Effect of Dissolved Organic Carbon on the Photoproduction of Dissolved Gaseous Mercury in Lakes: Potential Impacts of Forestry

5 AUTHORS, INCLUDING:

N.J. O'Driscoll

Acadia University

65 PUBLICATIONS **886** CITATIONS

David Lean

University of Ottawa

251 PUBLICATIONS **8,860** CITATIONS

Lisa Loseto

Fisheries and Oceans Canada

42 PUBLICATIONS **795** CITATIONS

Steven Douglas Siciliano

University of Saskatchewan

178 PUBLICATIONS **5,883** CITATIONS

Effect of Dissolved Organic Carbon on the Photoproduction of Dissolved Gaseous Mercury in Lakes: Potential Impacts of Forestry

N. J. O'DRISCOLL,*,[†] D. R. S. LEAN,[†] L. L. LOSETO,[†] R. CARIGNAN,[‡] AND S. D. SICILIANO[§]

Biology Department, Faculty of Science, University of Ottawa, P.O. Box 450, Station A, Ottawa, Ontario, Canada K1N 6N5, Département de Sciences biologiques, Université de Montréal, Box 6128, Montréal, Québec, Canada H3C 3J7, and Department of Soil Science, University of Saskatchewan, 51 Campus Drive, Saskatoon, Saskatchewan, Canada S7N 5A8

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 central Quebec: two with highly logged drainage basins and two with minimally logged drainage basins. On two separate days for each lake, water samples (filtered to remove >99% of microorganisms) with varying DOC concentrations were incubated in clear and dark Teflon bottles on the lake surface. DGM concentrations were measured at 3.5-h intervals over the course of 10.5 h. Levels of DGM concentrations increased with increasing cumulative irradiation for all lakes until approximately 4000 kJ m^{-2} (400–750 nm, photosynthetically active radiation (PAR)), when DGM concentrations reached a plateau (between 20 and 200 pg L^{-1}). When we assumed that DGM production was limited by the amount of photoreducible mercury, reversible first-order reaction kinetics fitted the observed data well (r^2 ranging between 0.59 and 0.98, $p < 0.05$ with the exception of N70 100% DOC, 0% DOC, and K2 0% DOC with $p = 0.06$, 0.10, and 0.11, respectively). The DGM plateaus were independent of DOC concentrations but differed between lakes. In contrast, photoproduction efficiency (DGM$_{prod}$) (i.e., the amount of DGM produced per unit radiation (fg L^{-1} (kJ/m^2)$^{-1}$) below 4000 kJ m^{-2} PAR) was linearly proportional to DOC concentration for both logged lakes ($r^2 = 0.97$, $p < 0.01$) and nonlogged lakes ($r^2 = 0.52$, $p = 0.018$) studied.

* Corresponding author phone: (613)562-5800, ext. 6655; fax: (613)562-5486; e-mail: nodrisco@science.uottawa.ca.
† University of Ottawa.
‡ Université de Montréal.
§ University of Saskatchewan.

Furthermore, logged lakes had a lower DGM$_{prod}$ per unit DOC ($p < 0.01$) than the nonlogged lakes. In these four lakes, the rate of DGM production per unit PAR was dependent on the concentration of DOC. The DGM plateau was independent of DOC concentration; however, there was a significant difference in DGM plateaus between lakes presumably due to different DOC structures and dissolved ions. This research demonstrates an important mechanism by which logging may exacerbate mercury levels in biota.

Introduction

Dissolved gaseous mercury (DGM) is believed to be primarily composed of dissolved elemental mercury (Hg^0) (*1*). 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 several diurnal cycles (*2*). Existing models, however, fail to predict accurately the measured DGM flux (*2*), which may reflect the uncertainty surrounding factors that affect rates of mercury photoreduction and photooxidation in freshwaters.

Solar radiation induces both chemical (*3*) and microbial (*4*) mercury reduction in lake water. These reactions probably involve other variables, including dissolved ions, availability of photoreducible mercury, and DOC concentration (*3, 5–8*). DOC is widely acknowledged to be important in the photoreduction of mercury (*9, 10*), but the exact manner in which DOC affects DGM production is not known. Watras et al. (*11*) 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. (*12*) spiked water samples with 100 nM mercury-(II) as Hg(OH)$_2$ and HgCl$_2$ and found that the presence of humics and fulvic acids (DOC) corresponded with significant increases in DGM photoproduction. Amyot et al. (*5*) sampled water from low DOC Artic lakes, spiked it with 1–8 mg of fulvic acids L^{-1}, and exposed it to varying levels of solar radiation without observing any significant changes in DGM. Yet, in another study Amyot et al. (*3*) 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 than in the two high DOC lakes. In contrast to these results, O'Driscoll et al. (*2*) report 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 than in a low DOC (3.6 mg L^{-1}) lake over a 48-h period ($n = 576$).

Part of the reason for such conflicting reports on the role of DOC in mercury photoreduction processes is that DOC may differ between lakes, not only in concentration but also in structure and composition. 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, to study the effects of DOC concentration on DGM production accurately, the DOC within a lake must be changed in concentration without changing other variables. Such an approach would allow for the assessment of photoproduction rates while avoiding the confounding effects of DOC structure and dissolved ions.

TABLE 1. Physical and Chemical Characteristics of the Lakes Sampled and Their Associated Drainage Basins

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
avg catchment slope	%	9.2	4.6	4.6	3.3
max lake depth	m	20.4	12.2	7.2	10.5
lake volume	m^3	4.4E+06	6.1E+06	2.3E+06	1.4E+06
% wetlands in catchment basin		2.5	4.4	11.0	3.2
cumulative % of basin logged since 2000		0	2	26	67
shoreline	km	4.04	11.85	5.37	2.95
oxygen saturation	%	100	100	100	100
Secchi depth	m	3.5	1.7	3.1	1.0
pH in-situ		6.4	5.7	6.1	6.3
chemical oxygen demand	mg L^{-1}	5.5	8.8	6.5	16.3
total phosphorus	μg L^{-1}	5.1	8.7	9.8	15.6
total nitrogen	μg L^{-1}	226	312	285	507
NO$_3^-$ as N	μg L^{-1}	0.5	8.8	0.5	7.0
Cl$^-$	mg L^{-1}	0.11	0.10	0.13	0.22
SO$_4^-$ as S	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}	0.23	0.21	0.30	0.77

The separation of DOC from lake water has been achieved in the past using various methods including XAD extraction, liquid chromatography (13), ultrafiltration, tangential ultrafiltration, and reverse osmosis (14, 15). 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 (16). Ultrafiltration can be prone to clogging of membranes and binding of metals to membrane surfaces and is generally used for samples of small volume (17). 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 (14) that may affect photoreduction processes (8). Tangential ultrafiltration is therefore the method of choice for altering DOC concentrations in large volumes of lake water since it involves no chemical alterations, it causes less clogging of pores due to a continuous tangential flow of solution on the filter, and the concentration of inorganic ions (smaller than the membrane pore size) remains largely unchanged during separations (18, 19).

Previous research has indicated that the logging of a drainage basin may increase mercury in the biota of the associated lake (20, 21). However, the mechanism that results in increased bioaccumulation with logging is unclear. We examined the effects of DOC concentration on the photoproduction of DGM in two freshwater lakes with logged drainage basins and two nonlogged lakes in central Quebec.

Site Description

Four lakes in central Quebec were chosen to represent a range of DOC concentrations within both logged and nonlogged drainage basins. Sampling and experiments were conducted during September 2002. Table 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 1 and 2). All lakes are relatively small (<1.5 km^2), and their surface waters are well-saturated with oxygen (~100%) (see Table 1).

TABLE 2. Total Mercury and Dissolved Organic Carbon Concentrations for each Series of Whole Water Dilutions Performed in the Four Lakes Sampled

lake	% whole water	total mercury (ng L^{-1})	SD	DOC (mg L^{-1})
K2	0	1.1	0.0	0.9
K2	10	0.8	0.0	1.3
K2	25	0.8	0.3	2.3
K2	50	1.2	0.1	5.1
K2	100	1.9	0.5	6.7
K3	0	1.6	0.3	0.4
K3	10	1.0	0.4	1.1
K3	25	2.0	0.3	1.6
K3	50	3.3	2.9	2.7
K3	100	3.3	0.3	4.9
DF9	0	1.6	1.2	2.3
DF9	10	2.6	1.0	3.8
DF9	25	2.9	0.7	5.0
DF9	50	5.2	1.3	8.1
DF9	100	8.7	2.3	13.7
N70	0	0.7	0.1	0.6
N70	10	0.5	0.6	1.0
N70	25	0.7	0.6	1.2
N70	50	0.9	0.3	1.6
N70	100	1.0	0.5	3.2

Methods

A single sample of surface water (>200 L) was collected at midday from each of the four lakes with contrasting DOC concentrations in central Quebec. Samples were taken near the water surface in the center of the lake. Each lake was sampled on a separate day over the course of four days. The water was collected in 25-L high-density polyethylene (HDPE) containers and transported in the dark to the analysis site within 1 h using a floatplane. HDPE was chosen for its cost-effectiveness, ease of handling, and suitability for subsequent mercury analysis (22).

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 ultrahigh 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
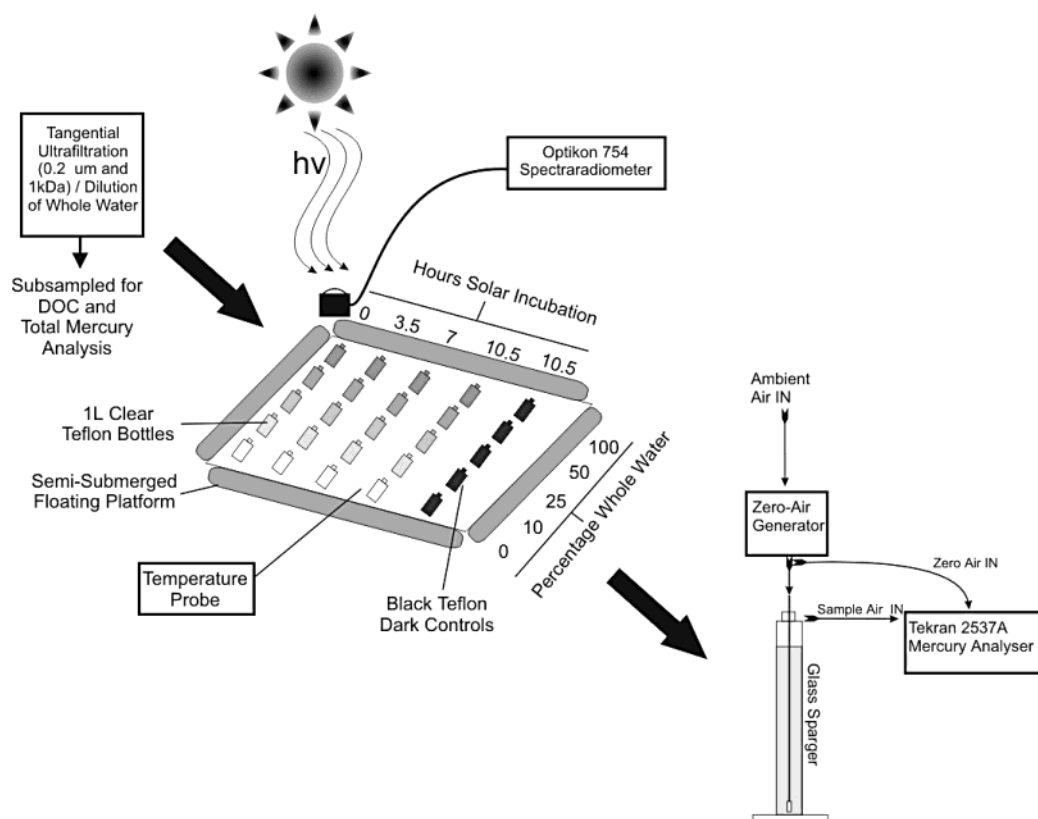
FIGURE 1. Flow diagram of sample preparation, incubation, and DGM analysis methods.

is referred to as "whole water" for the remainder of this study. Tangential ultrafiltration of the same series of lakes has been shown by previous work in our laboratory to remove >99% of microbes present (using visual counts and the DAPI method for bacterial counts). However, re-growth of the microbial population will occur over a 24-h period with minimal amounts occurring during the first 10 h after filtration (23). To account for this, all filtration was performed immediately prior to incubation of samples.

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. As previously outlined, tangential flow ultrafiltration is the technique best suited for studies of mercury and DOC fractionation (18, 19). As recommended (18, 19), membranes were preconditioned with lake water for 120 min 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 while leaving dissolved ions in the water unaltered. 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 fiber prefilter. A detailed explanation of this method has been given by Sun et al. (15). 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 were sampled and analyzed along with the rest of the dilutions to examine the effect of small molecular weight DOC on DGM photopro-duction.

Samples of each whole water dilution were subsampled for the analysis of DOC and total mercury. All subsamples were collected in 50-mL polypropylene tubes (Falcon). Total mercury samples were preserved by the addition of 1% BrCl (22) and refrigerated until analysis by cold vapor atomic fluorescence (U.S. EPA Method 1631). 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, and 100%) were placed in clear and black 1-L FEP Teflon bottles, which were then partially submerged in lake water using a floating platform (Figure 1) and exposed to sunlight for a total of 10.5 h. Solar radiation was measured every 15 min using an Optikon 754 spectra-radiometer equipped with a quartz spectral probe. Scans were taken at 10-nm intervals between 280 and 800 nm and integrated to obtain measurements of cumulative UVB (280−320 nm), UVA (320−400 nm), and photosynthetically active radiation (PAR) (400−750 nm). Water temperature was measured at 3.5-h intervals using a digital thermometer.

Samples for each whole water dilution were collected at 3.5-h 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 (1) is similar to methodology employed by Amyot et al. (3, 5, 6) and Lindberg et al. (24). The analysis system can be used to measure DGM in 1-L water samples (discrete mode) or continuously from a water reservoir (continuous mode) (1, 2). In short, the analysis system consisted of a 1-L glass volumetric sparger and Tekran 2537A air analysis unit. When analyzing a discrete sample, a 1-L sample was bubbled for 30 min using mercury-free air. The volatile mercury was then measured by gold amalgamation/atomic fluorescence spectrometry.

For each of the four lakes, the entire experiment from the original filtration and dilutions of whole water were 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.

Data Analysis. *Solar Radiation Measurements.* Visible or photosynthetically active (PAR) radiation is thought to be an important portion of the spectrum for DGM production. Amyot et al. (*6*) observed that seawater exposed to PAR, UVA, and UVB 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. Since all samples were exposed to the same full spectrum of incoming radiation, the relationship between UVA, UVB, and PAR will be similar for each sample during the course of the incubations. This was supported by strong Pearson correlations between PAR and UVA and between 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, 400–750 nm (mean = 78%, σ = 9.2%, n = 293); UVA, 320–400 nm (mean = 13%, σ = 3.4%, n = 293); and UVB, 280–320 nm (mean = 0.7%, σ = 0.42%, n = 293). Since the relative importance of UVA and UVB to photoreduction is unclear and since the proportion in surface waters is relatively 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 knew that only a portion of this radiation was absorbed by the samples. Amyot et al. (*3*) noted that 1-L Teflon bottles of the type used in these experiments have a longitudinal section of 0.016 m^2 and the number of photons received is relative to the absorption spectrum of the lake water and the radiant flux density. Similar Teflon bottles have been shown by Amyot et al. (*6*) to result in a decrease in irradiance of 18% of UVA, 34% of UVB, and 0.7% of 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.

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 photoreductants (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 photoreduction and photooxidation.

DGM dynamics can be modeled as a single reversible reaction, where the available photoreducible mercury ($Hg_{reducible}$) is converted to DGM by a number of photoreductants, as shown in eq 1. Assuming that photoreductants and oxidants are present in excess, their concentration can be considered unchanged throughout the reaction, and we can ignore them in the equation:

$$Hg_{reducible} + photoreductants \rightleftharpoons DGM + photooxidants \quad (1)$$
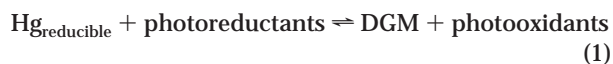
If we then assume that DGM is zero at time zero, with a forward rate constant k_1 and a backward rate constant k_2, we

can derive eq 2 (*25*):

$$[DGM] = (k_1[Hg_{reducible}]_0/(k_1 + k_2))[1 - e^{-(k_1+k_2)t}] \quad (2)$$

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 of L pg^{-1} $(kJ/m^2)^{-1}$ as opposed to the traditional L mol s^{-1}. It should be noted that by doing this we have assumed a linear relationship between time and cumulative solar radiation for each day. This seemed a reasonable assumption since a linear regression between time and cumulative solar radiation was found to fit very well for each of the eight days that experiments were performed (r^2 > 0.97; p < 0.001; n = 40). Since DGM is not equal to zero at the beginning of the incubations, an initial DGM constant has been added to eq 2. These changes result in

$$[DGM] = [DGM]_0 + (k_1[Hg_{reducible}]_0/(k_1 + k_2))[1 - e^{-(k_1+k_2)x}] \quad (3)$$

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

By setting parameters a and b as follows:

$$a = k_1[Hg_{reducible}]_0/(k_1 + k_2) \quad (4)$$

and,

$$b = k_1 + k_2 \quad (5)$$

we can rewrite eq 3 as

$$[DGM] = [DGM]_0 + a[1 - e^{-bx}] \quad (6)$$

Equation 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 nonlinear 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]. Since several of the days were cloudy, the cumulative radiation did not reach 10 000 kJ m^{-2} (particularly for lakes N70 and DF9 shown in Figure 2, panels c and d). Therefore, the plateau is an estimation using the equation for the curve fit.

Initial DGM Production Efficiency (DGM_{prod}) Calculations. Linear regression was used to determine the slope of DGM concentrations versus cumulative solar radiation (PAR), between 0 and 4000 kJ m^{-2}. Model 1 linear regression was considered appropriate since the error on the x-axis was considerably less than on the y-axis (<5%). A univariate general collinear model (ANCOVA) was used in the SPSS 10.0 statistical package to determine the relationships between photoproduction efficiency, DOC, and the fixed factors (logged and nonlogged sites).

Results and Discussion

In this investigation, we systematically varied DOC concentration with minimal changes in lake chemistry or DOC
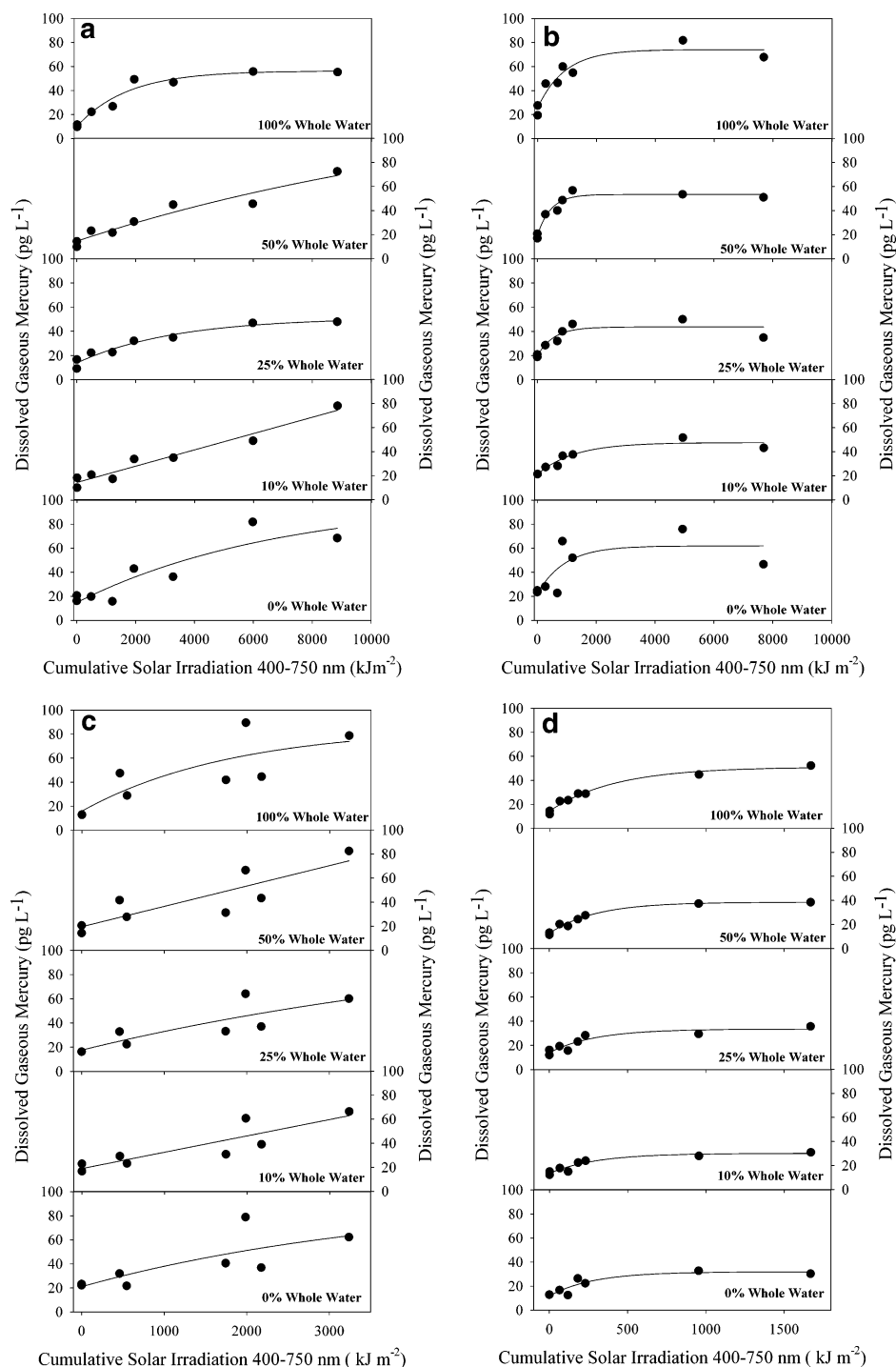
FIGURE 2. Cumulative PAR (kJ m^{-2}) versus dissolved gaseous mercury (pg L^{-1}) for each DOC dilution in (a) Lake K3, (b) Lake K2, (c) Lake N70, and (d) Lake DF9. Solid line represents regression of the form $y = y_0 + a(1 - e^{-bx})$; equation parameters given in Table 3. Data points were collected over two consecutive days.

structure and observed DGM dynamics in sterile lake water. Within our data set, we found that DGM production (DGM$_{prod}$) increased with DOC concentration and that lakes with logged drainage basins have lower efficiency of DGM production.

DOC and Total Mercury Analyses. 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 2) indicate that DOC concentrations were substantially decreased with dilutions using 1-kDa filtrate. The 1-kDa 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 in excess (5−90 times) of the DGM measured in the samples during incubation (<0.1 ng L^{-1}). The fraction of total mercury that is available for photoreduction is unknown. Reverse osmosis permeates for lakes K3 and N70 were found to contain DOC concentrations that were below detection limits (<0.002 mg L^{-1}).

Modeling DGM Dynamics. Plots of cumulative PAR against DGM for the five whole water dilutions for each of

TABLE 3. Variables and Statistics for Curve Fit of the Form $y = y_0 + a(1 - e^{-bx})$ for DGM Photoproduction in Each of the Lake Water Dilutions Shown in Figure 2

lake	% whole water	y_0	SE	a	SE	b	SE	r^2	p
K3	100	10.3	3.2	46.1	4.7	5.8E−04	1.6E−04	0.95	<0.01
K3	50	15.9	3.7	1.6E+05	3.2E+08	4.0E−08	8.0E−05	0.93	<0.01
K3	25	13.9	2.2	37.5	5.1	3.0E−04	1.0E−04	0.96	<0.01
K3	10	14.4	3.3	6.3E+05	2.5E+09	1.1E−08	4.3E−05	0.95	<0.01
K3	0	14.7	7.4	85.6	58.7	1.4E−04	1.8E−04	0.83	<0.01
K2	100	25.5	5.1	48.6	7.2	1.1E−03	3.7E−04	0.9	<0.01
K2	50	19.1	2.9	34.3	3.8	2.2E−03	6.6E−04	0.95	<0.01
K2	25	19.6	4.0	24.0	5.4	1.8E−03	1.0E−03	0.8	<0.01
K2	10	21.2	2.3	26.4	3.5	8.0E−04	2.6E−04	0.92	<0.01
K2	0	22.0	10.6	39.9	15.2	1.1E−03	9.4E−04	0.59	0.11
N70	100	16.0	12.5	70.0	54.5	5.5E−04	9.1E−04	0.68	0.06
N70	50	19.6	8.6	7.8E+06	3.6E+11	2.2E−09	1.0E−04	0.74	0.03
N70	25	17.6	7.1	98.0	285.1	1.7E−04	6.4E−04	0.73	0.04
N70	10	18.9	6.2	2.9E+06	1.0E+11	4.7E−09	1.6E−04	0.78	0.02
N70	0	21.0	9.9	75.1	181.1	2.6E−04	9.0E−04	0.6	0.10
DF9	100	14.5	1.5	36.7	2.6	2.4E−03	5.1E−04	0.98	<0.01
DF9	50	12.6	1.1	25.9	1.7	3.4E−03	5.9E−04	0.98	<0.01
DF9	25	14.0	2.4	19.5	3.5	3.4E−03	1.6E−03	0.86	<0.01
DF9	10	13.5	1.6	16.6	2.3	3.3E−03	1.2E−03	0.91	<0.01
DF9	0	11.8	3.7	20.1	4.6	3.6E−03	2.1E−03	0.83	0.03

the four lakes sampled are shown in Figure 2. Equation 6 was found to fit the measured data well with r^2 ranging between 0.59 and 0.98 ($p < 0.05$, with exception of N70 100%, 0%, and K2 0% with $p = 0.06$, 0.10, and 0.11, respectively) (Table 3). The lowest r^2 values were observed for data collected at Lake N70.

Both photoreduction and photooxidation of mercury are known to be important processes in DGM dynamics. Various mechanisms for mercury photoreduction and more recently mercury photooxidation (26) have been suggested. The following is a brief summary of this work and its application to our results.

(*i*) *Theoretical Mechanisms for Photoreduction.* There are many photoproduced reductants that may facilitate the conversion of inorganic mercury to DGM. Several researchers (27, 28) suggest that DOC absorbs solar radiation to emit aqueous electrons (eq 7), which are then available to reduce mercury (eq 8). The aqueous (or hydrated) electron is a highly reactive, strongly reducing species:

$$[DOC] + h\nu \rightarrow [DOC^{\bullet+}] + e^-(aq) \qquad (7)$$

$$2e^-(aq) + [Hg^{2+}] \rightarrow [Hg^0] \qquad (8)$$
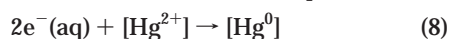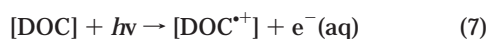
Using solar irradiated DOM solutions, Zepp et al. (28) determined aqueous electron photoproduction rates ranging between 0.2 and 0.4 μmol mg^{-1} DOC. Taking into account quenching by oxygen and normalizing for DOC, Zepp et al. (28) computed an average steady-state concentration of 2×10^{-17} mol L^{-1} for the aqueous electron in Swiss Lake Greifensee. 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 an aqueous electron concentration of 2×10^{-17} mol L^{-1} and assuming an excess of inorganic mercury is present and a 2:1 production of elemental mercury from the aqueous electron (i.e., two electrons for every inorganic mercury ion), we can determine a steady-state concentration of elemental mercury 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 photoreductants and reduction mechanisms probably 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 (29) determined that reduction by DOC is possible except at very low pH or with high chloride concentrations.

(*ii*) *Theoretical Mechanisms for Photooxidation.* LaLonde et al. (26), who discovered that DGM can be photooxidized, 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 photooxidation 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 photooxidation rates.

We modeled DGM dynamics by assuming that they represented a reversible first-order reaction (eqs 1−6). This model fitted the observed data well for the four lakes studied (r^2 ranging between 0.59 and 0.98, $p < 0.05$ with the exception of N70 100%, 0%, and K2 0% with $p = 0.06$, 0.10, and 0.11 respectively) (Table 3). The fit of the kinetic curve to the data indicated that parameter b ranged between 4.7×10^{-9} and 3.6×10^{-3} (kJ/m^2)$^{-1}$, with a mean value of 1.26 h^{-1} ($\sigma = 1.33$) for all dilutions in all four lakes (assuming a constant hourly radiant flux of 1000 kJm^{-2}). Since b is defined as the sum of the forward (photoreduction) and backward (photooxidation) first-order rate constants (eq 5), we conclude that while there is wide variation in the samples analyzed, the photooxidation rate constant suggested by LaLonde et al. (26) of 0.25 h^{-1} for freshwater is a reasonable estimate. With a photooxidation rate of 0.25 h^{-1} (26) and the mean value for b (1.26 h^{-1}), a mean abiotic DGM photoproduction rate constant of 1.01 h^{-1} ($\sigma = 1.33$) can be calculated for all samples analyzed in this study.

Note that in developing the equations for curve fitting we have assumed an excess of photoreductants and photooxidants due to the increasing levels of cumulative PAR throughout the incubations. This assumption must be carefully considered. It is known that not all absorbed light results in photochemical reactions, and Miller (30) 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. While we do not know for certain that the photoreductants and photooxidants are in excess, it is a plausible rationale for the development of the curve fitting equations, and it is supported by the current
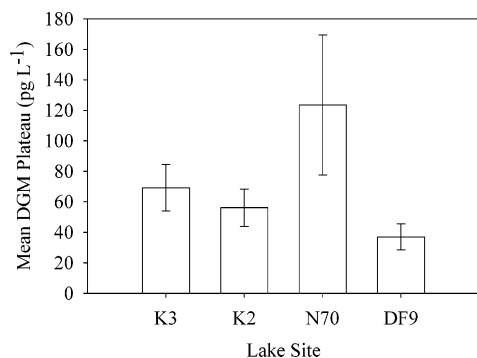
FIGURE 3. Mean DGM plateau for all whole water dilutions for each lake site. Error bars represent the standard deviation on the mean ($n = 5$).

literature. We believe this is a better approach than randomly selecting the curve of best fit.

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 (Figure 2a–d). On average 4000 kJ m^{-2} of PAR radiation was received after 6.1-h incubation on a sunny day but much longer for a cloudy day (>10.5 h). Note that several of the samples failed to show a distinctive plateau; in particular many of the samples from N70 did not plateau. This may be due, in part, to the lower levels of cumulative solar radiation received on the day these samples were irradiated (<3500 kJ m^{-2}). However, eq 6 was still found to fit the data reasonably well (as described in previous section). 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 3. The high standard deviation shown for N70 is likely due to the inability of several samples to reach a distinctive plateau. Also, due to the low levels of solar radiation received on that day much more extrapolation of the data was required. Concentrations of plateau DGM concentrations were verified for normality of residuals and homogeneity using the Anderson Daily normality test and Levene's test respectively and analyzed 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 3). Because of the small data set, combined interactions between factors could not be examined. We found that the DGM plateau was independent of DOC concentration but differed between lakes. 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. (3) 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 nonlinear production of DGM to the limited availability of photoreducible Hg(II) owing to its complexation with DOC.

While our data indicate that the balance between photooxidation and photoreduction is affected by site-specific factors, the actual mechanism is still unclear. Factors that affect mercury binding to ligands (Figure 4) such as DOC structure, the presence of ligands other than DOC, and the competition for binding by dissolved ions (31) may be important to the balance of photooxidation and reduction. Some of these factors are thought to influence photooxidation processes, as discussed by Lalonde et al. (26). The percentage
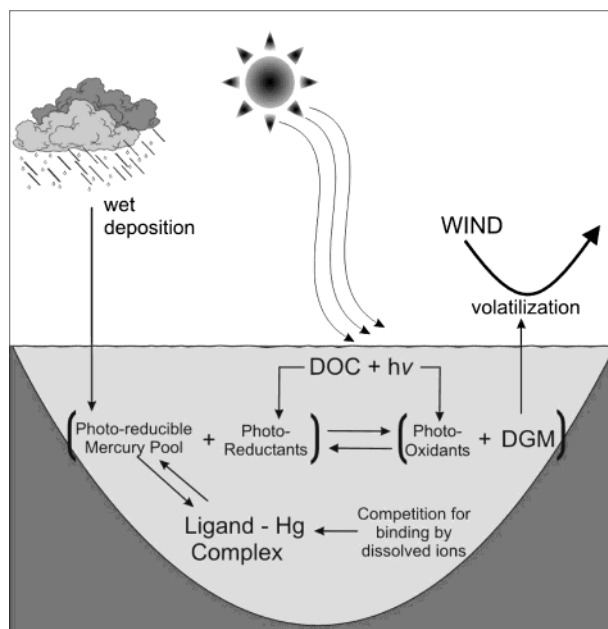

FIGURE 4. Conceptual diagram detailing the relationship between DOC, photoreducible mercury, and DGM dynamics.

of total mercury that was photoreduced 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%). It is interesting to observe that this is approximately an inverse relationship with DOC concentration in these samples, which may be attributed to a positive correlation between total mercury and DOC commonly observed in lake water. The amount of mercury reduction observed also corresponds well with results reported by Amyot et al. (3), who observed a range of 0.2–8% of total mercury being photoreduced during incubations in a series of freshwater lakes.

Reverse Osmosis Dilutions. As previously stated, 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 degree of 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 h with the same cumulative PAR exposure as the whole water dilutions. Subsequent linear regression analysis indicated that there was no significant relationship between DGM plateau concentrations and percentage dilution ($r^2 = 0.5$, $p = 0.185$ for lake K3; $r^2 = 0.02$, $p = 0.803$ for lake N70). In addition, the mean DGM for all reverse osmosis permeate dilutions (45 ($\sigma = 7.9$) pg L^{-1} for lake K3 and 73 ($\sigma = 7.7$) pg L^{-1} for lake N70) were similar to the results obtained with whole water dilutions and the same cumulative radiation exposure. These results indicated that changes in the dissolved ions and DOC concentrations that should have resulted from further dilutions of the 1-kDa filtrate did not affect the DGM plateau.

DGM Photoproduction Efficiency and DOC. DGM photoproduction 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}) versus cumulative PAR (kJ m^{-2}) below the plateau at approximately 4000 kJ m^{-2}. These linear regression calculations resulted in slopes that were
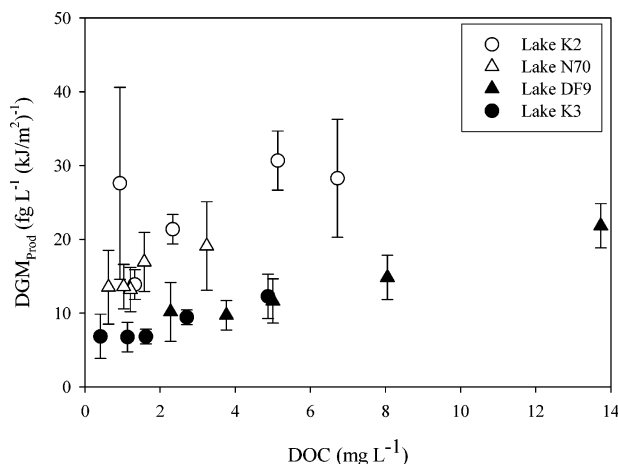
FIGURE 5. Relationship between DOC (mg L^{-1}) and DGM$_{prod}$ (fg L^{-1} (kJ/m^2)$^{-1}$). Open markers represent nonlogged lakes, and closed markers represent logged lakes. Data points represent the slope of the linear regression (n between 6 and 8 for each lake), and error bars represent the standard error.

significant ($p < 0.05$) with the exception of two slopes (lake K2 0% whole water and lake K3 0% whole water) that were close to being significant ($p = 0.093$ and 0.078, respectively). DGM$_{prod}$ ranged from 7 to 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 both the logged lakes ($r^2 = 0.97$, $p < 0.01$) and the nonlogged lakes ($r^2 = 0.52$, $p = 0.018$) studied (Figure 5).

The relationships between DGM$_{prod}$, DOC concentrations, and the logging of drainage basins were further analyzed using ANCOVA. The analysis indicated that DGM$_{prod}$ significantly increased with DOC concentration ($p < 0.001$). We also found that DGM$_{prod}$ in nonlogged lakes (mean = 20, σ = 7) was double ($p < 0.01$) that of logged lakes (mean = 10, $\sigma = 5$) investigated in this study. The combined interactions of DOC concentrations and logging of drainage basins were not found to affect DGM$_{prod}$ significantly ($p = 0.069$) in this study, but note that the interaction is close to being significant and may be significant within a larger dataset. This suggests that, in addition to logged lakes being less efficient at producing DGM, the DGM production efficiency (DGM$_{prod}$) in a logged lake might increase less than it would in a nonlogged lake subjected to a similar increase in DOC concentration.

This study demonstrates that initial rates of DGM production (DGM$_{prod}$) below 4000 kJ m^{-2} increased with increasing DOC concentrations for all lakes sampled (Figure 5). 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. (*3*) 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. (*11*) 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 photoreduction processes. Thus, the observed differences in DGM production may reflect other lake characteristics which, in turn, change in relation to DOC. A laboratory study performed by Xiao et al. (*12*) revealed 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 Xiao et al. (*12*) 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 photoreducible mercury between dilutions, since DOC structure and dissolved ions did not change between dilutions. Assuming that mercury bound to specific functional groups in DOC is available for photoreduction, then the amount of photoreducible mercury probably increases with increases in DOC concentration.

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 nonlogged lakes than for the logged lakes. We postulate that this relationship is due to differences in concentrations of photoreducible mercury arising from variations in DOC structure and dissolved ions between lake sites. Our data show 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. (*32*) 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 than in reference lakes. Garcia and Carignan (*20, 21*) found that methyl mercury concentrations were higher in the zooplankton of lakes with logged drainage basins than in nonlogged lakes and 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}).

Whereas 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. Although 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 photoreductants and photooxidants may not hold true at greater depths in the water column where sunlight is limited. We hypothesize that a portion of the mercury bound to DOC ligands may be available for photoreduction (Figure 4). Allard and Arsenie (*29*) have also 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-induced intra-molecular and extra-molecular photoreduction processes is currently unknown. The role of strong and weak ligands in the photoreduction of mercury is an area that requires more research to be clarified. Another source of error to be considered in reviewing the data is the effect of potential pH changes on mercury chemistry with DOC dilution. As pH was not monitored with DOC dilution in this study, this remains an unknown. However, since the pK_a of the dominant metal binding site (carboxylic) on DOC is approximately 4.5 (*33*), the carboxylic groups are predominantly negatively charged in all lakes studied (in-situ pH ranging from 5.7 to 6.4; Table 1), and small pH changes are unlikely to significantly alter the amount of mercury binding by DOC.

The results of this study are consistent with kinetics fitted using a reversible first-order reaction equation for the photoproduction of DGM in freshwater lakes. It is clear that, in surface waters, DOC plays an important role in DGM dynamics. Increases in DGM production rates were observed with increases in DOC concentration within each lake. We hypothesize that photoreductants and photooxidants are

present in excess such that the level of photoreducible mercury is the primary factor regulating DGM production with low levels of solar radiation. The level of photoreducible mercury is, in part, determined by its binding to ligands. A better understanding of DOC structure, inter-molecular and intra-molecular photoreduction processes, and factors affecting the competition for ligand binding is required in order to understand site-to-site differences in levels of photoreducible mercury. The balance of oxidation and reduction (i.e., DGM plateau) did not change with changes in DOC concentration but was found to be different between sites, which suggests an effect of DOC structure and dissolved ions. Also, lakes with logged drainage basins were observed to have lower rates of DGM photoproduction, which may indicate differences in mercury binding to ligands due to variations in DOC structure and composition. Our data predict that logging may reduce a lake's ability to produce DGM and may ultimately reduce mercury evasion. Thus, logged lakes may be more efficient at retaining mercury (as less is lost to the atmosphere in a given span of time). An increase in mercury in logged lakes may result in increased levels of methyl mercury and hence higher concentrations in the biota as observed by other researchers (*20, 21*). This research demonstrates an important mechanism by which logging may exacerbate mercury levels in biota.

Literature Cited

(1) O'Driscoll, N. J.; Siciliano, S.; Lean, D. R. S. *Sci. Total Environ.* **2003**, *304* (1−3), 285.
(2) O'Driscoll, N. J.; Beauchamp, S.; Siciliano, S. D.; Lean, D. R. S.; Rencz, A. N. *Environ. Sci. Technol.* **2003**, *37* (10), 2226.
(3) Amyot, M.; Mierle, G.; Lean, D.; McQueen, D. J. *Geochim. Cosmochim. Acta* **1997**, *61* (5), 975.
(4) Siciliano, S. D.; O'Driscoll, N. J.; Lean, D. R. S. *Environ. Sci. Technol.* **2002**, *36* (14), 3064.
(5) Amyot, M.; Lean, D.; Mierle, G. *Environ. Toxicol. Chem.* **1997**, *16* (10), 2054.
(6) Amyot, M.; Gill, G. A.; Morel, F. M. M. *Environ. Sci. Technol.* **1997**, *31* (12), 3606.
(7) Nriagu, J. O. *Sci. Total Environ.* **1994**, *154*, 1.
(8) Zhang, H.; Lindberg, S. E. *Environ. Sci. Technol.* **2001**, *35*, 928.
(9) Matthiessen, A. *Fresenius J. Anal. Chem.* **1996**, *354*, 747.
(10) Matthiessen, A. *Sci. Total Environ.* **1998**, *213*, 177.
(11) Watras, C. J.; Morrisson, K. A.; Host, J. S. *Limnol. Oceanogr.* **1995**, *40*, 556.
(12) Xiao, Z. F.; Stromberg, D.; Lindqvist, O. *Water, Air, Soil Pollut.* **1995**, *80*, 789.
(13) O'Driscoll, N. J.; Evans, R. D. *Environ. Sci. Technol.* **2000**, *34* (18), 4039.
(14) Clair, T. A.; Kramer, J. R.; Sydor, M.; Eaton, D. *Water Research.* **1991**, *25* (9), 1033.
(15) Sun, L.; Perdue, E. M.; McCarthy, J. F. *Water Res.* **1995**, *29* (6), 1471.
(16) Town, R. M.; Powell, H. K. J. *Anal. Chim. Acta.* **1993**, *271*, 195.
(17) Weber, J. H. In *Humic Substances and Their Role in the Environment*; Frimmel, F. H., Christman, R. F., Eds.; John Wiley & Sons: New York, 1988; p 165.
(18) Babiarz, C. L.; Hoffmann, S. R.; Hurley, J. P.; Andren, A. W.; Armstrong, D. E. *Environ. Sci. Technol.* **2000**, *34*, 3428.
(19) Hoffmann, S. R.; Shafer, M. M.; Babiarz, C. L.; Armstrong, D. E. *Environ. Sci. Technol.* **2000**, *34*, 3420.
(20) Garcia, E.; Carignan, R. *Can. J. Fish. Aquat. Sci.* **1999**, *56*, 339.
(21) Garcia, E.; Carignan, R. *Can. J. Fish. Aquat. Sci.* **2000**, *57*, 129.
(22) Hall, G. E. M.; Pelchat, J. C.; Pelchat, P.; Vaive, J. E. *Analyst* **2002**, *127*, 674.
(23) Lean, D. R. S.; Siciliano, S. D. *J. Phys. IV Fr.* **2003**, *107*, 743.
(24) Lindberg, S. E.; Vette, A. F.; Miles, C.; Schaedlich, F. *Biogeochemistry* **2000**, *48*, 237.
(25) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. Chapter 2. *Chemical Kinetics and Dynamics*; 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 1998; p 22.
(26) LaLonde, J. D.; Amyot, M.; Kraepiel, A. M.; Morel, F. M. M. *Environ. Sci. Technol.* **2001**, *35* (7), 1367.
(27) Cooper, W. J.; Zika, R. G.; Petasne, R. G.; Fischer, A. M. In *Aquatic Humic Substances: Influences on Fate and Treatment of Pollutants*; Suffet, I. H., MacCarthy, P., Eds.; American Chemical Society: Washington, DC, 1989; Chapter 22.
(28) Zepp, R. G.; Braun, A. M.; Hoigne, J.; Leenheer, J. A. *Environ. Sci. Technol.* **1987**, *21*, 485.
(29) Allard, B.; Arsenie, I. *Water, Air, Soil Pollut.* **1991**, *56*, 457.
(30) Miller, W. In *Ecological Studies, Vol 133. Aquatic Humic Substances*; Hessen, Tranvik, Eds.; Springer-Verlag; Berlin, 1998; Chapter 6.
(31) Benedetti, M. F.; Milne, C. J.; Kinniburgh, D. G.; Van Riemsdijk, W. H.; Koopal, L. K. *Environ. Sci. Technol.* **1995**, *29*, 446.
(32) Carignan, R.; D'Arcy, P.; Lamontagne, S. *Can. J. Fish. Aquat. Sci.* **2000**, *57*, 105.
(33) Perdue, E. M. In *Humic Substances in Soil, Sediment, and Water*, Vol. 1; Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley; New York, 1985; Chapter 20.