MERCURY FLUX MEASUREMENTS OVER AIR AND WATER IN KEJIMKUJIK NATIONAL PARK, NOVA SCOTIA

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Abstract. Mercury flux measurements were conducted at two lakes and three soil sites in Kejimkujik National Park, located in the eastern Canadian province of Nova Scotia. One of the lakes had high levels of both mercury and Dissolved Organic Carbon (DOC). Two of the soil sites were located under the forest canopy, while the other was in a small clearing surrounded by forest. Flux measurements were performed using the dynamic chamber method. Mercury concentrations in the air were measured with a TEKRAN mercury analyzer. Mercury fluxes over the two lakes were most strongly correlated with solar radiation, although the flux was also significantly correlated with water temperature, air temperature, and negatively correlated with relative humidity. The flux from the high DOC lake (Big Dam West) was especially high when the conditions were both sunny and windy (wind speed greater than 1.3 m s^{-1}) and the average flux measured was 5.4 ng m^{-2} h^{-1}. The mercury flux from this lake was well parameterized in terms of a simple expression involving solar radiation and a nonlinear dependence on wind speed. The flux measured from the low DOC lake (North Cranberry) tended to be lower than from the high DOC lake. The average flux measured was 1.1 ng m^{-2} h^{-1}, but was again strongly correlated with solar radiation. The flux was low during windy conditions in the absence of sunlight, suggesting that wind enhances mercury evasion from lakes only in the presence of solar radiation. Mercury fluxes measured over the soil sites tended to be smaller than those over water (a range of –1.4–4.3 ng m^{-2} h^{-1}). At one of the forest sites, mercury flux was very strongly correlated with 0.5 cm soil temperature, and this dependence was well described by an Arrhenius-type expression with an activation energy of 14.6 $kcal^{-1}$ mole, quite close to the heat of vaporization of mercury (14.5 $kcal^{-1}$ mol^{-1} at 20 °C). At the clearing, where there was direct exposure to the sun, the mercury flux was most strongly correlated with solar radiation.

Keywords: mercury, mercury fluxes, solar radiation

1. Introduction

Mercury is a metal which can assume a variety of chemical forms in the environment, and continuously cycle between the oceans, atmosphere, soil, lakes, and biota. In the atmosphere, it has a residence time of 1–2 yr (Slemr and Langer, 1992; Mason *et al*., 1994) and a near uniform global distribution. The main removal processes from the atmosphere are wet and dry deposition. Once entering a watershed via precipitation and dry deposition mercury can be transformed to more

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toxic forms such as monomethyl and dimethyl mercury. These compounds can bioaccumulate in the food chain, reaching high concentrations in wildlife such as fish and loons, and ultimately posing a health risk to humans. One of the most important pathways for removal of oxidized mercury (Hg^{II}) from a lake (its principal form) is reduction to elemental mercury (Hg^0) followed by volatilization back to the atmosphere (Schroeder *et al*., 1989; Fitzgerald *et al*., 1991; Vandal *et al*., 1995). Although the mechanisms by which this reduction occurs are not well understood, there is evidence for both biological pathways (Barkay *et al*., 1991; Mason *et al*., 1995) and chemical photo-reduction (Brosset, 1987; Munthe and McElroy, 1992; Xiao *et al*., 1995; Amyot *et al*., 1997).

Improvements in analytical techniques over the past ten years have increased our understanding of the factors that control mercury flux over soil and lake surfaces. Studies with flux chamber methods emphasized that rates of evasion from lakes were much larger during summer than winter, larger during the day than at night, and larger over water than surrounding soil surfaces (Schroeder *et al*., 1989, 1992; Xiao *et al*., 1991). Another study using a micrometeorological method found the rate of mercury evasion from a lake to be positively correlated with wind and solar radiation (Lindberg *et al*., 1995b). However, a chamber study found that the correlation between mercury flux and solar radiation at the surface of a large river was weak, and emphasized the importance of a strong stable thermal inversion close to the water surface in maintaining a mercury flux (Poissant and Casimir, 1998). They also found that the flux over water was negatively correlated with wind speed. A consistent theme from recent measurements over soil surfaces is that mercury fluxes are much larger over soils exposed to direct solar radiation than those soils which are protected from direct sunlight by a forest canopy, and that mercury flux is strongly correlated with soil temperature (Kim and Lindberg, 1995; Carpi and Lindberg, 1997, 1998; Poissant and Casimir, 1998).

The emission of mercury from water and soil surfaces can lower lake-water and soil mercury burden, and constitutes an important fraction of the 'natural' flux of mercury into the atmosphere (Vandal *et al*., 1995; Schroeder *et al*., 1989; Schroeder 1996; Kim *et al*., 1995; Fitzgerald *et al*., 1991) (although it should be kept in mind that much of this natural mercury can ultimately be of anthropogenic origin). Parameterizations for the dependence of mercury flux on its controlling variables are needed by both global scale models and smaller scale models of particular watersheds. In addition to the meteorological factors discussed above, the rate of evasion of mercury from a lake might be expected to depend on its depth, surface area, composition, and watershed soil geology. Mercury fluxes from soils may depend on soil type, soil mercury concentration, soil moisture, and vegetation cover. More mercury flux measurements are needed because many of these dependencies have not yet been characterized, and to determine if there is a consistent response in mercury flux to variations in solar radiation and wind. This paper discusses mercury flux measurements over soil and water in Kejimkujik National Park, Nova Scotia, Canada during the summer of 1997. Loons within the

TABLE I
Chemical and physical information for the lakes

Lake	DOC (mgL^{-1})	Total Hg (ngL^{-1})	pH	Area (ha)	Average depth (m)
BDW	8.85	6.45	5.1	104.7	2.47
NC	4.75	2.6	5.1	34.3	1.45

Park have been shown to have the highest concentrations of blood mercury in North America (Beauchamp *et al*., 1997; Evers *el al*., 1998). Mercury concentrations are highly variable from lake to lake within the Park, and are positively correlated with Dissolved Organic Carbon (DOC) concentrations (Beauchamp *et al*., 1997). We therefore made mercury flux measurements over two lakes, one with a high DOC concentration and the other with a low DOC concentration. We also measured the mercury flux at two soil sites within the forest adjacent to the lakes, and at an exposed grassy location. Although mercury fluxes over soil surfaces are usually much smaller than over water, their larger surface area can be expected to make their overall contribution to the mercury budget of a watershed significant.

2. Materials and Methods

2.1. Site descriptions

Kejimkujik National Park is located in the eastern Canadian Province of Nova Scotia (see Figure 1A). It is sensitive to anthropogenic pollution (including mercury), because it is situated downwind of major pollution sources in eastern North America. There are no known local anthropogenic atmospheric pollution sources in the area.

The two lakes selected for this study, Big Dam West and North Cranberry, were chosen on the basis of their chemistry and accessibility. Most of the water entering the lakes is from run-off, and the chemical composition, color, and DOC levels of the lakes indicates the amounts of dissolved or particulate material transported into the lakes from their watersheds. As shown in Table I, the DOC and total mercury concentrations at Big Dam West are about double that at North Cranberry. The difference in DOC concentration is probably attributable to the higher prevalence of bogs in the Big Dam West watershed. The lakes are also quite acidic, with high concentrations of organic acids (Kerekes *et al*., 1986). Big Dam West Lake is larger (104.7 ha) than North Cranberry (34.3 ha). Both lakes are quite shallow, with a mean depth of 2.47 m for Big Dam West and 1.45 m for North Cranberry. More details on the physical and chemical characteristics of the lakes are given in Table I.

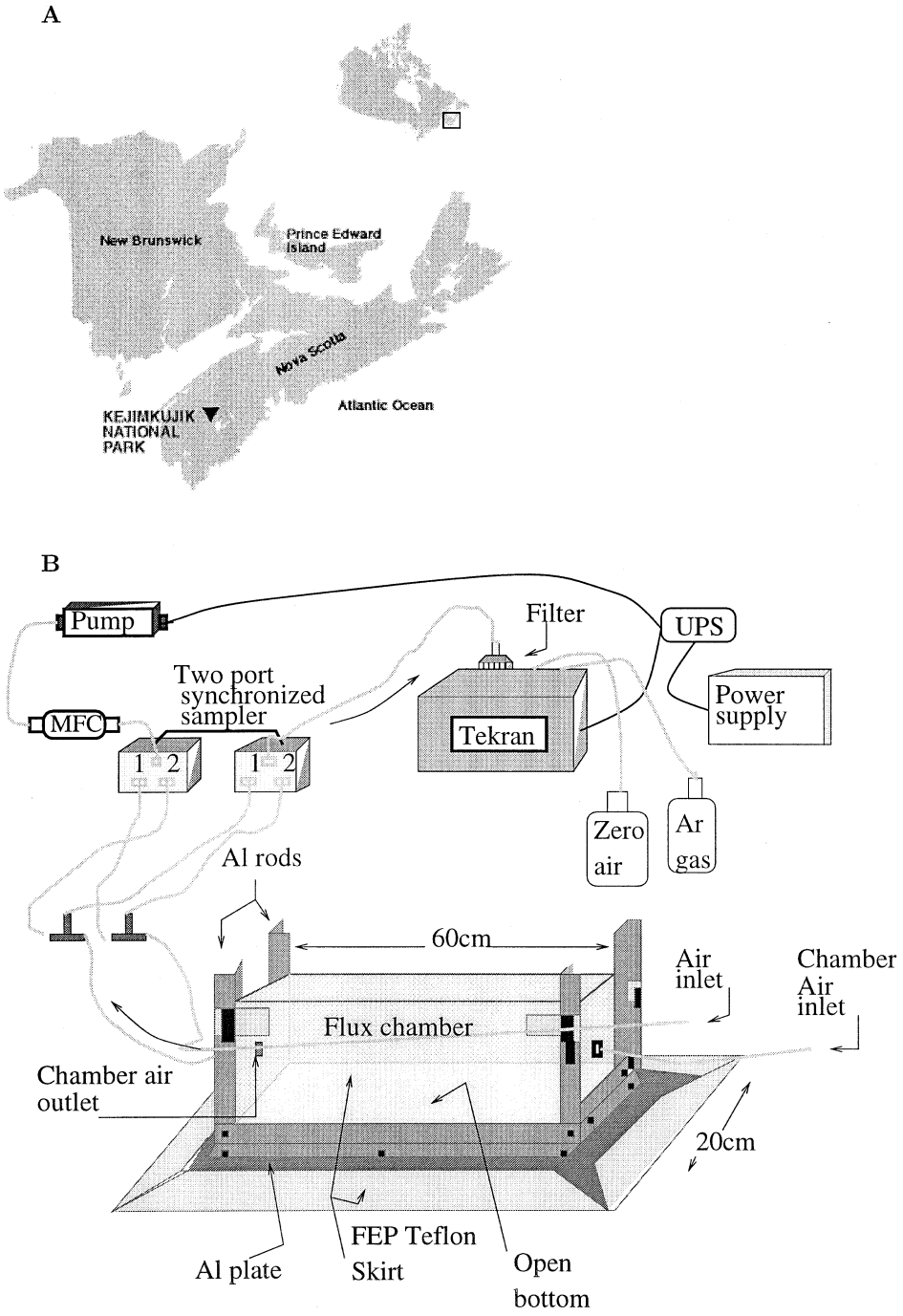

Figure 1. A map showing the location of the Kejimkujik National Park in Nova Scotia (A); the experimental set-up of the dynamic flux chamber with the TEKRAN mercury vapor analyzer (B); in Figure1B, UPS stands for uninterruptible power supplies and MFC for mass flow controller.

TABLE II

Mercury flux measurement over lake and soil results at Kejimkujik National Park. BDWw-Big Dam West over water; NCw-North Cranberry over water; BDWs-Big Dam West over soil; NCs-North Cranberry over soil

Date	Time (GMT)	Sampling site	TGM (air) average (ng m^{-3})	F_m (ng m^{-2} h^{-1}) range	Average (ng m^{-2} h^{-1})		
					Day	Night	All data
970810	18–24	BDWw	1.4	1.8–10.7	6	–	
970811	0–24	BDWw	1.5	0.7–43.8	12.5	1.3	
970812	0–24	BDWw	1.8	0.8–6.2	3.5	0.8	5.4
970821	22–24	NCw	1.3	0.2–0.8	0.7	0.3	
970822	0–24	NCw	1.3	–0.1–2.0	0.9	0.1	
970823	0–24	NCw	1.5	–2.0–13.5	4	–0.01	1.1
970627	4–23	CAPMoN	1.5	–0.15–4.3	1.9	–0.1	1.4
970709	23–24	BDWs	2.4	–0.1—0.2	–0.1	–	
970710	0–16	BDWs	2.4	–1.4–1.8	–0.8	–0.4	
970711	1–24	BDWs	2.4	–1.2–0.23	–0.28	–0.1	–0.3
970824	18–24	NCs	1	2.5–3.8	3.5	2.5	
970825	0–24	NCs	1.4	1.3–2.7	2.1	1.6	
970826	0–16	NCs	1	1.1–2.8	1.6	1.5	2.3

The soil sites adjacent to Big Dam West Lake and North Cranberry Lake, at which fluxes were measured, were located under a forest canopy of primarily hemlock trees. Very little solar radiation reaches the ground, and the soil was covered with forest litter. Mercury flux was also measured at one of the Canadian Acid Precipitation Monitoring Network (CAPMoN) sites. This is located on a grassy clearing within the forest, and is directly exposed to solar radiation.

Geological maps of the Kejimkujik National Park area show that the soils are derived from greenish-grey wacke and minor inter-bedded siltstone at Big Dam West and North Cranberry sites, and finely laminated slate and slate-stone at CAP-MoN site. Total mercury concentrations in the forest soil at Big Dam West and North Cranberry were 0.33 and 0.30 mg kg^{-1} respectively. The soil at the CAP-MoN site had a somewhat lower total mercury concentration of 0.1 mg kg^{-1}.

Daily average total gaseous mercury (TGM) concentrations were measured $\approx$ 10 cm above the ground and ranged from 1–1.8 ng m^{-3} for all sites except the Big Dam west forest soil site, which showed a slightly elevated concentration of 2.4 ng m^{-3} (see Table II). These concentrations are within the range of background levels (1–3 ng m^{-3}) (Porcella *et al.*, 1997).

2.2. ANALYTICAL

TGM concentrations were measured with a TEKRAN^{TM} automated mercury analyzer, which first captures the mercury on gold traps, heats the traps to release the mercury, and then measures the amount of gaseous mercury released (Fitzgerald and Gill, 1979). The analyzer uses two gold traps (A and B) and detects the gaseous mercury by cold-vapor atomic fluorescence spectrophotometry (CVAFS) (Bloom and Fitzgerald, 1988). The typical detection limit of the analyzer is close to 0.2 ng m^{-3}.

A schematic diagram of the experimental setup of the dynamic flux chamber with the TEKRAN mercury vapor analyzer is given in Figure 1B. The dimensions of the chamber were 20 × 20 × 60 cm (Xiao *et al*., 1991), and its volume was 0.024 m^3. When placed over a surface for flux measurements, the bottom is removed. Ports were placed in the front and back of the chamber. The chamber was constructed with transparent FEP Teflon film (Kim and Lindberg, 1995). A known volume of ambient air was drawn into the chamber through the inlet port, while the analyzer was connected to the outlet of the chamber.

For measurements over water, styrofoam blocks were used to provide buoyancy. To ensure a tight seal over both water and soil surfaces, six 11.24 kg lead weights were placed around the chamber. Mercury concentrations were measured twice in the ambient air entering the inlet of the chamber and twice in the air exiting through outlet of the chamber using the two parallel gold traps (A and B), with a 5 min sampling time at an air flow rate of 1.5 L min^{-1} (0.09 m^3 h^{-1}). The residence time of air in the chamber at this flow rate is about 16 min. Switching from the inlet to the outlet of the chamber every 10 min was achieved using a two port synchronized sampler from TEKRAN. When the mercury analyzer was sampling ambient air, air was kept flowing through the chamber by a separate pump at the same flow rate in order to keep the air inside the chamber from becoming stagnant. The air flow rate was controlled with a mass flow controller (Hastings). The measured mercury flux F_m (in ng m^{-2} h^{-1}) was computed using the following mass balance equation (Schroeder *et al*., 1989; Xiao *et al*., 1991).

$$F_m = \frac{([\mathrm{Hg}]_{\mathrm{out}} - [\mathrm{Hg}]_{\mathrm{in}}) \times \mathrm{Q}}{A}$$

$[\mathrm{Hg}]_{\mathrm{out}}$ is the mercury concentration in the air exiting through the outlet port of the chamber in ng m^{-3}; $[\mathrm{Hg}]_{\mathrm{in}}$ is mercury concentration in the air entering the inlet port of the chamber in ng m^{-3}; A is area of the open bottom surface of the chamber in m^2; and Q is air flow rate inside the flux chamber. For this calculation, a 10 min average TGM concentrations of air entering and exiting the chamber were used. The flux was measured with a resolution of 20 min.

Teflon tubing was used for the sampling lines to minimize mercury adsorption. This tubing had an outside diameter of 0.635 cm. A Li-COR silicon pyranometer sensor with a spectral sensitivity range (400–1100 nm) was used to measure the

solar radiation. The soil temperature at ≈0.5 and 2 cm depth, and the surface water temperature, were measured just beneath the chamber. Air temperature was measured at 2 and 100 cm above the ground near the chamber during flux measurements over soil and near the shore during flux measurements over water. The wind speed was measured at about 2 m above the ground. The flux chamber, and the water temperature and radiation sensors, were anchored at a distance of approximately 5 m from shore where the water depth was ≈1.5 m. All the meteorological parameters were collected with a datalogger (Campbell Scientific 21X) and downloaded to a laptop computer.

Both the mercury analyzer (TEKRAN) and the flux chamber were calibrated before field measurements began. The mercury concentration in the air exiting the chamber may include desorbed mercury from the interior sides of the chamber. This is referred to as the 'chamber blank'. Chamber blanks were measured in the laboratory, and in the field, before and after the flux measurements. The laboratory blanks ($n \approx 84$) were obtained by measuring the mercury flux over a clean Teflon sheet (Xiao *et al.*, 1991; Kim and Lindberg, 1995). These were found to be in the range 0.2–0.6 ng m^{-3}, close to the typical detection limit (0.2 ng m^{-3}) of the analyzer. Field blanks were obtained before and after the flux measurements at each sampling site. In this case, 6 to 9 10 min average mercury concentrations were measured at both the inlet and outlet for each site. The field blanks computed from these measurements ranged from 0.3 to 1.1 ngm^{-3}, with an average value of 0.63 ng m^{-3}, and a standard deviation of 0.42 ng m^{-3}. This average field blank was subtracted from all mercury flux measurements.

The calibration of the mercury analyzer was performed by direct injection of a known amount of mercury into mercury free air flowing into the analyzer. These injections were made with a precision gas-tight syringe, and a Saturated Mercury Vapor Calibration Unit (SMVCU) from TEKRAN, as the mercury source. Eight duplicate mercury samples, 96.95 pg each, were injected into the injection port of the analyzer. The injected samples were then measured by the analyzer, and the measured amounts then compared with the nominal amounts (e.g., Poissant and Casimir, 1998). The recovery rates of the gold traps of the analyzer were excellent, with an an average efficiency of greater than 94%.

To determine the recovery rate of mercury in the sampling lines, two Teflon sampling lines were joined with a tee fitting which had an injection port with a leak free septum. One end of the line was connected to a mercury free air supply, and the other end was connected to the analyzer. Mercury was injected into the port, and the injected mercury was then measured. The recovery efficiency of the traps are relatively low (88%). However, this should not affect our flux measurements, which are calculated by taking a difference.

The soil samples were collected and stored in polypropylene bottles just after the flux measurements, and kept frozen. During the analysis, the soil samples were suspended in distilled water. The organomercury compounds in the samples were oxidized to inorganic mercury by sulphuric acid, dichromate and UV photo-

oxidation. The oxidized mercury ions were reduced with stannous sulphate in hydroxylamine sulphate-sodium chloride solution to elemental form and detected using flameless atomic absorption spectrometry (Environment Canada, 1996).

3. Results and Discussion

3.1. Mercury flux over water

Mercury flux measurements for all sites are summarized in Table II. The daytime and nighttime averages shown in the table were calculated to segregate effects of solar radiation on the fluxes. This was achieved by assuming that the solar radiation flux is zero at night, the fluxes were averaged (nighttime vs daytime) for a given measurement period based on the solar radiation measurements. The average daytime flux over the 2 day measurement period at Big Dam West Lake was 7.3 ng m^{-2} h^{-1}, while the average nighttime flux was 1.1 ng m^{-2} h^{-1}.

The mercury flux at North Cranberry also showed a strong diurnal cycle, with an average daytime value of 2.0 ng m^{-2} h^{-1} over the 2 day measurement period, and an average nighttime value of 0.13 ng m^{-2} h^{-1}. As mentioned earlier, the existence of a strong diurnal cycle in mercury flux over water is consistent with the results of previous investigators (e.g., Schroeder *et al*., 1989; Xiao *et al*., 1991; Poissant and Casimir, 1998). The magnitudes of the mercury fluxes from Big Dam West and North Cranberry are also within the range of those observed over other lakes in Sweden using flux chamber and micrometeorological methods (Schroeder *et al*., 1989; Xiao *et al*., 1991; Lindberg *et al*., 1995b).

The response of the mercury flux over water to variations in meteorological parameters such as solar radiation and wind speed can be quite dramatic. The mercury flux over Big Dam West, together with supporting meteorological measurements, is shown in Figure 2. The lower panel shows that all three daytime periods had significant amounts of solar radiation although the third day was characterized by broken cloud. Extremely large fluxes (up to 44 ng m^{-2} h^{-1}) were observed on the second day, when it was both sunny and very windy. A linear regression analysis for all three days shows that the mercury flux was positively correlated with wind speed (r^2 = 0.45), positively correlated with solar radiation (r^2 = 0.50), weakly anti-correlated with relative humidity (r^2 = 0.24), and weakly positively correlated with water temperature (r^2 = 0.33) and air temperature (r^2 = 0.29). The correlations of flux with wind speed and solar radiation are shown in Figures 3A and b. It should be noted that, since all of the meteorological variables are correlated with each other, a correlation or anti-correlation of the flux with a particular meteorological variable does not necessarily imply that it was helping to increase or decrease the flux of mercury over the lake.

There are two mechanisms by which wind might be expected to increase mercury evasion. First, vertical mixing of elemental mercury within the water column

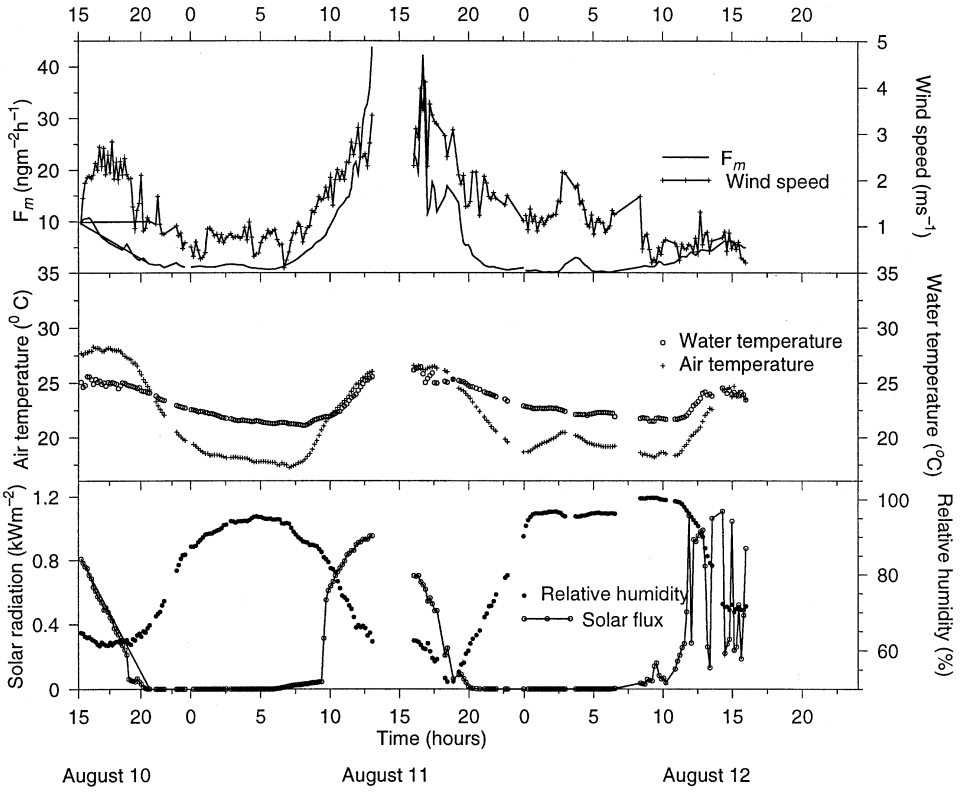

Figure 2. Mercury flux over Big Dam West Lake and meteorological variables.

can be expected to increase the rate of diffusion of pre-existing elemental mercury into the atmosphere. In this context, it is interesting to note that the nonlinear increase in flux shown in Figure 3A for wind speeds larger than 2 m s^{-1} is consistent with some other experiments in air/water gas exchange, which also found enhancements in exchange rate starting at 2 m s^{-1} associated with the generation of capillary waves (Jähne *et al.*, 1987; Broecker *et al.*, 1978; Wanninkhof *et al.*, 1987). As shown in the figure, the effect of wind speed on the flux started to occur at about 1.3 m s^{-1} which is even a little lower than 2 m s^{-1}. However, the measurements also indicate that this mechanism cannot be entirely responsible for the positive correlation between the mercury flux and wind speed, since the response of the flux to wind speed in the absence of solar radiation was weak. This was most clearly demonstrated at North Cranberry Lake, where strong winds on the first day of measurements did not drive an increase in flux, presumably because there was extensive low cloud and little solar radiation reached the surface (see Figures 5 and 6A). Figure 3B also shows that the flux was highest under conditions characterized by both high solar radiation and wind speed. A second mechanism by which wind can be expected to increase evasion, by working in concert with

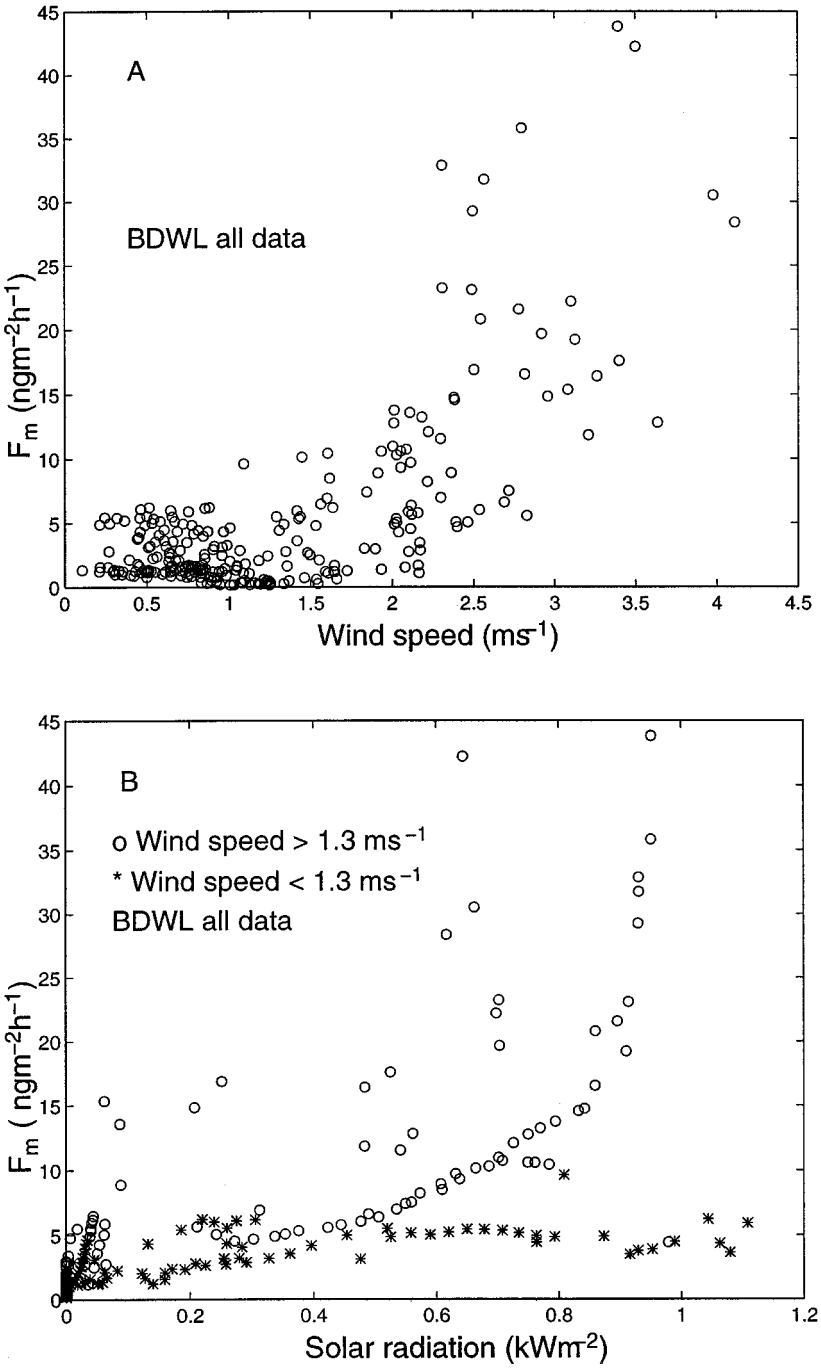

Figure 3. Mercury flux over Big Dam West Lake, wind speed (A) and solar radiation (B).

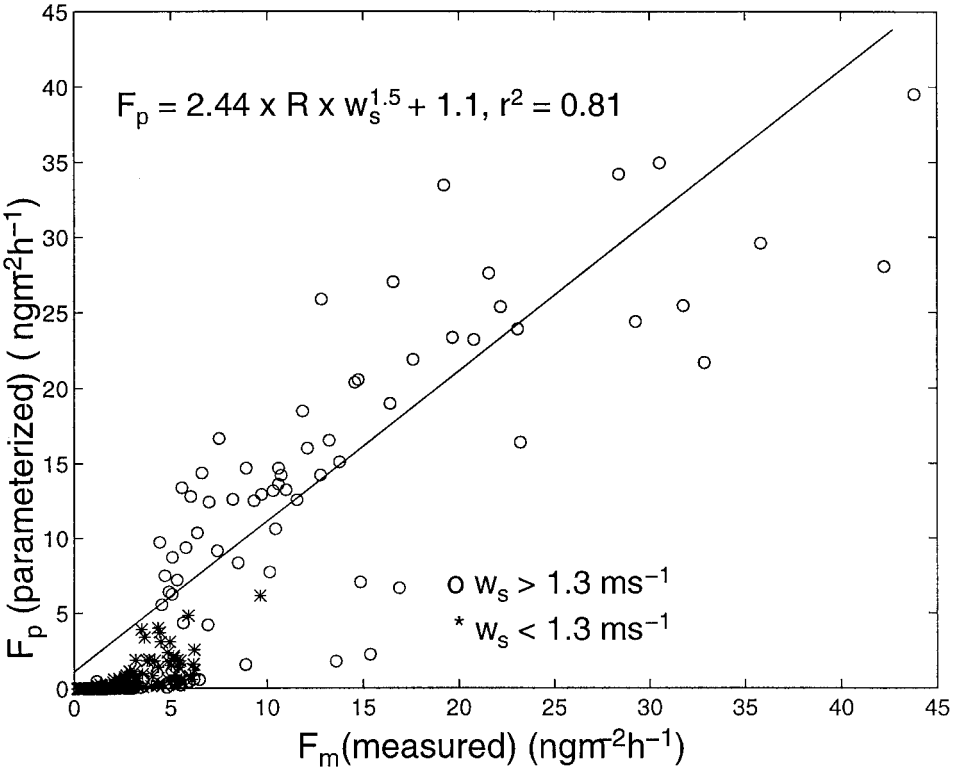

Figure 4. The mercury flux predicted by the parameterized equation is plotted against the measured flux.

solar radiation, is via the transport of photo-reducible mercury closer to the surface. Several recent experiments have shown that the photo-chemical production of elemental mercury from oxidized mercury in the water column was initiated by UV light (280–400 nm) (e.g., Amyot *et al.*, 1997). The UV penetration depth in high DOC lakes such as Big Dam West is probably about 3 to 6 cm (Kirk, 1994). It is quite easy to show that, in the absence of wind driven vertical mixing, the mercury flux from Big Dam West was sufficiently large to deplete photo-reducible mercury from the top 6 cm of the Lake within two days. As shown in Table II, the average mercury flux from Big Dam West was 5.4 ng m^{-2} h^{-1}. The total mercury concentration (Hg_T) in the lake was 4.3×10^3 ng m^{-3}. If all of this mercury is assumed to be photo-reducible, then it would take 2 days for the observed flux to deplete all of the photo-reducible mercury in the top 6 cm of the water column. The enhancement of mercury flux at high wind speeds may therefore be a consequence of the increased photo-reduction of elemental mercury within the water column, associated with the replenishment of mercury available for photo-reduction within the UV penetration depth of the surface.

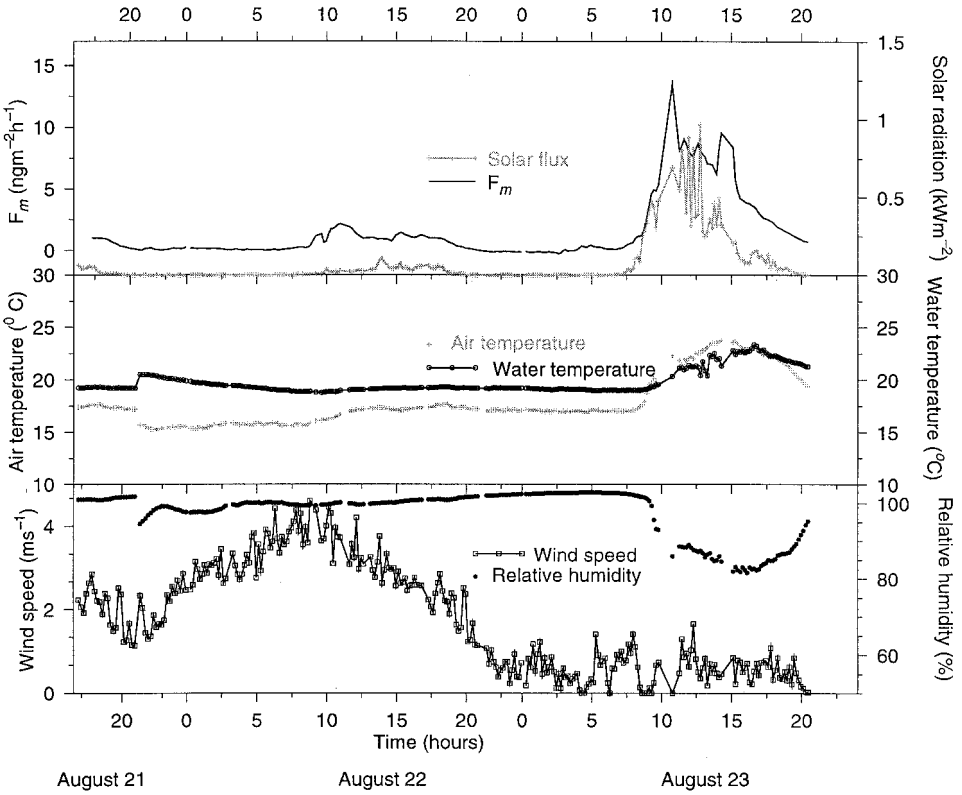

Figure 5. Mercury flux over North Cranberry Lake and meteorological variables.

Some studies of mercury cycling within watersheds have attempted to estimate the annual fluxes of mercury across air/water interfaces from fluxes measured using a flux chamber (e.g., Xiao *et al.*, 1991) and stagnant film model (Fitzgerald *et al.*, 1991; Vandal *et al.*, 1995). Such estimates are difficult because of the large variations in flux on diurnal, synoptic, and seasonal time-scales. Since it is impossible to measure the flux in all conditions, it is desirable to investigate the extent to which simple parameterization can predict mercury flux variations in terms of a small number of meteorological variables. We have used solar radiation and wind speed, since these are the variables with which the flux was most strongly correlated, and have assumed the following functional form,

$$F_p = BRw_s^i + c$$

where F_p (in ng m^{-2} h^{-1}) is the parameterized mercury flux, R the solar radiation (in kW m^{-2}), w_s the wind speed (in m s^{-1}), and B, i, and c are constants to be fitted. For Big Dam West, we obtain best fit values of B = 2.44, i = 1.5, and c = 1.1, which gives an r^2 of 0.81. A plot of the parameterized flux F_p against the measured flux F_m is given in Figure 4. The fit is quite good for the larger values of wind speed

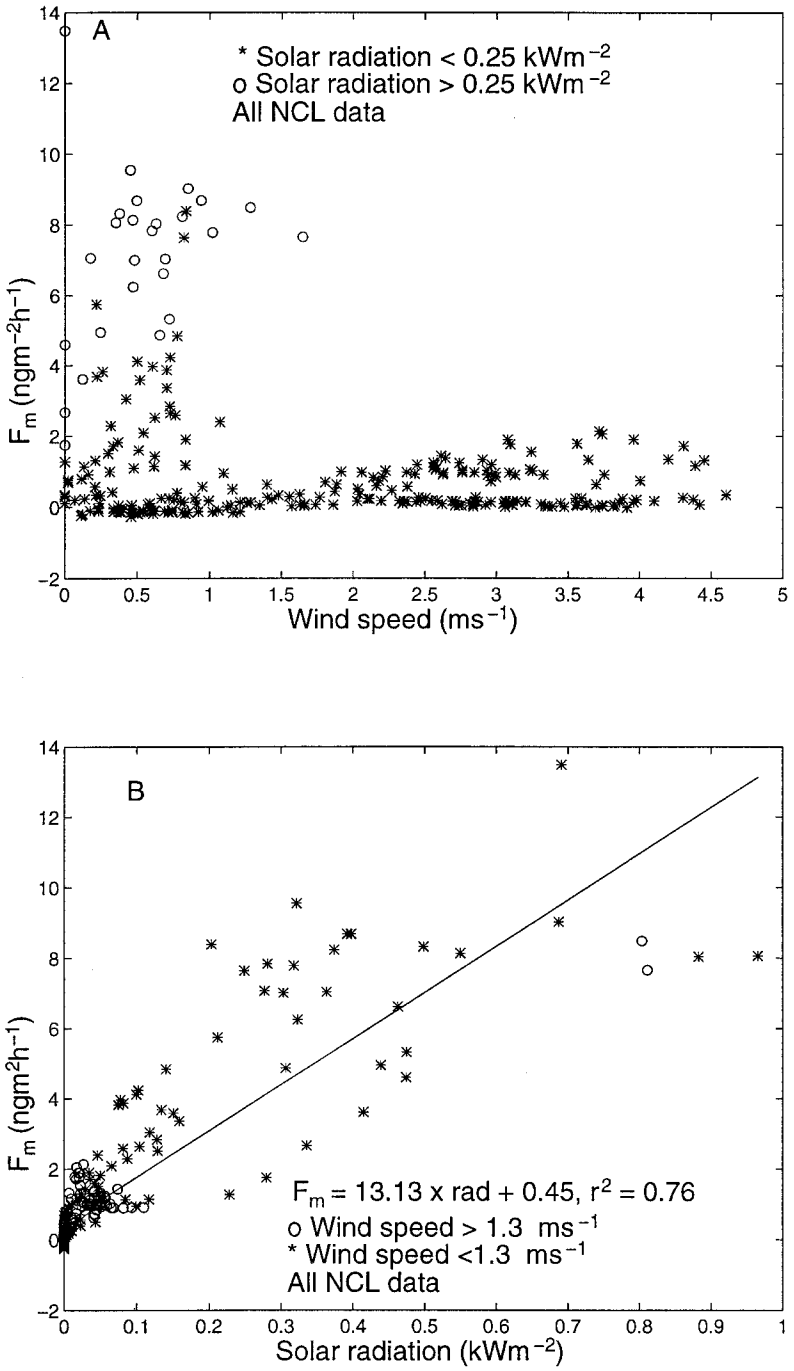

Figure 6. Mercury flux over North Cranberry Lake with wind speed for solar radiation less than 0.25 kW m^{-2} and greater than 0.25 kW m^{-2} (A); and solar radiation (B).

(w_s larger than 1.3 m s^{-1}) at which most of the evasion occurred. It tends to over predict the flux when the wind speed and solar radiation are low.

Mercury flux was measured over North Cranberry Lake for approximately two diurnal cycles. The flux and supporting meteorological measurements are shown in Figure 5. The first complete day of measurements (August 22) was characterized by heavy cloud cover, intermittent rain, high winds, little solar radiation, and very low flux. The second day had mostly clear skies, low winds, and somewhat higher levels of flux during the day. The flux chamber was covered by a tarpaulin suspended 1 m above the water surface between 20:00 August 21 and 15:00 August 22 to protect it from rain. The mercury flux measurements are plotted against wind speed and solar radiation in Figure 6. There was a strong positive correlation (r^2 = 0.76) between mercury flux and solar radiation (Figure 6B). There was essentially no correlation between mercury flux and wind speed (Figure 6A). This is probably because almost all of the flux measurements for which there existed significant solar radiation (R larger than 0.25 kW m^{-2}), had wind speeds less than 1.3 m s^{-1}. As shown in Figure 3A, wind driven enhancements in mercury flux are, for the most part, restricted to wind speeds of 2 m s^{-1} and larger. The measurements denoted by asterisks in Figure 6A, mostly taken on the first day, demonstrate quite clearly the lack of a response in flux to wind speed in the absence of solar radiation.

3.2. MERCURY FLUX OVER SOIL

Mercury fluxes were measured at forest soil sites adjacent to North Cranberry and Big Dam West Lakes, and at the CAPMoN site, a grass covered clearing. Table II shows average fluxes measured at the three sites. The magnitudes of the fluxes are comparable to those observed by investigators at other soil sites (e.g., Xiao *et al*., 1991; Schroeder *et al*., 1989).

Mercury flux and supporting meteorological measurements at the CAPMoN site are given in Figure 7A. The site was covered by fog from the beginning of the measurement period until 10:00 the following morning. Mercury flux and solar radiation rose rapidly after the fog dissipated, and were strongly correlated during the day as the mercury flux responded quite rapidly to the changes in solar radiation associated with the passage of low level cumulus clouds. Figure 7B also shows a plot of mercury flux against solar radiation (r^2 = 0.78). These results are consistent with other recent measurements of mercury flux over surfaces exposed to direct solar radiation (Carpi and Lindberg, 1997, 1998).

Measurements from the soil site adjacent to North Cranberry Lake are shown in Figure 8. Although both days of measurements were cloud free, little solar radiation reached the surface (and wind speeds were weak) because of the overlying forest canopy. The flux was most strongly correlated with 0.5 cm soil temperature. This dependence is often characterized by the following Arrhenius type relation

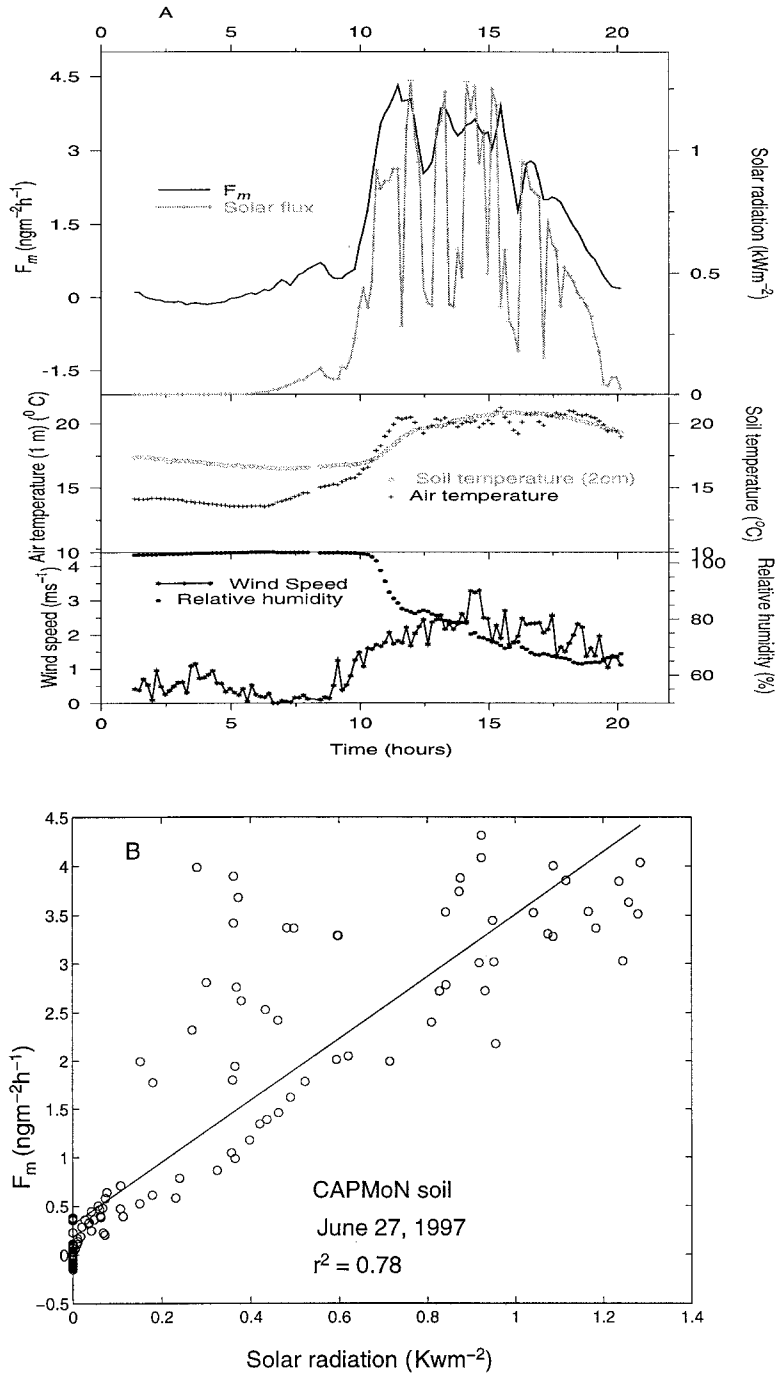

Figure 7. Mercury flux over soil at CAPMoN site, meteorological variables (A) and solar radiation (B).

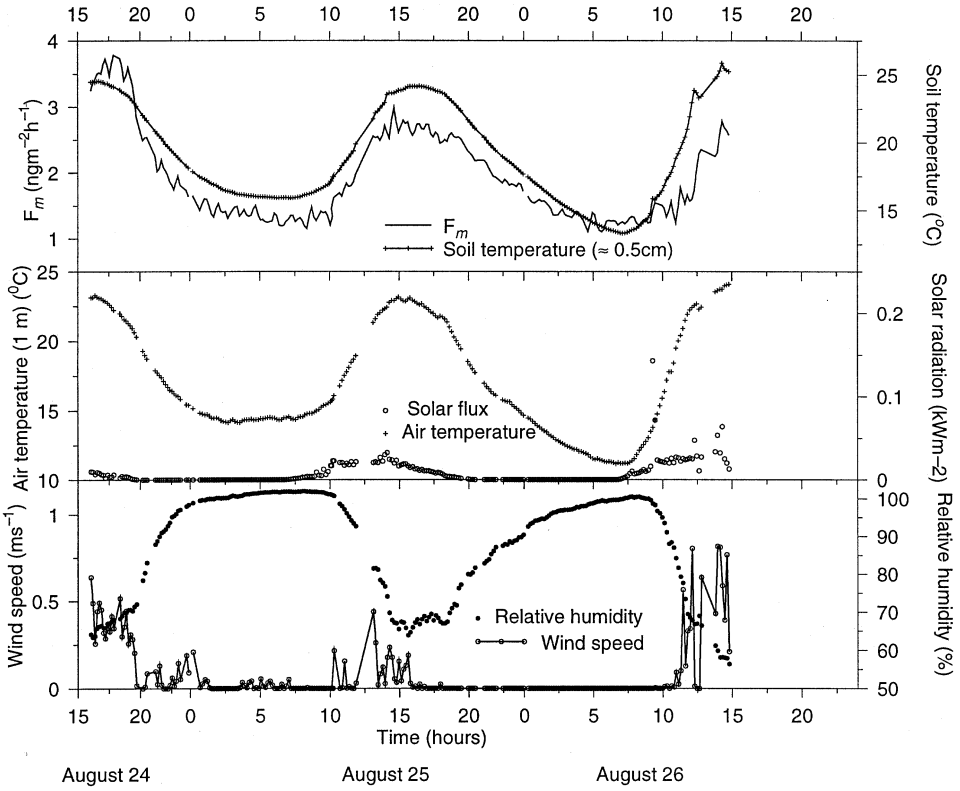

Figure 8. Mercury flux over soil at North Cranberry and meteorological variables.

(Carpi and Lindberg, 1997, 1998; Poissant and Casimir, 1998; Lindberg *et al.*, 1995a),

$$\ln(F_m) = \frac{-E_a}{RT} + c$$

where F_m is the mercury flux, T is the soil temperature in K, E_a is an activation energy, R the gas constant in kcal mol^{-1} K^{-1}, and c a constant. The natural logarithm of the mercury flux is plotted against inverse temperature in Figure 9. The slope of the best fit line through the data points gave an activation energy E_a of 14.6 kcal mol^{-1}, with an r^2 of 0.87, indicating that 0.5 cm soil temperature was a very good predictor of mercury flux at this site during the measurement period. The best fit E_a of 14.6 kcal mol^{-1} is very close to the mercury heat of vaporization of 14.5 kcal mol^{-1} at 20 °C (Carpi and Lindberg, 1997) which implies that the volatilization of mercury occurred as a result of vaporization of elemental mercury that may have been deposited via litterfall and throughfall or previously produced by some chemical and biological processes. The correlation of the mercury flux with 2 cm soil temperature (r^2 = 0.48) was much weaker. The mercury flux was also strongly

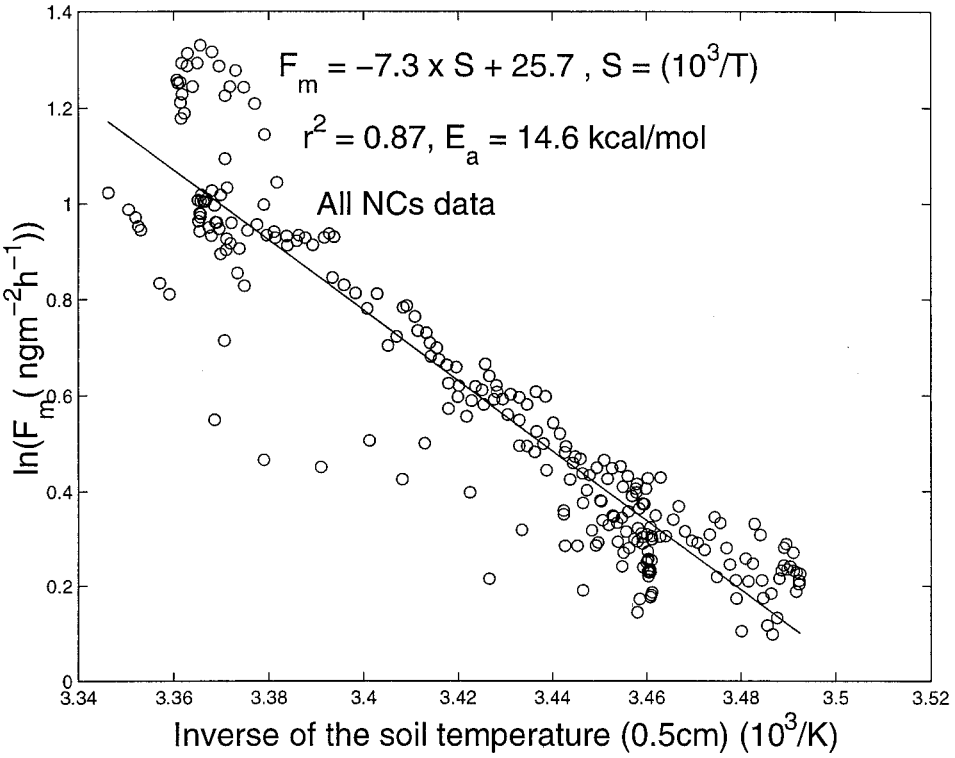

Figure 9. Natural log of mercury flux over soil and inverse of the soil temperature at ≈ 0.5 cm – the Arrhenius plot.

anti-correlated with relative humidity (r^2 = 0.78) and positively correlated with air temperature (r^2 = 0.77).

The average mercury flux at the forest site adjacent to Big Dam West Lake was –0.3 ng m^{-2} h^{-1}, substantially lower than the 2.3 ng m^{-2} h^{-1} observed at North Cranberry. This difference was probably attributable to the differing meteorological conditions of the two measurements periods. While conditions for the two days of soil measurements at North Cranberry were sunny and warm, the weather conditions for two days at Big Dam West were characterized by higher humidity, extensive cloud, little temperature variation, and intermittent rain. Fluxes were always depositional, or very weakly positive. There was no significant correlation between mercury flux and soil temperature, and the Arrhenius type relation given above cannot be expected to apply during periods of depositional flux.

4. Conclusions

The flux measurements over water strongly support the notion that mercury evasion from lakes is initiated by solar radiation. This is supported not only by the diurnal

cycles in mercury evasion over water, but also by the large differences in mercury flux between cloudy and sunny days. In the presence of solar radiation, wind speed can also play an important role in increasing the flux. There was a strongly non-linear increase in flux when the wind speed exceeded 2 m s^{-1}. On the other hand, when the solar radiation was weak, the flux did not increase with wind speed. It is likely that wind-induced mixing increases the flux both by increased vertical diffusion of pre-existing elemental mercury within the water column, and be increasing the production of elemental mercury by bringing photo-reducible mercury closer to the surface and exposing it to UV light. We have proposed a simple parameterization for the dependence of flux on solar radiation and wind speed. More measurements over a wider range of synoptic conditions would be desirable to determine the generality of this parameterization. Expressions of this kind would be useful both for small scale mercury mass balance studies of individual watersheds, and large scale models of the global mercury distribution.

In consistency with other recent measurements, the mercury flux was also strongly correlated with solar radiation at a soil site exposed to direct sunlight. We observed two types of behavior at two forest sites in which the soil was covered by leaf litter, and the forest canopy prevented direct solar radiation from reaching the surface. Under conditions associated with surface moisture (rain, dew, fog), fluxes were either negative or very weakly positive, and there was little if any diurnal cycle. Under dryer and warmer conditions, the flux was highly correlated with the 0.5 cm soil temperature, exhibited a strong diurnal cycle, and was always positive. The dependence of mercury flux on the 0.5 cm soil temperature was in this case well described by an Arrhenius type relation.

One of the objectives of the study was to determine whether lakes with differing DOC and total mercury concentrations also had different mercury fluxes across their surfaces. In this case, the lake with the larger DOC and total mercury concentration also had substantially larger average mercury fluxes (5.4 ng m^{-2} h^{-1} at Big Dam West as opposed to 1.1 ng m^{-2} h^{-1} at North Cranberry). Although suggestive, and consistent with previous studies (Xiao *et al.*, 1991), these differences are not conclusive because of the differing meteorological conditions of the measurements periods at the two lakes. In particular, the average fluxes at Big Dam West was strongly biased by the large fluxes observed on the second day, in which both levels of solar radiation and wind speed were large. However, the measurements do not support the notion that reduced mercury evasion from high DOC lakes (associated with the reduced light penetration) helps give rise to the positive correlation between DOC and mercury concentrations from lake to lake within Kejimkujik Park.

Our measurements indicate that evasion plays an extremely important role in the overall mercury budget of the lakes within Kejimkujik Park. For example, given that the average mercury flux over Big Dam West was strong enough to remove all of the mercury with the top 3 cm of the water column in one day, and that the lake

was only 2.47 m deep on average, the lifetime of mercury in the lake with respect to evasion in the summer would be only about 82 days.

Mercury fluxes over soil were on average approximately one third of that measured over water. It is interesting that soil mercury concentrations at the two forest sites were approximately three times larger than those measured at the grass covered CAPMoN site. This may be due to increased evasive fluxes at cleared sites exposed to direct solar radiation, or to the increased deposition of mercury to forest soils from litterfall (Schroeder and Munthe, 1998; Lindberg, 1996).

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