which were confirmed by comparison with an adjacent fixed mount standard rain gauge. The precipitation sample collection, analysis and QA/QC were carried out according to protocols developed by the National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN). Descriptions of instrumentation, sampling, analytical and QA/QC protocols are contained in NADP (1996a, 1996b).

2.3.3. Groundwater Sampling

Groundwater samples were obtained from 11 piezometers and 4 seepage meters

installed near shore at 60 – 90 cm depth. A galvanized stainless steel pipe (6' length; ¾" i.d.) was driven into the near shore sediment and a LDPE tube (7' length; ½ " o.d.) fitted with a piezometer tip was inserted into the steel pipe. The piezometer tip consists of a LDPE tube (5' length; ⅜" i.d.), with 1 cm holes and wrapped with 0.25 mm Nitex (nylon monofilament) screening. The metal pipe was slowly removed and the surrounding sediment compacted to ensure a good seal. Ground water was collected using a hand pump in line with a 1000 mL glass filtration flask connected to the LDPE tubing. Water was pumped prior to sampling to reduce silt content. Fitting the tube with an opaque HDPE bag below the water surface allowed for water collection over longer time spans (24 – 48 hours). After collection water samples were prepared for total mercury analysis as outlined above. Steel cylindrical seepage meters (area of 1.07 m^2) were installed in close proximity to the piezometers. An opening in the cylinder top was fitted with a rubber stopper connecting a HDPE tube and polypropylene reservoir bag. The water was collected over a 12 - 24 hour period.

2.3.4. Soil-Air and Water-Air Flux

Air-surface mercury exchange was measured on BDW Lake and the surrounding forested site using a rectangular Teflon flux chamber (Carpi & Lindberg, 1998) placed over the substrate enclosing an open surface area of 0.12 m^2 (Kim & Lindberg, 1995; Carpi & Lindberg, 1997). Teflon sampling lines and fittings were used throughout the mercury flux measurement system. Gaseous elemental mercury (GEM) concentration in air was measured using a Tekran Model 2537A

CV-AFS calibrated using an internal mercury permeation source and an external Tekran Model 2505 primary mercury vapor calibration system.

Unfiltered ambient air was sampled for 5 minutes alternating every 10 minutes (duplicate 5 min integrated samples) between ambient and chamber air. Switching between ambient and chamber air sampling was done using a Tekran Model 1110 Synchronized Automated Dual Sampling (TADS) switching system. To avoid stagnation of air in the system when samples were not being taken, air was continuously drawn through the system using an air pump set to 1.5 L min^{-1}. Flow rates in the analysis system (1.5 to 10 L min^{-1}) were controlled using Hastings-Teledyne mass flow controllers and mass flow meters. Mercury flux was calculated as the difference between the mercury concentrations in ambient air versus air which had passed through the chamber (Schroeder *et al.*, 1989 and Xiao *et al.*, 1991).

System quality control (QC) procedures including the use of standard operating procedures (SOPs), analyzer and sensor calibrations, chamber/system blanks and Hg injection-recovery tests were performed on a regular basis. Chamber blanks were performed in the laboratory and in situ using the complete system (lines, fittings, solenoid switches and the chamber). Flux rates presented in this study are blank corrected.

2.3.5 Sediment

Sediment samples were obtained using an open-barrel coring system that is best suited for sampling of soft-bottom sediments (Blomqvist, 1991; Stephenson *et al.*, 1996). Cores were obtained (July of 1999 and 2000) using a modified Kajak-Brinkhurst (KB) gravity corer, fitted with 1-metre long polycarbonate tubes (i.d. 3", 1/8 "wall). All cores (disturbed cores were discarded) were extruded and sectioned immediately in the field using a aluminum extruding stand. Supernatant water was siphoned off (to 5 cm water cover) prior to extrusion. Cores were sectioned as follows: every 0.5 cm for first 10 cm, every 1-cm from 10-30 cm, every 2 cm from 30-50 cm, and every 4 cm for depths greater than 50 cm. All equipment was rinsed with distilled de-ionized (d.d.) water and Kimwipes between samples. Sediment samples were collected in WhirlPak bags and kept cold until analysis.

Two cores were used to determine the down core changes in water content and bulk density using centrifugation and drying weights. Sediment samples were freeze-dried and then ground to a homogenous powder in a class-100 clean room using a mortar and pestle. The digestions were performed in a Questron QLAB 6000 Microwave Digestion Oven. Very High Pressure (VHP) Teflon digestion vessels were used to digest each 0.2 g of the dry, homogenized sediment. The following pressure control program was used for 25 minutes: 600 W power, 200°C temperature limit, and 200 psi pressure limit. 5 mL of HNO_3 and

2 mL of HF was added to the jar and digested to dryness. Once dry, 2 mL of environmental grade 8 N HNO_3 was added and digested to dryness again. This step was repeated one more time and then 2.5 mL of environmental grade 8 N HNO_3 was added to the vessel and digested until all of the sample dissolved. The contents of the jar were transferred to 125 mL HDPE container. The digestate was diluted with MQ water to a final weight of 100 g.

Dating of the sediment deposits and determination of the sedimentation rates were based on ^{210}Pb and ^{137}Cs methods, measured by γ-ray spectrometry at the USGS Geochronology Laboratory in Denver, Colorado. Four cores were taken from each lake and then the corresponding depth sections from each core were combined in a WhirlPak bag as one sample. From these samples, 30 were selected (15 from each lake) for freeze-drying and γ-ray spectrometry. Gamma-ray spectrometry for the determination of ^{210}Pb and ^{137}Cs was done with a high-purity Germanium well-type semiconductor of 16 mm diameter. From the activity of $^{210}Pb_{ex}$ and log $^{210}Pb_{ex}$ vs depth plots, the age and sedimentation rates can be determined. In attempt to verify the results of ^{210}Pb dating, ^{137}Cs was also measured as an independent chronostratigraphic marker.

Mercury in sediment samples were analyzed by aqua-regia (3:1 HCl : HNO_3, and 0.01% $K_2Cr_2O_7$) digestion method. 5 mL of aqua-regia was slowly added to 0.1 g of dry, homogenized sample in a pre-weighed 50 mL polypropylene Falcon centrifuge tube and left to stand for at least 5 hours. After this time, the caps

were tightened and the vessels were shaken vigorously for about one minute. The tubes were then placed in a hot water bath for 5 hours at 80°C, and then left overnight to cool. The digested sample was then diluted to 50 mL with 0.01% $K_2Cr_2O_7$ in distilled de-ionized water, re-capped, and the final weight recorded. The diluted digests were then shaken again for approximately one minute and then centrifuged for 10 minutes at 3500 rpm. The digested samples were analyzed by CV-AFS using a PS Analytical Millennium Merlin/Galahad mercury analyzer.

Sedimentation rates of mercury were also obtained using sediment traps to compare deposition with net accumulation. Four sediment traps collected sample over an 11-month period (August 14, 2000 to July 12, 2001). An aluminium frame (61 cm diagonal measurement) secured the traps in an upright position and prevented substantial movements. The sediment chambers consisted of polycarbonate plastic core tubes (10.2 cm diameter, 88 cm long) with 5 cm deep ABS caps on the bottom. This provided an aspect ratio (depth/width) of 9.5 to avoid sediment resuspension and loss during mixing events. The traps were located in Big Dam West at 3.6 m at a water depth of 6.1 m using polyethylene rope attached to a rock in the sediments and held in place using a subsurface float. The samples were collected, frozen, and then freeze-dried. The amount (+/- SD) for BDW was expressed on an areal basis by dividing by the area of the traps (0.08023 m^2) and correcting for 12 months to obtain annual sedimentation rates. The rates in BDW were 45.58 +/- 3.34 mg m^{-2} y^{-1} (n = 4).

The interpretation of sediment trap data has been widely debated due to problems of decomposition, sediment re-suspension, changing redox conditions, predation by zooplankton and other invertebrates, and death and decay by these opportunistic animals. Nevertheless, the data obtained provides some confirmation of the lead isotope results. From the sediment trap data the mercury sedimentation rate in BDW was found to be 91.2 μg m^{-2} y^{-1} or 95.73 g y^{-1}. In this study the lead isotope estimates of sedimentation have been used for all calculations.

2.3.6 Vegetation

Samples of leaf and twig tissue from the dominant tree species were collected in and around Kejimkujik Park. Dominant trees included: red maple (*Acer rubrum*), white pine (*Pinus strobus*), eastern hemlock (*Tsuga canadensis*) and white birch (*Betula papyrifera*). Duplicate samples were taken from adjacent trees at one in every 10 sites, however not all species were present at each of the sites. Samples were placed in paper bags, air-dried and returned to the lab for chemical analyses (Rencz *et al.*, 2003), along with control materials in order to verify lab accuracy. Mercury concentrations were determined by the Milestone Advance Mercury Analyzer (AMA-254).

In order to calculate the net uptake of mercury into vegetation surrounding Big Dam West Lake average mercury concentrations were calculated for coniferous and deciduous tree species. This was incorporated into a GIS analysis by producing a look-up table in PCI (version 6.3) for average mercury for each of the Canadian land classification units derived from remote sensing imagery. Using the look up table and the land classification index layer for Kejimkujik Park, a new GIS layer was created containing the average mercury concentrations in vegetation (ng Hg g^{-1} plant tissue). Primary productivity was then used provide an average net mercury in vegetation layer with units ng 25 m^{-2} y^{-1}(this is, the average mercury per 25 m^{-2} pixel block). Average net mercury in vegetation was then calculated for the Big Dam West Lake basin and multiplied by the terrestrial area in the basin to obtain the average net mass of mercury incorporated into the vegetation within the Big Dam West lake basin.

2.3.7. Mercury Conceptual Model

Figure 2-1 is a conceptual model of mercury movements in BDW watershed. The watershed was divided into 3 units based on the Canadian Land Classification Index and remote sensing data. Lake represents only the area covered by the lake surface, wetland is classified as areas that have standing water with vegetation, and the terrestrial portion as dry land that is covered by vegetation. These areas were calculated using remote sensing data.

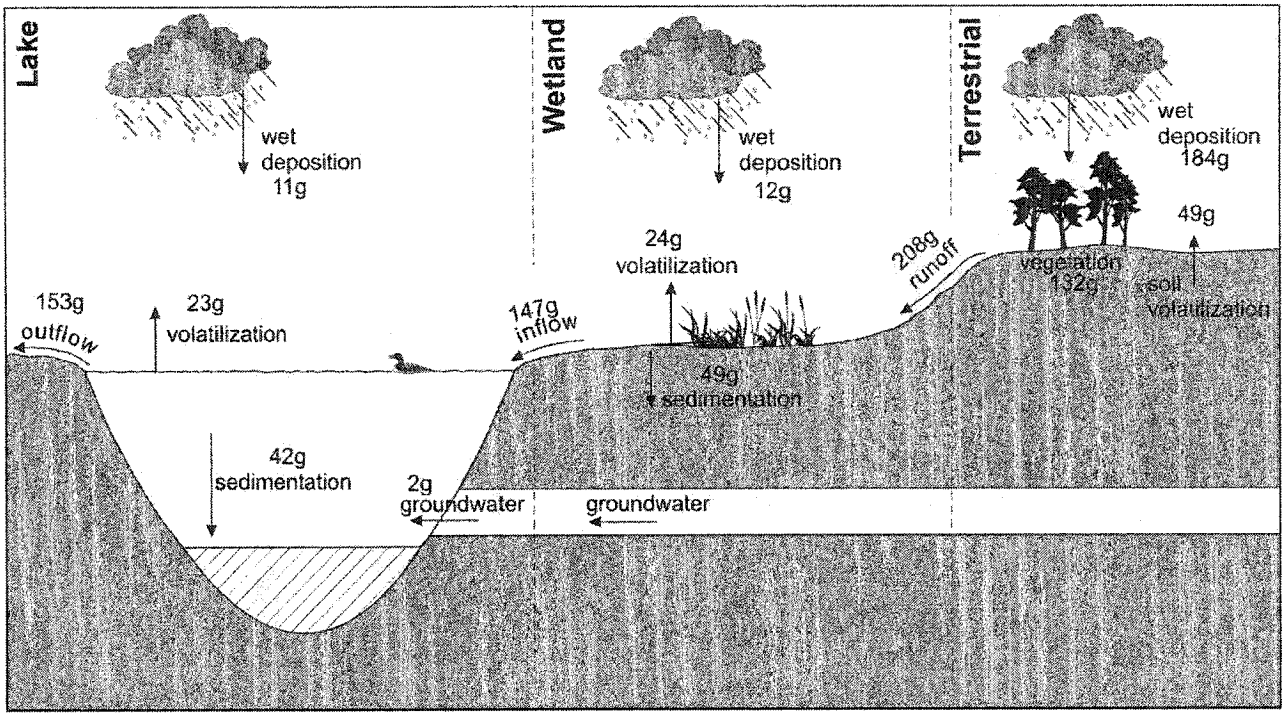

Figure 2-1:Conceptual diagram of mercury cycling in Big Dam West Lake, Kejimkujik Park, Nova Scotia. Values represent mean mass of mercury flux per year.

2.4. Results

2.4.1. Overview of Mass Balance

Variables for mercury mass balance calculations are shown in Table 2-2. Volatilization and precipitation values are published (Beauchamp *et al.*, 1998; 2001). Groundwater seepage areas derived from Kerekes (1973). Yearly averages were calculated from samples collected and analyzed during the times outlined. When data were unavailable, previously published values from other

studies were used. Watersheds were divided into 3 distinct units for examination of mercury flux based on the conceptual model shown in Figure 2-1. This model was thought appropriate since inflows from wetlands are the primary source of water flow in Big Dam West Lake, and negligible amounts of water inputs are due to direct runoff (as suggested by water balances of inflow and outflow budgets) (Clair *et al.*, In Press). Mass movement of mercury within and between these units was calculated using the equations outlined in Table 2-3.

The ecosystem data, estimated uncertainty, data source and time span are shown in Table 2-2, while the calculations and results used to populate the conceptual model are displayed in Table 2-3. When possible precision was expressed as one standard deviation.

Symbol	Desription	Time Span of Data	Value	SD
A_T	Terrestrial area within watershed (cm^2)	2001	2.76E+11	1.000E+09
A_L	Lake area within watershed (cm^2)	2001	1.70E+10	1.000E+09
A_W	Wetland area within watershed (cm^2)	2001	1.84E+10	1.000E+09
A_G	Groundwater seepage area (100 m shoreline) (m^2)	2001 monthly, June - Sept.	6.13E+05	1.000E+09
S_{Dep}	Sedimentation rate (cm y^{-1})	2000-2001 (summer)	9.2E-02	
S_{Dens}	Sediment particle density at 1 cm depth (g mL^{-1})	2000-2001 (summer)	9.8E-02	
V_{GW}	Mean groundwater seepage to lake (L m^2 y^{-1})	2001 (June - Sept.)	4.4E+03	7.29E+03
T_S	Ice-free hours per year (h y^{-1})		5.9E+03	1.00E-01
P_{Depth}	Mean depth of yearly precipitation (cm)	1997-2000 (weekly)	1.3E+02	2.89E+00
Hg_{LV}	Mean mercury volatilization from lake (ng m^{-2} hr^{-1})	1997, 2000, 2001 (24-hour means, summer)	2.3E+00	2.38E+00
Hg_{Sed}	Mean mercury in sediment (ng g^{-1})	2000-2001 (summer)	2.8E+02	
Hg_{Precip}	Mean mercury concentration in precipitation (ng L^{-1})	1997-2000 (weekly)	5.3E+00	4.39E-01
Hg_{SoilV}	Mean mercury volatilization from soil (ng m^{-2} h^{-1})	1999 (24-hour mean, summer)	3.0E-01	2.00E-01
Hg_{GW}	Mean total mercury in groundwater (ng L^{-1})	2001 monthly, June - Sept.	8.0E-01	2.09E-01
Hg_{Veg}	Mean mercury incorperation in vegetation (ng m^{-2} y^{-1})	1999-2002	4.8E+03	9.08E+00
BDW Outflow	Mean mercury leaving BDW Lake in outflows (g y^{-1})	1997, 1998, 2001	1.5E+02	5.05E+01
BDW Inflow	Mean mercury entering BDW Lake in inflows (g y^{-1})	1997, 1998, 2001	1.5E+02	3.67E+01

Table 2-2: Description of mass balance parameters

	Equation #	Mercury Flux	Equation	Predicted Value (g of Hg)	SD	Areal Flux (ug/m2/y)
Terrestrial						
INPUTS	2-1	Wet deposition	$(P_{Depth} \times A_T \times Hg_{Precip}) / 10^{12}$	184	20.2	6.6
			SUM	**184**	**20.2**	**6.6**
OUTPUTS	2-2	Volatilization	$(Hg_{Soilv} \times T_S \times A_T) 10^{13}$	49	0.0	1.8
	2-3	Incorporation in vegetation	$(Hg_{Veg} \times A_T) / 10^{13}$	132	0.0	4.8
	2-4	Runoff to wetland	Sum Wetland Outputs - Wet Deposition to Wetland	208	36.7	7.5
			SUM	**388**	**36.7**	**14.0**
Wetland						
INPUTS	2-5	Wet deposition	$(P_{Depth} \times A_W \times Hg_{Precip}) / 10^{12}$	12	0.0	6.6
	2-6	Input from terrestrial runoff	Sum Wetland Outflow - Wet Deposition to Wetland	208	36.7	113.0
			SUM	**220**	**36.7**	**119.7**
OUTPUTS	2-7	Inflow to lake	BDW Inflow	147	36.7	79.9
	2-8	Volatilization	$(Hg_{LV} \times T_S \times A_W) / 10^{13}$	24	0.0	13.3
	2-9	Sedimentation	$(S_{Dep} \times A_W \times S_{Dens} \times Hg_{Sed}) / 10^{9}$	49	5.8	26.4
			SUM	**220**	**42.5**	**119.7**
Lake						
INPUTS	2-10	Wet deposition	$(P_{Depth} \times A_L \times Hg_{Precip}) / 10^{12}$	11	0.0	6.6
	2-11	Lake inflow	BDW Inflow	147	36.7	86.4
	2-12	Groundwater inputs	$(V_{GW} \times A_G \times Hg_{GW}) / 10^{9}$	2	1.7	1.3
			SUM	**160**	**38.4**	**94.3**
OUTPUTS	2-13	Volatilization	$(Hg_{LV} \times T_S \times A_L) / 10^{13}$	23	0.0	13.3
	2-14	Lake outflow	BDW Outflow	153	50.5	90.2
	2-15	Sedimentation	$(S_{Dep} \times A_L \times S_{Dens} \times Hg_{Sed}) / 10^{9}$	42	5.1	24.8
			SUM	**218**	**55.6**	**128.3**

Table 2-3: Calculation of mass balance fluxes for lake, terrestrial, and wetland components of Big Dam West Lake basin.

2.4.2. Calculation of Uncertainty

The standard deviation for each flux calculation was calculated as consistently as possible given that the data was collected at different times and over different time scales. It should also be noted that calculated deviations are only methodological and sample analysis related and do not reflect all sources of environmental variations. In cases where too little data was available to assess sample variations, method detection limits were used for standard deviation (e.g. number of ice free hours, area calculations from remote sensing, etc).

The lake inlet and outlet numbers are calculated as the mean of samples collected over the years 1997, 1998, and 2001. If we calculate the standard deviation as the deviation between yearly means (with each yearly mean derived from 26 measurements), this results in a % RSD of 25 and 33 % for inflows and outflows respectively. Therefore differences observed between inflows and outflows are insignificant. It is likely that the calculated mean does not accurately represent the long-term yearly average due to the small sample size, and the above calculations of error are very rough estimates.

Variation between lake water flux numbers were calculated as the variation between the means of three 24-hour readings taken over BDW water in the summers of 1997, 2000, 2001. No variation is available for undisturbed forest soil as only one 24-hour mean was measured in the summer of 1999. Therefore, a

value for mean positive flux method detection limit was used (3X standard deviation of blank).

Detailed descriptions of sediment lead isotope calculations are available from Telmer and DesJardins (In Press). Variation for precipitation was taken from values of mean precipitation amounts measured weekly for the years 1997 - 2000. Similar variations were calculated for volume weighted mean concentrations of mercury in precipitation. These flux values were scaled up to a yearly flux value assuming that no significant flux occurs during the periods of ice and snow cover (December – March Inclusive).

2.5. Discussion

2.5.1. Comparison of Flux Values to Literature

The results obtained for mercury fluxes are consistent with the published literature. The mean water-to-air volatilization observed on Big Dam West Lake (2.3 ng m^{-2} h^{-1}, σ = 2.38) is less than what has been observed in contaminated wetland systems (mean = 43 ng m^{-2} h^{-1}, σ = 5) (Wallschlager *et al.* 2002). However, it is similar to readings over Lake Ontario and the upper St. Lawrence River (median = 1.85 and 1.76 ng m^{-2} h^{-1} respectively) using the gradient technique for flux measurement (Poissant *et al.* 2000). The mean soil-to-air volatilization (0.3 ng m^{-2} h^{-1}, σ = 0.20) was similar to Xiao *et al.* (1991) who (using

a stainless steel flux chamber) observed mercury fluxes ranging from –2 to 2 ng m^{-2} h^{-1} over uncontaminated forest soils.

The mean mercury in precipitation value of 5.3 ng L^{-1} (σ = 0.439 between annual means) observed in this study falls towards the lower end of the 5 – 100 ng L^{-1} range observed by several researchers (Lee and Iverfeldt, 1991; Pleijel and Munthe, 1995; US EPA, 1997, St. Louis *et al.*, 2001). The mercury in ground water observed in this study (0.80 ng L^{-1}, σ = 0.209) is similar to that found by Krabbenhoft and Barbiarz (1992) (2-4 ng L^{-1}). Krabbenhoft and Barbiarz (1992) also observed mercury inputs of 0.7 g y^{-1} to Pallete Lake, Wisconsin; which is similar to the 2.0 g y^{-1} (σ = 1.7) calculated for Big Dam West Lake in this study.

2.5.2. Relative Magnitude of Fluxes

Wet precipitation was the only source of mercury considered to the terrestrial system accounting for 184 (σ = 20.2) g of mercury deposited. The total outputs from the terrestrial system accounted for 388 g (σ = 36.7), of that, 34% (132 g, σ = 0.0) was incorporated into vegetation and, 13% (49 g, σ = 0.0) was volatilized from the soil surface. Although were unable to measure mercury runoff directly, 208 g would be necessary in order to balance the inputs and outputs of the wetland component. While this value is not significantly larger than what falls in wet deposition (given the error on the mean values), a larger output value might indicate mercury transport associated with soil erosion.

It should be emphasized that the source of mercury to vegetation and terrestrial runoff is unclear and is not necessarily wet precipitation. Direct atmospheric uptake and root uptake of mercury are possible mechanisms that were not accounted for in this budget. Therefore the imbalance of terrestrial inflows and outflows that results from this calculation would be improved with data for root to vegetation flux measurements. Runoff was the only flux in the mass balance that has been calculated by the difference of other inputs and outputs.

Of the mean 220 g (σ = 36.7) of mercury inputs to wetlands, 95% (208 g, σ = 36.7) was due to terrestrial runoff and 5% (12 g, σ = 0.0) was due to wet deposition. The total outputs from the wetland accounted for 220 g (σ = 36.7), 67% (147 g, σ = 36.7) was removed by outflow to the lake, 22% (49 g, σ = 3.6) was deposited to sediment and, 11% (24 g, σ = 0.0) was volatilized from the wetland surface.

Of the mean 160 g (σ = 38.4) of mercury inputs directly to the lake, 92% (147 g, σ = 36.7) was due to inflow from wetlands, 7% (11 g, σ = 0.0) was due to wet precipitation and, 1% (2 g, σ = 1.7) was due to groundwater inflow. The total outputs from the lake accounted for 218 g, 70% (153 g, σ = 50.5) was removed by outflow, 19% (42 g, σ = 3.6) was deposited to sediments and, 11% (23 g, σ = 0.0) was volatilized from the lake surface. It should be noted that total outputs were larger than inputs by 58 g (see section 13.5.4.), however this is not significant in light of the deviation observed in these values.

Henry *et al.* (1995) performed a mass balance on Onondaga Lake, NY and found that total mercury inputs accounted for 14.116 kg. Of the total inputs, 96.3% (13.6 kg) was due to terrestrial inflows, 3.1% (0.44 kg) was atmospheric deposition, 0.4% (0.056 kg) was sediment flux and, 0.1% (0.02 kg) was groundwater. Of the 13.916 kg of outputs, sedimentation accounted for 79.8% (11.1 kg), outflow 20.1% (2.8 kg), and volatilization 0.1% (0.016 Kg). These results compare well with what was observed in this study with inflows contributing the majority of the total mercury, followed by precipitation and groundwater. However, the outputs of the two lakes are quite different. Outflow is the primary sink in BDW Lake, whereas sedimentation is the dominant sink in Onondaga Lake. The lakes are in fact opposite in terms of outflow versus sedimentation. The level of volatilization is substantially higher in BDW as opposed to Onondaga Lake (11% and 0.1 % respectively) (See Figure 2-1)

2.5.3. The Role of Wet Deposition in Volatilization

The area within the BDW drainage basin is largely dominated by the terrestrial ecosystem. Of the 31.18 km^2 in the BDW watershed 88.7 % is terrestrial, 5.9 % is wetland, and 5.5 % is lake surface. The 207 g of mercury deposited in precipitation follows a similar distribution. Of the 96 g of mercury volatilized from all surfaces in the BDW watershed 51% is from the terrestrial soil, 26% is from the wetlands, and 24% is from the lake surface. In this context, it may appear that soil volatilization is the most important mercury removal process, however the percentage of volatilization relative to the amount of direct wet deposition

within the terrestrial, wetland and lake compartments is 27%, 200%, and 200% respectively. The high amounts of mercury volatilization relative to wet precipitation indicate that volatilization is an important process within this ecosystem, particularly over water (double the direct wet deposition). Over the entire basin area the mass of mercury volatilized is 46% of the mass deposited by wet deposition. It is likely that a combination of several factors limit mercury volatilization. Some limiting factors might include the availability of photo-reducible mercury in wet deposition, wind speed, or amounts of cumulative solar radiation.

Several researchers have found that levels of DGM formation and mercury volatilization from lake surfaces are linked to rainfall events. Vandal *et al.* (1994) observed that that the influx of reactive mercury in wet deposition may account for a large portion of elemental mercury production in Pallette Lake Wisconsin, USA. Similarly soil moisture contents have been linked to precipitation and volatilization. Johnson and Lindberg (1995) found that elemental mercury concentrations in soil increased exponentially with moisture content.

2.5.4. Sources of Error

The inputs and outputs of the lake component are close to being in balance, while the terrestrial is substantially out of balance (184 g inputs and 388 g outputs). The reason for the imbalance may be due either to error in measurements that were not accounted for, or due to missing inputs or outputs.

There are several possible fluxes of mercury that have not been adequately accounted for in this study. We were unable to account for mercury volatilization or scavenging by the forest canopy. The forest canopy has been found by many researchers to have dynamic exchanges with the atmosphere (St. Louis *et al*, 2001; Leonard *et al.*, 1998a; Leonard *et al.*, 1998b). St. Louis *et al.* (2001) found that through fall volumes at boreal ecosystem sites ranged between 43 - 69 % of the direct wet deposition, due to canopy interception and evapotranspiration. Litter fall is another source of mercury within the terrestrial system that has not been accounted for in this mass balance. Grigal (2002) estimates that deposition to lake surfaces is only about one fourth the deposition to forests by through fall and litter fall combined. We were also not able to account for mercury uptake by tree roots. We were also unable to measure any interaction between geology and mercury movement into runoff. An average value for mercury in the soil Ah horizon (silt size fraction) surrounding BDW lake is 466 ng g^{-1} (Rencz *et al.*, 2003). Since there is a large pool of mercury stored in soil and geology, any mobilization of this pool would affect our interpretation of mass movements.

Mobilization of mercury from the sediment storage pool was also not measured in this study and may constitute an important input to lake mercury levels. In addition, since no sediment sampling was performed for the wetland area of the catchment, the rate of sedimentation in the wetland portion of the mass balance was assumed to be equal to the lake portion of the catchment. This is likely a very rough estimate.

The importance of mercury dry deposition and reactive gaseous mercury deposition was not examined in this mass balance. This is an emerging area of research with the new analysis technology currently being assessed and tested. However we acknowledge that these unaccounted inputs may in part explain the imbalances observed. Future research may shed some light on the magnitude of these inputs.

2.5.5. Summary

In summary, volatilization of mercury was found to be an important process in the Big Dam West Lake catchment. The magnitude of volatilization appears to be approximately double the direct wet deposition over the lake and wetland areas, and 27% of the direct wet deposition to the terrestrial area of the catchment. Over the entire basin area the mass of mercury volatilized is 46% of the mass deposited by wet deposition. In addition, it was observed that the terrestrial catchment dominates the processes occurring in the BDW watershed. Terrestrial vegetation was found to play a significant role in mercury movement as evidenced by the large amount of mercury uptake found in this study (132g). The importance of terrestrial vegetation is not fully explored since 3 important mercury fluxes were not measured: (i) uptake from roots, (ii) volatilization from leaves, and (iii) litter fall.

Chapter 3

CONTINUOUS ANALYSIS OF DISSOLVED GASEOUS MERCURY IN FRESHWATER LAKES

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3.1. Abstract

The concentration of dissolved gaseous mercury (DGM) in freshwaters changes more quickly than the 40-minute processing time of current analytical methods. A new method for continuous field analysis of DGM was developed using a Tekran 2537A to achieve a DGM analysis time of 5 minutes. Samples are concurrently analyzed for temperature, oxygen, conductivity, pH, and oxidation-reduction potential using a Hydrolab. The method detection limit for DGM was 22.4 fmol L^{-1} with 99% removal efficiency. Control experiments showed that there was no interference due to methyl mercury (MeHg), which is present in similar concentrations to DGM. Controlled experiments comparing continuous DGM analysis with discrete DGM analysis showed that the results are not significantly affected by typical variations in water temperature (4- 30 ^{o}C), oxidation-reduction potential (135-355 mV), dissolved organic carbon (4.5- 10.5 mg L^{-1}), or pH (3.5-7.8). The continuous analysis was within 4.5% of the discrete analysis when compared across 12 samples analyzed in triplicate. The field performance of this method was tested over two 48-hour periods in two lakes in Kejimkujik Park, Nova Scotia where over 1000 data points were collected.

3.2. Introduction

Mercury exists in many different chemical forms in freshwater. In contrast, mercury in the atmosphere is predominantly elemental mercury (Hg^{0}) however,

when oxidized to inorganic mercury (Hg^{2+}) it is much more soluble in water and thus inorganic mercury is the predominant form in precipitation. Inorganic is also the predominant form of mercury found in freshwater (Morel et al., 1998). The interchange between the inorganic mercury present in water bodies and elemental mercury present in the atmosphere is critical to understanding the movement of mercury in an ecosystem (Zhang & Lindberg, 2001; Lalonde *et al.*, 2001; Lindberg *et al.*, 2000). Dissolved gaseous mercury (DGM) in the water column is generally present at concentrations that are 5 to 20% that of total mercury but due to it's high volatility, the production of DGM in water is a significant process in the mercury cycle as it is a major route of mercury removal from a water body (Amyot *et al.*, 2000). For example, once DGM is produced from other mercury species it is able to volatilize out of a watershed to the atmosphere. This volatilization in Kejimkujik Park can range from 1.1 to 5.4 ng m^{-2} h^{-1} (Boudala *et al.*, 2000), which is in a similar range to the average amount of mercury deposited to a lake in precipitation (Beauchamp *et al.*, 1998).

Despite the importance of DGM to the global mercury cycle, it is only present in pristine lakes at fmol L^{-1} concentrations compared to pmol L^{-1} concentrations of total mercury (ca. 5-20% of total mercury). The ability to measure such small quantities accurately has been one of the difficulties in performing DGM research. Current investigators use a purge and trap system with gold traps to accumulate volatile mercury purged out of solution by an inert gas (Amyot *et al.* 2000, Lindberg *et al.* 2000). This technique is accurate and reproducible but

analysis times range from 20 – 90 minutes. Since no preservation methods are available it is not possible to store samples without significant changes in DGM concentrations, with approximate DGM loss rate constants ranging between 0.1 - 0.2 h^{-1} in sealed containers (Lindberg *et al.*, 2000). Current methods of sampling for discrete samples include sampling from a plastic canoe using either 1 L black Teflon sample containers, solar radiation-shielded Pyrex glass bottles, or Go-Flow bottles. All sampling devices are generally pre-cleaned with acid and washed with large amounts of double distilled water (Amyot *et al.*, 1997a; Baeyens and Leermakers, 1998, Lanzillotta and Ferrara, 2001). Samples are then transported as soon as possible to a clean lab for analysis, however unless a clean lab is available on-site this may take some time.

Recent work has indicated that DGM fluxes occur very rapidly in lake water with DGM concentrations increasing or decreasing by 50% within a 20-minute period (Siciliano *et al*, 2002). Therefore, in order to see realistic changes in the mercury chemistry of lake water, an analysis method that can measure fM quantities over a very short time span is required. The method must also be portable for use in remote locations. Finally, to advance the science of mercury dynamics in aquatic ecosystems we must relate DGM changes to rapid biotic and abiotic processes.

While changes in water temperature, pH, oxidation reduction potential (ORP), and dissolved oxygen (DO) are common in freshwater, no research has explored the effect of these changes on DGM analysis or kinetics. The concurrent analysis of these variables and DGM concentration will allow relationships between DGM

and basic water chemistry to be explored in detail. In this paper we describe the novel use of a Tekran 2537A mercury analyzer for the continuous analysis of DGM and a Hydrolab Sonde 4a/ Surveyor 4a for the analysis of water chemistry, and compare this method with the discrete analysis method for DGM over a range of water chemistry.

3.3. Methods

The analysis system (Figure 3-1) consisted of a Hydrolab Sonde 4a in series with a sparger and Tekran air analysis unit. The 1 L glass volumetric sparger and Tekran 2537A were set to measure dissolved gaseous mercury in the water every 5 minutes. The Hydrolab was modified to serve as a flow through sample chamber by installing Teflon inlet and outlet connectors into the cup portion of the unit. Readings of pH, water temperature, ORP, DO, and specific conductivity (Sp. Cond.) were recorded via a Surveyor 4a set to auto log readings every 5 minutes with a 2-minute warm up period.

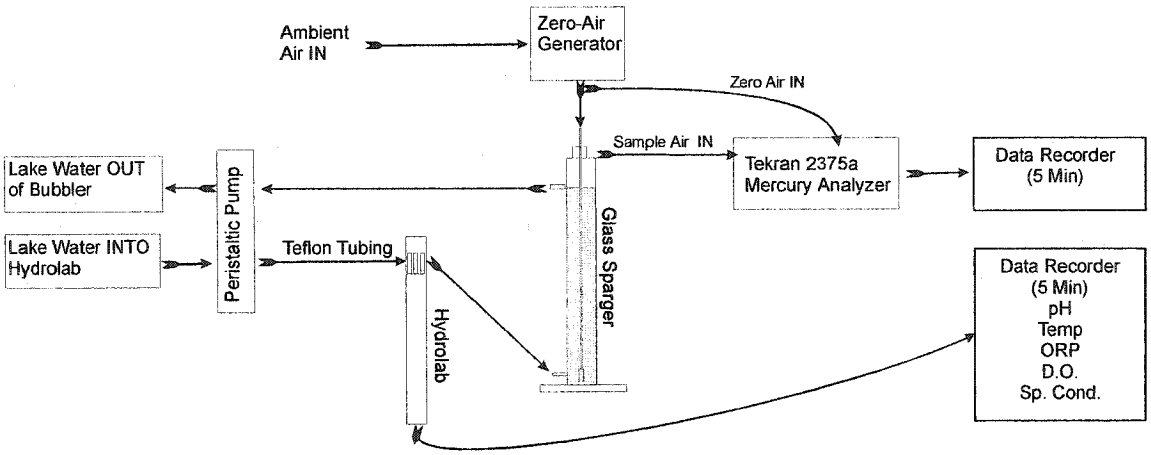

Figure 3-1: Schematic diagram of continuous DGM analysis instrumentation

The analysis system can be used to measure DGM in 1L water samples (discrete mode) or continuously from a water reservoir (continuous mode). When analyzing a discrete sample the peristaltic pump was turned off and a 1 L sample was bubbled for 30 minutes using mercury free air. The volatile mercury was then measured by gold amalgamation / atomic fluorescence spectrometry. This type of analysis is similar to the analysis methods used for previously published work on dissolved gaseous mercury (Lindberg *et al.*, 2000, Amyot *et al.*, 2000).

When in continuous mode, water was pumped from the Hyrdolab to the bottom of a 1 L graduated glass sparger with water exiting at the 1 L volume mark. The water flow rate was 50 mL min^{-1}, which means that 1 L of lake water was passed

through the analyzer every 20 minutes. Therefore, every 5 minutes, DGM levels in 250 mL of lake water were recorded. A Tekran 1100 zero air generator was used to supply mercury-free air to the glass sparger at a rate of 1.0 L min^{-1}. This was chosen instead of argon due to its mobility and its ease of use with the Tekran mass flow controller (that is set to measure ambient air volumes). The zero air pump uses ambient air and removes the mercury by passing it through a series of particulate and mercury removal filters. The mercury free air entered the water sample through a coarse glass dispersion tube that was placed at the bottom of the glass sparger (close to the lake water inlet). The DGM is carried with the analysis air from the sparger to the sample inlet of the Tekran 2537A (using ¼ inch Teflon tubing). Once in the Tekran, the DGM is amalgamated onto one of two gold sand traps arranged in parallel. The gold traps collect DGM for 5 minutes continuously, after which they are thermally desorbed and the released mercury is measured by atomic fluorescence spectrometry.

The Tekran 2537A was calibrated prior to this analysis using the internal mercury permeation calibration source which was further checked for accuracy through the use of standard air injection of elemental mercury using a Hamilton digital syringe and a Tekran 2505 mercury vapour calibration unit. The analysis system was allowed to warm up and stabilize for a minimum of 2 hours before readings were recorded for interpretation. Stripping efficiency was tested by filling the sampler with water from Big Dam West Lake and bubbling until a stable baseline of DGM concentration was achieved. This stable base line value was subtracted from the subsequent sample analysis when in continuous mode. After bubbling

for 60 minutes, the sample was poured back into the sample container and then back into the sparger to test for sources of contamination from the sampling routine. Interference from MeHg was evaluated by bubbling 1L of distilled de-ionized water to remove all traces of mercury and then spiking the sample with 1000 pg of methyl mercury chloride. This spiked sample was then analyzed in discrete sampling mode.

Effects on extraction efficiency by changes in water chemistry parameters were evaluated. For each of these tests a bulk water sample (250 L) from Meech Lake, Gatineau, Quebec was collected from the near surface (15 cm depth) using 25 L HDPE containers (Hall, 1998; Hall et al., 2002). Temperature effects were assessed by placing a 20 L sample of Meech Lake water in a temperature-controlled water bath. DGM analysis was performed in both continuous and discreet sampling modes between 4 and 30 ^{o}C. Temperature of the system was maintained by surrounding the sparger and the Teflon lines in bubble wrap for insulation. While the same bulk lake water sample was used for all tests, the total amount of DGM changed between each sample analysis. Total DGM for each sample was 450, 286, 282 and 519 fmol L^{-1} for 4, 10, 20, and 30 ^{o}C respectively. Therefore the results are represented as % Total DGM in Figure 3-6.

In order to test for the effect of pH and ORP separate 30 L samples from Meech Lake were adjusted to pHs of 7.8, 6.0, 5.0, and 3.5 with corresponding ORPs of 135, 214, 262, and 355 mV respectively using ACS grade nitric acid. All other parameters were kept constant for the analysis except for ORP, which changes

with pH (Wetzel, 1983). The continuous mode results were compared to the discrete mode results to determine if water temperature or pH had a perceptible effect on the results when in continuous mode.

Interference due to dissolved organic carbon (DOC) concentrations was evaluated. Dried humic substances were extracted from 150 L of Big Dam West Lake water in September of 1999 using solid phase extraction. The XAD-8 extraction method used was similar to that used by Thurman and Malcolm (1981) with the exception that the humic material was not separated into humic and fulvic acid fractions. Additions of 0, 2, 5, and 10 mg L^{-1} of extracted humic material were added to each 25 L lake water sample and the DOC measured through the use of an O.I. Analytical 1010 Total Organic Carbon analyzer (persulfate digestion with IR detection). The DOC of each sample of Meech Lake water as determined by persulfate digestion and IR detection was determined to be 4.5, 6.0, 6.8, and 10.5 mg L^{-1} DOC. Temperature was held constant at 23 °C and minimal changes in pH were observed through the use of the Hydrolab. The error on the mean sample DGM values was determined using a general linear model analysis.

The detection limits for the continuous analysis were calculated as 3 X the standard deviation of a blank sample (baseline fluctuation in discrete mode). The accuracy of the analysis system was determined by a general linear model analysis of a range of water samples with varying chemistries in discrete and continuous mode. The accuracy of the continuous analysis system is compared

against the discrete analysis system, which is assumed to be the standard. The precision of the analysis system was determined by the coefficient of variation (standard deviation/mean) for a set of 12 samples each run in triplicate.

The discrete and continuous DGM results were compared using a bivariate scattergram, as outlined by Sokal and Rohlf (1981, Chapter 15). We used a bivariate scattergram because the uncertainties in the X values (discrete DGM data) were also reflected in uncertainties in the Y values (continuous DGM data). Using a bivariate scattergram thus allowed us to calculate unbiased values for the slope and intercept of the principal axis of the relationship between the discrete and continuous analytical methods. The slope and intercept are indicators of the accuracy of the continuous technique compared to the discrete method; if the continuous method is exactly the same as the discrete, it would yield a unit slope and an intercept of zero. The slope of the principal axis of the relationship between the observed and predicted values is:

$$Slope\ (Principal\ Axis) = \frac{Covariance}{\lambda_1 - Variance\ (Observed\ Values)} \qquad \text{(Eq. 3-1)}$$

where λ_1 is the first eigenvalue of the variance-covariance matrix. We estimated the uncertainty of the slope and intercept using the eigenvalues of the principal and secondary axes (Sokal and Rohlf, 1981, Section 15.7).

The system testing sites were Big Dam West Lake and Puzzle Lake. Big Dam West Lake is located at 317825 Easting, 4925517 Northing and Puzzle is located at 322146 Easting and 4910233 Northing on the Nad83 GPS map, in Kejimukujik National Park in Nova Scotia, Canada. Big Dam West is an acidic (pH 5.0), low conductance (30 $\mu S\ cm^{-1}$), brown water (94 Hazens, Total Organic Carbon 10.5 $mg\ L^{-1}$) lake with a surface area of 105 hectares, a mean depth of 2.5 m and a flushing rate of 13 times yr^{-1}. Puzzle is also an acidic (pH 5.3), low conductance (20.6 $\mu S\ cm^{-1}$) lake but is clear (20 Hazens, Total Organic Carbon 3.6 $mg\ L^{-1}$) with a surface area of 34 hectares, a mean depth of 2.7 m and a flushing rate of 2 times yr^{-1} (Kerekes & Schwinghamer, 1973; Rencz, 2000)

Lake water was sampled at a depth of 15 cm using Teflon tubing attached to a floating Teflon platform. The platform was located 25 feet from the lake shoreline. A total of 50 feet of ¼ inch diameter Teflon tubing carried the lake water to the analysis system using a 2 channel peristaltic pump (Cole Parmer model no. 7553-07). The Teflon tubing was an average of 60 cm below the surface of the water until it reached the analysis tent on shore. A solar radiation extinction coefficient of 4.3 was calculated by extrapolating the dependence of two-year (1979-1981) extinction coefficients for Beaverskin, Kejimkujik and Pebbleloggitch on colour (Hazen units, r^2=0.979) to Big Dam West (Hazen unit = 94) (Beauchamp & Kerekes, 1989). Thus the tubing was exposed to only 7.6% of the surface incident radiation (3.8% of total radiation) for a total of 3 minutes while in transport to the analyzer (Environment Canada, 1982). Platinum cured silicone tubing (L/S 17) was used in the pump head and a flow rate of 50 mL min^{-}

[1] was maintained at all times. Big Dam West was sampled between 157.75 and 159.83 Julian day, 2001. During this period, air temperature averaged 16.7 °C (range: 8.6 - 23.7 °C), relative humidity 70% (range: 29 – 97%), visible light (400-1100 nm) during the day averaged 0.4 kW m^{-2} (range: 0.001 - 1.0 kW m^{-2}) and the wind speed averaged 0.8 m s^{-1} (range: 0-8.3 m s^{-1}). More details of the field study are available in Chapter 4.

3.4. Results

Water temperature had a significant effect on DGM removal efficiency during the first 5 minutes but after 20 minutes more than 98% of the DGM had been removed at all temperatures (Figure 3-2). At 4 °C less than 70% was recovered in the first 5 minutes as compared to greater than 90% at 30 °C. This is likely due to changes in the Henry's Law constant for elemental mercury, which decreases as temperature decreases (Sanemasa, 1975). For example the Henry's law constant changes from 0.33 at 23°C to 0.28 at 16 °C due to its temperature dependence (Schroeder *et al.*, 1991; Amyot *et al.*, 2000). Therefore, at higher temperatures elemental mercury prefers the vapour phase more then at lower temperatures. Other factors which are critical to the DGM removal efficiency include the aqueous viscosity and the molecular diffusivity which also change with temperature (Loux, 2000). Discrete and continuous analytical methods were found to give similar ($P<0.199$) responses between 4 and 40 °C using ANOVA. This is because each 250 mL aliquot is bubbled for 20 minutes offsetting the temperature dependence seen in the first five minutes (Figure 3-3).

When the same samples were re-analyzed in triplicate, no additional DGM was found. While it is clear from Figure 3-2 that there will be some carry-over of DGM between each five minute analysis time, the five-minute extraction efficiency is >80% for the temperature ranges encountered at the test site (20-25 °C). For colder temperatures (~4 °C) the analysis system would result in more carry-over of DGM from one five-minute reading to the next. This will result in less ability to see sharp peaks of DGM, since the peak would be spread over several readings (particularly at colder temperatures).

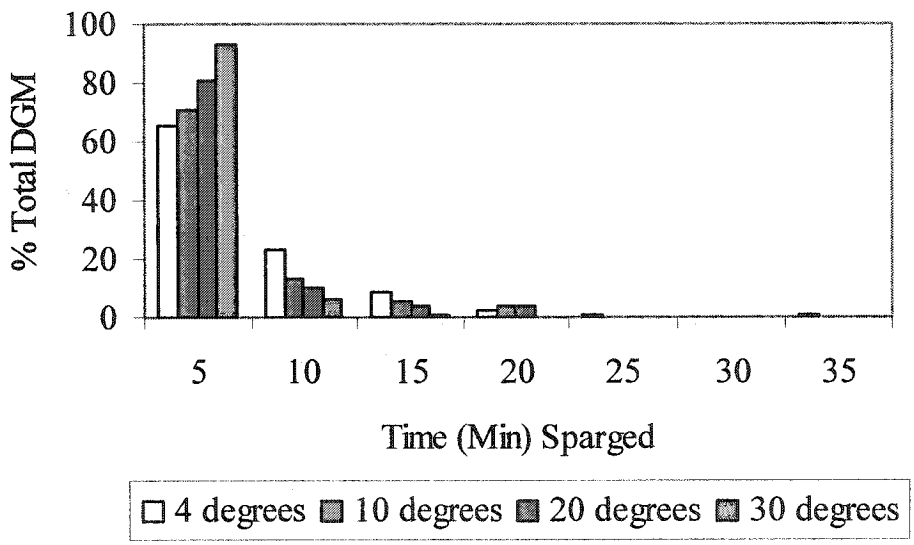

Figure 3-2: Percentage DGM sparged from lake water at various temperatures over time using discrete analysis.

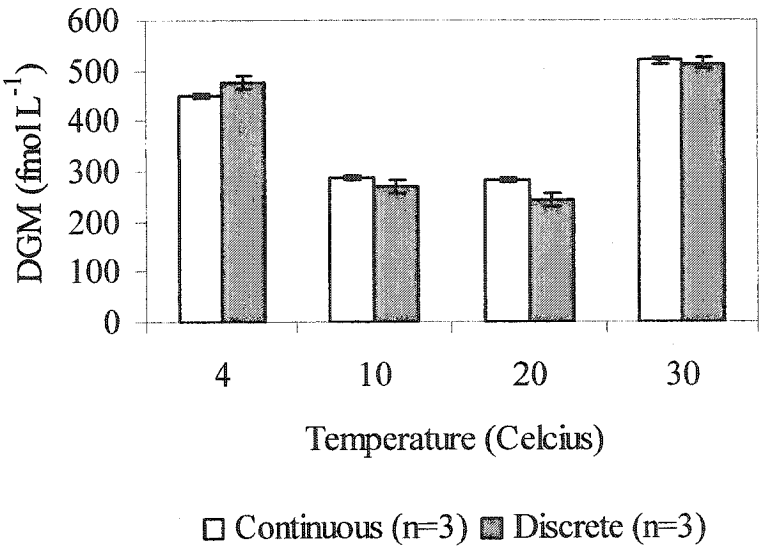

Figure 3-3: Difference between continuous and the discrete DGM analyses with varying temperature.

Discrete and the continuous analysis did not give comparable results for the typical ranges of pH, and DOC found in freshwater (Figures 3-4 to 3-5), however the percentage error of DGM concentrations between discreet and continuous analysis was not significantly related to pH or DOC concentrations (r^2= 0.40, p= 0.027 and r^2= 0.28, p=0.077 respectively). Therefore the differences between the discreet and continuous analysis was independent of temperature, pH, and DOC over the ranges tested. When both analysis techniques were used to analyze DGM in low DOC water (2.8 mg L^{-1}) from Puzzle Lake (Kejimkujik Park, Nova Scotia) very similar results were measured (153.2 +/- 9.97 fmol L^{-1} for continuous analysis and 144.6 +/- 8.9 fmol L^{-1} for discrete analysis). In order to calibrate the continuous analysis system, principal axis theory was used to calculate the slope between average continuous and average discrete measurements (n=12). The

slope of the principal axis was 1.045 with a 95% confidence interval of 0.937 and 1.168. The continuous analysis method had a bias of 4.5% compared to the discrete analysis method. Assuming that discrete analysis provides an accurate assessment of DGM concentration, this error can also be interpreted as a measurement of analysis method accuracy. The plot of discrete vs. continuous values is a type of calibration curve. Figure 3-6 shows this plot with principal axis (slope 1.045, intercept 6.7).

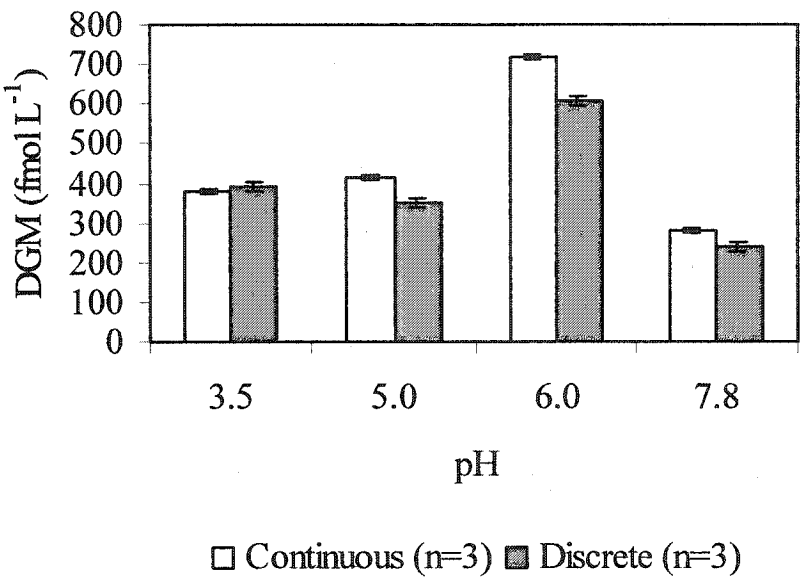

Figure 3-4: Difference between continuous and the discrete DGM analyses with varying pH.

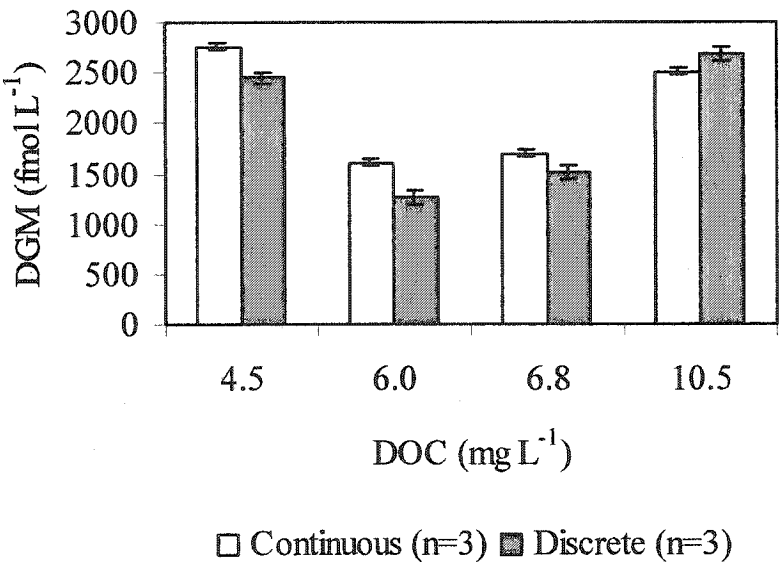

Figure 3-5: Difference between continuous and the discrete dissolved gaseous mercury (DGM) analyses with varying dissolved organic carbon (DOC) concentrations.

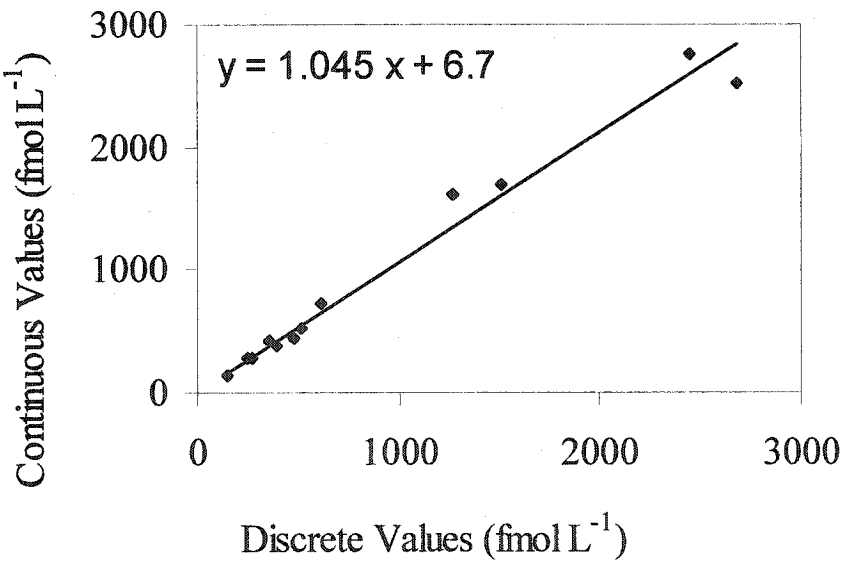

Figure 3-6: Scattergram of discrete versus continuous measurements.

The theoretical method detection limit (given that the detection limit of the Tekran 2357A is 1 pg of elemental mercury) for continuous analysis would be 20 fmol L^{-1}. The precision of the analysis system as determined as the average percentage relative standard deviation on a replicated sample was found to be 4.0 +/- 2.6% (n=36) giving an operational detection limit of 22.4 fmol L^{-1}. In order to test interference by MeHg in the analysis of elemental mercury, 4638 fmol of methyl mercury chloride was added to a 1 L water sample and analyzed in discrete sample mode and only 27.9 fmol DGM was detected or 0.6% of the methyl mercury spike. This suggests that for a typical environment containing 500 fmol L^{-1} MeHg, only 3 fmol or 0.75% of the DGM signal (using a typical DGM value of 400 fmol L^{-1}) would be due to MeHg. While more testing is needed to determine DGM speciation, it is likely that the predominant form of mercury measured is elemental.

Some of the results of the DGM and Hydrolab analyses performed at Big Dam West Lake are shown in Figures 3-7 and 3-8 respectively (similar data was collected for Puzzle Lake). Both lakes showed smooth changes in DGM, pH, ORP, and water temperature, (indicating reproducible readings in these parameters). The accuracy of the pH, ORP, and temperature probes used in the Hydrolab are +/- 0.2 pH units, +/- 1 mV, and +/- 0.1 °C respectively (Hydrolab, 1997). Over 1000 data points for each parameter was successfully collected over the two 48-hour testing periods with a loss of less than 1% of the data due to a power failure.

3.5. Discussion

DGM analysis has been the subject of many other research papers, however, it is still unclear what DGM actually is. Elemental mercury has been suggested by other researchers to be the primary constituent of DGM due to its high Henry's law constant and presence in the atmosphere (Schroeder *et al.*, 1991, Vandel *et al.*, 1991). We have demonstrated in this study that methyl mercury does not interfere with DGM analysis, but it is unknown if the same is true for other volatile mercury species.

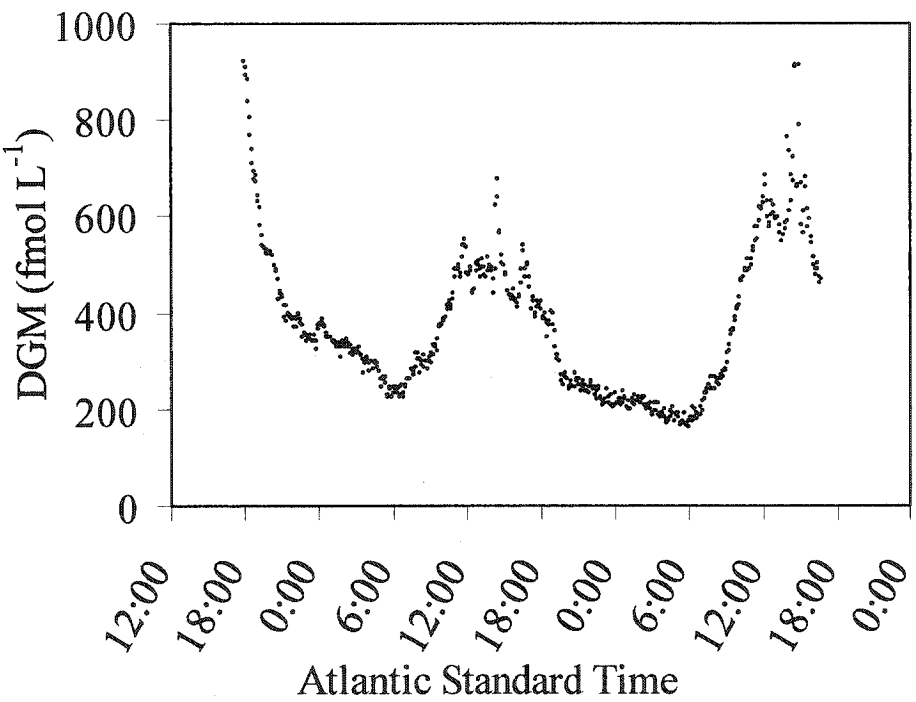

Figure 3-7: DGM measured in Big Dam West Lake on June 6-8, 2001 using the continuous analysis method for 48 hours

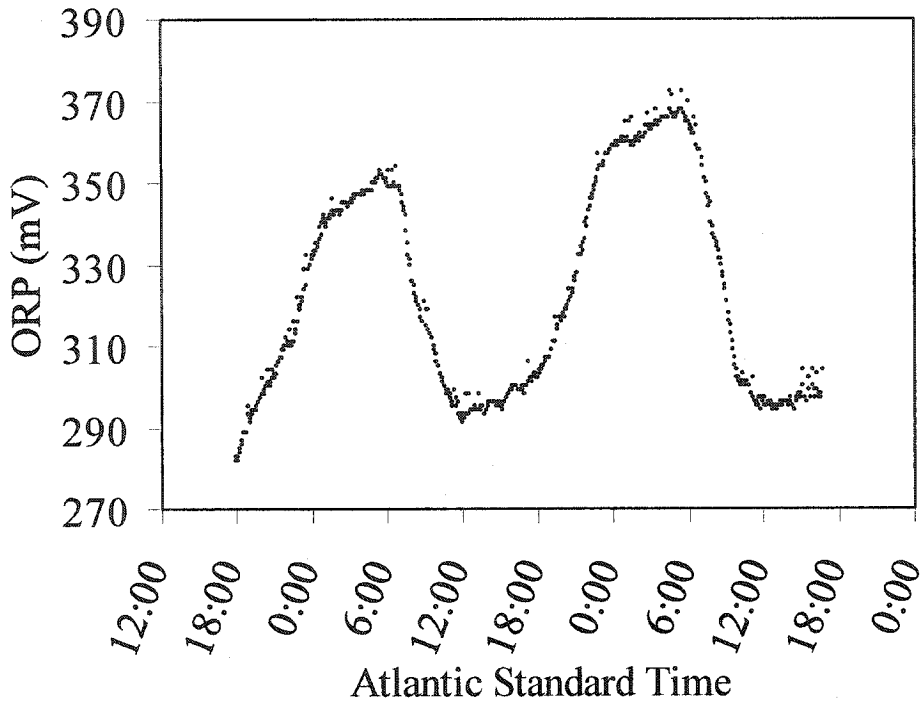

Figure 3-8: Oxidation Reduction Potential (ORP) measured in Big Dam West Lake on June 6-8, 2001 using the continuous analysis method for 48 hours

Most of the recently published papers on DGM analysis indicate a sample sparging time ranging from 20 to 90 minutes, which leads to very poor temporal resolution of DGM values (Krabbenhoft *et al.*, 1998; Bayens and Leermakers, 1998; Amyot *et al.*, 2000). This method gives a temporal resolution of 5 minutes, which allows for a detailed investigation of relationships between water chemistry and other variables that may affect DGM very quickly. Some of the sharp peaks observed in the diurnal studies indicate that very quick changes are occurring in the water concentration of DGM. Therefore fast processes are controlling both DGM production and loss in the water column. Past research has assumed that only discrete sample analysis could account for the difficulty in obtaining high DGM extraction efficiency with time. This method overcomes that problem by

using a large volume sparger with a relatively slow water circulation rate (50 mL min^{-1}). The lag time for sample transport from the lake to the analysis system was approximately 3 minutes at this speed.

If the water entering the sparger is thought of in discrete packets, then every 5 minutes 250 mL of lake water is introduced to the 1 L sparger. Therefore average turnover time for water in the sparger is 20 minutes which is the amount of bubbling time required to remove 99% of the DGM from an isolated water sample as shown in Figure 3-1. The 20-minute bubbling time has also been shown by other researchers to remove the majority of the dissolved gaseous mercury in water (Amyot *et al*, 2000, Lindberg *et al.*, 2000). The other advantage of this sampling method is that there is no possibility of contamination during sampling from external sources, and changes in sample composition are minimized due to the extremely quick processing time. During the field trials, the Teflon lines were run from the platform (at an approximate depth of 2 feet underwater) to an analysis tent located on the lakeshore to minimize interaction with solar radiation. We estimate that only 7.6% of incident solar radiation is available at this depth, therefore the effects of photoreduction would be minimal during the 3-minute sample tube residence time.

Since DGM extraction is temperature dependent (Figure 3-2) not all of the DGM in the 5-minute sampling is extracted during that time. Since there is some carry-over of DGM from one 5-minute sparging to the next we decided to give the sparger a 20-minute residence time. Therefore all DGM is removed from water

entering the sparger during its 20-minute residence time. It is noted that there will be some carry-over of DGM between each 5-minute data point (that will be most noticeable at low temperatures). However at water temperatures ~20 °C, each sampling point can be considered a composite value (i.e. approximately 80% of the current 5 minute sample plus 15% of the previous five minute sample, etc..). This gives the advantage of being able to observe sharp changes in DGM concentration every 5 minutes while avoiding the underestimation and temperature sensitivity of a 5-minute sparger residence time.

While calibration of analysis instrumentation has been a problem in previous DGM studies due to a lack of obtainable or stable standard reference materials for DGM, the Tekran 2357A mercury analyzer contains an internal elemental mercury calibration standard for the measurement of mercury in air. The Tekran is calibrated both to this standard and to standard injections of gaseous elemental mercury in air to check the calibration source. While no liquid calibration samples were analyzed (due to the unavailability of a suitable stable standard for DGM) it was assumed that all volatile mercury is removed from the sample within the analysis time. This was checked by re-sparging a sparged sample and finding little DGM. Since 1 L of analysis air per minute is passed through the sparger it is a safe assumption that the removal efficiency is high. The removal efficiency is also aided by the sparger design, which is tall and thin to allow for maximum sample interaction with the analysis air.

The close relationship between near-continuous and discrete measurements

over a range of pH, DOC, and temperature conditions indicates that the near-continuous method gives consistent results within 4.5%. It is likely that this is just due to analytical error that is involved with any chemical analysis. Sources of this error may include changes in sample flow during the analysis or changes in redox conditions during sample bubbling.

An example of the data collected for Big Dam West Lake is shown in Figures 3-7 and 3-8. The sharp peaks observed in DGM readings indicate the necessity of having a fine time resolution for diurnal DGM data. Diurnal cycles were obvious in both lakes for DGM and many Hydrolab parameters (ORP shown in Figure 3-8). Recent research has identified a number of processes that can influence the levels of DGM in lake water. The balance between photoreduction and photooxidation processes (initiated by solar radiation principally in the UVA and UVB spectrum) has been identified as important determinants of DGM concentrations (Amyot *et al.*, 1994). More recently, the role of microbial oxidation and reduction processes in DGM diurnal cycles has been identified (Siciliano *et al.*, 2002). The Hydrolab parameters that were measured may also have an effect on DGM production and volatilization, however they have not been previously examined in detail over a diurnal cycle. Redox processes and reaction rates are intimately linked to water temperature, pH, and ORP measurements in lake water. A detailed examination of the data collected at both lakes is available in Chapter 4.

In conclusion this method has been thoroughly tested and found to provide

consistent results when compared with the discrete analysis method. This method has been determined to have a low detection limit, high accuracy and precision, and a much reduced sample analysis time as compared with discrete sample analysis. The automated system was tested at two remote freshwater lakes and was found to collect 99% of the data (over 1200 data points) during two 48-hour periods. Applications of this method may include the examination of quick ecosystem processes that alter DGM concentrations in water or real time surveying of water chemistry both spatially and with depth in the water column.

Chapter 4

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

Reproduced in part with permission from: O'Driscoll, N.J., Beauchamp, S., Siciliano, S.D., Lean, D.R.S., and Rencz, A.N. 2003. Continuous analysis of dissolved gaseous mercury (DGM) and mercury flux in two freshwater lakes in Kejimkujik Park, Nova Scotia: Examining flux models with quantitative data. *Environmental Science and Technology*. 37(10): 2226-2235. Copyright (2003) American Chemical Society.

4.1. Abstract

Diurnal patterns for dissolved gaseous mercury (DGM) concentration, mercury flux, several water variables (pH, oxidation reduction potential (ORP), water temperature), and meteorological variables (wind speed, air temperature, % relative humidity, solar radiation) were measured in two lakes with contrasting dissolved organic carbon (DOC) concentrations in Kejimkujik Park, Nova Scotia. A continuous analysis system made it possible to measure quick changes in DGM over time. Consistently higher DGM concentrations were found in the high DOC lake as compared to the low DOC lake. An examination of current mercury flux models using this quantitative data indicated some good correlations between the data and predicted flux (r ranging from 0.27 to 0.83) but generally poor fit (standard deviation of residuals ranging from 0.97 to 3.38). Cross-correlation analysis indicated that DGM dynamics changed in response to solar radiation with lag-times of 65 and 90 minutes. This relationship with solar radiation was used to develop new predictive models of DGM and mercury flux dynamics for each lake. We suggest that a generalized approach using time-shifted solar radiation data to predict DGM can be incorporated into existing mercury flux models. It is clear from the work presented that DOC and wind speed may also play important roles in DGM and mercury flux dynamics, and these roles have not been adequately accounted for in current predictive models.

4.2. Introduction

Dissolved gaseous mercury (DGM), which is composed primarily of elemental mercury, can volatilize from a lake's surface to the atmosphere thus reducing the amount of total mercury present (Baeyens *et al.*, 1991; Vandal *et al.*, 1991; Amyot *et al.*, 1997a). There is a positive correlation between the total amount of mercury in freshwater lakes and the amount of methyl mercury (MeHg) present during summer months (Driscoll *et al.*, 1994; Watras *et al., 1995; O'Driscoll et al., 2001*). Thus, predictive models of DGM flux to the atmosphere would help identify ecosystems likely to retain more total mercury and accumulate MeHg, which is the form of mercury that will bioaccumulate in aquatic food webs (Morel *et al.*,1998).

There are significant changes in DGM over a diurnal cycle for both freshwater and seawater systems (Amyot *et al.*, 1994; 1997c; Lanzillotta and Ferrara, 2001). These changes are the result of several oxidation and reduction processes occurring simultaneously. Supporting the early work of Amyot *et al.* (1994), Zhang & Lindberg (2001) found that iron-mediated photo-reduction and photo-oxidation processes play a role in DGM dynamics. In addition to these chemical processes, photo-induced microbial reduction and oxidation processes also contribute to DGM dynamics (Siciliano *et al.*, 2002).

In addition to studies of DGM, several recent publications have examined mercury flux between water and air. Loux (2000) found that temperature effects

on chemical properties such as Henry's law constants, and diffusive layer properties may explain up to 44 % of diurnal mercury flux variations. Zhang and Lindberg (*2000*) produced a box model of DGM evasion rates based primarily on solar radiation and dissolved reactive mercury availability. All of the current research indicates that solar radiation is directly or indirectly the driving force behind diurnal variations in DGM and mercury flux.

Researchers often use predictive models to estimate mercury flux given a known DGM concentration (*Baeyens et al.,* 1991; Schroeder *et al.,* 1992). Most of the current mercury flux models are based on modified measurements of carbon dioxide water-to-air transport (Schroeder *et al.,* 1992; Poissant *et al.,* 2000). Some authors have also attempted to incorporate wind parameters into these flux models based on theoretical calculations involving changes to the diffusive layer. Current flux models have not been rigorously tested using large datasets of quantitative field measurements due to significant challenges associated with DGM analysis in lake water (as outlined in Chapter 3). Our group recently developed and calibrated (under a wide range of DOC, pH, and water temperatures) a continuous analysis system capable of measuring DGM and Hydrolab readings (ORP, water temperature, pH, specific conductivity, dissolved oxygen) every 5 minutes (O'Driscoll *et al.,* 2003a). An alternative continuous DGM analysis system was independently and simultaneously developed by Amyot *et al.* (*2001*).

Several researchers (Schroeder *et al.,* 1992; Boudala *et al.,* 2000; Poissant *et*

al., 2000) have investigated spatial and temporal trends in mercury flux over water using various chamber and micrometeorological designs. While it is recognized that mercury movement between water and air is an important part of the mercury cycle, only a few papers have measured DGM and mercury volatilization at the same time, and none have done so continuously to examine diurnal patterns (Poissant *et al.*, 2000). The purpose of this paper was to examine diurnal patterns in DGM and mercury flux continuously in two lakes with contrasting DOC contents, and then use this data to evaluate current predictive models for mercury flux from water.

4.3. Methods

4.3.1. Continuous analysis of DGM

Water was sampled from each lake site using ¼ inch diameter Teflon tubing that had been pre-cleaned by passing 5 L of 5% HCl through it, followed by large amounts (~20 L) of distilled de-ionized water. The Teflon tubing was also rinsed with 5-10 L of the lake water being sampled, prior to starting the sampling system. The sample inlet was fixed 10-15 cm below a floating Teflon platform that was located approximately 15 meters from shore. The sample depth was chosen to give a representation of near-surface water while avoiding flux chamber interferences and air sampling during high wave conditions. The Teflon tubing was 60 cm below the surface of the water until it reached the shore and then was exposed to sunlight over a 1 m interval between the tent and shoreline.

A solar radiation extinction coefficient of 4.6 m^{-1} was calculated by extrapolating the dependence of two-year (1979-1981) extinction coefficients for Beaverskin, Kejimkujik and Pebbleloggitch Lakes on colour (Hazen units, $r^2 = 0.979$) to Big Dam West Lake (Hazen unit = 94) (Beauchamp *et al.*,1989). Thus the tubing was exposed to only 7.6% of the surface incident radiation (3.8% of total radiation) for a total of 3 minutes while in transport to the analyzer (Environment Canada, 1982). A detailed description of the analysis system is available in Chapter 3.

When in continuous mode, water was pumped (using a two channel peristaltic pump with silicone pump tubing) from the lake to the Hydrolab™ for analysis of water chemistry (Hydrolab, 1997), and then to the bottom of a 1 L graduated glass sparger. Water was then pumped from the sparger at the 1 L volume mark back to the lakeshore. With a flow rate of 50 mL min^{-1} the volume of sample analysed was 250 mL every 5 minutes. This flow rate and sparge time has been shown to be comparable with previous discrete analysis methods (O'Driscoll *et al.*, 2003a). A Tekran™ 1100 zero air generator was used to supply mercury-free air to the glass sparger at a rate of 1.0 L min^{-1}. The mercury-free air bubbled the sample through a coarse glass dispersion tube that was placed at the bottom of the glass sparger close to the lake water inlet. The DGM is carried from the sparger to the sample inlet of the Tekran™ 2537A and analyzed for mercury content. Each Tekran™ 2537A used for this study was calibrated prior to this analysis using the internal mercury permeation calibration source. The internal mercury calibration source was checked for accuracy with a standard air injection

of elemental mercury using a Hamilton™ digital syringe and a Tekran™ 2505 mercury vapour calibration unit. The analysis system was allowed to warm up and stabilize for a minimum of 2 hours before readings were recorded for interpretation. Using this method the detection limit for DGM was 20 fmol L^{-1} and the relative standard deviation (RSD) of duplicates (n=36) was 4.0 +/- 2.6 % (O'Driscoll *et al.*, 2003b).

4.3.2. Continuous Analysis of Gaseous Elemental Mercury in Ambient Air

Gaseous elemental mercury (GEM) concentration in air was measured using a Tekran™ Model 2537A cold vapour atomic fluorescence (λ=253.7nm) spectrophotometer (CVAFS) calibrated using an internal mercury permeation source and an external Tekran™ Model 2505 primary mercury vapour calibration system. Ambient air was continuously sampled at a rate of 1.5 L min^{-1} for 5 min through a heated sampling line. GEM in ambient air was trapped onto the gold cartridges then thermally desorbed at 800 °C. The Tekran™ analyzer underwent automatic calibrations every 25 hours using an internal mercury permeation source in addition to quarterly calibrations done manually using an external Tekran™ Model 2505 primary mercury vapour calibration system. Quality assurance (QA) and quality control (QC) checks were performed regularly including injection testing for line loss, zero air-flow checks for line source and flow meter/controller calibrations.

4.3.3. Continuous Analysis of Mercury Flux from Water

Air-surface mercury exchange was measured using a rectangular Teflon flux chamber (Carpi and Lindberg, 1998) placed over the substrate enclosing an open surface area of 0.12 m^2 (Kim and Lindberg, 1995; Carpi and Lindberg, 1997). Teflon sampling lines and fittings were used throughout the mercury flux measurement system. Unfiltered ambient air was sampled for 5 minutes alternating every 10 minutes (duplicate 5 min integrated samples) between ambient and chamber air. Switching between ambient and chamber air sampling was done using a Tekran™ Model 1110 Synchronized Automated Dual Sampling (TADS) switching system. Since the Tekran™ draws air samples alternately from the flux chamber line and the ambient air line there is a possibility of air stagnating in the areas of the system not being measured. Stagnation of air in the system may result in adsorption of mercury on the Teflon lines. To avoid this, a solenoid valve system and air pump was used to maintain flow rates of 10 L min^{-1} when the Tekran™ was not measuring GEM. Flow rates in the system (10 L min^{-1}) were controlled using Hastings-Teledyne™ mass flow controllers and mass flow meters. Mercury flux was calculated as the difference between mercury concentrations in ambient air versus air that had passed through the chamber (Scroeder *et al.,* 1989; Xiao *et al.,1991*).

System quality control (QC) procedures were performed on a regular basis, including the use of standard operating procedures (SOPs), analyzer and sensor calibrations, chamber/system blanks and Hg injection-recovery tests. Chambers

were closed with a clean Teflon sheet to perform blanks in the laboratory and *in situ* using the complete system (lines, fittings, solenoid switches and the chamber). Mean blank fluxes for the system were 0.07 ng m^{-2} h^{-1} (σ = 0.11, n = 48). Flux rates presented in this study are blank-corrected.

A RM Young™ model 05103 wind monitor was used to collect data on wind speed and direction. This instrument is a Meteorological Service of Canada (MSC) standard instrument and has a sensitivity of 1.0 m s^{-1} and an accuracy of 0.1 m s^{-1}. Monitors were calibrated prior to use. The wind monitor was located at a height of 1 m above the lake surface, near shore. The following calculation (Eq. 4-1) was used to convert the readings to a 10 m height for use in some predictive models (assuming an unstable atmosphere during the day and smooth surface conditions).

$$\text{Wind Speed}_{10\text{ meter height}} = \text{Wind Speed}_{1\text{ meter height}} (10/1)^{0.11} \qquad \text{(Eq. 4-1)}$$

4.3.4. Flux Model Evaluation and Description

Three mercury flux models were chosen from the current published literature to be evaluated in comparison to the collected quantitative data. Predicted flux values were calculated using each model and the Pearson correlation coefficient between the predicted data and measured flux was assessed. The residual values for each model prediction were calculated by subtracting the measured flux values from the predicted flux values (Eq. 4-2).

Residual Values = Predicted Flux – Measured Flux (Eq. 4-2)

The distribution (Appendix 2, Figures A2-1 to A2-6), mean and standard deviation of each set of residual values was calculated and (in combination with the correlation coefficient) served as an assessment of the fit of the corresponding flux model. For example, a mean residual value of 1 would indicate that the model over-predicted the measured flux by 1 ng m^{-2} h^{-1} on average, over the duration of the experiment. In the case of the Poissant *et al.* (2000) model, manipulations of a constant wind speed parameter were performed to observe the effects of wind speed on the predictions.

3.3.5. Mass Transfer Mercury Flux Model

Schroeder *et al.* (1992) adapted the two-layer gas transfer model of Liss and Slater (1974) (Eq. 4-3) for use with mercury. In the work of Schroeder *et al.* (1992) the mass transfer coefficients for mercury are calculated relative to carbon dioxide measurements (example Eq. 4-4).

$$F = (C_a - HC_w) / (1/K_a + H/K_w) \quad \text{(Eq. 4-3)}$$

Where: F = flux of mercury from water to air (ng m^{-2} h^{-1}), C_a = concentration of volatile Hg in air (ng m^{-3}), C_w= Concentration of DGM in water (ng m^{-3}), H = dimensionless Henry's Law constant, K_a= air mass transfer coefficient (9 m h^{-1}),

and K_w = water mass transfer coefficient (0.09 m h^{-1}).

$$K_w(Hg^0) = K_w(CO_2) \times (M_{CO2}/M_{Hg})^{0.5} = 0.09 \text{ m } h^{-1} \quad \text{(Eq. 4-4)}$$

Where: M_{CO2} = molecular mass of carbon dioxide (g mol^{-1}), M_{Hg} = molecular mass of mercury (g mol^{-1})

For elemental mercury the air mass transfer coefficient is negligible in the calculations (i.e. $1/K_a = 0.11$).

4.3.6. Temperature- and Wind-Sensitive Mass Transfer Mercury Flux Models

The Poissant *et al.* (2000) flux model was adapted for mercury from the two-layer Liss and Slater (1974) model and the Wanninkhof *et al.* (1985) model. Like Schroeder *et al.* (1992), they also calculate mass transfer coefficients based on carbon dioxide measurements (Eq. 4-5). However, the mass transfer calculations are based on Schmidt numbers that are calculated for mercury as the ratio of kinematic viscosity to diffusivity. In the work of Poissant *et al.* (2000), kinematic viscosity, diffusivity, and the Henry's Law constant are corrected for temperature using equations drawn from the published literature (Schroeder *et al.*, 1989; Poissant and Pilote, 1998; Mason and Sullivan, 1997). The mass transfer coefficient for water is also modified by a wind speed parameter measured at a 10-meter height (U_{10}) (Eq. 4-5).

$$K_w \sim (0.45\ U_{10}^{1.64})\ [Sc_w(Hg) / Sc_w\ (CO_2)]^{-0.5} \quad \text{(Eq. 4-5)}$$

Where: K_w= the water mass transfer coefficient (m h^{-1}), U_{10} = wind speed at 10 meter height above water (m s^{-1}), and Sc_w = is the Schmidt number in water for mercury or carbon dioxide.

4.3.7. Solar Radiation and Wind Speed (Empirically-Derived) Mercury Flux Model

The Boudala *et al.* (*2000*) mercury flux model is an empirically-derived model based on measurements taken at Big Dam West (BDW) lake for mercury flux, solar radiation and wind speed. A multiple linear regression approach was taken to produce a predictive model based on these variables for BDW Lake (Eq. 4-6). In this case the wind speed raised to the power of 1.5 is derived from empirically fitted data rather than theory.

$$F = 2.44\ R\ w_s^{1.5} + 1.1 \quad \text{(Eq. 4-6)}$$

Where: F = mercury flux (ng m^{-2} h^{-1}), R = solar radiation (kW m^{-2}), and w_s= wind speed near surface (m s^{-1}).

4.3.8. Empirical Approach with Continuous Data

Multiple linear regression analysis was used on the continuous data presented in this paper, to produce models based on solar radiation and wind speed raised to

the exponent of 1.5 (similar to the Boudala *et al.* (*2000*) model). The predicted flux from these models was then correlated to measured data.

Predictive multivariate equations for DGM and mercury flux were produced using the Hydrolab™ and meteorological data. The data was transformed where appropriate (using logarithms, etc.) and tested for normality using the Kolmogorov-Smirnov statistic, with a Lilliefors significance (or Shapiro-Wilk statistic when appropriate) in an SPSS statistical package. The normalized data were analysed using a stepwise multiple linear regression to determine the important variables for predictive models (F-value: entry value = 0.001, removal value = 0.01). The most significant variables (variables with highest standardized beta coefficients) were then used in a multiple linear regression to determine the best predictive relationship. The robustness of the predictive model was then tested by re-entering the data and examining the difference in observed versus predicted values. No obvious trends were observed between the residual values and changes in the time of day or the DGM concentration, and this indicated a model that worked well under the range of conditions tested. While this multivariate analysis produced accurate predictive models, it did not produce models that were intuitive or causal in nature. In addition the models did not work outside of the dataset used to produce them, i.e. the BDW Lake empirical model did not predict well for the Puzzle Lake data.

In consideration of the poor performance of the multivariate regression models,

simplified models were created employing linear regression with time-shifted solar radiation as the driving parameter. Cross-correlation analysis was performed on time-shifted solar radiation and DGM data to find the maximum correlation. This allowed observation of time-delayed relationships, which may give indications as to the dominant mechanisms of DGM production. Since the peak correlations between solar radiation and DGM (0.90 and 0.75 for Puzzle and BDW respectively) were found to occur with different time-lags in each lake, an average positive lag-time of 75 minutes was used as a predictor of DGM. Simple models of mercury flux based on the time-shifted solar radiation data were produced to investigate the potential for creating modified flux models that incorporate the variables that govern DGM dynamics.

4.3.9. Site Description

Kejimkujik Park is located in southern Nova Scotia, Canada, in an area of relatively flat topography. BDW Lake and Puzzle Lake are located within Kejimkujik Park (see Table 4-1 for eastings and northings) and have different physical and chemical properties. The physical and chemical properties of both lakes are shown in Tables 4-1 and 4-2, respectively. It can be seen that while the lakes are situated relatively close to each other (< 25 km), have similar mean depths (2.5 - 2.7 m), and are both at an elevation close to sea level (120 m), they have very different lake and catchment characteristics. In comparison to Puzzle Lake, BDW Lake has a much larger lake surface area, a much more rapid flushing rate, and a greater area of wetlands in the catchment basin (20.2 km^2 for

BDW as compared to 0.6 km^2 for Puzzle). The higher flushing rate combined with the large area of wetlands in the catchment basin suggests that BDW Lake's DOC, pH, and cation content is determined largely by the inputs from the surrounding wetlands. In contrast, Puzzle Lake's DOC, pH, and cation content is not substantially affected by wetland inputs. The importance of the wetland interaction is obvious when examining the water chemistry parameters (Table 4-2). It can be seen that while both lakes are acidic, the amount of total organic carbon (TOC) is much higher in BDW Lake (10.5 mg L^{-1}) than in Puzzle Lake (3.6 mg L^{-1}). The higher DOC in BDW results in higher colour (94 Hazens), and higher specific conductance due to slightly higher inputs of cations such as Na, K, Ca, Mg, Al, and Fe (See Table 4-2) (Kerekes and Schwinghamer, 1973). These observations are in line with those of D'Arcy and Carignan (1997), who found that the DOC content of a lake is largely predicted by the slope of the drainage basin. Therefore, a lake with a low slope and a high ratio of drainage basin to lake area would be expected to have a high DOC content.

Physical Parameter	**Big Dam West**	**Puzzle**
Easting Nad83	317825	322146
Northing Nad83	4925517	4910233
Lake Elevation (m)	120	120
Surface Area (hectares)	105.0	33.7
Total Catchment Area (km^2)	40.0	2.1
Wetland Area (km^2)	20.2	0.6
Volume (m^3)	2593000	911000
Mean Depth (m)	2.5	2.7
Max Depth (m)	9.5	6.1
Shoreline Length (km)	6.1	4.6
Flushing Rate (times/yr)	13.1	2.0

Table 4-1: Physical parameters for Big Dam West Lake and Puzzle Lake.

Water Chemistry	Big Dam West	Puzzle
pH	5.0	5.3
Dissolved Oxygen	11.05	10.73
Total Organic Carbon (mg L^{-1})	10.5	3.6
Color (Hazens)	94	20
Alkalinity (mg L^{-1})	0.07	0.09
Specific Conductance (uS cm^{-1})	30.1	20.6
Total Hg - unfiltered (ng L^{-1})	5.01	0.87
Cl (mg L^{-1})	4.84	3.41
SO_4 (mg L^{-1})	1.69	1.69
Total N_2 (mg L^{-1})	0.111	0.093
Na (mg L^{-1})	3.52	2.26
K (mg L^{-1})	0.307	0.238
Ca (mg L^{-1})	0.641	0.383
Mg (mg L^{-1})	0.364	0.290
Al (mg L^{-1})	0.198	0.061
Fe (mg L^{-1})	0.165	0.105

Table 4-2: Chemical parameters for Big Dam West Lake and Puzzle Lake.

4.4. Results

Some of the results from the DGM, Hydrolab, and meteorological analyses performed at Puzzle Lake are shown in Figure 4-1 and similar results for BDW Lake are shown in Figure 4-2. Results are presented in Julian Time, which is a standardized system of representing time relative to Greenwich Mean Time (GMT). A Julian Day of 163 refers to the 163rd day of the year at 12:00 AM GMT, and 163.5 Julian Day would be equivalent to 12:00 PM GMT on that same day. 12:00 PM GMT is equivalent to 8:00 AM in Atlantic Standard Time (AST). For the purposes of the following discussion we will refer to Atlantic Standard Time (AST).

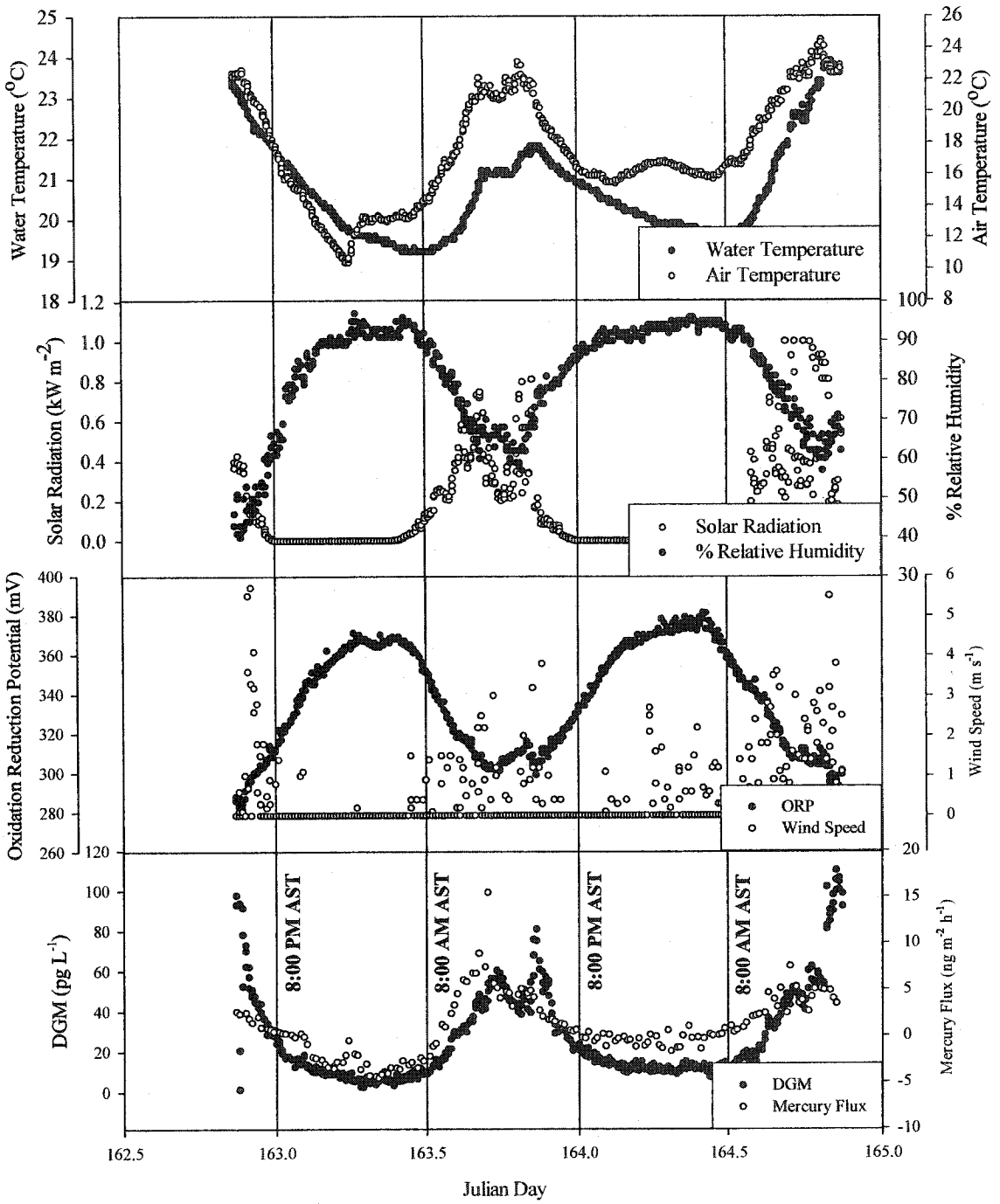

Figure 4-1: Water temperature, air temperature, solar radiation, % relative humidity, oxidation reduction potential, wind speed, dissolved gaseous mercury, and mercury flux readings for Puzzle Lake over 48 hours.

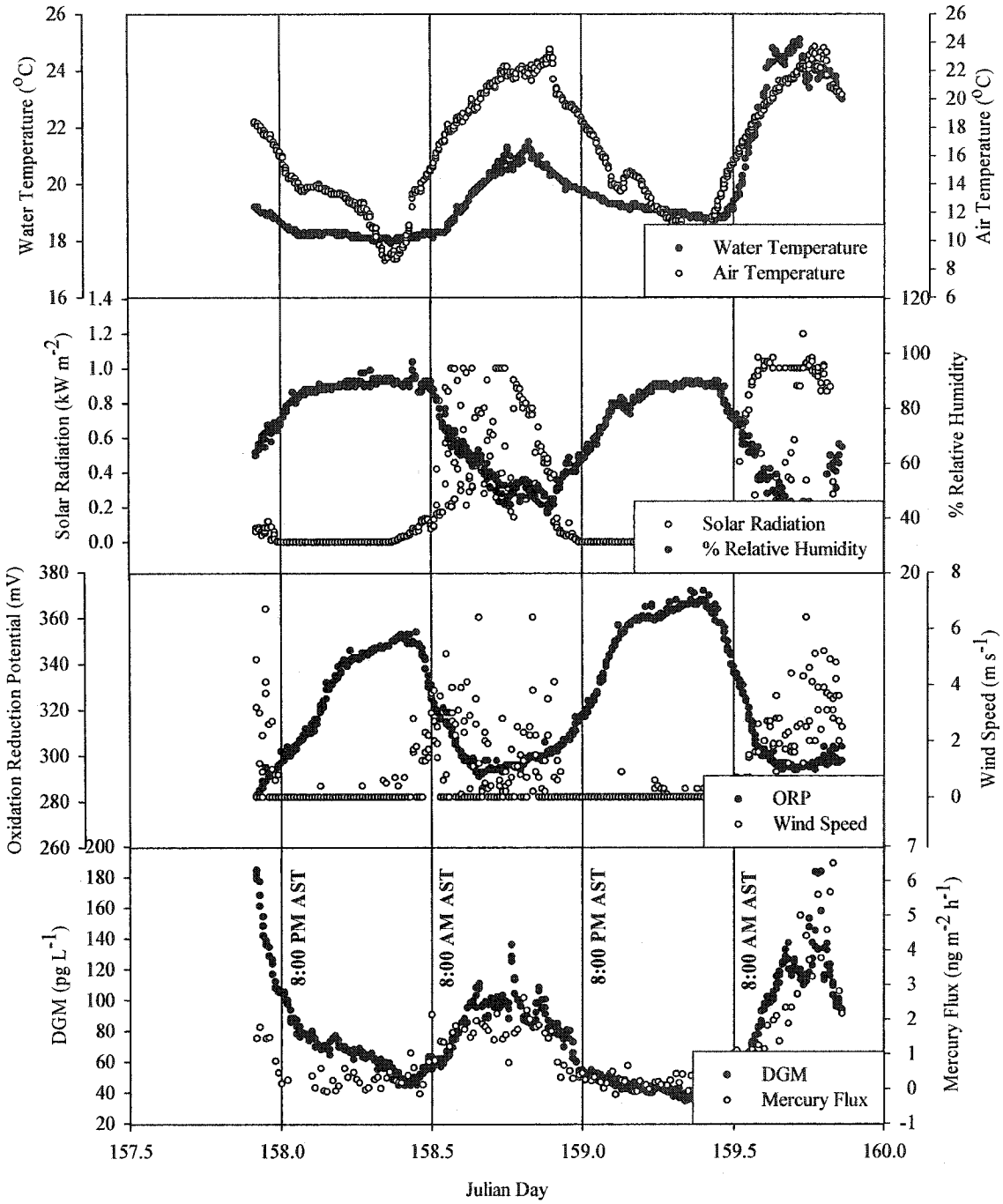

Figure 4-2: Water temperature, air temperature, solar radiation, % relative humidity, oxidation reduction potential, wind speed, dissolved gaseous mercury, and mercury flux readings for Big Dam West Lake over 48 hours.

It can be seen that water and air temperatures follow diurnal patterns with peaks occurring at midday (10:00AM - 2:00PM AST) and lows at midnight (10:00PM - 2:00AM AST). Wind speed can be seen to follow a similar diurnal pattern for both lakes with the highest values occurring during daylight (6:00AM - 6:00PM AST) and very little wind at night. The wind speed readings are somewhat erratic, ranging between 0 – 7.0 m s^{-1}. Oxidation-reduction potential (ORP) and % relative humidity followed an inverse diurnal pattern with lows at midday and highs at midnight. It can be seen in Figures 4-1 and 4-2 that water and air temperatures, ORP, and % relative humidity readings had similar ranges for both lakes (19 - 25 °C, 8 – 24 °C, 270 – 390 mV, and 40 – 90 % respectively). Solar radiation for both lakes ranged between 0 - 1.0 kW m^{-2}. Little change was observed in the specific conductivity or dissolved oxygen concentration in either lake during the course of the sampling.

Diurnal patterns for DGM concentration and water-to-air mercury flux were observed in both lakes with highs occurring at midday and lows at midnight. More detail is available for the DGM measurements and quick changes in concentration can be observed. Sharp changes in DGM concentration are observed during the daylight hours for both BDW and Puzzle Lake, with values changing as much as 40 pg L^{-1} over a 20-minute period. It can be seen that the range of DGM values and the average DGM concentration is consistently higher for BDW Lake (range: 32.4 – 182.6 pg L^{-1}, mean 76, σ = 31.1 pg L^{-1}) than for Puzzle Lake (range: 1.3 – 110.0 pg L^{-1}, mean 27, σ = 21.8 pg L^{-1}).

As seen in Figures 4-1 and 4-2, generally wider ranges in mercury flux were measured in Puzzle Lake (-4.55 to 9.00 ng m^{-2} h^{-1}) than in BDW Lake (-0.15 to 6.50 ng m^{-2} h^{-1}). The average daytime flux for BDW was 2.1 +/- 1.30 ng m^{-2} h^{-1} and the average night time flux was 0.4 +/- 0.40 ng m^{-2} h^{-1}. In contrast, the average daytime flux for Puzzle was 3.8 +/- 2.60 ng m^{-2} $h^{-1}$and the average night time flux was –1.3 +/- 1.70 ng m^{-2} h^{-1}. While there was not a significant difference between the average flux of the two lakes (given the standard deviations on the average flux), the range of flux values is wider for Puzzle Lake than for BDW Lake.

The data produced by the Schroeder *et al.* (1992) mercury flux model correlated well with the measured flux data from both Puzzle Lake and BDW Lake (r = 0.72 and 0.69 respectively) (Table 4-3). The mean of the residuals for the Puzzle Lake data was much closer to zero (mean = 1.0, σ = 2.29) than it was for BDW Lake (mean = 5.6, σ = 2.35). As observed by the means and distributions of the residuals, the model consistently over-predicted the flux for BDW Lake (by 400 - 800%), whereas the predictions for Puzzle Lake randomly over-predicted and under-predicted flux (See Figures A2-1 and A2-2, Appendix 2). While the high Pearson correlations indicate similar trends between the model data and the measured data, the high standard deviation of the residuals indicated the modeled data did not accurately predict the measured data.

	Puzzle Lake		
Model	Pearson Correlation	Mean of Residuals	Standard Deviation of Residuals
Schroeder et al, 1992	0.72	1.0	2.29
Poissant et al., 2000	0.27	-0.7	3.03
3 m/s Wind	0.69	0.1	2.59
Boudala et al., 2000	0.32	0.9	3.38
	BDW Lake		
Model	Pearson Correlation	Mean of Residuals	Standard Deviation of Residuals
Schroeder et al, 1992	0.69	5.6	2.35
Poissant et al., 2000	0.47	0.0	1.53
3 m/s Wind	0.83	2.0	0.97
Boudala et al., 2000	0.63	1.0	2.45

Table 4-3: Pearson correlation, mean of residuals, and standard deviation of residuals for mercury flux predictive models in comparison to measured flux data.

The data produced by the Poissant *et al.* (2000) mercury flux model did not correlate well with the measured mercury flux data ($r = 0.27$ and 0.47, for Puzzle and BDW Lakes, respectively). The replacement of the wind speed variable with a constant wind speed of 3 m s^{-1} resulted in a better correlation between the predicted flux and the measured flux ($r = 0.69$ and 0.83 for Puzzle and BDW Lakes, respectively). The mean of the residuals for Puzzle Lake was –0.7 (σ = 3.03) for the model with variable wind speed and 0.1 (σ = 2.59) for the model with a constant wind speed of 3 m s^{-1}. The mean of the residuals for BDW Lake was 0.0 (σ = 1.53) for the model with variable wind speed and 2.0 (σ = 0.97) for the model with a constant wind speed of 3 m s^{-1} (Table 4-3). The distribution and means of the residuals indicated the model with variable wind under-predicted the measured flux while the model with constant wind speed over-predicted (Figures SI-3 to SI-6, Appendix 2). The lower standard deviations of the

residuals for the model with a constant wind speed of 3 m s^{-1} indicates that the constant wind speed results in a more accurate prediction of the measured flux for Puzzle Lake.

The mercury flux model produced by Boudala *et al.* (2000) was found to work well with the dataset from which it was produced ($r = 0.81$ for BDW Lake). However, as shown in Table 4-3, the data produced by the same predictive equation for the lakes in this current dataset did not correlate with the measured flux data as well ($r = 0.32$ for Puzzle and 0.63 for BDW). This is likely due to the lack of wind during the study period, and the strong wind dependence implicit in the model. The mean of the residuals for the Boudala *et al.* (2000) model were 0.9 ($\sigma = 3.38$) for Puzzle Lake and 1.0 ($\sigma = 2.45$) for BDW Lake. The distribution and means of the residuals indicated that the model over-predicted the measured flux (Figures SI-7 and SI-8, Appendix 2). The high standard deviation of the residuals also indicated that the modeled data did not accurately predict the measured data (Table 4-3).

Initial attempts were made to produce multivariate predictive equations based on the meteorology and Hydrolab™ readings collected during this study. Stepwise linear regression was performed on all variables and the standardized beta coefficients were examined to determine key variables. A multiple linear regression was performed on these key variables to produce predictive models for DGM in Puzzle and BDW Lakes. The predictive equations produced by this

type of analysis were found to fit the data quite well within the dataset used to produce the equations ($r > 0.80$, significance < 0.001), but did not show a causal relationship between the variables. The variables most important to DGM and mercury flux prediction often included water and air temperature, pH, and % relative humidity. Initial tests to develop more generalized predictive equations for DGM and flux were performed, based on the temperature difference between water and air. However, this approach did not accurately predict DGM or mercury flux either ($r < 0.2$). Predictive equations based on solar radiation and wind speed raised to the exponent of 1.5 (similar to the Boudala *et al.* (2000) model) were then created for Puzzle and BDW Lakes using multiple linear regression on the current dataset. These models were also found to have a poor relationship with measured flux.

Since the correlations with measured data were not high for empirical models based on wind and solar radiation (Boudala *et al.* (2000) models), we decided to examine the role of solar radiation in more detail. The high degree of temporal resolution in the dataset permitted an analysis of time-lags in the photo-production of DGM. Solar radiation was significantly correlated with DGM for both Puzzle and BDW Lakes ($r = 0.65$ and 0.55 respectively) but when the solar radiation data was time-shifted the correlations increased substantially. By time-shifting the solar radiation data (cross-correlation analysis), maximum correlations of 0.90 and 0.75 were observed between DGM and solar radiation for Puzzle and BDW Lakes respectively. This corresponds with time shifts of 65 and 90 minutes (Figure 4-3). That is, peaks and lows in solar radiation were

observed to occur 65 to 90 minutes before corresponding peaks and lows in DGM. Predictive models for DGM were then created based on solar radiation readings time-shifted by 75 minutes. Since DGM is a key variable in the determination of mercury flux, similar models based on solar radiation were developed for mercury flux.

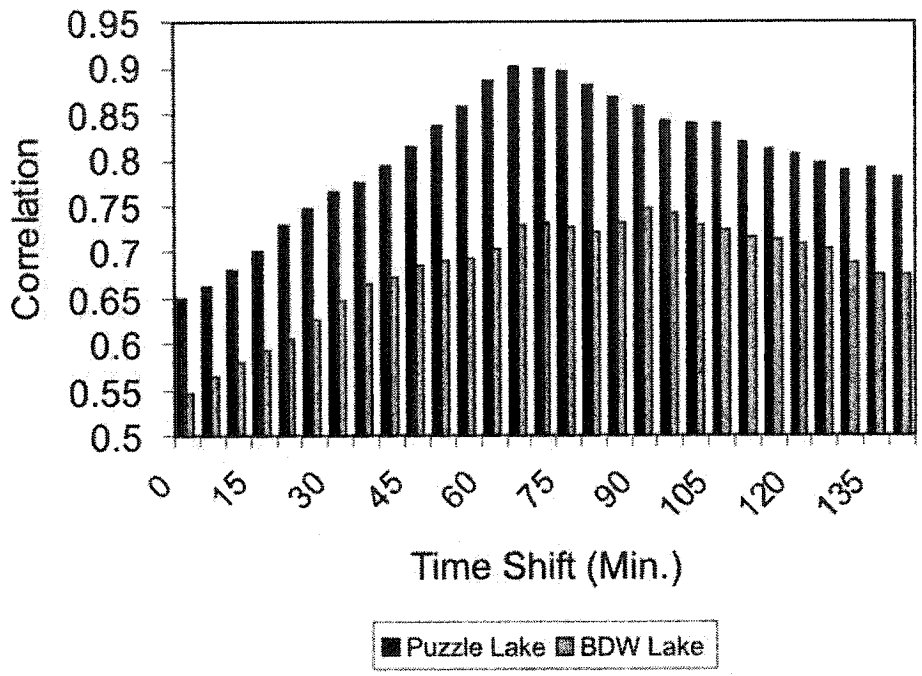

Figure 4-3: Cross-correlation analysis for DGM production and solar radiation in Puzzle Lake and Big Dam West Lake.

The equations developed using linear regression analysis for DGM and mercury flux are shown in equations 4-7 to 4-8 and 4-9 to 4-10, respectively.

$$DGM_{Puzzle}\ (pg\ L^{-1}) = 81.9\ Solar\ Radiation_{(75\ min\ prior)} + 12.8 \qquad \text{(Eq. 4-7)}$$

(r^2 = 0.80, significance <0.001)

DGM_{BDW} (pg L^{-1}) = 59.2 Solar Radiation $_{(75\ min\ prior)}$ + 59.2 (Eq. 4-8)

(r^2 = 0.53, significance <0.001)

$Flux_{Puzzle}$ (ng m^{-2} h^{-1}) = 9.48 Solar Radiation $_{(75\ min\ prior)}$ – 0.62 (Eq. 4-9)

(r^2 = 0.47, significance <0.001)

$Flux_{BDW}$ (ng m^{-2} h^{-1}) = 2.64 Solar Radiation $_{(75\ min\ prior)}$ + 0.46 (Eq. 4-10)

(r^2 = 0.53, significance <0.001)

4.5. Discussion

In this study we have evaluated previously published DGM flux models with continuously measured data and have found that these models were not good predictors of mercury flux over a diurnal period. Time-shifted solar radiation was found to be a good predictor of diurnal changes in DGM. Our results highlight the strengths of the current mercury flux models and suggest that incorporation of time-delayed photo-dependent processes may improve the models fit to measured data.

The continuous DGM analysis system was found to perform well in remote environments. The use of a closed-loop sampling system reduced the likelihood

of contamination, which can occur during manual sampling. The quick changes in DGM concentrations observed in samples by Siciliano *et al.* (2002) in a laboratory setting were confirmed during this analysis. The quick changes in DGM concentrations observed indicate that the maximum sample storage time may be much shorter than previously believed. Lindberg *et al.* (2000) indicate that loss rates in sample containers approaching 1 h^{-1} may be appropriate for DGM; this study suggests that significant changes can occur over a 20-minute period in lake water.

The data obtained at BDW and Puzzle Lakes compares well with previously published values for DGM in lake water. Krabbenhoft *et al.* (1998) observed similar diel patterns in the Florida Everglades (DGM concentrations ranging from 5 pg L^{-1} to 39 pg L^{-1} at solar noon). Amyot *et al.* (1994) found that lake water showed diel patterns in DGM concentrations ranging from approximately 40 – 120 pg L^{-1}. Zhang and Lindberg (2000) have also reported DGM values for Whitefish Bay, MI, of 29 +/- 12 pg L^{-1}.

There are several variables that have been proposed to affect DGM production in lakewater and the resulting mercury flux. Loux (2000) examined diel temperature effects on the water-to-air exchange of mercury, and observed significant changes in Henry's law constants that are not currently accounted for in mercury flux models. Another important factor in the production and volatilization of DGM is the level of dissolved organic carbon present in the lake water. DOC may act as a ligand, an intermediate photosensitizer of abiotic and biotic redox reactions,

or be directly involved in the redox reactions of mercury (Mackay and Yeun, 1983). Matthiessen (1998) found that an increase in pH resulted in an increase in elemental mercury production. This pH dependence was explained by the dissociation of phenolic functional groups in DOC. While Matthiessen (1998) observed no changes in DGM with changes in DOC, changes in the structure of the DOC were not explored in detail. Several researchers have observed diurnal patterns of hydrogen peroxide in surface waters and others have suggested that hydrogen peroxide can act as an oxidizing or reducing agent depending on the water's ORP, ionic strength, and the presence of ligands such as DOC (Brosset, 1987; Cooper and Lean, 1989; Cooper *et al.*, 1989b; Schroeder *et al.*, 1990).

In this study DGM concentrations were found to be consistently higher in the dark water lake (BDW) than in the clear water lake (Puzzle). BDW has a DOC concentration of 10.5 mg L^{-1} while Puzzle has only 3.6 mg L^{-1}. Nriagu (1994) reviewed the role that DOC may play in the photo-reduction of Hg(II) in lake waters. He noted that the interaction might be complicated by the ability of DOC to bind inorganic mercury as well as other reactions that might inhibit the role of DOC in photosensitization. Chlorine was also suggested as a competing ion that may inhibit photo-reduction in high concentrations. While admittedly the concentrations of chlorine are low, this relationship does not seem to hold true in this study since the chlorine concentration in BDW (4.84 mg L^{-1}) is higher than that of Puzzle (3.41 mg L^{-1}) (Table 4-2). The relationship between DOC content and freshwater photo-reduction is still unclear, as other researchers have observed no reduction of mercury by humic substances (Matthiessen, 1998).

While the mechanisms for producing DGM are still being explored, it is clear from the literature that solar radiation plays a major role (Amyot *et al.*, 1994; Boudala *et al.*, 2000; Zhang and Lindberg, 2001). Researchers have suggested photo-reductive processes and photo-induced microbiological processes follow trends in solar radiation. While a correlation has been observed between DGM and solar radiation in previous papers (Amyot *et al.*, 1994; Amyot *et al.*, 1997a), the level of detail was not sufficient to explore time-lag effects in a natural setting. In this study the maximum correlation between solar radiation and DGM occurred with a time-lag of 65 and 90 minutes for Puzzle and BDW Lakes, respectively. This suggests that the mechanisms involved in these photo-induced processes require over an hour to take place. It is also possible that the longer time-lag in BDW Lake is linked to lake water characteristics such as the quality and amount of DOC present. Hydrogen peroxide has been found to follow similar diurnal photo-production dynamics in freshwater lakes and also has recently been linked to microbial reduction mechanisms (Siciliano *et al.*, 2002; Sculley *et al.*, 1995). Interestingly, lab studies on Lake Ontario water found that modulation of DGM levels by hydrogen peroxide-induced microbial processes occurred with a time-lag on the order of 75 minutes (Appendix 1).

The DGM and mercury flux models examined in this study were linear regression models based on empirical data (Boudala *et al.*, 2000) or parameter-derived models based on lab experiments for a number of different chemicals such as in the work of Schroeder *et al.* (1992) and Poissant *et al.* (2000) The Poissant *et al.*

(2000) mercury flux model was found to be highly dependant on the wind speed variable due to its prominence in the calculation of the water mass transfer coefficient (see Eq. 4-5). Since the water mass transfer coefficient dominates the overall mass transfer equation, wind has a large effect on the predictive flux. While the use of this wind speed parameter seems intuitive, the model does not work well for low wind conditions. When a constant wind speed of 3 m s^{-1} (or 10.8 km h^{-1}) was applied to the Kejimkujik data the Pearson correlation between the predicted and actual flux increased from 0.27 to 0.69 for Puzzle Lake and from 0.47 to 0.83 for BDW Lake (Table 4-3). Previous tests of this model were performed with data collected under high wind speed conditions (25 – 30 km h^{-1} during the day) and therefore its applicability to low wind speed conditions was not explored (Poissant *et al.*, 2000).

Other researchers have had similar problems incorporating wind speed into predictive equations for mercury flux. Boudala *et al.* (2000) produced a flux model based on measurements of wind speed and solar radiation (taken over a 48-hour period) for BDW Lake. The parameters gave an equation of best fit with $r^2 = 0.81$. It was observed that the predicted values fit well with wind speeds in excess of 1.3 m s^{-1}, but tended to over-predict the flux when the wind speed was low. Unfortunately there were no extended periods with high wind speeds during the experiment, however we speculate that similar inaccuracies would have occurred with high winds. An examination of the Boudala *et al.* (2000) model displays its sensitivity to wind. A wind speed of 0 m s^{-1} will result in a 1.1 ng m^{-2} h^{-1} flux. However, with increasing wind speed the flux increases exponentially such

that with a constant solar radiation of 0.5 kW m^{-2}, increasing wind speeds of 0.5, 1, 5, and 10 m s^{-1} result in fluxes of 1.5, 2.3, 14.7, and 39.7 ng m^{-2} h^{-1}; respectively.

Wangberg *et al.* (2001) created a model similar to the Poissant *et al.* (2000) mercury flux model, however a slightly different calculation was employed for the effects of wind speed. Gas transfer velocities were calculated using equation 4-11 (Wanninkhof, 1992). However, wind speed still dominates the calculation, and the model will again in this case be inaccurate for low and high wind speed conditions.

$$K_w = 0.31\ U^2_{10}\ (Sc_{Hg}/\ Sc_{CO2})^{-0.5} \qquad \text{(Eq. 4-11)}$$

Where: K_w= the water mass transfer coefficient (m h^{-1}), U_{10} = wind speed at 10 meters above water (m s^{-1}), and Sc_{Hg} = the Schmidt number of mercury, and Sc_{CO2} = the Schmidt number of carbon dioxide (assumed to be 600 in freshwater at 20°C).

Similarly, a water-air mercury flux model proposed by Xu *et al.* (1999) attempts to account for changes in wind speed over 5 m s^{-1}, but does not work for very low wind speeds. The k_w for normal wind speeds in this model (< 5 m s^{-1}) is similar to that used in the work of Poissant *et al.* (2000) but is based on the experiments of Mackay and Yeun (1983) for organic molecules (Eq. 4-12). For wind speeds over 5 m s^{-1}, equation 13 is employed which attempts to account for changes in

friction velocities due to changes in surface roughness (Eq. 4-13).

$$K_w = 1.0 \times 10^{-6} + 144 \times 10^{-4} (U^*)^{2.2} Sc^{-0.5} \quad \text{(Eq. 4-12)}$$

Where: k_w = the mass transfer coefficient for water (m s^{-1}), U^* = wind speed <5 (m s^{-1}), and Sc = the Schmidt number of mercury.

$$K_w = 2.778 \times 10^{-6}\{[(69.8U-236.4)+W_c[115200-(69.8U-236.4)]\}Sc^{-0.5} + 2.778 \times 10^{-6}(-37/\alpha + 6120\alpha^{-0.37}Sc^{-0.18})W_c$$

(Eq. 4-13)

Where: k_w = the mass transfer coefficient, U = wind speed at 10 m (m s^{-1}), W_c = the fractional whitecap coverage linked to wind speed, and α = the Ostwald solubility.

None of the models presented in this paper are capable of modeling negative flux (deposition) values such as those observed in our dataset. This may either be a criticism of the models themselves or a problem with the flux measurement technique. Gustin *et al.* (1999) found that mean mercury flux rates on Nevada soil measured using the micromet method were nearly 3 times higher than those measured with the chamber method. It is still unclear whether these observed differences were due to actual analysis errors, differences in analytical design, or differences in site heterogeneity.

Issues related to the chamber method for the analysis of mercury flux have previously been examined in detail (Wallschlager *et al.*, 1999). One of the main criticisms of the chamber method has been the possible isolation of the water surface from the effects of wind. Assuming that increased wind increases water-to-air flux of mercury, this would imply that the flux values measured with the chamber are low. This, however, does not explain the over-predictions observed with the Schroeder *et al.* (1992) mercury flux model, since this model is largely based on changes in elemental mercury concentrations between air and water. In comparison, the Poissant *et al.* (2000) and Boudala *et al.* (2000) model predictions (which are largely wind biased) are periodically lower. The high flow rate through the Teflon chamber should have captured all volatile mercury such that any changes in flux would be detectable. When an artificial wind speed inside the chamber was assumed, the models still indicated a poor fit to measured data. The consistent flux rates and low levels of wind observed in this study indicate that wind was not a critical variable controlling mercury flux within this dataset.

While accurate and sensitive wind measurement techniques are clearly crucial to the testing of the models outlined in this paper, it is also obvious that the models themselves do not accurately reflect the role of wind in mercury volatilization over a wide range of wind speeds. The wind readings in this study are among the most accurate and sensitive that can be taken. The instrument employed would have easily recorded wind speeds less than 3 m s^{-1}, which is the wind speed required for the Poissant *et al.* (*2000*) mercury flux model to produce modeled

flux values close to the measured flux values. Interestingly, wind speeds less than 3 m s^{-1} have been found to result in laminar flow conditions over water (Valhos *et al.,* 1995). This fits well with the results obtained in this study that mass transfer models such as the Schroeder *et al.* (1992) estimate the observed flux as well as wind-adapted models.

The result of the modeling on Puzzle and BDW lakes indicates that diurnal trends in DGM can be predicted within a lake using time-shifted solar radiation values (Eq. 4-7 and Eq. 4-8). The slope of these equations are relatively close considering the differences between the two lake sites (81.9 in Puzzle and 59.2 in BDW). This suggests that solar radiation influences the diurnal dynamics of DGM in both lakes in a similar manner. Changes in the constant values in these equations are likely related to variations between lakes that do not display a strong diurnal pattern, but do vary substantially between lake sites and seasons (such as DOC and total mercury content). Such parameters must be assessed in the absence of photo-dependant reactions. The night time DGM value represents the level of DGM in each lake in the absence of solar radiation (13 pg L^{-1} for Puzzle and 59 pg L^{-1} in BDW). Since this night time value is quite different between the two lakes, a simplified DGM model for inter-lake variability would be useful to underlie the diurnal model. A combination of two such models would give the capability to predict DGM in any lake at any time of day. It is possible that night time DGM values could be used as a baseline for future DGM and mercury flux models. What has not yet been adequately described are variations in DGM with seasonal changes. This may yet prove to be an important area of

research and in the meantime the predictive equations presented here may only be considered valid for summer readings within these lake sites.

It is clear from this work that none of the mercury flux models examined were capable of accurately predicting the measured mercury flux in our dataset. In addition, time-shifted solar radiation alone was not found to be a good predictor of mercury flux with r^2 values of 0.47 and 0.53 for BDW and Puzzle lakes respectively (Eq. 4-8 and Eq. 4-9). However, these mercury flux models may be improved by the incorporation of variables that govern DGM dynamics, such as time-shifted solar radiation and DOC concentration. Wind speed is also an important variable affecting mercury flux, however it is not accurately incorporated into current models (predictions show poor fit to measured data particularly during low wind speed conditions). This work emphasizes the usefulness of on-site continuous analysis for examining diurnal trends in DGM. The observed time-lag between DGM and solar radiation is similar to recent time-lag observations by Siciliano *et al.* (2002) which link DGM production and destruction to sunlight-induced microbial processes (Appendix 1).

Chapter 5

EFFECTS OF DISSOLVED ORGANIC CARBON ON THE PHOTO-PRODUCTION OF DISSOLVED GASEOUS MERCURY (DGM) IN FRESHWATER LAKES

Reproduced in part with permission from: O'Driscoll, N.J., Lean, D.R.S., Losetto, L.L. and Siciliano, S.D. 2003. The effect of DOC on the photo-production of dissolved gaseous mercury (DGM) in freshwater lakes: Examining the potential impacts of forestry. *Environmental Science and Technology*. Submitted.

5.1. Abstract

The production of dissolved gaseous mercury (DGM) in freshwater lakes is induced by solar radiation, and is also thought to be linked to processes mediated by dissolved organic carbon (DOC). Studies investigating these processes using comparisons between lakes are often confounded by differences in DOC content and structure. In this study, we investigated the link between DOC concentrations and DGM production by using tangential ultrafiltration to manipulate DOC concentrations in water samples taken from a given lake. In this way, a range of samples with different DOC concentrations was produced without substantial changes to DOC structure or dissolved ions. This was repeated for four lakes in northern Quebec; two with highly logged drainage basins and two with minimally logged drainage basins. On two separate days for each lake, water samples (filtered free of microorganisims) with varying DOC concentrations were incubated in clear and dark Teflon bottles on the lake surface. Temperature and DGM concentrations were measured at 3.5-hour intervals over the course of 10.5 hours. Levels of DGM increased with increasing cumulative irradiation for all lakes until approximately 4000 kJ m^{-2} (400-750 nm, photosynthetically active radiation (PAR)), when DGM concentration reached a plateau (between 20 and 200 pg L^{-1}). If we assume that DGM production was limited by the amount of photo-reducible mercury, reversible first-order reaction kinetics fit the observed data well (r^2 ranging from 0.59 to 0.98). The DGM plateaus were independent of DOC concentrations but differed between lakes. In contrast photo-production efficiency (DGM_{prod}), *i.e.* the amount of DGM

produced per unit radiation (fg L^{-1} $(kJ/m^2)^{-1}$) prior to 4000 kJ m^{-2} PAR, was linearly ($P<0.0005$) proportional to DOC concentration. Furthermore, logged lakes had a lower DGM_{prod} per unit DOC ($P<0.006$) than the non-logged lakes. In these four lakes, the rate of DGM production per unit PAR was dependent on the concentration of DOC, with significant differences between lakes presumably due to different DOC structures and dissolved ions. These results are consistent with the observation that elevated levels of mercury exist in biota in lakes with logged drainage basins.

5.2. Introduction

Production of DGM is an important process in lakes, as DGM is the primary form of mercury that can volatilize from the water surface to the atmosphere. The production and evasion of DGM from lakes is an important means by which lakes can reduce their mercury pool. Our recent research observed a direct link between the formation of DGM in lake water and water-to-air mercury flux over a diurnal cycle (O'Driscoll *et al.*, 2003b). Existing models failed to accurately predict the measured DGM flux (O'Driscoll *et al.*, 2003b), which may reflect the uncertainty surrounding factors that affect rates of mercury photo-reduction and photo-oxidation in freshwaters.

Solar radiation induces both chemical (Amyot *et al.*, 1997a) and microbial (Siciliano *et al.*, 2002) mercury reduction in lake water. These reactions likely involve other variables, including dissolved ions, availability of photo-reducible

mercury, and DOC concentration (Amyot *et al.*, 1997a; 1997b; 1997c; Nriagu, 1994; Zhang and Lindberg, 2001). DOC is widely acknowledged to be important in the photo-reduction of mercury (Matthiessen, 1996, 1998), but the exact manner in which DOC affects DGM production is not known.

Watras *et al.* (1995) sampled surface water from 23 Northern Wisconsin lakes and found that increasing DOC concentration was related to an exponential decrease in the ratio of DGM to total mercury. Xiao *et al.* (1995) spiked water samples with 100 nM of mercury and found that increases in DOC concentration corresponded with significant increases in DGM photo-production. Amyot *et al.* (1997b) sampled water from low DOC Artic lakes, spiked it with 1-8 mg L^{-1} of fulvic acids and exposed it to varying levels of solar radiation without observing any significant changes in DGM. Yet, in another study Amyot *et al.* (1997a) compared a low DOC lake (2.2 mg L^{-1}) with two higher DOC lakes (8.7 and 5.0 mg L^{-1}) and found that hourly DGM production was 1.8 and 7.7 times higher in the low DOC lake as compared to the two high DOC lakes (Amyot *et al.* 1997a). In contrast to these results, we have observed DGM concentrations in surface water in southern Nova Scotia that were 2-4 times higher in a high DOC (10.5 mg L^{-1}) lake as compared to a low DOC (3.6 mg L^{-1}) lake over a 48-hour period (n = 576) (See Chapter 4; O'Driscoll *et al.*, 2003b).

Part of the reason for such conflicting reports on the role of DOC in mercury photo-reduction processes is that DOC may differ between lakes, not only in

concentration but also in structure. Thus, comparing DGM production in lakes of differing DOC contents is confounded by inherent differences in DOC structure and the unknown impact that these may have on the processes being examined. Consequently, in order to accurately study the effects of DOC concentration on DGM production, the DOC within a lake must be changed in concentration without changing other variables. Such an approach would allow for the assessment of photo-production rates while avoiding the confounding effects of DOC structure.

The separation of DOC from lake water has been achieved in the past using various methods, including XAD extraction, liquid chromatography (O'Driscoll and Evans, 2000), ultrafiltration, tangential ultrafiltration, and reverse osmosis (Clair *et al.*, 1991; Sun *et al.*, 1995). XAD extraction and liquid chromatography involve drastic pH changes (2-10) or the addition of buffers that may alter DOC structure or result in aggregation and physical trapping of adsorbed material (Town and Powell, 1993). Ultrafiltration can be prone to clogging of membranes and binding of metals to membrane surfaces, and is generally used for samples of small volume (Weber, 1988). Reverse osmosis has been found to be an efficient method for concentrating large volumes of DOC in lake water, however, the small pore sizes used in this process result in a concentration of inorganic ions in the retentate (Clair *et al.*, 1991) that may affect photo-reduction processes (Zhang and Lindberg, 2001). Tangential ultrafiltration is therefore the method of choice for altering DOC concentrations in large volumes of lake water, since it involves no chemical alterations, causes no clogging of pores, and the concentration of

inorganic ions (smaller than the membrane pore size) remains largely unchanged during separations (Barbiarz *et al.*, 2000; Hoffmann *et al.*, 2000).

Previous research has indicated that logging of a drainage basin may increase mercury in the biota of the associated lake (Garcia and Cariganan 1999; 2000). However, the mechanism that results in increased bioaccumulation with logging is unclear. The purpose of this study was to examine the effects of DOC concentration on the photo-production of DGM in two freshwater lakes with logged drainage basins and two non-logged lakes in northern Quebec. For each lake, tangential ultrafiltration was used to produce water samples of different DOC concentrations while minimizing the changes in dissolved ions and DOC structure that can occur with alternative DOC extraction methodologies.

5.4. Site Description

Four lakes in northern Quebec were chosen to represent a range of DOC concentrations within both logged and non-logged drainage basins. Table 5-1 lists some of the physical and chemical characteristics of each lake. Lakes K2 and N70 have catchments where very little logging has occurred (0 and 2 % of basin, respectively), and have DOC concentrations of 6.7 and 3.2 mg L^{-1}, respectively. In contrast, lakes K3 and DF9 have logged catchments (26 and 67 % of basin, respectively) and DOC concentrations of 4.9 and 13.7 mg L^{-1}, respectively (See Tables 5-1 and 5-2). All lakes are relatively small (< 1.5 km^2) and are well saturated with oxygen (>94%) (See Table 5-1).

Characteristic	Units	N70	K2	K3	DF9
Latitude	(° ' ")	48°05'12"	48°17'56"	48°18'26"	48°42'31"
Longditude	(° ' ")	75°29'09"	75°10'08"	75°16'18"	75°01'03"
Altitude Above Sea Level	(m)	439	415	414	406
Lake Area	(km^2)	0.654	1.421	0.829	0.421
Averae Catchment Slope	(%)	9.2	4.6	4.6	3.3
Maximum Lake Depth	(m)	20.4	12.2	7.2	10.5
Lake Volume	(m^3)	4,417,080	6,144,649	2,321,023	1,398,745
% Wetlands in Catchment Basin	%	2.46	4.44	10.98	3.18
Cumulative % of Basin Logged Since 2000	%	0	2	26	67
Shoreline	(km)	4.04	11.85	5.37	2.95
Oxygen Saturation	%	94.9	95.2	95.2	95.3
Secchi Depth	(m)	3.53	1.72	3.11	1.04
Chemical Oxygen Demand	($mg\ L^{-1}$)	5.5	8.8	6.5	16.3
Total Phosphorous	($ug\ L^{-1}$)	5.1	8.7	9.8	15.6
Total Nitrogen	($ug\ L^{-1}$)	226	312	285	507
NO_3	($ug\ L^{-1}$)	0.5	8.8	0.5	7.0
Cl^-	($mg\ L^{-1}$)	0.113	0.100	0.129	0.218
SO_4^-	($mg\ L^{-1}$)	0.75	0.67	0.49	0.46
Na^+	($mg\ L^{-1}$)	0.66	0.53	0.50	0.61
K^+	($mg\ L^{-1}$)	0.232	0.212	0.298	0.774

Table 5-1: Physical and chemical characteristics of the lakes sampled and their associated drainage basins.

5.5. Methods

Surface water (>200 L) was collected from each of four lakes with contrasting DOC concentrations in northern Quebec. Samples were taken near the water surface in the centre of the lake. The water was collected in 25 L high-density polyethylene (HDPE) containers and transported in the dark to the analysis site within one hour using a floatplane. High-density polyethylene was chosen for its

cost-effectiveness, ease of handling and suitability for subsequent mercury analysis (Hall *et al.*, 2002).

At the analysis site near Lake Berthelot, Quebec, the lake water was sterilized using a Centramate PE Lab Tangential Flow System (Pall Corporation), which is constructed with ultra-high molecular weight polyethylene. All tubing was Teflon, with the exception of a 20 cm piece of polypropylene used for the peristaltic pump. Omega™ polyethersulfone cassette filters were used to remove all particles greater than 0.2 µm. The 0.2 µm filter was used with an inlet pressure of 8 PSI and no backpressure. The resulting sterilized lake water is referred to as "whole water" for the remainder of this study.

A portion of the whole water for each lake was then filtered further through an Omega™ polyethersulfone 1 kDa filter (1 kDa water) to remove most of the DOC while allowing dissolved ions to remain in the filtrate. The 1 kDa filter was used with an inlet pressure of 10 PSI and a back pressure of 8 PSI. Tangential flow ultrafiltration has been found to be a useful technique for mercury and DOC fractionation (Barbiarz *et al.*, 2000; Hoffmann *et al.*, 2000). As recommended (Babiarz *et al.*, 2000; Hoffmann *et al.*, 2000), membranes were preconditioned with lake water for 120 minutes before use and a concentration factor of 2 was used during filtrations.

Dilutions of the "whole water" from each lake were prepared using the 1 kDa filtered water, to produce samples with a range of DOC concentrations with

minimal changes to dissolved ions. Dilutions were prepared in 1 L Teflon bottles at 0, 10, 50 and 100%.

A DOC-free permeate (R.O. Permeate) from the lake water at two of the four lakes (K2 and N70) was obtained using a RealSoft™ portable reverse osmosis system PROS/1S with 0.5 µm glass fibre pre-filter. A detailed explanation of this method has been given by Sun *et al.* (1995). The R.O. permeate was used to make further dilutions of the 1 kDa filtrate from the two lakes, and dilutions were incubated with the whole water dilutions. These additional dilutions with negligible DOC and dissolved ion concentrations were sampled and analyzed along with the rest of the dilutions to examine the effect of small molecular weight DOC on DGM photo-production.

Samples of each whole water dilution were sub-sampled for the analysis of DOC and total mercury. All sub-samples were collected in 50 mL polypropylene centrifuge tubes (Falcon). Total mercury samples were preserved by the addition of 1% BrCl (Hall *et al.*, 2002) and refrigerated until analysis by EPA method 1631 (cold vapour atomic fluorescence). DOC samples were kept cold until analysis by 100° C persulfate wet oxidation and CO_2 detection by infrared spectroscopy (OI Corporation Model 1010 wet oxidation TOC analyzer).

For each lake, the dilutions of whole water (0, 10, 50, 100%) were placed in clear and black 1L FEP Teflon bottles, which were then partially submerged in lake water using a floating platform (Figure 5-1) and exposed to sunlight for a total of

10.5 hours. Solar radiation was measured every 15 minutes using an Optikon™ 754 spectra-radiometer with quartz spectral probe. Scans were taken at 10 nm intervals between 280 – 800 nm and integrated to obtain measurements of cumulative UVB (300-320 nm), UVA (320-400 nm), and photosynthetically active radiation (PAR) (400-700 nm). Water temperature was measured at 3.5-hour intervals using a digital thermometer.

Samples for each whole water dilution were collected at 3.5-hour intervals and analyzed for DGM on-site (in order to minimize the changes in DGM concentration that can result from delays in sample analysis). The method employed for discrete DGM analysis (see Chapter 3; O'Driscoll *et al.*, 2003a) is similar to methodology employed by Amyot *et al.* (1997a; 1997b; 1997c) and Lindberg *et al.* (2000). The analysis system can be used to measure DGM in 1L water samples (discrete mode) or continuously from a water reservoir (continuous mode) (O'Driscoll *et al.*, 2003a). In short, the analysis system consisted of a 1L glass volumetric sparger and Tekran™ 2537A air analysis unit. When analyzing a discrete sample a 1 L sample was bubbled for 30 minutes using mercury-free air. The volatile mercury was then measured by gold amalgamation / atomic fluorescence spectrometry.

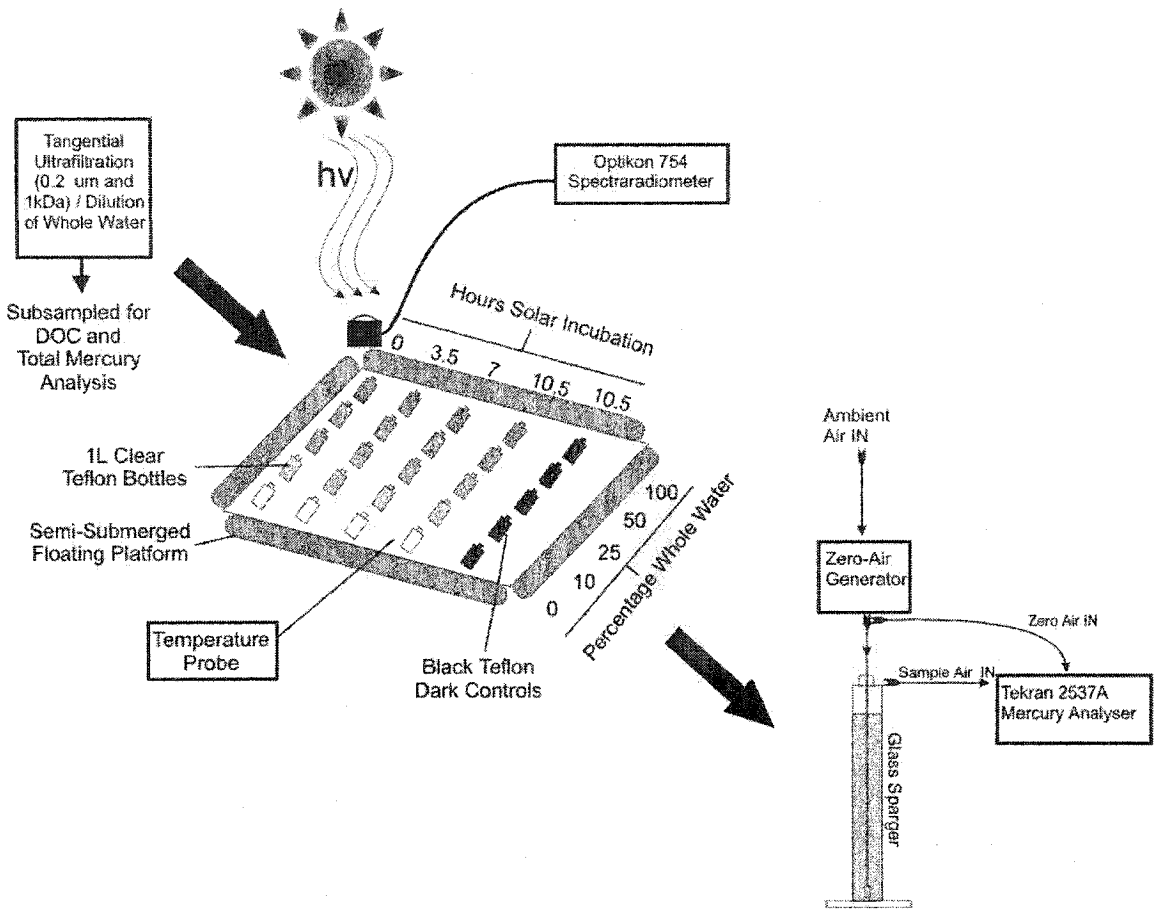

Figure 5-1: Flow diagram of sample preparation, incubation, and DGM analysis methods.

For each lake, the entire experiment from the original filtration and dilutions of whole water was repeated twice on two consecutive days. This allowed us to investigate the influence of a wider range of cumulative solar radiation values on DGM production.

5.6. Data Analysis

5.6.1. Solar Radiation Measurements

Visible, or photosynthetically active (PAR) radiation has been suggested to be an important portion of the spectrum for DGM production. Amyot *et al.* (1997c) observed that seawater exposed to PAR, UV_A, and UV_B radiation resulted in 46, 31, and 23% of total DGM production respectively. To date, however, no quantum yield estimates have been made for specific wave bands. In this study, PAR is the portion of the total incoming irradiance that is discussed relative to DGM. It is assumed that since all samples were exposed to the same full spectrum of incoming radiation, the relationship between UVA, UVB, and PAR will be relatively constant for each sample during the course of the incubations. This was supported by strong Pearson correlations between PAR and UVA, and PAR and UVB values measured in this study (0.99 and 0.95, respectively, with significance at the 0.01 level (two-tailed). The distribution of total incoming radiation (280 – 800 nm) was found to be consistent over the course of the incubations for each range of wavelengths. The following percentages were observed relative to total radiation: PAR 400 to 750 nm (mean = 78%, σ = 9.2 %, n = 293), UVA 320 to 400 nm (mean = 13%, σ = 3.4%, n = 293), and UVB 280 to 320 nm (mean = 0.7%, σ = 0.42%, n = 293). Since the relative importance of UVA and UVB to photo-reduction is unclear, and since the proportion in surface waters is constant PAR is a useful and easily measured surrogate.

When discussing PAR relative to changes in DGM, we used total cumulative incoming PAR, even though we know that only a portion of this radiation is absorbed by the samples. Amyot *et al.* (1997a) noted that 1 L Teflon Bottles of the type used in these experiments have a longitudinal section of 0.016 m^2 and therefore the number of photons received is relative to the absorption spectrum of the lake water and the radiant flux density. Teflon bottles have been shown by Amyot *et al.* (1997c) to result in a decrease in irradiance of 18 % of UVA, 34 % UVB, and 0.7 % PAR. Again, since all samples were consistently exposed to the same incoming radiation, we have presented our results in terms of total cumulative PAR to simplify interpretations and make application to modeling efforts easier.

5.6.2. Kinetic Equations and DGM Dynamics

The data show that DGM levels in all samples reached a plateau after approximately 4000 kJ m^{-2} of cumulative radiation (samples from lake DF9 plateau slightly before 4000 kJ m^{-2}). Since cumulative solar radiation continued in each experiment to increase beyond 4000 kJ m^{-2} throughout the day, it is hypothesized that availability of photo-reductants (created by interaction of solar radiation with dissolved ions and DOC) was not the factor limiting DGM production during the course of the incubations. Instead, the observed plateaus of DGM values are attributed to the balance of photo-reduction and photo-oxidation.

DGM dynamics can be modeled as a single reversible reaction, where the available photo-reducible mercury ($Hg_{reducible}$) is converted to dissolved gaseous mercury (DGM) by a number of photo-reductants, as shown in Eq 5-1. Assuming photo-reductants are present in excess, their concentration can be considered unchanged throughout the reaction and we can ignore them in the equation.

$$[Hg_{reducible}] + \text{Photo-Reductants} \leftrightarrow [DGM] \qquad \text{(Eq. 5-1)}$$

If we then assume that DGM is zero at time zero and the kinetic equation for products has a forward rate constant k_1 and a backward rate constant k_2, we can derive equation 5-2 (as outlined by Steinfeld *et al.*, 1998; Chapter 2).

$$DGM = (k_1[Hg_{reducible}]_0 / (k_1 + k_2))\ [1-e^{-(k1 + k2)\, t}] \qquad \text{(Eq. 5-2)}$$

In order to fit these equations to graphs of cumulative solar radiation versus DGM concentrations, we can replace time with cumulative solar radiation (x). This results in equations that have rate constants with units L pg^{-1} $(kJ/m2)^{-1}$ as opposed to the traditional L mol sec^{-1}. Since DGM is not equal to zero at the beginning of the incubations, an initial DGM constant has been added to equation 5-2. These changes result in equation 5-3.

$$DGM = [DGM]_0 + (k_1[Hg_{reducible}]_0 / (k_1 + k_2))\ [1-e^{-(k1 + k2)\, x}] \qquad \text{(Eq. 5-3)}$$

Where: [DGM] = concentration of DGM (pg L^{-1}) at cumulative radiation x, $[DGM]_0$ = the amount of DGM present at the onset of incubations (pg L^{-1}), $[Hg_{reducible}]_0$ = the amount of photo-reducible mercury available at the onset of incubations, k_1 =the rate constant for the forward (reduction) reaction (L pg^{-1} $(kJ/m^2)^{-1}$), k_2 = the rate constant for the backward (oxidation) reaction (L pg^{-1} $(kJ/m^2)^{-1}$), and x = cumulative PAR (kJ m^{-2}).

By setting parameters a and b as follows:

$$a = (k_1[Hg_{reducible}]_0/ (k_1 + k_2) \quad \text{(Eq. 5-4)}$$

and

$$b = k1 + k2 \quad \text{(Eq. 5-5)}$$

we can re-write equation 5-3 as equation 5-6:

$$DGM = [DGM]_0 + a[1-e^{-b\,x}] \quad \text{(Eq. 5-6)}$$

Equation 5-6 was fit to the data for DGM production with cumulative PAR and parameters a and b derived. Sigma Plot 2001 software was used for the non-linear regression. All equations converged such that the tolerance was satisfied within the following equation options; iterations = 100, step size = 100, and tolerance = 1×10^{-10}.

The DGM concentration at the plateau for each of the fractions was calculated by setting x = 10,000 kJ m^{-2}, which is the approximate daily maximum cumulative PAR during the incubation time, and then solving for [DGM].

5.6.3. Initial DGM Production Efficiency (DGM_{prod}) Calculations

Linear regression was used to determine the slope of DGM concentrations vs. cumulative solar radiation (PAR), prior to 4000 kJ m^{-2}. Linear regression was considered appropriate since the error on the x-axis was considerably less than on the y-axis (< 5%).

A univariate general co-linear model (ANCOVA) was used in the SPSS 10.0 statistical package to determine the relationships between photo-production efficiency, DOC and the fixed factors (logged and non-logged sites).

5.7. Results

5.7.1. Analysis of DOC and Total Mercury

The original DOC levels in the four lakes sampled (i.e. 100 % whole water) ranged from 3.2 to 13.7 mg L^{-1}. The DOC results for the whole water dilutions for each lake (Table 5-2) indicate that DOC concentrations were substantially

decreased with dilutions using 1 kDa filtrate. The 1kDa filtrate should have contained only the fraction of DOC smaller than 1 kDa, and the data show that this ranged between 8 and 19 % of the total DOC found in the whole water samples from the four lakes. Total mercury in the whole water dilutions from the four lakes ranged between 0.5 and 8.7 ng L^{-1}, which was far in excess (5 to 90 times) of the DGM measured in the samples during incubation (< 0.1 ng L^{-1}). The fraction of total mercury that is available for photo-reduction is unknown. Reverse Osmosis Permeates for lakes K3 and N70 were found to contain DOC concentrations that were below detection limits (<0.01 mg L^{-1}).

Lake	% Whole Water	Total Mercury (ng L^{-1})	SD	DOC (mg L^{-1})
K2	0	1.1	0.01	0.9
K2	10	0.8	0.02	1.3
K2	25	0.8	0.25	2.3
K2	50	1.2	0.15	5.1
K2	100	1.9	0.50	6.7
K3	0	1.6	0.26	0.4
K3	10	1.0	0.35	1.1
K3	25	2.0	0.34	1.6
K3	50	3.3	2.93	2.7
K3	100	3.3	0.33	4.9
DF9	0	1.6	1.18	2.3
DF9	10	2.6	0.97	3.8
DF9	25	2.9	0.72	5.0
DF9	50	5.2	1.30	8.1
DF9	100	8.7	2.30	13.7
N70	0	0.7	0.07	0.6
N70	10	0.5	0.63	1.0
N70	25	0.7	0.55	1.2
N70	50	0.9	0.30	1.6
N70	100	1.0	0.49	3.2

Table 5-2: Total mercury and dissolved organic carbon concentrations for each series of whole water dilutions performed in the four lakes sampled.

5.7.2. Modeling DGM Dynamics

Graphs of cumulative PAR versus DGM for the five whole water dilutions for each of the 4 lakes sampled are shown in Figures 5-2 to 5-5. Equation 5-6 was found to fit the measured data well, with r^2 ranging between 0.59 and 0.98. The lowest r^2 values were observed for data collected at Lake N70.

5.7.3. Examination of DGM plateaus

Within each whole water dilution for the four lakes studied, DGM concentration was observed to increase with cumulative solar radiation until approximately 4000 kJ m^{-2}, where it began to plateau. The DGM concentration at which this plateau was reached was calculated for each of the dilutions. The mean DGM concentration (for all dilutions) at plateau for each lake site is shown in Figure 6. The mean DGM concentration at plateau for all samples was 72 pg L^{-1} (σ = 40.3). DGM plateau concentrations were tested for normality of residuals and homogeneity using the Anderson Daily normality test and Levene's test, respectively, and analysed by ANOVA to test for differences between dilutions and between lakes. The ANOVA results indicated that DGM plateau concentrations were independent of dilution factor ($p<0.41$), but differed ($P<0.001$) between lake sites (Figure 5-6). Due to the small data set combined interactions between factors could not be examined.

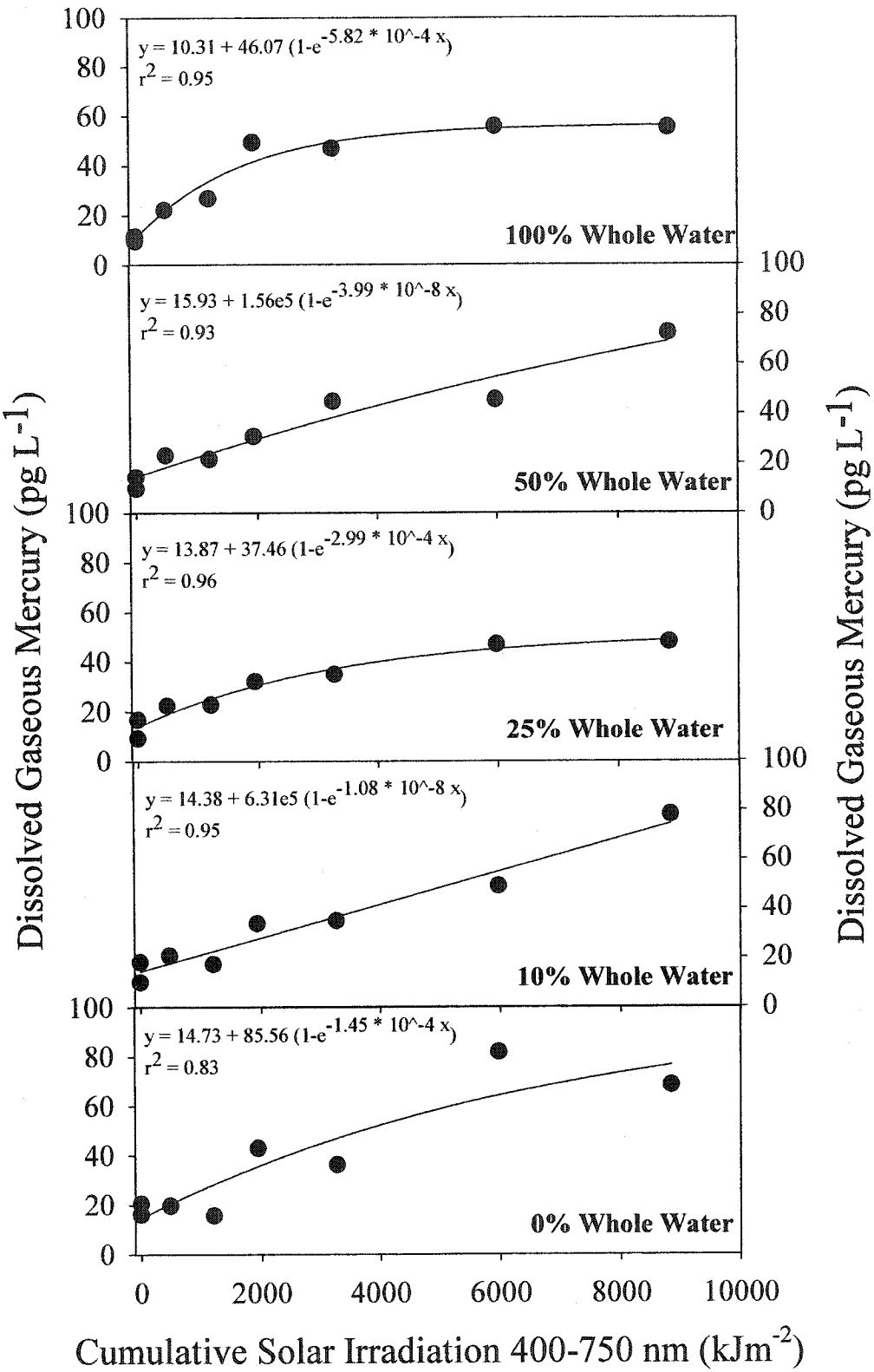

Figure 5-2: Cumulative PAR (kJ m^{-2}) versus dissolved gaseous mercury (pg L^{-1}) for each DOC dilution in Lake K3. Solid line represents regression of the form $y = y_o + a\,(1-e^{-bx})$ with equation on graph.

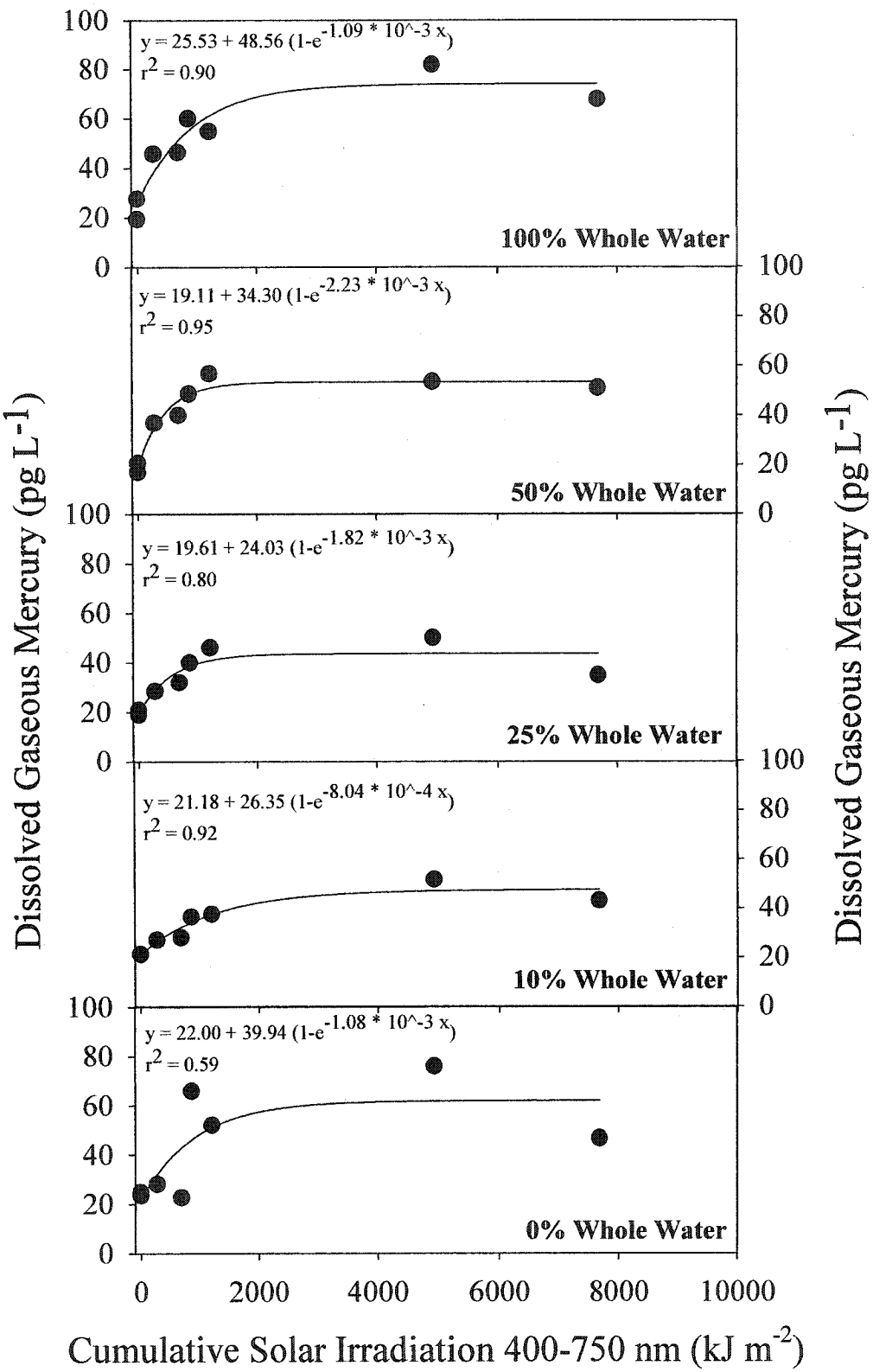

Figure 5-3: Cumulative PAR (kJ m^{-2}) versus dissolved gaseous mercury (pg L^{-1}) for each DOC dilution in Lake K2. Solid line represents regression of the form $y = y_o + a\,(1-e^{-bx})$ with equation on graph.

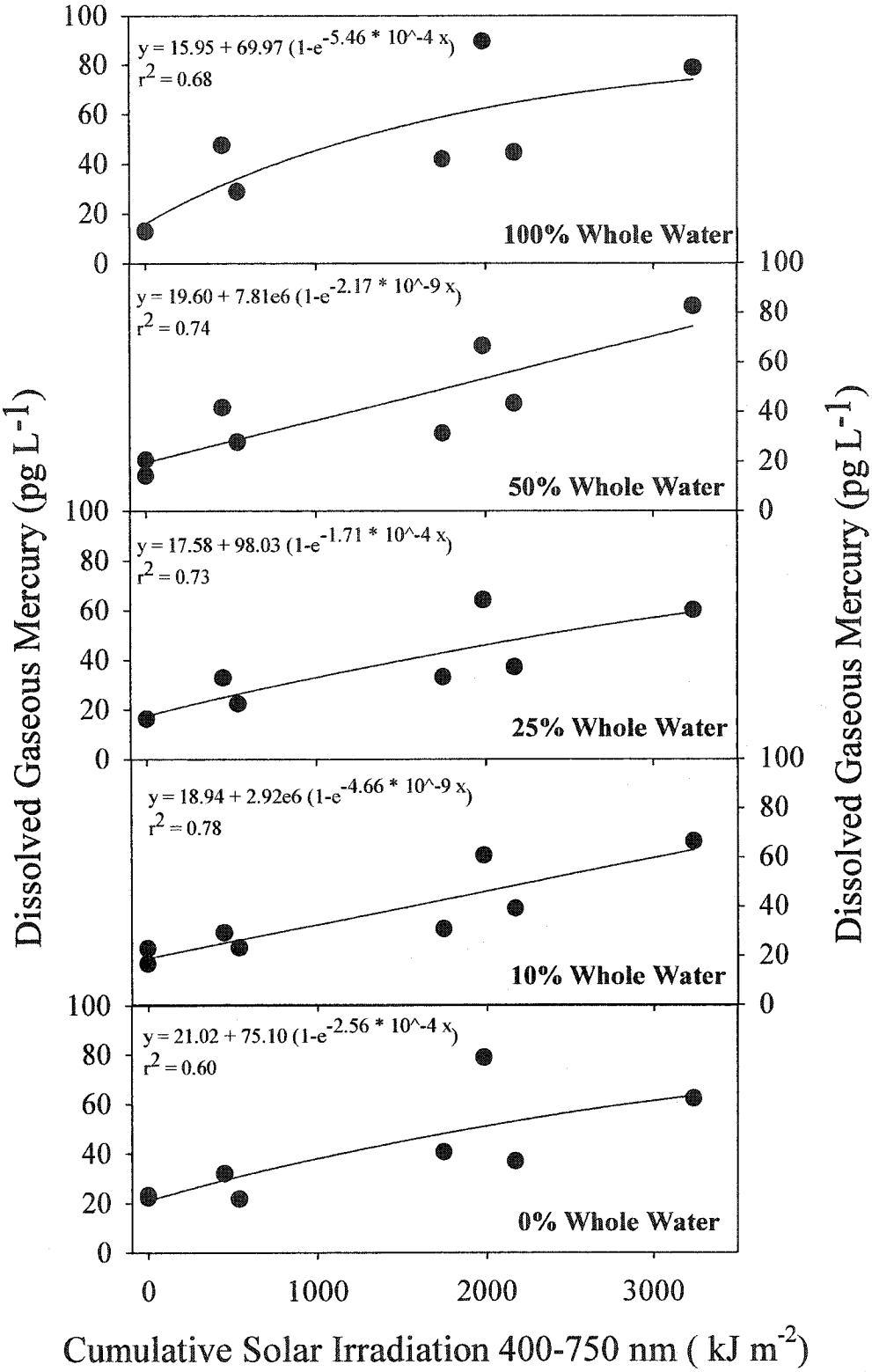

Figure 5-4: Cumulative PAR (kJ m^{-2}) versus dissolved gaseous mercury (pg L^{-1}) for each DOC dilution in Lake N70. Solid line represents regression of the form $y = y_o + a\,(1-e^{-bx})$ with equation on graph.

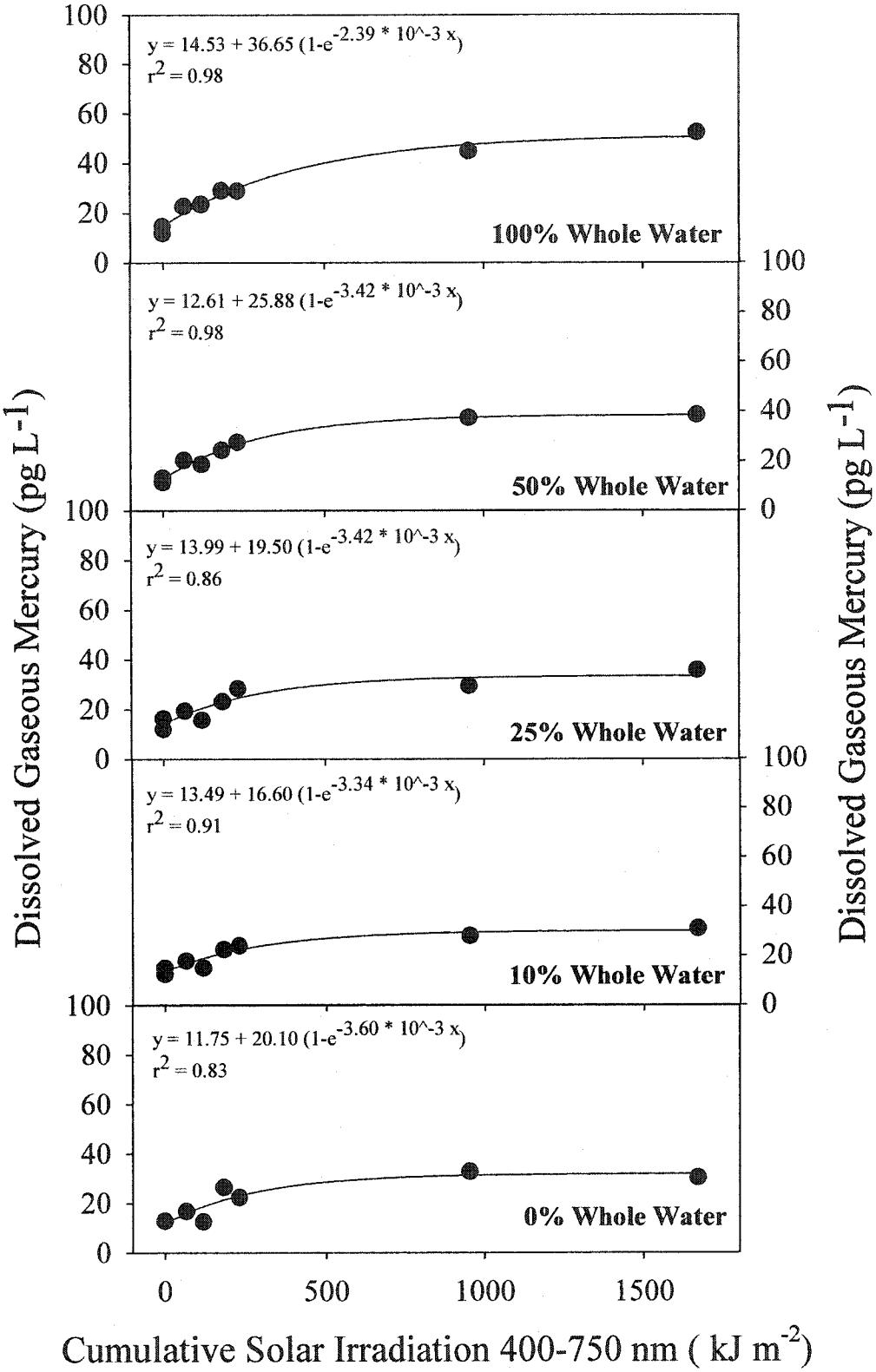

Figure 5-5: Cumulative PAR (kJ m^{-2}) versus dissolved gaseous mercury (pg L^{-1}) for each DOC dilution in Lake DF9. Solid line represents regression of the form $y = y_o + a\,(1-e^{-bx})$ with equation on graph.

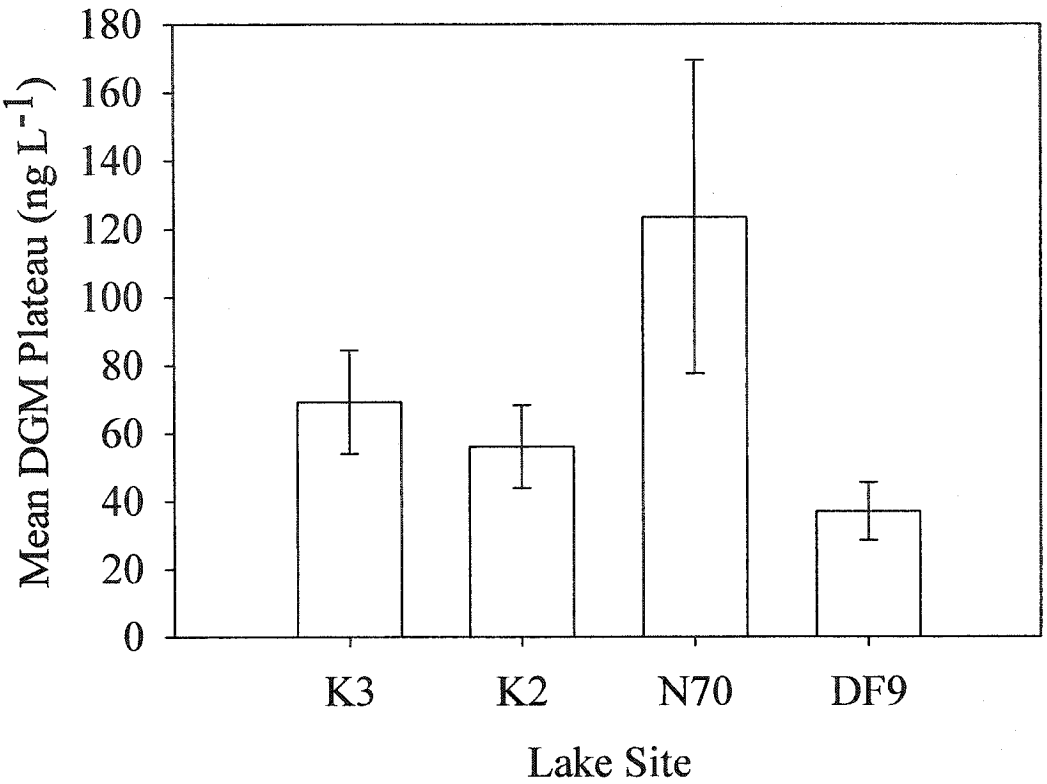

Figure 5-6: Mean DGM plateau for all whole water dilutions for each lake site.

5.7.4. Reverse Osmosis Dilutions

As shown in section 5.7.3., no significant differences between DGM plateaus for different dilutions were observed ($p<0.41$); that is, within a given lake, DGM production appeared to be leveling off at about the same concentration regardless of the strength of the DOC dilution. This suggested that whatever was

affecting the balance between DGM production and oxidation (dissolved ions or DOC) was present in sufficient quantity even in the weakest of our whole water dilutions (1 kDa filtrate). To test this, 1 kDa filtrates from lakes K3 and N70 were further diluted with reverse osmosis filtrate to 1 kDa filtrate concentrations of 100, 50, 25, and 10%. These dilutions were incubated for 7 hours with the same cumulative PAR exposure as the whole water dilutions. Subsequent linear regression analysis indicated that there was no significant relationship between DGM concentrations and percentage dilution (r^2 = 0.5, $p<0.185$ for lake K3 and r^2 = 0.02, $p<0.803$ for lake N70). However, average DGM for all reverse osmosis permeate dilutions was 45 (σ = 7.9) pg L^{-1} for lake K3 and 73 (σ = 7.7) pg L^{-1} for lake N70 were similar to the results obtained with whole water dilutions. These results indicated that changes in the dissolved ions and DOC concentrations that should have resulted from further dilutions of the 1kDa filtrate did not affect the DGM plateau.

5.7.5. DGM Photo-Production Efficiency and DOC

DGM photo-production efficiency (DGM_{prod}) was calculated for each whole water dilution as the slope of the best-fit line obtained for DGM concentration (fg L^{-1}) vs. cumulative PAR (kJ m^{-2}), prior to the plateau at approximately 4000 kJ m^{-2}. These linear regression calculations resulted in slopes that were significant (<0.043) with the exception of two slopes (lake K2 0% whole water and lake K3 0% whole water) that were close to being significant (0.093 and 0.078, respectively). DGM_{prod} ranged between 7 and 30 fg L^{-1} $(kJ/m^2)^{-1}$ for all samples

analyzed. In contrast to the DGM plateau concentrations, a positive relationship was observed between DGM_{prod} and DOC concentration for the four lake sites studied (Figure 5-7).

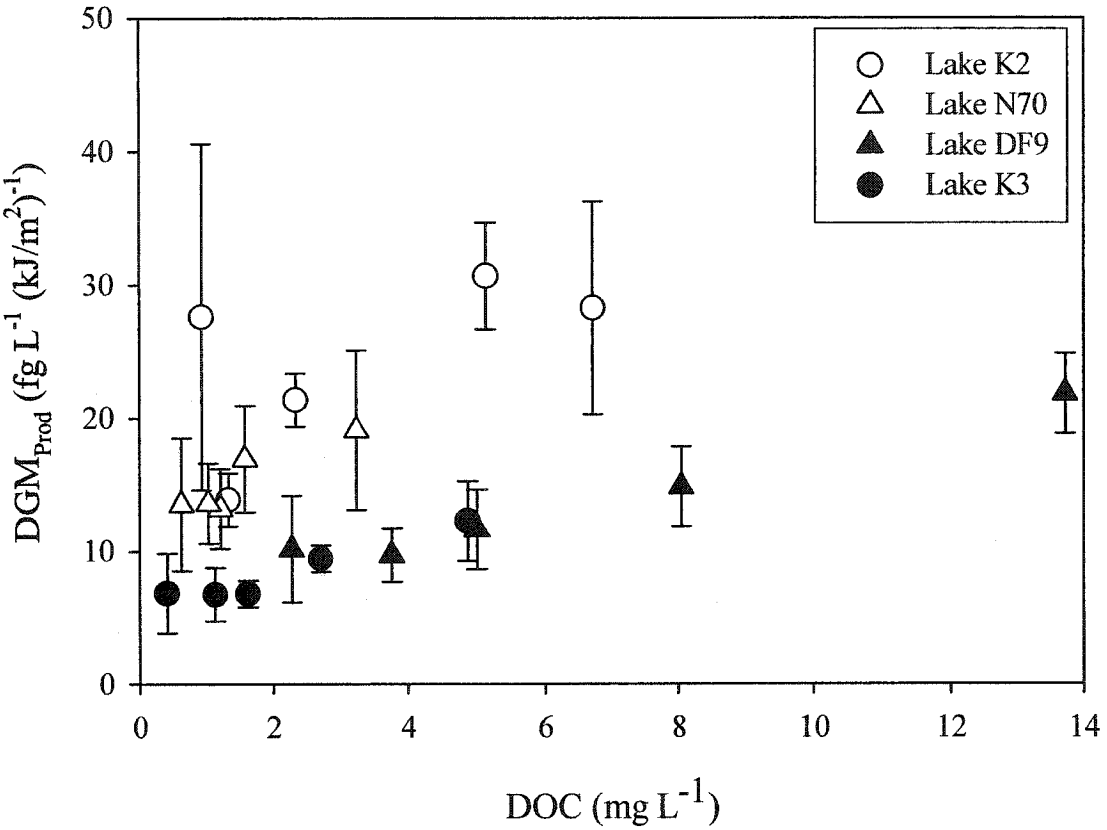

Figure 5-7: Relationship between DOC (mg L^{-1}) and DGM Prod (fg L^{-1} $(kJ/m^2)^{-1}$). Open markers represent non-logged lakes and closed markers represent logged lakes.

The relationship between DGM_{prod}, DOC concentrations, and logging of drainage basins was further analyzed using ANCOVA. The analysis indicated that DGM_{prod} in non-logged lakes (mean = 20, σ = 7) was double ($p<0.006$) that of logged lakes (mean = 10, σ = 5) investigated in this study. It was also found that DGM_{prod} significantly increased with DOC concentration ($p<0.0005$). The combined interactions of DOC concentrations and logging of drainage basins were not found to significantly affect DGM_{prod} ($p<0.069$) in this study, but it should be noted that the interaction is close to being significant and may be significant within a larger dataset.

5.8. Discussion

In this investigation, we systematically varied DOC concentration with minimal changes in lake chemistry or DOC structure and observed DGM dynamics in sterile lake water. We found that DGM production was closely linked to DOC concentration and that within our dataset lakes with logged drainage basins have lower efficiency of DGM production.

5.8.1. Modeling DGM Dynamics

Both photo-reduction and photo-oxidation of mercury are known to be important processes in DGM dynamics. Various mechanisms for mercury photo-reduction and more recently mercury photo-oxidation (Lalonde *et al*, 2001) have been

suggested. The following is a brief summary of this work and its application to our results.

5.8.1.1. Theoretical Mechanisms for Photo-Reduction

There are many photo-produced reductants that may result in the conversion of inorganic mercury to DGM. Several researchers (Cooper *et al.*, 1989; Zepp *et al.*, 1987) suggest that DOC absorbs solar radiation to emit aqueous electrons (Eq. 5-7), which are then available to reduce mercury (Eq. 5-8).

$$[DOC] + hv \rightarrow [DOC?^{+}] + e^{-}_{(aq)} \qquad \text{(Eq. 5-7)}$$

$$2\ e^{-}_{(aq)} + [Hg^{2+}] \rightarrow [Hg^{0}] \qquad \text{(Eq. 5-8)}$$

Zepp *et al.* (1987) suggest that a realistic quantum yield for the aqueous electron in natural waters is 0.17×10^{-3} to 1.2×10^{-3}. Taking into account quenching by oxygen and normalizing for DOC, Zepp *et al.* (1987) determined a steady state concentration of 2×10^{-17} mol L^{-1} for the aqueous electron. It should be noted that this calculation overestimates the role of the aqueous electron since it assumes a constant concentration equal to that which would be found at noon after a morning of continuous sunlight. Using the concentration of 2×10^{-17} mol L^{-1}, and assuming a 2:1 production of DGM from aqueous electrons (i.e. two electrons for every inorganic mercury ion) we can determine a steady state concentration of DGM that is 1×10^{-17} mol L^{-1} (equivalent to 2×10^{-3} pg L^{-1}). Since this is 10,000

times less than the DGM concentrations observed in this study, other photo-reductants and reduction mechanisms likely predominate. An alternative to reduction by the aqueous electron is direct reduction of mercury by humic substances. While the exact reduction mechanism is not clear, semiquinones (which are present in humic acids) are thought to act as redox intermediates. Allard and Arsenie (1991) determined that reduction by DOC is possible except at very low pH or with high chloride concentrations.

5.8.1.2. Theoretical Mechanisms for Photo-Oxidation

Lalonde *et al.* (2001), who discovered that DGM can be photo-oxidized, claimed that chloride ions stabilize Hg(I) in solution and decrease the Hg(I)/Hg(0) potential such that electron transfer to semiquinones may take place. They determined that photo-oxidation of Hg(0) follows pseudo-first-order kinetics with a rate constant of 0.25 h^{-1} for freshwater and 0.6 h^{-1} for saline waters. These results suggest that dissolved ions may play an integral role in determining photo-oxidation rates.

We modeled DGM dynamics by assuming that DGM dynamics were the result of a reversible first-order reaction (see Eqs 5-1 to 5-6). This model fit the observed data very well (r^2 ranging between 0.59 and 0.98) for the four lakes studied. The fit of the kinetic curve to the data indicated that parameter b ranged between 4.66×10^{-9} and 3.60×10^{-3} $(kJ/m^2)^{-1}$, with a mean value of 1.26 h^{-1} (σ = 1.33) for all dilutions in all four lakes (assuming a constant radiant flux of 1000 kJm^{-2}).

Since b is defined as the sum of the forward (photo-reduction) and backward (photo-oxidation) first-order rate constants (Eq. 5-5), we must conclude that while there is a wide variation in the samples analyzed, the photo-oxidation rate constant suggested by Lalonde *et al.* (2001) of 0.25 h^{-1} for freshwater is a reasonable estimate. With a photo-oxidation rate of 0.25 h^{-1} (Lalonde *et al.*, 2001) and the mean value for b (1.26 h^{-1}), a mean abiotic DGM photo-production rate constant of 1.01 h^{-1} (σ = 1.33) can be calculated for all samples analyzed in this study. .

It should be noted that we assumed a linear relationship between photo-reductants and cumulative PAR throughout the incubations, while the relationship may in fact be more complicated. It is known that not all absorbed light results in photo-chemical reactions, and Miller (1998) has outlined several other processes resulting from absorbed light, including: (i) internal conversion (energy loss within singlet spin states); (ii) intersystem crossing (transition between singlet and triplet spin states, and; (iii) emission of light energy by fluorescence or phosphorescence.

5.8.2. DGM plateaus and DOC

In contrast to close dependence of DOC concentration on DGM production, we found that the DGM plateau was independent of DOC concentration but differed between lakes (see Section 5.7.3.). Differences in dissolved ions, concentration

of ligands, and DOC structure between lake sites may have affected the balance between oxidation and reduction (DGM plateau).

Other authors have also reported plateaus of DGM concentration such as those observed in this study. Amyot *et al.* (1997a) observed that on different sampling dates a plateau of DGM concentration was reached in Ranger Lake after incubations were exposed to approximately 2000 - 6000 kJ m^{-2} total incident radiation. The authors attributed this non-linear production of DGM to the limited availability of photo-reducible Hg(II) due to its complexation with DOC.

While our data indicates that the balance between photo-oxidation and photo-reduction is affected by site-specific factors, the actual mechanism is still unclear. Factors that affect mercury binding to ligands (Figure 5-8), such as DOC structure, the presence of ligands other than DOC, and the competition for binding by dissolved ions (Benedetti *et al.*, 1995) may be important to the balance of photo-oxidation and reduction. Some of these factors have been suggested to influence photo-oxidation processes as described by Lalonde (2001). The percentage of total mercury that was photo-reduced in each 100% whole water sample over the course of the incubations ranged from 0.4 to 12.4% (lake DF9 0.4%, lake K3 2.1%, lake K2 3.0%, and lake N70 12.4%). This also corresponds well to results reported by Amyot *et al.* (1997a), who observed a range of 0.2 to 8% of total mercury being photo-reduced during incubations in a series of freshwater lakes.

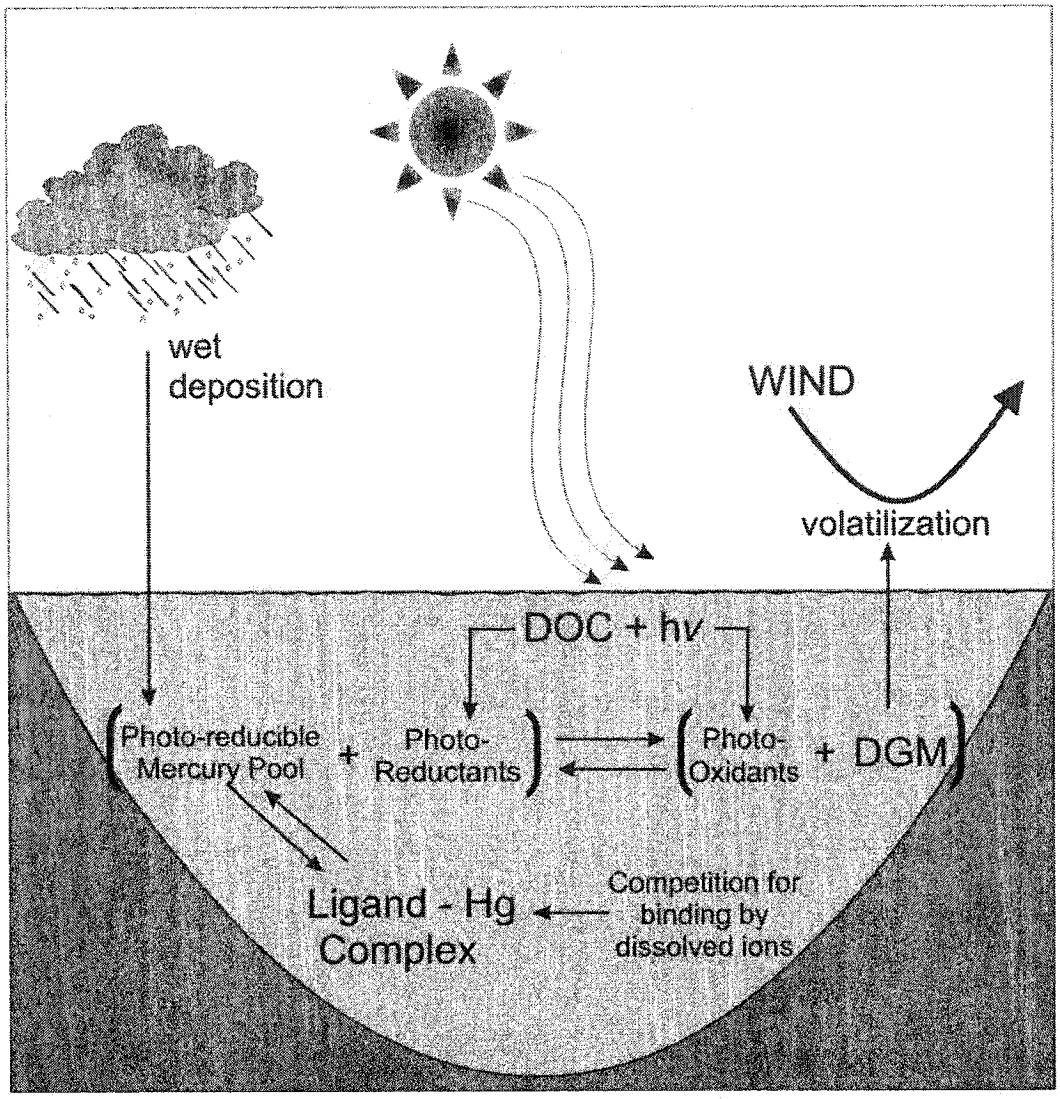

Figure 5-8: Conceptual diagram detailing the relationship between DOC, photo-reducible mercury and DGM dynamics.

5.8.3. DGM Photo-Production Efficiency and DOC

This study demonstrates that initial rates of DGM production (DGM_{Prod}) prior to 4000 kJ m^{-2} increased with increasing DOC concentrations for all lakes sampled (Figure 5-7). The published literature is not consistent on the relationship between DOC and DGM production, and our results stand in contrast to those of

several researchers who have observed a negative relationship between DOC and DGM production. For example, Amyot *et al.* (1997a) found that solar radiation induced higher DGM yields in a low DOC lake (2.3 fM DGM kJ^{-1}) than in two high DOC lakes (1.0 and 1.3 fM DGM kJ^{-1}). Similarly Watras *et al.* (1995) found that the ratios of DGM:total Hg decreased exponentially with increasing DOC in a series of lakes, suggesting lower DGM production in high DOC lakes. The reasons for the negative relationship observed in these studies may lie in experimental designs that could not exclude the effects of other inter-site differences that may affect photo-reduction processes. That is, it is possible that the observed differences in DGM production reflect other lake characteristics that change in relation to DOC.

A laboratory study performed by Xio *et al.* (1995) found that Hg(II) in the form of $HgCl_2$ and $Hg(OH)_2$ is reduced to Hg(0) more efficiently in the presence of humic and fulvic acids. The work of Xio *et al.* (1995) clearly indicates that some level of DOC is required for efficient production of DGM, though the effects of changing concentrations and DOC binding were not explored. We propose that the positive relationship between DOC concentration and DGM production observed in this study is due to changes in photo-reducible mercury between dilutions, and is not related to changes in DOC structure or dissolved ions. Assuming mercury that is bound to strong ligands is unavailable for photo-reduction, an increase in photo-reducible mercury with increases in DOC concentration may represent mercury that is weakly bound to DOC, and therefore available for photo-reduction.

The relationship of DGM dynamics to forestry is an important global issue that requires more research. In this study DGM_{prod} was significantly higher for the non-logged lakes than for the logged lakes used in this study. We hypothesize that this relationship is due to differences concentrations of photo-reducible mercury arising from variations in DOC structure, and dissolved ions between lake sites. This data shows that logging may reduce a lake's ability to produce DGM and thus may ultimately reduce mercury evasion. A reduction in mercury evasion may result in an increase in the mercury pool of lakes with extensive logging in their drainage basins. Several researchers have examined the effects of forestry on water quality and mercury fate. Carignan *et al.* (2000) found that DOC concentrations were up to 3 times higher and K^+, Cl^-, and Ca^{2+} concentrations were up to 6 times higher in lakes with logged drainage basins as compared to reference lakes. Garcia and Carignan (1999) found that methyl mercury concentrations were higher in the zooplankton of lakes with logged drainage basins than in non-logged lakes. Garcia and Carignan (2000) found that mercury concentrations in northern pike were significantly higher in lakes with logged drainage basins (3.4 μg g^{-1} wet wt.) than in reference lakes (1.9 μg g^{-1}).

It should be noted that while there is a direct relationship between DOC concentrations and DGM production observed in this study, this does not necessarily imply greater overall amounts of DGM in high DOC lakes. Our results were obtained with incubations at the lake surface. While the creation of DGM at the lake surface is important, the effects of solar radiation attenuation with depth, water column mixing, and volatilization of mercury to the atmosphere would need

to be accounted for in a whole lake model. In addition, our assumption of excess photo-reductants may not hold true at greater depths in the water column where sunlight is limited. It should also be noted that we have assumed that mercury bound to strong ligands is unavailable for photo-reduction (Figure 8). In contrast, Allard and Arsenie (1991) have speculated that binding of mercury to DOC could facilitate the reduction by electron transfer if intra-molecular processes are important. The relative importance of DOC-instigated intra-molecular and extra-molecular photo-reduction processes is currently unknown. The role of strong and weak binding sites in the photo-reduction of mercury is also unclear, however we suspect that weakly bound mercury may be available for photo-reduction as evidenced by our results.

The results of this study indicate that a reversible first-order reaction equation for the abiotic photo-production of DGM can accurately describe DGM dynamics in freshwater lakes. The balance of the photo-oxidation and photo-reduction processes may in part explain the lag time between solar radiation and DGM observed in chapter 4. More research is required to clarify the role of abiotic and biotic reactions in this lag effect.

It is clear that in surface waters, DOC plays an important role in DGM dynamics. Increases in initial DGM production rates were observed with increases in DOC concentration within each lake. We hypothesize that photo-reductants are present in excess such that the level of photo-reducible mercury is the primary factor regulating DGM production with low levels of solar radiation. The level of

photo-reducible mercury is, in turn, determined by its binding to ligands. A better understanding of DOC structure and factors affecting competition for ligand binding is required in order to understand site-to-site differences in levels of photo-reducible mercury. The balance of oxidation and reduction (i.e. DGM plateau) was found to be different between sites, which suggests an effect of DOC structure and dissolved ions. In this study, lakes with logged drainage basins were observed to have lower rates of initial DGM production, which may indicate differences in mercury binding to strong ligands. Our data predicts that logging may reduce a lake's ability to produce DGM and may ultimately reduce mercury evasion.

Chapter 6

DISSOLVED GASEOUS MERCURY PROFILES IN FRESHWATERS

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6.1. Abstract

The importance of dissolved gaseous mercury (DGM) profiles in shallow and deep freshwaters has not been previously investigated in detail. In this study we evaluate DGM depth profiles for four sampling stations on Lake Ontario and several bays of Jack's Lake near Apsely, Ontario. When DGM concentrations are expressed on an areal basis, DGM concentrations above the thermocline in Lake Ontario average 1.5 μg m^{-2} and in small freshwater lakes it ranged between 0.1 and 0.8 μg m^{-2}. Further, it was demonstrated that the majority of DGM in large freshwater lakes such as Lake Ontario exists below the thermocline where photochemical oxidation and reduction processes cannot occur. The importance of this DGM to atmospheric flux rates is discussed. In addition the results indicate that microbial processes may be an important factor regulating DGM in the water column of freshwater lakes, particularly in the hypolimnion.

6.2. Introduction

The evasion of Hg^0 from freshwater bodies is believed to be major route of mercury loss (Loux, 2000). Previous models of mercury volatilization (See Chapter 4) have focused mainly on surface water DGM concentrations and have not incorporated the effects of DGM distribution in the water column, which would be necessary in a whole-lake model. Areal concentrations of DGM may be a useful point of comparison between ecosystems in such a whole lake model.

The areal extent of DGM in freshwater has not yet been determined but it is known that DGM profiles in lake water can vary significantly. For example, DGM in the water column of Ranger Lake varied from 240 fM to 6 fM (Amyot *et al*, 1994) and in Lake Ontario it varied from 1290 fM to 696 fM (Amyot *et al*, 2000). Elemental mercury in freshwater lakes is regulated by a combination of photochemical and biological processes. Zhang and Lindberg (2001) hypothesized that the photochemical process is mediated by reactive iron in the water column, which initiates a free radical reaction scheme that reduces Hg^{2+} to Hg^0. Other parameters such as Cl and organic carbon also mediate the photochemical transformations of Hg^0 (Lalonde *et al.*, 2001). Recently our laboratory group demonstrated that microorganisms play an important role in DGM cycling in freshwater systems. The photochemical production of hydrogen peroxide initiates the microbial oxidation of Hg^0 to Hg^{2+} and mercury reductase activity reduces this Hg^{2+} back to Hg^0 (Siciliano *et al.*, 2002; See Appendix 1). The majority of DGM research has taken place in the uppermost portion of the water column. Little is known about deep-water DGM processes but these deep waters may contain the majority of DGM and thus play an important role in modulating DGM over a seasonal cycle.

In addition to the atmosphere-water boundary, there are other boundaries in lake water that are known to influence the distribution of contaminants in freshwaters. At the thermocline sharp gradients of NO_3, NH_4, SO_4, H_2S, Fe^{3+}, Fe^{2+}, CH_4, N_2O, and H_2O_2 have been observed (Knowles and Lean, 1987; Lean and Knowles, 1987; Taylor *et al.*, 1987; Cooper *et al.*, 1989). Changes in the redox state of

water might also influence biologically mediated transformations of DGM because as metal's move from one redox state to another, H_2O_2 is produced (Cooper *et al.*, 1989) and this may influence the H_2O_2 dependent mercury oxidase enzyme. In this work, we investigate DGM concentrations and associated enzyme activities in detailed depth profiles under a variety of conditions. The purpose of this study was to characterize the distribution of DGM through the water columns of deep and shallow water lakes.

6.3. Materials and Methods

Samples from two bays, Brookes and Williams, in Jack's Lake, (44° 41' 20" N, 72° 02' 54" W), were collected from a fiberglass boat using a Go-Flo sampler on July 21, 2000. Jack's Lake is a mesotrophic lake near the Canadian Shield with an average of 14 mg of Ca^{2+} L^{-1}, 12 µg P L^{-1} and pH of 7.22. Brookes Bay has a dissolved organic carbon (DOC) concentration of 7.8 mg L^{-1} and Williams Bay has a DOC of 6.0 mg L^{-1}. Samples from Lake Ontario were collected using a Go-Flo sampler on September 12, 2000 at 10:26 from Station 29 (43° 49' 51" N, 78° 52' 08" W) and at 18:30 from station 743 (43° 31' 13" N, 78° 11' 16" W). On September 14, 2000 samples were collected at 09:08 from Station 73 (43° 38' 01" N, 76° 17' 12" W) and at 17:49 from station 586 (43° 29' 07" N, 77° 02' 48" W).

DGM was analyzed by bubbling approximately 20 L (1 L min^{-1} for 20 minutes) of mercury free air produced by a Tekran 1100 Zero Air Generator through a 1 L

water sample contained in a glass graduated sparger. The bubbled gas was analyzed for dissolved gaseous mercury using a Tekran 2537A with pre-cleaned Teflon lines and connections. This analytical system had a daily detection limit of 5-25 fM. Daily detection limit was determined as three times the standard deviation of the baseline. The average percent difference between duplicates was 32 % (n = 24). After analysis of DGM in Jack's Lake, 500 mL of lake water was combined with 100 mL of glycerol and the samples were frozen in amber glass bottles for microbial analysis.

Microbial mercuric reductase and oxidase activity was assessed on protein extracts of 500 mL of unfiltered lake water. Microbial cells were concentrated and lysed as previously described (Ogunseitan, 1997) and assessed for mercury reductase activity (Ogunseitan, 1998). Mercuric reductase consumes NADPH to reduce mercury. To assess mercuric reductase, NADPH consumption over a 20 minute time period is compared between samples with or without 20 nmoles of Hg^{2+}. One unit of enzyme activity (U) was defined as the equivalent to 1 µmole of NADPH consumed in response to the Hg^{2+} aliquot, i.e. NADPH consumption in the presence of mercury – NADPH consumption without mercury. Microbial oxidation of elemental mercury was measured using 1 mL additions of water saturated with Hg^0 to 200 µL enzyme extracts of lake water (Smith *et al.*, 1998). Enzyme extracts were incubated at 22 °C for 1 hour and a U designated as 10 fmoles of inorganic mercury formed. Boiled controls were prepared by heating enzyme samples (100°C) for 10 minutes and background mercury oxidation is subtracted from the reported value. Protein levels were quantified using the

Lowry Protein Assay (Koch, 1994).

Areal concentrations of DGM were calculated by estimating the mass of DGM present in a m^2 of the water column that extends to the bottom of that section of lake. For surface water samples, the thermocline was assumed to be the bottom. Hence the amount of DGM present in a 1 m^2 area that extends from the surface to the thermocline was calculated. Similarly, areal concentrations below the thermocline were calculated by extending the 1 m^2 column to the lake bottom and calculating DGM present in that column.

6.4. Results and Discussion

Dissolved gaseous mercury concentrations in Brookes Bay increased with depth throughout the epilimnion and decreased immediately above the thermocline (Figure 6-1). In the hypolimnion, DGM concentrations were highest just below the thermocline and then decreased with depth. Levels of mercury reductase activity in the epilimnion followed a similar pattern with maximal mercury reductase activity co-inciding with the maximum DGM concentrations. However, in the hypolimnion this trend did not continue with mercury reductase activity remaining relatively constant despite decreasing DGM concentrations with depth. Mercury oxidase activity was highest in the surface waters, corresponding with a low DGM concentration and then steadily decreased until 7 meters where a sharp increase in activity was evident. This is consistent with the observation that mercury oxidase activity is closely linked to H_2O_2 (Siciliano *et al.*, 2002; Appendix 1). The

increase at 7 meters co-incided with the lowest level of DGM observed in the hypolimnion.

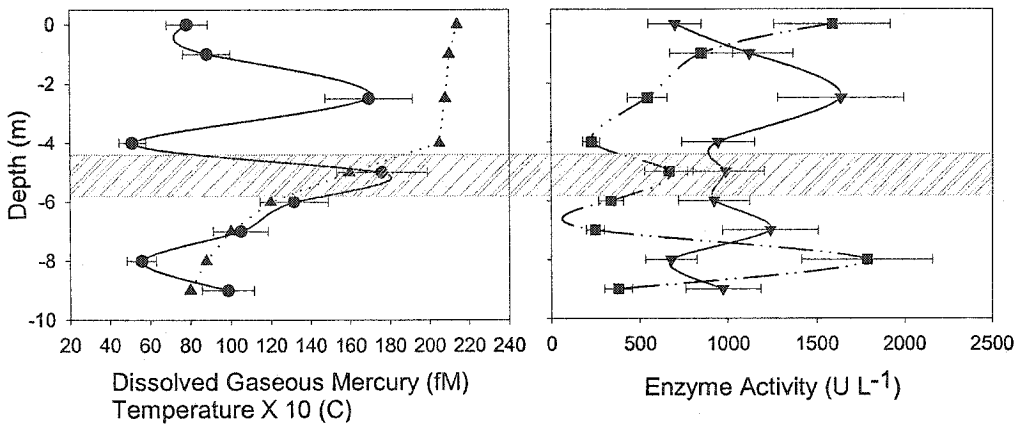

Figure 6-1: Depth profiles of dissolved gaseous mercury (●), temperature (▲), mercury reductase activity (▼) and mercury oxidase activity (■) in Brookes Bay, Jack's Lake. Each data point is the average of duplicate samples taken at each depth with error bars indicating the range. The shaded box indicates the water depth at which the maximum change in water temperature was observed.

In William's Bay (Figure 6-2), similar trends were observed with DGM concentrations reaching a peak in the epilimnion at 2.5 meters followed by a sharp decrease within the thermocline and oxocline and then an increase in the hypolimnion just below the thermocline. In contrast to Brookes Bay, mercury reductase activity was higher in the hypolimnion compared to the epilimnion and bore little relation to observed DGM concentrations. Mercury oxidase activity in

William's Bay was 10 times less than that observed at Brooke's Bay but it followed a similar pattern with maximal activity observed near the surface and a rapid decrease with depth. Perhaps reflecting low mercury oxidase activity, the concentrations of DGM are 4 times greater in William's compared to Brooke's Bay and there is a correspondingly large differential between mercury reductase and oxidase activity in William's Bay. This suggests that both DGM formation and transformation by microrganisms are important in regulating DGM concentrations in freshwaters.

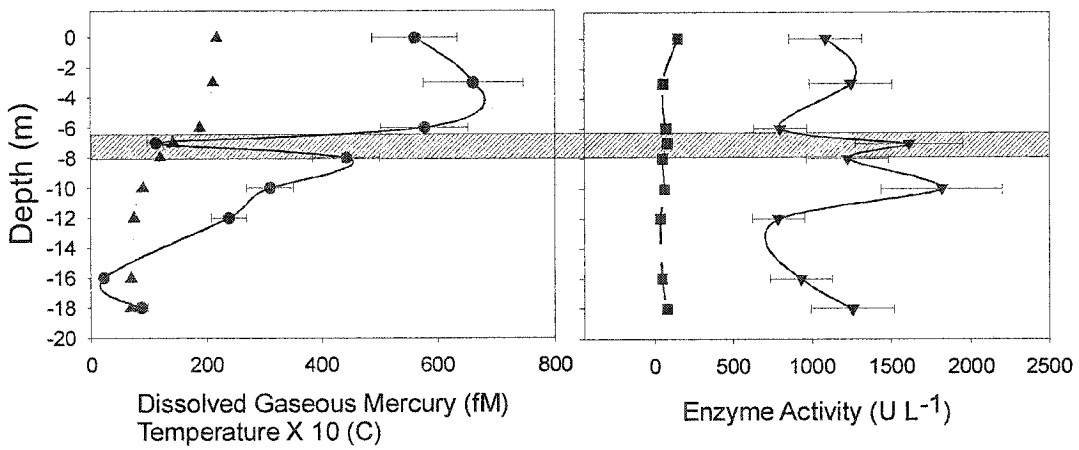

Figure 6-2: Depth profiles of dissolved gaseous mercury (●), temperature (▲),mercury reductase activity (▼) and mercury oxidase activity (■) in Williams Bay, Jack's Lake. Each data point is the average of duplicate samples taken at each depth with error bars indicating the range. The shaded box indicates the water depth at which the maximum change in water temperature was observed.

Our results in Jack's Lake are similar to that observed in Pettaquamscutt (Mason *et al.*, 1993) and Kejimikujik (O'Driscoll *et al.*, 2003b) in which DGM and temperature were closely linked but differ from results obtained at Ranger Lake (Amyot *et al*, 1994). Dissolved gaseous mercury is formed by a combination of photochemical and biological processes (Siciliano *et al.*, 2002; Appendix 1). It is likely that basis for the differences in DGM concentrations observed in different lakes is the result of a complex interaction between iron cycling, Cl levels, organic matter and microbial activity (Zhang and Lindberg, 2001; Lalonde *et al.*, 2001). Figure 6-3 illustrates the complexity of reactions regulating DGM concentrations in freshwaters. This figure suggest that redox based processes may be largely responsible for deep water DGM transformations. However, as of yet, few investigations have assessed the interaction between abiotic and biotic transformations of DGM in deep water.

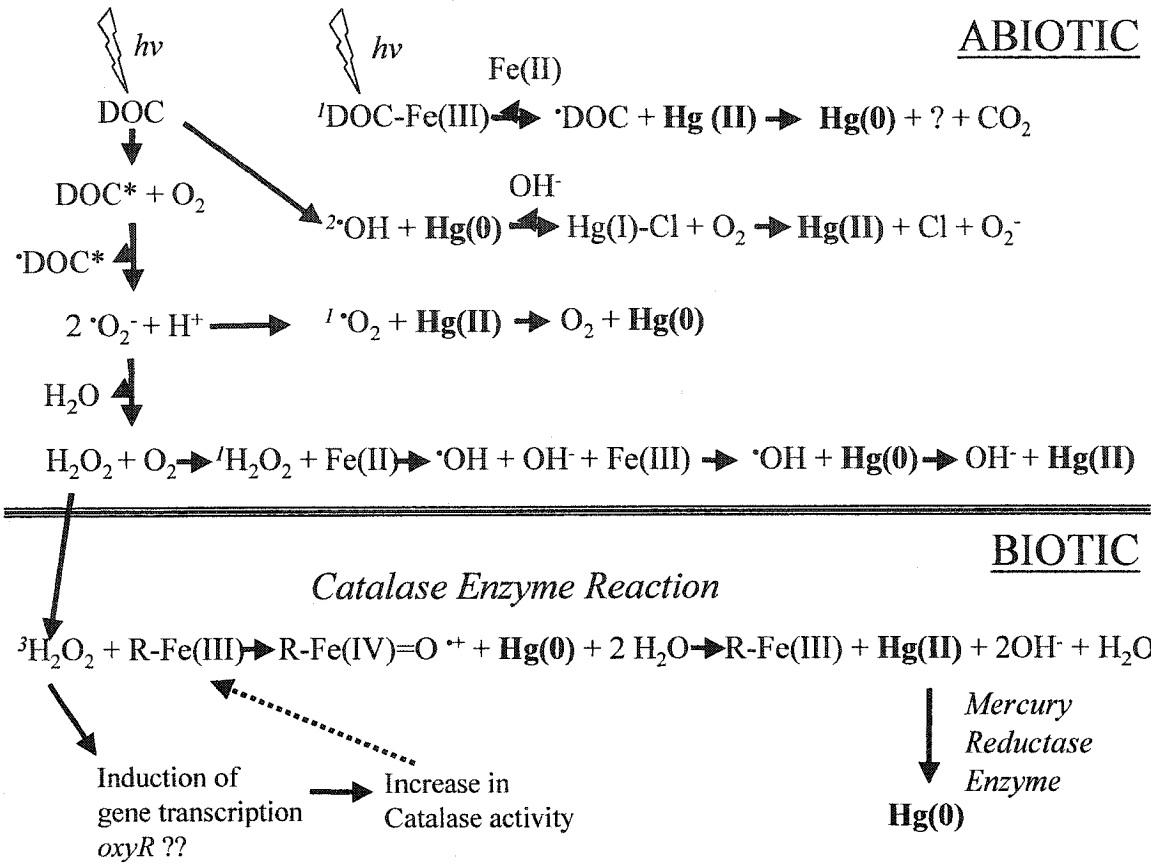

Figure 6-3: Conceptual diagram outlining the importance of sunlight for the two known biological and four known abiotic transformations of divalent and elemental mercury in freshwaters. 1-reactions described by Zhang and Lindberg (2001), 2-reactions described by Lalonde *et al.* (2000) and 3-reactions described by Siciliano *et al.* (2002). The relative importance of each reaction pathway has yet to be determined.

Profiles of DGM in the shallow stations of Lake Ontario were similar to that observed at Jack's Lake (Figure 6-4). DGM concentrations were their highest at the lake surface and then rapidly decreased with depth. Just above lake bottom, DGM concentrations increased again, in the case of Lake Ontario from approximately 200 fM to 400 fM and in the case of Jack's Lake from 30 fM to 100 fM. DGM concentrations in Lake Ontario shallow stations bore little relation to

changes in temperature. At Station 73, DGM concentrations remained at approximately 200 fM despite a 10 °C drop in temperature from 21 °C to 9 °C. Similarly, at Station 29, DGM concentrations dropped from 1000 fM to less than 200 fM with no change in water temperature. Similar results were obtained in 1998 at a depth profile for Station 983, 35 m deep, in which DGM concentration increased from 400 fM to 500 fM despite a 20 °C decrease in temperature (Amyot *et al.*, 2000). Similarly, at station 988, 27 m deep, DGM concentrations increased from 700 fM to 1300 fM and a corresponding 10 °C decrease in water temperature. It appears that DGM concentrations in shallow stations are linked to parameters other than temperature.

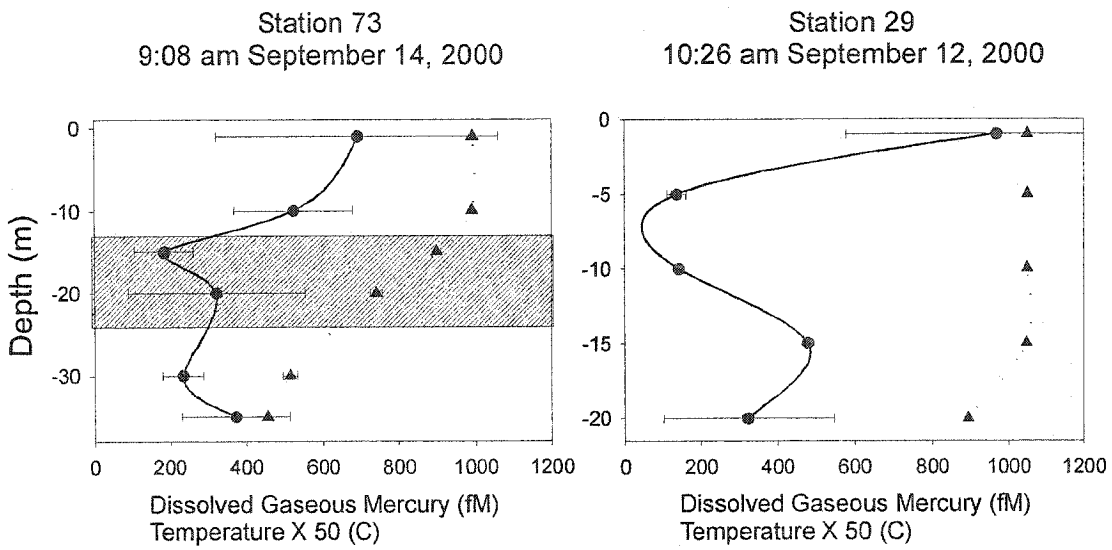

Figure 6-4: Depth profiles of dissolved gaseous mercury (●) and temperature (▲) in shallow stations of Lake Ontario. Each DGM data point is the average of duplicate samples taken at each depth with error bars indicating the range. The shaded box indicates the water depth at which the maximum change in water temperature was observed.

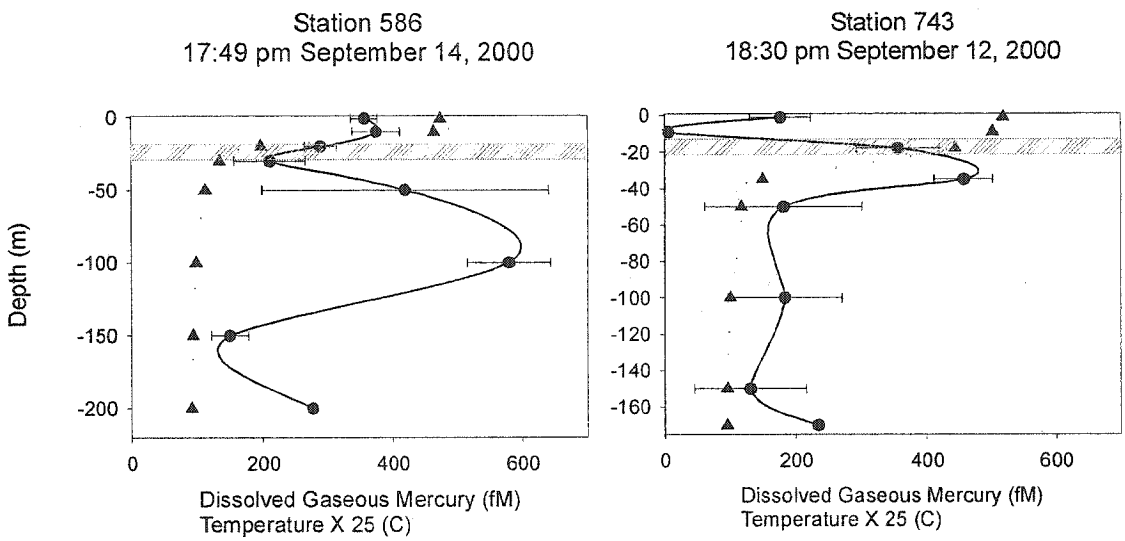

Figure 6-5: Depth profiles of dissolved gaseous mercury (●) and temperature (▲) in deep stations of Lake Ontario. Each DGM data point is the average of duplicate samples taken at each depth with error bars indicating the range. The shaded box indicates the water depth at which the maximum change in water temperature was observed.

In contrast to the shallow stations, deep stations of Lake Ontario displayed high concentrations of DGM in the hypolimnion (Figure 6-5). Similar DGM patterns were observed in the surface waters with a high concentration at the surface followed by a rapid decline but underneath the thermocline, DGM concentrations increased to double that seen in the surface waters. This is now the second study that has observed significant concentrations of DGM near the lake bottom (Amyot *et al.*, 2000). As of yet there is no explanation for this increase in DGM. It is unlikely that it is a H_2O_2 mediated pathway. However, up-core enrichment of mercury in lake sediments has been repeatedly observed. It is possible, that microorganisms exposed to inorganic mercury are reducing it to Hg^0. The mer gene has been observed in sediments (Hobman *et al.*, 2000) but the prevalence of this pathway in Lake Ontario is not known. Alternatively, sediment redox processes may be contributing to Hg^0 production. The importance of sediment processes on DGM in the water column is an area that warrants further investigation.

Areal concentrations of the surface of Lake Ontario remained relatively constant at approximately 1.5 μg m^{-2} (Table 6-1) and are very similar to those obtained previously for lake Ontario (Amyot *et al.*, 2000). The high concentration of DGM near Pickering may be related to higher total mercury (0.99 ng L^{-1}) in the area compared to the remainder of Lake Ontario (0.33 ng L^{-1}). Jack's Lake had a much more variable areal concentration that was at least 50% lower than that observed in Lake Ontario. Previous areal values obtained for Ranger Lake (Amyot *et al.*, 1994) are between the areal DGM concentrations of Brookes and

William's bays in Jack's Lake. Average water-to-air mercury flux rates recorded for a three-day period for two shallow freshwater lakes, North Cranberry and Big Dam West, were 1.1 ng m^{-2} h^{-1} and 5.4 ng m^{-2} h^{-1} respectively (Boudala *et al.*, 2000). The values for Big Dam West are skewed by a one day period during the day in which mercury flux was 12.5 ng m^{-2} h^{-1}, trimming this value gives an average flux rate of 2.5 ng m^{-2} h^{-1}. The following year flux rates at Big Dam West over a 48-hour period were 1.2 ng m^{-2} h^{-1} and for another small lake, Puzzle Lake, they were 0.9 ng m^{-2} h^{-1} (unpublished observations). In contrast, flux rates over the deep water of Lake Ontario were found to be between 2 and 4 ng m^{-2} h^{-1} (Poissant *et al.*, 2000).

DGM flux to the atmosphere is partially controlled by the concentration of DGM in the uppermost region of the epilimnion. In turn, these DGM concentrations are the result of two processes, net production / destruction in the irradiated layer and the diffusion of DGM from the remainder of the epilimnion. In deep lakes diffusion of DGM from the large available pool observed the hypolimnion may offset periods when DGM is being destroyed by photochemical or biological processes in the uppermost layer of the epilimnion. This is a possibility, which awaits further experimental verification.

Portion of Water Column[2]	*Lake Ontario*						*Jack's Lake*		*Range r Lake*[4]
	Station 586	*Station 743*	*Station 73*	*Station 29*	*Station 983*[3]	*Station 988*[3]	*Brooke's Bay*	*William's Bay*	
Above Thermocline	1.4	1.5	2.0	1.5	1.3	4.9	0.10	0.85	0.24
Below Thermocline	13	5.6	0.89	0	1.5	0	0.094	0.53	0.10
Water Column Depth (m)	210	171.5	38	21.5	35	27	9	18	12

Table 6-1: Areal concentrations[1] of dissolved gaseous mercury at the surface and at the thermocline in freshwater lakes

[1]Areal dissolved gaseous mercury concentrations are expressed as total μg of DGM m^{-2} of water at the boundary. This is calculated by determining the amount of DGM in a one m^3 column of lake water that extends from the surface to the thermocline and for the thermocline value, from the thermocline to the lake bottom.

[2]The water column was divided into that region above and below the thermocline. Stations 29 and 988 did not have a detectable thermocline.

[3]Value computed from Figure 2, Amyot *et al.* 2000. Distribution and transformation of elemental mercury in the St. Lawrence River and Lake Ontario. Can. J. Fish. Aquat. Sci. 57 (Suppl. 1): 155-163. Station 988 is near Pickering, Nuclear Power Plant and has concentrations on inorganic mercury three times that (0.99 ng L^{-1}) that found elsewhere in Lake Ontario.

[4]Value computed from Figure 6. Amyot *et al.* 1994. Sunlight-induced formation of dissolved gaseous mercury in lake waters. Environ. Sci. Technol. 28 (13): 2365-2371.

Areal concentrations beneath thermocline are much higher than the areal DGM concentration for surface water with the majority of DGM in the deep stations being below the thermocline where photochemical processes are not occurring. This hypolimnotic DGM is likely not available for flux to the atmosphere while the thermocline is in existence. But come fall turnover, stations such as Station 586

have 15 µg DGM m^{-2} whereas Station 73 has only 2.8 µg DGM m^{-2}. The influence this has upon DGM flux to the atmosphere is not known.

This study has illustrated that DGM concentration changes substantially with depth in freshwater lakes. We have also found that the deep stations of Lake Ontario contain a substantial amount of DGM in the hypolimnion. We suggest that microbial processes are an important regulator of DGM concentrations at depth in freshwater lakes.

Chapter 7

THESIS SUMMARY

7.1. Conclusions

The research presented in this thesis has led to many important advances in the areas of DGM dynamics and mercury volatilization. The mercury mass balance described for Big Dam West Lake (BDW) (Kejimkujik Park, Nova Scotia) in Chapter 2 is unique as it is based primarily on original data collected by a multidisciplinary research team. This mass balance indicates that mercury volatilization from BDW lake surface is equivalent to 200% of mercury deposited in wet deposition directly to lake. This demonstrates that volatilization is a significant process determining mercury fate in the BDW ecosystem. The mass balance also suggests that the terrestrial portion of the catchment is important for mercury movement in the BDW system (since the terrestrial portion receives the majority (88.7%) of the mercury deposited in wet deposition).

Chapter 3 describes a new method that was developed for the continuous analysis of DGM and found to work well for a wide range of water temperature, pH, ORP, and DOC concentrations. QA/QC indicated that it compared quite well to older methods of discrete DGM analysis and had a method detection limit of 22.4 fmol L-1 with an RSD of 4.0 +/- 2.6 % on duplicates. This is an important advance in DGM research, as for the first time DGM can be measured accurately and continuously in field locations. In this study, methyl mercury was not found to interfere with DGM analysis. Water temperature was found to affect DGM extraction such that the best data resolution for continuous analysis was at higher temperatures.

The new method outlined in Chapter 3 was used in Chapter 4, in conjunction with water-to-air mercury flux measurements, to observe relationships between these variables and some additional meteorological measurements. Correlations were observed between solar radiation and DGM as well as between solar radiation and mercury flux. Cross-correlation analysis indicated that the maximum correlation between solar radiation and DGM occurred at a time-lag of approximately 75 minutes. These results support the theory that solar radiation is the driving force behind DGM formation and mercury flux from the water surface, and suggest that there is a time lag of 75 minutes between solar radiation reaching the water, and the initiation of photo-reduction. It was also noted in this study that there were substantial differences in the DGM concentrations measured for a low DOC lake as compared to a high DOC lake over a diurnal cycle. This suggested that DOC might be an important factor affecting DGM production and led to the work outlined in chapter 5.

The data collected for Chapter 4 were further used to test a series of mercury flux models found in the current published literature. The data showed that the predictive models did not accurately represent the relationship between DGM and mercury flux. Attempts to produce a new predictive model using the data were also unsuccessful, and it was concluded that water chemistry and meteorological measurements alone are not sufficient to produce an accurate predictive model of mercury flux. It is suggested that the models examined in this chapter could be improved with the incorporation of time-delayed solar radiation

measurements, measurements of site-specific factors such as DOC concentration, and a more thorough understanding of the relationship between wind and mercury flux.

In Chapter 5, the relationship between DOC and DGM production was examined in more detail. DGM was found to increase with increasing solar radiation in all samples from four lakes studied, to a point (approximately 4000 kJ m^{-2}) at which it reached a plateau. The level of the DGM plateau differed somewhat between lake sites but was independent of DOC concentration. However, the initial rate of DGM production prior to the plateau was shown to increase with increasing DOC concentrations in all lakes studied. These results suggest that DOC concentration is linked to the production rate of DGM, perhaps by regulating the availability of photo-reducible mercury. Differences in the DGM plateaus between lakes may be due to differences in water chemistry and DOC structure that regulate the balance of photo-oxidation and photo-reduction.

Interestingly, the rates of initial DGM production observed in this study were significantly lower in the two logged lakes than in the two lakes whose catchments had not been logged (independent of DOC concentration). This suggests the possibility that less mercury is being volatilized from logged lakes, and corresponds with the results of some other researchers who have reported elevated levels of mercury in the biota of logged lakes (Garcia and Carignan, 1999; 2000). Overall, the results of this study demonstrate that DOC plays an important role in the regulation of photo-reducible mercury and production of

DGM in lakes. However, the effects of solar attenuation with depth and DGM distribution in the water column need to be accounted for in a whole lake model.

In Chapter 6, the distribution of DGM was examined in the water columns of both shallow and deep freshwater lakes. In all lakes studied, DGM concentration was generally observed to be highest at the surface, decreasing steadily with depth through both the epilimnion and hypolimnion (apart from an increase in DGM above the thermocline in Jack's Lake). In the deeper parts of the hypolimnion of the deep lake (Lake Ontario) an increase in DGM was observed that might be due to sources other than photo-reduction. This research demonstrates that vertical mixing in the water column will substantially affect DGM concentrations in the surface of these freshwater lakes and therefore will affect rates of DGM volatilization. The importance of DGM concentration in the hypolimnion is unclear, though it may be significant in lakes where a buildup of DGM in the hypolimnion could become available for volatilization with lake turnover.

7.2. Significance of Findings

The conclusions outlined in the previous section are significant for DGM and mercury research in several ways. The first and most straightforward contribution of the thesis is the development of a new analysis system for DGM that can take continuous on-site measurements in a way that was previously impossible. This new method was used throughout the rest of the research presented in the thesis, and we believe it will be instrumental to new discoveries in the future.

Overall, the research presented in the rest of the thesis shows that the relationship between DGM and mercury volatilization in freshwaters is complex and not accurately represented by current predictive models. Two fundamental problems with these models are that: (i) they do not incorporate the parameters necessary to make them applicable to a wide range of ecosystems, and (ii) the incorporation of wind speed in the calculation of the mass transfer co-efficient leads to many inaccuracies in predicting mercury diurnal dynamics. It is proposed that a new model needs to be developed that is specific to mercury volatilization, and that it should incorporate factors important to DGM surface dynamics. Three such factors that have emerged from the work presented here are time-delayed photo-reactions, DOC concentration and structure, and mixing in the water column.

It has long been accepted that solar radiation is a driving force behind DGM formation, but our work suggests that there is a time lag of about 75 minutes between sunlight reaching the water surface and DGM being formed. DOC has also been proposed before as a factor affecting DGM dynamics, but the results presented in this thesis demonstrate specifically that DOC concentration is positively correlated with rates of DGM photo-production. We propose that DOC regulates photo-reducible mercury and that this must be considered in models describing DGM dynamics in surface water. While our results suggest that a high DOC lake may produce DGM more easily than a low DOC lake, changes in solar attenuation with depth and DGM distribution must also be considered.

The depth profile work presented here has highlighted several ways in which water column mixing can alter concentrations of DGM at the lake surface. An important finding was the presence of large amounts of DGM below the thermocline in deep lakes, which indicates a source of DGM that is not related to photo-reduction processes. The importance of such a process in DGM distribution and mercury volatilization has yet to be evaluated. However, it suggests that turnover of such lakes may result in increased DGM concentrations in surface waters, and a periodic increase in mercury volatilization.

More research into the relationship between DGM and mercury volatilization may help to identify other key variables required to improve our ability to model these processes.

Finally, another important discovery of this research was the observation that logging is related to lower rates of DGM photo-production in freshwater. This suggests that levels of logging near freshwaters will directly affect DGM production and potentially alter levels of mercury volatilization. While we cannot specifically say why logging affects DGM production, we suggest it is related to changes in dissolved ions that balance photo-oxidation and photo-reduction processes. It is possible that these changes are linked to soil erosion (instigated by tree removal). The potential impacts of logging and its affects on the mercury cycle will need to be evaluated globally

7.3. Recommendations for Future Research

The results and conclusions discussed in this thesis highlight several areas in which further research is critical to a better understanding of DGM dynamics and mercury volatilization.

Chapter 2 demonstrates the need for more research into the terrestrial portions of lake catchments and the role they play in mercury cycling in lake ecosystems. In particular, the role of vegetation in the mobilization of mercury is an area that requires more attention. It is also not clear to what extent differences in mercury volatilization affect the available mercury pool and the bioaccumulation of mercury in different ecosystems. The development of more mass balances would facilitate comparisons between ecosystems and would help to answer questions such as this one.

The new method presented in Chapter 3 is a significant advance for DGM analysis. Future research with this new analysis method will take advantage of the ability to analyze continuously in remote locations with contamination-free sampling. Several such analyzers would give the ability to measure DGM dynamics with depth in the water column over time, something which was previously not possible. Laboratory experiments may involve kinetic analyses of DGM photo-production that may shed more light on the observed time-lag between solar radiation and DGM production.

While this new method is a major improvement there are still several analysis issues that need to be clarified with more research. The problem of temperature effects on extraction, as well as the current inability to obtain an aqueous DGM standard is an area that needs to be resolved. While limited research has been performed on DGM speciation the complete speciation of DGM in freshwaters has never been clarified. Current extraction and analysis techniques for DGM primarily measure elemental mercury, so that the term DGM continues to be defined in part by limitations of methodology.

The study of the mechanisms responsible for photo-reduction and photo-oxidation (Chapter 4) is an area in which much progress can be made. New evidence has been reported for biotic redox mechanisms (Siciliano *et al.*, 2002) however, more research is required to identify the relative importance of abiotic and biotic reduction and oxidation reactions in different ecosystems. The discovery of a time lag between solar radiation and DGM formation requires more investigation, particularly to see if it is apparent in different ecosystems. The role of abiotic and biotic reactions in determining this time-lag should be explored further. The incorporation of time-delayed, solar-induced mechanisms in current flux models may improve their accuracy. The calibration of these predictive models with quantitative data is also an area in which much progress can be made. It is apparent that meteorological variables are important to flux calculations, however more work is required on incorporating parameters such as wind into predictive models, as the current approach does not work well for extreme conditions.

Chapter 5 provides a very preliminary look at the complex relationship between DOC concentration, forestry practices, and the photo-production of DGM. The development of a whole-lake DGM model would have to account for solar radiation attenuation with depth in the water column. The role of specific wavebands in the production of DGM is also an area that has not been examined in detail. While our preliminary research suggests that forestry may decrease the rate of DGM formation in lakes, more data is required in order to confirm this important discovery. The effects of forestry on DGM production and mercury evasion is a new area of research that may be critically important to understanding increases in mercury bioaccumulation observed in logged lakes. A larger-scale study linking forestry practices to DGM production and mercury volatilization is warranted.

While Chapter 6 shows differences in DGM distribution between shallow and deep lakes, the reasons for these differences are unclear. The large amounts of DGM found in the hypolimnion of deep lakes has yet to be explained and should be explored over a seasonal time-span in a range of stratified lakes. It is possible that substantial quantities of DGM are introduced into the water column with lake turn over. The mechanisms that govern DGM formation in the absence of solar radiation are currently unknown. However, biotic mechanisms are a potentially important source of DGM in the hypolimnion of deep lakes.

Overall, this thesis has contributed substantial new knowledge to the area of DGM dynamics and mercury volatilization. In particular the following advances have been made; (i) the creation of new methodology for DGM analysis, (ii) the observation of a time lag between solar radiation and DGM production, (iii) the assessment of flux model weaknesses with quantitative data, (iv) the clarification of the role of DOC in DGM production, (v) the identification of possible effects of forestry on DGM production, and (vi) the examination of DGM distribution in the water column with potential implications for a whole lake mercury model. While the relationship between DGM and mercury volatilization is complex and will continue to present us with many challenges, we are ever closer to a more complete understanding of the fate of mercury in freshwater ecosystems.

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Appendix 1

MICROBIAL REDUCTION AND OXIDATION OF HG IN FRESHWATER LAKES

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Abstract

The evasion of elemental mercury represents a significant pathway for reducing the level of this toxic material in aquatic ecosystems. The evasion rate is controlled by the concentration of dissolved gaseous mercury (DGM) across the air-water interface, water and air temperature as well as wind speed. Here we investigate the role of microbial mercury oxidation and reduction in regulating DGM diel patterns in two freshwater lakes, Jack's Lake and Lake Ontario. Three replicate diurnal cycles of DGM in Brookes Bay, Jack's Lake peaked at 313 fM between 9:00 and 10:30 and decreased to 79.6 fM by 16:00. Microbial mercury reductase activity (converts Hg^{2+} to Hg^{0}) increased with DGM concentrations and mercury oxidase activity (converts Hg^{0} to Hg^{2+}) increased as DGM concentrations decreased in the mid-afternoon. This suggested that mercury oxidase activity was linked to hydrogen peroxide (H_2O_2) diurnal patterns. Thirty minutes after spiking Lake Ontario water with H_2O_2, mercury oxidase activity increased by 250% and sixty minutes after the H_2O_2 spike, DGM decreased to 28% of it's initial value. Two hours after the H_2O_2 spike, mercury oxidase activity had declined but mercury reductase activity and DGM both increased. Four hours after the spike, mercury reductase and DGM levels had returned to original levels. Our results suggest that in the morning, microbial activity produces DGM but by mid-day, photochemically produced H_2O_2 induces the biologically mediated decrease in DGM concentrations throughout the afternoon. To predict concentration of DGM in surface waters and relate changes to flux rates, the

contribution of photoreduction and photooxidation must be placed in context with reduction and oxidation rates due to microbial activity.

Introduction

A significant route of mercury loss from lakes, rivers and wetlands occurs by evasion of elemental mercury into the atmosphere. It is a function of the mercury concentration gradient across the water-air interface, the temperature and the wind speed *(1, 2, 3)*. Strong diel fluctuations in DGM concentrations have been observed in most lakes with levels of DGM peaking at noon*(4, 5)*. Investigators have attributed this increase to photochemical processes that involve the production of reductive species or direct electron transfer*(6, 7, 4)*. However, neither the reactive species involved nor the mechanism of direct electron transfer initiated by solar radiation has been shown*(8)* although reactive iron is thought to play a role(*9*). The reduction in DGM levels commonly observed in mid-afternoon is thought to be due to increased flux of DGM from lake water as well as mixing of surface water within the epilimnion of lakes*(3, 10)*.

The role of microbial activity in regulating freshwater diel patterns of DGM has been largely ignored. In marine waters, DGM concentrations and phytoplankton pigments are correlated*(11)* but investigators have attributed this correlation to non-specific reactions occurring as a consequence of microbial growth*(10)*. In fresh waters it has been postulated that microbial activity, especially heterotrophic bacteria, may play a role in DGM production in freshwaters*(12, 13)*.

These investigators spiked isolated lake water with Hg and observed the production of DGM. However, microbial production of DGM in unpolluted freshwaters has been discounted because mercury concentrations, 3-20 pM, in pristine freshwater environments are below that required for the induction of the bacterial *mer* operon, between 10pM (George Golding, U of Manitoba, unpublished data) and 50 pM*(8)* However, bacteria maintain a basal level of mercury reductase activity that is able to efficiently reduce even very low concentrations of Hg^{2+} to Hg^0 *(14)* and the expression of mercury reduction activity by bacteria is dependent on factors other than mercury concentrations in water*(15)*. In addition to theoretical arguments discounting microbial DGM production, investigators observed that DGM was produced in filtered (0.7 µm) lake water at rates comparable to unfiltered water*(5)* suggesting that microorganisms were not a significant source of DGM production in lake water. Many bacteria in oligotrophic environments are well known to have diameters <0.7 µm and could pass through the filters used in that study. Thus, the role of microorganisms in DGM production in pristine freshwaters cannot be discounted.

We postulate that in addition to being a source of DGM, microbial activity may also reduce levels of DGM in lake water. Bacterial enzymes induced by H_2O_2, *e.g.* hydroperoxidase-catalase (*Kat*G) and other unidentified catalases, oxidize Hg^0 to Hg^{2+} *(16)*. These enzymes are not restricted to a particular group of organisms but are widely distributed amongst the eubacteria*(16)*. The oxidation of Hg^0 to Hg^{2+} has not been shown to be a specific reaction of a distinct catalase

but rather, may be a non-specific reaction of microbial catalases. H_2O_2 follows a strong diel pattern with increasing levels of H_2O_2 in lake water typically occurring in late afternoon*(17, 18)* but H_2O_2 is not capable of directly reducing Hg^{2+} to elemental mercury*(19)*. H_2O_2 induces bacterial catalase activity because bacteria need to protect themselves from the harmful effect of H_2O_2 on intracellular processes. This induction may occur through a stimulation of genetic transcription, *e.g.* via *oxyR,* or an increase in catalase activity may be the result of increasing the co-substrate, H_2O_2, for the catalase reaction. Hence, the induction of microbial oxidase activity by H_2O_2 is a possible explanation for the decrease in DGM levels observed in freshwater lakes during the afternoon. In this study, we investigated the role of microbial activity and its interaction with photochemical processes, in the diel patterns of DGM in lake water.

Experimental Section

Site Description

We measured DGM concentrations every 45-90 minutes as well as microbial mercury reductase and oxidase activity in three bays at Jack's Lake, located approximately 200 km northeast of Toronto, Canada (44°,41',20" N, 72°,02',54" W) on July 21, 22, and 23, 2000 and in Lake Ontario during the week of September 10-14, 2000. Similar weather prevailed over the three day period of July 21, 22 and 23 at Jack's Lake with no rain occurring and each day being sunny and clear. Jack's Lake, which has been the site of detailed H_2O_2

studies*(20)*, is a mesotrophic lake on the edge of the Canadian Shield with an average of 14 mg of Ca^{2+} L^{-1}, 12 µg P L^{-1} and pH of 7.2*(21)*. Brookes Bay is shallow, coloured, and shows pronounced anoxia below 5m with a shallow mixing depth. In contrast, Sharpes Bay is clear and shows little hypolimnetic oxygen depletion to the max depth of 43m. Williams Bay has features that are between the other bays but has metalimnetic peaks of chlorophyll and sulfate reducing bacteria*(22)*. Together these three bays which are present in a single water body, represent the physical features of most temperate lakes.

Analysis of Dissolved Elemental Mercury in Lake Water

Samples of Jack's Lake water were collected from a fiberglass boat 15 cm below the surface by placing a narrow mouth Teflon^R bottle directly into water by hand. Samples of Lake Ontario water were collected using a Go-Flo sampler. DGM was analyzed by bubbling approx. 20L (1 L min^{-1}) of mercury free air produced by a Tekran Zero Air Generator through a 1 L water sample contained in a closed glass graduated cylinder. The bubbled gas was analyzed for elemental mercury using a Tekran 2537A with pre-cleaned Teflon lines and connections. This instrument first amalgamates mercury onto a pure gold cartridge, then thermodesorbs this mercury, which is analyzed by cold vapour atomic fluorescence spectrophotometry every 5 minutes. This closed analytical system removes 99% of the DGM from a 1 L sample within 20 minutes with a daily detection limit of 5-25 fM. Daily detection limit was determined as three times the

standard deviation of blanks. The average coefficient of variation of 17 samples analyzed in triplicate was 13%. To the best of our knowledge, no di-atomic volatile Hg species have been reported in freshwaters. Consequently, values are expressed in fM based on the assumption that only mono-atomic Hg species were detected with this instrument. After analysis of DGM, 500 ml of lake water was combined with 100 ml of glycerol and the samples were frozen for microbial analysis.

Analysis of Microbial Mercury Reductase and Oxidase Activity

Microorganisms were extracted from water by centrifugation of 1L of lake water, lysed and the amount of protein extracted was quantified*(23)*. Protein extracted varied between 95 and 170 μg L^{-1} throughout the three day sampling period. Protein, *i.e.* enzyme, extracts were assessed for their mercury reductase activity*(24)*, with a U equivalent to 1 μmole of NADPH consumed in response to an aliquot of inorganic mercury. Microbial oxidation of elemental mercury was measured using 1 ml additions of water saturated with Hg^0 to 200 μL enzyme extracts of lake water*(16)*. Enzyme extracts were incubated at 22°C for 1 hour and a U designated as 10 fmoles of inorganic mercury formed. Boiled controls were prepared by heating enzyme samples (100°C) for 10 minutes and background mercury oxidation is subtracted from the reported value. The oxidation of Hg^0 was found to be proportional to the amount of enzyme.

Hydrogen Peroxide Experiments

DGM concentrations for Lake Ontario were from seven different stations encountered over the five day cruise. Weather patterns varied considerably over this time. Lake Ontario surface (sampler was set to 1m) water was collected with a GoFlo Sampler from Stations 9 (43°,35',12" N, 79°,23',42" W), 81(44°,01',00" N, 76°,40',18" W) and 752 (43°,29',55" N, 79°,28',58" W) in the morning for the H_2O_2 experiments and station 83 (44° 00' 00"N, 76° 50' 36"W) was sampled around 11 am for the sunlight incubation experiments. The sunlight incubations were performed on the rear deck on the Limno's cruise vessel between 13:00 until 18:00 on a clear and sunny day with dark samples kept inside a cupboard on board. Isolated samples were spiked with 100 nM H_2O_2 that is a typical mid-day concentration of H_2O_2 in Lake Ontario*(25)*. DGM, mercury reductase and oxidase activities were determined every thirty minutes for 5 hours. Data was normalized to the DGM concentrations observed immediately (< 5 minutes) after lake water was spiked with 100 nM H_2O_2. Lake water was filtered in an attempt to determine the relative contribution of abiotic and biotic processes on DGM production. Lake water was filtered through a 0.22 µM syringe top Sterivex^{TM} filter*(26)* and protein concentration*(27)* used to detect biological activity.

Results and Discussion

DGM concentrations in all three bays in Jack's Lake peaked at *ca.* 159 fM (n=6, standard deviation of 26%) at 12:00 and decreased to *ca.* 90 fM, by 18:00 for the remainder of the day (Figure A1-1). These DGM concentrations are similar to that observed in Ranger lake*(5)*. Microbial reductase and oxidase activity patterns were similar in all three bays with a strong increase in mercury reductase activity in the morning followed by mercury oxidase activity peaking in late afternoon. Similarly, DGM concentrations in Lake Ontario were the highest before noon peaking at 736 fM (standard deviation of 209 fM, n=3) and the lowest, 284 fM (standard deviation of 100 fM, n=4) in the afternoon. This pattern is also similar to that previously observed in Ranger lake*(5)* and the Florida Everglades*(4)* suggesting that we are observing a general pattern of DGM in the uppermost surface water of freshwaters lakes. Levels of DGM in lake Ontario were somewhat higher than that previously observed, 145 ±85 fM n=5, in Lake Michigan *(12)* but it is not clear at what time of day these samples were collected.

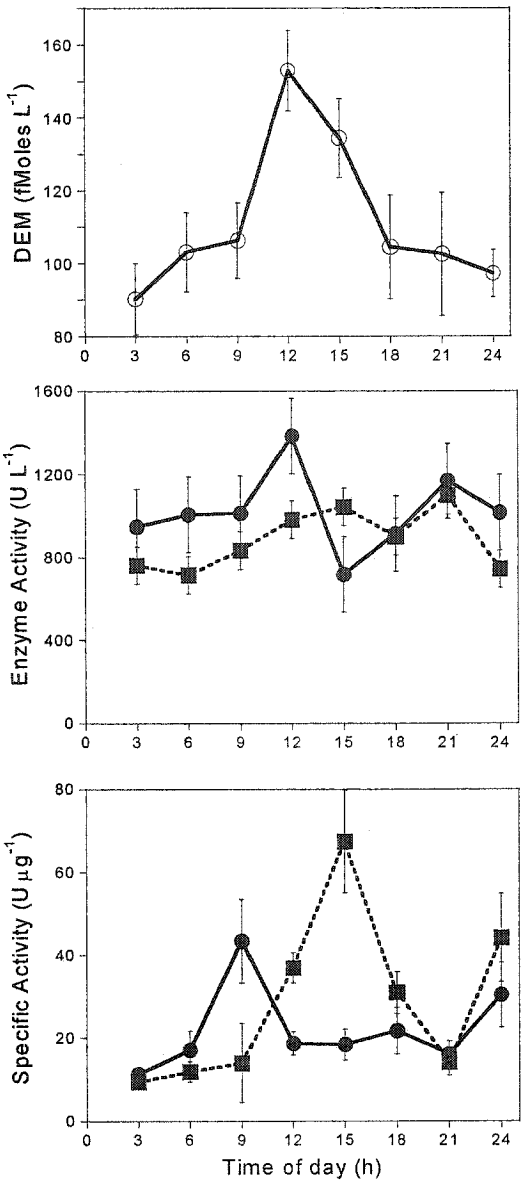

Figure A1-1. Diel pattern of DGM (○), mercury oxidase (■) and reductase (●) activity extracted from three bays in Jack's Lake on July 21, 2000. Each data point is the average of three bays that were measured in duplicate (n=6) and error bars represent the standard error of the estimate.

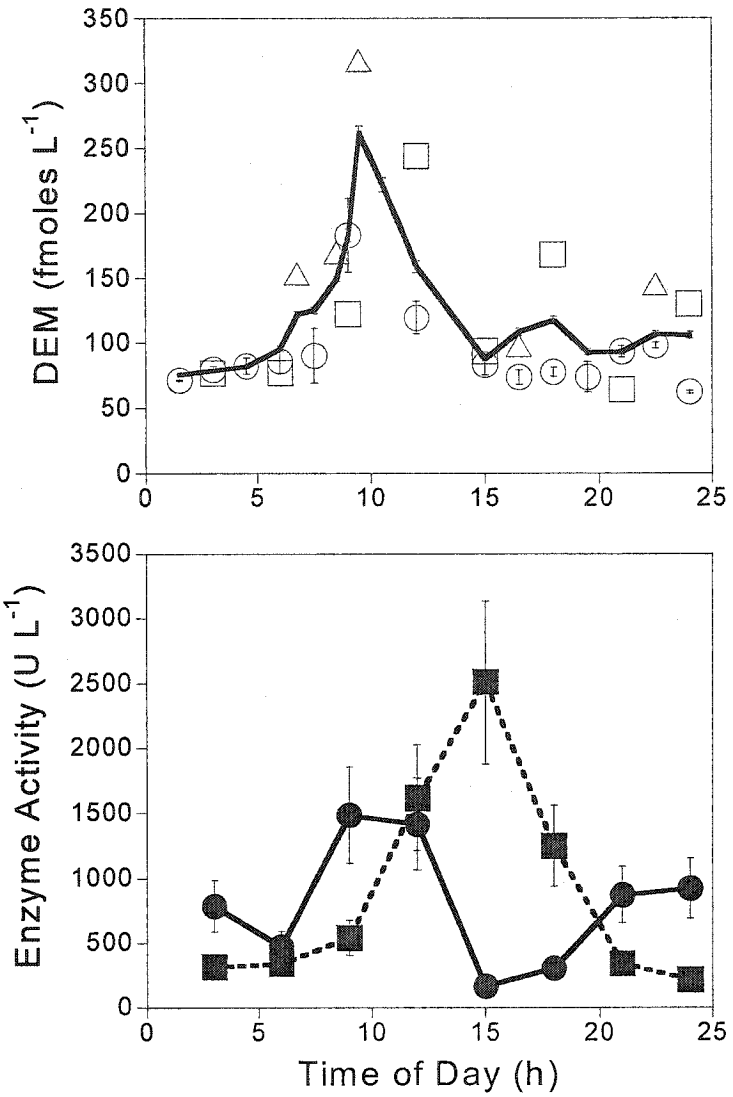

Figure A1-2. Diel pattern of DGM, mercury oxidase (■) and reductase (●) activity over a three day period in Brookes Bay, Jack's Lake. Each data point for DGM for July 21(Δ) and July 22(□) is a single sample with duplicate samples analyzed on July 23(○). The moving average (—) is the average of observations taken over the three-day period immediately before, at and after the indicated time of sampling with error bars indicating the standard error of this estimate. Each data point for microbial mercury oxidase and reductase activity is the average of duplicate samples taken on July 22 and 23.

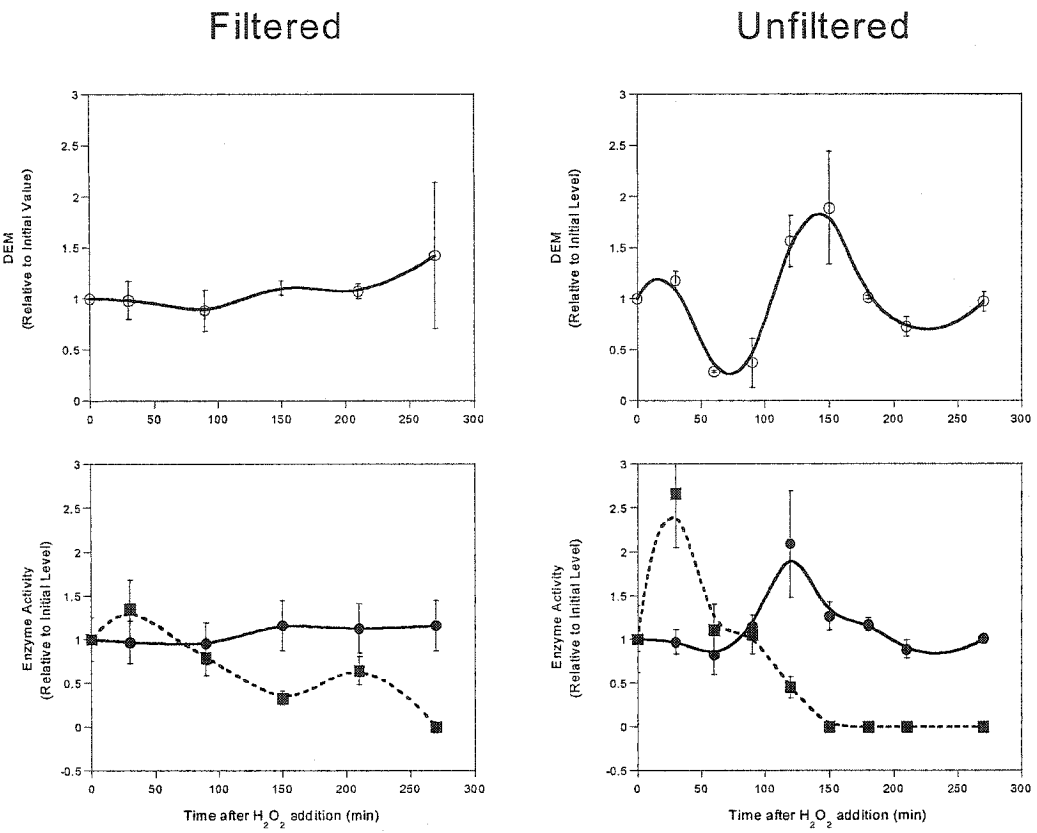

Figure A1-3. Induction of microbial mercury oxidase (■) and reductase (●) activity and resulting DGM (○) concentrations by the addition of H_2O_2 to Lake Ontario water. Each data point for DGM is the average of independent incubations from three different sampling locations on Lake Ontario. Each data point for enzymes from unfiltered water is from the three different sampling locations but for filtered water, it is the average of two different sampling locations only.

Diel patterns of DGM in Brookes Bay (Figure A1-2) were highly reproducible over a three-day period peaking between 10:00 and 12:00 followed by a steady decrease to the baseline concentration of DGM of *ca.* 100 fM by 16:00. Mercury reductase activity paralleled DGM levels in lake water with a sharp increase in reductase activity occurring in the early morning, peaking by 12:00 and decreasing by 15:00. Mercury oxidase activity, i.e. DGM consumption, did not significantly increase until later in the day, peaking at 15:00. Mercury reductase activity increased again after 15:00 but at that point mercury oxidase activity was elevated and thus, the net result on DEM concentrations was minimal. The regulation of mercury reductase activity at environmental mercury concentrations and in *in situ* communities is an area that requires further research. The strong reproducibility of the diel patterns in Brookes bay supports our assertion that these diel patterns are a general phenomenon of freshwater lakes.

The diel pattern of mercury oxidase activity observed in all three bays as well as Lake Ontario was similar to previously published diel patterns of hydrogen peroxide*(21, 17)*. However, no H_2O_2 additions were made at Jack's Lake because other researchers had observed no effect on DGM levels measured four hours after H_2O_2 addition in samples from Rangers Lake*(5)*. At that time, DGM analysis was more time consuming and thus, it was not possible for researchers to develop more detailed time course data. The strong similarity between H_2O_2 and DGM patterns convinced us that H_2O_2 may be related to DGM

concentrations in water but that it may occur over a time scale, that previous investigators were unable to determine. Additions of H_2O_2 increased mercury oxidase activity by 250% within 30 minutes, and 60 minutes after H_2O_2 addition, DGM had decreased to 28% of the initial value (Figure A1-3). At time 0, unfiltered samples contained 390 fM (stdev of 95fM, n=3) DGM and for filtered samples 467 fM (stdev of 130 fM, n=3) DGM which is well within the range observed at other sampling stations on Lake Ontario. At time 0, there was 1060 U L^{-1} mercury reductase and 720 U L^{-1} mercury oxidase activity in unfiltered water but only 58 U L^{-1} mercury reductase and 60 U L^{-1} mercury oxidase activity in filtered water. Hydrogen peroxide may increase mercury oxidase activity by either inducing peroxidase enzymes such as *katG* or alternatively, by increasing the amount of intracellular co-substrate for the oxidation of Hg^0*(16)*. In a manner similar to that observed at Jack's Lake, mercury reductase activity and DGM concentrations in water paralleled one another with only a short time lag of 30 minutes occurring between the increase in mercury reductase activity and an increase in DGM concentrations. This increase in mercury reductase may be related to the stimulation of mercury reductase activity by the increase in divalent mercury, *c.a.* 246 fM, in the environment. DGM stabilized by 240 minutes at levels comparable to that initially seen. Previous investigator's DGM data, measured 0 and 240 minutes after H_2O_2 addition, does not reflect the remarkable transformations which may take place over this four hour period*(5)*. Hydrogen peroxide induced DGM fluctuations were not observed in filtered lake water suggesting that the changes in DGM concentrations observed in non-filtered lake water were a result of biological activity and confirm earlier work that H_2O_2 is not capable of reducing

Hg^{2+} to elemental mercury*(19)*. The H_2O_2 spiking experiments implicate microbial oxidation activity in the regulation of DGM concentrations in lake water. The sine-wave pattern observed with the H_2O_2 spiking experiments was not observed during the diel patterns and is likely due to the continuous production of H_2O_2 throughout the peak periods of the day. These experiments illustrate that a cascade of microbial driven mercury transformations is triggered by H_2O_2 production in lake waters. From our results it is not clear the mechanism by which H_2O_2 induces mercury oxidase activity. It could be the induction of the mercury oxidase gene as observed in pure culture studies*(16)*. Alternatively, the increase in electron acceptor concentrations for the catalase reaction, in this case H_2O_2, may result in an increase in the oxidation of mercury by pre-existing catalase's present in the water column.

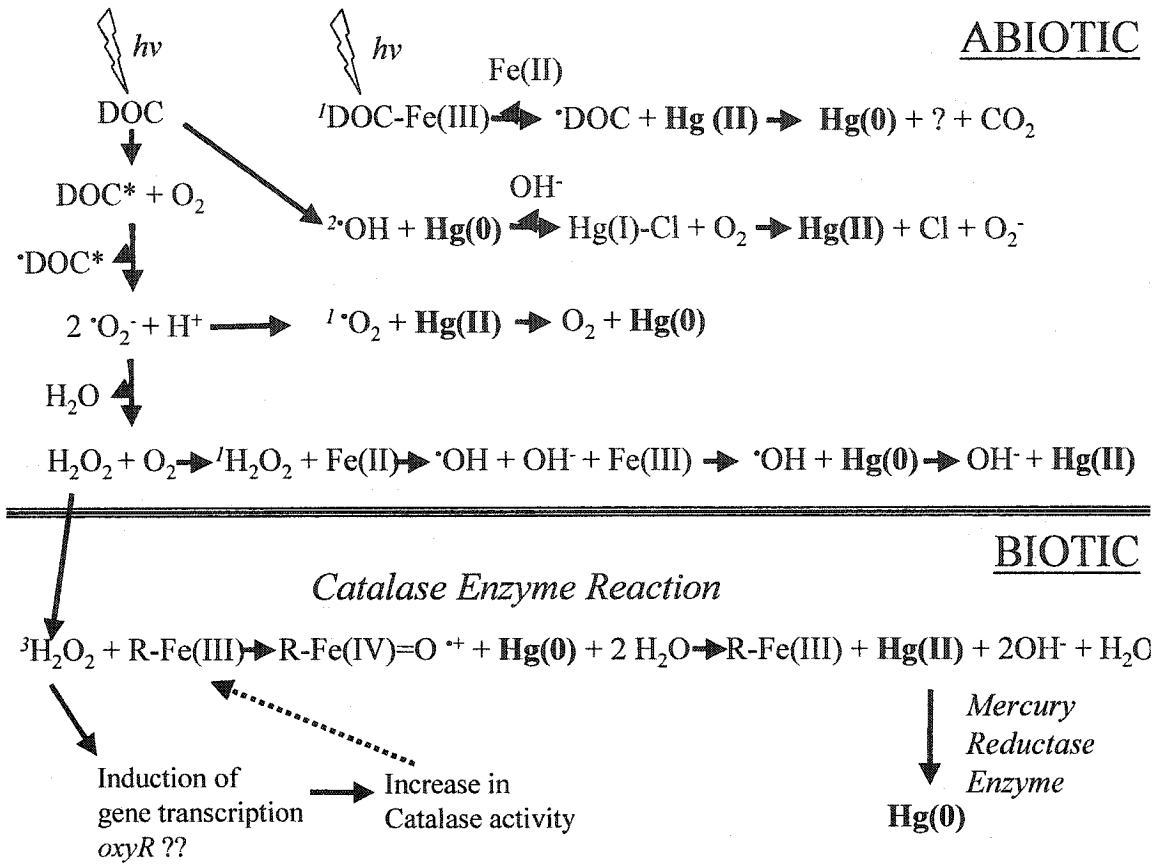

Figure A1-4. Conceptual diagram outlining the importance of sunlight for the two known biological and four known abiotic transformations of divalent and elemental mercury in freshwaters. [1]-reactions described by Zhang and Lindberg*(9)*, [2]-reactions described by Lalonde *et al. (28)* and [3]-reactions described in this study. The relative importance of each reaction pathway has yet to be determined.

Our work suggests that H_2O_2 produced by solar radiation stimulates mercury oxidase activity in lake water, which results in a decrease in DGM levels during the afternoon. We acknowledge that our work in unable to determine the *in situ* activity of mercury oxidase, but rather our work highlights that the potential mercury oxidase activity increases in response to H_2O_2 produced by solar radiation. Further, our results illustrate the interplay of microbial reduction and

oxidation activities with photochemical processes in controlling levels of DGM in surface water of lakes. This interplay is illustrated in Figure A1-4. Irradiation of lakes begins a cascade of photochemical reactions that in turn trigger four known abiotic and two known biotic transformations involving elemental mercury. Important co-factors in these reactions such as benzoquinones and Fe(III) are just now beginning to be uncovered by investigators*(9,28)*. The relative contribution of photoreduction and photooxidation must now be placed in context with reduction and oxidation rates due to microbial activity in order to develop an accurate model for DGM levels in surface waters. Future investigations will focus on a comparison of actual *in situ* rates of photooxidation/reduction to *in situ* rates of microbial mercury oxidation and reduction.

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Appendix 2

Supplementary Information for Chapter 4

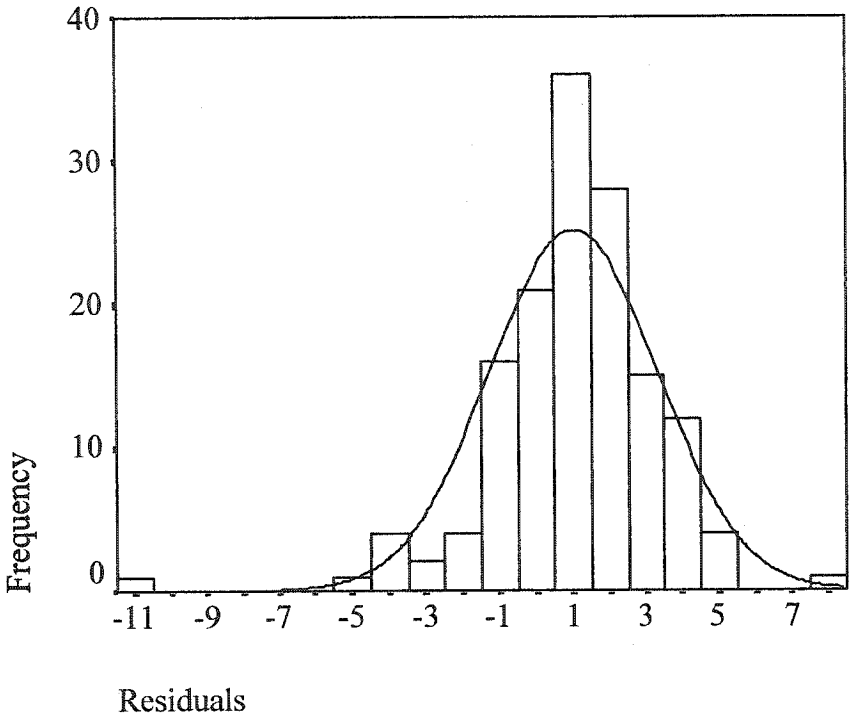

Figure A2-1: Distribution of residuals for Schroeder *et al.* model on Puzzle Lake with normal curve displayed as a solid line.

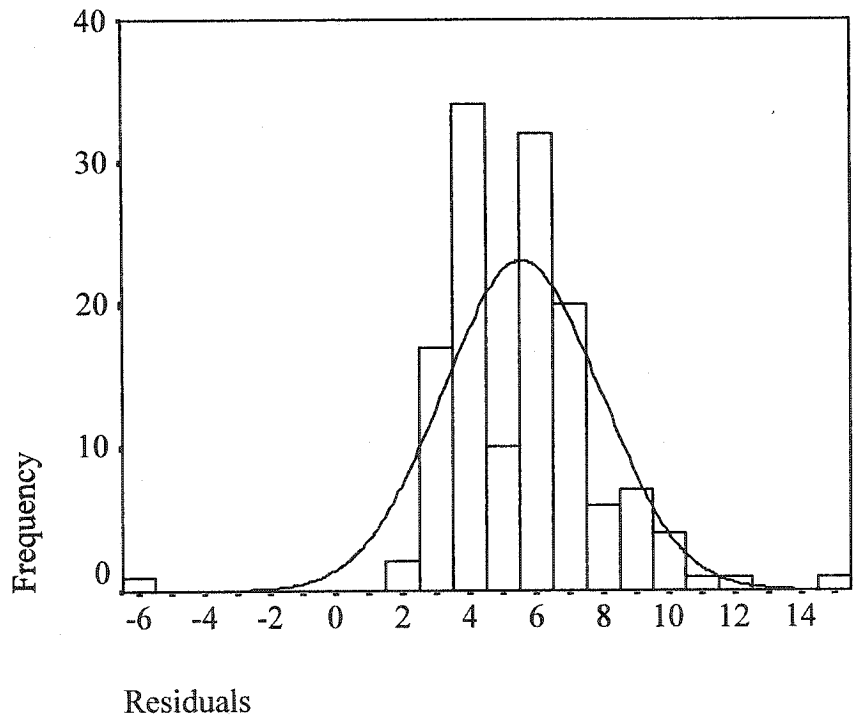

Figure A2-2: Distribution of residuals for Schroeder *et al.* model on Big Dam West Lake with normal curve displayed as a solid line.

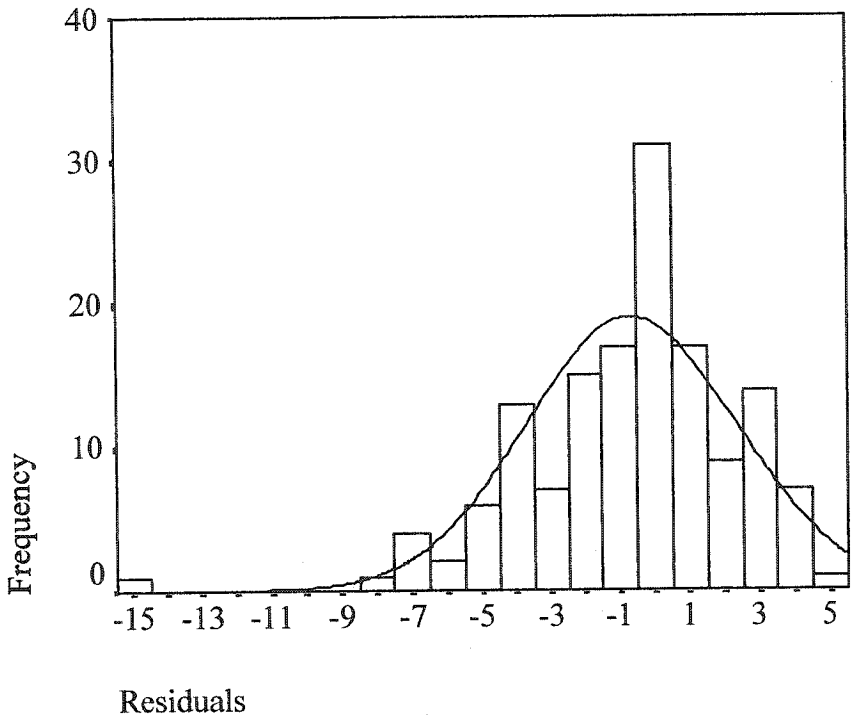

Figure A2-3: Distribution of residuals for Poissant *et al.* model on Puzzle Lake with normal curve displayed as a solid line.

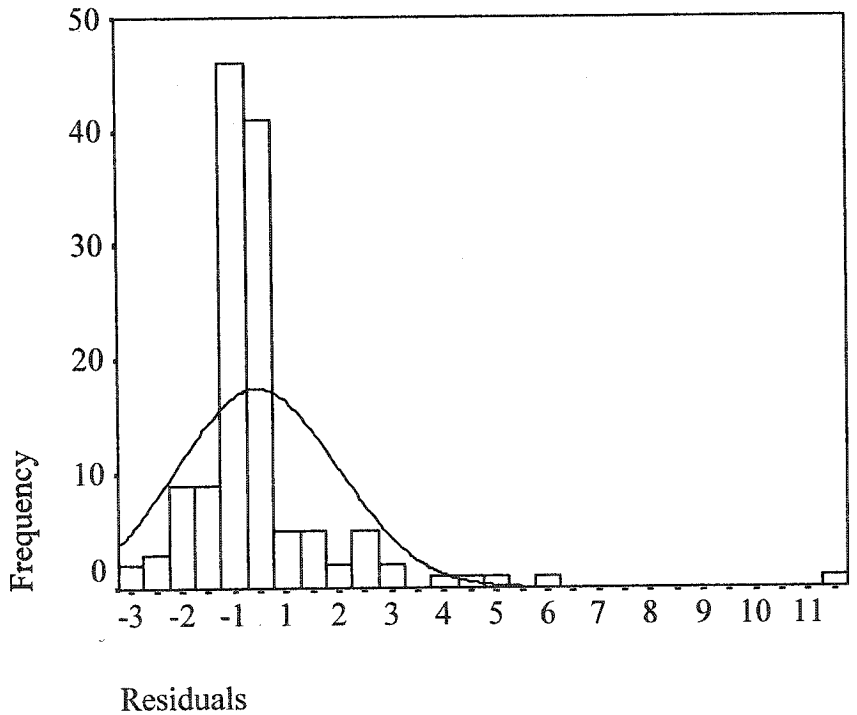

Figure A2-4: Distribution of residuals for Poissant *et al.* model on Big Dam West Lake with normal curve displayed as a solid line.

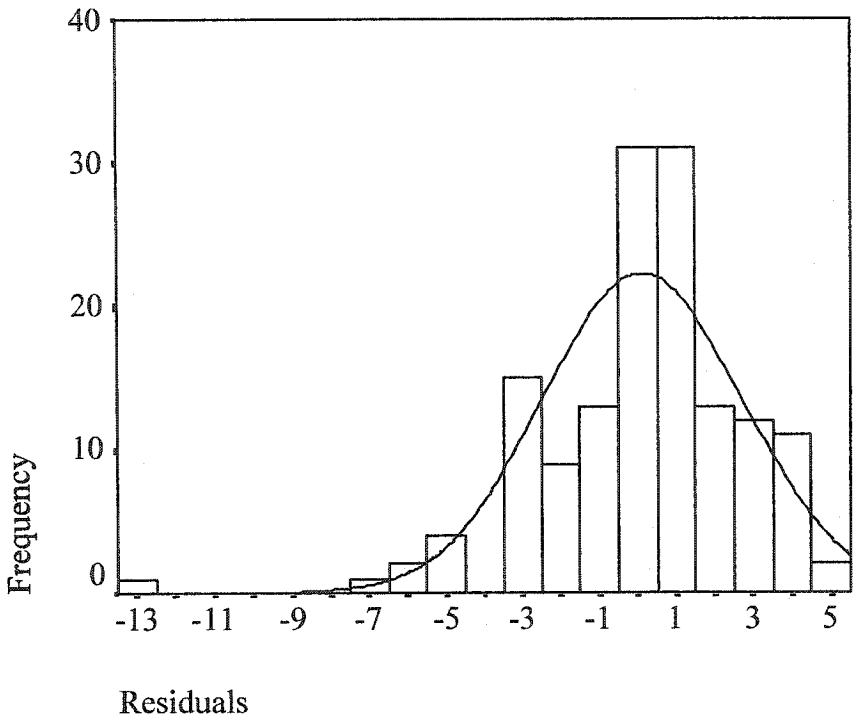

Figure A2-5: Distribution of residuals for Poissant *et al.* model with constant 3 ms^{-1} wind speed on Puzzle Lake with normal curve displayed as a solid line.

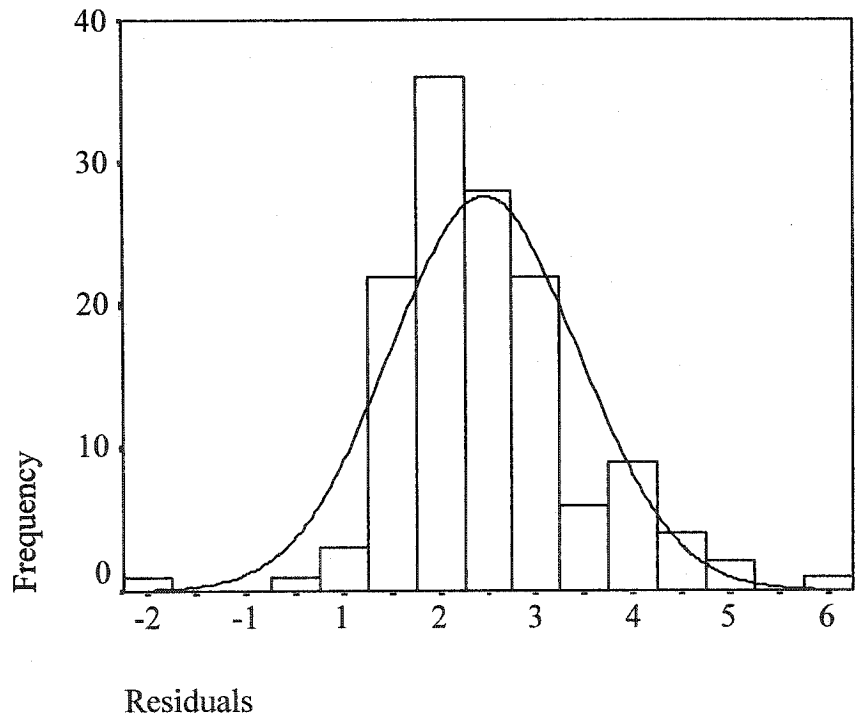

Figure A2-6: Distribution of residuals for Poissant *et al.* model with constant 3 ms^{-1} wind speed on Big Dam West Lake with normal curve displayed as a solid line.

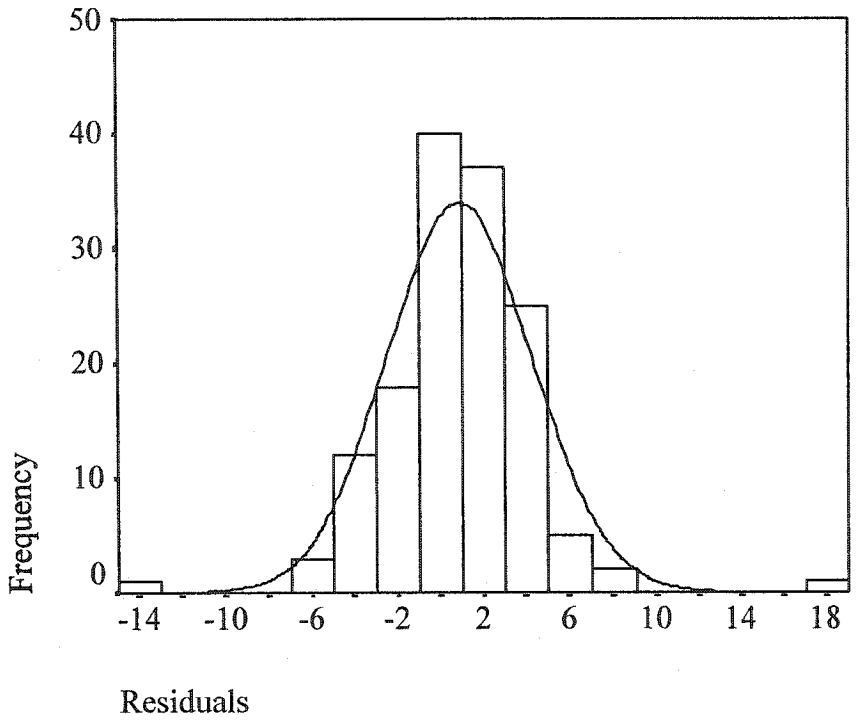

Figure A2-7: Distribution of residuals for Boudala *et al.* model on Puzzle Lake with normal curve displayed as a solid line.

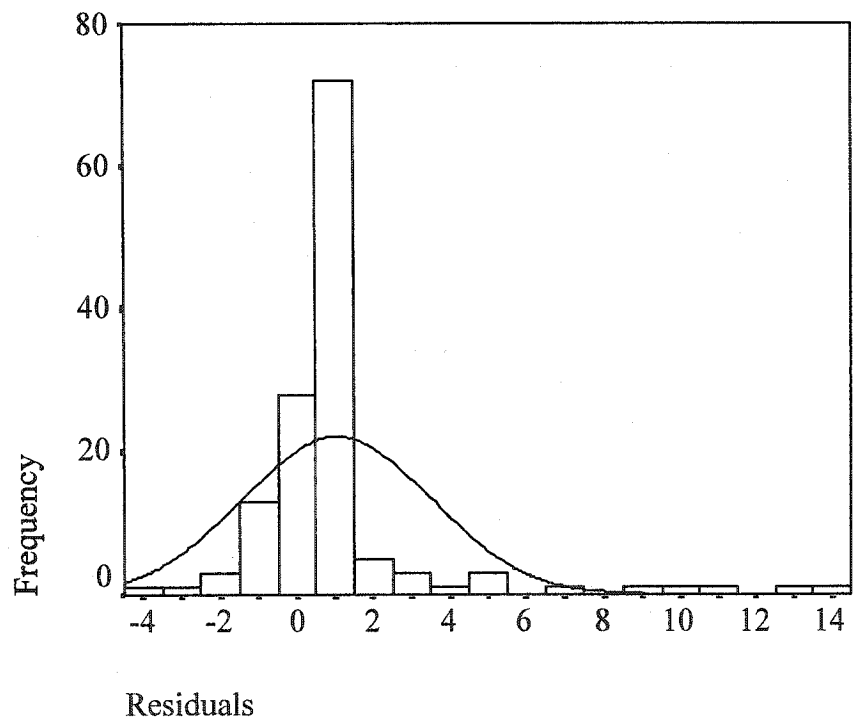

Figure A2-8: Distribution of residuals for Boudala *et al.* model on Big Dam West Lake with normal curve displayed as a solid line.