MERCURY IN ADIRONDACK WETLANDS, LAKES AND TERRESTRIAL SYSTEMS (MAWLTS)

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NEW YORK STATE
ENERGY RESEARCH AND
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Final Report

Prepared for the
**NEW YORK STATE
ENERGY RESEARCH AND
DEVELOPMENT AUTHORITY**

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Chapter 6. Hydrologic Factors Influencing Mercury Release from an Adirondack Wetland

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Chapter 7. Characteristics and Hg Behavior within an Adirondack Wetland

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EXECUTIVE SUMMARY

Mercury (Hg) is a powerful neurotoxin of significant environmental concern. High concentrations of mercury in fish represent a health concern to people and wildlife that eat fish. Nearly all of the mercury is found in the edible muscle tissue and is in the form of methylmercury (MeHg). Most of the mercury comes from a fish's diet with only a small part derived from water taken up through the gills. As of 2006, 3,080 fish consumption advisories due to Hg contamination had been issued for 48 states, including 34 statewide advisories for freshwaters and 12 statewide advisories for coastal waters and one territory. These advisories represent approximately 56,800 km^2 of lakes and 1,421,000 km of rivers (US EPA 2007).

Most of the mercury entering remote lake-watershed systems, such as the Sunday Lake Watershed in the Adirondacks is from atmospheric deposition and is in the inorganic form. Mercury entering lake-watersheds as direct deposition or indirect deposition that then becomes terrestrial runoff or groundwater undergoes a variety of transformations that affect its ultimate concentration in fish. The specific characteristics of a lake and its surrounding watershed can significantly affect how much of the mercury entering the system is converted to the organic form, methylmercury (MeHg), and how efficiently that MeHg is bioaccumulated in fish.

The conversion of inorganic Hg to MeHg, called methylation, is the most important step in the pathway leading to mercury accumulation in fish and wildlife. Methylation occurs in regions with anoxic (oxygen-deprived) conditions and sufficient organic carbon and sulfate to support sulfate-reducing bacteria. Investigations of wetlands for this project showed that riparian wetlands where all three requirements were met had the highest methylmercury concentrations in the shallow groundwater. These conditions can also occur in shallow lake sediment or in the water column near the oxic-anoxic interface. Typically, shallow lake waters are oxygenated due to diffusion from the atmosphere. Microbial activity leads to the depletion of oxygen. As depth increases, diffusion from the atmosphere cannot keep up with microbial demand, and the dissolved oxygen concentration goes to zero. In this environment, bacteria that derive their energy by reducing sulfate in water become active. In the process of reducing sulfate, these bacteria also methylate mercury. MeHg typically constitutes a small fraction of the total mercury in lakes, but it is the critical form that bioaccumulates up the food chain into fish.

Mercury research conducted in the Adirondacks in the early 1990s resulted in the following observations:

- Mercury concentrations in the muscle tissue of Yellow Perch are often elevated above the U.S. FDA action level (1 ppm).
- Mercury concentrations in both fish and water are higher in the Adirondacks than in other remote areas in the U.S. In fact, the highest mercury concentrations measured in water for Adirondack lakes are comparable to concentrations reported for lakes with a point source of mercury from mining or industrial activity.
- Total and methylmercury concentrations in water and fish increase with increasing concentrations of dissolved organic carbon and percent wetlands in the watershed.

These results led to the initiation of the Mercury in Adirondack Wetlands, Lakes, and Terrestrial Systems (MAWLTS) project. The overall objective of the MAWLTS project was to develop an understanding of the behavior of mercury in drainage lake-watershed systems through a mass balance analysis and to produce an integrated mathematical model with the capability of simulating the terrestrial, wetland, and in-lake processes that influence the levels of mercury in fish. This report describes the major findings from the field, laboratory, and modeling investigations. The focus of this project was primarily to evaluate the influence of the watershed, so a drainage lake was selected that has a variety of types of vegetation and wetlands. The Adirondack region is an acid-sensitive forested area with soft-water lakes that receive elevated atmospheric deposition of mercury. The Sunday Lake Watershed has extensive northern hardwood forest cover and both natural and beaver-produced wetlands. This lake-watershed was suitable for investigating the influence of the forested canopy and wetlands on transport of mercury from the atmosphere to the lake, and ultimately uptake by fish.

Major Findings

Watershed Characteristics

Sunday Lake Watershed is located in the western part of the Adirondack Park in New York State, just west of the Stillwater Reservoir (Figure ES-1). Sunday Lake is a small lake (7.8 hectares) surrounded by a large watershed (1,340 hectares). The total surface area of the nine lakes and streams in the watershed is 23.2 ha, which represents about two percent of the watershed. Because the watershed feeding the lake is much larger than the lake itself, water moves through the lake rapidly, resulting in a retention time of about one week. Wetlands cover approximately 20 percent of the watershed, and border 66 percent of the stream channels and lake shorelines.

Figure ES-1 **The Sunday Lake Watershed is located in the western part of the Adirondack Park in New York State.**

The average precipitation from 1999-2001 in the watershed was 127.1cm, of which 77.4cm (61 percent) became streamflow. Wetland areas are important as 70 percent of the streamflow comes from runoff from wetland areas (37 percent) and shallow groundwater flow through the riparian wetland areas (33 percent). Four types of wetlands were investigated in the Sunday Lake watershed: fringe, sedge, shrub, and riparian. Mercury concentrations in surface water and groundwater samples from these types of wetlands are discussed in Chapter 6. The average total mercury in the riparian groundwater, defined as water flowing within the upper 1 meter of the wetland, was 21.15 ng/L, and the average methylmercury concentration was 2.96 ng/L. Hydrologic factors explain why riparian wetlands produce more MeHg than the other wetland types. The riparian wetlands discharge water to the streams from surrounding soils throughout most of the year, but during rain storms and snowmelt events, water from the stream recharges the groundwater. This recharge may transport mercury and organic matter into riparian wetlands, which have active microbial communities capable of methylating mercury. During the growing season, evapotranspiration of riparian vegetation creates an upflux that draws fresh supplies of sulfate and DOC into the riparian groundwater allowing for the maintenance of high methylation rates by sulfate-reducing bacteria, as discussed in Chapters 7 and 9.

The dynamics of Hg fluxes were also studied within upland coniferous and deciduous forest plots, as presented in Chapter 8. The flux of Hg to the forest ecosystem was dominated by dry deposition, estimated as throughfall (water that falls to the ground following interaction with the forest canopy) plus litter fall. Dry deposition accounted for 70 percent of total deposition. Throughfall mercury concentrations were higher at the coniferous plot than at the deciduous plot. Leaf litter mercury concentrations differed among individual tree species; MeHg was higher in deciduous than coniferous species. Concentrations of MeHg in soil were relatively uniform throughout both forest soil profiles, whereas porewater MeHg concentrations were highly variable.

The data from different aspects of the research were combined to estimate mercury fluxes and to develop a lake watershed mass balance. The measured wet deposition of mercury from the Huntington NADP/MDN Station was used to quantify wet deposition for the watershed. The total mercury wet deposition flux was calculated as 9.4 $\mu g/m^2/yr$ and the methylmercury flux as 0.05 $\mu g/m^2/yr$. The estimated quantities of total and methylmercury input to the watershed and lake are shown in Figure ES-2, as discussed in Chapter 13. The direct wet deposition of total mercury to Sunday Lake is 0.7 g/yr. The wet deposition of total mercury to the upland (99.1 g/yr) and wetland areas (25.4 g/yr) is greater than the estimated total mercury flux reaching the lake (40.7 g/yr), indicating that much of the mercury is retained in the largely forested watershed. Dry deposition represented a greater flux to the watershed than wet deposition for both total and methylmercury.

The pools of total and methylmercury present in the soil layers and estimated drainage fluxes to underlying layers are also shown in Figure ES-2. Mass balance calculations show that the soil was a net sink for inputs of THg and MeHg at both the coniferous and deciduous plots. Most of the mercury is retained in the deeper soil layer, the Bs horizon. The pool of total mercury retained in all the soil layers is over 500 times the annual flux to the watershed. The primary flux out of the soil plots, the flux from the Bs soil horizon, was small for total mercury (30.8 g/yr), representing about 12 percent of the total flux to the forest floor. The methylmercury flux from the Bs soil horizon was 1.2 g/yr, representing about five percent of the total flux to the forest floor. Due to the large pool of mercury already present in the soil horizons, changes in the flux out of the deeper soil horizons are expected to be slow in response to changes in mercury concentrations of the atmospheric deposition.

The total mercury flux from the watershed to the lake was estimated as 40.7 g/yr based on the total lake inflow of 77.4cm and the average total mercury concentration of 3.95 ng/L. This total inflow represents the combination of surface stormflow, riparian groundwater in the top 1 meter, and deeper non-wetland groundwater. The methylmercury flux to the lake from the watershed was 7.7 g/yr based on the above flow rate and an average methylmercury concentration of 0.75 ng/L. Based on the mass balance shown in Figure ES-2, the lake is a sink for total mercury.

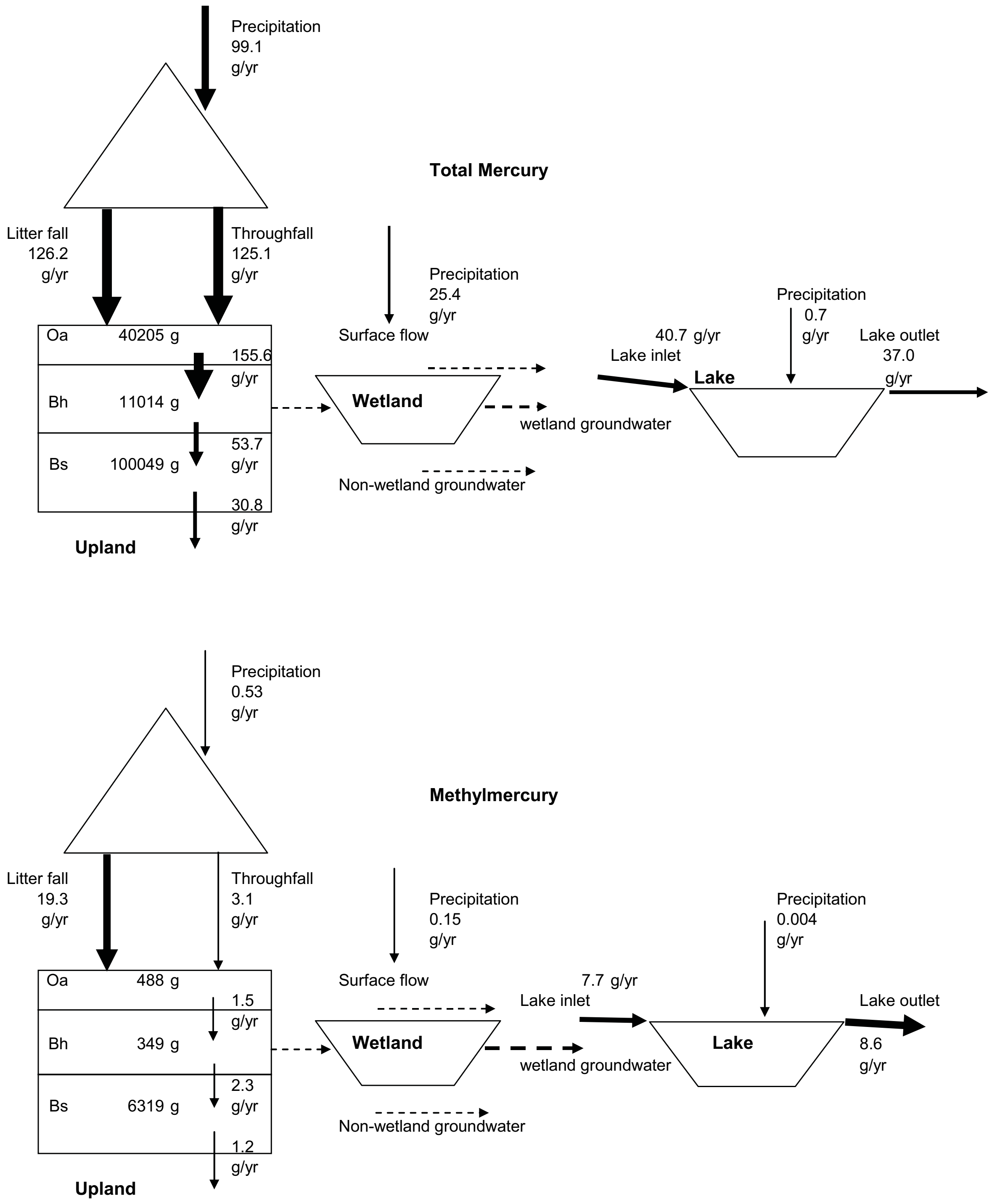


Figure ES-2. Mass Balance Diagram of Total and Methylmercury for Sunday Lake and Watershed

The trophic transfer of MeHg was evaluated in Sunday Lake by measuring mercury concentrations in water, Zooplankton, Forage fish, and Yellow Perch samples. Mercury concentrations in the lake epilimnion averaged 3.6 ng/L THg and 0.86 ng/L MeHg over the period from August 1999 to October 2002. Higher THg and MeHg were observed in spring and late summer, as shown in Chapter 4. Zooplankton MeHg concentrations were lower than values observed in Wisconsin lakes, and differed between species, as discussed in Chapter 10. Mercury concentrations in Yellow Perch of Sunday Lake averaged 1.0 ± 0.47 ppm, and were higher than values observed in many remote regions. The log BF values were similar to the 1992 study for Yellow Perch in Sunday Lake and in general increased with fish age.

Application of the Mercury Cycling Model for Headwater Drainage Lakes (MCM-HD)

The Mercury Cycling Model for Headwater Drainage Lake Systems (MCM-HD) was developed to simulate Hg interactions in headwater drainage lakes and their adjacent watersheds, including wetlands. It was applied to the Sunday Lake watershed based upon project data, as presented in Chapter 12. The model was parameterized using observed lake-watershed physical characteristics and precipitation quantity and quality as driving variables. Calibration parameters were adjusted where necessary to achieve a best fit between simulated and observed values. Model results are in agreement that both the watershed and the lake are sinks for total Hg.

Following calibration, a scenario analysis was conducted to evaluate the response to 15 and 50 percent decreases in atmospheric deposition of total Hg. The modeling results for Sunday Lake estimated that a 50 percent decrease in atmospheric deposition could decrease THg in the water from an average of 0.7 ng/L to 0.58 ng/L and in the fish from 0.88 µg/g to 0.73 µg/g after 10 years and to 0.64 µg/g after 50 years. The reduction in fish mercury concentrations represented a 27 percent decrease after 50 years. The simulated concentrations in both the lake water and Yellow Perch decreased relatively rapidly in the first 35 years following deposition, and then declined slowly. The timing of the response is highly uncertain, since it is dependent on the retention of mercury within the watershed soils and the bioavailability of THg for methylation.

Research related to retention of mercury was investigated. Concentrations of total Hg were measured in sediment cores collected from eight Adirondack lakes as discussed in Chapter 11. Although there were lake-to-lake variations, on average sites showed a 5.8-fold increase in sediment Hg deposition from background values (before 1900) to peak values. Mercury deposition peaked from 1973 to 1995 and has decreased in recent years. Current sediment Hg deposition is 3.5 times background values. Using sediment deposition data across the study lakes, watershed Hg retention by year was estimated and may be decreasing.

MAWLTS Research Questions

The researchers of the MAWLTS project identified seven questions or hypotheses to be evaluated using the results of the field and laboratory investigations at the Sunday Lake watershed. These questions are listed below:

1. DoesAl/Hg-DOC affect the concentration of Hg in fish in Sunday Lake?

2. To what extent do Sunday Lake wetlands account for Hg-mass loading?

3. How does water quality affect Hg availability?

4. How does soil Hg content correlate with Hg-mass loading in the Sunday Lake ecosystem?

5. How do aqueous and fish mercury concentrations change in the modeled system in response to changes in atmospheric deposition of mercury?

6. What impacts do changes in water quality characteristics have on aqueous and fish mercury concentrations?

7. How quickly does the modeled system respond to changes in atmospheric deposition of mercury or lake water quality characteristics?"

Each of these questions are addressed using data and findings from the MAWLTS project.

1. Does Al/Hg-DOC affect the concentration of Hg in fish in Sunday Lake?

Driscoll et al. (1994) observed that some lakes in the Adirondack region, including Sunday Lake, had higher fish Hg levels than other lakes. A previous study by Yan (1996) also reported relatively high THg and MeHg concentrations in Sunday Lake, as compared to 15 other Adirondack lakes, and high Hg for fish in this lake. The average mercury concentrations in both lake water and fish in Sunday Lake are shown in Table ES-1. Mercury concentrations averaged 3.6 ng/L THg and 0.86 ng/L MeHg in the epilimnion of Sunday Lake. Yellow Perch averaged 0.21 µg/g ww for age +1, 0.93 µg/g ww for age 4+, and 1.1 to 1.9 µg/g ww for age 5+ to 7+ , as discussed in Chapter 10.

One of the study hypotheses was that aluminum concentrations may be a factor controlling fish mercury concentrations. The hypothesis was that competition between aluminum and mercury for organic binding sites may result in greater bioavailability of mercury in lakes with a high Al/DOC ratio, because more of the Al would be complexed with DOC rather than the Hg. This factor is particularly relevant for areas such as the Adirondacks where some lakes (typically acidic drainage lakes) exhibit elevated concentrations of aluminum (Driscoll et al. 1994). Previous research showed that aluminum is higher in surface waters with pH values less than five (Driscoll 1985). Such acidic waters have a low inorganic buffering capacity. Under such conditions aluminum hydrolysis and protonation/deprotonation of natural organic acids can occur providing some buffering capacity.

The average aluminum in the epilimnion of Sunday Lake over three years of sampling (August 1999 – October 2002) was 4.3 +/- 2.7 µmol/L for Al_m and 3.2 +/- 1.2 µmol/L Al_o (Table ES-2). The mean pH over the same period was 5.4 +/- 0.49 and the mean DOC was 7.0mg C/L +/- 2.8, which is equivalent to 586.7 µmol/L C. The Al/DOC ratio in the lake using the mean values was 0.013. Because the lake was not highly acidic, the aluminum concentrations are not high relative to other Adirondack lakes (Driscoll 1985). There was a weak negative relationship between the Al/DOC ratio and MeHg in lake surface water, which was primarily due to the influence of DOC. There was no relationship between the individual Al parameters and MeHg in the lake surface water. Thus, DOC was more important than aluminum in this lake.

Table ES-1.
Concentrations of THg, MeHg, and log bioconcentration factor (BF) for Zooplankton, Forage fish, and Yellow Perch in Sunday Lake

species	n	average THg	average MeHg	units	%MeHg	average log BF
Lake water	37	3.6 ± 1.8	0.86 ± 1.1	ng/L	24	
Combined Zooplankton	32	39 ± 56	25 ± 40	ng/g dw	67	3.5
Cladocera						
Bosmina longirostris	2	197	156	ng/g dw	79	
Holopedium gibberum	4	35 ± 4.4	25 ± 11	ng/g dw	70	
Daphnia pulex	16	38 ± 38	22 ± 17	ng/g dw	58	
Copepoda						
Mesocyclops edax	10	9.4 ± 11	4.3 ± 3.3	ng/g dw	46	
Fish						
Golden Shiners						
size class 1	13	0.20 ± 0.07		μg/g ww	*	5.4
size class 2	15	0.40 ± 0.07		μg/g ww	*	5.7
size class 3	5	0.45 ± 0.14		μg/g ww	*	5.7
Yellow Perch						
age 1+	4	0.21 ± 0.07		μg/g ww	*	5.4
age 2+				μg/g ww		
age 3+				μg/g ww		
age 4+	24	0.93 ± 0.19		μg/g ww	*	6.0
age 5+	33	1.1 ± 0.45		μg/g ww	*	6.1
age 6+	3	1.5 ± 0.51		μg/g ww	*	6.2
age 7+	2	1.9 ± 0.37		μg/g ww	*	6.3

*Assumed to be > 95% (Bloom, 1992)

Table ES-2.
Epilimnion water chemistry for Sunday Lake, – Data represent the average over three years of sampling (August 1999 – October 2002).

	average	standard deviation	units
pH	5.4	0.49	
DOC	7.0	2.8	mg C L^{-1}
ANC	16.4	32.5	μeq L^{-1}
THg	3.6	1.8	ng L^{-1}
MeHg	0.86	1.1	ng L^{-1}
Ca^{2+}	1.8	0.33	mg L^{-1}
Mg^{2+}	0.36	0.08	mg L^{-1}
K^{+}	0.49	0.13	mg L^{-1}
Na^{+}	0.86	0.18	mg L^{-1}
Cl^{-}	9.8	6.5	μmol L^{-1}
NO_3^{-}	15.9	17.8	μmol L^{-1}
SO_4^{2-}	44.7	11.3	μmol L^{-1}
Al_m	4.3	2.7	μmol L^{-1}
Al_o	3.2	1.2	μmol L^{-1}

A correlation between total dissolved Al and fish Hg has been reported (Driscoll, et al. 1994). A possible link is the release of aluminum from soils as acidic water moves as subsurface stormflow through the upper soil horizons. Similarly, Hg accumulates in fish from watersheds where shallow subsurface stormflow is dominant instead of deep subsurface flow through higher ANC soils. In the Sunday Lake watershed, wetland areas are clearly important in generating streamflow, as 70 percent of the streamflow is coming from either runoff from wetland areas (37 percent) or shallow groundwater flow through riparian wetlands (33 percent), as discussed in Section 5.2.7. While much of the riparian groundwater flow may originate in adjacent upland areas, it enters the stream after passing through the riparian wetlands. The effect of flow through the wetlands is seen in the relatively high DOC in the lake water (7mg C/L, see Table ES-2). The riparian wetland groundwater had the highest MeHg, as discussed in Chapter 10, but a low Al/DOC ratio. In this lake watershed, DOC has a stronger influence on MeHg than aluminum species, most likely because it is not highly acidic.

Driscoll, et al. (1994) found that fish THg concentrations in Adirondack Yellow Perch were positively correlated with DOC up to DOC concentrations of 8mg C/L. As shown in Table ES-2, average DOC in Sunday Lake was 7mg C/L. The 1994 study reports that although water MeHg concentrations were higher in high DOC lakes, bioavailable MeHg appeared to be lower. Decreasing log BF values with increasing DOC concentrations indicate that complexation with DOC reduces bioavailable MeHg in Adirondack lakes. Sunday Lake log BF values were generally lower than lakes with low DOC concentrations (See Figure ES-3 and discussion in Section 10.4). DOC concentrations are one influence on Hg concentrations of Sunday Lake, although mercury concentrations in Yellow Perch are affected indirectly, first through methylation and second, uptake through the food chain.

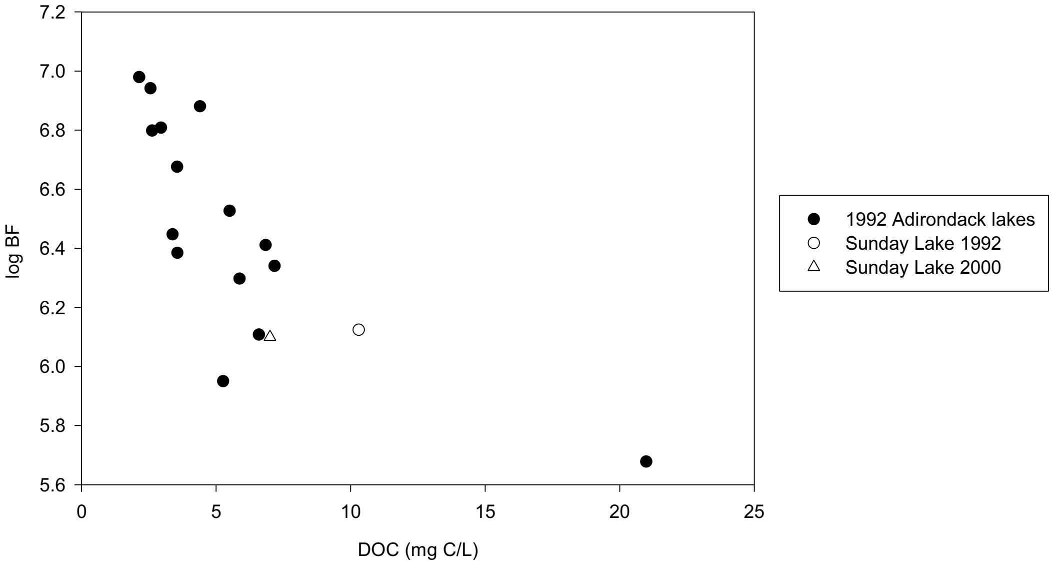


Figure ES-3. **Log bioconcentration (BF) values for age 3+ to 5+ perch vs. DOC (mg C/L) for 16 Adirondack lakes in 1992 (Yan, 1996) and Sunday Lake in 2000**

2. To what extent do Sunday Lake wetlands account for Hg-mass loading?

Wetlands cover approximately 20 percent of the Sunday Lake watershed, with most located adjacent to lakes and streams (riparian wetlands). Wetlands border 66 percent of all the stream channels and much of the lake shorelines. From a hydrologic perspective, the wetlands are important because of their position relative to the lake. Precipitation averaged 127.1cm per year over the study period (Table ES-3). Evapotranspiration, determined as the difference between precipitation and streamflow, averaged 39 percent of precipitation (See Chapter 5). The remaining 61 percent of precipitation left the watershed via streamflow. Streamflow was divided into three components; surface stormflow, riparian wetland groundwater flow, and non-wetland groundwater flow. The riparian component, at 25.9cm/yr, represents water flowing through the upper-most meter of the saturated zone under riparian wetlands. Wetland areas are clearly important in generating streamflow as 70 percent of the streamflow is coming from either runoff from wetland areas (37 percent) or groundwater flow through riparian wetlands (33 percent).

Table ES-3.
Sources of Water in the Sunday Lake Watershed from January 1999 through December 2001

Source	cm
Precipitation	127.1
Infiltration	98.5
Evapotranspiration	49.6
Streamflow	77.4
Surface Stormflow	28.6
Riparian wetland groundwater	25.9
Non-wetland Groundwater	22.9

Wetlands are also important from a mercury perspective. In the Sunday Lake watershed, there are four contrasting wetland types based largely on the traditional classification system of Cowardin et al. (1979): fringe, shrub, sedge, and riparian types, described in Chapter 6. The riparian wetland was distinguished from the other three sites by significantly greater ($P < 0.05$) concentrations of THg and MeHg. Groundwater samples from the riparian wetlands, the major tributary to the lake, had higher average concentrations (21.15 ng/L THg, 2.96 ng/L MeHg) than those found in the main tributary, Inlet 2 (3.95 ng/L THg and 0.75 ng/L MeHg). Mercury and the DOC released by the riparian wetlands does influence the Hg cycling in Sunday Lake. This is evident through the strong correlation between MeHg and DOC concentrations in Inlet 2 and the epilimnion (r^2=0.53 and 0.75, respectively discussed in Chapter 10).

3. How does water quality affect Hg availability?

The water quality of the lake outlet was typical of the high DOC, thin till class of Adirondack lakes in the ALSC classification system (Newton and Driscoll 1990). This lake class is considered to be sensitive to acidic deposition and expected to have high mercury concentrations. The average THg and MeHg in the Sunday Lake outlet stream are high compared to the Adirondack lakes studied in 1994 (Driscoll, et al. 1994). Previous monitoring of Adirondack lakes showed a positive relationship between DOC and THg, and a more complex, but still positive relationship between DOC and MeHg (See Figure 3-2 in this report from Driscoll, et al. 1995). Positive relationships were also observed between THg and DOC in throughfall in both the coniferous and deciduous plots and in soil water beneath these two types of plots, as discussed in Chapter 8.

Detailed investigations were conducted in the wetlands of Sunday Lake watershed. Of the four types of wetlands present in the watershed, the riparian wetland had the highest mean THg, MeHg, and SO_4, as discussed in Chapter 6. The highest MeHg in the riparian wetland was much higher than in the other wetlands, and three of the five samples from riparian wetlands had high DOC. The DOC present in the wetland groundwater was considered to facilitate Hg methylation, as discussed in Chapter 7. Other relationships discussed in Chapter 7 included a negative relationship between ANC and THg, but none THg or MeHg and nitrate.

4. How does soil Hg content correlate with Hg-mass loading in the Sunday Lake ecosystem?

The THg concentrations in the soil beneath coniferous and deciduous plots varied more than MeHg, as seen in Figure ES- 4 and discussed in Chapter 8. While the highest THg content was in the upper soil horizon for both plots, the largest pool of THg was in the deeper soil horizons (Table ES-4). The mass balance for the watershed (See Figure ES-2) showed that the THg input from wet and dry deposition were larger than the fluxes from the soil layers, indicating that THg is accumulating in the soil. Further discussion of the mercury mass loading is presented in Chapter 13.

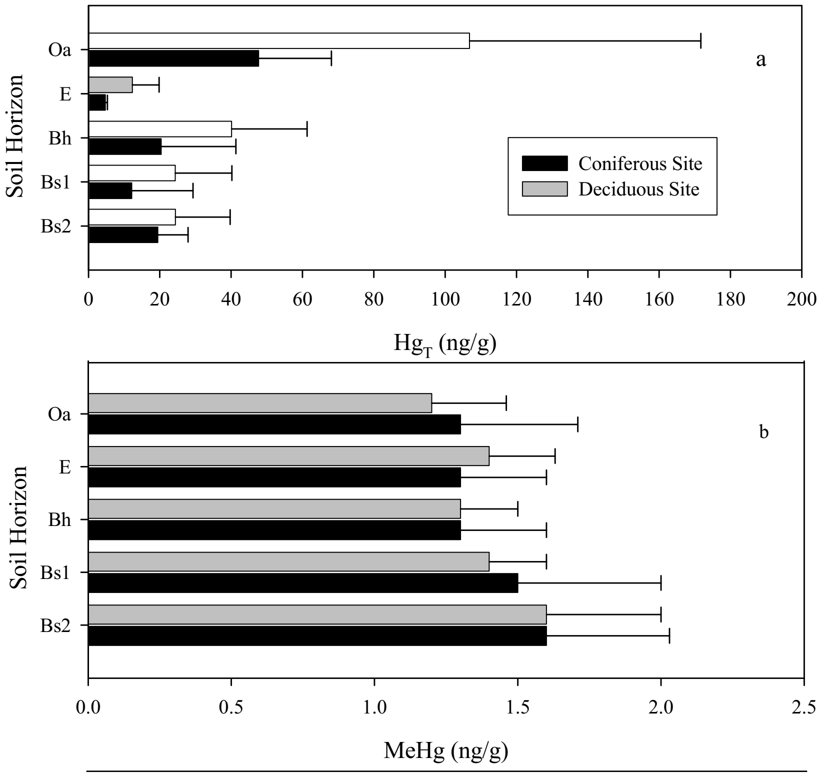


Figure ES-4. Concentrations and standard deviations of THg (a) and MeHg (b) in soil at coniferous and deciduous plots within Sunday Lake Watershed

Table ES-4.
Pools of THg and MeHg by soil horizons at Sunday Lake Watershed

	Pools (g/ha)			
	Coniferous		Deciduous	
Soil Horizon	THg	MeHg	THg	MeHg
Oa	17.53	0.40	46.97	0.49
E	1.67	0.45	7.19	0.77
Bh	1.95	0.10	14.09	0.43
Bs1	14.48	1.52	25.94	1.4
Bs2	43.78	3.06	84.67	5.2
Total	79.4	5.53	178	8.29

5. How do aqueous and fish mercury concentrations change in the modeled system in response to changes in atmospheric deposition of mercury?

The modeling results for Sunday Lake, presented in Chapter 12, showed that a 50 percent decrease in atmospheric deposition decreased THg in the water from an average of 0.7 ng/L to 0.58 ng/L and in the fish from 0.88mg/g to 0.73 µg/g after 10 years and 0.64 µg/g after 50 years. The reduction in fish mercury concentrations represented a 27 percent decrease after 50 years. The plots of simulated fish mercury concentrations showed that concentrations decrease faster for the first 35 years and then slowly after that (See Figure 12-10 in this report). Part of the reason for the slow response is the retention of deposited mercury in the soils. A faster response would be expected in a seepage lake where most of the mercury input comes from direct deposition.

Predictions of fish response times for ecosystems receiving most of their Hg from terrestrial runoff also strongly depend on assumptions made in the model, discussed in Chapter 12, regarding the watershed response and the bioavailability for methylation of this Hg source. If newly added Hg is more available for methylation, the response times would be expected to shorten compared to current simulations. However, part of the mercury deposited on the uplands would still be retained in the soil pools.

6. What impacts do changes in water quality characteristics have on aqueous and fish mercury concentrations?

An analysis was conducted using the model to evaluate the impact of reductions in atmospheric sulfur and nitrogen inputs on lake and fish Hg concentrations. Reductions in sulfur emissions related to the requirements of the Clean Air Act Amendments have resulted in statistically significant decreases in the sulfate concentrations of Adirondack Lakes. Some of these lakes have also experienced increases in ANC and pH. Mercury uptake by biota is influenced by aqueous pH, and this influence is reflected in the model. Further reductions in sulfur emissions, as well as nitrogen emissions, have been proposed, and may result in further increases in lake water pH. If the sulfate concentrations of surface waters and porewaters are reduced as a result of decreases in sulfur deposition, net methylation may decrease, potentially resulting in lower lake and fish MeHg concentrations.

This analysis, discussed in Section 12, used a 50 percent reduction in lake and porewater sulfate concentrations and a 1-unit change in lake water pH. The simulated response to these changes was smaller than the simulated response to a 50 percent decrease in atmospheric THg deposition, which was estimated as a reduction of 27 percent.

7. How quickly does the modeled system respond to changes in atmospheric deposition of mercury or lake water quality characteristics?

The plots of simulated fish mercury concentrations showed that concentrations decrease gradually in the first five years as shown in Figure 12-9 and continue at about the same rate for 35 years, but then decrease at a slower rate, as shown in Figure 12-10. Part of the reason for the slow response is the retention of deposited mercury in the soils, which is leached slowly over time. A faster response would be expected in a seepage lake where most of the mercury input comes from direct deposition. In contrast, all surface waters in the Sunday Lake watershed represent only 2 percent of the total watershed. The direct deposition to the lake was <2 percent of the total mercury influx to the lake, as shown in the lake-watershed mass balance (See Figure ES-2), and discussed in Chapter 13.

Changes to lake water characteristics were simulated for pH and sulfate, as discussed in the response to question 6. Decreases in acidity or increases in ANC would have the most effect.

1 Introduction

1.1 Background

Mercury concentrations in many regions of the globe have risen as a result of industrial activities (Munthe et al. 2007). Mercury contamination can occur as a localized issue near industrial releases and as a longer range transboundary issue arising from atmospheric emissions, transport and deposition. While most of the mercury (Hg) released to the environment is inorganic, a small but important fraction is converted by bacteria to methylmercury (MeHg), a toxic form that bioaccumulates through aquatic food webs to fish, which are the primary exposure pathway for methylmercury in humans and many wildlife species.

The discovery of elevated mercury levels in fish from remote lakes led the regulatory community to devote increased attention to mercury cycling and accumulation (e.g. WHO 1990, Porcella 1994, US EPA 1997 and 2001a). Much research has been undertaken in the past two decades to better understand factors explaining elevated fish mercury concentrations in remote areas. Fewer studies conducted to-date have investigated mercury cycling in temperate drainage lake-watershed systems, which comprise over 85 percent of the lakes in the Adirondacks. Improved understanding of mercury cycling in uplands and wetlands is important because terrestrial mercury loads typically exceed direct deposition rates to lakes. Previous research has indicated that terrestrial and wetland processes play a vital role in determining the aqueous chemical characteristics and fish tissue mercury concentrations in these types of systems (Driscoll, et al. 1994a, b, c). Without research in temperate drainage lake systems, the benefits of emissions controls in these types of systems are uncertain.

The U.S. Food and Drug Administration (FDA) set the Action Level for mercury in fish involved in interstate commerce at 1 ppm (wet weight basis). Above this level, fish cannot be sold in interstate commerce. The equivalent standard in Canada is 0.5 ppm, as it is for the World Health Organization (WHO, 1990). To protect the human population, the USEPA established a MeHg criterion for fish tissue at 0.3 µg/g under Section 304(a) of the Clean Water Act (USEPA 2001b). As of 2006, 3,080 fish consumption advisories due to Hg contamination had been issued for 48 states, including 34 statewide advisories for freshwaters and 12 statewide advisories for coastal waters, and one territory. These advisories represent approximately 56,800 km^2 of lakes and 1,420,991 km of rivers (US EPA 2007). The number of advisories is increasing with time, although this is due at least partly to more sites being sampled (Wiener, et al. 2003). Based on the FDA action level, the New York State Department of Health (NYDOH) issued health advisories for several lakes in the Adirondacks indicating that eating more than one meal per month of fish caught in these lakes may be hazardous to human health.

The New York State Department of Environmental Conservation (NYDEC) began monitoring fish and wildlife for mercury and organic compounds in the early 1970s under the Statewide Toxic Substances Monitoring Program (STSMP) and other, smaller projects. Samples were collected from surface waters throughout the state. However, sampling locations and methods varied considerably from year-to-year. Much of the sampling effort was focused on large water bodies such as Lake Ontario, Lake Erie, and Lake Champlain. Only 12 Adirondack lakes were sampled, but 8 of those 12 had fish containing over one ppm mercury (Boulton and Hetling 1972; NYDEC, 1981, 1982, 1987).

A comparison of data from sites sampled in 1970-1972 and again in 1976-1979 showed decreases in fish tissue mercury concentrations for most New York waters (Armstrong and Sloan 1980). Included among the waters with decreasing fish tissue mercury concentrations was Onondaga

Lake, which received direct discharges of over 160,000 pounds of mercury from an industrial facility on its shoreline prior to 1970. However, fish from five of the six Adirondack lakes that were sampled during both of the above time periods showed increases in mercury concentration. Fish samples from four of the six Adirondack lakes had higher mercury concentrations than the samples from Onondaga Lake (Fourth Lake, Great Sacandaga Reservoir, Indian Lake, and Raquette Lake). On the basis of these observations, NYDEC targeted the Adirondacks as an area of concern with respect to mercury in fish. Simonin et al. (1994) investigated concentrations of mercury in fish tissue in 12 Adirondack lakes and found relatively high concentrations in fish and increasing concentrations with decreasing pH. However, the lakes sampled were not representative of all of the different classes of Adirondack lakes (Newton and Driscoll 1990).

In 1992 the Empire State Electric Energy Research Corporation (ESEERCO) and the New York State Energy Research and Development Authority (NYSERDA) initiated the Mercury Survey of Adirondack Lakes (MSAL) project. For the MSAL project, the concentrations of total and methylmercury in lake water and concentrations of mercury in fish tissue in 16 lakes representative of the lake classes described by Newton and Driscoll (1990) were determined. The project results can be summarized as follows (Driscoll, et al. 1994c):

- Mercury concentrations in the muscle tissue of Yellow Perch were elevated above the U.S. FDA action level (one ppm) in one or more individual fish from 9 of the 16 lakes sampled.

- Both fish mercury and aqueous phase total mercury concentrations were higher in the Adirondacks than in other remote areas in the U.S. In fact, the highest aqueous phase total mercury concentrations measured for Adirondack lakes were comparable to concentrations reported for lakes with a point source of mercury from mining or industrial activity.

- Aqueous concentrations of total and methyl mercury increased with increasing concentrations of dissolved organic carbon and percent wetlands in the drainage basin.

- For 3- to 5-year-old Yellow Perch, tissue concentrations of mercury generally increased with increasing concentrations of dissolved organic carbon and percent wetlands in the drainage basin. However, in a lake with very high concentrations of dissolved organic carbon (26 ppm), fish concentrations were lower. Previous data sets did not include fish mercury measurements in lakes with DOC this high.

A subsequent project, the Mercury in Adirondack Wetlands and Watersheds Study, supported the results of the MSAL project by measuring aqueous and fish tissue mercury concentrations in an additional 10 lakes. A second component of the study involved a mass balance analysis on an Adirondack wetland. This study showed that during the summer, when microbial activity is high, MeHg concentrations leaving the wetland were elevated relative to the concentration entering the wetland (Driscoll, et al. 1998). One of the products of the mass balance analysis was the Mercury in Adirondack Wetlands and Watersheds Model (MAWWM). This model incorporated the understanding of mercury biogeochemistry within wetland and terrestrial systems at that time. The model simulates three major mercury species (Hg(0), Hg(II), and MeHg) in up to five soil layers and in wetland surface waters.

Previous work on seepage lakes in Wisconsin resulted in the development of the Mercury Cycling Model (Hudson, et al. 1994), which represents the understanding of mercury biogeochemistry within lakes. This model tracked three major mercury species in the water column (epilimnion and hypolimnion), sediments, and a food web consisting of four biotic compartments in each lake layer (phytoplankton, Zooplankton, a Forage fish population, and a piscivore fish population

(Hudson, et al. 1994). More recent work updated the mercury cycling routines for lakes such as the Dynamic Mercury Cycling Model (D-MCM, EPRI 2002) and extended the model to the Florida Everglades, resulting in the development of the Everglades Mercury Cycling Model (E-MCM, Harris, et al. 2003). E-MCM simulates mercury cycling in wetlands including surface waters, underlying soil layers, and vegetation, and represented a significant advance in simulating wetland mercury cycling.

Many lakes receive important mercury contributions from their surrounding watershed. The mercury lake models are effective tools for simulating mercury cycling and bioaccumulation within lakes, but were not designed for drainage lake systems, which receive most of their total inflow from the surrounding watershed. The E-MCM model simulates mercury cycling in soils, surface waters, and vegetation, but does not have the ability to simulate watershed hydrology. The MAWWM model effectively simulates watershed hydrology, but the mercury cycling routines are not appropriate for lakes. Because drainage lake-watershed systems comprise a large component of the surface water systems throughout North America, including over 85 percent of the lakes in the Adirondacks (Kretser, et al., 1989), the development of a model for use in headwater drainage lake systems was necessary. The development of the Mercury Cycling Model for Headwater Drainage Lake Systems (MCM-HD) used previous models as building blocks as well as the results of a mass balance analysis in an Adirondack watershed that characterized flows and mercury fluxes and transformations throughout the system.

1.2 Objectives and Approach

The overall objectives of the Mercury in Adirondack Wetlands, Lakes, and Terrestrial Systems (MAWLTS) project were due to the following:

- Develop a better understanding of the behavior of mercury in drainage lake-watershed systems through a mass balance analysis, and

- Produce an integrated mathematical model with the capability of simulating the terrestrial, wetland, and in-lake processes that influence the levels of mercury in fish tissue.

The following steps were used to meet these objectives:

- A lake-watershed system (Sunday Lake) was selected for mass balance analysis with both wetland and upland influences on mercury cycling and accumulation in fish. Sunday Lake is located in the western part of the Adirondack Park in New York State, just west of the Stillwater Reservoir (75˚ 5’ west longitude, 43˚ 51’ north latitude).

- The system was hydrologically characterized to determine volumetric inputs and outputs and to establish flowpaths of water through the lake-watershed. This involved surficial geologic mapping and measurements of inlet and outlet stream flows.

- The system was chemically characterized with respect to surface waters and groundwater to track mercury movement and transformations through the lake-watershed system. This was done by measuring total mercury and methylmercury concentrations in water samples from the lake inlets, outlet and water column, standing water in wetlands, and limited shallow groundwater samples.

- Mercury concentrations were determined in Zooplankton and fish. This was done using the same techniques applied in previous Adirondack mercury studies described above.

- An integrated mathematical simulation model was developed that accounts for terrestrial, wetland, and in-lake processes that influence mercury cycling and accumulation in fish tissue.

1.3 Organization of Report

Section 2 gives a general description of the MAWLTS project organization, project team and schedule. Sections 3 and 4 describe mercury cycling in terrestrial and aquatic environments, and provide a description of the study watershed. Sections 5 through 9 discuss hydrology and mercury field studies in the Sunday Lake watershed uplands, wetland and lake waters. Section 10 presents results of mercury studies related to the Sunday Lake food web. Section 11 discusses historical mercury deposition trends for the Adirondacks, based on sediment records from eight lakes in the Adirondacks, including Sunday Lake. Section 12 describes the development of the watershed-scale mercury cycling model and its application to the Sunday Lake watershed. Section 13 integrates the results of the field investigations and discusses mass balances for Sunday Lake and its watershed.

2 Project Organization and Schedule

The Mercury in Adirondack Wetlands, Lakes, and Terrestrial Systems (MAWLTS) project was a multli-disciplinary study to develop an understanding of the behavior of mercury in a drainage lake-watershed system. Major study components are outlined in Figure 2-1 and included field and modeling studies. Key project investigators are shown in Table 2-1. The general project schedule is summarized in Figure 2-2. MAWLTS field studies were carried out primarily from 1999-2002. Modeling and reporting were conducted following the field studies.

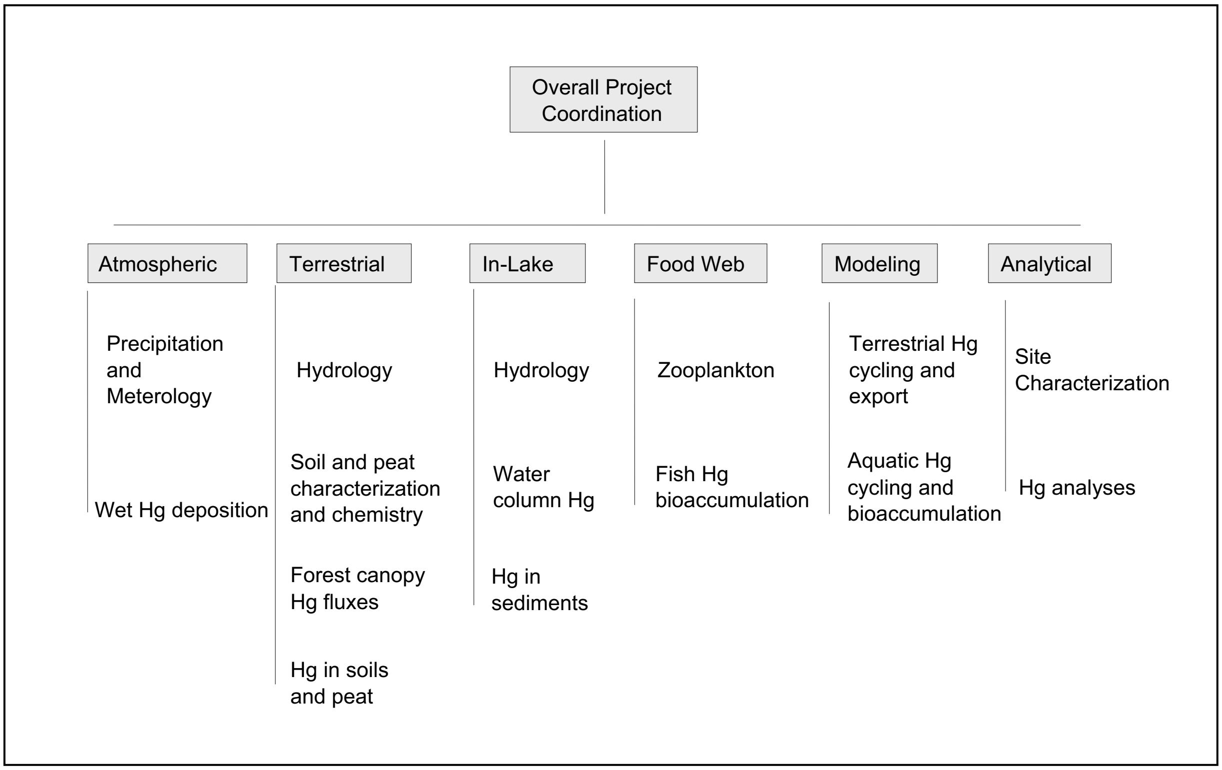


Figure 2-1. MAWLTS Project Organization

Study Component	1999	2000	2001	2002	2003	2004	2005	2007	2007
Hydrology	▬	▬	▬	▬	▬				
Mercury in Sunday Lake watershed wetlands	▬	▬	▬	▬	▬				
Mercury in Sunday Lake watershed uplands	▬	▬	▬	▬	▬				
Water column and sediment mercury in streams and Sunday Lake	▬	▬	▬	▬	▬				
Food web MeHg	▬	▬	▬	▬	▬				
Historical Hg deposition analysis	▬	▬	▬	▬	▬				
Modeling	▬	▬	▬	▬	▬	▬	▬	▬	▬
Reports and Publications			▬	▬	▬	▬	▬	▬	▬

Figure 2-2. Project Schedule

Table 2-1.
MAWLTS Investigators

Investigator	Organization	Study component
Charles T. Driscoll	Syracuse University	Watershed Hg cycling and bioaccumulation
Robert M. Newton	Smith College, MA	Terrestrial hydrology and Surficial geology
Joseph Yavitt	Cornell University	Wetland Hg cycling and MeHg production
Ron Munson	Tetra Tech	Mass balance modeling
Ann Pufall	Smith College, MA	Terrestrial hydrology and Hg cycling
Jason Demers	Cornell University	Wetland Hg cycling and MeHg production
Melissa Kalicin	Syracuse University	Hg cycling in upland forests
Erin McLaughlin	Syracuse University	Hg in terrestrial vegetation
James Sutherland	New York State Dept. of Environmental Conservation	Hg bioaccumulation
Peter Lorey	Syracuse University	Hg sedimentation and historical Hg deposition
Daniel Engstrom	Science Museum of Minnesota	Hg sedimentation and historical Hg deposition

3 Mercury Cycling in Watersheds

3.1 Mercury in Watersheds and Wetlands

Terrestrial mercury export is an important source of mercury to rivers and many lakes. When runoff mercury export is compared to rates of wet Hg deposition, less mercury is currently being exported than deposited to terrestrial systems (e.g. ranging from 10-50%, Balogh, et al. 2005, Munthe and Hultberg, 2004). This is even more evident if dry deposition rates, which may be comparable to or exceed wet deposition (Driscoll, et al. 1994c; Munthe, et al., 1995a, b; Lindberg, 1996; Rea, et al., 2001; St. Louis, et al. 2001), are included as part of atmospheric deposition. These ratios suggest that once watershed/lake ratios exceed roughly 10:1, and often at lower values, terrestrial loads currently exceed wet deposition rates to drainage lake surfaces. It should be noted that the origin of terrestrial mercury export in remote areas is still largely atmospheric deposition unless there are localized geologic sources, mining, or industrial point sources (Fitzgerald, et al. 1998).

It is conceptually incorrect however to think of export/deposition ratios as reflecting what portion of Hg deposition in a given year is actually exported. Evidence from the METAALICUS study (Krabbenhoft, et al. 2006, Hintelmann, et al, 2002) has shown that atmospheric Hg deposition to terrestrial systems is mixed into very large pools of Hg in soils and peat that accumulate over long periods. While terrestrial Hg loads to lakes can be large, most of the mercury exported in runoff is not derived from the current year's deposition. The average terrestrial delay time for the delivery of atmospheric Hg deposition to streams and lakes is not known, but could involve decades or centuries.

The retention and export of mercury in terrestrial systems is strongly linked to hydrology and organic carbon. These factors are in turn influenced by watershed features including the type of terrain (e.g. wetland or upland), the size and topography of watersheds, the ratio of watershed to surface water area, land cover, and land use (Munthe, et al. 2007, Balogh, et al., 2005; Hurley, et al., 1995; Farella, et al 2001, Shanley, et al., 2005; Warner, et al., 2005, Porvari, et al, 2003; Munthe and Hultberg, 2004). Higher levels of dissolved organic carbon or color in runoff are associated with higher levels of Hg export (Grigal 2002, Driscoll, et al. 1995; Johansson and Iverfeldt, 1994; Joslin 1994; Lee et al. 1998; Kolka, et al. 1999a,b; Mierle and Ingram 1991, Lee and Iverfeldt 1991). Grigal (2002) reported an increase of roughly 0.2 ng Hg/L per mg/L DOC for various lakes in the US northeast and midwest, as shown in Figure 3-1 with differences in intercepts probably related to whether or not particulate Hg is included.

In contrast to the overall tendency of watersheds to be traps for inorganic mercury, wetlands are net producers of methylmercury, and can be important sources of carbon and MeHg to aquatic systems (Grigal 2002, Bishop, et al., 1995a; Grigal, et al., 2000; Lee, et al., 1998; Rasmussen, et al., 1998, St Louis, et al., 1996). Statistical relationships that have been identified between wetland-derived constituents, like dissolved organic carbon (DOC), and Hg. (Driscoll, et al. 1995) found that in Adirondack lakes, both HgT and MeHg increased with increasing (DOC) and percent shoreline wetlands (Figure 3-2). Watershed factors such as land-use, the distribution of wetlands, and the flow path of water through the watershed are important in determining how much MeHg will be released and available for fish uptake (Babiarz, et al. 1998; Driscoll, et al. 1994c).

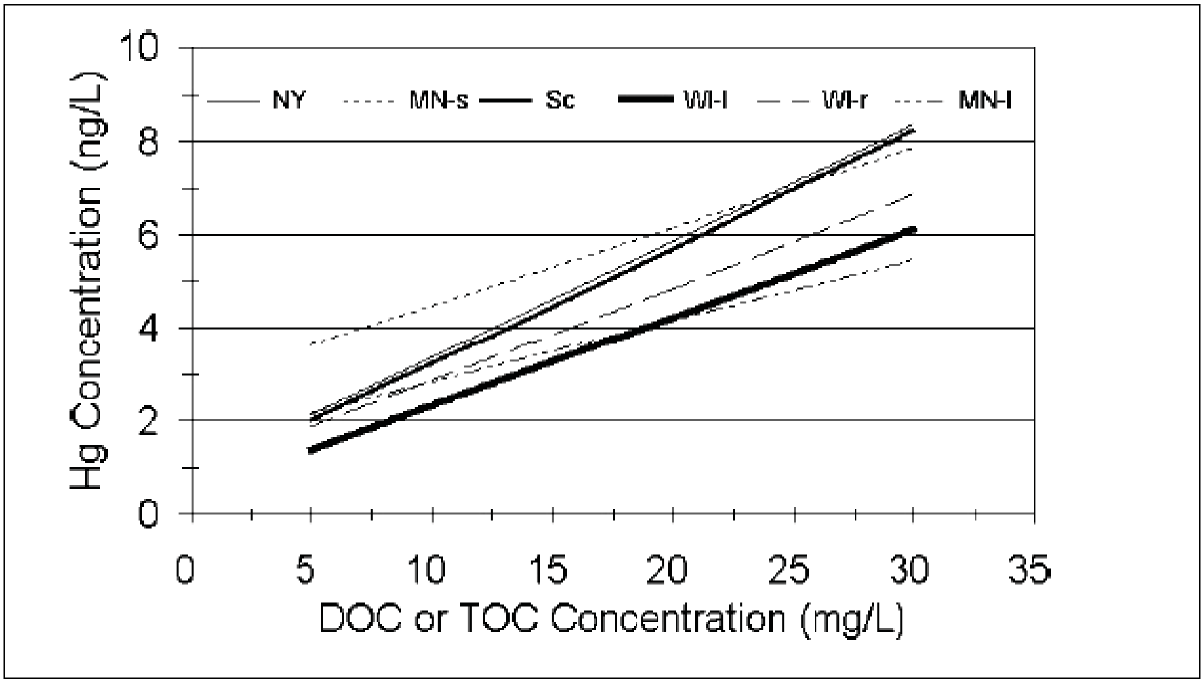


Figure 3-1. Reported empirical relationships between total Hg concentration and dissolved or total carbon concentration in solution. (Source: Grigal 2002)

NY = lakes in the Adirondack Mountains, New York, U.S.A. (Driscoll, et al. 1995); MN-s = first-order streams in northern Minnesota, U.S.A. (data from Fleck 1999); Sc = forest streamflow in Sweden (from Meili 1991); WI-l = lakes in northern Wisconsin, U.S.A. (Watras, et al. 1996); WI-r = rivers in Wisconsin, U.S.A. (Babiarz, et al. 1998); MN-l = lakes in northern Minnesota (Sorensen, et al. 1990).

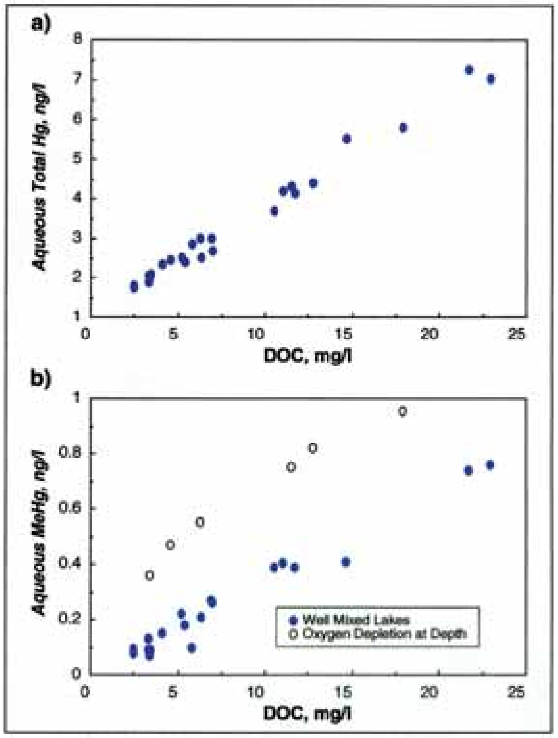


Figure 3-2. **Total mercury and methylmercury versus dissolved organic carbon in Adirondack Lakes, - In general, dissolved mercury concentrations are higher in waters with higher concentrations of DOC. Lakes that have oxygen depleted bottom waters have higher methylmercury concentrations, but within this group the relationship of higher methylmercury with higher DOC still holds (Driscoll, et al. 1995).**

3.2 Mercury Cycling in Lakes

Mercury enters lakes via atmospheric deposition and terrestrial runoff, principally as inorganic Hg(II). A complex cycle of transport and transformations results in a small portion of the inorganic mercury pool being converted to methylmercury and bioaccumulating in fish (Figure 3-3). Site conditions such as pH, dissolved organic carbon, and trophic structure can strongly influence the efficiency of individual ecosystems to translate a given mercury load into mercury burdens in fish. Once exported to a lake, inorganic mercury can accumulate or be removed by outflow, buried, reduced to elemental mercury and volatilized, or converted to methylmercury. Site conditions can shift the relative balance of these removal pathways, sometimes favoring methylation. Particular attention has been given by the research community to determine which conditions favor the activity of methylating microbes, e.g. sulfate reducing bacteria, and which dissolved inorganic Hg(II) species are available for methylation. Figure 3-4 shows how water quality factors can influence the inorganic Hg(II) species likely to be present in the water column of a lake or in sediment porewater.

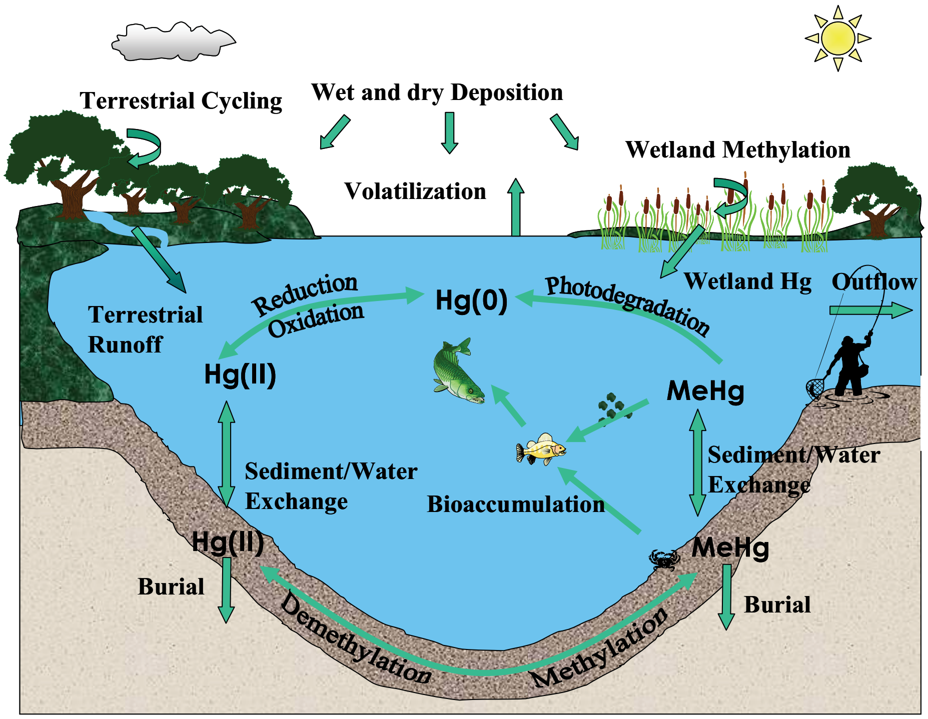


Figure 3-3. Mercury cycling in lakes as represented in D-MCM

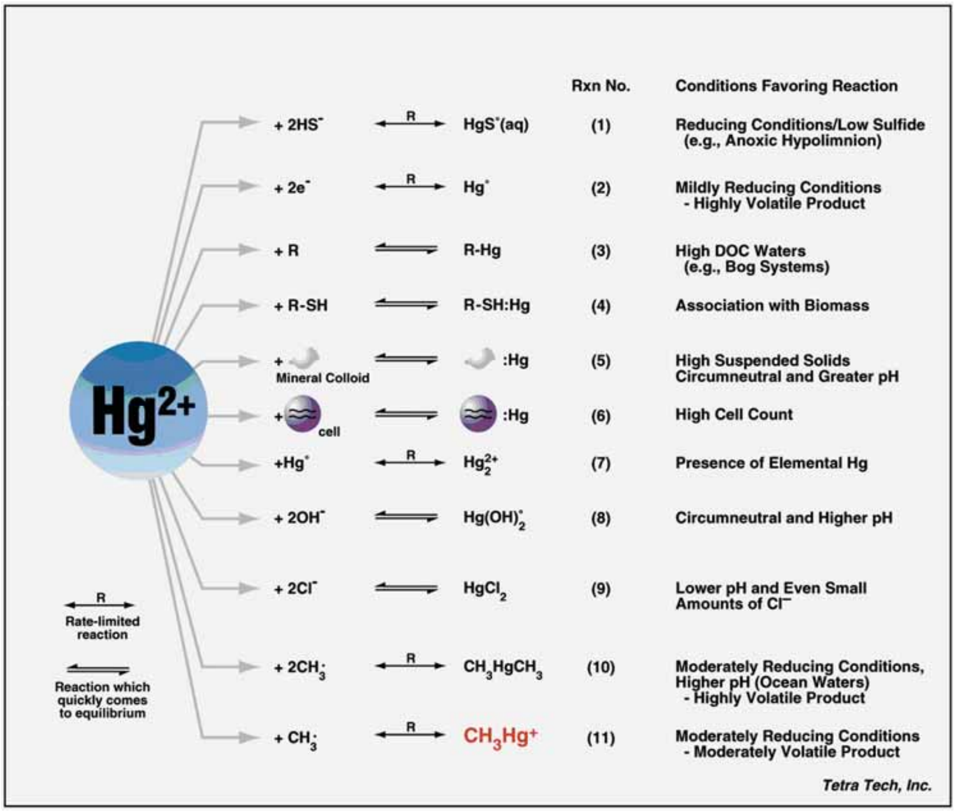


Figure 3-4. Examples of competitive reactions (parallel reactions with Hg(II)). Data for characterizing the above reactions in natural systems are of variable quality. Reactions 1-8 all compete with reactions 10 and 11 that form methylmercury.

H, dissolved organic carbon (DOC) and sulfides, for example, have been widely documented to affect the mercury cycle, although in complex ways still being investigated:

- **pH** has been widely linked to mercury cycling and bioaccumulation (e.g Driscoll, et al. 2007, Wiener, et al., 2006, Kamman, et al. 2004, Spry and Wiener 1991, Winfrey and Rudd 1990, Grieb, et al. 1990). For example, pH has been studied in connection with the availability of inorganic Hg(II) for methylation directly (e.g. Kelly, et al. 2003, Xun,et al. 1987) and indirectly via increased Hg(II) photoreduction at higher pH (e.g. Zhang 2006), which could lead to greater evasion losses and less remaining Hg(II) in the lake system for methylation (Watras, et al. 1994).

- **DOC** has also been widely linked to mercury cycling and bioaccumulation. DOC is a strong complexing agent for inorganic Hg(II) and methylmercury (e.g. Ravichandran et al. 2004, Haitzer, et al., 2003, Hintelmann, et al. 1995, Hudson et al. 1994). As a result, higher DOC concentrations tend towards higher concentrations of total and methylmercury in the surface waters of aquatic systems (in addition to the effects of co-transport of Hg with DOC from terrestrial runoff). DOC has also been implicated as a factor both enhancing (Golding et al. 2002) and inhibiting (Kelly, et al. 2003, Barkay, et al. 1997, Miskimmin, et al. 1992) inorganic Hg(II) bioavailability for methylation. Different types of DOC (e.g. large versus small) molecular weight may partially explain the contrary trends, although the mechanistic understanding of these effects is still inadequate. Recently, (Miller, et al. 2007) investigated interactions between mercury, DOC and sulfides, identifying a potential DOM-Hg-sulfide complex, or hydrophobic partitioning of neutral Hg-sulfide complexes into higher molecular weight DOM. Increased DOC levels have also been noted to decrease the bioavailability and partitioning of methylmercury into the base of the food web (Watras, et al. 1998, Driscoll, et al. 1995). As a result, it does not always follow that increased DOC and methylmercury in surface waters correspond to increased methylmercury in fish.

- **Sulfur Cycling**: The balance between sulfate and sulfide is a key control on MeHg production in many ecosystems (Munthe, et al. 2007). Sulfate stimulates Hg-methylating sulfate reducing bacteria. This has been shown in studies ranging from pure cultures (King, et al. 2000; Benoit, et al. 1999a, b) to sediment and soil amendments (Compeau and Bartha, 1985; Gilmour, et al. 1992; Harmon, et al. 2004; King, et al. 2001; Benoit, et al. 2003), and field amendments to lakes and wetlands (Watras, et al. 1994; Branfireun, et al. 1999; Benoit, et al. 2003). Sulfides, the product of sulfate reduction, have been found to enhance (neutral complexes) or inhibit (charged complexes) uptake of inorganic Hg(II) by methylating microbes. It has been hypothesized that higher concentrations of total sulfide favor charged complexes, resulting in less bioavailable Hg(II) for methylation (e.g. Benoit, et al. 1999a,b, Marvin-DiPasquale and Agee, 2003). Among these studies, the optimal concentration for methylation ranges from 10 to about 300 µM sulfate, while the optimal sulfide concentration is quite low, about 10 µM (Munthe, et al 2007). Part of the complexity is that there are multiple types of sulfate-reducing bacteria, which can also use other compounds as energy sources.

3.3 Mercury in Fish

Most of the mercury in water, sediments, and the base of the food web is inorganic Hg(II). While methylmercury represents small fractions of total mercury in these compartments, it biomagnifies, i.e. concentrations increase in organisms that feed at higher levels of the food chain, while inorganic Hg(II) does not. As a result, methylmercury represents an increasing portion of total Hg in biota as one progresses up the food web, and is the dominant form in fish (greater than 95 percent in fish muscle, (Bloom 1992 and Grieb, et al, 1990). Biomagnification in fish occurs largely because food is the dominant pathway for MeHg uptake in fish (Hall, et al., 1997; Harris and Bodaly, 1998), and methylmercury is more efficiently retained than the food, which is used for growth (Harris, et al. 1996). As a result, mercury concentrations in fish generally increase with weight, length, and age.

Relationships between fish mercury concentrations and surface water mercury are not straightforward. Studies in seepage lakes and low-organic western drainage lakes have shown linear relationships between fish mercury concentrations and aqueous methylmercury concentrations (Watras, et al., 1994; Gill and Bruland, 1990). In contrast, when high-DOC drainage lakes were included in studies in Sweden and in the Adirondacks, a relationship between fish mercury and aqueous methylmercury concentrations was not observed (Lee and Iverfeldt, 1991; Driscoll, et al. 1994c). Since drainage lakes make up a large proportion of the lakes in the Northeast (e.g., 85 percent in the Adirondacks - Kretser, et al. 1989), this complicates the use of simple relationships. Data from the Adirondacks and the results of modeling analyses suggest that an increase in DOC concentration above some level greater than 8mg/l results in a decrease in fish Hg (Driscoll, et al. 1994c; Hudson, et al. 1994; Watras, et al. 1995b). pH has also been examined as a correlate with fish mercury concentrations. Several studies have shown that low pH is associated with high fish tissue mercury, but even this observation is tenuous when high-DOC lakes are included.

Bioconcentration factors (BCFs) provide another perspective on fish methylmercury accumulation. The bioconcentration factor for MeHg is defined as the ratio of the MeHg concentration in fish tissue to the methylmercury concentration in water. For Adirondack Yellow Perch, the bioconcentration factor ranged from about 500,000 to 10,000,000. The bioconcentration factor decreased significantly with increasing concentrations of DOC, but showed no significant effects due to pH. As indicated earlier, wetlands play a significant role in determining DOC concentrations in lakes, and given the effects of DOC on bioconcentration factors, wetlands may also influence mercury bioaccumulation (Driscoll, et al. 1994).

Aluminum concentrations may also be a factor controlling fish mercury concentrations. While it appears that concentrations of both metals in the water column may be linked by similar transport mechanisms, the competition between aluminum and mercury for organic binding sites may result in greater bioavailability of mercury in lakes with a high Al/DOC ratio. This process is particularly relevant for areas such as the Adirondacks where some lakes (typically acidic drainage lakes) exhibit elevated concentrations of aluminum (Driscoll, et al. 1994c).

4 Sunday Lake Watershed

The Sunday Lake watershed, located in the western Adirondacks of New York State, has 1,314 hectares draining to the lake outlet and is a third order catchment lying within the larger, Oswegatchie-Black watershed. The watershed area above the outlet gauging station downstream of the lake includes additional land and has an area of 1,340 hectares, as shown in Table 4-1. The Sunday Lake watershed was chosen for this study because it is representative of drainage lakes in the Adirondacks and has both wetland and upland influences on mercury cycling and accumulation in fish.

The watershed has 202 m of relief, with elevations ranging from 488 m at the outlet gage station to 690 m at Stillwater Mountain on the eastern edge of the watershed. There are nine small lakes and ponds within the watershed with a total surface area of 23.2 ha. Sunday Lake (7.8 hectares) is located at the outlet of the catchment and is second in size to Fifth Creek Pond (10.6 ha) located near the southern watershed divide.

Sunday Lake watershed is largely forested with 75 percent deciduous forest and 15 percent coniferous forest cover bounding streams and wetlands, part of which are also forested. The major tree species include American beech, red spruce, and balsam fir. The watershed is covered by a variety of surficial materials deposited during the last glaciation that ended approximately 14,000 years ago (Muller and Calkin, 1993). The lower part of the watershed (21 percent) lies within an area of stratified drift characterized by a complex esker system composed of well-sorted sands and gravels that are generally over 5m in thickness. A thin (<3 m), discontinuous veneer of till covers (62 percent) the Precambrian age granite gneiss over the upper part of the watershed. Between lies an area of thicker till (17 percent) that completely masks the underlying bedrock. Soils are well-drained Apodosols (Typic Haplorthods) in the uplands consisting of sandy loam to loamy sands.

The watershed also contains 20 percent wetlands, (274 ha), which is a relatively large percentage of wetlands for Adirondack Mountain watersheds. The total wetland area is comprised of 1.6 percent emergent, 58.7 percent forested, and 39.7 percent scrub-shrub wetlands (Roy, et al., 1996; R. Newton, personal communication). These wetlands have been mapped as part of the State Wetlands Protection Program (Primack, et al., 2000). Wetland types were classified using the Cowardin system in accordance with the National Wetland Inventory (Cowardin, et al., 1979). Most of the wetlands are located adjacent to the lakes and streams, and 66 percent of the lengths of stream channels are bordered by wetlands.

The geology of the watershed is typical of the glaciated Canadian Shield. The middle Proterozoic metamorphic bedrock is mainly a biotite, hornblende, granite gneiss except at the western edge of the watershed where charnockite and granitic and quartz syenite gneiss outcrops. Overlying the bedrock are a variety of sediments deposited in association with the last glaciation, approximately 14,000 years ago (Muller and Calkin, 1993). The upper areas of the watershed are covered by a discontinuous deposit of glacial till which is typically less than 3 m thick and is composed of an unsorted, unstratified, mixture of sand silt and clay-sized material with abundant cobbles and boulders. The matrix is mostly sand sized material with lesser amounts of silt and clay. The till is overlain, in some areas, by a thin (<20cm) layer of aeolian silt. There are some areas at lower elevations where the till is relatively thick (>3m) and masks the underlying bedrock topography. The lower part of the watershed lies within a zone of meltwater deposits that extend from the Stillwater Reservoir eastward toward the Black River valley. Stratified drift in this part of the watershed includes numerous eskers that are generally orientated northeast-southwest. The stratified drift is composed of sorted, stratified, sands and gravels that are generally greater than 5 m thick. Like the till areas, a thin layer of aeolian silt covers some of these deposits.

The distribution of surficial deposits (62 percent thin till, 17 percent thick till, 21 percent Stratified drift) make this a thick till/stratified drift dominated watershed in the Adirondack Lakes Survey Corporation (ALSC) lake classification system (Newton and Driscoll1990). It would, therefore, be expected that the acid neutralizing capacity (ANC) of the surface waters would be relatively high as the areas of thick till and stratified drift provide high ANC baseflow from their extensive groundwater reservoir systems. The actual ANC was lower than expected. This is likely due to a combination of factors including the position of the deposits at the lower end of the watershed and the abundance of riparian wetlands that help isolate the streams from the groundwater system.

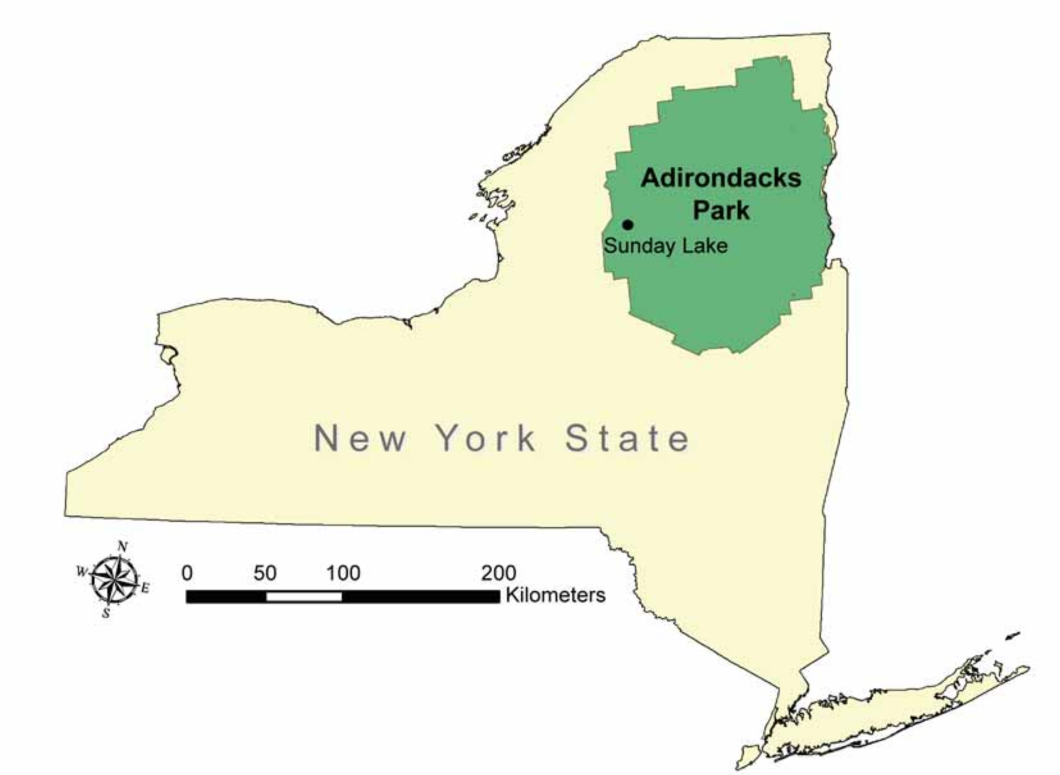


Figure 4-1. The Sunday Lake Watershed is located in the western part of the Adirondack Park in New York State.

Table 4-1.
Watershed Characteristics

Watershed Areas	hectares	Percent
Watershed (outlet gage station)	1,340	100
Watershed (Sunday Lake outlet)	1,314	98
Stratified Drift	226	17
Thick Till	202	15
Thin Till	611	46
Wetlands	274	20
Lakes	23	2
Streams	4	<1
Stream Lengths	**km**	
Total stream length	16.8	
Length of stream bordered by wetlands (km)	11.1	
Relief (m)	190	

Annual precipitation from 1999 through 2001 averaged 127.1cm while total streamflow averaged only 77.4cm. The difference is due to evapotranspiration losses that total 39 percent of precipitation. Much of the winter precipitation falls as snow and is released during a spring snowmelt event that can account for as much as 28 percent of the total streamflow. The source areas of precipitation-generated stormflow change seasonally with wetland areas being more important than uplands during the summer. Although only 20 percent of the watershed is covered by wetlands, their location next to stream channels causes about 70 percent of the water moving to streams to pass through them. We estimate that almost half of this is water moving as shallow groundwater flow through riparian wetlands.

Sunday Lake (7.8 hectares) is located at the downstream end of the catchment. The lake is fed by two main tributaries, Inlets 1 and 2, and is drained by one outlet stream (Figure 4-2). The mean lake depth is 2.5 m, while the maximum depth is 5.5 m. The lake stratifies and mixes twice per year (dimictic) and is moderately productive biologically (mesotrophic, average mid-summer chlorophyll-α concentration = 6.7 μg/L). Relatively high DOC concentrations (average mid-summer DOC = 9.8mg C/L) in Sunday lake can be attributed to the large quantity of wetlands.

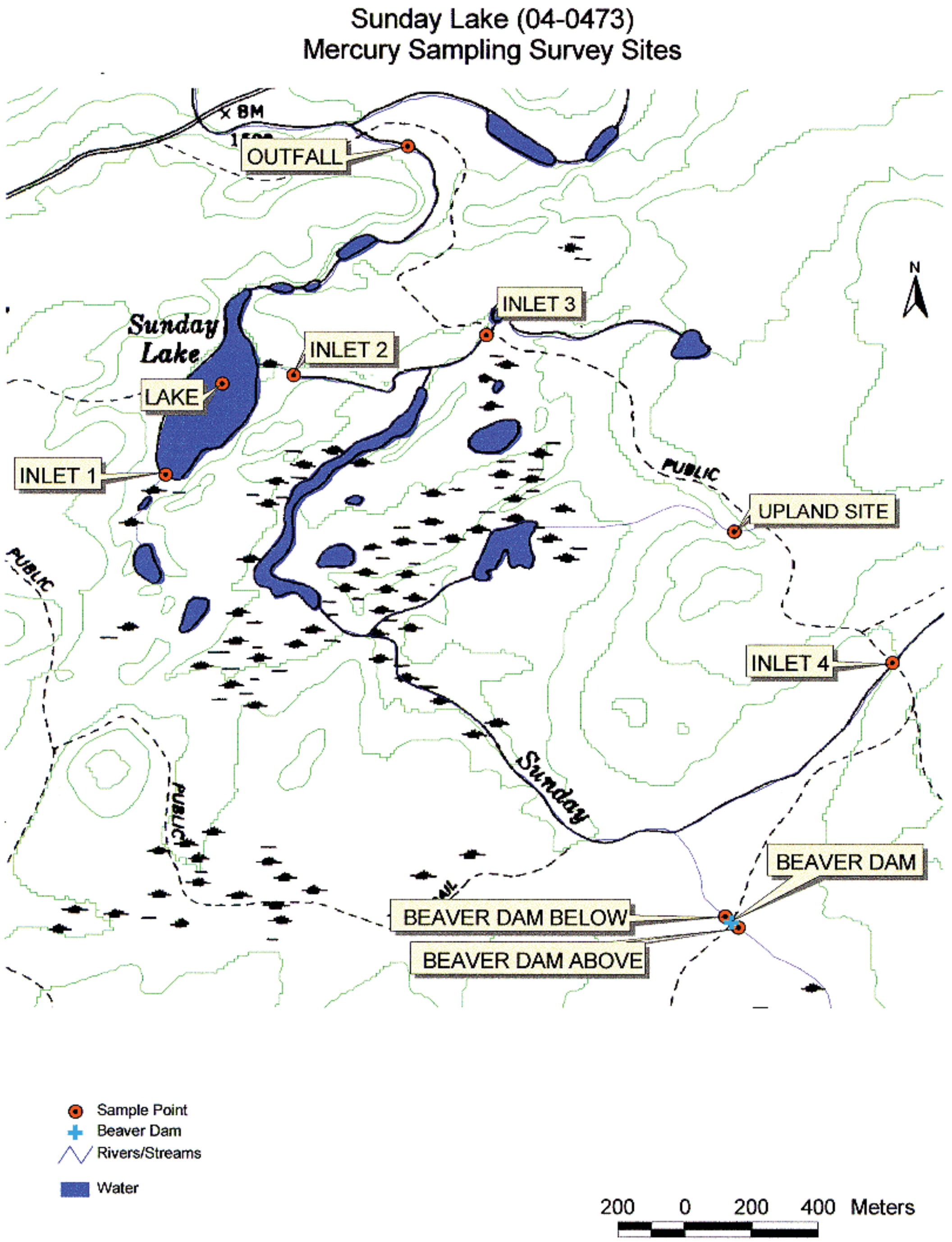


Figure 4-2. **Sunday Lake surface water sampling locations**

Samples were collected at nine stations on the tributaries to the lake and the lake outlet, and analyzed for water chemistry and total methylmercury on a monthly basis. In addition, porewater samples were collected from Teflon lysimeters in upland areas and piezometers in riparian wetlands monthly. Other sampling efforts involved collection and analysis of throughfall, litter, and soils under both coniferous and deciduous canopy and lake sediment cores. Finally, a mercury wet deposition sampler was installed in a nearby watershed at Huntington Forest, as part of the MDN network. All surface and porewater samples were analyzed for total Hg, methylmercury, major anions and cations, pH, ANC, DOC, DIC, and aluminum.

Mean concentrations from 1999-2002 in the inlet, lake surface, and outlet samples are provided in Table 4-2. Inlet 2 is the major flow to the lake, and had slightly higher mean total mercury than the lake outlet. The mean methylmercury concentration was similar between the lake surface and Inlet 2. Inlet 1 discharges into the lake at the upstream end, whereas Inlet 2 is located near the middle of the lake on the eastern side, as seen in Figure 4-2. Total and methylmercury were lower in this inlet than Inlet 2. The other inlets are upstream sampling locations on the stream of Inlet 2.

Surface water total and methylmercury concentrations are shown in Figures 4-3 and 4-4, respectively. Total mercury plots show the string seasonal variation in both inlet and lake samples with low total mercury in the winter and higher concentrations in the summer. The total mercury concentrations in all the inlets were higher in the summer of 2001 than in 2000, although Inlet 1 had less seasonal variation, perhaps because it drains a smaller area than Inlet 2 (See Figure 8-1). The combined total and methylmercury concentrations in the lake at the surface and at a depth are shown in Figure 4-5, although both measurements were not available for all dates. The deeper lake samples had higher total Hg on some dates, but not all. The difference between the MeHg concentrations was small for most of the dates. The deeper samples did not have higher MeHg, which is common in deep lakes with anoxic hypolimnion.

The highest methylmercury concentrations were observed in the sample collected from below a beaver dam on one of the streams leading to Inlet 2 (Figure 4-6). Comparison of the two sets of samples shows that methylmercury can be higher downstream of a beaver pond due to in-situ methylation if reducing conditions are generated in the pond. The higher methylmercury occurred in July 2001 when the total mercury was high as well. The lowest methylmercury concentrations were observed in Inlet 1, which had concentrations less than 1 ng/L instead of occasional values above 2 ng/L in the summer. The upland inlet had less increase in the summer than the other inlets.

The plots of total mercury and methylmercury concentrations in the two lake samples show that the levels of methylmercury were similar at the surface and at depth, although this is a shallow lake. There was one high value for methylmercury in August 2001 in the deep lake sample, which may indicate the effect of having an oxic-anoxic interface in the summer.

Table 4-2.
Mean Concentrations of Total and Methylmercury Mercury, DOC, and pH in Surface Water Samples from Sunday Lake Watershed, 1999-2002

Site	pH	DOC (ppmC)	HgT (ng/L)	MeHg (ng/L)
Lake Surface	5.39	7.04	3.59	0.53
Inlet 1	5.27	4.29	2.49	0.26
Inlet 2	5.41	7.41	3.87	0.52
Inlet 3	5.59	7.40	4.01	0.48
Inlet 4	5.61	7.22	4.14	0.47
Inlet Upland	4.68	9.51	4.51	0.40
Lake Outlet	5.45	6.58	3.51	0.49
ABD	4.91	6.26	4.30	0.58
BBD	4.91	6.34	4.73	0.95

ABD is above beaver dam, BBD is below beaver dam.

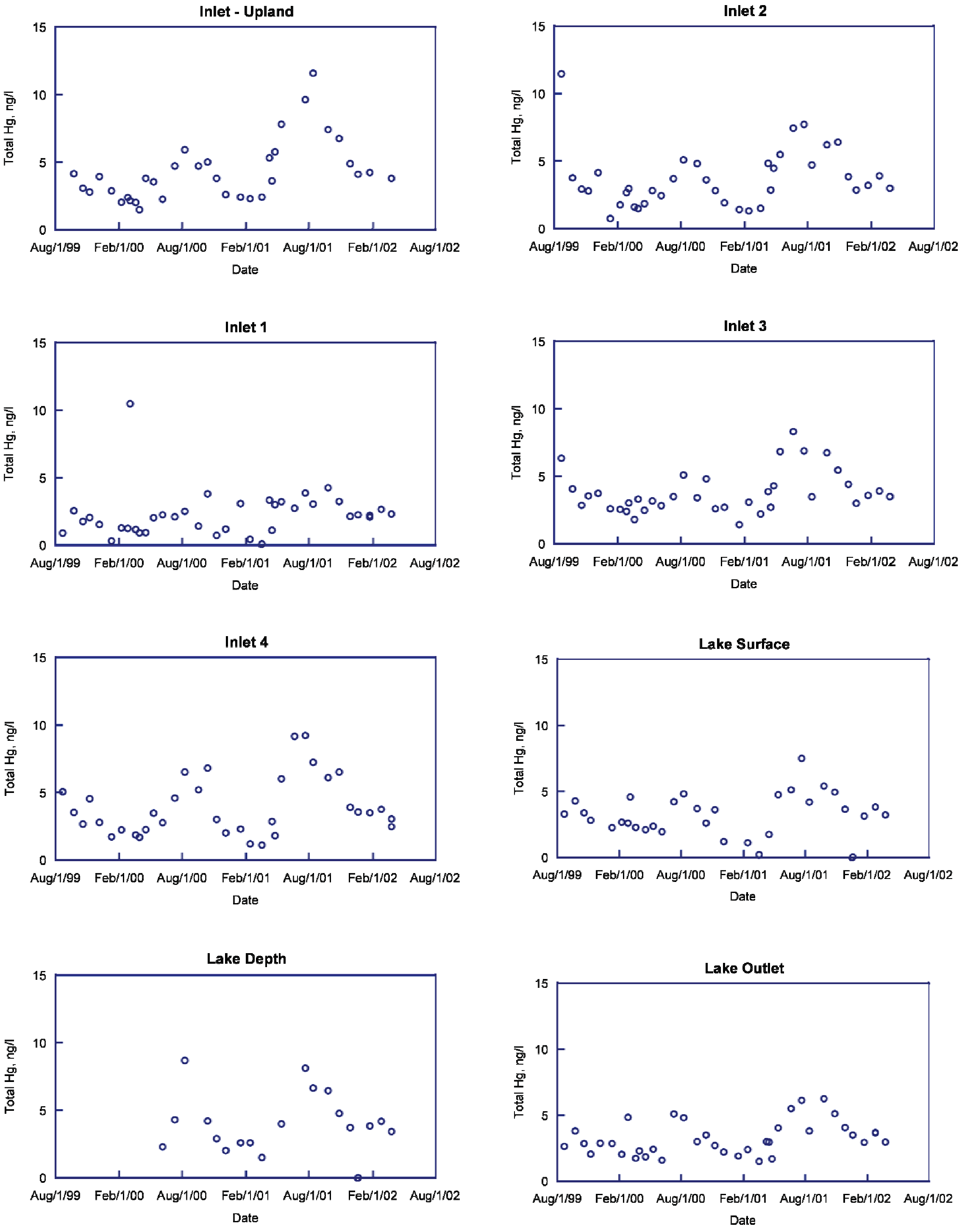


Figure 4-3. Total Hg concentrations at surface water sampling stations throughout the Sunday Lake Watershed

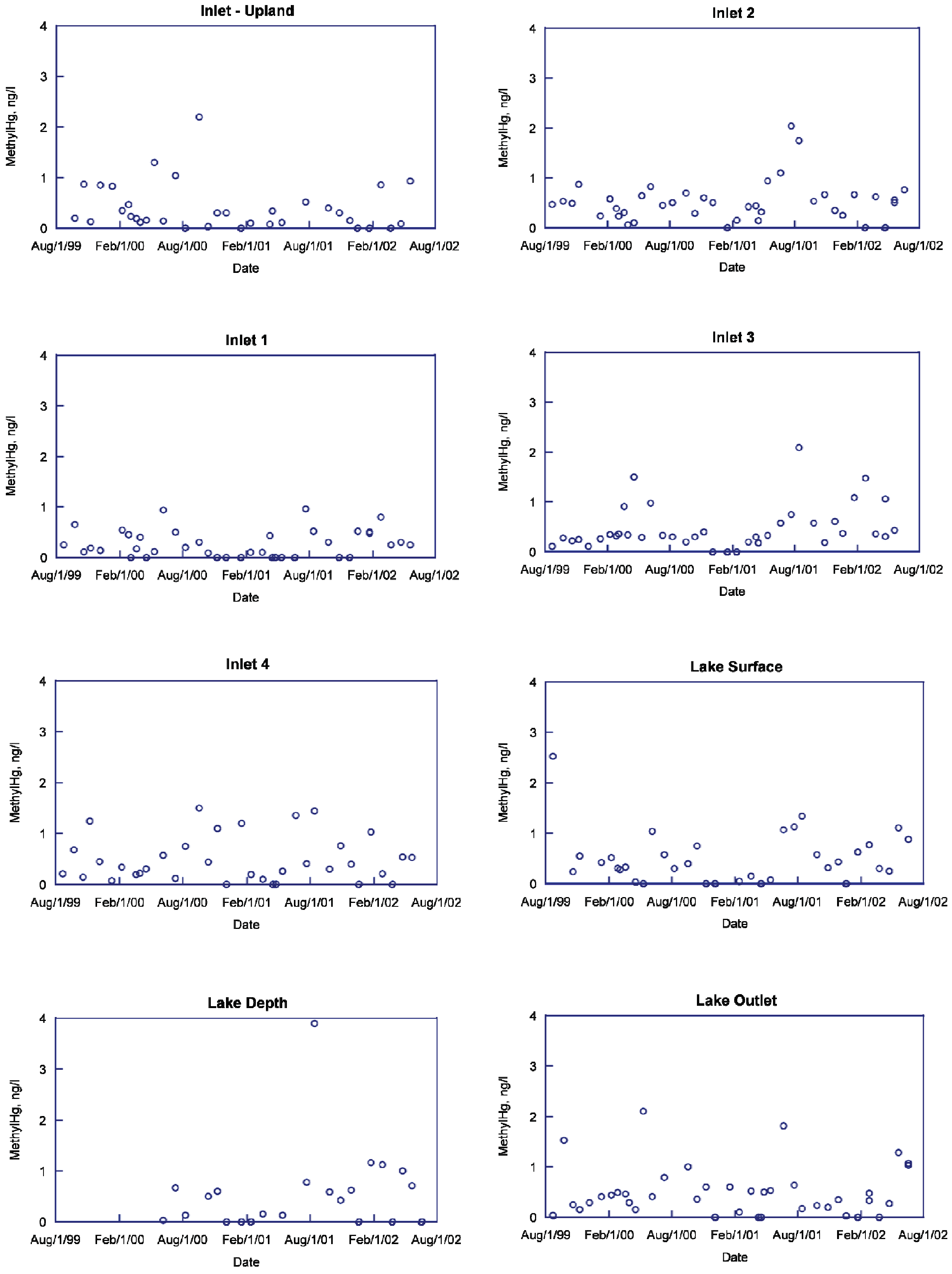
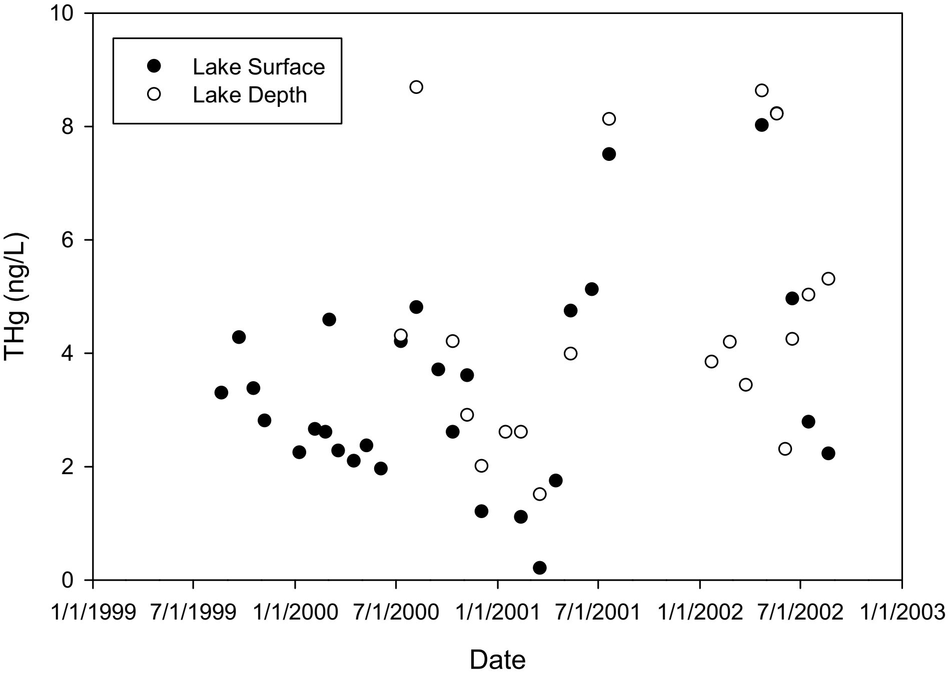


Figure 4-4. Methylmercury concentrations at surface water sampling stations throughout the Sunday Lake watershed



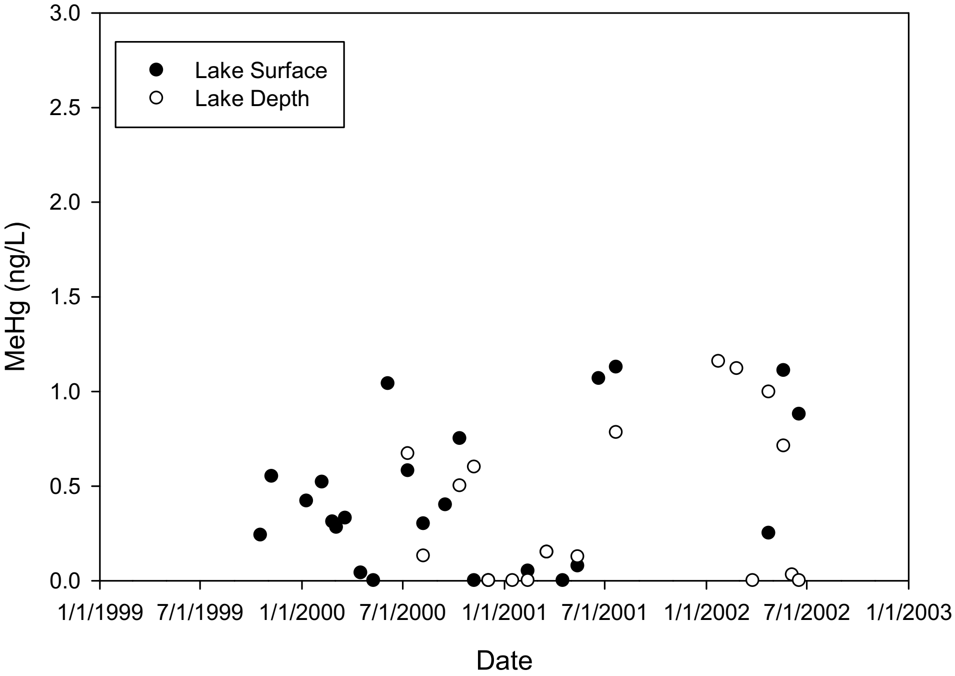


Figure 4-5. Total and methylmercury concentrations in the lake at the surface and at depth

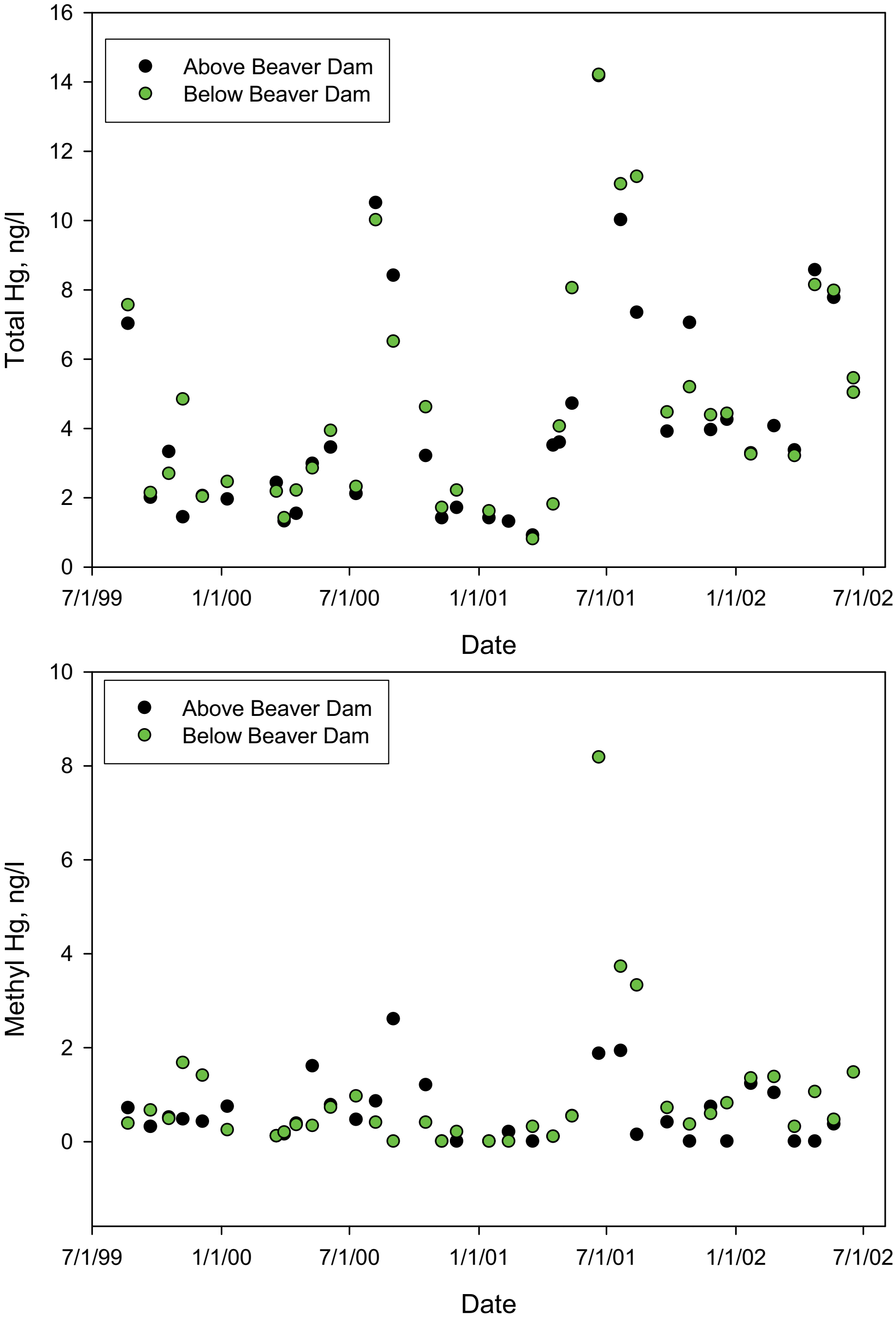


Figure 4-6. **Total and Methylmercury concentrations above and below Beaver Dam**

5 Hydrology of the Sunday Lake Watershed

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Hydrologic flow pathways are important in determining the fate of Hg in a watershed (Bishop and Lee, 1997). Allan, et al. (2001) in their study of Precambrian Shield headwater catchments, found that there was little retention of Hg by water moving as surface runoff over bedrock surfaces and consequently water moving along this pathway provided a net source of HgT to surface waters. This is in contrast to the retention that occurs as water infiltrates upland soils (Kalicin, et al., this volume; Driscoll, et al. 1998; Grigal 2002; Schwesig and Matzner 2001; St Louis, et al. 1996). Thus, in catchments where shallow interflow and surface runoff dominates, there is less retention and consequently more export of HgT from upland sources.

This chapter presents the results of hydrologic studies from January 1999 to December 2001 in the Sunday Lake watershed and a watershed-scale assessment of the influence of hydrology on mercury cycling and delivery to Sunday Lake. Characteristics of the watershed and lake were presented in Chapter 4.

5.1 Methods

5.1.1 Watershed Areas

A Geographic Information System (GIS) was used to analyze spatial data. Watershed and sub-watershed boundaries were determined from a georeferenced scanned raster image of a portion of the 1989 Number Four 7.5 x 15 minute USGS topographic map. Watershed areas calculated by the GIS system were found to be significantly different from those reported by the Adirondack Lake Survey Corporation (ALSC). The values determined in this study are close to those estimated from a hydrologic modeling analysis of a 10 m Digital Elevation Model (DEM) of the area and are therefore thought to be more accurate than those reported by the ALSC.

5.1.2 Hydrology

Three gaging stations, two on the stream and one in a wetland next to the lake used to measure lake stage, and 14 piezometers were installed in the watershed. Two stream gaging stations were established, one on the major inlet (#2), 200m upstream from Sunday Lake and the other on the outlet stream approximately 700m downstream of the lake (Figure 5-1). The downstream gaging station defines a watershed that is approximately 25 hectares larger than that defined by the lake outlet. These stations were equipped with Campbell Scientific CR10X dataloggers with Druk 5psi transducers for measuring stream stage. Measurements at the gaging stations were made at one-second intervals with averages calculated every ten minutes. Discharge was determined from stage discharge relationships established for each station. Discharge was measured at various stages throughout the study period using a Swoffer model 3000 current meter equipped with a six-tenths rod. During discharge measurements, each stream cross section was subdivided in such a way as to limit the section discharge to less than 10 percent of the total flow.

Precipitation and temperature were also measured at the three gaging stations from January 1999 to December 2001. Thermistors recorded air and stream temperature, and the outlet gage was equipped with a tipping bucket rain gauge. Additional climate data were obtained from a station at the Stillwater Reservoir (COOP Station #308248) located approximately 5 km northeast of the watershed centroid.

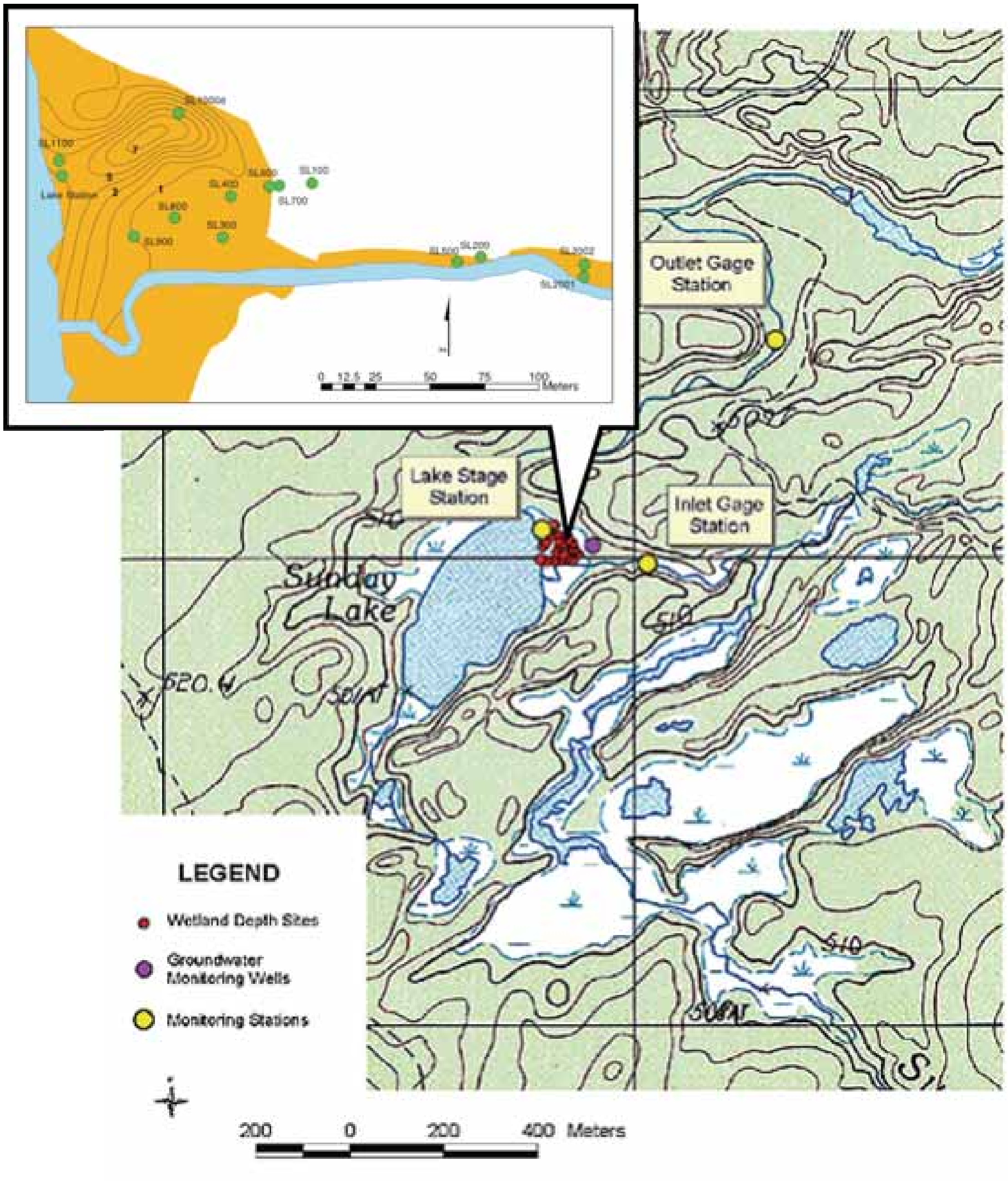

Figure 5-1. **Sunday Lake hydrologic monitoring stations**

A third gaging station, called lake stage in Figure 5-1, similarly equipped to the outlet station was established in a wetland adjacent to Sunday Lake. This gaging station monitored lake stage as well as water temperature near the lake surface and at a depth of approximately 3 m. Groundwater stage in a deep piezometer located in thick peat deposits near the lake was also monitored for a short period of time until a nearby lightning strike disabled the transducer.

Runoff deficits were calculated from the difference between measured precipitation and total streamflow. Total streamflow was determined by integrating the unit hydrograph at the watershed outlet over the period of interest. For event-based calculations, streamflow was integrated from the start of precipitation to 3 days after the precipitation ended to ensure enough time for all the runoff water to exit past the outlet stream gage. Estimates of the potential runoff from various landscape elements were calculated by multiplying precipitation totals by the total area of the landscape element. Areas were determined by the GIS software.

Estimates of groundwater flow through riparian wetlands were based on Darcy's Law calculations. Hydraulic conductivities were measured by slug tests, and hydraulic gradients were determined from monitoring water levels at piezometers located at the upslope edge of the wetland and at the stream (Newton, et al. Chapter 6). Flow was calculated using the 10-minute water level data collected by the data loggers and summed for the period of record. For the purposes of this calculation it was assumed that groundwater flow through the riparian zone was limited to the upper one meter of the saturated zone. Estimates of the whole catchment riparian groundwater contribution were based on the total length of stream bordered by wetlands as measured by the GIS software.

Precipitation from the outlet station and surface water samples from the three gaging stations were collected monthly, for isotope analysis, during the non-ice period, usually April through November of each year. Mountain Mass Spectrometry Inc. analyzed samples for the stable isotopes ^{18}O and deuterium and all results are reported in reference to Standard Mean Ocean Water (SMOW). In addition, a "snapshot sampling" of surface waters throughout the watershed was done on August 10, 2000.

5.1.3 Water Chemistry

Surface water samples for chemical analysis were collected monthly at the gage stations. Samples for major ion analysis were collected in acid washed plastic bottles and were analyzed by the methods described by Driscoll (Driscoll, et al. 1996). Dissolved oxygen was measured in the field using an YSI model 58 dissolved oxygen meter.

5.1.4 Mercury in Surface Waters

Samples for mercury analysis were collected in 500-mL Teflon bottles using clean procedures (US EPA, 1995b). They were acidified in the field using 0.4 percent by volume HCL, double bagged, and packed in ice for transport to the laboratory. Prior to analysis, samples in the lab were stored in a dark refrigerator at 4˚C. Total mercury was determined using cold vapor atomic fluorescence spectrophototmeter (CVAFS) in accordance with EPA Method 1631(US EPA, 1995b and 2002). Methylmercury was analyzed following the method described by Kalicin et al. (Chapter 8).

5.2 Results

5.2.1 Climate

The mean annual temperature at the meteorology station near Stillwater Reservoir during the period from 1987 to 2000 was 4.9˚C. Monthly mean temperatures over the same period ranged from 19.7˚C in July of 1995 to -17.3 ˚C in December of 1989 (Table 5-1). July is usually the warmest month while January or February is the coldest. Annual precipitation averaged 126cm during this same period. The maximum annual precipitation (144cm) occurred in 1998 while the minimum (101cm) occurred in 1988. Winter precipitation is mainly in the form of snow and snowfall totals varied from 270cm in 1998 to 681cm in 1997. The average annual snowfall for the period of record was 446cm. Snow pack depths were also measured daily and generally show that the ground was snow covered from the beginning of December through the end of March. The maximum measured snow depth of 120cm occurred on March 31 of 2001.

Table 5-1.
Mean Monthly Temperature and Precipitation at Stillwater, New York 1987-2000

Month	˚C	cm
January	-9.4	10.37
February	-9.0	6.94
March	-3.8	7.81
April	3.8	9.26
May	11.0	11.20
June	16.0	10.99
July	18.1	12.85
August	17.2	11.69
September	12.8	12.79
October	6.7	10.91
November	0.5	12.01
December	-6.6	9.13
Annual	5.1	125.95*

* Average total precipitation

5.2.2 Streamflow

During the monitoring period for this study from January 1999 to December 2001, mean daily streamflow ranged from less than 1mm per day to 19mm/day during the spring melt in April of 2001. High flows tended to occur in the fall and spring while the lowest flows generally occurred in late summer (Figure 5-2). The largest direct precipitation event occurred during the fall of 2001 when 116mm of rain fell in a 16-hour period resulting in a peak flow (10 minute average) of 21mm/day. In contrast, several combined snowmelt/precipitation events during the study resulted in peak flows in excess of 23mm/day. Generally, over 50 percent of total streamflow occurs during a 3-month period, starting with snowmelt that usually begins in late March, and runs through the end of April. Another 20-30 percent of total stream flow occurs from October to December. In some years a significant amount of total stream flow is directly associated with melting of the snow pack. For example, in 2001, 28 percent of the total annual streamflow occurred during an 18 day snowmelt event in April. During this period the mean daily temperature rose to 5˚C with a maximum temperature just over 25˚C.

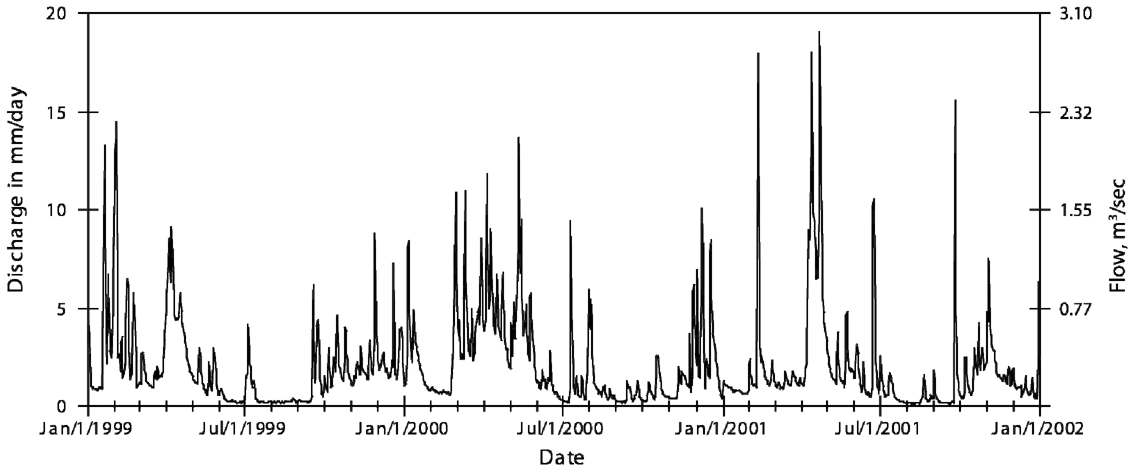

Figure 5-2. Mean daily stream flow at the outlet gage station from January of 1999 through December of 2001. (Total flow is based on watershed area of 1340 hectares. $1m^3/sec=6.448mm/day$)

Stream discharge at the outlet ranged from 0.02 m^3/sec to 3.7 m^3/sec. A flow duration curve constructed from mean daily discharge measurements at the outlet gage shows that discharge at the outlet exceeded 1 m^3/s 5 percent of the time (Figure 5-3). The flow duration curve was fairly straight for flows higher than the 85 percent exceedance value. Beyond this point the curve flattened in steps. Low flows were controlled by the sequential draining of various natural reservoirs. Upstream ponds and wetlands contributed to stream flow as long as water levels were above the elevation of the outflow control point. Once water levels dropped below this, these reservoirs ceased to contribute to stream flow. The lowest base flows were maintained by the groundwater reservoir.

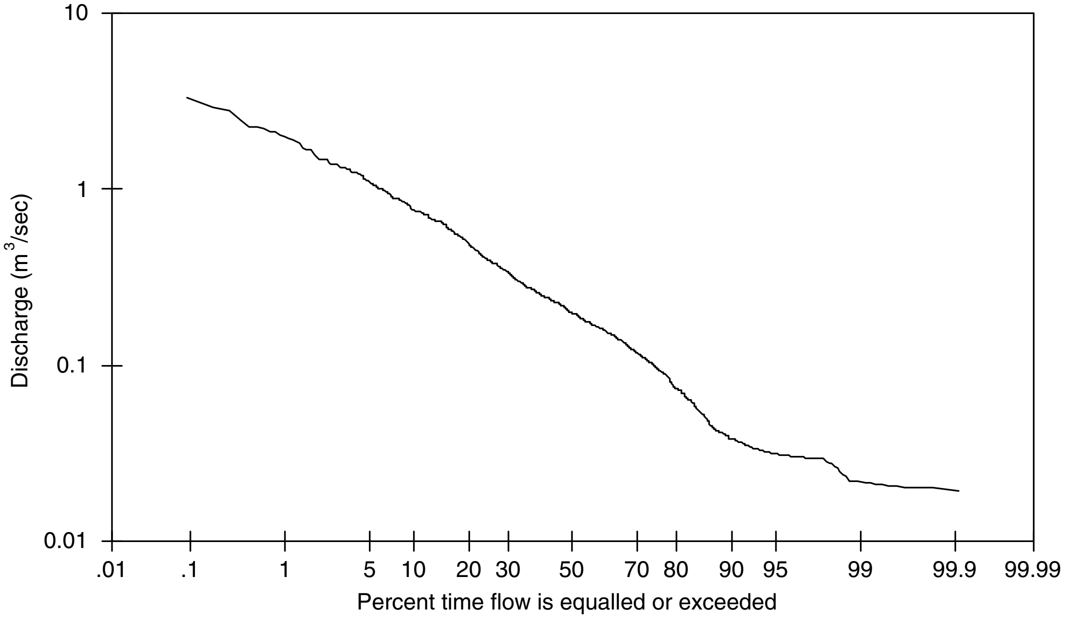

Figure 5-3. Flow duration curve constructed from mean daily discharge measurements taken at the outlet gage.($1 m^3/sec = 6.448 m/day$)

5.2.3 Sunday Lake Hydrology and Temperatures

Sunday Lake has a surface area of 7.8 ha, a mean depth of 2.5 m, and maximum depth of 5.5 m. A summary of the watershed and lake characteristics are presented in Chapter 4. Lake water is replaced rapidly, with a mean hydraulic residence time of approximately one week (0.02 year). The lake showed intermittent seasonal thermal stratification. During the winter, when the lake was frozen, the temperature of deeper water (3 m) generally ranged from 2˚ to 4˚ C except during mid winter melt events when the temperature dropped to near 0˚C. During the summer the deeper waters ranged from 10˚ to 14˚C. Summer deepwater temperatures were generally steady with a slight diurnal fluctuation except during major precipitation events when up to 4˚C warming occurred (Figure 5-4). Lake surface (0.5m) temperature varied from 0˚C during ice covered periods to 30˚C during summer warm spells. Summer diurnal temperature fluctuations were as much as 10˚C. During major summer precipitation events the thermal stratification broke down and the lake became isothermal for a brief period of time.

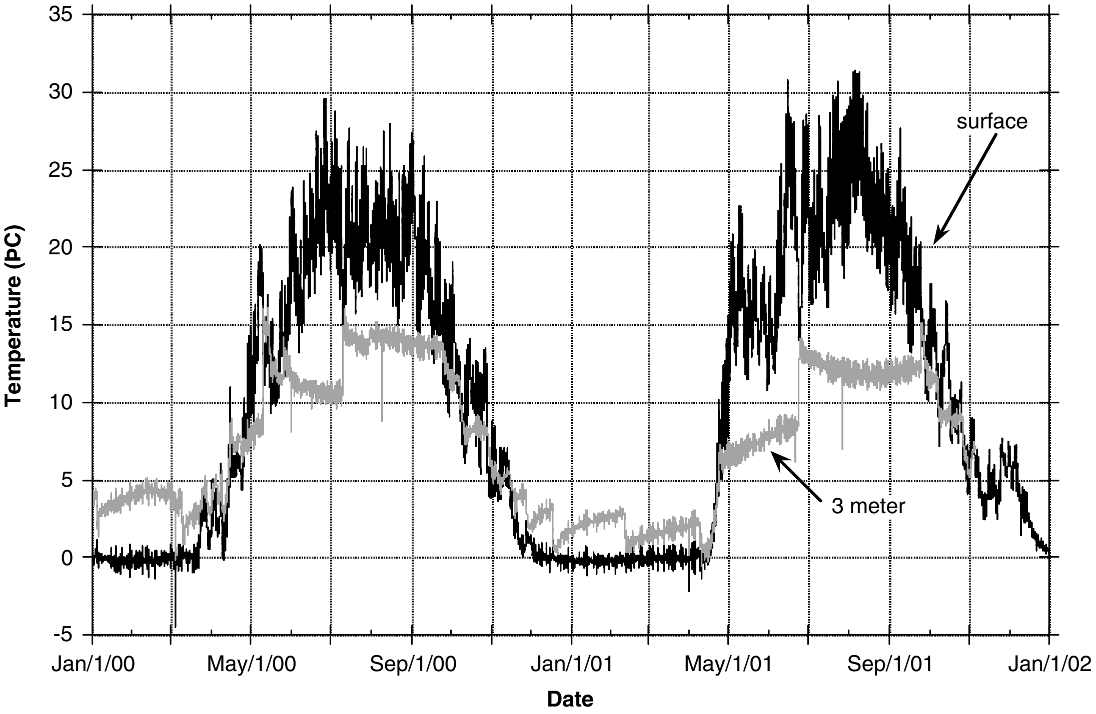

Figure 5-4. Temperature variations in Sunday Lake from thermocouples near the surface and at a depth of 3 m

The temperature data showed that ice out in 2000 occurred on approximately April 13 when the lake became isothermal and surface temperatures rose above 0˚C. Isothermal conditions persisted until May 25 when the deepwater temperature started to cool slightly while the surface water temperatures continued to rise. The deep-water temperature remained at approximately 11˚C until July 10 when a large rain event caused the lake to briefly become isothermal at approximately 15˚C. This event caused a sudden rapid rise in the deepwater temperature after which it stayed almost 4˚C higher than it was prior to the event (Figure 5-4). Sunday Lake became isothermal again in the fall on September 24 and essentially remained isothermal until about November 15 when the surface temperature cooled below 4˚C. After that time the surface temperature stayed cooler than the deeper temperature except for a couple of midwinter melt events on December 17 and February 10 when deepwater temperatures briefly dropped to near 0˚C. Ice out in 2001 appeared to occur on April 15, and isothermal conditions persisted until April 26 when surface temperatures rose above the deep-water temperature. There was an isothermal event on June 24 during the summer of 2001, similar to the July 2000 event, when an influx of warm runoff water to the lake caused an approximately 5˚C rise in the temperature of the deepwater (Figure 5-4). Isothermal conditions returned in the fall on approximately September 30.

Variations in lake stage are both seasonal and event driven. The seasonal variation shows a gradual rise usually beginning in early November and reaching a peak at the time of the spring melt in mid April. Minimum stage usually occurs sometime in late summer. The seasonal variation in stage is approximately 15cm and is seen as a gradual oscillation in the base of the hydrograph (Figure 5-5). A series of rapid stage changes are superimposed on this gentle oscillation. These are associated with hydrologic events that cause as much as a 45cm rise in lake stage in as little as 12 hours. Rates of water rise can exceed 7.5cm/hr for brief periods of time. Recovery from these events is also rapid with water levels typically returning to pre-event levels within 2-3 days. Some of the rise in water level shown on the hydrograph during the spring of 2000 was due to ice deflection of the staff gage that held the pressure transducer.

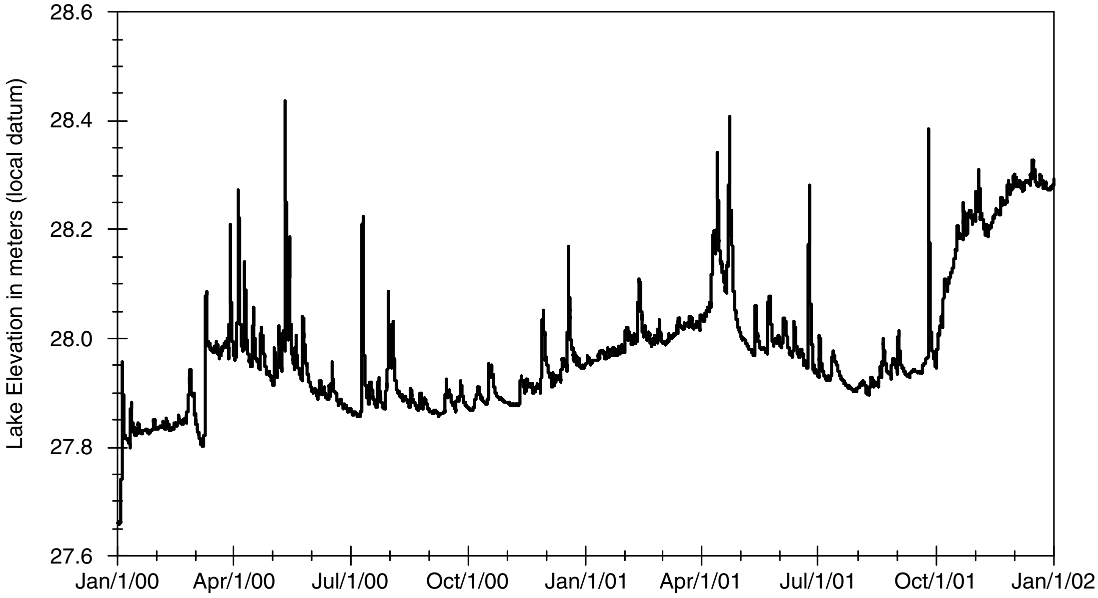

Figure 5-5. **Hydrograph showing changes in stage at Sunday Lake from January 2000 through December 2001**

5.2.4 Flow Paths using Stable Isotopes

Measurements of deuterium and $\delta^{18}O$ were used to estimate the relative importance of different flow paths as well as to determine the residence time of waters in different parts of the system. Precipitation samples were used to generate a watershed water line (Deuterium on the y axis and $\delta^{18}O$ on the x axis) that was found to have a slope of 7.1 ($r^2 = 0.99$). This is close to the 7.3 to 7.9 slopes reported for the streams at nearby Woods Lake (Burns and McDonnell, 1998) and the value reported at Ottawa (7.68) (IAEA, 1981).

A snapshot sampling of groundwater and surface waters on August 10, 2000 showed a wide range in isotopic composition; however, most samples fell on a line between groundwater and precipitation end-member samples (Figure 5-6). Only a seepage lake had an isotopic composition heavier than the rain. Using the groundwater and precipitation samples as end-members, the percentage of groundwater making up each surface water sample was calculated. The percent of groundwater in each surface water sample is shown in Figure 5-7. The larger upstream pond had a low percent of groundwater.   Tributaries draining thick till had a higher percentage groundwater, than tributaries draining stratified drift areas.

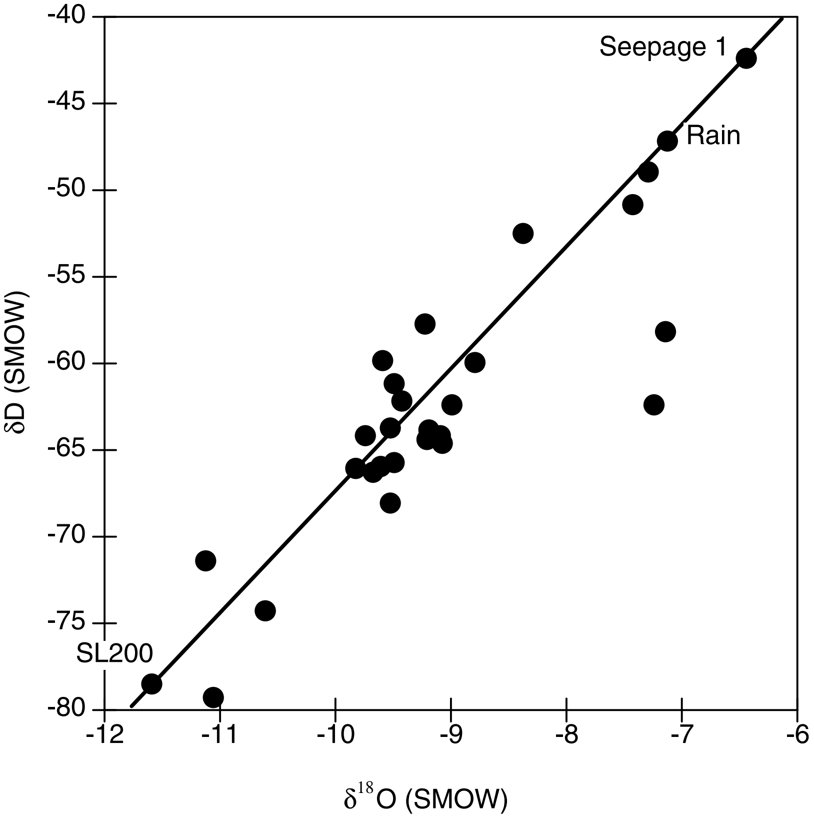

Figure 5-6. **Results of surface water snapshot sampling on August 10, 2000 - Most samples fell between the groundwater end-member collected at SL200 and the monthly composite rain sample collected on that date.**

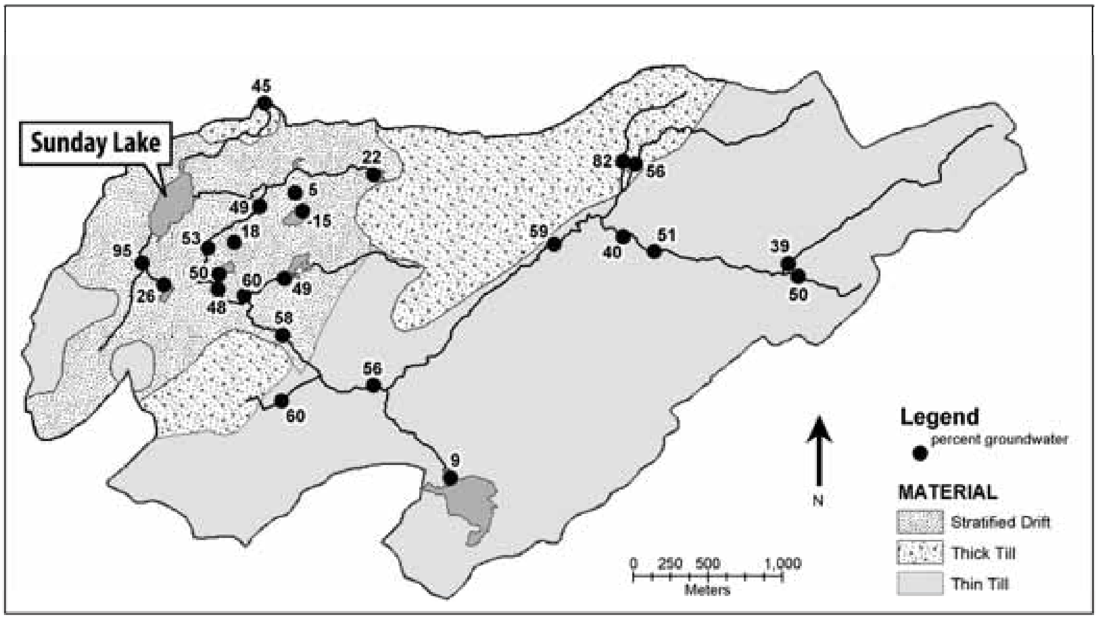

Figure 5-7. Estimated percent groundwater contribution to surface water samples taken during the snapshot sampling on August 10, 2000

5.2.5 Monthly Water Budgets – Sunday Lake Watershed

Monthly water balances (Figure 5-8) showed that more water entered the watershed through precipitation than left via stream flow for all periods except during spring snow melt. In the winter, these runoff deficits were due to the accumulation of the snow pack, and in the summer they were due to losses to evapotranspiration. There was generally net accumulation of snow pack during January, February, and March, but this was highly variable. Midwinter melting events can lead to a net monthly loss at any time. In February of 1999, for example, the runoff deficit was negative, meaning that there was more runoff than precipitation. The main melt that year came in April when the runoff deficit was over 100mm. In 2000, only a relatively small melt occurred in March, while in 2001 a large pack was melted in April. Melting of this pack accounted for 185mm of the 216mm of total stream flow that occurred in April of that year. In contrast, the melt in 2000 occurred mainly in March and only accounted for about 45mm of the 140mm of stream flow.

Runoff deficits are greatest in the summer. The average deficit starts to rise, in May, with the beginning of the growing season. The average, as a percentage of total precipitation, rises from about 35 percent in May to a maximum of 82 percent in August, then declines steadily to about 20 percent in December. These changes are in large part due to water losses to evapotranspiration during the growing season. Beginning in late November or early December, the snow pack starts to form, and water deficits during these times are largely due to pack accumulation. Since snow pack storage is temporary, any deficits associated with pack formation are accounted for during the spring melt and therefore, the total annual deficit is mainly due to evapotranspiration losses. If we assume that on an annual basis there is no change in any of the various watershed storage reservoirs (soil moisture, groundwater, and surface water), then the annual deficit is a measure of total evapotranspiration. During the period of study (1999-2001), precipitation averaged 127.1cm while stream flow averaged 77.4cm (Table 5-2). Stream flow thus accounted for only 61 percent of total precipitation and the remaining 49.1cm (39 percent) can be assumed lost to evapotranspiration.

5.2.6 Hydrologic Response to Precipitation Events

The hydrologic response of the outlet stream to precipitation events was examined for five events during the spring and summer of 2001 (Figure 5-9). For each event, total precipitation was compared to water yield (Hewlett, 1982), and the potential streamflow from direct precipitation to surface waters and wetlands was calculated. In all cases more precipitation fell during the rain event than was measured at the outlet gage. The amount of this deficit increased through the summer due to the progressive drying of watershed soils. In the fall it decreased as evapotranspiration losses declined.

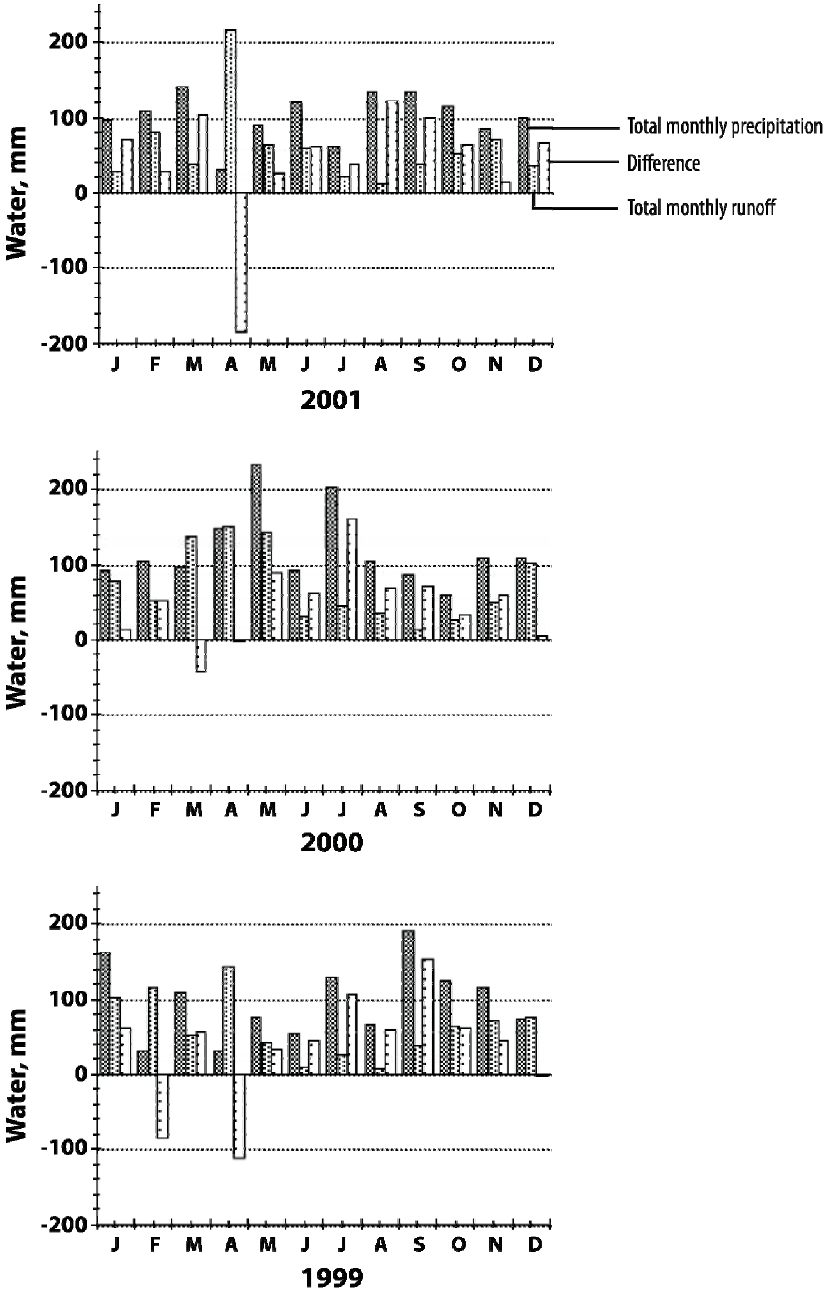

Figure 5-8. Monthly water balances determined from a comparison of total monthly precipitation to total monthly runoff - Negative values represent loss of accumulated snowpack.

Table 5-2.
Annual Inputs of Precipitation versus Streamflow and Evapotranspiration for 1999-2001

	Precipitation	Streamflow		Evapotranspiration	
Year	cm	cm	%	cm	%
1999	116.4	75.0	64	41.0	36
2000	143.2	86.3	60	56.9	40
2001	121.7	70.9	58	50.8	42
Average	127.1	77.4	61	49.6	39

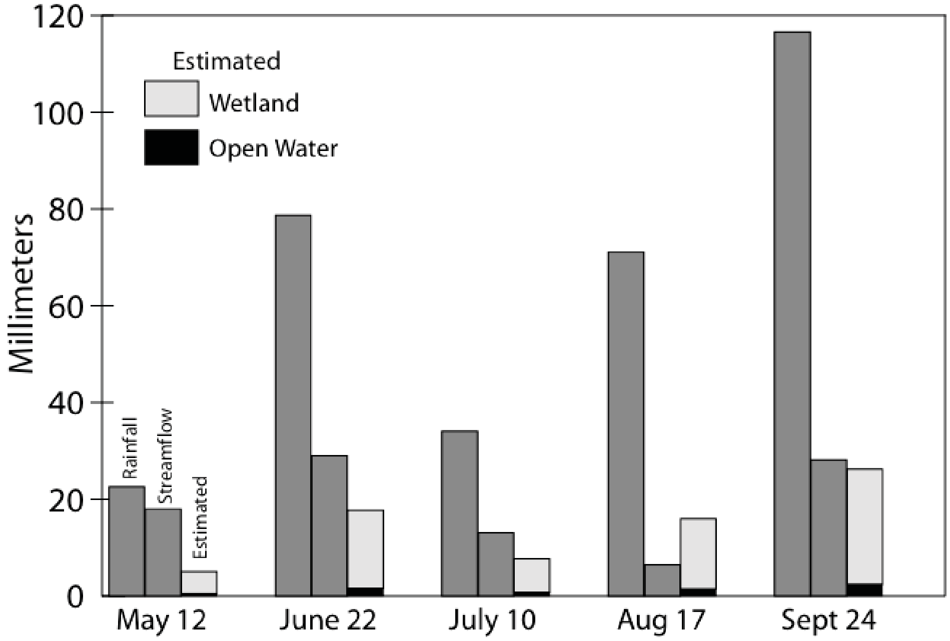

Figure 5-9. Precipitation, streamflow and potential stormflow (direct precipitation on surface waters and wetlands) for a series of precipitation events during the summer of 2001

Early in the growing season, soil moisture conditions are high causing relatively high runoff rates. During the May 12 event, 80 percent of the rainfall that fell in the watershed, left as streamflow. Direct precipitation to surface waters and wetland areas could account for only 28 percent of the observed streamflow. As the summer progressed, drier soils caused less runoff. During both the June 22 and July 10 events less than 40 percent of precipitation left the watershed as streamflow while direct precipitation to surface waters and wetlands could account for about 60 percent of the observed streamflow. By late summer 75-90 percent of precipitation was either retained in the watershed or lost to evapotranspiration. During the August 17 event more rain fell as direct precipitation to surface waters and wetlands than was observed in streamflow. Prior to this event groundwater levels in a wetland adjacent to Sunday Lake reached their lowest levels in the 3-year study period (Newton, et al. Chapter 6). Therefore, much of the water that fell during this event was stored within the wetland-surface water system. During the September 24 event, over 11cm of rainfall was measured at the Sunday lake gage station. Only about 25 percent of this was observed in streamflow and most of what was measured, could be accounted for by direct precipitation on surface waters and wetlands.

Surface water samples, collected from the major inlet to Sunday Lake during two of these events, show markedly different dissolved organic carbon (DOC) concentrations. During the May 12 event, when over 80 percent of event precipitation was observed in streamflow, DOC was relatively low (5.9mg/L C). During the September 24 event, when almost all of the streamflow could be accounted for by rain falling as direct precipitation to surface water and wetlands, the DOC was high (15.6mg/L C). These chemical results support the hydrologic analysis that shows that wetland areas are an important source of streamflow during the late summer as wetlands are a prime source of DOC (Grigal, 2002).

5.2.7 Flow Path Analysis

The amount of water moving along hydrologic pathways was estimated from the hydrologic equation and measurements of precipitation, runoff, and groundwater flow (Table 5-3). Precipitation averaged 127.1cm per year over the study period (January 1999 —December 2001). Surface stormflow, calculated from the volume of precipitation falling on wetlands and surface water bodies, averaged 28.6cm. This is probably an overestimation as there are times when the surfaces of some wetlands are not fully saturated as shown by the analysis of the August 17 event. Most of the precipitation falling on upland areas infiltrates the soil. Some is held in the canopy but this is incorporated into evapotranspiration. Infiltration, calculated from the difference between precipitation and surface stormflow, averaged 98.5cm. It includes water that moves as subsurface stormflow, groundwater flow, and water lost to evapotranspiration.

Evapotranspiration, determined from the difference between precipitation and streamflow, averaged 39 percent of precipitation or 49.6cm per year. The remaining 61 percent of precipitation left the watershed via streamflow. Streamflow was divided into three components; surface stormflow, riparian wetland groundwater flow, and non-wetland groundwater flow. The riparian component, at 25.9cm/yr, represents water flowing through the upper-most meter of the saturated zone under riparian wetlands. Non-wetland groundwater flow at 22.9cm/yr includes groundwater flowing under the 1-meter riparian wetland zone as well as groundwater entering through non-wetland riparian areas. Wetland areas are clearly important in generating streamflow as 70 percent of the streamflow is coming from either runoff from wetland areas (37 percent) or groundwater flow through riparian wetlands (33 percent). While much of the riparian groundwater flow may originate in adjacent upland areas, it enters the stream after passing through the riparian wetlands.

Table 5-3.
Sources of Water in the Sunday Lake Watershed from January 1999 through December 2001

Source	cm
Precipitation (P)	127.1
Infiltration (P-SS)	98.5
Evapotranspiration (P-S)	49.6
Streamflow (S)	77.4
Surface Stormflow (SS)	28.6 (part of S)
Riparian wetland groundwater (W-G)	25.9 (part of S)
Non-wetland Groundwater (Non W-G)	22.9 (part of S)

5.2.8 Discussion of Mercury Concentrations and Water Chemistry

Seasonal average THg and MeHg concentrations in the samples from the three gaging stations (inlet, outlet, and Sunday lake station) are shown in Table 5-4. Concentrations of both MeHg and THg varied seasonally with the lowest concentrations occurring in winter and the highest in summer (Table 5-4). Seasonal average MeHg concentrations in Sunday Lake varied from a low of 0.38 ng/L in winter to a high of 1.66 ng/L in summer. The major inlet stream varied from a winter average of 0.30 ng/L to 1.28 ng/L in summer while concentrations in the outlet stream generally fell between these values. The highest seasonal average THg (5.70 ng/L) occurred in the inlet stream and was significantly higher than the summer seasonal averages at both Sunday Lake (4.20 ng/L) and the outlet stream (4.09 ng/L). The percentage of THg that was MeHg was also highest in the summer. Sunday Lake had the highest MeHg percentage (39.5 percent) while the inlet stream experienced the lowest (22.4 percent). Winter values were as low as 9.9 percent in the lake at the lake stage gaging station.

Table 5-4.
Seasonal average concentrations for THg and MeHg

Location	n	MeHg ng/L	THg ng/L	MeHg % of THg
Inlet*				
Winter	10	0.30	2.10	14.2
Spring	12	0.42	4.07	10.3
Summer	10	1.28	5.70	22.4
Fall	11	0.76	3.81	20.0
Lake				
Winter	9	0.38	2.51	15.3
Spring	9	0.41	4.14	9.9
Summer	9	1.66	4.20	39.5
Fall	10	0.97	3.63	26.8
Outlet				
Winter	9	0.39	2.65	14.7
Spring	12	0.59	3.70	15.9
Summer	9	1.45	4.09	35.4
Fall	12	0.48	3.40	14.2

*The main inlet to Sunday Lake is called Inlet 2. The location of the inlet, outlet, and lake stations are shown in Figure 4-2. The complete data sets are shown in Figures 4-3 and 4-4.

The average chemistry of the outlet stream (Table 5-5) is typical of watersheds that fall into the high DOC, thin till, class of Adirondack Lakes according to the ALSC lake classification system (Newton and Driscoll 1990). This lake class has been found to be most sensitive to acidic deposition and may also be expected to have high Hg concentrations. The average THg and MeHg concentrations observed in the outlet stream are high in comparison to the group of Adirondack lakes studies by Driscoll, et al. (Driscoll, et al. 1994c).

Table 5-5.
Average water quality and Hg concentrations of streamwater at the outlet gage station

Constituent	Concentration	SD*
pH	5.33	0.46
ANC	22.1	18.9
DOC	550.0	189.2
Ca	44.9	9.2
Mg	15.6	3.3
Na	39.1	10.0
K	12.8	3.1
SO_4	43.4	9.7
NO_3	16.8	15.3
Cl	7.9	2.3
THg	3.57	1.58
MeHg	0.83	1.26

* SD - standard deviation
Concentrations in µmoles/L except pH, ANC (µeq/L) and THg and MeHg (ng/L)

Some systematic variations between streamflow and stream chemistry were observed at the gage stations. The best relationship was between streamflow and sodium (sodium = 0.98 – 0.313 $\log Q_{mm/day}$; $r^2 = 0.66$) at the outlet gage (Figure 5-10). The relationship at the inlet gage was weaker but still statistically significant (sodium = 0.915 – 0.248 $\log Q_{mm/day}$; $r^2 = 0.44$). Acid Neutralizing Capacity (ANC) also varied with streamflow (ANC=25.84 – 27.13log $Q_{mm/day}$; r^2=0.57) at the outlet gage (Figure 5-11), but there was no statistically significant relationship at the inlet gage. Finally, MeHg was observed to increase as a power function with decreasing discharge at the inlet gage (MeHg=0.47 x $Q^{-0.22}{}_{mm/day}$; r^2=0.41) (Figure 5-12).

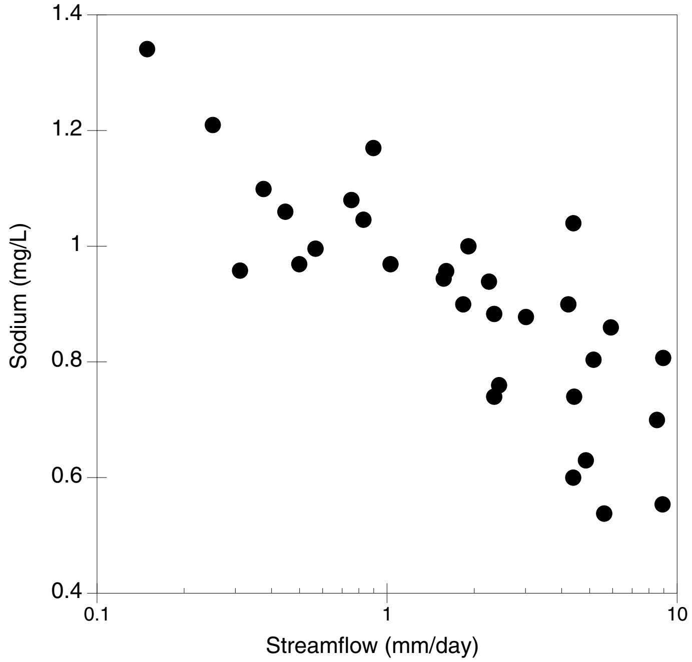

Figure 5-10. **Relationship between the concentration of Na in the outlet stream and streamflow, (sodium = 0.98 – 0.313 $\log Q_{mm/day}$; r^2 = 0.66)**

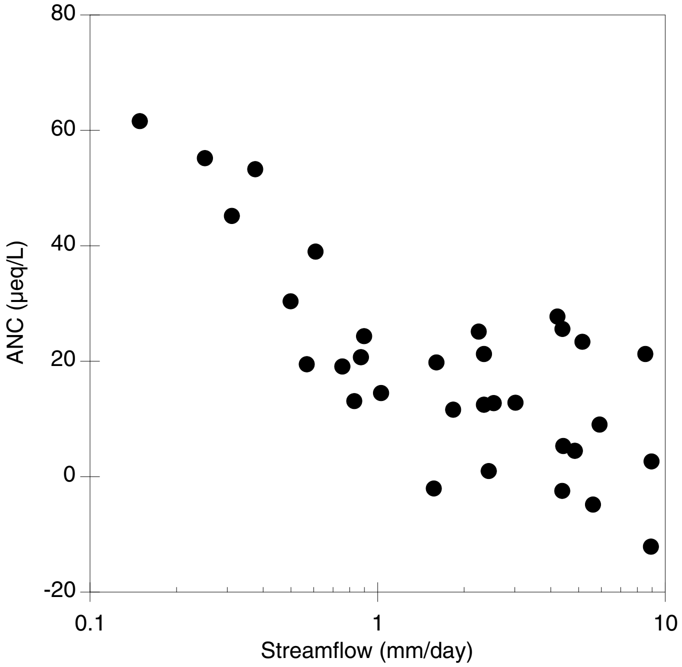

Figure 5-11. Relationship between stream ANC and streamflow at the outlet gage station, (ANC=25.84 – 27.13log $Q_{mm/day}$; r^2=0.57)

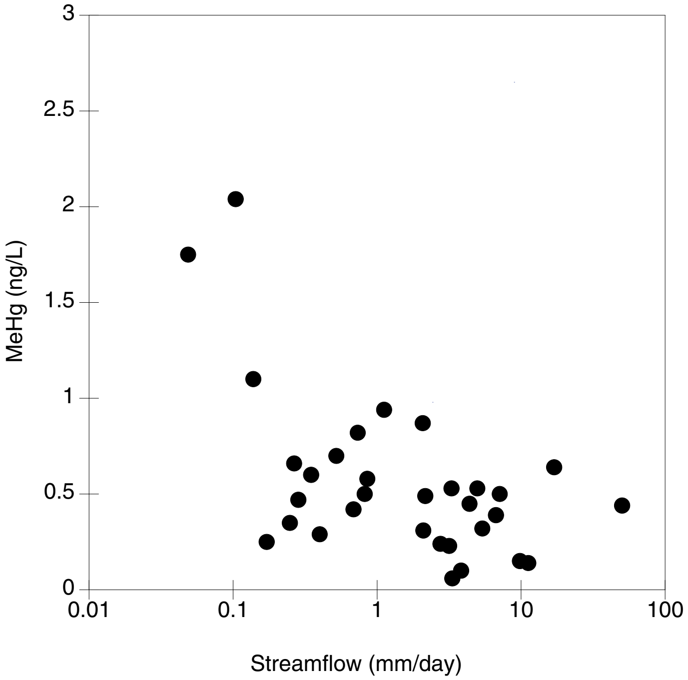

Figure 5-12. Relationship between MeHg and streamflow at the inlet gage (MeHg=0.47 x $Q^{-0.22}{}_{mm/day}$; r^2=0.41)

5.3 Discussion - The role of hydrology at the watershed scale

Hydrologic pathways play a critical role in the behavior and export of mercury deposition as it moves through the watershed. Our results show that wetlands strongly influence the export of MeHg from the Sunday Lake Watershed. Although wetlands make up only 20 percent of the watershed area, we estimate that as much as 70 percent of the streamflow moves through them either as surface stormflow or as riparian groundwater flow. This exaggerated influence is due, in part, to the location of most wetlands at lower elevations adjacent to stream channels. Approximately 66 percent of the total lengths of stream channels in the Sunday Lake watershed, are bordered by wetlands. This means that most of the upland water moving as surface stormflow or subsurface stormflow is funneled through the riparian zone before entering surface waters. Thus the riparian zone is last to influence surface water chemistry (Bishop, et al., 2004).

Our estimate of the amount of water moving along the riparian groundwater pathway is based on two assumptions. The first is that the hydrologic characteristics at the two instrumented sites are representative of the riparian wetlands in the rest of the watershed. We feel that this is a valid assumption given the similarity of the results from the two stations and the similarity of these wetlands to others across the watershed. The second assumption is that riparian groundwater flows in a 1 meter thick saturated zone under the surface. The riparian groundwater is chemically distinct, having high MeHg and low SO_4 as compared to deep groundwater (Newton, et al., Chapter 6). However, we did not have deep enough piezometers to determine where this transition occurs. The one-meter value is a best estimate and will need to be refined by further research. A deeper flowpath would increase the total volume of water moving through the organic-rich horizon that could contribute to transport of MeHg. However, methylation occurs primarily at the oxic-anoxic interface, and thus does not extend to deep depths in the subsurface.

Deep groundwater flow could be an important component of streamflow during base flow periods, however, during the summer snapshot sampling, groundwater made up only about 50 percent of streamflow. Streamflow at this time was at the 68th percentile on the flow duration curve. This is above the steps in the duration curve and it is likely that at this stage many of the upstream ponds were still contributing water to streamflow that was isotopically similar to precipitation. We suspect that the higher plateau in the flow duration curve represents the time when flow from upstream ponds supports baseflow. Deep groundwater supports baseflow when flows drop below this plateau.

The relative contribution of groundwater to baseflow increases with decreasing discharge. This is demonstrated by the negative correlations between both ANC and Na with discharge. High ANC and Na concentrations are the expected result of weathering reactions that occur as water reacts with minerals as it slowly moves through the groundwater reservoir. At higher flows, the groundwater influence on chemistry is diluted. That MeHg shows a similar relationship and suggests that it too is derived from reactions occurring within the groundwater system. However, in this case, it is in the shallow groundwater beneath riparian wetlands.

It is somewhat surprising that deep groundwater flow is not more important in this watershed given that 17 percent of it is covered by well-sorted stratified drift, and an additional 15 percent is covered by thick till. Using the relationship between thick surficial sediments and ANC proposed by Newton (Newton, et al., 1987), the ANC at the outlet gage station should be in excess of 100 μeq/L. Yet the average is only 22 μeq/L. It may be that the position of these deposits at the downstream end of the catchment limits their impact by allowing groundwater to exit the watershed under the outlet gage. Also, the presence of large peatlands with low permeability, adjacent to the stream in the lower part of the watershed, serves to isolate the groundwater from the surface water.

Our results show that the sources of stream water change seasonally with the summer being the period when wetland areas become relatively more important. This is also the time when MeHg production can be expected to reach its maximum. Mercury methylation is a biological process involving SO_4 reducing bacteria (Gilmour, et al., 1992). Increasing biological activity with increasing temperature results in more methylation. This may in part explain the seasonality of the variations in MeHg with highs in the summer associated with high biologic activity due to the warm temperatures. Summer and fall are also periods when streamflow is low as evapotranspiration rates are high. Little streamflow is generated from upland areas so there is little dilution of the MeHg released from wetlands.

A comparison of the seasonal average MeHg concentration in Sunday Lake with its outlet and major inlet shows the highest concentrations occurring in the lake during the summer. This suggests in-lake methylation processes may be important. It should also be noted that the MeHg concentrations in the inlet stream, although lower than in the lake, are relatively high in comparison with values reported by Driscoll, et al. (Driscoll, et al. 1994c). It may be that most of the MeHg is generated in the wetlands and in-lake processes add incrementally to this amount. Driscoll (Driscoll, et al. 1994b, c) reported high MeHg concentrations in Adirondack lakes having an anoxic hypolimnion. Sunday Lake was one of the anoxic lakes included in this study. It may be that the location of the major inlet stream at the same end of the lake as the outlet stream, allows anoxic conditions favorable to methylation in part of the lake despite the rapid flows.

The role of hydrologic pathways in determining MeHg concentrations is similar to their role in determining the sensitivity of surface waters to acidic deposition. In both cases, infiltration into upland soils leads to retention of contaminants, and runoff as stormflow causes them to be released. The correlation between total dissolved Al and fish Hg reported by Driscoll, et al. (Driscoll, et al. 1994c) demonstrates this relationship. Aluminum is released from soils as acidic water moves as subsurface stormflow through the upper soil horizons. Similarly, Hg accumulates in fish from watersheds where subsurface stormflow is dominant as high volumes of stormflow are flushed through the MeHg producing riparian zone.

Release of Hg to surface waters in the Sunday Lake watershed is primarily determined by watershed characteristics that influence the flow pathways of water moving through wetland systems. The impact of atmospheric deposition of Hg on the level of Hg in fish is primarily determined by watershed processes rather than by in-lake processes in Sunday Lake because of the high flowrates and associated stream Hg loads compared to direct atmospheric Hg deposition. In-lake methylation processes contribute, but watershed processes dominate in this ecosystem.

6 Hydrologic Factors Influencing Mercury Release from an Adirondack Wetland

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6.1 Introduction

Chapter 5 identified watershed hydrologic processes, particularly flow paths through uplands and wetlands, as playing an important role in the delivery of total and methylmercury to Sunday Lake. Here, we further examine the importance of hydrologic factors in determining mercury transport through a small, complex series of wetlands that border the eastern end of Sunday Lake and its main inlet stream.

The hydrology of wetlands is a critical controlling factor in the release of Hg. Branfireum, et al. (1996) noted a threefold increase in MeHg concentrations in a stream flowing through a peatland. These high concentrations were maintained even during hydrologic events when stream flow increased tenfold. Although groundwater flow in peatlands can be complex, the low hydraulic conductivity of the humified peat below the acrotelm generally limits deep groundwater flow (Branfireun, et al., 1996). Only the upper 50cm has a high enough hydraulic conductivity to allow significant flow rates to transport Hg to streams (Yavitt et al., Chapter 7).

The position of wetlands relative to streams and lakes is important. Because of their position next to streams, even small riparian wetlands can be important modifiers of stream chemistry (Schiff, et al., 1998). Burns, et al. (2003) found that groundwater from riparian zones was the major source of ions in streamwater at Panola Mountain in Georgia. Riparian wetlands can also be important sources of MeHg (Bishop, et al., 1995a, b; Lee, et al., 1998). They accumulate HgT, and their high biological productivity leads to high methylation rates (Moore, et al., 1995). High groundwater flux through these wetlands makes them a potentially significant source of MeHg to surface waters.

Wetlands cover approximately 20 percent of the watershed (274 hectares) with most located adjacent to the lakes and streams. These wetlands have been mapped as part of the State Wetlands Protection Program (Primack, et al., 2000). Wetland types were classified using the Cowardin system in accordance with the National Wetland Inventory (Cowardin, et al., 1979). Sixty-six percent of all stream channels by length are bordered by wetlands.

6.2 Methods

Fourteen shallow groundwater piezometers were installed in the wetland adjacent to the inlet of Sunday Lake (Figure 6-1). The piezometers were constructed of 5cm PVC pipe screened in the lower 30cm with 0.25mm slots. They ranged in depth from 61 to 279cm below surface. Four were installed in riparian wetlands adjacent to the inlet stream, seven were installed in the ‘sedge’ wetland at the east end of the lake, and two were located in the forested area just outside the wetland. All but two piezometers terminated below the organic wetland sediments, although the upper part of some screens extended into the organic horizons. Hydraulic conductivity of the materials at the piezometer screen was determined by slug tests using the Hvorslev method (Hvorslev, 1951). The relative elevations of all piezometers were determined by standard survey methods using a Topcon GTS-2B Total Station. Water levels were measured monthly using a Solinst Water Level Meter. Water levels in four piezometers were continuously monitored using Campbell Scientific CR10X data loggers equipped with Druk 5 psi pressure transducers. Measurements were made at 1 second intervals and averaged every 10 minutes.

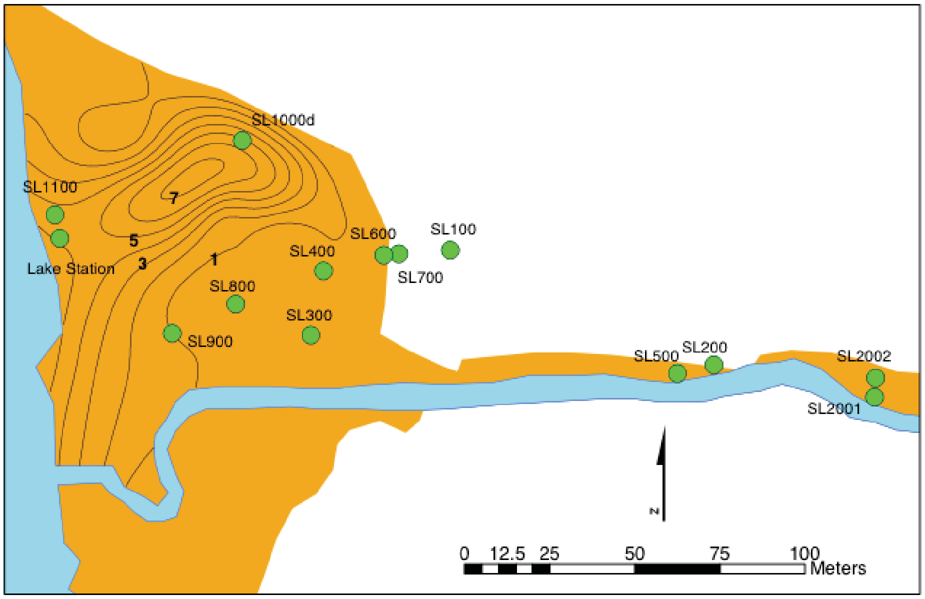

Figure 6-1. Map showing instrumentation and thickness of peat at the east end of Sunday Lake and its inlet stream

Wetland groundwater and surface waters were sampled monthly from April through November of each year between 2000 and 2002, from the 14 shallow groundwater piezometers installed in the wetland adjacent to the inlet of Sunday Lake. Samples were analyzed for major ion chemistry and the stable isotopes ^{18}O and deuterium. The sampling and analytical methods are described in Section 5-1.

Mean residence time was calculated for groundwater and streamwater by comparing the amplitude of annual fluctuations of ∂^{18}O to that observed in precipitation. Burns and McDonnell (1998) used this method to determine the mean residence time of stream water in subcatchments of the nearby Woods Lake watershed. The sinusoidal variation in precipitation ∂^{18}O in temperate latitudes reflects the seasonal changes in tropospheric temperature. The attenuation of signal amplitude in the surface and groundwater reservoirs is a function of mean residence time, assuming a steady-state, well-mixed reservoir, having an exponential distribution of residence times (Eriksson, 1958). The amplitude of the best-fit sine curve for precipitation ∂^{18}O is compared to that from the sample site, and the residence time is calculated from:

$$T = \omega^{1}[(A/B)^{2} - 1]^{1/2} \tag{1}$$

Where T is the residence time (days), ω the angular frequency of variation ($2\pi/365$ days), A the amplitude of the precipitation sine curve, and B the amplitude of the sample site curve (Burns and

McDonnell, 1998). This method was applied to both groundwater and surface waters in the Sunday Lake watershed.

Mean monthly precipitation ∂^{18}O values were estimated from mean monthly temperatures using a linear regression model (∂^{18}O =0.32 x temperature -13.25; $r^2 = 0.71$) derived from 9 years of data collected at Ottawa, Ontario (IAEA, 1981). The estimated values are close (± 1 ∂^{18}O) to measured values collected in the Sunday Lake watershed during the summer and fall of 2000 and 2001.

6.3 Results

6.3.1 Wetland Hydrology

The 1.5 ha wetland system at the east end of Sunday Lake has components that are representative of most of the watershed's wetlands. Yavitt, et al. (Chapter 7) identified four different wetland types in the area. 'Fringe' and 'shrub' wetlands are underlain by thick peat deposits and make up a large part of the study area (Figure 6-1). The thick peat underlies an area between the extension of two eskers that border the lake-wetland system. The hydraulic conductivity of the thick peat, below the acrotelm, is extremely low ($<1\text{x}10^{-6}$ cm/sec). A 'sedge' wetland is located between the 'shrub' wetland and the stream and merges with a riparian wetland that extends upstream. Both the 'shrub' and riparian wetlands have thin organic horizons at the surface that are generally less than 50cm thick, underlain by a poorly sorted, silty sand, with numerous cobbles. The boundary between the 'shrub' and 'sedge' wetlands is relatively sharp suggesting that the steep esker slopes to the east extend into the subsurface in the area of the large wetland at the end of the lake. The poorly sorted, cobble rich, sediment was probably deposited by meltwater streams that formed the esker system. This material may have also been partially reworked by the modern stream. Hydraulic conductivities of these sediments ranged from $2.4 \text{ x } 10^{-2}$ to $7.9\text{x}10^{-3}$cm/sec.

Water levels in the 4 m deep piezometer screened within thick peat deposits in the 'fringe' wetland was continuously monitored for 4 days during the summer of 1999 before a nearby lightning strike permanently disabled the pressure transducer. During this time, water levels rose continuously as the piezometer slowly recovered from pumping associated with the collection of an initial water sample. The four days yielded only about half or 1.5 m of recovery, from the initial 3 m drawdown. This dramatically shows the very low hydraulic conductivity of the thick peat.

Four of the nine piezometers in the 'sedge' and riparian wetlands, were equipped with pressure transducers for continuous water level monitoring and the rest were measured monthly. Two piezometers (SL100, SL700) were located outside the wetland in the adjoining stratified drift deposits, in order to determine groundwater fluctuations outside the influence of the stream and wetlands.

Water levels in piezometer SL400 were monitored from July 2000 through June 2002 (Figure 6-2). This piezometer is located in the 'sedge' wetland at the east end of Sunday Lake approximately 35 m from the inlet stream (See Figure 6-1). It is screened 90cm below the surface in mineral soil overlain by about by about 40cm of organic material. From July through March of 2000 the water table was located just below the bottom of the organic horizon except during large rain events when water levels rose briefly into the organic horizon. The spring melt in April of 2001 drove the water table all the way to the surface, and head elevations suggest a brief flooding event near the end of April. The water table remained within the organic horizon from April until about the middle of June. A large rain event near the end of September drove the water table back into the organic horizon and although it briefly fell back into the mineral horizon after this event, this marked the beginning of a prolonged period when the water table remained within the organic horizon. This period extended from the fall of 2001 through the spring and early summer of 2002. Like the spring of 2001, a brief flooding event occurred near the middle of April 2002.

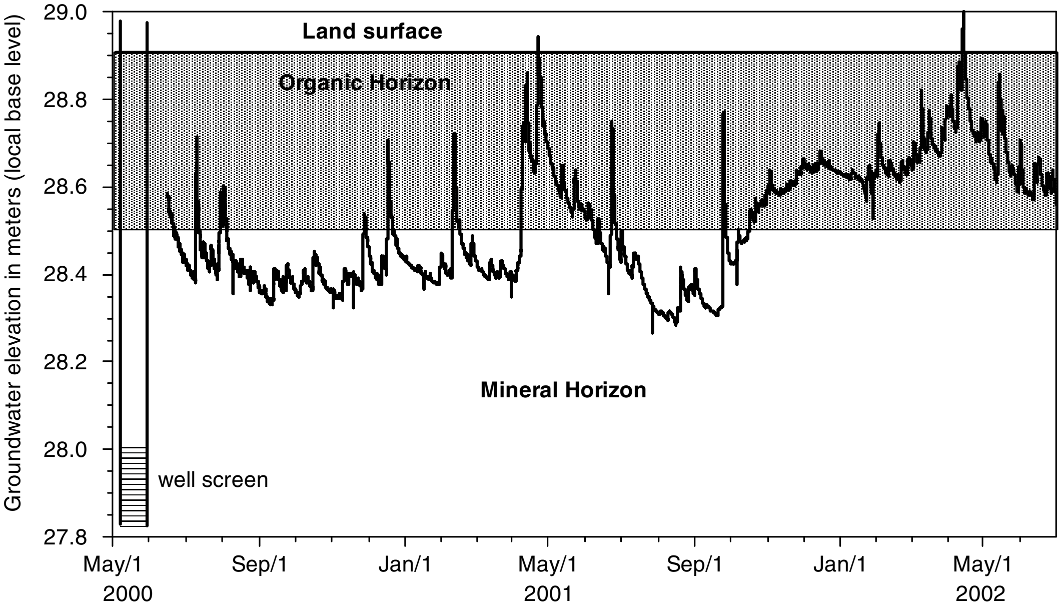

Figure 6-2. **Hydrograph of piezometers SL400 located in the wetland approximately 35 meters from the inlet stream**

A pair of piezometers was installed approximately 50 m upstream of the inlet gage station, in an alder dominated ‘riparian’ wetland. Piezometer SL2001 is located within 1 m of the inlet stream and is screened 55cm below the surface in cobble alluvium. Piezometer SL2002 is screened 60cm below the surface and is 7m from the stream. Organic horizons are only about 20cm thick in this area.

The hydrograph from SL2002 (Figure 6-3) shows that water levels are maintained at relatively high levels until summer when they drop dramatically. Groundwater levels recover during rain events in late September. This is typically the time that marks the end of the growing season as deciduous trees begin to drop their leaves. Precipitation events throughout the period of record cause rapid short-term oscillations in water levels similar to that observed at SL400. These events do not appear to result in any long-term recharge. The water that enters the system is rapidly discharged to surface water. Long-term variations in groundwater levels appear to be controlled by factors outside the immediate area of the wetland. In this case the level of the water table in the surrounding stratified drift appears to control these long-term oscillations and it is only when evapotranspiration ceases at the end of summer, that recharge occurs in the stratified drift aquifer. Most of the recharge occurs in the fall, when the maximum water level rise is observed. Spring recharge is limited by high water tables that force most of the meltwater to flow laterally through the upper levels of the soil.

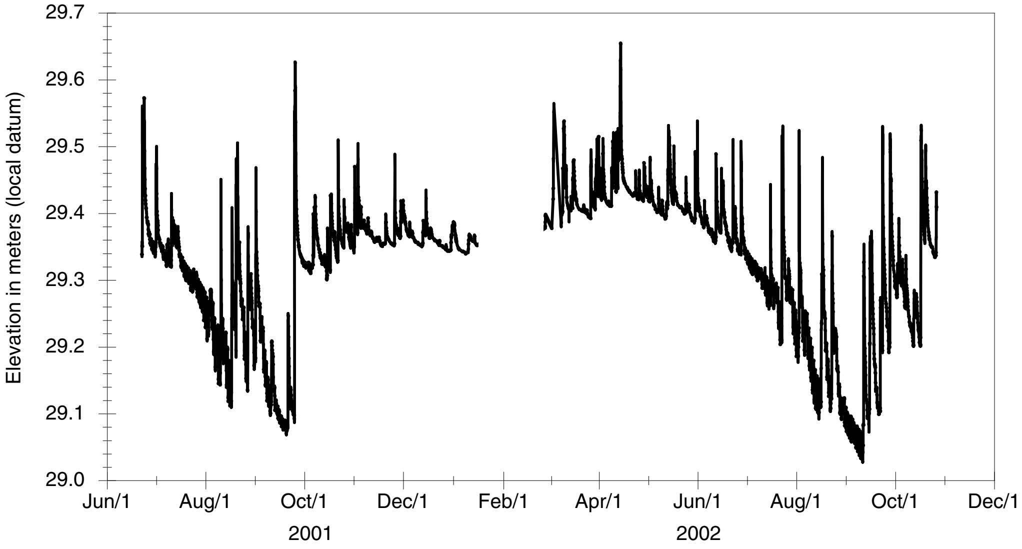

Figure 6-3. **Hydrograph for SL2002 (7 m from inlet stream)**

Evapotranspiration is significant in the riparian wetlands. Hydrographs from SL2002 during a dry period in early September 2002, show a daily oscillation of as much as 40mm in response to daytime temperatures as high as 30 ˚C (Figure 6-4). Each day water levels began to fall near 0800hrs EST and continued to drop until approximately 1700 hrs when recovery began. Differentiation of the hydrograph shows that maximum evapotranspiration rates occurred near 1100 EST when the rate of water level decline reached a maximum of 10mm/hr. Recovery was slower with a maximum rate of 4mm/hr reached at about 2000 EST. No seasonal shifts were observed in the timing of the ET signal, unlike findings from a study of ET in Canada (Meyboom, 1967).

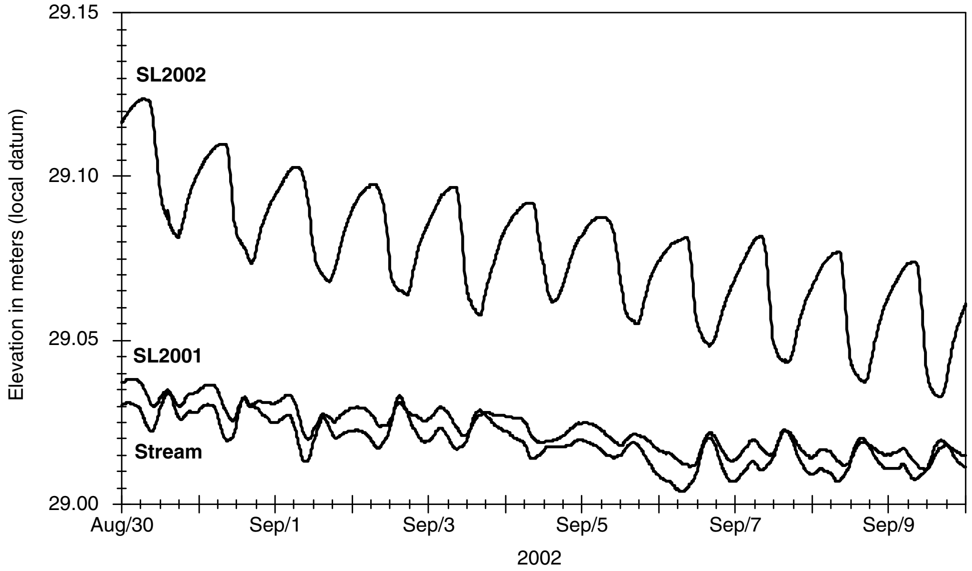

Figure 6-4. **Oscillations in water levels in piezometers located in the Alder riparian wetland, - Piezometer SL2002 is located 7m from the stream while SL2001 is located 1m from the stream. Elevations are relative to an arbitrary datum**

Calculation of the evapotranspiration rate for the September 6 – 10, 2002 period using the Penman-Monteith model (Dingman 2002) yields an average rate of 3mm/day. It is also possible to estimate evapotranspiration from the piezometer hydrographs provided specific yield is known. Nachabe (Nachabe 2002) developed expressions to show the dependence of specific yield on time and depth to water table. Using his relationships for fine loamy sand together with the method of White (White 1932) for estimating hydrograph evapotranspiration yields values from 4.7-5.5mm/day. Although there are uncertainties associated with both of these methods, this analysis suggests that evapotranspiration in the riparian wetlands is a significant hydrologic process that draws water upward into the shallow riparian. Ultimately, this recharge water must come from the adjacent groundwater system in the stratified drift aquifer. It cannot come from the stream as the elevation of the stream is lower than the riparian water table. The stratified drift aquifer discharges to the stream under the riparian system and thus can readily supply an upflux of water to the riparian zone in response to an evapotranspiration stress.

Water levels in the stream also display a daily oscillation, but it is more complex and has a much lower amplitude. Typically, stream stage drops from about 0400 hrs until 1000 hrs when water levels begin to rise peaking from 1400hrs to 1500hrs before dropping again. Piezometer SL2001 follows this same pattern indicating a close connection between stream and groundwater at this location.

6.3.2 Rain Event September 24-25, 2001

Most of the time, groundwater flows from the riparian wetlands into the stream as indicated by higher head in the wetlands than in the stream. However, during some hydrologic events, the water level in the stream rises above the groundwater level in the adjacent wetlands. During these times, there is a reversal of flow, and stream water infiltrates into the riparian zone. This phenomenon was observed during a rain event in late September 2001 (Figure 6-5). During this event, 116mm of rain fell during the afternoon and evening of September 24 and early morning of September 25. Piezometers SL2001 and 2002 began to rise within 30-40 minutes of the start of precipitation. By 2100 hours on September 24 the stream began to overflow its banks and SL2001 was flooded. After that time, fluctuations in water levels at SL2001 essentially parallel, at a slightly lower level, the changes in stream stage. SL2002 did not become flooded until 0200 hrs on September 25. Prior to that, water levels rose rapidly to within about 5cm of the land surface where, but for a couple of brief events, they remained until the area was flooded. This rapid initial rise of 42cm was driven by the first 26mm of rainfall and was accomplished by 1745 EST. Peak rainfall rates of 40mm/hr at 1830 hrs and 32mm/hr at 2100 EST briefly drove the piezometer levels to the land surface. Most of the rain (109mm of 116mm) had fallen by the time SL2002 was flooded at 0200 EST. The peak in the stream hydrograph occurred at 0440 EST, which was also the time that water levels in SL2001 and SL2002 peaked. Floodwaters receded from SL2002 by 1000 EST but water levels in the stream remained higher than the piezometers until noon on September 25. The flooding event was essentially over at 2230 EST when the stream level dropped below the land surface elevation at SL2001.

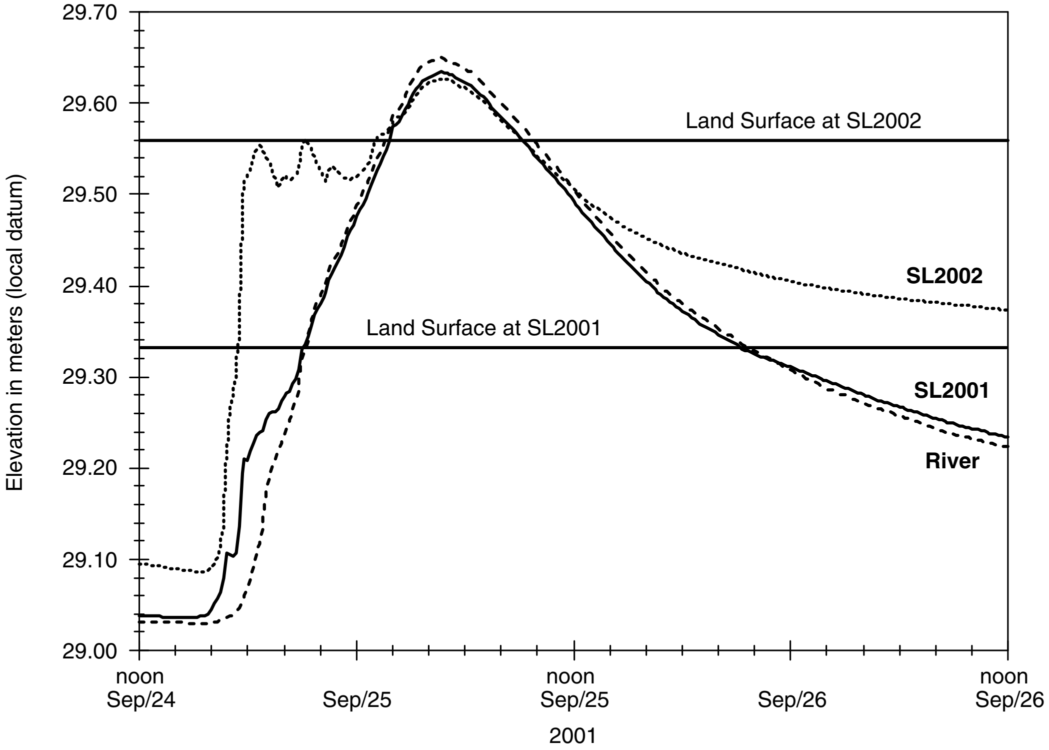

Figure 6-5. **Changes in water levels in piezometers SL2001, SL2002, and the adjacent stream during a 116mm rain event during the afternoon and evening of September 24, 2001**

Water level measurements in wetland piezometers can potentially be influenced by two different phenomena that cause them to become disconnected from the water table. The Lisse effect (Meyboom, 1967; Weeks, 2002) occurs when infiltration during intense rain events seals the surface of the soil, compressing vadose air and causing a rapid water level rise in piezometers screened below the water table. This rise does not reflect changes in the water table. The magnitude of the Lisse effect can be calculated by

$$\Delta h = \frac{n}{s-n} P \qquad (2)$$

Where Δh is the change in piezometer head; n is the depth of rain penetration; s is the distance from the land surface to the top of the capillary fringe; and P is atmospheric pressure head in water equivalents.

Rapid piezometer response can also be caused by the reverse Wieringermeer effect (Gillham, 1984; Jaber, et al., 2006; Meyboom 1967) that occurs when the capillary fringe extends to the land surface prior to the start of precipitation. Infiltration at the beginning of a rain event produces an almost instantaneous rise in the water table. The rise associated with the reverse Wieringermeer effect is less than that observed for the Lisse effect and is always followed by an equally fast water level decline (Heliotis and DeWitt 1987).

The rapid response of SL2002 at the beginning of the September rain event was likely due to the Lisse effect. Calculations using equation 2 show that virtually all the initial rise can be explained by this effect. It is also likely that much of the flashy component of the annual hydrograph at this site (Figure 6-3) is due to this effect.

Water levels were continuously monitored at three other stations during this precipitation event. The response at SL400, located in the sedge wetland, was different from that observed in the upstream riparian wetland. The initial rise in water levels at the start of the event was much less and there were no distinct peaks associated with peaks in rainfall intensity, indicating no Lisse effect at this site. Instead there was a steady increase in groundwater level until it peaked at 0700 EST on September 25. This was similar to the rise in lake level that peaked slightly earlier at 0600 EST. Although lake level is lower than groundwater, the channel of the inlet stream that flows through this area is higher due to the presence of a low beaver dam. This difference in elevation was measured during a base flow period, and the difference was used to estimate water levels in the channel during the event (Figure 6-6). These estimates show water levels in the stream become higher than groundwater in the adjoining ‘sedge’ wetland during the event. This suggests recharge from the stream could influence water levels at SL400.

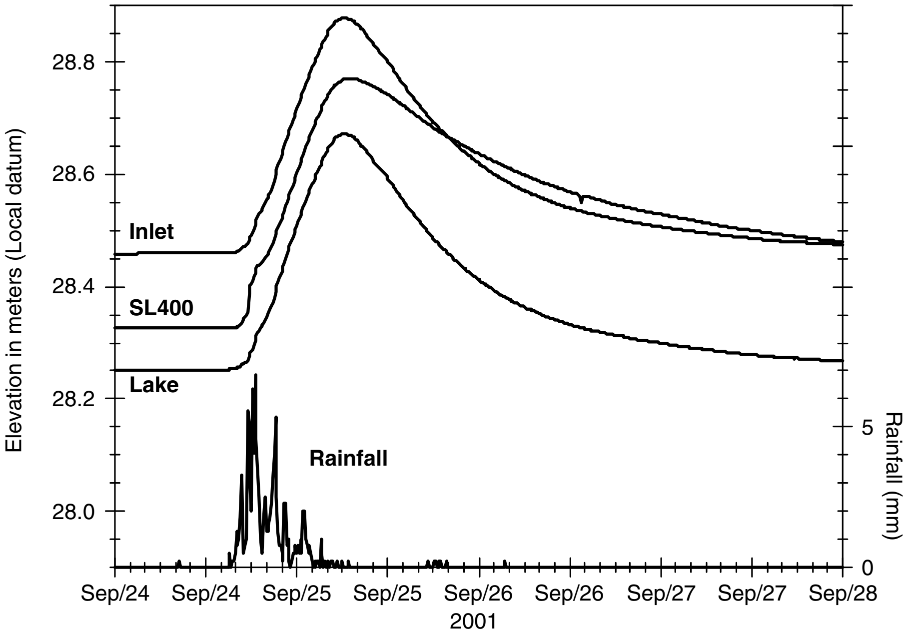

Figure 6-6. Groundwater levels at SL400 together with lake levels and an estimate of the level of water in the inlet channel during the September 24-25, 2001 event

Recharge of ‘sedge’ groundwater also occurred from direct infiltration of rainwater as indicated by variations in groundwater temperature during the event. Groundwater temperatures at SL400 vary from 3.3 ˚C in mid February to 14.5 ˚C in mid August. The temperature just prior to this event was 12.7 ˚C. As precipitation began falling and infiltrating into the ground, groundwater temperatures increased as did the air temperature, and therefore the temperature of the precipitation was warmer (16 ˚C). Groundwater temperature rose to a maximum of 13.9 ˚C before beginning to fall towards end of the precipitation event. This temperature spike reflects advective transport of warm rainwater into the shallow groundwater system. The temperature continued to fall as the level of groundwater reached its peak elevation. The minimum temperature was reached at about 1000 EST after which there was a gradual rise over the next 24 hours before temperatures began to fall once more (Figure 6-7). This secondary temperature peak likely represents infiltration of stream water into the groundwater system.

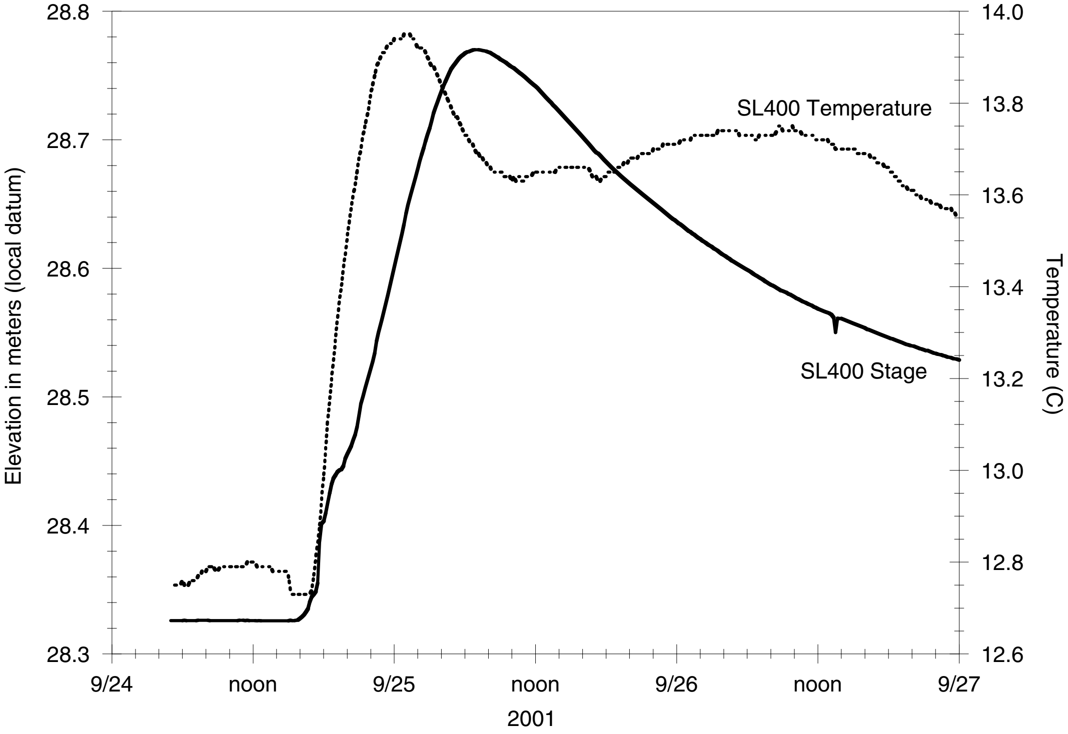

Figure 6-7. Changes in stage and temperature at SL400, —Temperature changes suggest much of the recharge was the result of infiltration from the stream located about 40 m away

Groundwater levels at SL400 rose 45cm in response to the 11.6cm of precipitation that fell during this storm. If all the precipitation that fell on the wetland infiltrated, then the specific yield for the sediments would be approximately 0.22. This seems a little high given that the piezometer is screened in poorly sorted cobble sand that underlies the organic horizons but is consistent with specific yield estimates from other parts of the wetland.

6.3.3 Rain Event July 9-10, 2001

Wetland groundwater levels were continuously monitored in the ‘sedge’ (SL400) and riparian (SL200) wetlands during an 82mm rain event on July 9-10, 2001. Piezometer SL200 is located in the riparian wetland adjacent to the inlet stream gage, located approximately 50 m downstream of SL2002 (Figure 6-1). The SL200 hydrograph shows a strong Lisse effect in response to three pulses of precipitation (Figure 6-8). During each pulse, water levels rose rapidly, at rates that ranged from 20 – 27cm/hr with peak heights from 21 – 28cm. Recovery from each Lisse effect event was rapid (generally less than 5 hours). While rapid recovery is a feature normally associated with the Wieringermeer effect, the depth to water (70cm) and nature of the materials (cobble sand) make it unlikely that the capillary fringe could be at the land surface prior to the start of precipitation.

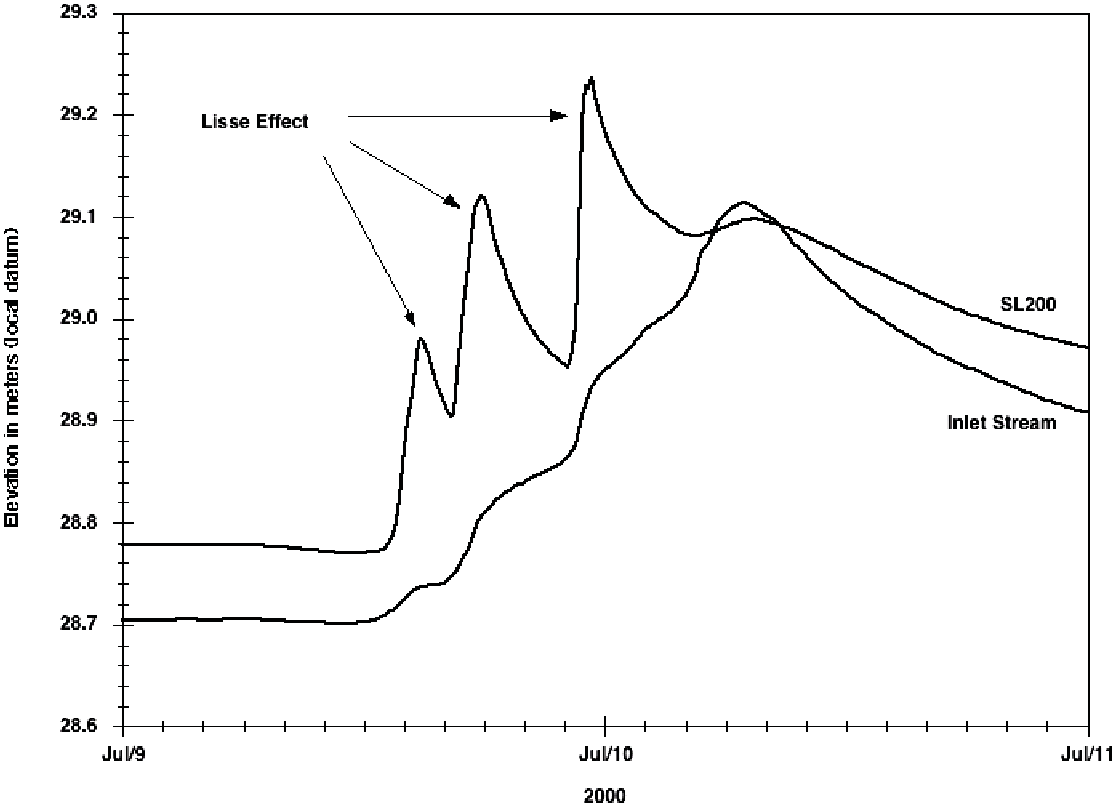

Figure 6-8. Response of groundwater and stream to an 82mm rain event that occurred on July 9-10 2001 —The peak in groundwater levels came within 26cm of the land surface

Towards the end of the rain event, water levels in the stream rose above the water level in SL200. At about this time, the water level in SL200 stops decreasing and begins to rise (Figure 6-8). The rise continues until 2.5 hours after the peak in the stream hydrograph. This reversal in hydraulic gradient near the peak in stream flow indicates a period of bank storage when stream water infiltrates into the riparian wetland. Distances are short as SL200 is located less than 4 m from the stream, but the land surface at SL200 is high enough that it is not flooded by the rising stream.

The response of peizometer SL400 in the 'sedge' wetland to this event was similar to that observed for the September 2001 event. There was no Lisse effect but there was some warming associated with advection of warm rainwater recharge. The total rise in groundwater level (33cm) was similar to that observed at SL200 (32cm) and the apparent specific yield 0.25 was very close to that observed for the September 2001 event (0.22).

6.3.4 Riparian versus Sedge Hydrology

Groundwater flow through upstream riparian wetlands is different from that in the 'sedge' wetland. During the summer dry periods, flow through the upstream riparian wetlands is fed from the adjoining stratified drift uplands. A portion of the flow is directed upward to replace water lost to evapotranspiration. As water levels drop in the adjoining stratified drift aquifer, hydraulic gradients decline from 0.038 immediately after recharge events to 0.006 during dry periods. Recharge in the wetland comes from either direct precipitation falling on the wetland surface or recharged from the stream either in the form of the lateral movement of bank storage or from the vertical infiltration during flooding.

During summer dry periods groundwater flow through the ‘sedge’ wetland comes mainly from the adjoining stratified drift uplands but here discharge is not to the stream, but directly to the lake. Equipotential lines determined from water levels measured on June 21, 2001, indicate flow essentially parallel to the line of piezometers (Figure 6-1). Hydraulic gradients range from 0.0041 at the beginning of the summer to 0.0004 at its end. Major changes in ‘sedge’ wetland water levels parallel changes in lake level.

Evapotranspiration is less important in the ‘sedge’ wetland than in the riparian wetland. The maximum evapotranspiration signal was <2mm at SL400 compared to >40mm at SL2002 in the riparian wetland. This likely reflects differences in vegetation as the sedge wetlands are mainly grass covered while the riparian wetlands are alder covered.

Flow was not determined from within the ‘shrub’ wetland that borders the ‘sedge’ wetland to the north as hydraulic conductivity below the acrotelm was very low. However, water levels measured in mineral sediments below the thick peat (SL1000d), were similar to levels in SL400 suggesting that both are part of the same groundwater system. In the spring and early summer, water levels at SL1000d were slightly higher than its shallow pair (SL1000s) indicating some upflux, but the low hydraulic conductivity makes this quantitatively insignificant. Later in the summer the water levels in the two piezometers were essentially identical. It is likely that the upper acrotelm receives most of its recharge directly from precipitation and that the high hydraulic conductivity in this zone results in rapid runoff during precipitation events.

6.3.5 Hydraulic Residence Time

Mean residence time in the wetland was calculated at those piezometers that displayed a statistically significant annual oscillation in ∂^{18}O using the method of Burns and McDonnell (1998). Sine curves were fit to both calculated precipitation ∂^{18}O and observed groundwater and surface water ∂^{18}O data (Figure 6-9). The peak in precipitation ∂^{18}O generally occurred in mid-August while the peak in surface water ∂^{18}O occurred in late September and in late October to early November in groundwater. The displacement of the surface water and groundwater ∂^{18}O peaks is likely due to either, delays in inputs associated with the melting of the snowpack or to differences in the size of the groundwater and surface water reservoirs.

Mean residence times for waters collected from the shallow ‘sedge’ wetland piezometers generally change with distance along groundwater flow lines (Table 6-1). The shortest residence times are associated with piezometers nearest the upstream edge of the wetland (SL700) while the longest times are found at piezometers directly adjacent to the stream. The mean residence time of water from the piezometers during base-flow conditions was 194 days. This is identical to the residence time calculated for piezometer SL500 located within 80cm of the stream suggesting a close hydrologic connection between the two. Burns and McDonnell (1998) report mean residence times of 102 and 103 days for base-flows from two small headwater streams in the nearby Woods Lake watershed. They found groundwater had a longer residence time (160 days) while soil water from the O-horizon had the shortest residence time (63 days). The increase in residence time of shallow groundwater moving along a flow line is not simply a function of the rate of advective transport. The addition of new recharge water to groundwater moving along a flow line reduces the mean residence time. Similarly, upwelling of deep groundwater in the vicinity of the stream will add an older component to mean residence time. The similarity of residence times between the stream and the riparian groundwater directly adjacent to the stream (SL500, <1 m from stream) either reflects the dominance of deep groundwater discharge or perhaps more likely, stream water has infiltrated into the near shore riparian zone.

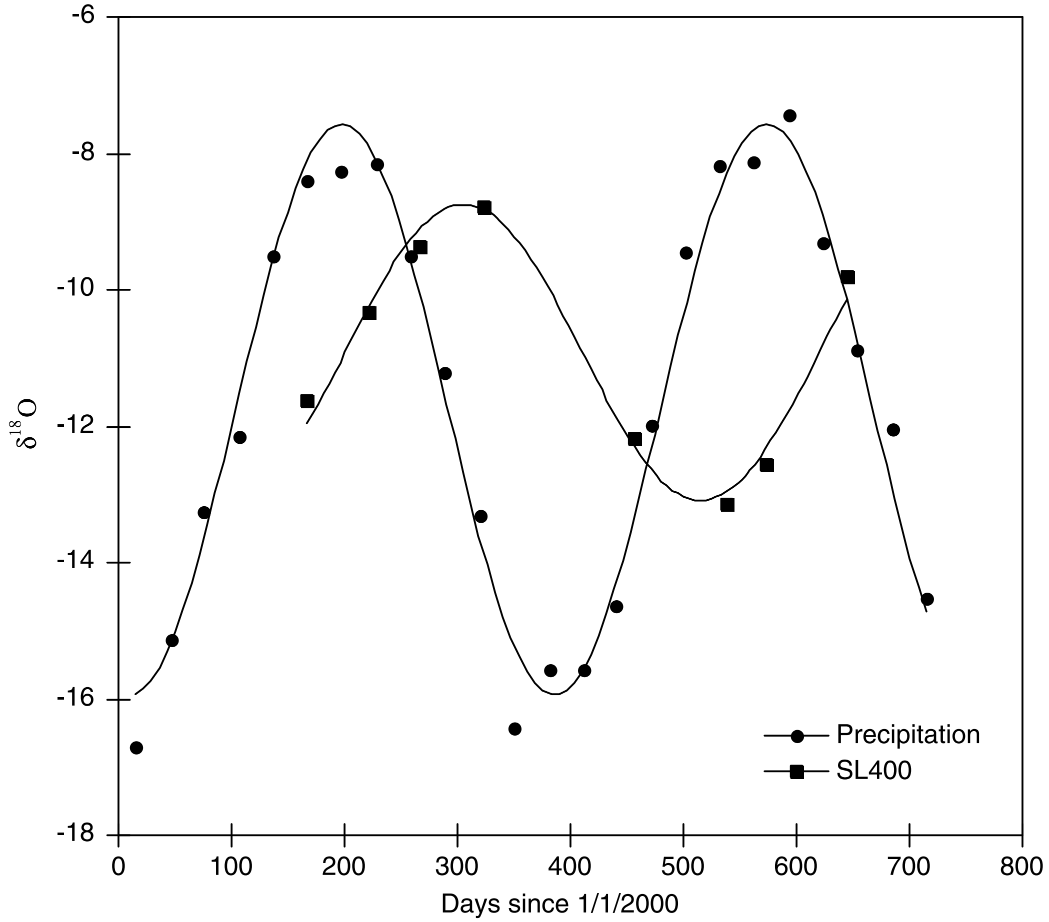

Figure 6-9. Sine curves fit to the variation in estimated precipitation $\delta^{18}O$ and measured changes at piezometer SL400

Table 6-1.
Calculated residence times

Site	Transect Distance (m)	Residence time (days)	r^2
Sedge Wetland			
SL700	0	73	0.97
SL400	38	96	0.98
SL300*	48	92	0.98
SL800	65	131	0.95
Riparian Wetland			
SL500		194	0.89
Inlet Stream		194	0.86

*SL300 is offset from the flow line

6.3.6 Wetland Chemistry

Sunday Lake is classified as a thin till and bedrock dominated catchment using the lake classification system of Newton and Driscoll (1990). The relatively low Ca concentration at the outlet (mean Ca = 45 µm) is surprising given the relatively high percentage of stratified drift (21 percent) in the watershed. Normally, the stratified drift aquifer would be expected to provide high ANC base flow to surface waters. It may be that the location of the stratified drift in the lower part of the watershed allows much of the groundwater to discharge outside the watershed boundary.

Shallow groundwater in the stratified drift was sampled at SL100, screened at a depth of 2.5 m and located just up gradient from the 'sedge' wetland. The shallow groundwater here was dilute and acidic (pH 4.69; ANC -4 µeq/L). Calcium (20 µm/L) and Na (24 µm/L) were the dominant base cations while SO_4 (61 µm/L) was the dominant anion. The chemistry of the groundwater at this location is likely influenced by several factors. First, the piezometer is located in a recharge area where the water has a very short residence time, as this site is only 15 m upgradient from SL700, the piezometer with the shortest residence time (73 days). Second, sediment here is well-sorted sand with low specific surface area, reducing mineral weathering rates. Finally, the low pH and ANC may, in part, be due to oxidation of Fe^{2+} produced in the wetland. Sediment collected during installation of the piezometer shows a prominent red staining.

SL100 is at the upstream end of the piezometer transect orientated along a flow line through the 'sedge' wetland. Concentrations of Ca, $SiO_{2\ aq}$ and pH increase with downgradient distance (Figure 6-10) but there is no significant change in sodium concentrations. These increases are likely due to mineral weathering reactions given the increase in mean residence time along the flow line from 73 days at SL700 to 131 days at SL800 (Table 6-1). Burns, et al. (2003) similarly noted a positive correlation between age of riparian groundwater and Ca, Na, and $SiO_{2\ aq}$ concentrations at the Panola Mountain Research Watershed that they interpreted to be the result of weathering of plagioclase feldspar (Burns, et al., 2003). Here the observed ratio of Ca/ $SiO_{2\ aq}$ (0.39; r^2=0.95) is similar to that that would result from congruent weathering of plagioclase feldspar of An_{85} composition. This is too mafic a composition for plagioclase feldspar in the underlying hornblende granitic gneiss. April and Newton (1983 and 1985) found that, in the Adirondacks, hornblende was the major source of Ca from primary mineral weathering. Hornblende stoichiometry predicts a Ca/ $SiO_{2\ aq}$ ratio of 0.29 which is still significantly lower than the observed 0.39. This suggests that either the weathering reaction was incongruent (April et al., 1986) or perhaps there was an additional source of Ca.

Weathering rates can be estimated by dividing the increase in solute concentration along a groundwater flow line with the change in mean residence time along the line. The release rate for Ca and Si $O_{2\ aq}$ is higher than that observed by Burns, et al. (Burns, et al., 2003) at Panola Mountain in Georgia. Release rates at Panola ranged from 1.3mg/L yr for $SiO_{2\ aq}$ to 0.3mg/L yr for Ca. It is possible to estimate the release rates from the sedge wetland by comparing the change in concentration with distance along a flowpath with the change in mean residence time of groundwaters at each piezometer as a function of distance. The results show a release rate for Ca of approximately 18mg/L yr and $SiO_{2\ aq}$ of approximately 66mg/L yr. Although it is expected that the fresher mineral surfaces in the Adirondacks might yield higher weathering rates, uncertainties with respect to the residence time calculations make these results somewhat questionable.

Groundwater in riparian wetlands had lower $SiO_{2\ aq}$ concentrations than that observed in the 'sedge' wetland. Concentrations of $SiO_{2\ aq}$ were highest in piezometers located directly adjacent to the stream (SL500, SL2001) while those located on the upland side of the wetland were lower

(SL200, SL2002). Fluctuations in $SiO_{2\,aq}$ concentrations at SL500 paralleled changes observed in the inlet stream except the groundwater concentrations were approximately 100 µmol/L higher. Similarly, along the transect from SL2002 and SL2001 to the stream, it was found that the lowest $SiO_{2\,aq}$ concentrations were in the stream with an intermediate concentration at SL2002. The higher concentrations immediately adjacent to the stream are likely due to an upflux of deep groundwater.

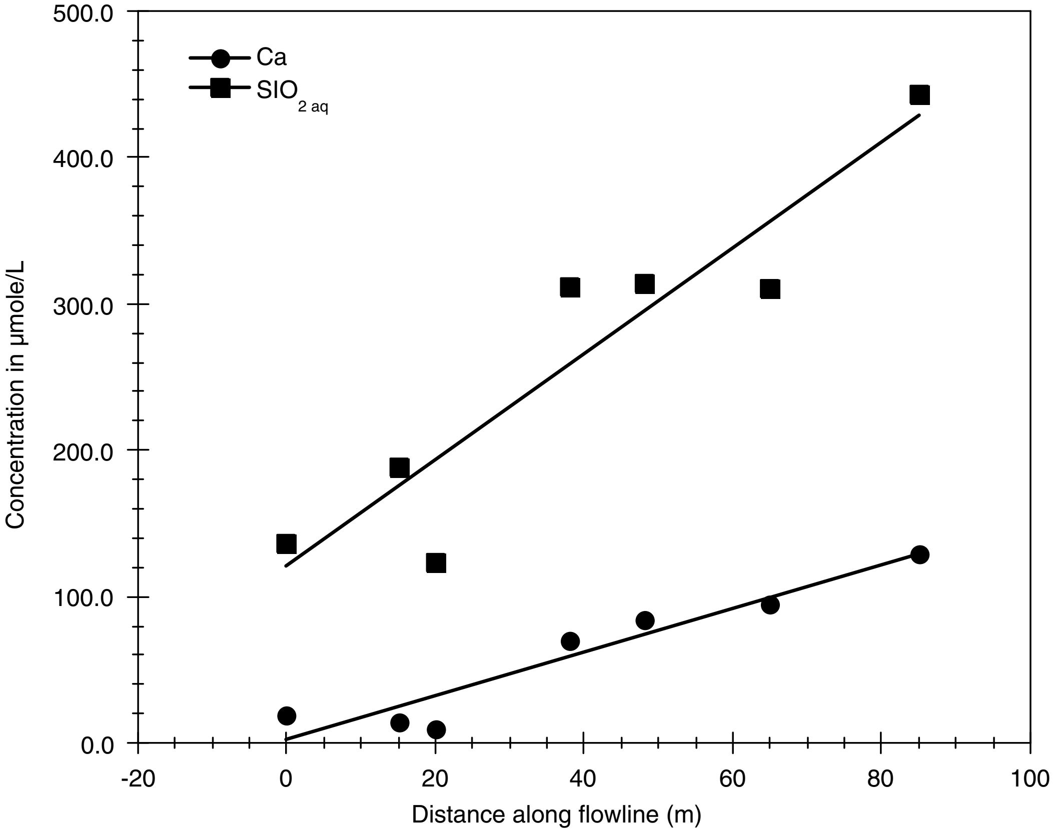

Figure 6-10. **The concentrations of Ca and $SiO_{2\,aq}$ increase in the direction of flow moving from SL100 to SL900. Linear regressions are Ca = 2.41 + 1.49 x distance (r^2= 0.91) and $SiO_{2\,aq}$ = 120.6 + 3.62 x distance (r^2 = 0.87).**

During the summer, SO_4 concentration decreased across the riparian wetland from a high of approximately 55 µm/L at SL2002 to 45 µm/L at SL2001 to 35µm/L at the stream. The odor of reduced sulfur was observed at both of the piezometers located directly adjacent to the stream (SL2001 and SL500).

Dissolved oxygen was at least partially depleted from all wetland piezometers. Values ranged from a high of 10.3mg/L at SL700 to a low of 0.52mg/L for the deep piezometer in the 'shrub' wetland. Riparian wetland values were generally lower than those found in the 'sedge' wetland (Table 6-2)

Table 6-2.
Average chemical composition of groundwater and surface water samples taken from the piezometers and adjacent stream

Site	pH	SD	ANC	SD	CB	SD	SO_4	SD	NO_3	SD	Cl	SD	$SiO_{2\,aq}$	SD	DO
Upland															
SL100	4.85	0.44	7.32	42.02	50.56	10.46	61.83	8.79	2.77	1.65	20.49	2.83	135.79	15.02	9.73
SL700	5.03	0.22	7	12.03	29.59	8.44	26.56	4.15	2.15	1.84	12	1.68	123.18	19.29	10.32
Sedge Wetland															
SL300	5.5	0.38	94.33	74.05	134.11	24.93	55.53	10.86	125.34	101.49	17.93	4.56	313.85	89.98	3.84
SL400	4.97	0.2	32.5	43.84	113.25	32.27	49.62	5.4	121.97	70.62	16.08	4.77	311.93	27.67	4.91
SL600	4.9	0.15	15.1	16.34	41.26	9.45	33.88	8.58	7.45	6.32	13.3	8.07	188.36	19.67	7.9
SL800	5.27	0.64	58	71.75	150	51	60.41	10.82	158.79	164.34	19.37	7.82	310.06	44.85	5.74
SL900	6.33	0.42	464.2	127.64	237.43	66.29	11.72	10.79	3.45	4.05	20.25	18	442.91	30.86	1.71
Shrub Wetland															
SL1000S	4.55		51		156.86		69.75		20.08		23.98		170.03		
SL1000D	5.8	0.43	223	73.08	132.75	26.43	0.9	0.78	2.1	2.18	13.26	0.75	512.75	12.26	0.52
Riparian Wetland															
SL200	5.12	0.21	13.6	11.23	108.99	12.4	90.28	12.92	4.98	3.66	22.82	6.95	184.01	12.32	1.78
SL500	5.32	0.47	94.9	110.12	62.27	16.29	45.18	17.24	3.11	4.4	22.54	7.73	352.75	82.78	2.08
SL2001	5.6	0.39	57.33	27	83.86	12.11	44.21	5.74	6.02	5.07	11.99	3.77	211.97	29.09	
SL2002	5.58	0.3	46.2	22.31	83.16	11.7	48.51	5.31	3.03	2.45	11.11	1.29	188.23	40.74	
Surface Waters															
Inlet	5.62	0.53	39	34.49	95.13	21.13	39.49	8.93	8.57	6.8	14.52	9.62	134.71	64.13	9.25
Outlet	5.72	0.51	41.5	36.05	88.18	12.86	43.81	15.5	11.21	8.92	12.92	4.81	119.78	41.49	

All concentrations in µmoles/L except pH, ANC (µeq/L) and DO (dissolved oxygen – mg/L).
CB= sum of base cations, SD is the standard deviation of the mean when more than three samples averaged.

6.3.7 Wetland Mercury Concentrations

Groundwater THg concentrations were highly variable across the wetlands but generally higher than THg observed in surface waters (Table 6-3). The lowest average concentration (1.90 ng/L) was observed in the deep piezometer located in the 'shrub' wetland while the highest average concentration (40.08 ng/L) occurred in piezometer SL2002 located in an alder dominated riparian wetland. There were extreme temporal variations in the concentration of THg at this location. Concentrations exceeded 100 ng/L at three times during the summer of 2001 then dropped to below 10 ng/L by the end of the summer of 2002. Although other samplers showed similar temporal trends none had the extremely high THg found at this site.

Table 6-3.
Average Mercury and DOC concentrations at mercury sample sites in wetlands and adjacent surface waters.

Piezometer	Hg Sampler	n	DOC	SD	THg	SD	MeHg	SD
Upland								
SL100	P1	8	0.95	0.67	5.91	3.70	0.17	0.26
Sedge Wetland								
SL600	P2	9	2.57	0.96	3.21	2.64	0.18	0.29
SL400	P3	7	2.20	1.14	2.56	1.90	0.33	0.63
SL800	P4	6	2.98	0.75	28.01	24.01	0.21	0.18
SL900	P5	8	3.64	2.47	3.87	2.20	0.61	0.86
SL300	P7	7	2.35	1.01	33.17	60.17	0.30	0.55
Average for Sedge			2.75	1.34	13.81	29.82	0.28	0.44
Fringe Wetland								
SL1100	P8	9	16.44	6.97	4.24	1.77	0.35	0.42
Shrub								
SL1000s	P9	7	13.57	3.86	20.68	16.33	0.54	0.53
SL1000d	P10	9	15.23	1.83	1.90	1.25	0.21	0.23
Average for Shrub			14.40	2.98	10.57	14.38	0.38	0.43
Riparian Wetland								
SL500	P6	5	27.07	19.86	18.62	15.49	7.98	3.70
SL500	RWN1	9	9.76	10.14	22.98	10.95	5.37	1.24
	RWF1	9	12.05	13.59	27.60	38.79	1.15	1.09
SL2001	RWN2	9	2.82	1.61	20.12	22.32	0.77	0.57
SL2002	RWF2	7	2.60	2.09	40.08	42.63	1.03	0.81
Average for Riparian			7.00	10.35	21.15	26.16	2.96	3.87
Surface Waters								
Inlet	Inlet 2	45	7.34	3.44	3.95	2.17	0.75	0.83
Lake	Lake	38	7.04	2.78	3.64	1.74	0.86	1.12
Outlet	Outlet	49	6.60	2.27	3.57	1.58	0.83	1.26
Average for Surface Waters			7.01	2.85	3.73	1.83	0.83	1.10

All concentrations in nanograms per liter except Dissolved Organic Carbon (DOC) which is in ppm carbon per liter. SD= standard deviation of the mean. MeHg is methylmercury.

Groundwater in riparian wetlands had the highest THg concentrations of all the wetlands sampled. The average of 21.15 ng/L was significantly higher than that observed for the 'sedge' (13.81 ng/L), 'shrub' (10.57 ng/L) and 'fringe' (4.24 ng/L) wetlands (Table 6-3). The average THg concentration of riparian wetland groundwater was over 5 times greater than the average

THg concentration in surface waters. Seasonal variations in the surface water samples for THg and MeHg are discussed in Chapter 4.

Groundwater in the riparian wetlands also had the highest MeHg concentrations with one sampler (SL500), located directly adjacent to the stream, having an average concentration of almost 8 ng/L MeHg. This sampler (at SL500) was relocated to a site approximately 2m away from its original position during June of 2001. Although concentrations dropped, the newly positioned sampler still had an average MeHg concentration of 5.37 ng/L. At 4 of the 5 riparian wetland sites, the concentration of MeHg in the groundwater averaged above 1 ng/L (Table 6-3). Concentrations of MeHg in other wetland areas were much lower, with none averaging more that the 0.83 ng/L observed in the surface water.

6.4 Discussion

Riparian wetlands in this study were hotspots of THg accumulation and MeHg production. McClain, et al. (2003) defines biogeochemical hot spots as areas of disproportionately high biogeochemical reaction rates that commonly occur at the boundary or ecotone between two landscape features. These high reaction rates are often sustained by converging hydrologic flow paths where each carries materials essential to the reaction. The riparian wetlands in the Sunday Lake watershed receive water from three different sources, and biogeochemical reactions that result from the interactions of these different waters account for the high Hg levels.

Riparian wetlands can accumulate THg during high flow events through the deposition of Hg-rich sediment, although data to prove this hypothesis were not obtained in this study. Particulate matter often carries important fractions of mercury loads in terrestrial runoff, since mercury sorbs to clays and organic matter. Flooding of riparian wetlands during high flow events can deposit POC on the surface and bank storage can deposit it in the subsurface. The net result is accumulation of THg and, in addition, this POC can serve as a nutrient base for microbial activity. Increasing the available carbon increases the microbial activity needed for methylation (Regnell, 1994).

The riparian groundwater zone is the saturated zone beneath the riparian wetland where microbial reactions with organic carbon have reduced dissolved oxygen concentrations. The zone exists as a diffuse lens, transitioning downward into oxygen-rich upland groundwater at depth. The flow in both is toward the stream during base flow conditions.

Sulfate reducing bacteria are important contributors to the methylation of inorganic mercury (Gilmour, et al, 1992). Increasing SO_4 stimulates methylation (Benoit, et al., 2003). The riparian groundwater zone sits atop a large SO_4 source in the form of the upland groundwater moving to the stream. Fresh SO_4 can be brought into the riparian zone through evapotranspiration-induced upflux. The importance of groundwater upwelling to MeHg production was described by Branfireun (Branfireun, et al, 1996). The topographic position of the riparian wetlands, relative to the surrounding stratified drift uplands, makes it likely that upwelling also occurs during significant recharge events associated with major rain events and spring snow melt. It is likely that infiltration recharge is inhibited during events that displayed Lisse effects in the riparian piezometers. Formation of the saturated cap that compresses air in the vadose zone inhibits further infiltration, stimulating runoff. The non-Lisse effect rise in piezometer water levels is most likely due to upwelling.

Riparian wetlands are unique in that they receive water from both the stream and from upland groundwater and it is the ready mixing of these two sources that enables the wetlands to be an ecological hotspot for mercury methylation.

6.5 Conclusion

Wetlands are an important source of MeHg in Adirondack watersheds, but not all wetlands are of equal importance. Hydrologic factors explain why riparian wetlands produce more MeHg than other wetland types. Access of wetlands to upland groundwater and surface water appears to be a critical factor. Where wetlands are isolated from underlying upland groundwater by a catotelm in peatlands, for example, SO_4 and nutrient deficiencies can develop that lessen MeHg production. Even where there appears to be no isolating layer, such as in the ‘sedge’ wetland of this study, the lack of a mechanism to bring upland groundwater into the wetland prevents high methylation rates. The residence time of groundwaters in these wetlands is relatively short at least as compared to the average residence time of water in the stream, but there is time for weathering reactions to occur that release Ca and SiO_2 and raise the pH. In watershed systems, MeHg has been found to increase with decreasing pH (Driscoll, et al. 1995) so it is also possible that the increase in pH along the groundwater flow path reduces the rate of MeHg production.

Groundwater in riparian wetlands has the highest MeHg concentrations ultimately because of interactions between the riparian wetland water and the stream and upland groundwater. The stream deposits organic carbon that serves as a carbon source for methylating sulfate reducing bacteria. During the growing season, evapotranspiration of riparian vegetation creates an upflux that draws fresh supplies of SO_4 into the riparian groundwater zone allowing for the maintenance of high methylation rates. The distribution of riparian wetlands may help explain variations in MeHg concentrations observed in watersheds across the Adirondacks.

7 Characteristics and Hg Behavior within an Adirondack Wetland

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7.1 Introduction

The role of wetlands in MeHg dynamics is uncertain, in part, because 'wetlands' is a generic term for a diverse group of neither terrestrial nor aquatic systems. As shown in Chapter 6, concentrations of total and methylmercury varied among different types of wetland habitats present in the Sunday Lake watershed. Hg dynamics in four contrasting wetlands in the Sunday Lake watershed were investigated to identify wetland characteristics associated with microbial activity and inorganic Hg(II) levels, both of which affect MeHg production. Factors examined included: (i) soil characteristics and rates of microbial activity at different depths in the wetland soils; and (ii) solute chemistry in soil waters. The relative activity of microorganisms in a soil can be elucidated using metabolic inhibitors (Oremland and Capone, 1988). For instance, molybdate is a specific inhibitor of SO_4^{2-} reduction (Oremland and Silverman, 1979), whereas 2-bromoethane sulfonate (BES) targets methanogenesis (Zinder, et al., 1984). Chloroform ($CHCl_3$) inhibits several anaerobic microorganisms, including acetate-using SO_4^{2-} reducers and methanogens (Scholten, et al. 2000). Methyl fluoride (CH_3F) is a specific inhibitor of acetate-using methanogenesis (Frenzel and Bosse 1996). Acetate-using SO_4^{2-} reducers have the largest Hg methylation rates (King, et al. 2000).

We collected soil solutions approximately monthly to characterize conditions during high water yields and low-flow conditions. We hypothesized that riparian wetlands would be especially large sources of THg and MeHg due to their position between uplands and surface waters. We also expected that riparian wetlands would have thinner soil leading to more bioavailable Hg(II) and less soil trapping and Hg retention. Riparian wetlands should be flushed regularly with surface water and/or ground water, which would help stimulate microbial metabolism by removing toxic products and bringing in fresh reactants.

7.2 Methods

Wetland is a generic term to describe systems that are flooded at least periodically, dominated by plants that tolerate flooding, and have hydric soil. Wetlands are usually associated with large, flat, poorly drained landscapes, although they can occur on fairly steep slopes if fed regularly by surface water or ground water. There are several systems for naming and classifying wetlands, but no single system is used universally. We identified four contrasting wetland types based largely on the traditional system of Cowardin, et al. (1979): fringe, shrub, sedge, and riparian.

The ‘fringe’ wetland was a floating mat over the edge of Sunday Lake. The soil was >8 m deep. Vegetation was an open cover of ericaceous shrubs (*Ledum groenlandicum*, *Chamaedaphne calyculata*) with a continuous ground cover of *Sphagnum* mosses. There were open pools of water on the wetland surface throughout the year, indicating that the water table was always near the surface vegetation.

The ‘shrub’ wetland was located at the base of an upland esker. A narrow open-water trench (lagg) divided the peat soil and esker. The soil was >11 m deep. Vegetation was a dense cover of myrtle (*Myrica gale*). Ground cover was discontinuous cover of *Sphagnum* mosses. There was evidence of ephemeral rivulets running from the esker across the wetland surface. However, we did not observe flow in these channels, suggesting that only large flood events send surface water across the soil surface. The wetland had open pools of water soon after snowmelt, but the pools drained by mid August, indicating that the water table dropped below the surface vegetation in mid summer.

The ‘sedge’ wetland was located between the shrub wetland and a second-order tributary stream that drained into the lake. Soil was only 45cm deep with sand beneath. Vegetation was a dense cover of *Carex* sp. sedges. The major source of water appeared to be ground water, although flooding across the wetland surface occurred at snowmelt and possibly in summer associated with large thunderstorms that increased stream flow.

The ‘riparian’ wetland was sandwiched between the banks of a second-order stream and an esker with upland forest. Soil was only 20cm deep with sand and cobbles beneath. Vegetation was mostly *Carex* sedges, although speckled alder (*Alnus rugosa*) was present in small, dense patches. Water was a mixture of interflow plus groundwater derived from the esker, although there was evidence of frequent over bank flooding.

7.2.1 Soil Sampling and Analyses

We collected three replicate soil cores per site using a Russian-style, side-cutting peat corer. The cores were divided into 10-cm depth intervals in the field, each of which was placed into a separate plastic bag. The bags were taken to Cornell University, and processing began 24 hours after collection. Each section was weighed at field moisture content before a known volume was removed, dried at 105°C, and reweighed to estimate moisture content and bulk density. A small portion of the dried sample was combusted at 550°C to determine loss on ignition (LOI).

The remaining soil was mixed and woody pieces larger than 0.5cm diameter were removed. A 5-g portion of field-moist soil was mixed with 5 mL of de-ionized water and pH (pH_{H2O}) was measured using an electrode. A second 5-g portion was mixed with 5 mL of 1 mol/L KCl and pH (pH_{KCl}) was measured. The degree of soil humification was determined by the pyrophosphate index (Kaila, 1956). One hundred mg of soil was extracted in 10 mL of 0.025 mol/L sodium pyrophosphate for 18 hr. After extraction, the solution was centrifuged and 5 mL of solution was diluted to 25 mL in distilled water. The absorbance of the solution was measured at 550 nm on a variable wavelength spectrophotometer. The absorbance is an index of humification.

We quantified rates of microbial activity using an *in vitro* incubation technique described in detail in Yavitt and Lang, (1990). Briefly, a separate 50 - 60 g portion of field-moist soil was taken and placed into a 125-mL Erlenmeyer flask along with 10 to 25 mL Milli-Q water. The flask was sealed immediately with a red-rubber stopper (Subaseals, Aldrich Chemical Company, Inc., Milwaukee, Wisconsin), and the headspace exchanged three times with O_2-free N_2 to establish anoxic conditions. Flasks were incubated for 48 hours at 21°C, and gas samples were removed at 0, 8, 24 and 48 hours using syringes fitted with needles and three-way stopcocks. To avoid changes in headspace pressure, 10 mL of O_2-free N_2 was injected into the flask prior to removing the 10 ml sample. Concentrations of CH_4 and CO_2 in the gas samples were quantified using a gas chromatograph equipped with a thermal conductivity detector for CO_2 and a flame ionization detector for CH_4. Gases were separated on a Poropak-R column using He carrier gas. Gas chromatograph temperatures were 50°C for the oven, 100°C for the injector, and 180°C for the detector. Gas concentrations were corrected for the amount that remained dissolved in soil water using a variation of Henry's Law (Flett, et al., 1976) and temperature dependent Bunsen coefficients for CH_4 (Yamamoto, et al, 1976) and CO_2 (Wilhelm, et al., 1977). At the completion of the incubation period, the headspace volume in each flask was determined gravimetrically by adding water to fill the flask. Dry matter was determined by drying the soil to a constant mass at 70°C. Production rates are reported as moles of gas per gram dry matter.

A second set of soil samples was used to examine microbial activity with added SO_4^{2-} plus ethanol. Previous research indicated that ethanol stimulated CH_4 production (Coles and Yavitt, 2002) and many non-marine SO_4^{2-} reducers use ethanol (Laanbroek and Pfennig, 1981). The flasks were established as described above, and we added SO_4^{2-} to a final concentration of 0.25 mmol/L using a Na_2SO_4 solution and ethanol to a final concentration of 0.24mmol/g.

Concentrations of NH_4^+ and NO_3^- were determined on separate 5-g portions of soil per sample by extracting in 50 mL of 2 mol/L KCl. The soil and solution were shaken for one hour, and after standing overnight, the liquid was removed for colorimetric estimations of NH_4^+ and NO_3^- (NO_3^- after cadmium reduction to NO_2^-). A second 5-g portion was placed into a separate plastic cup, covered with a lid that had a hole to allow aeration and incubated in the dark at 20°C for 14 days. Each cup was weighed every other day to check for water loss, which was replaced as necessary. Following incubation, NH_4^+ and NO_3^- were extracted as described above. Net N mineralization was calculated as the sum of NH_4^+ and NO_3^- (mg N/kg dry soil) in the incubated soil (final) minus NH_4^+ and NO_3^- in the soil prior to incubation (initial). Net nitrification was final NO_3^- minus initial NO_3^-.

7.2.2 Soil Solution Sampling and Analyses

Soil water was collected using custom-fabricated tension Teflon lysimeters installed permanently in each site. The lysimeters were installed into auger holes with the collecting tip placed immediately below the soil in the sedge and riparian wetlands, and 6 m deep in the fringe and shrub wetlands. The auger holes were filled with soil and the lysimeters were allowed to equilibrate seven months before the first collection. We installed five collectors in the riparian wetland, four in the sedge wetland, one in the fringe wetland, and one in the shrub wetland. There was a second collector in the shrub wetland that captured soil water near the soil surface, and it was sampled only during the spring snowmelt period.

The lysimeters were sampled using a hand pump, and water was collected in acid-cleaned 2.5-l glass bottles. A portion of the water sample was transferred to 500-ml Teflon bottles. Clean collection procedures were used at all times. Water samples for Hg analyses were acidified in the field using 0.4 percent by volume HCl, double-bagged, and packed on ice packs for transport to the laboratory. These samples were stored in a dark 4^oC cooler until analysis.

Total mercury was determined after acid oxidation and reduction to Hg^o. The Hg^o was analyzed by cold-vapour atomic fluorescence spectroscopy (CVAFS) following EPA Method 1631.

Analysis of MeHg used CVAFS following acidic chloride digestion and sub-boiling distillation. The distillate was buffered with 200 µl of sodium acetate buffer, ethylated with 100 µl of sodium tetraethyl borate ($NaBEt_4$) and reacted for 15 minutes. Following distillation, the Hg species were purged with ultra high purity N_2 and trapped on Tenax TA. Mercury was thermally desorbed from the Tenax TA in an ultra high purity N_2 stream, speciated chromatographically, and combusted to Hg^o in a pyrolytic column before analytical detection with a Brooks Rand Model III CVAFS.

Water samples were analyzed for concentrations of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) by Atomic Absorption Spectroscopy and for concentrations of strong acid anions (NO_3^-, SO_4^{2-}, Cl^-, F^-) by ion chromatography. Solution pH was determined potentiometrically with a combination electrode. Ammonium was determined colorimetrically using the phenate method on a continuous flow analyzer. Dissolved organic carbon was determined by persulfate enhanced ultraviolet oxidation followed by infrared detection (IR). Dissolved inorganic carbon was measured by acidification followed by IR detection of CO_2. Total (Al_m) and organic (Al_o) monomeric Al were determined analytically using the method of Driscoll (1984). The concentration of organic anion (OA^-) was calculated by an electroneutrality approach as the anion deficit (Driscoll, et al. 1994b), i.e., the sum of inorganic cations minus the sum of inorganic anions. This approach assumes that all of the inorganic solutes contributing to charge balance have been measured analytically so that unanalyzed OA^- accounted for the discrepancy in electroneutrality.

Concentrations of inorganic Al_i were calculated as the difference between Al_m and Al_o. The Al_i charge (Al^{n+}) was determined as the sum: $3[Al^{3+}] + 2[AlOH^{2+}] + [Al(OH)_2^+] + [AlF^{2+}]$. These inorganic Al species were calculated by an approach combining mass balance and chemical equilibrium using the thermodynamic data presented in Driscoll (1984).

7.2.3 In vitro Incubation Experiment

A more extensive incubation experiment was done using soil from the riparian wetland to elucidate several microbial processes. A bulk soil sample was collected in September 2002, and within 24 hours of collection was divided into 108 replicate portions. Each was prepared for *in vitro* incubation as described above. These were randomly assigned to one of four groups, i.e., 27 portions per group. One group was amended with 10 mL of distilled, de-ionized water; the second group received SO_4^{2-} as Na_2SO_4 (1mmol/L final concentration); the third group received ethanol (2mg C/g soil); and the final group received SO_4^{2-} plus ethanol.

Following these treatments, the jars incubated for seven days before a second set of nine treatments was applied to each group. The treatments were applied to three jars per group: distilled, de-ionized H_2O control; MoO_4 to inhibit SO_4^{2-} reduction; BES to inhibit CH_4 production; $CHCl_3$; CH_3F to inhibit acetate-utilizing methanogens; $CHCl_3$; MoO_4 plus BES; MoO_4 plus CH_3F; MoO_4 plus $CHCl_3$; and, MoO_4, CH_3F plus $CHCl_3$. The MoO_4 was added as Na_2MoO_4 to a final concentration of 5mmol/L. The BES was a final concentration of 10mmol/L. The $CHCl_3$ had a final concentration of 0.1mmol/L.

7.2.4 Statistical Analyses

We used repeated measures analysis of variance (ANOVA) to analyze the effect of wetland type and depth on soil characteristics. The repeated measure is necessary because sampling occurred at various depth intervals in the same soil core, and thus depth was a fixed repeated measure or within-subjects effect. Wetland type was a fixed between-subjects effect, and replicate cores per wetland type were a random effect nested in wetland type. We also used repeated measures ANOVA to analyze differences in solute chemistry of soil solutions. Analyses were done separately for each solute, wetland type was the between-subjects effect, and date was the within-subjects effect.

7.3 Results

7.3.1 Soil Characteristics

Soil in the four wetlands was organic rich (>85 LOI) and had low bulk density (< 0.35 g/cm^3) in the top 15 to 25cm of the soil profile (data not shown). We sampled to >6.5 m in the fringe wetland and encountered organic-rich, low bulk density peat throughout the entire depth profile. In the shrub wetland, the soil was mostly organic rich, except for the presence of distinct buried sand and gravel layers often 10cm thick. For instance, there was a prominent gravel layer 55 to 65 cm below the surface in the core we used for chemical and microbiological analyses.

Soil pH_{H2O} was <4.75 in the top 50cm, except for significantly less acid soil pH in the fringe wetland (Figure 7-1). Soil pH_{H2O} increased progressively with depth in the fringe wetland. The pH measured in KCl solution includes H^+ on soil exchange sites, and pH_{KCl} was 0.5 to 1.5 units lower than pH in water indicating a large net negative charge on the exchange sites (data not shown). The pyrophosphate index (Figure 7-1), which indicates organic matter decomposition, was greater in surface soil and decreased with depth. The index was significantly greater ($P < 0.01$) in soil from the sedge and shrub wetlands than in soil from the other two sites.

The riparian and sedge wetlands were distinguished from the other two sites by significantly greater ($P < 0.01$) rates of net N mineralization and net nitrification in the top 15cm (Figure 7-2). Net N mineralization occurred sporadically in deeper soil in the other two sites, although net nitrification was restricted to the top 30cm.

The largest rates of CH_4 production and anaerobic CO_2 production in each wetland occurred in the top 25cm (Figure 7-3). We encountered large variation in gas production rates among seemingly replicate samples. For example, the coefficient of variation calculated using the uniformly minimum variance unbiased estimator (Method 3 in Parkin et al., 1988) for gas production rates per depth interval was frequently > 100 percent, indicating non-normally distributed data. Therefore, we used the geometric mean rather than the arithmetic mean as an estimate of central tendency in a data set. The geometric mean corrects for data showing a lognormal distribution (Parkin and Robinson, 1993). Soil in the fringe wetland supported significantly ($P < 0.5$) greater rates of CH_4 production, and the shrub wetland had low rates of anaerobic CO_2 production throughout most of the deep soil.

Our indirect assay for SO_4^{2-} reduction revealed increased rates of anaerobic CO_2 production in soil with added SO_4^{2-} for only three soil cores, and only in the 0-10cm depth interval in each of those soil cores. Two of the cores were in the sedge wetland (30 percent increase and 23 percent increase in anaerobic CO_2 production), and the third core was in the in fringe wetland (27 percent increase). These were the three cores taken closest to the lake or tributary, excluding the riparian soil cores. The added SO_4^{2-} in the riparian soil produced an unexpected response: no change in rates of anaerobic CO_2 production, but 20 to 60 percent greater CH_4 production rates. We repeated this experiment three times with freshly collected soil on three dates and found the same SO_4^{2-} stimulated rates of CH_4 production.

7.3.2 Solute Chemistry

Solutions had acidic pH, and site means were statistically similar (Table 7-1). Mean concentrations of dissolved cations showed a 2 to 3-fold difference among sites. The sum of cations, on a charge basis, was greater in the sedge and shrub wetlands (260 µeq/L) than in the riparian wetland (190 µeq/L) and fringe wetland (140 µeq/L). Mean concentrations of Cl^- were relatively uniform among sites, whereas NO_3^- concentrations were significantly greater ($P < 0.05$) in the sedge wetland and SO_4^{2-} concentrations were larger in the fringe wetland and shrub wetland. Concentrations of DOC and ANC were much greater in the fringe and shrub wetlands than in the riparian and sedge wetlands. Water in the shrub wetland had the greatest concentrations of OA-.

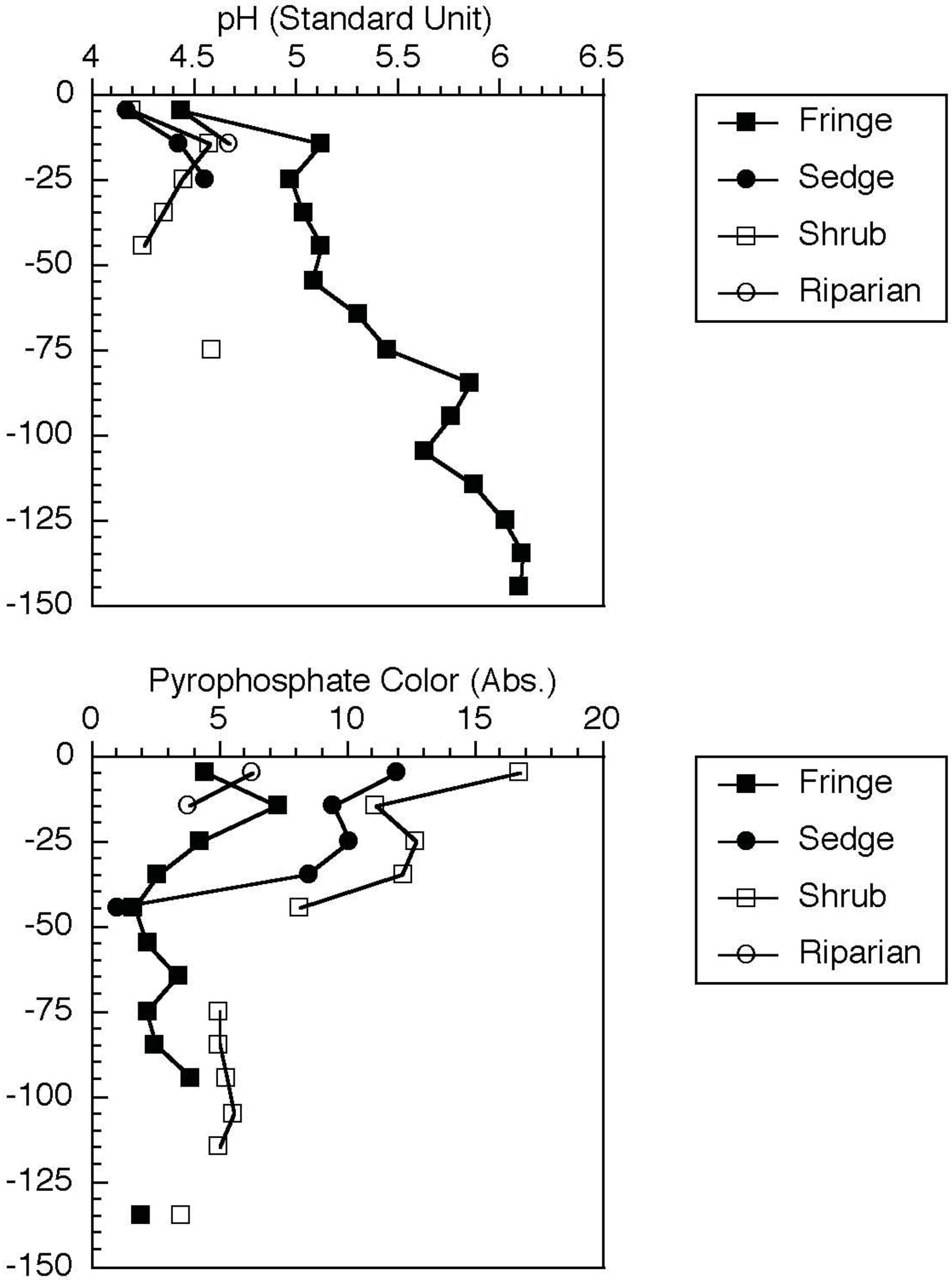

Figure 7-1. Vertical profiles of pH and pyrophosphate adsorption in soil from four wetlands in the Sunday Lake catchment, New York State, - The vertical axis is depth below ground surface in cm.

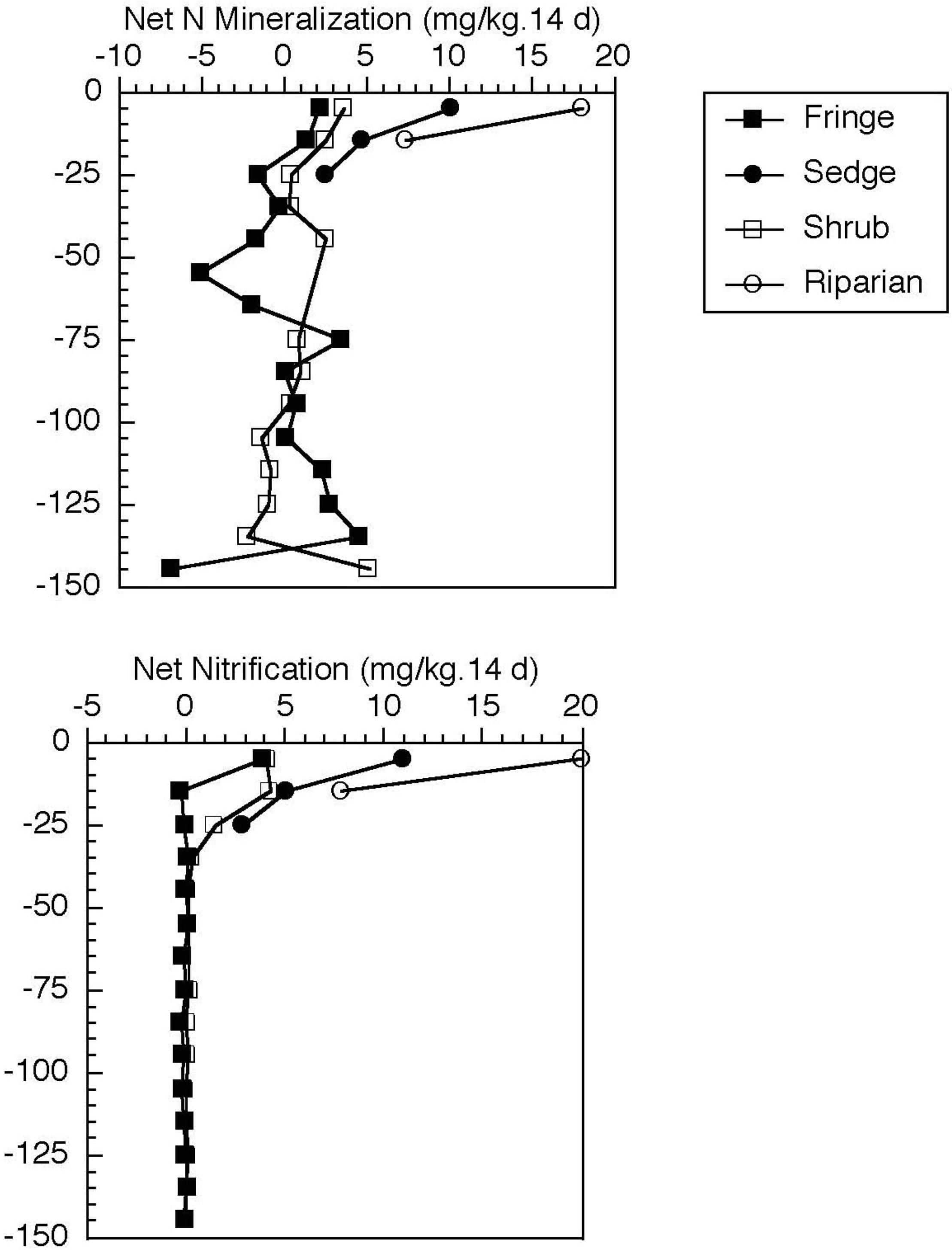

Figure 7-2. Vertical profiles of net N mineralization and net nitrification in soil from four wetlands in the Sunday Lake catchment, New York State —The vertical axis is depth below ground surface in cm.

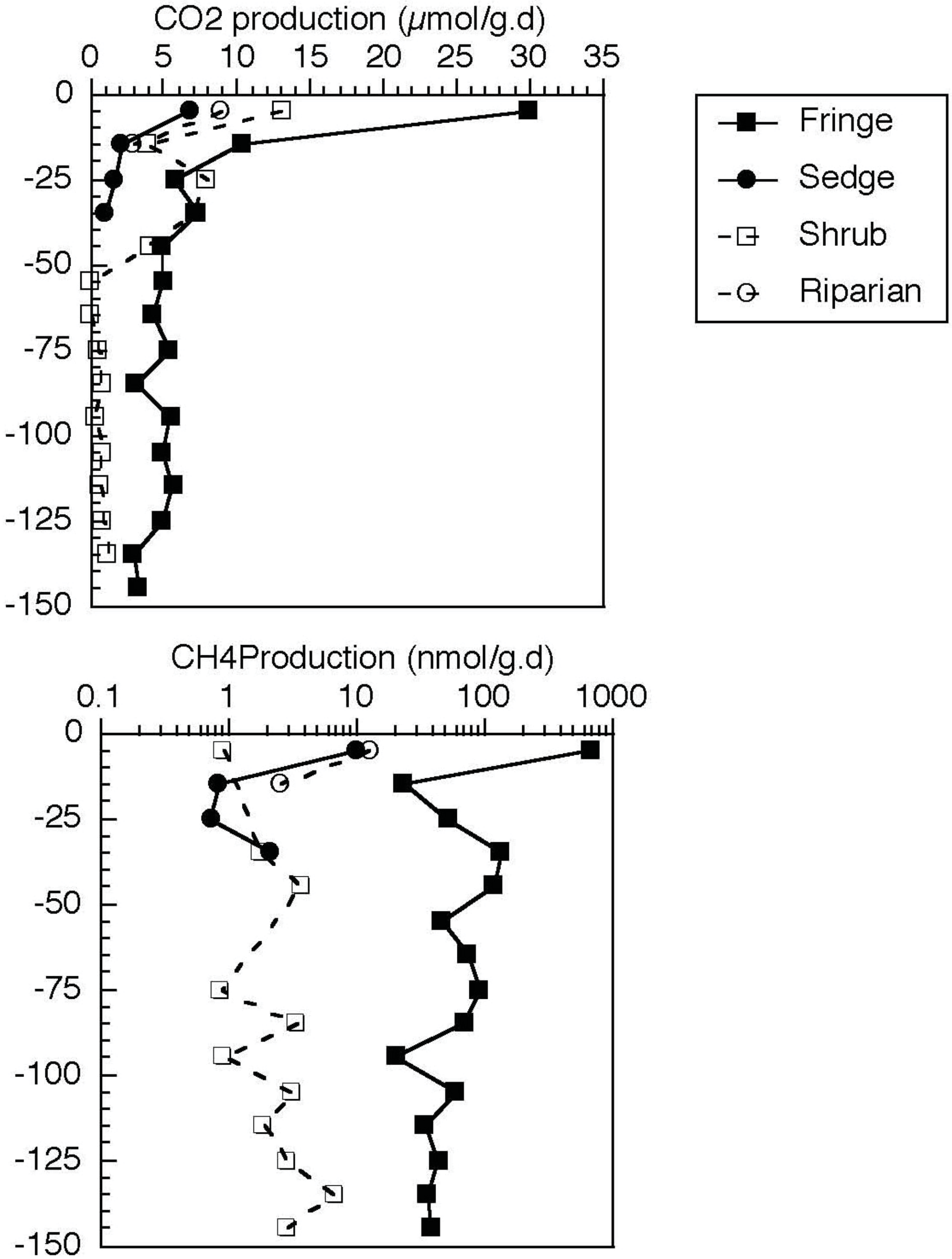

Figure 7-3. **Vertical profiles of anaerobic CO_2 production and net CH_4 production in soil from four wetlands in the Sunday Lake catchment, New York State—The vertical axis is depth below ground surface in cm.**

Table 7-1.
Mean solute concentrations in soil solutions, based on one collector each in fringe and shrub wetlands; four collectors in the sedge wetland; and five collectors in the riparian wetland—Values are mean with 1 S.E. in parentheses (below).

Wetland	pH	DOC	ANC	THg	MeHg	Ca	Mg	K	Na
Fringe	5.05	16.44	96.3	4.24	0.35	43.8	11.5	4.3	15.2
Sedge	4.95	2.79	27.0	16.90	0.37	81.2	17.3	11.2	26.5
	(0.26)	(0.33)	(19.8)	(7.90)	(0.09)	(3.0)	(4.9)	(3.1)	(0.9)
Shrub	5.49	15.23	152.4	1.90	0.21	54.8	21.8	10.2	45.6
Riparian	5.20	8.56	31.2	34.37	3.51	37.2	9.9	11.8	42.6
	(0.11)	(3.67)	(13.5)	(17.2)	(1.58)	(6.5)	(1.2)	(2.0)	(8.3)
	Cl	NO3	SO4	Ali	Alo	OA			
Fringe	11.40	6.7	17.9	3.08	6.33	91.20			
Sedge	10.13	100.0	55.2	12.45	2.04	52.21			
	(2.37)	(34.5)	(4.0)	(3.67)	(0.17)				
Shrub	16.50	0.0	7.8	3.13	8.05	184.78			
Riparian	13.20	7.3	43.6	3.65	2.60	53.52			
	(1.72)	(4.0)	(7.9)	(0.72)	(1.26)				

All values are μmol L^{-1} except ANC (μeq L^{-1}), DOC (mg L^{-1}) and THg and MeHg (ng L^{-1}).

The riparian wetland was distinguished from the other three sites by significantly greater ($P < 0.05$) concentrations of THg and MeHg. Concentrations of THg, but not MeHg, were greater in the sedge wetland than in the other two sites. The sedge and riparian wetlands also had lower concentrations of DOC, ANC and Al_{om}, and OA-. We found that MeHg was approximately 10 percent of THg, except for a lower value (2.2 percent) in the sedge wetland.

We compared solute chemistry during the spring snowmelt period (high flow) versus the combined summer and autumn period (low flow) to assess seasonal differences (Table 7-2). During high flow, soil solutions had less ANC, which was associated with lower concentrations of dissolved cations (12 to 50 μeq/L less charge). Mercury concentrations did not vary seasonally, except in the riparian wetland where concentrations of THg and MeHg were lower during high flow. Concentrations of DOC did not vary seasonally. Concentrations of Cl^- and NO_3^- were 40 to 60% less during high flow than low flow, except in the shrub wetland. The concentration of Al_i was much lower at high flow, except in the riparian wetland. As a result, OA^- generally decreased during high flow.

The collection of water near the soil surface in the shrub wetland, only at high flow, revealed an acidic solution with negative ANC, a large concentration of THg, but a low concentration of MeHg. The concentrations of base cations were quite large, and thus, the acidity was the result of large NO_3^- and SO_4^{2-} concentrations.

7.3.3 Riparian Soil

In vitro incubation of riparian soil showed no CH_4 production for the first 150 hours of incubation, followed by essentially exponential increase in CH_4 production after that. Addition of either BES or $CHCl_3$ inhibited CH_4 production completely (data not shown). The addition of either SO_4^{2-} or EtOH stimulated CH_4 production after the initial lag period, and the addition of both SO_4^{2-} and EtOH stimulated the most CH_4 production. Addition of CH_3F along with added SO_4^{2-} and EtOH reduced CH_4 production, indicating that some of the CH_4 production came from acetate.

Table 7-2.
Mean solute concentrations in soil solutions collected during high flow at spring snowmelt versus low flow in summer and autumn—Values are means across multiple collectors per wetland type.

	Flow	pH	DOC	ANC	THg	MeHg	Ca	Mg	K	Na
Fringe	high	5.35	19.70	41.9	5.55	0.33	41.0	11.1	5.4	16.2
	low	4.87	13.17	137.1	3.27	0.36	48.0	11.9	3.6	14.8
Sedge	high	5.00	2.54	18.4	17.17	0.26	71.0	14.4	11.5	24.0
	low	4.82	3.17	18.9	16.68	0.36	100.0	19.7	12.3	29.7
Sedge surface	high	4.59	13.57	-17.2	24.44	0.65	101.2	14.8	10.7	18.3
Shrub	high	5.45	14.50	134.6	2.73	0.11	57.5	21.0	11.3	41.0
	low	5.56	16.33	170.2	1.28	0.31	52.0	22.2	9.2	51.1
Riparian	high	5.02	6.70	8.1	13.92	2.72	35.0	9.5	8.2	31.0
	low	5.37	7.17	47.1	45.16	3.09	44.0	11.1	14.1	55.0

	Flow	Cl	NO3	SO4	Ali	Alo	OA
Fringe	high	7.70	0.87	21.80	0.97	7.86	79.8
	low	13.62	10.26	15.55	5.19	4.81	109.2
Sedge	high	7.37	84.78	53.82	10.84	1.81	39.3
	low	13.67	128.36	56.90	15.75	2.42	80.1
Sedge, surface	high	5.82	62.3	53.8	4.48	7.08	119.9
Shrub	high	18.70	0.00	15.12	1.27	8.44	165.8
	low	14.31	0.00	0.54	5.93	7.48	205.0
Riparian	high	10.56	5.29	45.09	4.71	2.00	41.6
	low	14.63	9.43	45.22	3.30	1.41	75.7

All values are μmol L^{-1} except ANC (μeq L^{-1}), DOC (mg L^{-1}) and THg and MeHg (ng L^{-1}).

At the onset of incubation, soil with no added SO_4^{2-} or EtOH showed a CO_2 production rate of 9.3 μmol g^{-1} d^{-1}. After that, the rate decreased by 17 percent (to 7.7 μmol g^{-1} d^{-1}) and stayed constant during the following 300 hours of incubation (i.e., basal CO_2 production rate). The addition of inhibitors did not affect CO_2 production in the soil incubated with no added SO_4^{2-} or EtOH (Table 7-3). The addition of SO_4^{2-} resulted in a 14 percent larger initial CO_2 production rate, which eventually declined to the basal CO_2 production rate. The addition of EtOH induced the largest initial CO_2 production rate, which also declined to the basal CO_2 production rate. Notably, the addition of MoO_4^{2-} with added EtOH decreased the initial CO_2 production rate by 27 percent, and the final rate decreased below the basal CO_2 production rate. This same pattern occurred in the soil with the addition of both SO_4^{2-} and EtOH, although rates of CO_2 production were lower than soil incubated with EtOH alone.

Table 7-3.
Rates of anaerobic CO_2 production per gram of soil from the riparian wetland in the Sunday Lake catchment, New York State, incubated *in vitro* with different solutes or inhibitors

		CO_2 (µmol g^{-1} d^{-1})	
Matrix	Inhibitor	Initial	Final
H_2O	None	9.3	7.7
SO_4^{2-}	none	10.6	7.0
Ethanol	none	16.7	7.7
	MoO_4^{2-}	12.2	5.2
	$CHCl_3$	12.6	4.8
	BES	7.2	6.5
	MoO_4^{2-} & BES	9.0	3.9
Ethanol & SO_4^{2-}	none	12.4	6.0
	MoO_4^{2-}	9.1	5.2
	$CHCl_3$	10.4	5.0
	BES	6.3	5.6
	MoO_4^{2-} & BES	9.9	4.6

7.4 Discussion

Knowing the characteristics of wetlands that influence concentrations of THg and MeHg helps to evaluate spatial and temporal patterns of Hg pollution in surface waters. The four wetlands studied had organic-rich peat soil material, and thus, these results are most comparable with wetland research done in northern wetlands that have developed peat soil (St Louis, et al., 1994; Bishop, et al., 1995a, 1995b; Branfireum and Roulet, 2002). Peat is particularly good at trace metal adsorption and retention (Wieder, 1990), and thus, peat soils should accumulate a relatively large Hg inventory. On the other hand, peat-forming processes can generate large amounts of DOC (Dalva and Moore, 1991), which bound to Hg can result in a soluble complex. Therefore, the role of wetlands in THg dynamics is uncertain. Peatlands that harbor anaerobic SO_4^{2-}-reducing bacteria have a clear role in the net production of MeHg, as SO_4^{2-} reducers methylate Hg (Compeau and Bartha, 1985). However, SO_4^{2-} reduction in northern peatlands is highly uncertain (Vile, et al., 2003).

Soils in our sedge and riparian wetlands did not classify as peat soils (Histosols) *per se* because they were shallower than the 60cm deep requirement (USDA Soil Survey Staff, 1999). Rather soils in these two wetlands were similar to the peaty gley soils in British moorlands (Avery, 1980) derived from grasses and sedges rather than *Sphagnum* mosses. Soils in the fringe and shrub wetlands were considerably deeper and derived from *Sphagna* in the top 160cm, which fit a criterion of a histic epipedon and a Histosol in the US soil classification system (USDA Soil Survey Staff, 1999). *Sphagnum*-derived peat typically has acidic pH and also can have a large net surface charge (Yavitt, et al., unpublished manuscript). For instance, the difference between pH_{H2O} and pH_{KCl} indicated net negative charge in these soils. As a result *Sphagnum*-derived peat scavenges and adsorbs positively charged solutes, which is one reason why *Sphagna* have been implicated in Hg retention (Moore, et al., 1995; Grigal, 2003).

Finding significantly greater concentrations of THg in the two wetlands with shallower soil (sedge and riparian wetlands) than in the two sites with deeper soil (fringe and shrub wetlands) is noteworthy. Soils and geomorphic setting of the fringe and shrub wetlands are typical of wetlands in which water flows much more quickly through the upper less decomposed peat material (i.e., acrotelm) than in deeper peat (i.e., catotelm; Ingram, 1978; Holden and Burt, 2003). For example, the distinct lagg zone around the shrub wetland indicates that water coming from the upland esker does not, for the most part, penetrate deeply in the wetland. Also, near neutral pH of the deep peat in the fringe wetland indicates little exchange with solutes in the acidic lake water. Very deep peat soils (> 6.5 m deep) are common in many temperate-zone peatlands in contrast to shallower peat soil in more northern counterparts (Lavoie and Richard, 2000). Very deep peat limits the type of upwelling groundwater described by Branfireum and Roulet (2002) that fuels SO_4^{2-} reduction and methylation of atmospherically derived Hg in surface peat. For example, Branfireum and Roulet (2002) showed the highest SO_4^{2-} concentrations in subsurface peat in a zone of upwelling groundwater, whereas deep peat in our shrub and fringe wetlands had very low SO_4^{2-} concentrations.

We were surprised by net nitrification in surface soil of the riparian and sedge wetlands, indicating that oxic conditions occur frequently enough to allow the development of an aerobic microbial community. Lower rates of net N mineralization (<1.5mg N kg^{-1} dry soil 14 $days^{-1}$) and no net nitrification in soil >25cm deep is consistent with the notion that N mineralization does occur, albeit slowly, in peat soils. The general notion for peat soil is that infrequent oxygenation and little available NH_4^+ limit aerobic nitrification (Williams and Wheatley, 1988; Bridgham, et al., 1998). There is also some evidence that acidic soil pH can inhibit net nitrification, although, acid-tolerant nitrifiers have been found in drained peat soils (Lang, et al., 1993). Our rates of net nitrification agree with rates found in peat gley soils derived from grasses (Williams, et al., 2003), indicating presence of acid-tolerant bacteria.

Rates of CH_4 production and anaerobic CO_2 production in the top 45cm of the fringe wetland agree with gas production rates for other peat soils from northern peatlands (Yavitt, et al., 1997). Consequently, CH_4 production rates in the other three wetlands were towards the low end of values for northern peat soils. Except for the top 30cm of the peat soil, where typical rates of anaerobic CO_2 production occurred, microbial decomposers are not particularly active in these soils, which accounts for the accumulation of deep peat soil in the fringe and shrub wetlands. Erosion likely accounts for thin soil in the sedge and riparian wetlands; albeit, this hypothesis requires data on soil accumulation rates.

At the onset we hypothesized that riparian soil might be a particularly good site for either Hg methylation or for focusing bio-available THg from terrestrial soil into surface water for subsequent methylation. Our results do not confirm one or the other hypothesis but do provide insight. For instance, results from the *in vitro* incubations of soil can be used to estimate the amount of SO_4^{2-} reducer biomass in the soil. The amount of CO_2 production coming from SO_4^{2-} reduction was estimated at 3.3 μmol g^{-1} d^{-1}, which is the difference between soil with added EtOH and 1mmol/L SO_4^{2-} versus added EtOH, 1mmol/L SO_4^{2-} and 20mmol/L MoO_4^{2-} (i.e., inhibitor). Such substrate (EtOH) induced rates of CO_2 production can be used as an index of microbial biomass (Anderson and Domsch, 1978) assuming that the CO_2 production comes from endogenous biomass before microbial growth occurs (i.e., within the first 12 hours after the substrate addition). Using the modification of West and Sparling (1986) for saturated soil, we estimated a SO_4^{2-} reducer biomass of 165 μg/g in the riparian soil.

Although there are many published estimates of SO_4^{2-} reduction rates in soil and sediments, there are very few accurate estimates of SO_4^{2-} reducer biomass. Recently, however, Kondo, et al. (2004) estimated 1 x 10^8 cells/mL of SO_4^{2-} reducers in estuary sediment. Non-marine soils typically have 1/10th that cell number (Nedwell, 1984). Assuming the mass of one bacterial cell is 1 x 10^{-12} μg and a sediment bulk density of 1 g/mL of sediment, our estimate is very similar to the calculated biomass of 100 μg/g. Moreover, our finding that $CHCl_3$ had significantly less effect than MoO_4^{2-} on CO_2 production in soil with added EtOH and SO_4^{2-}, suggests that SO_4^{2-} reducers in the riparian soil are not acetate users, which is typical of non-marine soil (Pfenning, 1989). Acetate-using SO_4^{2-} reducers are thought to have the largest Hg methylation rates (King, et al., 2000). Therefore, we can tentatively conclude that the riparian soil harbors a typical population of SO_4^{2-} reducers for a non-marine soil, and it is not a zone of unusual SO_4^{2-} reduction.

We did not measure instantaneous SO_4^{2-} reduction rates, because they are difficult to resolve with overall microbial activity in peat soil (cf., Vile, et al., 2003). Rather our *in vitro* assay for microbial activity with added SO_4^{2-}, using fresh soil samples incubated for only two days (See Table 7-1), represents SO_4^{2-} reduction by the endogenous population whereby SO_4^{2-} availability does not limit activity. In the absence of added SO_4^{2-}, concentrations of dissolved SO_4^{2-} are low enough to limit SO_4^{2-} reduction, i.e., <200 µmol/L (Vile et al., 2003). Spatial patterns in SO_4^{2-} reduction did not conform to wetland types. Rather our results suggest that populations of SO_4^{2-} reducers occur adjacent to the lake and depend on inundation by lake water for SO_4^{2-}. The riparian site is an exception because oxic conditions and thin soil limit the development of a large SO_4^{2-} reducer population.

Measurements of CH_4 production shed light on the question of whether the riparian soil is a site of net MeHg production because microbial demethylation does not occur there. Marvin-DiPasquale, et al. (2000) have shown that methanogenic bacteria and SO_4^{2-} reducing bacteria can demethylate MeHg, in particular, in anoxic soil with atmospherically derived Hg. However, in our case, the most likely site for demethylation of MeHg by methanogenic bacteria would be in the fringe wetland, which supported the largest rates of CH_4 production. While methanogens were present in riparian soil, their populations were quite constrained by other bacteria. This was evident in the long lag time before the onset of CH_4 production in soil incubated *in vitro*.

Bishop, et al. (1995a) recognized the importance of the riparian zone for Hg in streams draining forest-wetland catchments. They found that much of the MeHg arose from the riparian zone, whereas large peatlands were the source for THg and DOC. Skyllberg, et al. (2003) confirmed preferential net methylation in the riparian zone, in part, based on an elevated MeHg/THg ratio. We found a similar MeHg:/THg ratio in the fringe wetland (8.2 percent), shrub wetland (11 percent), and riparian wetland (10.2 percent), suggesting equal net methylation in these sites, versus a markedly low ratio in the sedge wetland (2.2 percent).

Although DOC interacts with Hg, we found a poor relationship between THg and DOC (Pearson r = 0.22) for our entire data set. The largest DOC concentrations in the deep soils of the fringe and shrub wetlands were not associated with large THg concentrations. Rather concentrations of THg were exceptionally large in the riparian and sedge wetlands. The sedge wetland had the reverse pattern with very low DOC concentrations but high THg concentrations. Data for the pyrophosphate index help resolve the poor THg, DOC relationship. The pyrophosphate index measures color in a soil extract, and it is related to the concentration of soluble aromatic compounds (Volk and Schnitzer, 1973). The large index in the sedge and shrub sites reflects aromatic compounds derived from vascular plants regardless of a low DOC concentration (sedge site) or a high DOC concentration (shrub site). A much lower index in the fringe wetland is consistent with the dominance of *Sphagna*, which are composed largely of carbohydrates rather than aromatic compounds (Williams, et al., 1998). Therefore, the riparian soil had the unique combination of moderate DOC concentrations but a low phyrophosphate index.

Furthermore, the relationship between DOC and base cations (C_b) was negative (r = -0.56), suggesting that DOC and base cations might compete for exchange sites. Indeed, we found only a moderate positive relationship between DOC and OA- (r = 0.63), indicating that not all of the organic compounds carry a net negative charge at the low pH of soil solutions. Theses results show that the chemical characteristics of the DOC are variable across the four wetlands, which merit study to determine DOC charge and binding ability to Hg.

Bishop, et al. (1995b) and others (cf., Shanley, et al., 2002) have argued that, for catchments that develop a large winter snow pack, Hg leaching into streams occurs primarily during the spring snowmelt period. Mercury is one of the few elements that will exhibit an increase in concentration as flow increases (Bishop, et al., 1995b), rather than dilution. Shanley, et al. (2002) found that episodic Hg export was associated with DOC, and NO_3^- to a lesser extent. Although we did not sample soil solutions on an event basis, we did sample repeatedly during the spring snowmelt high-flow period and at lower flow throughout the year. Analyses of our data by wetland type and seasonal flow period revealed some interesting relationships (Table 7-3). For example, THg in soil water did not exhibit larger concentrations at high flow versus low flow, with dilution of THg in the riparian wetland, in contrast to stream water (Shanley, et al., 2002). It is likely that much of the Hg in stream water soon after snowmelt comes directly from terrestrial soils and bypasses wetlands. Notwithstanding, in the riparian wetland, we found a much larger MeHg:/THg ratio at high flow (19.5 percent) than at low flow (6.8 percent), suggesting greater net Hg methylation during this snow melt period.

One other relationship in our data merits attention, - namely, a negative relationship between ANC and THg. This relationship suggests that Hg mobility is linked to soil and water acidification. Acid-neutralizing capacity of water is, in part, a function of acidic deposition of S and N oxides that maintain acidic pH, decrease ANC, and increase Al_m concentrations (Driscoll et al. 2003). For instance, our data revealed a stoichiometric relationship between $H^+ + Al^{n+}$ acidity and SO_4^{2-} rather than naturally occurring organic acids, which is typical of soil impacted by acidic S deposition (Fitzhugh, et al. 1999). Microbial SO_4^{2-} reduction in the deep peat soil of the fringe and shrub wetlands produced ANC. The sharp decrease in ANC during high flow in the fringe and riparian wetlands resulted from a pulse of acidic water during the spring snowmelt period rather than dilution of C_b. No evidence of the acidic pulse in the shrub wetland is evidence that very little snowmelt water penetrates the peat soil deposit. Overall, ANC showed a negative relationship with SO_4^{2-} ($r = -0.54$), as expected, a positive relationship with OA- ($r = 0.50$), and no relationship with C_b ($r = -0.11$).

The relationship between ANC and THg involves a cascade of events depending on concentrations of DOC and Al_m. In particular, ANC and DOC concentrations exhibit a positive relationship ($r = 0.64$), as do concentrations of DOC and Al_o ($r = 0.91$). Therefore, soil water with high ANC is associated with large DOC concentrations, and Al_m is a better competitor than Hg for exchange sites on the DOC. Although there is much less DOC at low ANC, there is also less Al_o and more THg. Presumably, this THg is bioavailable for methylation, as the only significant relationship between MeHg, and other dissolved solutes was a negative correlation with Al_o ($r = -0.60$).

Although NO_3^- exhibited some relationships with other solutes, it showed no relationship with THg or MeHg. The concentration of C_b showed a much stronger positive correlation with NO_3^- (Pearson $r = 0.84$) than with SO_4^{2-} ($r = 0.40$).

In summary, three aspects distinguished wetlands associated with higher dissolved THg: (i) shallow soil, (ii) derived mostly from decomposing sedges (rather than *Sphagna*), and (iii) located between terrestrial soil and surface water. Therefore, specific information on soil depth, composition and hydrology is necessary to predict how wetlands affect Hg in watersheds. Although microbial processes are thought to largely govern methylation and demethylation of

Hg, abiotic processes might play a large role in wetland Hg dynamics. For instance the high concentration of MeHg in the riparian wetland was not associated with an obvious hot spot for anaerobic SO_4^{2-} reduction. The DOC here facilitated Hg methylation, much like the abiotic Hg methylation that has been observed in high Arctic wetlands (Loseto, et al., 2004).

8 The Dynamics of Mercury in Upland Forests of the Adirondack Region of New York

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8.1 Introduction

Atmospheric deposition is a significant source of Hg to remote forest ecosystems; yet its transport through the terrestrial environment and ultimate fate, including delivery to lakes, has not been well characterized. The objectives of this study were to gain a better understanding of the following: (i) the total inputs of THg and MeHg to a forest catchment, (ii) the cycling of Hg within upland stands of coniferous and deciduous tree species, and (iii) the soil, retention, storage, and loss of Hg from upland forest ecosystems through the investigation of THg and MeHg dynamics in precipitation, throughfall, leaf litter, soil, and soil water.

8.2 Methods

Two plots, coniferous and deciduous, were instrumented in the Sunday Lake Watershed to study Hg cycling in upland forests with differing dominant vegetation types (Figure 8-1). At each site leaf litter, throughfall, soil, and soil water were collected and analyzed for THg, MeHg, and dissolved organic carbon (DOC) or total carbon (C_T). The coniferous forest plot included predominantly *Picea rubens* (red spruce), *Abies balsamea* (balsam fir), *Tsuga Canadensis* (eastern hemlock), and *Pinus strobes* (eastern white pine), whereas the deciduous forest plot predominantly included *Fagus grandifolia* (American beech), *Betula alleghaniensis* (yellow birch), and *Acer saccarum* (sugar maple).

One soil pit was excavated at each plot where acid-cleaned Teflon® gravity lysimeters were installed below three soil horizons (Oa, Bh, and Bs). Soil water samples were collected approximately every two months and during major hydrologic events such as snowmelt and precipitation events during 2000 to 2002. Precipitation quantity was estimated from a station established at Stillwater Reservoir, approximately 5 km from Sunday Lake Watershed.

Wet deposition of THg and MeHg were collected at the National Atmospheric Deposition Program/ Mercury Deposition Network (NADP/MDN, 1999) site at Huntington Forest, Newcomb, NY (approximately 100 km from Sunday Lake Watershed). To estimate wet Hg and MeHg deposition at Sunday Lake Watershed, we used precipitation quantity obtained from Stillwater Reservoir and precipitation chemistry measured at the Huntington Forest. Throughfall collectors were constructed out of acid-cleaned glass funnels modified with Teflon® fittings, tubing, and reservoirs. Three throughfall collectors were installed at each forest plot located randomly under the full forest canopy. Through fall samples were collected on an event basis usually within 12 to 48 hours after significant rain events.

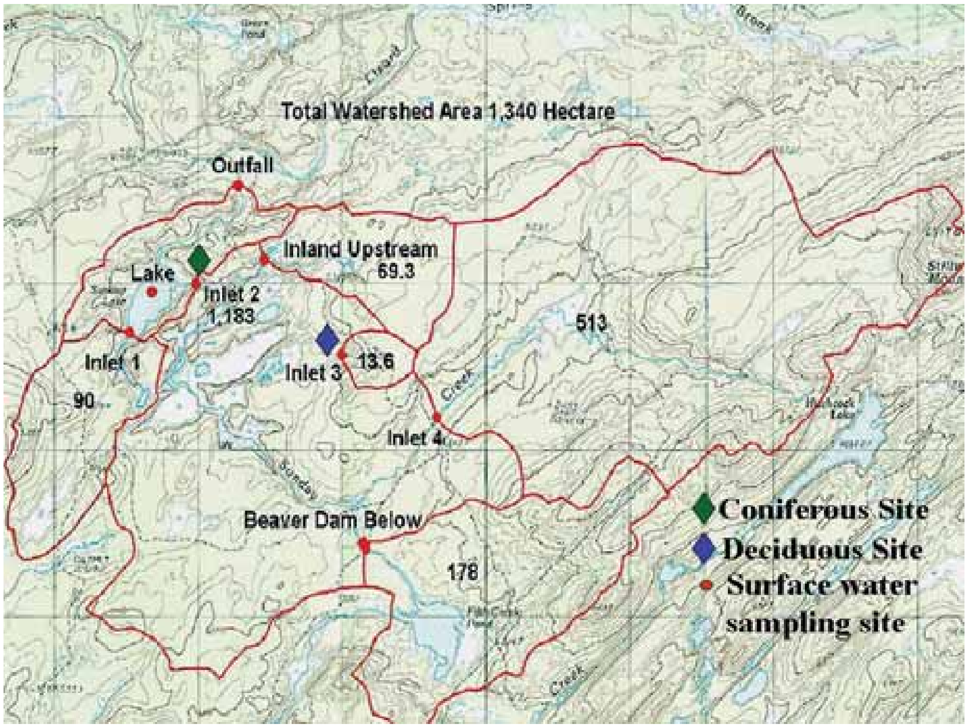

Figure 8-1. Map of Sunday Lake Watershed showing coniferous and deciduous forest plot sampling locations and surface water sampling locations

Leaf litter was collected for Hg analysis during a four-week period (October 2000) of peak fall of deciduous foliage. Acid cleaned 4'x 4' plastic tarps were set out on dry days to collect fresh litter for several hours. Leaves were collected by hand with particle free gloves and samples were then returned to the laboratory and air-dried. Before analyses, leaves were sorted by species, freeze-dried, crumbled, and homogenized. Traps were also deployed at each plot to collect litter in order to determine the total annual mass of litter fall.

Mercury samples were collected using ultra clean techniques and the clean hand/dirty hands method (U.S. EPA, 1995b) to prevent sample contamination. Water, soil, and leaf litter were analyzed for THg and MeHg using the techniques described by PTI Environmental Services (1991) and the U.S.EPA Method 1631 (Mercury in Water by Oxidation, Purge and Trap and Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) USEPA 1995a and 2002).

Annual inputs, outputs, and fluxes of THg, MeHg, and DOC were calculated for each plot for 2000 to 2002. These calculations included concentrations and fluxes associated with precipitation, throughfall, leaf litter, and soil water. Annual throughfall flux at the deciduous plot was determined by summing the precipitation flux for the non-growing season and the throughfall flux determined for the growing season. The soil leachate flux was estimated using precipitation inputs and measured surface water discharge (see Newton, et al., Chapter 5). Evapotranspiration was assumed to occur during the growing season and was partitioned according to the distribution of fine roots following the approach of Driscoll, et al. (1985) and Romanowicz, et al. (1993). These fluxes were determined and summed for the growing and non-growing seasons. Soil Hg pools were estimated using relationships determined by Huntington, et al. (1989) using percent C_T, bulk density, Hg concentrations, soil thickness, and coarse fragment volume. Statistical analyses of Hg content by tree species in throughfall, leaf litter, soil and soil water data were performed using a statistical general linear model and SAS®.

8.3 Results

8.3.1 Precipitation

Total Hg concentrations in precipitation at Huntington Forest ranged from 1.3-29.2 ng/L, with an average (± standard deviation) of 7.3 ± 5.0 ng/L. Although there were large temporal fluctuations in THg concentrations, no apparent seasonal pattern prevailed. The average MeHg concentration for precipitation at this site was 0.042 ± 0.001 ng/L.

8.3.2 Throughfall

Concentrations of THg in throughfall varied from greater than to less than concentrations found in precipitation. Average MeHg concentrations in throughfall were consistently greater than concentrations in precipitation. Mean THg concentrations were significantly different between the two plots ($p=0.000$); however, mean MeHg concentrations were not significantly different ($p=0.959$). There was a relationship between THg and DOC in throughfall for both plots ($r^2=0.59$; Figure 8-2); however, this relationship was largely the result of variations in concentrations in the coniferous plot. MeHg concentrations in throughfall were lower at the deciduous plot than concentrations at the coniferous plot.

Concentrations of THg, MeHg, and DOC in throughfall followed different patterns during the growing season. There was a strong negative relationship between THg concentrations and quantity of rainfall during each event (Figure 8-3). There was a weak correlation between THg concentrations and antecedent dry period prior to precipitation events sampled. Concentrations of THg in throughfall, however, were inversely related to the amount of rainfall for an event. There was a correlation between the antecedent dry period prior to sampling events and MeHg concentration within the deciduous throughfall ($r^2=0.99$), whereas this relationship was weak in coniferous throughfall ($r^2=0.12$).

8.3.3 Leaf Litter

Total Hg concentrations in leaf litter (LL) varied significantly between tree species (Figure 8-4); however, average concentrations in litter were similar at both plots. Average THg concentrations in leaf litter varied from 40.4± 3.7 ng/g in eastern white pine litter to 74.3± 7.5 ng/g in red spruce needles. MeHg in deciduous litter largely varied from 5 - 10 ng/g with means of about 7-8 ng/g and were higher than in the two coniferous species. Values measured for coniferous litter were low and no differences were evident between the two coniferous species (Figure 8-5).

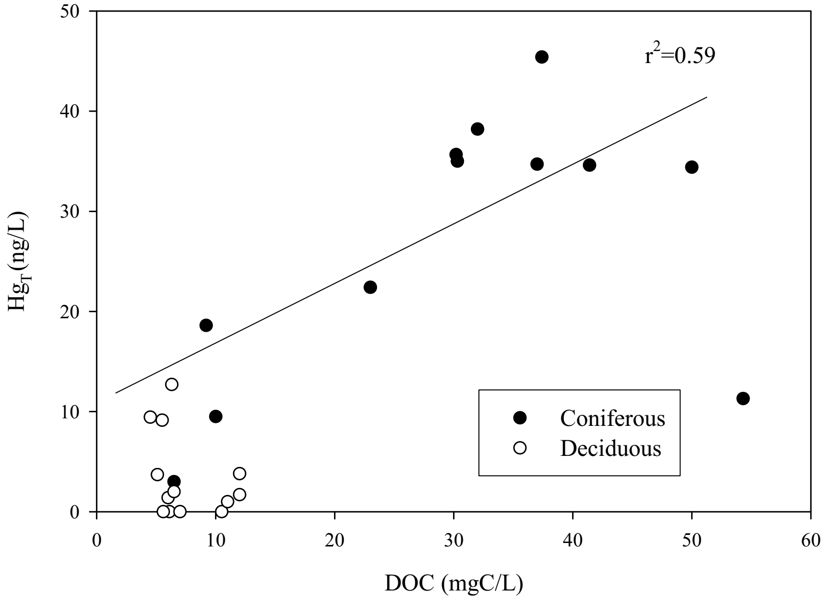

Figure 8-2. Total mercury concentrations as a function of DOC concentrations in throughfall from both coniferous and deciduous plots at Sunday Lake Watershed

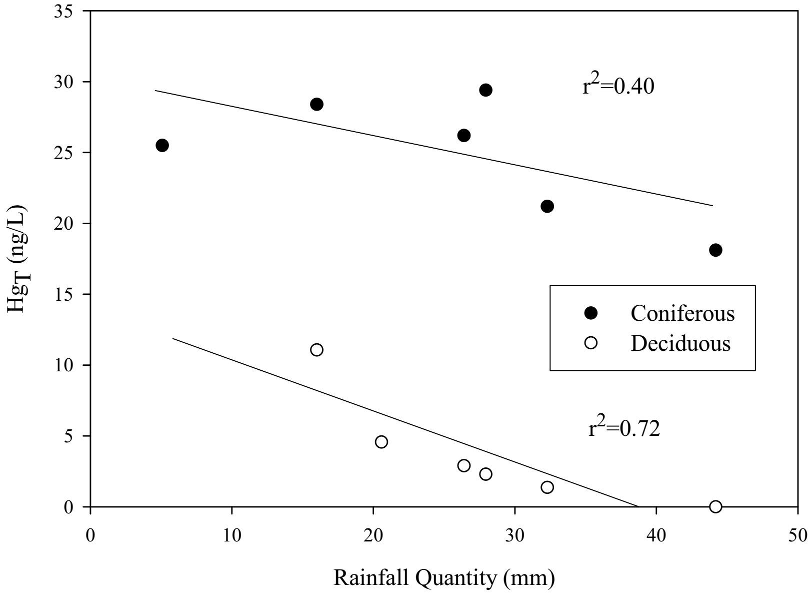

Figure 8-3. Total mercury concentration in throughfall as a function of quantity of rainfall event at Sunday Lake Watershed under coniferous and deciduous forest stands

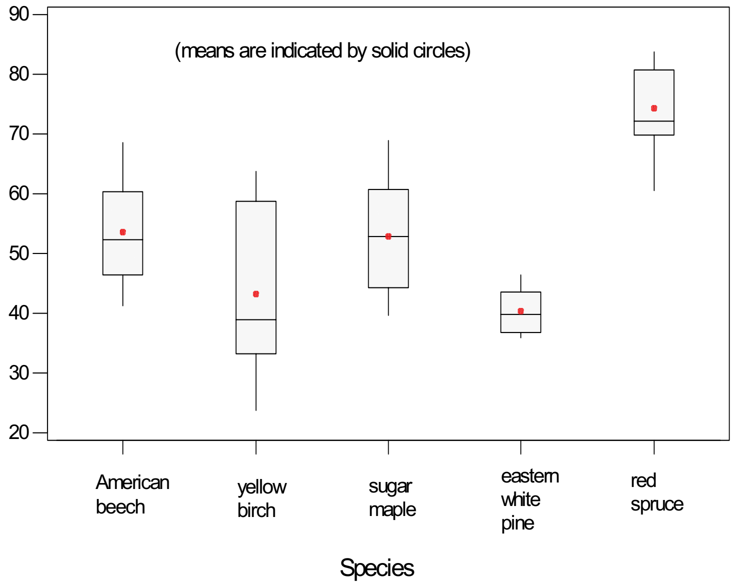

Figure 8-4. Box plots of THg concentrations in leaf litter by tree species—the line indicates the median value. The shaded area represents where 50% of the data lie. The lines to the top and bottom represent the maximum and minimum values, respectively

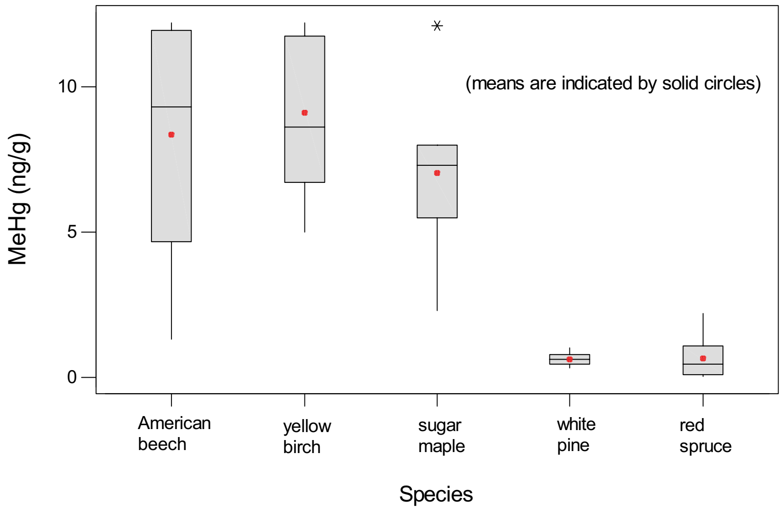

Figure 8-5. Box plots of MeHg concentrations in leaf litter by tree species—the line indicates the median value. The shaded area represents where 50% of the data lie. The lines to the top and bottom represent the maximum and minimum values, respectively. The star represents an outlier.

8.3.4 Soil

Patterns of soil carbon varied by horizon at both plots (Figure 8-6c). Carbon concentrations decreased between the forest floor and E horizon, increased in the Bh horizon, and decreased with increasing soil depth in the Bs horizon. The carbon content of the forest floor was significantly greater in the deciduous plot than the coniferous plot (p=0.05), while the carbon content in the mineral soil horizons were similar for both plots. The concentrations of THg varied with soil horizon following the same pattern as the carbon content. (Figure 8-6a). MeHg concentrations in Sunday Lake watershed soils were relatively consistent between plots and soil horizons (Figure 8-6b), ranging from 1.0-2.2 ng/g, with a mean of 1.4± 0.3 ng/g.

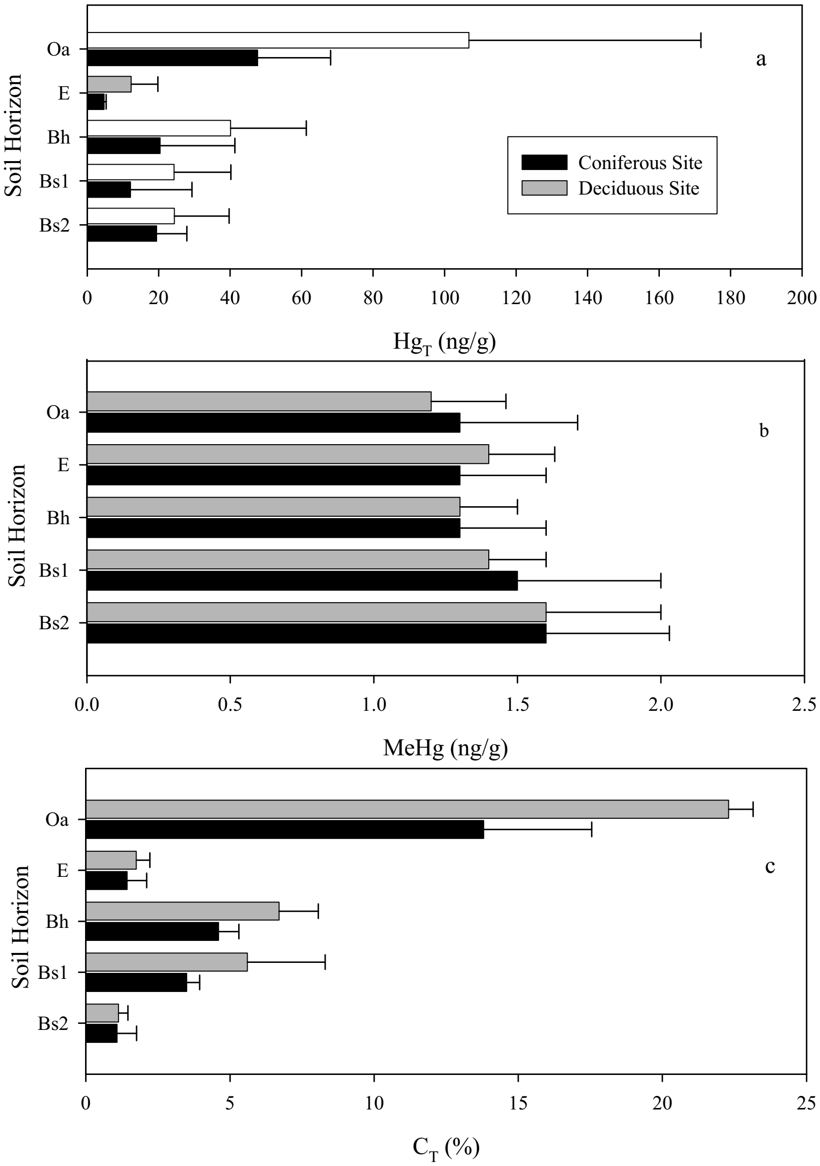

Figure 8-6. **Concentrations and standard deviations of THg (a), MeHg (b), and total carbon (c) in soil at coniferous and deciduous plots within Sunday Lake Watershed**

A strong relationship was evident between the carbon content and THg concentrations in the soil for both plots (r^2=0.51; Figure 8-7). As observed for carbon content, concentrations of soil THg were only significantly different between plots in the forest floor (p=0.009).

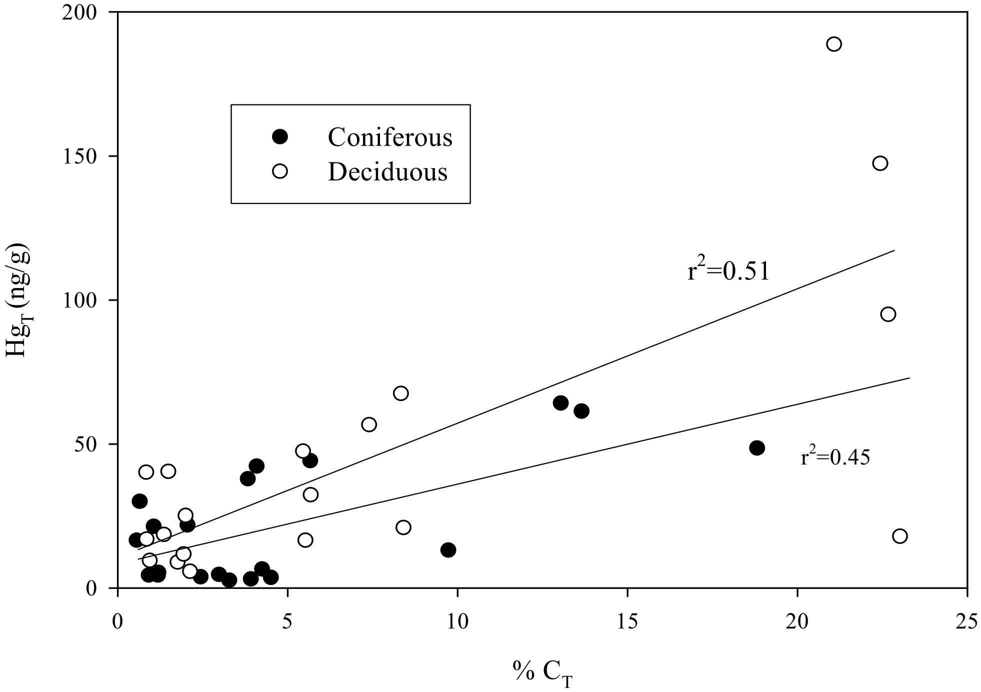

Figure 8-7. Total mercury concentrations as a function of % total carbon in soil at Sunday Lake Watershed

Soil pools were estimated at each plot and soil horizon. Soil within the coniferous plot contained less than half of the THg than soil within the deciduous plot largely due to differences in the bulk density of soil (Table 8-1). Soil pools of MeHg also were less within the coniferous plot (5.5 g/ha) than at the deciduous plot (8.3 g/ha) and followed the pattern evident for THg. Soil pools of THg were highest in the Bs2 horizon and lower in the Oa, E, and Bh horizons for both the coniferous and deciduous plots, as shown in Figure 8-8.

Table 8-1.
Pools of THg and MeHg by soil horizons at Sunday Lake Watershed

	Pools (g/ha)			
	Coniferous		Deciduous	
Soil Horizon	THg	MeHg	THg	MeHg
Oa	17.53	0.40	46.97	0.49
E	1.67	0.45	7.19	0.77
Bh	1.95	0.10	14.09	0.43
Bs1	14.48	1.52	25.94	1.4
Bs2	43.78	3.06	84.67	5.2
Total	79.4	5.53	178	8.29

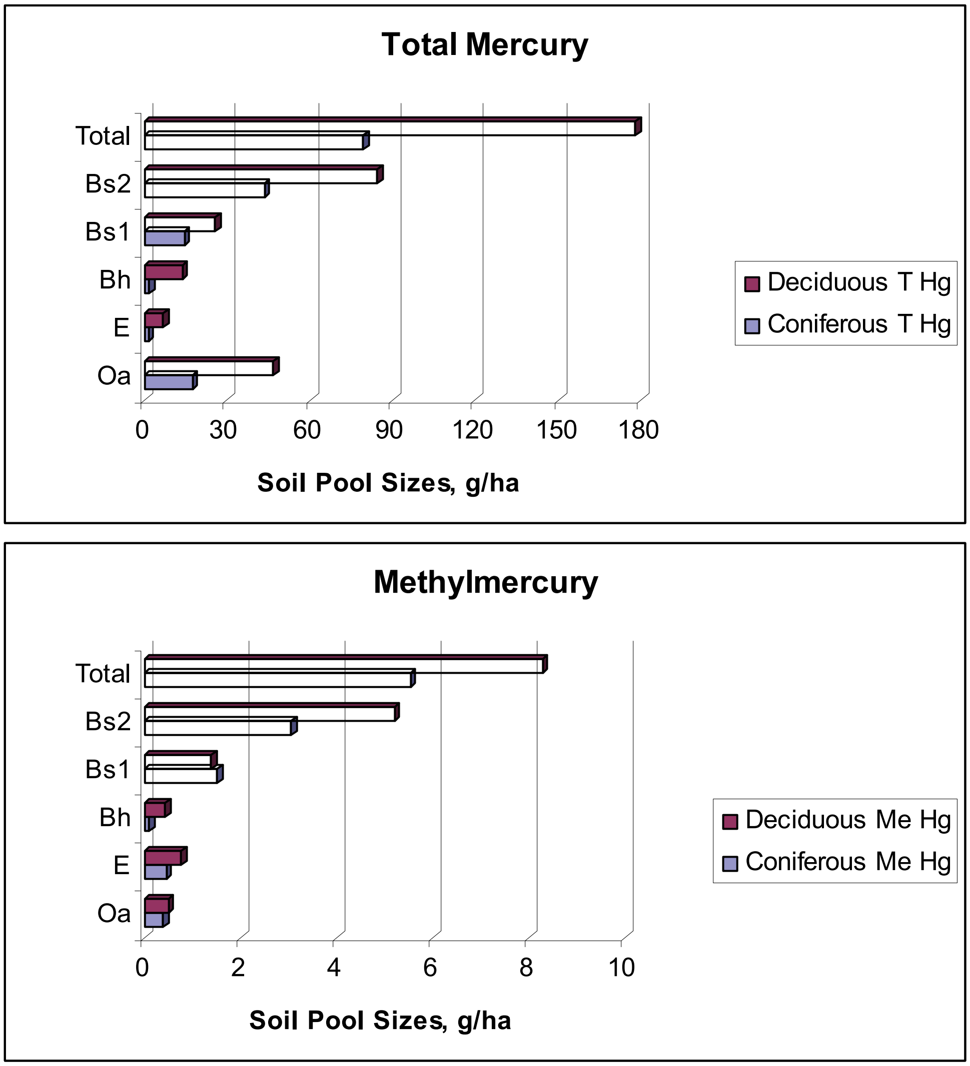

Figure 8-8. **Sunday Lake Watershed pools of total mercury (a) and methylmercury (b) in coniferous and deciduous soil plots**

8.3.5 Soil Water

MeHg concentrations in soil water (Figure 8-9b) were highest in the Bh horizon solution, lower in the Bs horizon solution, and lowest in the Oa horizon solution. In contrast, THg concentrations followed the same pattern as DOC concentrations in soil leachate (Figure 8-9a,c). A relatively strong relationship was evident between THg and DOC concentrations in soil water from values for both plots (r^2=0.33; Figure 8-10); although this relationship was more prominent within the deciduous plot (r^2=0.66) than the coniferous plot (r^2=0.18).

There was little seasonal fluctuation in THg concentrations in soil solutions. Concentrations of THg in forest floor leachate were relatively uniform throughout the year, with the exception of marked decreases during snowmelt, concentrations of THg decreased below 10 ng/L and DOC 20mgC/L. Mineral soil solutions showed no seasonal patterns in THg and DOC concentrations (data not shown).

8.3.6 Total Inputs and Fluxes

Total inputs of Hg, estimated as the sum of throughfall and leaf litter, were 32 µg/m^2-yr for the coniferous plot and 20.7 µg/m^2-yr for the deciduous plot (Figure 8-11). The THg and MeHg fluxes via precipitation were used to estimate net throughfall (NTF) flux from total throughfall inputs at Sunday Lake watershed. Wet deposition was 9.4 µg/m^2-yr for THg and 0.05 µg/m^2-yr for MeHg. Net throughfall inputs of THg and DOC were significantly greater at the coniferous plot than at the deciduous plot. At the coniferous plot, net throughfall was a significant source of THg (17.2 µg/m^2-yr) and MeHg (0.58 µg/m^2-yr), contributing 53 percent of the THg inputs to the forest floor, whereas precipitation contributed 29 percent of THg inputs to the forest floor.

Throughfall patterns were significantly different at the deciduous plot than the coniferous plot. Within the deciduous plot, throughfall inputs were 5.7 µg/m^2-yr for THg and 0.15 µg/m^2-yr for MeHg. The net throughfall of THg at this plot was negative, indicating a net uptake of 3.7 µg/m^2-yr THg by the deciduous canopy. Net throughfall flux of MeHg was 0.10 µg/m^2-yr at the deciduous forest plot.

Leaf litter (LL) was a more important source of THg to the forest floor at the deciduous plot than within the coniferous stand. Litter inputs were 72 percent of the THg input to the forest floor of the deciduous plot and 18 percent of the THg input to the coniferous plot. Deciduous LL inputs for THg were 15 µg/m^2-yr, whereas coniferous LL inputs were 5.7 µg/m^2-yr for THg and 0.06 µg/m^2-yr for MeHg.

Soil waters draining the Bs horizon were considered the primary outputs of Hg from the forest plots. The flux patterns of THg and DOC were similar through the soil profile, however, there were greater amounts of DOC draining from each horizon of the coniferous plot than from the deciduous plot (Figure 8-11). In contrast, THg fluxes draining coniferous forest soils were generally lower than values observed for the deciduous plot. MeHg fluxes from forest soils did not show distinct patterns by horizon. Both stands exhibited a maximum soil water MeHg flux in waters draining the Bh horizon.

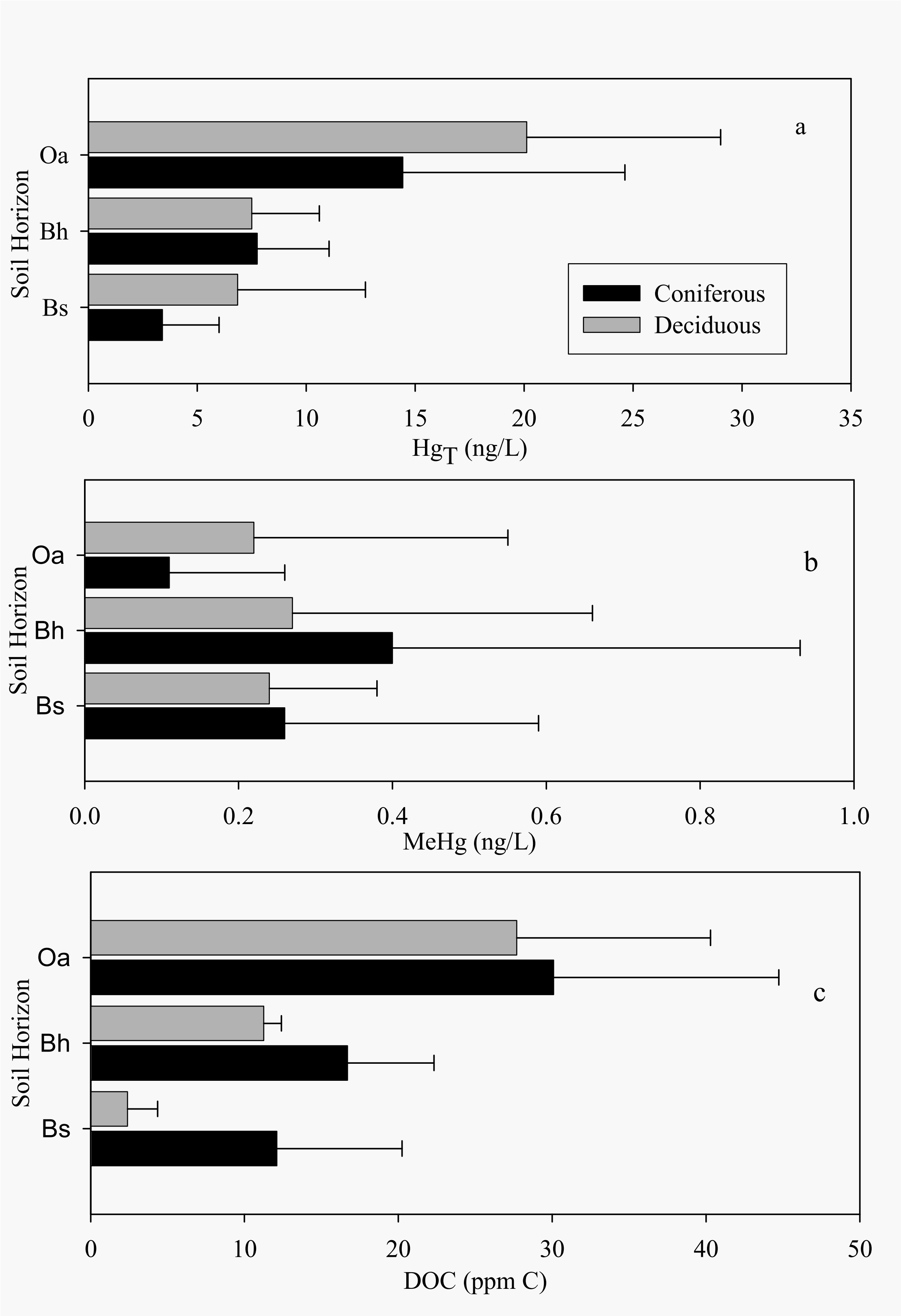

Figure 8-9. Soil water concentrations of THg (a), MeHg (b), and DOC (c) in deciduous and coniferous stands in the Sunday Lake Watershed

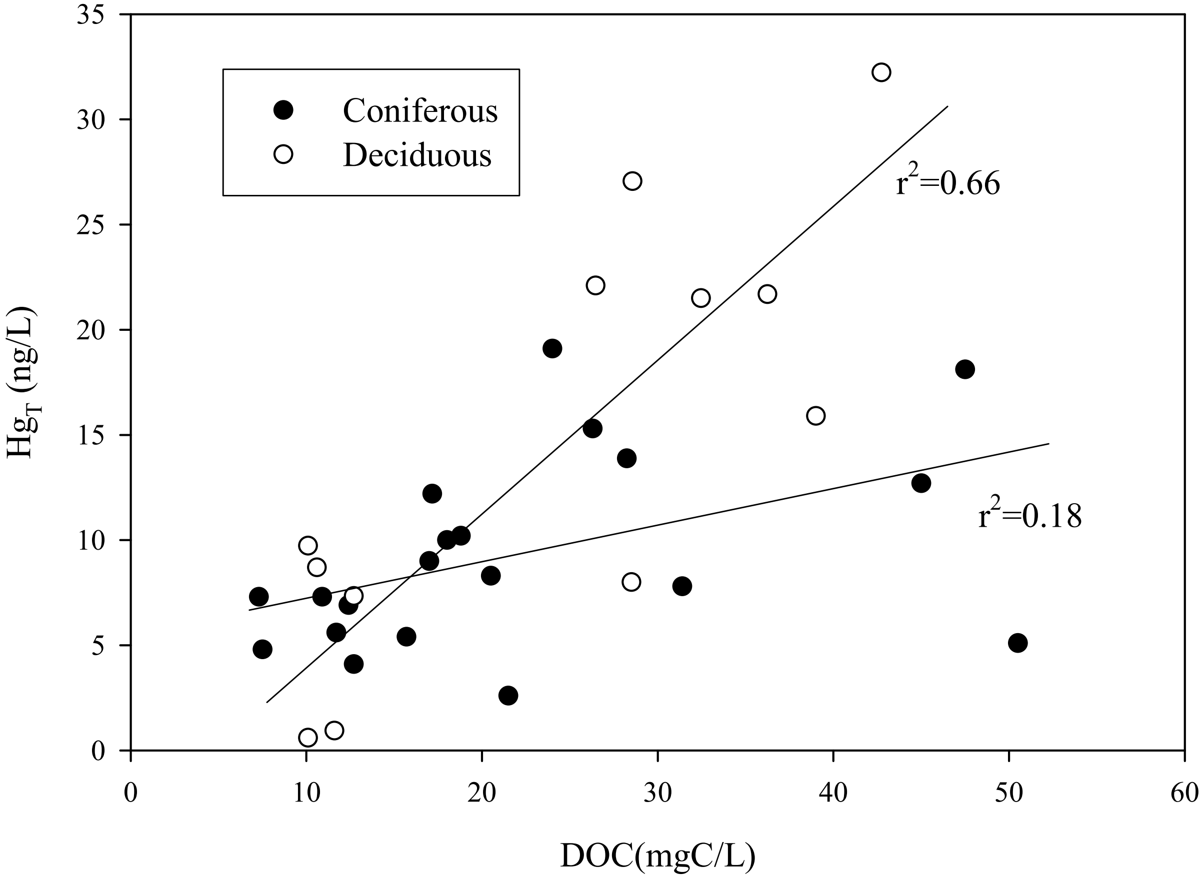

Figure 8-10. Total mercury concentrations as a function of DOC concentrations in soil water at Sunday Lake Watershed

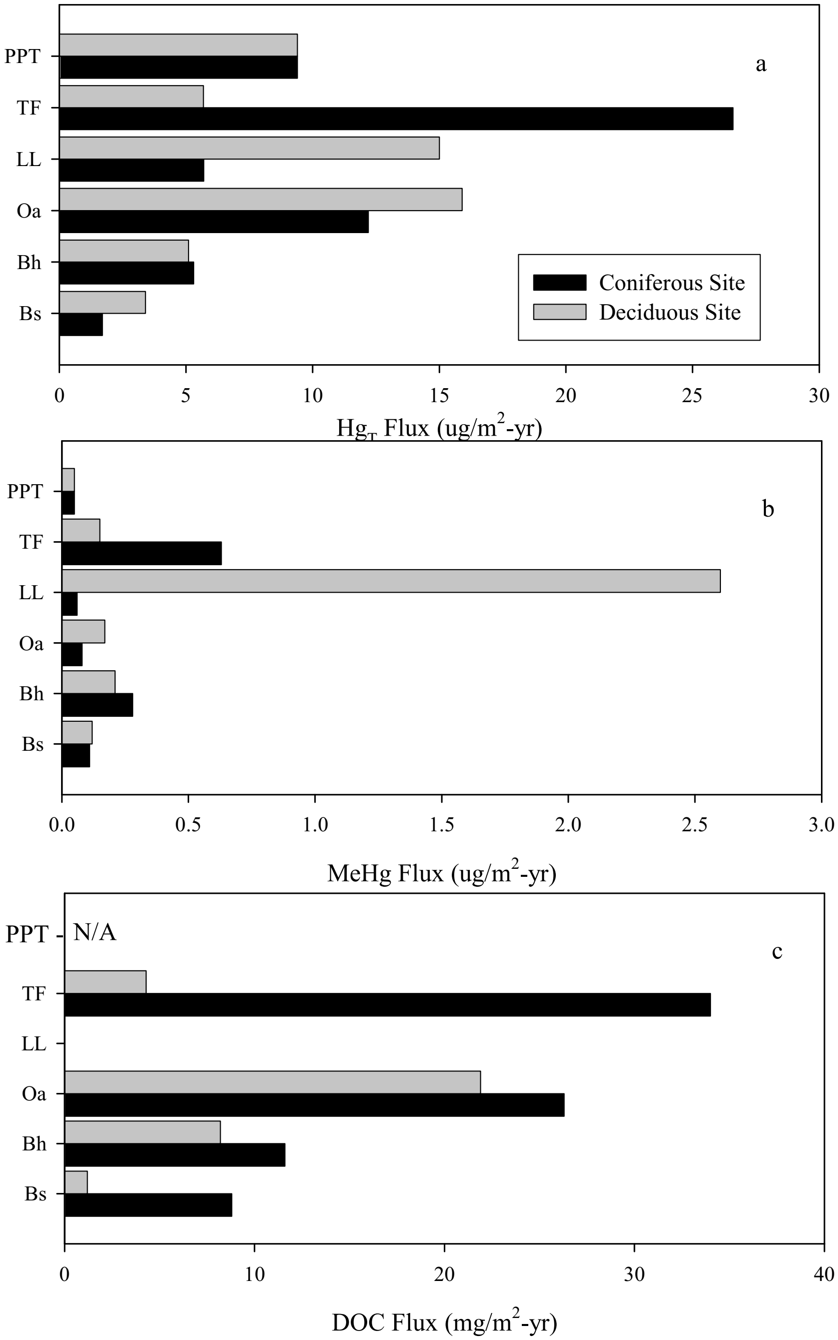

Figure 8-11. Fluxes for total mercury (a), methylmercury (b), and DOC (c) for the coniferous and deciduous plots at Sunday Lake Watershed

8.4 Discussion

8.4.1 Role of Tree Species in Mediating Mercury Deposition to a Temperate Forest

The quantity and pathway of Hg deposition to Sunday Lake watershed is influenced by vegetation type. Deposition of THg was higher within the coniferous stand than within the deciduous stand.

Mercury cycling within the plots appeared to be closely linked to the dynamics of organic matter and varied with vegetation type.

Concentrations and fluxes of THg and MeHg in bulk deposition measured at Huntington Forest and estimated for Sunday Lake watershed were similar to other areas within the northeastern region of the U.S. (Guentzel, et al., 1995; Rea, 1998; NADP/MDN, 1999; Grigal, et al., 2000). The average throughfall concentrations and fluxes of THg for the watershed were also comparable to literature values reported for North America (Rea, 1998; Grigal, et al., 2000) and Europe (Iverfeldt, 1991; Munthe, et al., 1995a, b; Schwesig and Matzer, 2000).

Concentrations of THg in throughfall were three times greater than average precipitation under the coniferous canopy; whereas THg concentration and flux under the deciduous canopy were roughly half that of mean precipitation THg values. Concentrations of THg in coniferous throughfall were similar to observations elsewhere (Iverfeldt, 1991; Munthe et al., 1995b; Schwesig and Matzner, 2000), however, the concentrations in deciduous throughfall (mean of 3.3 ng/L) were lower than values reported in the literature.

The low concentrations of THg in throughfall at the deciduous plot corresponded with low DOC concentrations compared to the values at the coniferous plot, given the positive relationship between THg and DOC concentrations in throughfall (r^2=0.59; See Figure 8-2) for values from both plots. We did not observe a relationship between THg and DOC concentrations (r^2=0.12) in throughfall from the deciduous plot alone.

Throughfall within the deciduous plot exhibited a relatively constant DOC concentration independent of rainfall quantity. Total mercury on the other hand, exhibited a strong negative relationship with quantity of rainfall. This suggests that THg is diluted with increasing quantities of precipitation whereas DOC continues to be released from the deciduous canopy regardless of the intensity of the precipitation event. This pattern was not evident for the coniferous canopy where THg concentrations increased as precipitation passed through the canopy along with perhaps associated DOC; the correlation between THg and DOC concentrations was relatively strong in coniferous throughfall (Figure 8-2).

Concentrations of THg in deciduous throughfall in the Sunday Lake plots were lower than in precipitation concentrations even though throughfall has been observed to contribute to greater concentrations of many chemical constituents (Lovett, et al., 1996), including THg at other sites (Munthe et al., 1995b; Rea and Keeler, 1996; Schwesig and Matzner, 2000). A significant contribution of THg deposition in many forested areas has been net throughfall, although negative net throughfall values were observed at the Sunday Lake watershed deciduous plot, dominated by American beech. It seems as though the deciduous tree species at this plot were efficient in scavenging THg from precipitation. Net retention or uptake of THg by a forest canopy has only been reported in two other studies including European beech and certain tropical tree species (Heinrichs and Mayer, 1977; Lindberg and Harris, 1985). The low concentrations and fluxes of THg at the deciduous plot were unexpected. The low fluxes of THg may, in part, be explained by stemflow fluxes, particularly for beech. Stemflow was not measured at Sunday Lake watershed but stemflow can be large for some tree species including beech (Johnson and Lindberg, 1992).

Mean MeHg concentrations and fluxes in throughfall the Sunday Lake plots were similar to values reported in Sweden (Munthe, et al., 1995a), which were roughly twice those found in the German catchments (Schwesig and Matzner, 2000). The concentrations and fluxes of MeHg were greater at the coniferous plot than the deciduous plot at Sunday Lake watershed; this pattern was similar to that observed in the coniferous and deciduous plots within the German catchments. Net throughfall MeHg concentrations and fluxes were negative at Lake Gardsjon, Sweden (Munthe, et al., 1995a). Hence there was a retention, transformation, or uptake of MeHg in the coniferous canopy in Sweden that was not observed in Germany or at Sunday Lake Watershed. In fact, in both these sites (including coniferous and deciduous forest stands) the forest canopy was a net source of MeHg in throughfall. At Sunday Lake watershed, MeHg concentrations in coniferous throughfall increased with increasing antecedent dry period between rainfall events suggesting that MeHg accumulated on leaf surfaces between precipitation events and was flushed from the leaf surface during precipitation events.

Leaf litter was an important component of total Hg deposition at the Sunday Lake watershed. Total Hg litter fluxes at the deciduous plot were about three times greater than THg litter fluxes at the coniferous plot. Even though mean THg concentrations in litter were similar between different forest stands (Figure 8-4), the higher deciduous THg fluxes were due to the greater mass of litter fall from the deciduous species. This pattern was also observed in German catchments where litter quantities were also three times greater at the deciduous plot than at the coniferous plot (Schwesig and Matzner, 2000).

The litter flux of MeHg within the coniferous stand at Sunday Lake Watershed was not as significant as suggested in other studies. At Lake Gardsjon, Sweden Munthe (1993) and Hultberg, et al. (1995) both observed an uptake of MeHg in coniferous forest canopy and greater fluxes through litter fall.

The inputs of Hg to the terrestrial ecosystem were dominated by dry deposition, as estimated as the difference between litter inputs plus throughfall less wet deposition; at Sunday Lake Watershed the dominant pathway of THg inputs varied by overstory canopy type. Within the forest ecosystem dry deposition was the most important input of Hg to the forest floor; the foliage captured atmospheric Hg releasing it either with litter fall (as particulate sorbed or soluble mercury) or as precipitation passed through the canopy.

Mass balance calculations for the two plots in Sunday Lake Watershed (See Figure 8-11) suggest that Hg inputs were retained or lost that have not been accounted for in this study such as volatilization, root uptake and/or soil storage. At the coniferous site, total THg inputs to the forest floor were greater than drainage outputs by 20 $\mu g/m^2$-yr (62 percent retention/loss); whereas at the deciduous site the total THg inputs exceeded drainage outputs from the forest floor by 4.4 $\mu g/m^2$-yr (21 percent retention/loss). It would seem that soil volatilization would be the most likely pathway explaining this discrepancy in mass balance. Forest floor pools and drainage fluxes of THg were lower at the coniferous plot, which is inconsistent with the high net retention of THg. An Hg input not considered within Sunday Lake Watershed is stemflow, which may be significant for certain tree species (Johnson and Lindberg, 1992). If stemflow inputs of Hg were significant at Sunday Lake Watershed, estimates of forest floor retention would increase. We hypothesize that throughfall Hg would be more readily available for reduction than litter Hg. Reduction of inorganic Hg^{2+} to Hg^0 in the forest floor might explain the observed discrepancy between inputs and outputs of THg at the coniferous plot. Moreover, the relatively strong relationship between THg and DOC in soil water at the deciduous plot, compared to the coniferous plot, may reflect the release of Hg associated with the mineralization of deciduous litter.

At the coniferous site the inputs of MeHg to the forest floor were 0.61 $\mu g/m^2$-yr (88 percent retention/loss/transformation) greater than the outputs. Within the forest floor there may be retention, demethylation, or plant uptake of MeHg explaining the major losses suggested in mass balance calculations within Sunday Lake Watershed.

8.4.2 Mercury Soil Storage, Retention, and Residence Time within Soils at Sunday Lake Watershed

Soil storage of Hg varied with depth at both plots within Sunday Lake Watershed (Table 8-1). The soil pools of THg showed a different pattern with horizons than was found in a German catchment studied in the 1970s (Heinrichs and Mayer, 1977). In that study, Hg pools were greater in the forest floor than in the mineral soil, whereas, at Sunday Lake watershed mercury pools were greater in the mineral soil than in the forest floor for both THg and MeHg. This difference could be due to several factors including soil Hg volatilization from the forest floor due to vertical transport of Hg through the soil profile, or decreases in Hg deposition over this time frame, or soil depths as discussed below.

In a study of German catchments, the coniferous soil pools of Hg exceeded the deciduous soil pools by 4.6 times (Schwesig et al., 1999). The soil Hg pools found at Sunday Lake Watershed were considerably lower than the soil pools found in these European soils; values of THg storage at Sunday Lake Watershed were 79 g/ha for the coniferous stand and 178 g/ha for the deciduous stand. In contrast, soil Hg pools at Sunday Lake Watershed were higher than a watershed in Minnesota, U.S. (Grigal et al., 2000); these THg pools were 39 g/ha in a bog and 53 g/ha in an upland forest. These differences, in part, reflect differences in the soil depth samples. Minnesota soils were determined to 25-35cm in soil depth, whereas the German values were estimated for a soil depth of 60cm, and at Sunday Lake Watershed the mean soil depth was 75cm.

Methylmercury pools at Sunday Lake Watershed were higher than in the catchments studied in Europe (pools were determined for similar depth 75 and 60cm, respectively). Similar to THg, the deciduous plot at Sunday Lake Watershed had a larger storage value for MeHg than in the soil at the coniferous plot. This pattern was also different than observed at the German catchments, where THg and MeHg pools were both greater within the coniferous forest than within the deciduous forest. These differences largely reflect differences in soil bulk density between sites.

The average residence time of THg in the forest floor (mean depth 15cm) at the coniferous plot was 50 years and 210 years for the total soil profile (mean soil depth 75). At the deciduous plot the average residence time for THg in the forest floor was 210 years (mean depth 15cm) and was 810 years for the total soil profile (mean depth 75cm). These residence times were similar to those calculated from the soil storage data and total measured inputs from another watershed within the U.S. Using data from a watershed in Minnesota, U.S. (Grigal, et al., 2000), the calculated residence time of THg in soils (25-35cm depth) of 240 years for an upland plot (Aspen dominated forest) and 120 years for a bog area dominated by black spruce. However, using the data from a watershed in Germany (Schwesig and Matzner, 2000) the retention times of Hg in the soils (60cm depth) were 10 times longer than Sunday Lake Watershed soils (1600-3100 years). The long residence times of THg within the German watershed were due to the particularly high soil pools. The difference between residence times calculated for coniferous and deciduous plots at Sunday Lake Watershed is noteworthy. The long residence time of Hg in soil at the hardwood stand may reflect the input of THg largely occurring via leaf litter. It seems likely that this input of Hg might be readily incorporated into soil organic matter than throughfall inputs.

8.5 Conclusions

Deposition of Hg to forest catchments is influenced by vegetation type. Fluxes and concentrations of THg and MeHg in throughfall, leaf litter, and soil/soil water varied between plots with differing tree species. Therefore, coniferous and deciduous trees exhibit different cycling mechanisms of Hg through the terrestrial ecosystem. The mobilization and deposition of organic carbon appeared to mediate the mobilization and retention of inorganic Hg in these plots.

Relationships between THg and DOC (Percentage of C in soil) were exhibited throughout the forested plots including throughfall, soil, and soil water.

Dry deposition as manifested in throughfall and litter fall was an important flux of THg deposition to the forest plots, as precipitation quantities of THg (9 $\mu g/m^2$-yr) and MeHg (0.1 $\mu g/m^2$-yr) were low. However, the pathway of deposition differed between stands. Coniferous throughfall flux of THg (32 $\mu g/m^2$-yr) was greater than of litter flux (6 $\mu g/m^2$-yr) whereas, deciduous throughfall flux of THg (7 $\mu g/m^2$-yr) was half than of the litter flux (15 $\mu g/m^2$-yr). Deciduous trees exhibited an uptake or retention of THg in their canopies, as the net throughfall values were negative at this plot. Litter fall was not a significant MeHg flux at the coniferous plot.

Soil storage of Hg may be a serious concern as a potential source of THg to downstream aquatic ecosystems. The residence time of THg in soils was long; the time for Hg to be retained within soils of Sunday Lake watershed is on the order of several decades to several centuries. Even if Hg deposition is drastically reduced, soil leaching may pose future risks if the quantity is sufficient to account for the toxic levels found in aquatic life.

9 Mercury in Upland and Riparian Wetland Vegetation

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9.1 Introduction

As discussed in Chapter 8, vegetation plays an important role in Hg loading, processing, and transport within a watershed. This section discusses mercury dynamics in upland and wetland vegetation during a growing season, compares sun and shade leaf Hg concentrations, and examines the role of a riparian wetland in the supply of Hg within an Adirondack lake or watershed ecosystem.

9.2 Methods

9.2.1 Vegetation

Upland vegetation for this study included American beech (*Fagus grandifolia*) and balsam fir (*Abies balsamea*). (See Figure 8-1 for location of coniferous and deciduous study sites.) Leaves and needles were collected from trees growing just upland from the riparian wetland along Inlet 2, the main tributary for Sunday Lake, using hand-held branch cutters. Sampling height was approximately 6 m. Both sun and shade samples were collected from five trees of both species. Sun leaves and needles were collected from the ends of branches on the outside of the canopy, and shade leaves and needles were collected from branches close to the tree trunk. Following the same procedures, five additional balsam fir samples were collected from a large wetland adjacent to Sunday Lake. However, two of the wetland balsam trees were only 2.5 m tall and sampling height was approximately 2 m. Leaves from five individual speckled alder (*Alnus rugosa*) shrubs, and five patches of sedge (*Carex spp.*) and moss (*Sphagnum spp.*) were sampled from the riparian wetland along Inlet 2. Upland and wetland vegetation were sampled four times during the 2002 growing season: June 2 (just after leaf out), July 2, August 1, and September 25 (just prior to litterfall). Sampling sites were permanently marked with stakes and tags for the sedge and moss samples, and tree tags for the tree and shrub samples. Samples were collected following clean procedures, double-bagged in zip-lock bags, and packed on ice packs for transport to the laboratory. Upon return to the laboratory, bags of vegetation samples were placed (open) in a non-metallic laminar-flow hood located in a class 1,000 clean room. A large, dark-colored tarp was doubled over and attached to the front of the hood to block ambient light from reaching the samples. Samples were dried in this manner to constant weight. Once samples were dry, they were frozen until analysis.

For analysis, five leaves of each beech, alder, and sedge sample were homogenized by hand in the sample bags. A recorded weight of all vegetation samples was digested with 10 mL of nitric and sulfuric acid (7:3 v/v) and heat. An aliquot of digestate was then diluted and analyzed with a

Tekran cold vapor atomic fluorescence spectrophotometer (CVAFS) following EPA Method 1631 (U.S. EPA, 2002).

9.2.2 Water

Groundwater samples were collected from nested piezometers installed at 10 and 40cm depths in the upland forest and riparian wetland. The piezometers were constructed of 3.8cm PVC pipe and were screened to prevent debris from entering the pipe. Piezometers were sampled using a hand pump, and the groundwater was collected in acid-cleaned 2.5 L glass bottles. The groundwater samples were then transferred to 500 mL Teflon bottles. Surface water samples were collected directly into 500 mL Teflon bottles from Sunday Lake and Inlet 2. Clean procedures were used for collection. Mercury water samples were acidified in the field using 0.4 percent by volume HCl, double-bagged, and packed on ice packs for transport to the laboratory. These samples were stored in a dark 4°C cooler until analysis. Total Hg samples were analyzed by CVAFS following EPA Method 1631. MeHg samples were buffered with 200 µL of sodium acetate buffer, ethylated with 100 µL of sodium tetraethyl borate ($NaBEt_4$), and then allowed to react for 17 minutes. Following reaction, the bubbler contents were purged onto carbotraps with ultra high purity nitrogen gas for 17 minutes, after which the carbotraps were dried for seven minutes. After drying, the carbotraps were analyzed with a Brooks Rand Model III CVAFS.

9.2.3 Quality Control

Acid blanks and National Institute of Standards and Technology (NIST) certified reference material (CRM) samples (apple leaves) were digested and analyzed in the same manner as the vegetation samples. At least one CRM sample was analyzed with every 10 samples, along with a triplicate, matrix spike, and matrix spike duplicate sample. Ongoing precision and recovery and continuing calibration verification samples were analyzed prior to sample analysis, and after each batch of 20 samples. A continuing calibration blank was analyzed at the beginning of each run and after every group of 10 samples. All glassware and Teflon vials were acid-cleaned by soaking in heated (70°C) 20 percent nitric acid overnight. Teflon vials were then filled with 1 percent hydrochloric acid and heated overnight in a 65°C oven. High purity (18.2 mΩ/s) distilled deionized water was used for all cleaning and analysis procedures.

9.2.4 Statistical Analysis

Data were analyzed using Pearson correlations, regressions, paired-t tests, two-sample t tests, and ANOVA at $\alpha = 0.05$. The Minitab (v. 13.32) program was used for all statistical analyses. Vegetation Hg concentrations are reported as averages ± SD.

9.3 Results and Discussion

American beech leaves ranged from 22.9 ± 11.1 to 41.7 ± 32.6 ng/g THg (dw) and from 24.0 ± 16.0 to 49.0 ± 20.6 ng/g THg (dw) for sun and shade samples, respectively, over the growing season (Figure 9-1). These ranges are comparable to literature values for mixed hardwood leaves including beech (3.4 – 39.8 ng/g THg dw; Rea, et al., 2002). Samples were not collected immediately after bud break for this study, which may explain why the minimum values are higher. In addition, no litterfall samples were collected. Unlike Rea, et al. (2002), no significant differences in leaf THg concentrations were observed between months of the study. Total Hg concentrations did not differ significantly between sun and shade leaves.

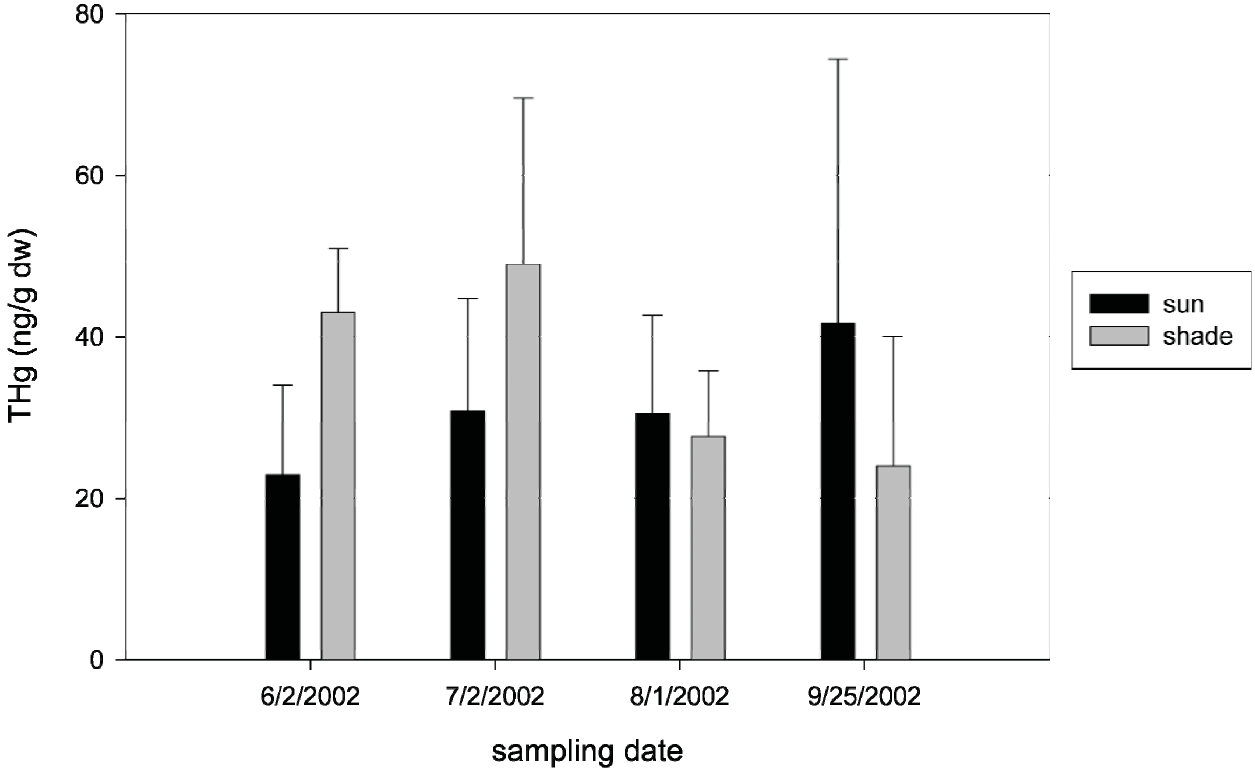

Figure 9-1. **Mean total mercury concentrations and standard deviations for American beech at Sunday Lake Watershed over the growing season—values are shown for sun leaves and shade leaves.**

Upland balsam fir needles ranged from 10.9 ± 5.8 to 31.5 ± 5.5 ng/g THg (dw) and from 3.8 ± 8.9 to 59.2 ± 22.2 ng/g THg (dw) for sun and shade samples, respectively (Figure 9-2a). Differences between the sun and shade needle concentrations were not statistically significant. THg concentrations were roughly within the range of literature values of 5 – 16 ng/g THg (dw) (Lin, et al., 1995) and 15 – 26 ng/g THg (dw) (Rasmussen 1995). However, the highest shade needle concentrations were approximately twice the highest literature values. Decreases in THg in balsam fir sun needles over the growing season are most likely due to growth dilution, since sun needles were taken from the tip of the branches. There were significant differences in THg concentration between the June, July, and August sun needles, and the August and September shade needles.

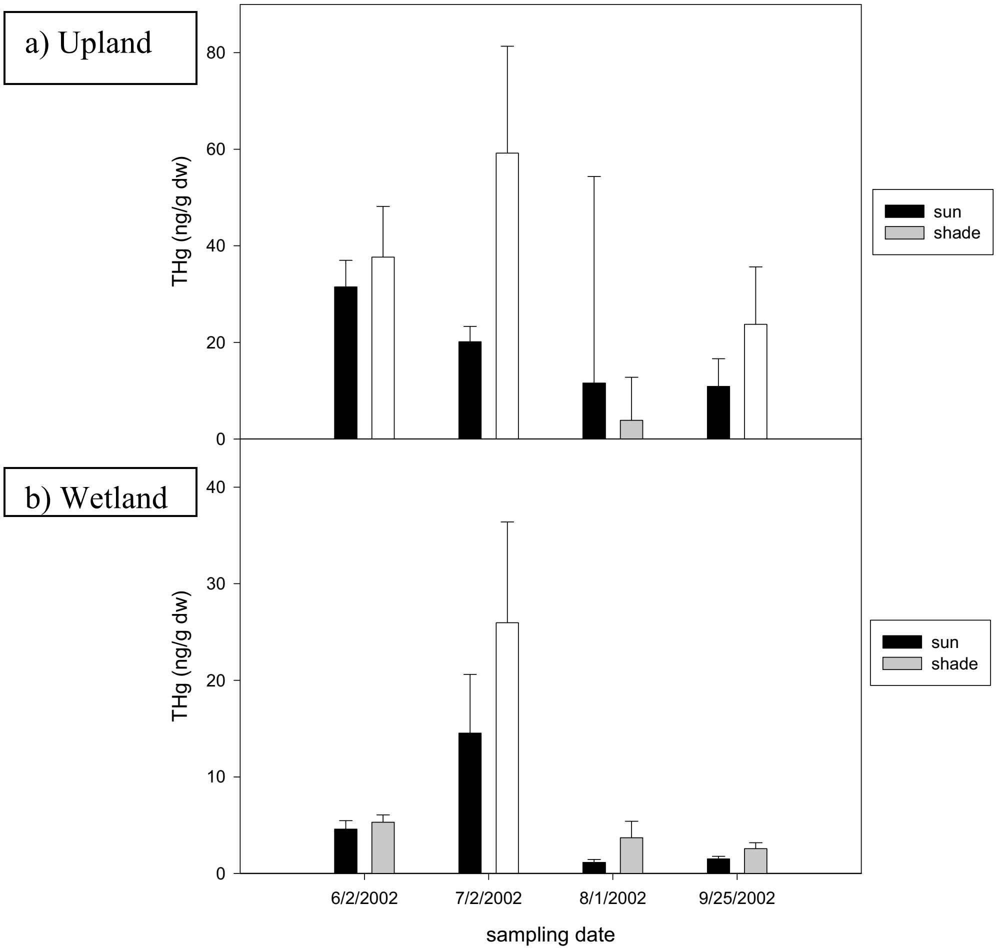

Figure 9-2. Mean total mercury concentrations and standard deviations in needles of balsam fir at Sunday Lake Watershed over the growing season—values are shown for upland (a) and wetland (b) vegetation and for sun and shade leaves.

The wetland balsam fir needles ranged from 1.1 ± 0.3 to 14.5 ± 6.1 ng/g THg (dw) and from 2.6 ± 0.6 to 26.0 ± 10.4 ng/g THg (dw) for sun and shade samples, respectively (Figure 9-2b). Sun and shade needle values were not statistically different. Concentrations of THg in the wetland balsam needles were generally lower than concentrations in the upland balsam needles, but the difference was not significant. There were significant differences in THg concentrations between all sampling dates for the wetland balsam sun needles, and all sampling dates except between August and September for the shade needles.

Sun leaves and needles were expected to have higher THg concentrations than shade leaves and needles, since they are located on the outside of the canopy and receive greater deposition. However, no statistically significant difference was observed between sun and shade leaf Hg concentrations in the Sunday Lake watershed. Other factors influencing vegetation Hg concentrations include volatilization from leaf surfaces and wash-off by precipitation events (Leonard, et al., 1998; Lindberg, et al., 1998; Ericksen, et al., 2003; Rea, et al., 2001). Findings from previous studies show greater Hg volatilization with greater solar radiation and air temperature (Leonard, et al., 1998; Lindberg, et al., 1998). Both air temperature and solar radiation are expected to be greater for sun leaves than for shade leaves. Large precipitation events can remove dry deposition from leaves, thus reducing mercury concentrations in foliage (Rea, et al., 2001). The amount of Hg removed by wash-off depends on the species of Hg deposited to leaves. Reactive gaseous Hg (Hg^{2+}) may be more susceptible to wash-off since it is deposited to the leaf surface. Inorganic Hg can accumulate in stomata making it less susceptible to wash-off (Rea, et al., 2002; Rea, et al., 2001). However, Ericksen, et al. (2003) determined that only 1.5 – 3 percent of foliar Hg could be removed by wash-off. Therefore, the decrease in leaf Hg concentrations by precipitation events would be minimal compared to decreases from volatilization. The main factors influencing foliar Hg concentrations are most likely atmospheric deposition and volatilization. The sun leaves receive more atmospheric deposition, but the Hg deposition appears to be balanced by greater volatilization from sun leaves.

Sphagnum samples had THg concentrations ranging from 7.6 ± 4.6 to 155.4 ± 65.8 ng/g THg (dw) (Figure 9-3), which were comparable to literature values (27 – 199 ng/g (dw); Moore, et al., 1995). Except for between July and August, there were significant differences in THg concentrations between sampling dates. The *Carex* samples had THg concentrations ranging from 4.7 ± 1.8 to 62.6 ± 24.0 ng/g THg (dw) (Figure 9-3), with the maximum concentration three times the maximum value of 18.8 ng/g THg (dw) reported in Moore, et al. (1995). Since the *Carex* samples analyzed by Moore, et al. (1995) were collected in October and May, the authors may have missed the late summer THg peak observed in this study, and only captured the early season and post-season THg concentrations. There were significant differences between all sampling dates for the sedge samples. The alders had a range of 3.3 ± 1.4 to 57.7 ± 13.4 ng/g THg (dw) (Figure 9-3). Alder THg concentrations differed significantly between all sampling dates.

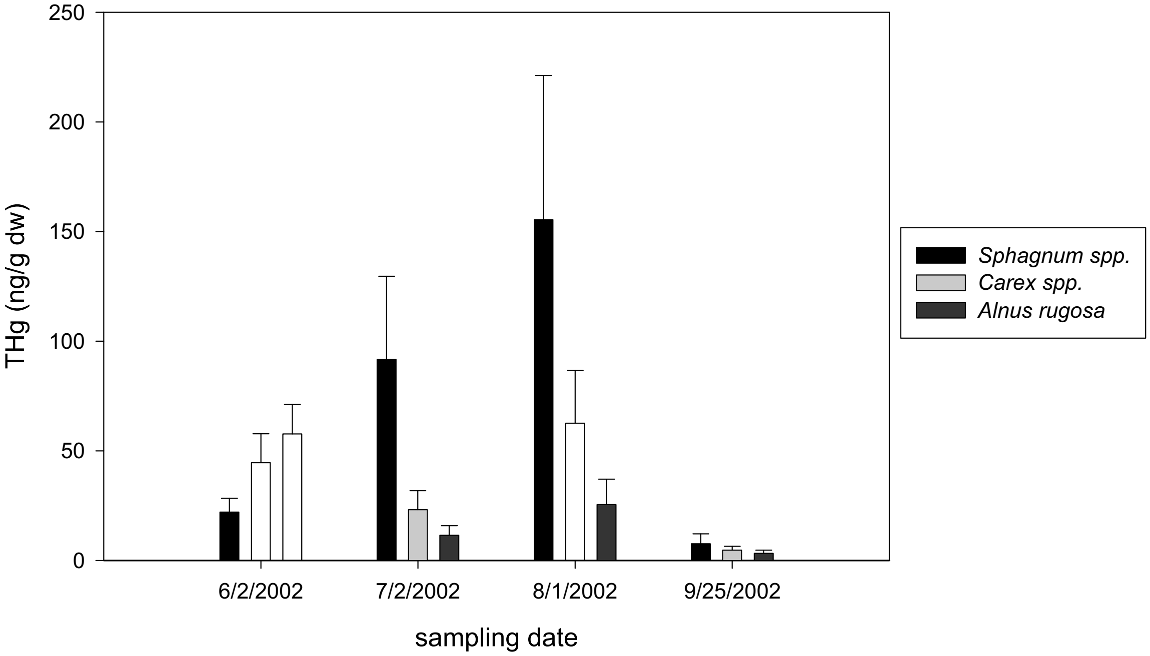

Figure 9-3. Mean total mercury concentrations and standard deviations in wetland vegetation of Sunday Lake Watershed over the growing season

Total Hg concentrations for the three wetland species decreased significantly at the end of the growing season. End of season declines in foliar Hg concentrations have not been reported in the literature (e.g. Rea, et al., 2002; St. Louis, et al., 2001). St. Louis, et al. (2001) reported an average Hg concentration for speckled alder litterfall of 34 ng/g THg, which is an order of magnitude greater than concentrations in alder leaves at the end of the growing season at Sunday Lake watershed. Plants are known to reabsorb nutrients such as N, P, and K during leaf senescence for reuse in the subsequent growing season (Schlesinger, 1997; Solomon, et al., 1993). Resorption of trace metals including Fe and Zn has been reported in some species of deciduous trees (Killingbeck, 1985). However, increased foliar concentrations of Cu and Mn were also reported for some species at senescence. These increases may be a mechanism for removing non-essential or potentially toxic metals from the plant (Killingbeck, 1985). The possible existence of a THg exclusion mechanism in roots of conifer species (Bishop, et al., 1998) suggests that plants would be more likely to remove Hg rather than reabsorb it. Therefore, the reason for the observed decreases in THg concentrations for the three wetland species is unclear.

10 Trophic Transfer of Mercury in an Adirondack Lake Ecosystem

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10.1 Introduction

High Hg levels have been reported in fish collected from remote lakes, including the Adirondack Mountains (Driscoll, et al. 1994c; Watras, et al. 1995a, b; Quemerias, et al. 1998). Driscoll, et al. (1994c) observed that some lakes in the Adirondack region, including Sunday Lake, had higher fish Hg levels than other lakes. The factors influencing fish Hg concentrations are not fully understood. As elevated Hg concentrations in wildlife and fish are observed in an increasing number of remote regions, resource managers realize the need to better understand the sources of Hg contamination in biota and the processes within the watershed and lake ecosystem that influence Hg levels in top game species. This study was designed to (1) determine levels of Hg in water, Zooplankton, Forage fish, and Yellow Perch for Sunday Lake; (2) calculate the bioconcentration factors (BF) for different trophic levels in the lake food chain; and (3) identify processes controlling Hg transfers in the food chain.

10.2 Methods

10.2.1 Yellow Perch

A previous study by Yan (1996) reported relatively high THg and MeHg concentrations in Sunday Lake, as compared to 15 other Adirondack lakes. In addition, high Hg concentrations were also reported for fish in the lake (Yan, 1996). Yellow Perch (*Perca flavescens*) were chosen for this study because they are a common fish species found in lakes throughout the Adirondack Mountains. Gill nets were used to collect 66 Yellow Perch, ranging in age from one to seven years, in October 2000. The fish were collected, measured (mm), weighed (g), and aged by Adirondack Lake Survey personnel. A portion of muscle filet was then transferred to small borosilicate glass jars, frozen, and shipped on ice to the analytical laboratory where they remained frozen until analysis. A portion of muscle filet (approximately 0.3 g) for each fish was digested using 10 mL of nitric and sulfuric acid (7:3 v/v) and heat. Dilutions of the digestates were then analyzed for THg concentration, following EPA Method 1631, using a Tekran cold vapor atomic fluorescence spectrophotometer (CVAFS). The predominant form of mercury in fish is MeHg; however, it is acceptable to measure only THg, as it has already been well-established that 95 percent of the mercury in fish is MeHg (Grieb, et al, 1990).

10.2.2 Golden Shiners

Thirty-three Golden Shiners (*Notemigonus crysoleucas*) of varying size were collected in June 2003 using experimental trap nets. The fish were double-bagged in Zip-Lock® bags, frozen, and then shipped to the analytical laboratory for whole-fish analysis. Partially thawed fish were homogenized in a stainless steel blender (Waring) following the procedures of Stober (1991). The blender was rinsed copiously with Milli-Q distilled, deionized (ddi) water (18.2 MΩ*cm) between each fish. A subsample of the homogenate was then digested with 10 mL of nitric and sulfuric acid (7:3 v/v) and heat. Digestates were diluted and an aliquot was used for total mercury analysis by CVAFS.

10.2.3 Zooplankton

Zooplankton were collected roughly every two weeks between May and October, 2002. Collection was achieved by replicate vertical hauls using a 30cm diameter, 153 µm mesh Nitex net (Wildco). Sampling was performed from an inflatable raft at the deepest area of Sunday Lake, by sampling personnel wearing shoulder-length gloves. A surface float tied to an anchor permanently marked the sampling site. Contents of the net were collected in 1-L acid-cleaned Teflon® bottles. These bottles were double-bagged in Zip-Lock® bags and placed on ice for transport to the sorting laboratory. On each sampling date, separate hauls were taken for Zooplankton species identification and enumeration.

Processing of the Zooplankton samples occurred in a laminar flow hood. Nitrile gloves and acid-cleaned Teflon® Petri dishes, Teflon® wash bottles, and glass Pasteur pipettes were used for sorting the Zooplankton samples. Zooplankton samples were allowed to thaw to room temperature under the hood, prior to being narcotized with filtered carbon dioxide. After being narcotized, the Zooplankton settled to the bottom of the sampling bottle and the majority of the sample water was then decanted. Zooplankton were then sorted into the main species present during each respective collection. Sorting was conducted by placing an aliquot of the narcotized Zooplankton into a Teflon® Petri dish, sorting individual species through a minimum of two separate washes, and then transferring the sorted Zooplankton to 5 mL Teflon® vials. A binocular dissecting microscope was employed during the sorting process. In addition, an ocular micrometer was used to measure the length of individual Zooplankton, which was then recorded. A known number of each species was transferred to each 5 mL vial, after which any excess water was removed, and the vials were placed in a –80°C freezer awaiting shipment to the analytical laboratory.

For analysis, Zooplankton samples were first thawed. Following the procedures outlined by Back, et al. (1995), the thawed samples were transferred to 1mL borosilicate glass microtissue grinders (Fisher Scientific), along with 100 µL of Milli-Q ddi water. The specimens were finely ground, and then 400 µL of Milli-Q ddi water was used to rinse the mortar and grinder tube. The contents of each sample vial were ground in a separate grinder, and then half of the grinder contents were transferred to each of two 5 mL vials. To one vial, 200 µL of 25 percent KOH/methanol solution was added for MeHg analysis. To the second vial, 200 µL of nitric and sulfuric acid (7:3 v/v) was added for THg analysis. All vials were placed in a 65°C oven overnight for digestion.

For THg analysis, an aliquot of the digestate was added to Milli-Q ddi water, and the sample was then analyzed by CVAFS. For MeHg analysis, an aliquot of the digestate was added to 100 mL ddi water in a 200 mL borosilicate glass bubbler. The bubbler contents were buffered with 200 µL of acetate buffer, ethylated with 100 µL ethylating agent, and then allowed to react for 17 minutes. Following reaction, the bubbler contents were purged with UHP nitrogen gas for 17 minutes, after which the carbotraps were dried for seven minutes. After drying, the carbotraps were analyzed using a BrooksRand Model III CVAFS. Zooplankton dry weights were calculated using the Zooplankton lengths (L) and the equation: $W_{(dry,\ \mu g)} = 7.4\ L_{(mm)}^{3.85}$ (Culver, et al., 1985).

10.2.4 Water

Surface waters were sampled at nine locations throughout the watershed; sample locations are shown in Figure 10-1. Water chemistry samples were collected on a monthly basis between August 1999 and October 2002, and analyzed to assess factors influencing Hg accumulation in the food chain of Sunday Lake. Both Hg and ancillary water samples were collected from inlet streams within the watershed, the epilimnion and hypolimnion of Sunday Lake, and the outlet stream. Mercury water samples were acidified in the field using 0.4 percent by volume HCl. Correlations between the various water chemistry variables (pH, ANC, DOC, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, and Al^{3+}) and lake THg and MeHg were examined for this analysis. The bioconcentration factor, defined as the ratio of the concentration of MeHg in Zooplankton or fish to the concentration of MeHg in the water column, was calculated for the Zooplankton and each fish age class. Although MeHg was not measured in fish, the fish THg was assumed to be >95 percent as MeHg, as discussed previously (Grieb, et al, 1990 and Bloom 1992).

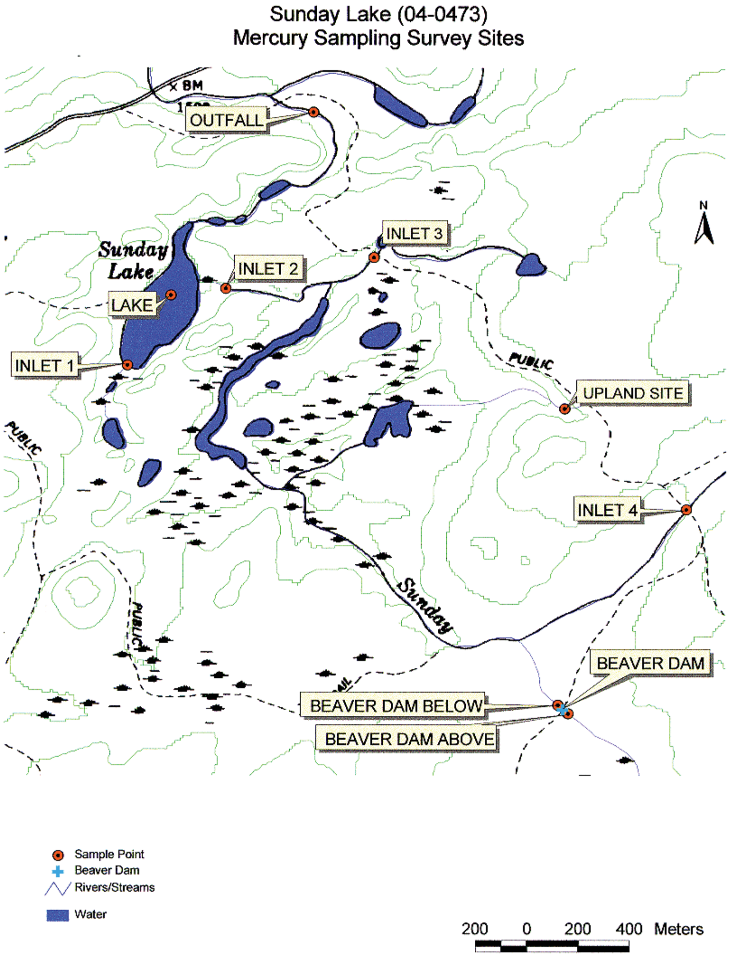

Figure 10-1. Sunday Lake surface water sampling locations

10.2.5 Quality Control

Acid blanks and DORM-2 certified reference material (CRM) samples were digested and analyzed in the same manner as the fish and Zooplankton samples. At least one CRM sample was analyzed with every 10 samples, along with a triplicate, matrix spike, and matrix spike duplicate sample. Ongoing precision and recovery and continuing calibration verification samples were analyzed at the beginning of each run, and after each batch of 20 samples. A continuing calibration blank was analyzed at the beginning of each run and after every group of 10 samples. All bottles, vials, Petri dishes, microtissue grinders, and Pasteur pipettes were cleaned by first soaking overnight in heated (70°C) 20 percent nitric acid. They were then filled with one percent hydrochloric acid and heated in a 65°C oven overnight. Milli-Q ddi water (18.2 MΩ*cm) was used for all Hg cleaning and analyses.

10.2.6 Statistical Analysis

Minitab (v. 13.32) software was used for all statistical analyses of the water, Zooplankton, and fish data. Data were analyzed using Pearson correlations, regressions, paired-t tests, and 2-sample t tests at $\alpha = 0.05$.

10.3 Results

10.3.1 Water

Mercury concentrations averaged 3.6 ng THg L^{-1} and 0.86 ng MeHg L^{-1} in the epilimnion over three years of sampling (Table 10-1). Higher THg and MeHg concentrations were typically observed in spring and late summer (Figure 10-2). Sulfate concentrations were usually greater during the winter months, whereas DOC concentrations were usually greatest in late summer and fall. Analysis of the relationships between Inlets 1 and 2, the lake, and the outlet stream revealed that epilimnion THg concentrations were most correlated with the outlet and hypolimnion THg concentrations (r^2=0.82 and 0.69, respectively). Epilimnion MeHg concentrations were most correlated with Inlet 2 MeHg concentrations (r^2=0.53). Plots of the lake epilimnion and hypolimnion data are shown in Figure 4-5. Because this lake is shallow, there was not a consistent difference between the shallow and deep samples, and the MeHg concentrations in the hypolimnion were not significantly greater than near the surface. Mercury in the water column did not correlate strongly with any of the ancillary water chemistry data.

Table 10-1.
Epilimnion water chemistry for Sunday Lake—Data represent the average over three years of sampling (August 1999 – October 2002).

	average	standard deviation	units
pH	5.4	0.49	
DOC	7.0	2.8	mg C L^{-1}
ANC	16.4	32.5	µeq L^{-1}
THg	3.6	1.8	ng L^{-1}
MeHg	0.86	1.1	ng L^{-1}
Ca^{2+}	1.8	0.33	mg L^{-1}
Mg^{2+}	0.36	0.08	mg L^{-1}
K^{+}	0.49	0.13	mg L^{-1}
Na^{+}	0.86	0.18	mg L^{-1}
Cl^{-}	9.8	6.5	µmol L^{-1}
NO_3^{-}	15.9	17.8	µmol L^{-1}
SO_4^{2-}	44.7	11.3	µmol L^{-1}
Al_m	4.3	2.7	µmol L^{-1}
Al_o	3.2	1.2	µmol L^{-1}

10.3.2 Zooplankton

Due to possible contamination, Hg data from the first three months of Zooplankton sampling are not included with these results. Only Hg concentrations for the four major Zooplankton species analyzed from samples collected in August, September, and October 2002 were used for Zooplankton calculations. Thus, these data were not collected at the same time as the fish data. *Bosmina longirostris*, *Daphnia pulex*, and *Holopedium gibberum* are cladocerans. *Mesocyclops edax* is a cyclopoid copepod. No patterns were seen in Zooplankton Hg over the course of the three-month period (five sampling events). However, differences were observed between species. *Daphnia pulex* and *H. gibberum* averaged 38 and 35 ng/g (dw) THg, and 22 and 25 ng/g (dw) MeHg, respectively (Table 10-2). *Bosmina longirostris* and *M. edax* had the highest and lowest concentrations of any species, averaging 197 and 9.4 ng/g (dw) THg, and 156 and 4.3 ng/g (dw) MeHg over the study period, respectively. Total Hg and MeHg concentrations were significantly lower in *Mesocyclops edax* than in *D. pulex* and *H. gibberum* ($p=0.011$ and 0.001, respectively). Although *B. longirostris* Hg concentrations were much higher than the other three species, due to the small sample size ($n=2$), the concentrations could not be included in the statistical analysis. *Bosmina longirostris* was the smallest specie of Zooplankton, averaging only 0.42 ± 0.05mm in length. *Mesocyclops edax* was the largest species, averaging 1.44 ± 0.03mm. *Holopedium gibberum* averaged 0.99 ± 0.06mm in length. *Daphnia pulex* ranged in length from 0.88 ± 0.09 to 1.37 ± 0.09mm, but *Daphnia* Hg levels were not correlated with length and no significant differences were seen between the different sizes. For the calculation of the bioconcentration factor (log BF = 4.46), the average MeHg concentration, 25 ng/g (dw) MeHg, for all four Zooplankton species was used (Table 10-2). *Bosmina longirostris* biomass was consistently lower than *D. pulex* ($p=0.037$), *M. edax* ($p=0.002$), and *H. gibberum* ($p=0.038$) (Figure 10-3). Note that *Mesocyclops edax* and *D. pulex* values are totals for both adults and juveniles. Chlorophyll-α concentrations were greatest (13.1 µg L^{-1}) around the September 17, 2002 sampling.

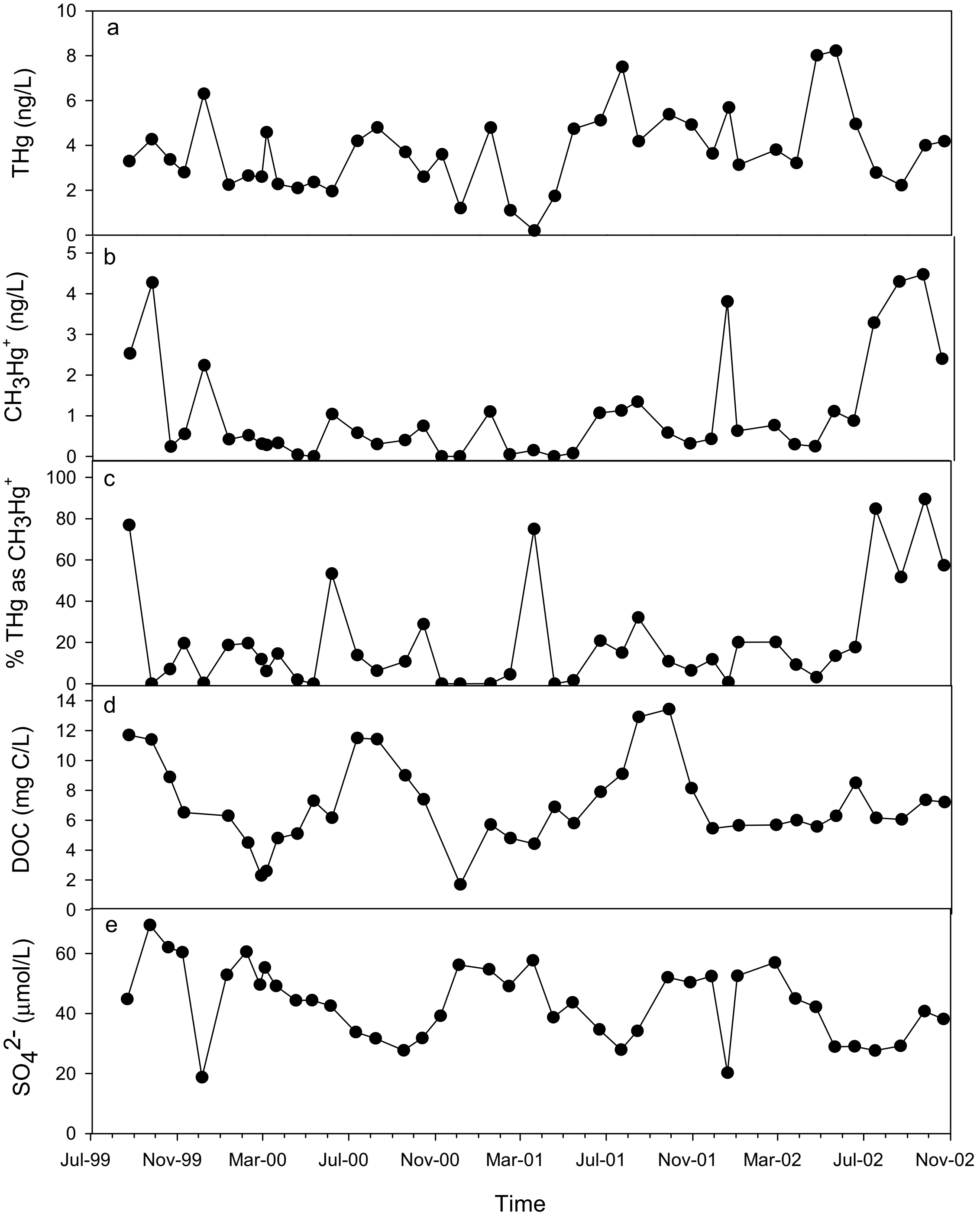

Figure 10-2. Temporal patterns of concentrations of THg (a), MeHg (b), % THg occurring as MeHg (c), DOC (d), and SO_4^{2-} (e) for the epilimnion of Sunday Lake

Table 10-2.
Concentrations of THg, MeHg, and log bioconcentration factor (BF) for Zooplankton, Forage fish, and Yellow Perch in Sunday Lake

species	n	average THg	average MeHg	units	%MeHg	average log BF
Lake water	37	3.6 ± 1.8	0.86 ± 1.1	ng/L	24	
Combined Zooplankton	32	39 ± 56	25 ± 40	ng/g dw	67	3.5
Cladocera						
Bosmina longirostris	2	197	156	ng/g dw	79	
Holopedium gibberum	4	35 ± 4.4	25 ± 11	ng/g dw	70	
Daphnia pulex	16	38 ± 38	22 ± 17	ng/g dw	58	
Copepoda						
Mesocyclops edax	10	9.4 ± 11	4.3 ± 3.3	ng/g dw	46	
Fish						
Golden Shiners						
size class 1	13	0.20 ± 0.07		µg/g ww	*	5.4
size class 2	15	0.40 ± 0.07		µg/g ww	*	5.7
size class 3	5	0.45 ± 0.14		µg/g ww	*	5.7
Yellow Perch						
age 1+	4	0.21 ± 0.07		µg/g ww	*	5.4
age 2+				µg/g ww		
age 3+				µg/g ww		
age 4+	24	0.93 ± 0.19		µg/g ww	*	6.0
age 5+	33	1.1 ± 0.45		µg/g ww	*	6.1
age 6+	3	1.5 ± 0.51		µg/g ww	*	6.2
age 7+	2	1.9 ± 0.37		µg/g ww	*	6.3

*Assumed to be > 95% (Bloom, 1992)

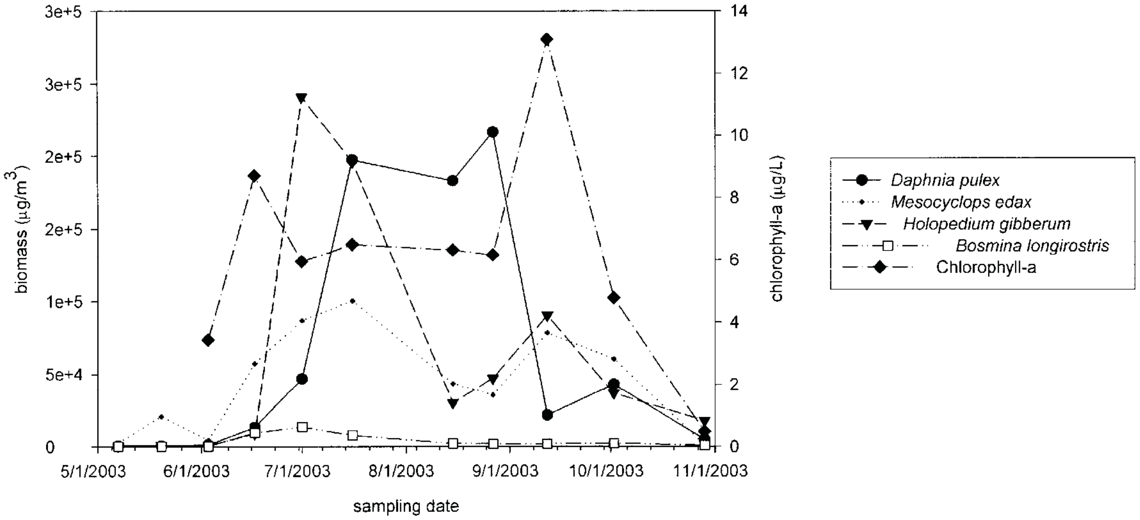

Figure 10-3. Zooplankton biomass and chlorophyll-α concentration over the six-month sampling period at Sunday Lake—*Daphnia pulex* and *Mesocyclops edax* numbers are totals for both adult and juvenile individuals.

10.3.3 Golden Shiners

For calculation purposes, the 33 Golden Shiners were divided into three size classes based on length and weight. Size class one ranged in length from 50-73mm and from 1.87-6.88 g. Size class two ranged from 77-109mm and 7.89-27.85 g, and size class three ranged from 120-140mm and 33.91-58.00 g. Golden Shiner THg concentrations were most correlated with fish length (r^2 = 0.53), and less correlated with weight (r^2=0.37). The average Hg concentrations were 0.20, 0.40, and 0.45 µg/g (ww) THg for size class one (n=13), two (n=15), and three (n=5), respectively (Table 10-2). Mercury concentrations increased significantly from the first to the second size class ($p<0.001$). The second size class fish had similar mercury concentrations to many of the third size class fish, although the average mercury increased slightly from the second to the third size class (Figure 10-4). The log BF values were 5.37, 5.67, and 5.72 for the first, second, and third size classes, respectively (Table 10-2).

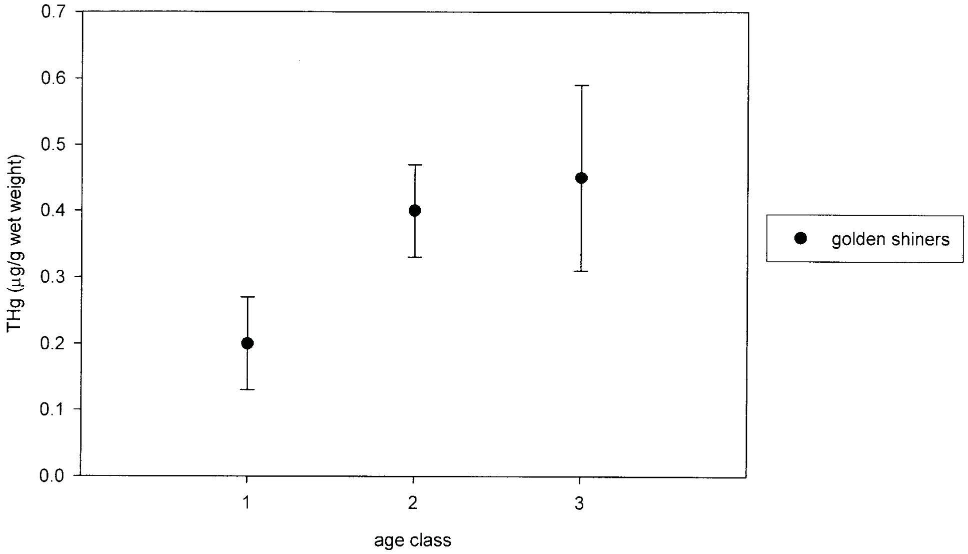

Figure 10-4. Concentrations of THg for three size classes of Golden Shiners

10.3.4 Yellow Perch

Yellow Perch ranged in age from 0+ to 7+ years. No age 2+ or 3+ fish were collected in the October 2000 sampling. Fish THg was most correlated with fish length (r^2=0.45), and more weakly correlated with fish age (r^2=0.36) and weight (r^2=0.30). Total Hg concentrations increased from age 0+ to age 7+ perch (Table 10-2), and averaged 1.0 ± 0.47 µg/g (ww). There was a significant difference between age 1+ and 4+ perch ($p<0.001$), but no significant difference was evident between the 4+, 5+, 6+, and 7+ perch despite large differences in weight and length. There was no significant difference in THg concentrations between the 1992 (Yan, 1996) and 2000 Yellow Perch ($p=0.608$) (Figure 10-5). Average fish Hg exceeded the FDA consumption advisory of 1 µg/g at age 5+, although wide variation existed in Hg concentrations in fish of the same age class. According to the literature, Yellow Perch are typically insectivores until roughly age 5+, at which time they shift their primary diet to piscivory (Driscoll, et al. 1994c). This pattern depends on the dynamics of the food chain within a particular lake. The Sunday Lake fish appear to follow this pattern, as Hg concentrations increased dramatically after age 5+. The log BF values were similar to the 1992 study for Yellow Perch in Sunday Lake, and increased with fish age (Table 10-2). There was a significant difference between Yellow Perch and Golden

Shiner THg concentrations as a whole ($p<0.001$). Very similar THg concentrations were observed between size class one Golden Shiners and age 1+ Yellow Perch, although the 1+ perch had greater weights and lengths ($p=0.001$ and <0.001, respectively).

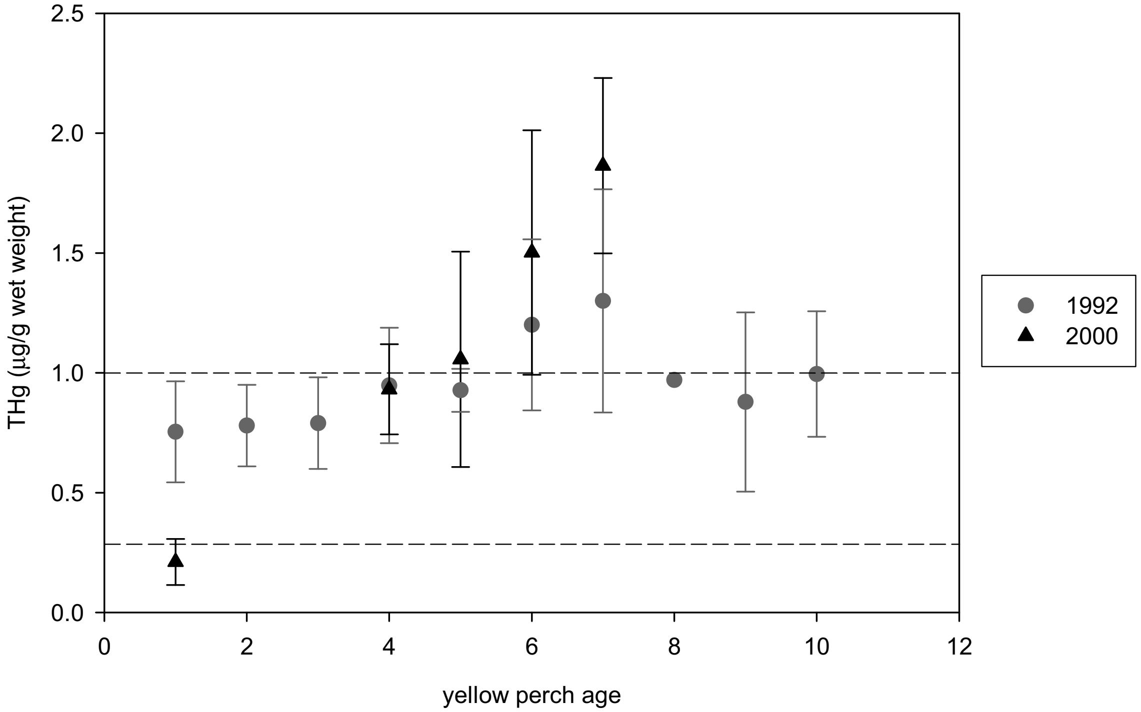

Figure 10-5. Comparison of THg concentrations for different age classes of Yellow Perch in Sunday Lake for 1992 (Yan, 1996) and 2000—Dashed lines represent the FDA consumption advisory level of (1 µg/g) and EPA MeHg criterion (0.3 µg/g) for fish.

10.4 Discussion

10.4.1 Zooplankton

It is well known that MeHg is transferred to a much higher degree than inorganic Hg(II) between trophic levels. Mason, et al. (1995b) identified the process behind this phenomenon in Zooplankton, determining that MeHg is more readily transferred from phytoplankton to Zooplankton than inorganic Hg(II) because of differences in the storage sites for Hg species in the cells of phytoplankton. MeHg is stored in the cytoplasm, which the Zooplankton readily digest. However, inorganic Hg(II) is stored in the cell membranes, which are not digested and simply pass through the Zooplankton predators (Mason, et al., 1995b). The MeHg transfer from water to phytoplankton has been shown to be the major bioaccumulation step in lake food chains. Log BF values may increase five-fold at this step, compared to only two to four-fold at other trophic steps (Back and Watras, 1995). Watras et al. (1998) determined that MeHg concentrations in Crustacean Zooplankton, such as the four reported in this study, were strongly correlated with the modeled CH_3HgOH fraction in the water column of 15 Wisconsin lakes. Epilimnion MeHg concentrations for Sunday Lake averaged 0.86 ± 1.12 ng L^{-1}. This value represents ~24 percent of the THg for the lake and is at the high-end of the range for the Wisconsin lakes studied. However, *Daphnia*, *Holopedium*, and cyclopoid species (*Mesocyclops*) in Sunday Lake had lower MeHg concentrations than the Wisconsin lakes. This suggests that MeHg in Sunday Lake waters is less available for uptake by plankton than was the case for the Wisconsin lakes. Dissolved organic carbon concentrations in Sunday Lake were higher than the median DOC concentration in the Wisconsin lakes. A previous Zooplankton study observed that log BF values for MeHg decrease with increasing DOC concentrations (Back and Watras 1995). Lower Zooplankton MeHg in Sunday Lake may be due to complexation by DOC, which is known to reduce the bioavailability of MeHg (Wright and Mason 2000).

Unlike other studies (e.g. Monson and Brezonik 1998), THg and MeHg concentrations of the four Zooplankton species did not vary significantly over the three-month study. However, this study represents a short period of time in late summer and fall, and Zooplankton concentrations may have already reached maximum levels. As reported in the literature, Hg concentrations in Zooplankton were not correlated with concentrations of Hg species in water over the three months of sampling (Monson and Brezonik 1998).

In another study, experimental acidification of a basin was found to increase the MeHg fraction in Zooplankton compared to a reference basin (Watras and Bloom 1992). In the reference basin *Daphnia* and *Holopedium* had <30 percent THg as MeHg, whereas the acidified basin had >90 percent THg as MeHg. The pH was 6.1 and 4.7 in the reference and acidified basin, respectively. Sunday Lake pH averaged 5.4 (See Table 10-2), which is intermediate between the pH of the reference and experimentally acidified basins. Average percentage of THg as MeHg values for *Daphnia* and *Holopedium* in Sunday Lake were between 30 percent and 90 percent (See Table 10-2), which corresponds well with the concentrations in the experimental acidification study (Watras and Bloom 1992).

Holopedium is reported to be restricted to calcium-poor lakes, most likely because other cladocerans may outcompete it in high calcium, higher pH lakes (Cole 1994). Sunday Lake is characterized by low calcium concentrations and the presence of *Holopedium* may suggest that other species in the lake are not as adapted for low-calcium lakes, allowing *Holopedium* to compete. Over the six-month sampling period, *Holopedium gibberum* biomass decreased in late July (See Figure 10-3). However, *Daphnia pulex* biomass remained high during this same period. *Daphnia pulex* is a preferred prey specie of Golden Shiners (Ehlinger 1989). Therefore, since fish do not preferentially feed on *Holopedium* unless other prey species are sparse (Ehlinger 1989), it is unlikely that the decrease in *Holopedium* biomass was due to planktivore predation.

In Sunday Lake, cyclopoid copepod species such as *Mesocyclops edax* were the dominant copepod species. Cole (1994) reported that *Mesocyclops edax* is most likely a predatory species, feeding on smaller Zooplankton species such as *Bosmina longirostris*. However, in Sunday Lake *M. edax* had lower Hg concentrations than the suspected prey species such as the cladoceran *B. longirostris*. This relationship was also observed by Watras, et al. (1998). *M. edax* is most likely feeding on some other species with low Hg concentrations.

10.4.2 Golden Shiners

Gorski, et al. (1999) studied Hg accumulation in the mimic shiner, a Forage fish filling a similar niche as the Golden Shiner. The smallest Golden Shiners in Sunday Lake corresponded to the largest, or age 2, mimic shiners in terms of length, and THg concentrations were comparable. Results of the mimic shiner study found that between 3 percent and 100 percent of fish stomach contents were comprised of *Daphnia*. When *Daphnia* populations were low, the mimic shiners added other Zooplankton to their diet (Gorski, et al., 1999). In Sunday Lake, *Daphnia* biomass increased rapidly in July 2002 and decreased markedly in late September (Figure 10-3). Since

Daphnia are a preferred prey species, Golden Shiners in Sunday Lake most likely fed primarily on *Daphnia* in July and August, and a mixture of other Zooplankton the rest of the year. Gorski, et al. (1999) found that THg in mimic shiners increased in winter months when fish growth was negligible, and decreased somewhat in summer months due to rapid fish growth. In Sunday Lake, Golden Shiners were collected in early June, 2003, and hence the THg concentrations in the fish include the previous summer, fall, and winter THg accumulations. Total Hg concentrations most likely had not been diluted greatly by rapid fish growth this early in the season.

Ehlinger (1989) determined that Golden Shiners use two feeding methods—particulate feeding (visual) and pump filter-feeding (non-visual), and could switch between them depending on prey species composition. When fed equal portions of prey species, Golden Shiners were observed to particulate-feed disproportionately on cladocerans, especially larger species, rather than copepods. Ehlinger (1989) attributed the disproportionate feeding to the copepods' superior swimming ability, giving them an advantage over the cladocerans in escaping filtering suction produced by the feeding shiners. Among cladocerans, Golden Shiners exhibited preferential consumption of *Daphnia* over *Bosmina*. When *Daphnia* populations decrease or light conditions are poor, Golden Shiners have the advantage of switching from particulate-feeding to filter-feeding (Ehlinger, 1989). In Sunday Lake, light conditions are poor due to the high color of the water. Consequently, Golden Shiners in Sunday Lake would be expected to frequently use filter-feeding. Therefore the golden shiner is expected to be non-selective in its prey. As in the mimic shiner (Gorski, et al., 1999), golden shiner diet varies depending on prey densities and environmental factors.

10.4.3 Yellow Perch

As mentioned earlier, size class-1 Golden Shiners and 1+ Yellow Perch had similar THg concentrations (Table 10-2). The log BF values for both species classes were comparable as well, implying that the smallest members of these two species feed on similar diets or at least prey with similar MeHg concentrations. The age 1+ Yellow Perch had similar concentrations despite having greater lengths and weights. Growth dilution of Hg concentrations may be greater in the perch at this age than in the shiners. Post, et al. (1996) reported that age 0+ Yellow Perch growth rates were rapid during the first spring and summer, but reached an asymptote in fall similar to mimic shiners (Gorski, et al., 1999). No age 2+ or 3+ perch were collected; therefore a comparison between age class-2 and 3 shiners is not possible. Around age 5+, Yellow Perch in Sunday Lake most likely switch to piscivory and start consuming Golden Shiners and other small fish. This is evident in the greater increases in perch THg concentration after age 5+ (Figure 10-5).

The Sunday Lake Yellow Perch collected in October 2000 averaged 1.0 ± 0.47 µg/g THg, just at the FDA consumption advisory level. Thirty of the 66 Yellow Perch exceeded the FDA advisory level, and all but three perch exceeded the EPA fish tissue MeHg criterion of 0.3 µg/g. The levels in Sunday Lake were greater than Yellow Perch collected from Western and Central Maryland (Castro, et al., 2002; Gilmour and Riedel, 2000), New Jersey (Sprenger, et al., 1988), northern Wisconsin (Greenfield, et al., 2001; Watras, et al., 1998), the Upper Peninsula of Michigan (Grieb et al., 1990), and a survey of northeastern U.S. lakes (Stemberger and Chen 1998). Driscoll, et al. (1994c) found that fish THg concentrations in Adirondack Yellow Perch were positively correlated with DOC up to DOC concentrations of 8mg C/L. The study reports that although water MeHg concentrations were higher in high DOC lakes, bioavailable MeHg appeared to be lower. Decreasing log BF values with increasing DOC concentrations indicate that complexation with DOC reduces bioavailable MeHg in Adirondack lakes, where Sunday Lake log BF values were generally lower than lakes with low DOC concentrations (Figure 10-6). Theories about why fish are high in Hg implicate both food chain transfers (e.g. Mason, et al., 1997; Chen, et al., 2000) and lake DOC concentrations (e.g. Driscoll, et al. 1994c). Both of these pathways are likely influencing Hg concentrations of Sunday Lake Yellow Perch.

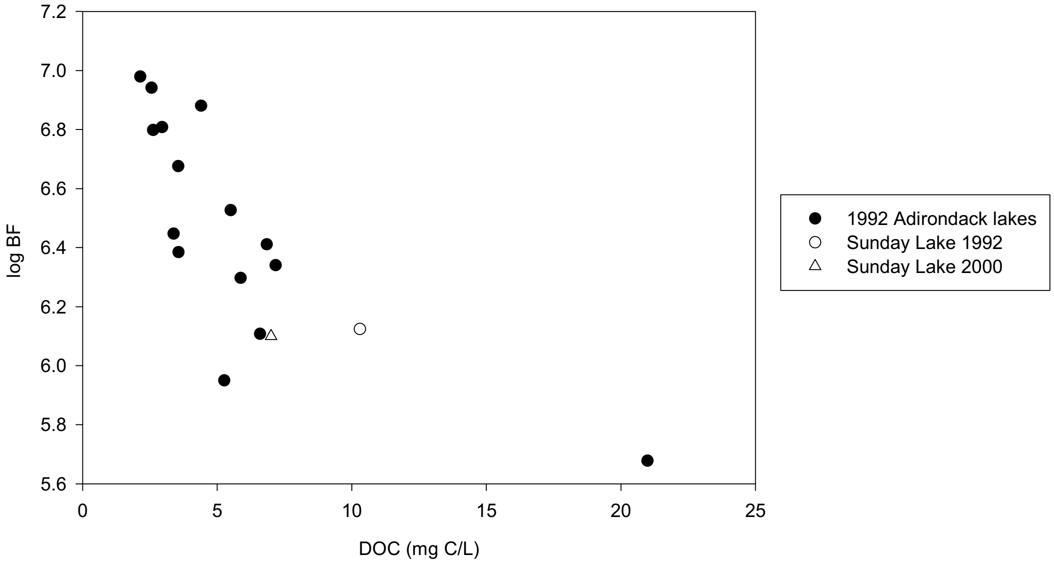

Figure 10-6. **Log bioconcentration (BF) values for age 3+ to 5+ perch vs. DOC (mg C/L) for 16 Adirondack lakes in 1992 (Yan, 1996) and Sunday Lake in 2000**

11 Changes in Historical Mercury Deposition in Adirondack Lake Sediments and Lagged Response from Watershed Contributions

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11.1 Introduction

Anthropogenic emissions and deposition of Hg have globally enriched the content in soils above their preindustrial levels (Benoit, et al., 1994; Engstrom, et al., 1994; Engstrom and Swain, 1997; Hudson, et al., 1995; Kamman and Engstrom, 2002; Lockhart, et al., 1998; Swain, et al., 1992; Lamborg, et al., 2002). Even with reductions in Hg emissions and atmospheric deposition, the Hg contained in the watershed soils of a lake ecosystem could delay any apparent recovery of lake and fish Hg levels. The Adirondack region of New York is a significant area to study as it has many acidified lakes which are more sensitive to Hg contamination in fish, and it has a relatively close proximity to upwind Hg emission sources (Driscoll, et al. 1994c).

Increased industrial activities led to increases in atmospheric Hg emissions after 1850. The increases have resulted in a 2-5 fold increase in Hg burdens and pools above preindustrial levels, even in remote areas (Benoit, et al., 1994; Engstrom, et al., 1994; Engstrom and Swain 1997; Hudson, et al., 1995; Kamman and Engstrom 2002; Lockhart, et al., 1998; Swain, et al., 1992; Lamborg, et al., 2002). Anthropogenic emissions of Hg occur as elemental Hg (Hg^o), reactive gaseous mercury (RGM) and particulate Hg (Hg_P) (Mason, et al., 1994a, b). The majority of atmospheric Hg occurs as Hg^o. This form has an atmospheric residence time of about 1 year and is a global scale pollutant (Porcella 1994). Atmospheric Hg^o is oxidized (Porcella 1994) and Hg is largely deposited from the atmosphere in this form (Lindqvist 1994; Olmez, et al., 1998). The degree to which oxidized Hg is transported will depend on the size of the particle to which it is associated. If Hg is in a gaseous form or associated with large particles, it remains in the atmosphere for only a few days, and is deposited in a region local to the source (Olmez ,et al., 1998). If oxidized mercury is associated with small particles or aerosols, it may remain in the atmosphere for a week or so, and be deposited on a regional scale relative to the source (Olmez, et al., 1998). Large sources of Hg deposition to the Adirondack region of New York include emissions from the U.S. (37 percent; NYSERDA, 2002) and from countries as far away as Asia.

Lake sediment and peat bog cores have been used to investigate historical changes in atmospheric Hg deposition (Benoit, et al., 1994; Engstrom, et al., 1994; Engstrom and Swain, 1997; Gobeil, et al., 1999; Kamman and Engstrom 2002; Lockhart, et al., 1998; Swain, et al., 1992). In this study we used sediment cores to examine historical deposition of Hg and recent changes in Hg deposition in remote lakes of the Adirondack region of New York.

11.2 Study Area Description and Methods

The eight lakes in this study are located throughout the Adirondack region of New York State (Figure 11-1), and exhibit a wide range of watershed and chemical characteristics. Lake surface areas ranged from 1 to 521 ha, while the watersheds ranged from 1 to 9,481 ha. These lakes were among those cored in the early 1980's as part of the PIRLA project, and these older cores were analyzed for Hg (Lorey and Driscoll 1999). Seven of the lakes are drainage lakes that receive water inputs from precipitation, groundwater, and stream discharge while also having a surface outlet. Little Echo Pond is a groundwater-recharge seepage lake that receives most of its water from direct precipitation, with some runoff through the upper sections of a surrounding peat bog (Driscoll, et al. 1991).

Sediments were collected during the open-water season of 1998 using a piston corer operated from the lake surface by rigid drive-rods. A surface piston corer equipped with a 7cm diameter polycarbonate core barrel was used to collect a continuous 1 m section of the upper sediments (Wright 1991). This device recovers the watery, uncompacted sediment surface as well as deeper strata without disturbance or displacement (core-shortening) (Blomqvist 1991). The cores were sectioned vertically in the field at 1cm increments from 0 to 30cm and 2cm increments from 30 to 70cm. The cores were stored in ice packed coolers until being returned to the laboratory, where they were stored at 4^{o}C.

Sediment chronology was determined by standard 210Pb methods. Lead-210 was analyzed by alpha spectrometry using thermal distillation and isotope dilution (Eakins and Morrison 1978), and dates and sediment accumulation rates were calculated according to the constant rate of supply (c.r.s.) model (Appleby 2001).

THg was extracted from aliquots of wet sediment by digestion in concentrated trace metal grade nitric and sulfuric acids at boiling with reflux for two hours. The digestate was diluted with a solution of 1 percent (v/v) bromine monochloride which provided further oxidation. After pre-reduction with hydroxylamine hydrochloride, the samples were reduced with tin (II) chloride and the resultant Hg^{o} was quantified by cold vapor atomic fluorescence spectrometry (CVAFS). The concentrations were converted to a dry weight basis using water content as determined on separate aliquots of sediment. Each analytical batch contained a method blank, sample duplicate, and a matrix spike or spiked blank sample.

Table 11-1.
Lake characteristics and surface water chemistry results for the study lakes

Lake	Watershed Area[a] (ha)	Surface Area (ha)	WA/SA Ratio	DOC (mg C·L^{-1})	THg (ng·L^{-1})	MeHg (ng·L^{-1})
Big Moose	9481	520.59	18.2	6.47	2.60	0.31
Little Echo	1	1.00	1	17.70	8.90	0.89
Merriam	53	8.78	6.0	6.51	3.78	0.38
West	133	12.30	10.8	10.01	5.09	0.41
Bear[b]	78	21.90	3.6	N/A	N/A	N/A
Queer	371	54.50	6.8	3.84	1.46	0.11
Upper Wallface	59	6.54	9.02	4.34	1.94	0.20
Clear	573	70.82	8.1	3.95	1.21	0.25

a – watershed area includes lake surface area, because the intent is to compare total fluxes to the ratio
b – no water sample was obtained from Bear Pond
There are some differences in the watershed and lake surface areas from values previously reported for these lakes (Lorey and Driscoll 1999). The current lake surface area values are from recent Adirondack Park Agency digital coverages, which are believed to be more accurate than previous estimates (K. Roy, personal communication). The watershed areas are based on the latest metric U.S. Geological Survey 7.5 minute quads (Newton, personal communication).

Figure 11-1. **Map of the Adirondack Park, including location of the lakes where sediment cores were collected**

In addition, a surface water sample was collected from seven of the lakes using the “clean hands/dirty hands” technique (US EPA, 1995b). These water samples were analyzed for THg, MeHg, and dissolved organic carbon (DOC). The THg method was the same as for soils, without the concentrated acid digestion. The MeHg analysis was accomplished through distillation, followed by aqueous phase ethylation, and purging and trapping on an organic adsorbent trap. The traps were heated to release the organo-Hg compounds which were separated by gas chromatography, and quantified with CVAFS. DOC samples were filtered and analyzed with an automated TOC instrument. The instrument removed inorganic carbon with acid oxidation and purging. The organic carbon was then converted to carbon dioxide by a UV/persulfate oxidation.

The resulting carbon dioxide was detected by IR. We compared current rates of sediment THg deposition with wet Hg deposition that is measured at Huntington Forest (site ID = NY20) in the central Adirondacks as part of the National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN). (http://nadp.sws.uiuc.edu/nadpdata/mdnsites.asp)

11.3 Results and Discussion

THg concentrations ranged from 1.2 to 8.9 ng·L^{-1}, while MeHg concentrations ranged from 0.11 to 0.89 ng·L^{-1}. There was no apparent relationship between the surface water Hg concentrations and the concentrations of Hg found in surface sediments.

THg concentrations in deeper sections of the Adirondack lake sediment cores ranged from 0.07 to 0.24 µg·g^{-1} dry wt. The THg concentrations were relatively constant over several centimeters and began increasing with decreasing sediment depth around 11-25cm below the sediment-water interface. The upper sections of the sediment cores had THg concentrations that ranged from 0.18 to 0.50 µg·g^{-1} dry wt. The uppermost section of all eight cores showed a decrease in THg concentration from the maximum value. The decreases in THg in surface sediments ranged from 6-34 percent (average = 16 percent) of peak concentration. Further sampling using multiple cores per lake would be needed to confirm whether mercury concentrations in sediment are decreasing in response to decreased deposition, particularly since variations in precipitation result in interannual variability.

Several sediment core studies have shown an increase above background levels beginning around 1850 (Engstrom, et al., 1994; Engstrom and Swain 1997), while another shows this increase around 1875 (Kamman and Engstrom 2002). Two of the sediment cores in this study showed an increase in sediment THg accumulation above background just before 1850 (Figure 11-2), while four other sites showed an increase around 1880. The earliest increase in THg accumulation began around 1820 and the latest around 1910.

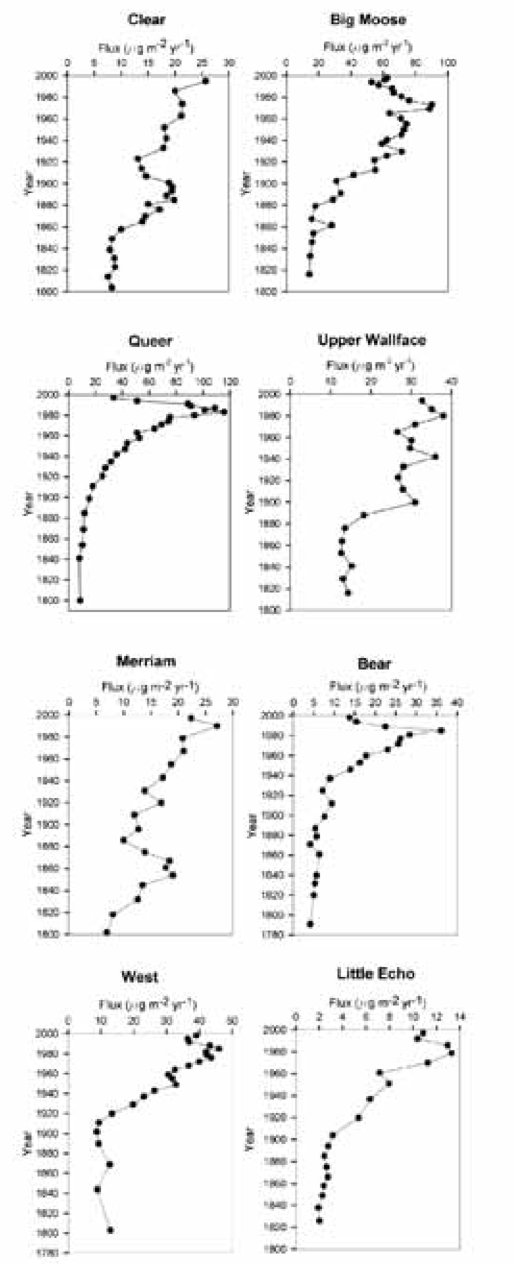

Figure 11-2. Total mercury accumulation profiles in the ^{210}Pb dated sediment cores of the eight study lakes

Preindustrial values of sediment Hg accumulation ranged from 5.2 to 15.8 $\mu g \cdot m^{-2} \cdot y^{-1}$ for drainage lakes, and was 2.3 $\mu g \cdot m^{-2} \cdot y^{-1}$ for the seepage lake, Little Echo, (Table 11-2). Maximum THg fluxes, which ranged from 25.7 to 115.6 $\mu g \cdot m^{-2} \cdot y^{-1}$ in drainage lakes and were 13.3 $\mu g \cdot m^{-2} \cdot y^{-1}$ in the seepage lake, occurred during the period from 1973 to 1995. Modern values ranged from 13.7 to 62.5 $\mu g \cdot m^{-2} \cdot y^{-1}$ for the drainage lakes while the seepage lake THg flux was 10.9 $\mu g \cdot m^{-2} \cdot y^{-1}$. Seven of the eight lakes had a modern THg flux that was lower than the maximum flux for the core. The decreases from maximum values ranged from 14-71 percent (average = 33 percent).

Table 11-2.
Fluxes of the study lakes, along with the ratios obtained relative to background values

Lake	Preindustrial Flux (years averaged)	Maximum Flux (year)	Maximum Flux Ratio	Modern Flux (year)	Modern Flux Ratio
Big Moose	15.81 (1816-1879)	90.05 (1973)	5.70	62.49 (1998)	3.95
Little Echo	2.30 (1826-1885)	13.30 (1979)	5.78	10.88 (1997)	4.73
Merriam	6.90 (1802)	27.09 (1990)	3.93	22.31 (1997)	3.23
West	10.28 (1803-1890)	46.00 (1985)	4.47	39.05 (1998)	3.80
Bear	5.20 (1791-1887)	36.07 (1985)	6.94	13.74 (1998)	2.64
Queer	8.34 (1800&1841)	115.58 (1983)	13.86	33.40 (1997)	4.00
Upper Wallface	13.64 (1816-1876)	37.96 (1980)	2.78	32.71 (1994)	2.40
Clear	8.24 (1804-1849)	25.69 (1995)	3.12	25.69 (1995)	3.12
		Avg. =	5.82	Avg. =	3.48

The maximum THg fluxes showed an average enrichment (flux ratio) of 5.8 fold (range = 2.8 – 6.9, excluding 13.9 for Queer Lake) above background levels. For fluxes in the most recent sediments, the mean flux ratio has decreased by 40 percent to 3.5 fold (range = 2.4 – 4.7) above background. This value is within the 2-5 fold range that is found in studies from other sites in the northern hemisphere (Benoit, et al., 1994; Bindler, et al., 2001; Engstrom, et al., 1994; Engstrom and Swain 1997; Hudson, et al., 1995; Lamborg, et al., 2002; Lockhart, et al., 1998; Swain, et al., 1992), and agrees well with values from the midwestern U.S. (Engstrom, et al., 1994; Engstrom and Swain, 1997; Swain, et al., 1992) and Vermont/New Hampshire (Kamman and Engstrom, 2002).

As part of this study, we compared the results for these cores with results from cores of the same eight lakes that were taken in 1982 for the PIRLA study and analyzed previously by the authors (Lorey and Driscoll 1999). The THg concentration profiles for the 1982 and 1998 cores show relatively good agreement for the majority of the eight cores (Figure 11-3). The largest discrepancies occur during the early 1900's for the Merriam core, and the 1980's for the Clear and Little Echo cores. Likewise, the THg flux profiles for the 1982 and 1998 cores also show relatively good agreement (Figure 11-4). The most notable differences occur after 1950 in the Merriam, Bear, and Little Echo cores.

Noted differences between the two sets of cores are most likely due to differences in core locations for the two studies. Because the exact locations of the 1982 cores are unknown, the 1998 cores were most likely collected in a somewhat different part of the basin. Lake sediments typically exhibit large spatial differences in sediment accumulation and THg concentrations across the lake basin (Engstrom, et al., 1994; Engstrom and Swain 1997; Swain et al., 1992). Due to this spatial heterogeneity, the most accurate determination of whole basin THg fluxes requires multiple cores from each lake (EPRI, 1996). However, a single lake core can still provide reliable information about stratigraphic trends and the magnitude of change in Hg loading to the lake (EPRI, 1996).

Although assumed to be less significant, difference in results between the two studies may reflect a change in analytical method from CVAAS to CVAFS and the associated sample preparations (see Lorey and Driscoll 1999). Also, the ^{210}Pb dating and sediment accumulation rate determinations were done in different laboratories with different equipment. The modeling of ^{210}Pb data in particular requires interpretations that could vary from one individual to another. Taking these differences into account, the 1998 cores do a reasonably good job of confirming the trends evident in the 1982 cores, and now add an additional 15 years of information about the historic trends of sediment THg deposition in these lakes. Declining rates of Hg accumulation, barely apparent in 1982, are clearly evident by 1998. Moreover, the similarity of the two sets of cores provides strong evidence the stratigraphic trends in THg are well preserved over time and are not appreciably altered by diagenetic processes (e.g. diffusion) as some papers have suggested (e.g., Rasmussen 1994).

There are several pathways of THg to lake sediments. Prior to increases in atmospheric Hg and deposition associated with human activities, a remote lake would receive THg inputs from direct atmospheric deposition to the lake surface and from the watershed via stream and surface runoff. THg is supplied to the watershed principally from atmospheric deposition (directly to the lake surface or indirectly through the watershed) and to a much lesser extent (except in Hg-rich terrains) from the weathering of primary minerals. With increases in atmospheric Hg emissions, loading of Hg to lakes via direct atmospheric deposition and watershed runoff should increase. Much of the atmospheric input of THg to forested watersheds is retained in the soils or re-emitted to the atmosphere, with a smaller fraction (10-25%) exported to surface waters. Under conditions of lower atmospheric Hg deposition associated with emission controls, one might expect watershed pools to continue to supply Hg to drainage waters through mineralization of soil organic matter or net desorption from soil surfaces.

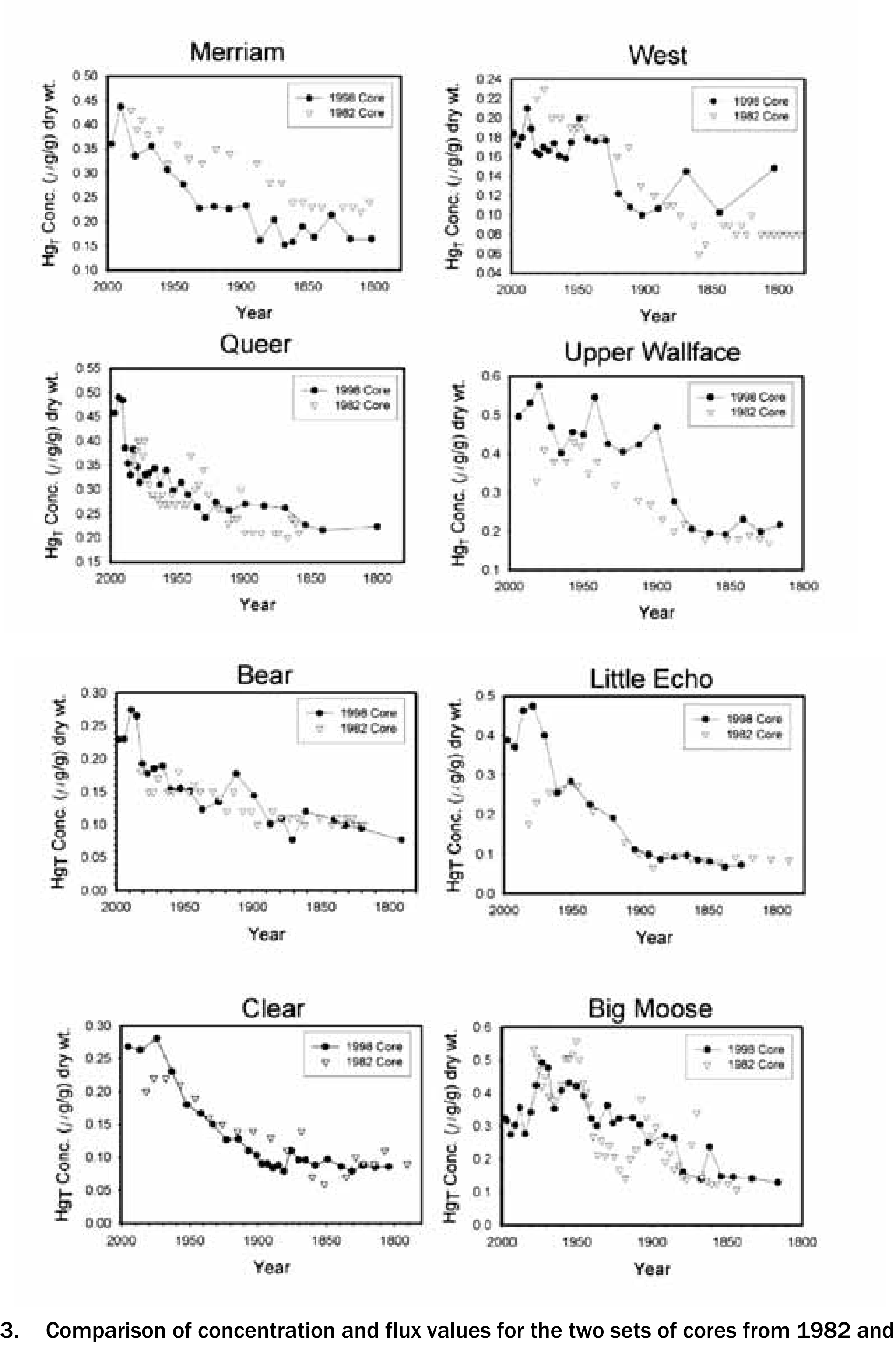

Figure 11-3. Comparison of concentration and flux values for the two sets of cores from 1982 and 1998

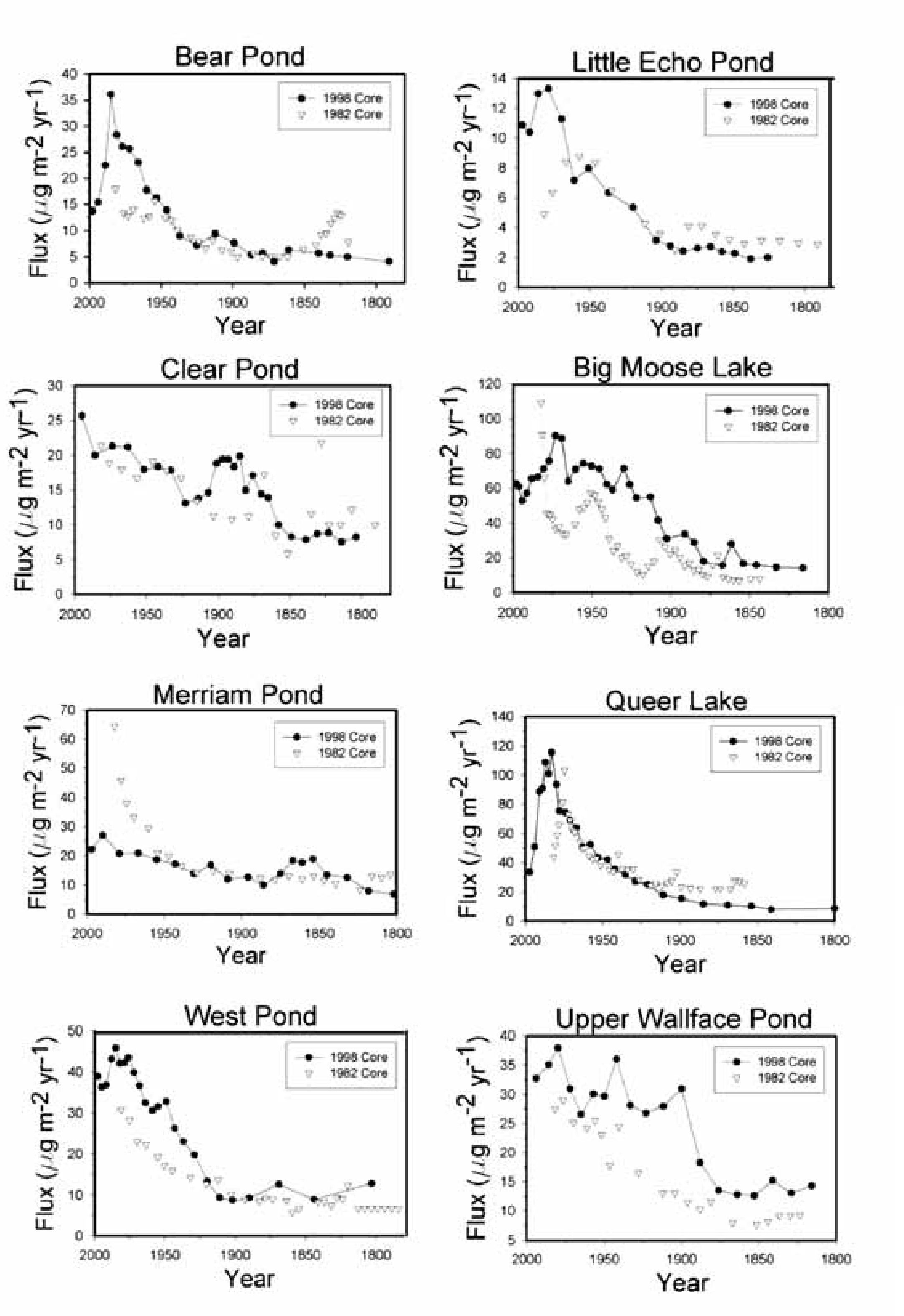

Figure 11-4. **Comparison of Total Mercury Fluxes from Watershed from 1998 and 1992 Cores**

The relative contribution of Hg to a lake ecosystem from direct atmospheric deposition and watershed sources has been shown to depend on the ratio of the watershed area to lake surface area (Swain, et al., 1992), the magnitude of atmospheric THg deposition, and the processes regulating retention/release of THg within the watershed. The eight Adirondack lakes in this study all showed a strong linear relationship between sediment THg accumulation and the ratio of watershed area to lake surface area, both in preindustrial ($r^2 = 0.85$) and modern times ($r^2 = 0.95$) (Figure 11-5). The slope of the lines in this relationship are a measure of the relative importance of Hg inputs from the watershed as compared to direct Hg deposition to the lake surface to THg accumulation rates in the sediments. The slope of the modern line (3.1 ± 0.28) has increased by almost a factor of 4 over the preindustrial value (0.78 ± 0.13). This pattern indicates that the supply of THg from the watershed has increased markedly relative to increases in direct atmospheric deposition to the surface of drainage lakes, particularly for those sites with large watershed area to lake surface area.

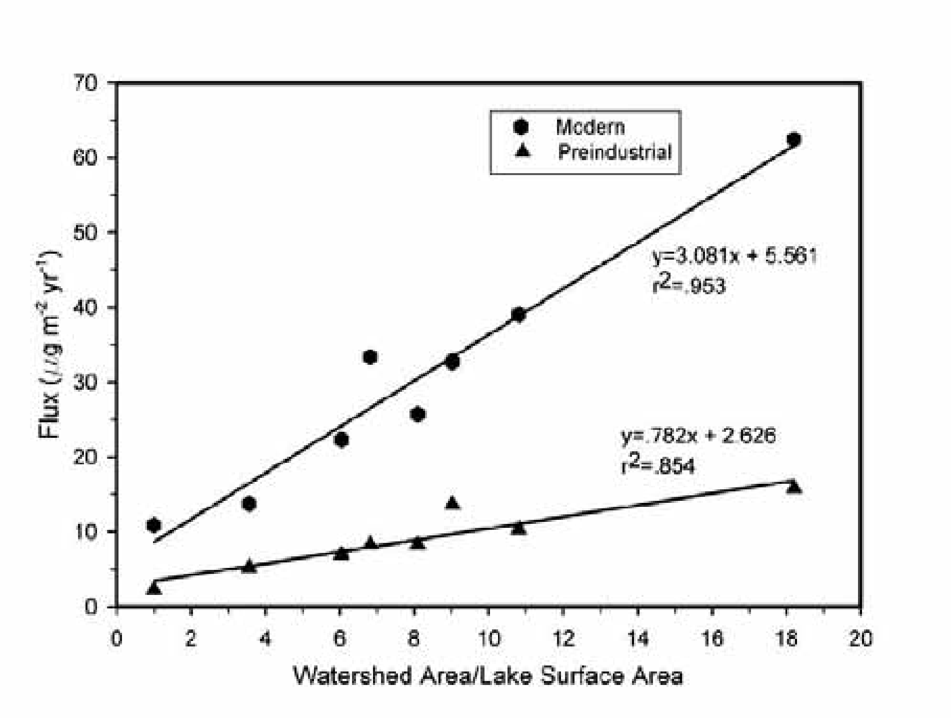

Figure 11-5. The preindustrial and modern sediment THg fluxes as a function of the watershed area to lake surface area ratio

An extrapolation of the regression lines to a watershed/lake area ratio of 1 provides an estimate of the atmospheric Hg deposition to the lake surface (Swain, et al., 1992). At this value the watershed area is equivalent to the lake surface area and the lake acts as a perched seepage lake. In preindustrial times this intercept was $3.4 \pm 1.1\ \mu g \cdot m^{-2} \cdot y^{-1}$ while in modern times the value increased to $8.6 \pm 2.4\ \mu g \cdot m^{-2} \cdot y^{-1}$. These estimates represent the flux of THg to the sediments that entered the lake by direct wet or dry deposition and that was not lost by evasion or outflow. The modern value is very similar to wet Hg deposition measured at the Huntington Forest MDN site ($7.1\ \mu g\ m^{-2}\ y^{-1}$ in 2000).

Other studies of Hg cycling in temperate-region lakes indicate relatively small evasive losses – on the order of 10 percent of Hg inputs (e.g., Fitzgerald, et al., 1991). A mass balance study of seven

Wisconsin seepage lakes (Watras, et al., 1994) found an atmospheric deposition of 10.3 $\mu g \cdot m^{-2} \cdot y^{-1}$ of which 70 percent was from wet deposition while 30 percent was from dry deposition. Of this input, one lake showed over 90 percent was deposited in the sediments, while approximately 7 percent was lost by evasion of Hg^o with the remainder lost to groundwater. There was a range in the sedimentation to evasion ratio from 9:1 to 1:1 for the lakes in that study (Watras, et al., 1994).

Although atmospheric Hg deposition began to decline in the 1980's, some of these lakes did not show a decreasing Hg accumulation until 1990 or later. Thus, there can be a delay in the recovery of a lake from decreases in atmospheric Hg deposition. This delay in response to decreases in atmospheric Hg deposition along with the strong relationship of sediment Hg deposition with watershed area to lake surface area ratios indicates some watershed processes affect transport of Hg to lakes. One measurement that is of particular interest is the amount of deposited THg that is retained in the watershed. This can be determined from Figure 11-5 numerically by dividing the slope of the regression line by its intercept at a ratio value of one, and subtracting this from 100 percent (Swain, et al., 1992). Watershed retention of THg, calculated thus for each individual decade from 1820 until present, shows a significant decrease over the past 200 years ($r^2 = 0.65$) (Figure 11-6). Based on the regression line for the most recent time period, present-day watershed THg retention in Adirondack lakes is 70 percent. This value is in relatively good agreement with several other studies of Hg delivery from forested catchments (Driscoll, et al. 1998; Engstrom, et al. 1994; Lockhart, et al. 1998; Scherbatskoy, et al. 1998; St. Louis, et al. 1996; Swain, et al. 1992).

Our core data also indicate recent declines in Hg flux to Adirondack lakes. Hg accumulation rates peak (circa 1973-1995) for seven of the eight study sites, suggesting declining rates of atmospheric Hg inputs, as observed previously in sediment cores from nearby Vermont and New Hampshire (Kamman and Engstrom 2002) and Minnesota (Engstrom and Swain 1997). Because sedimentation rates can have a large influence on THg accumulation for a given core, it is important to examine trends in THg concentrations as well, especially as several of our cores exhibit a decrease in sedimentation in recent years. However, as previously noted, all eight of the cores show a decrease in THg concentrations in the past 1-3 decades, reinforcing the conclusion that Hg inputs to the lakes have declined during this time.

The characteristics of the watershed can have a large effect on the speciation and transport of Hg. Several studies have concluded that upland areas are sinks for THg (Hurley, et al. 1995; Scherbatskoy, et al. 1998; St. Louis, et al. 1996) and this study.

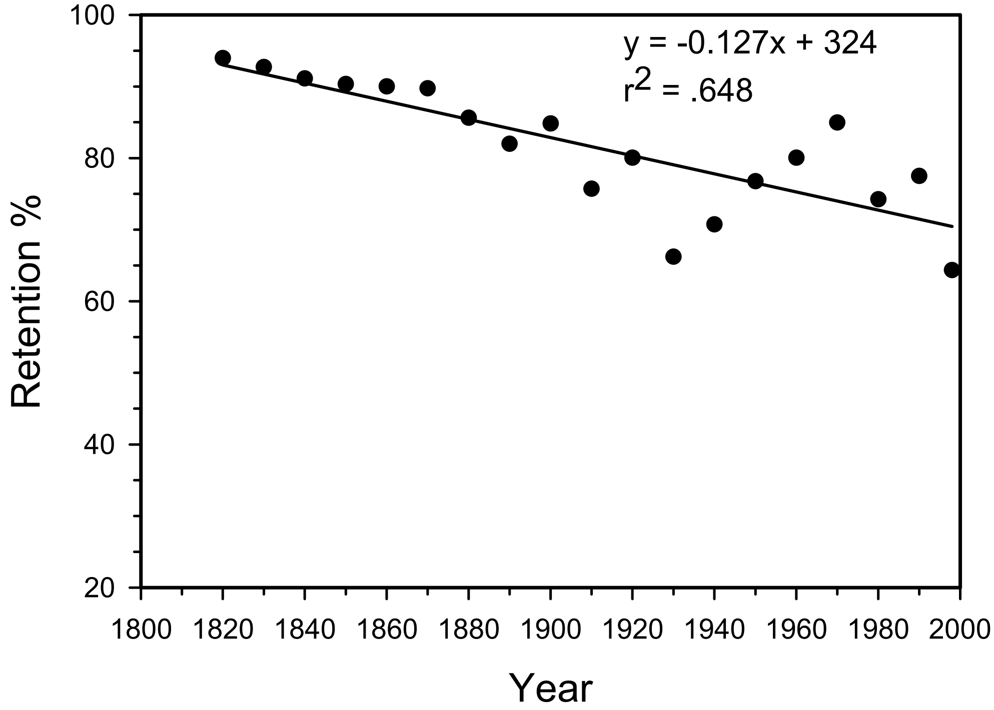

Figure 11-6. **Percent retention of total mercury in the watersheds for individual decades from 1820 to the present**

At Sunday Lake in the Adirondacks, the percent of THg retained is 77 percent if the mass balance is based on wet Hg deposition and 93 percent if it is based on total Hg deposition. The wet deposition based mass balance is close to our modern estimate of watershed Hg retention from sediment cores. It is difficult to know how to interpret this. On one hand, dry deposition of Hg largely occurs by litterfall in deciduous forests (Kalicin, et al., Chapter 8). This Hg may be sequestered in soil organic matter and not readily transmitted to surface waters. On the other hand, the Sunday Lake watershed mass balance (and other Hg mass balances) fails to consider losses of Hg by volatilization**,** and this may be an important pathway of Hg removal (Grigal, 2002). Losses from the lake would tend to lower sediment-based estimates of watershed Hg retention. And in fact, what we are really calculating from cores is not retention, but rather delivery to the lake. A large portion of the Hg that doesn't get to the lake is probably retained in the soil pool, although some of it could be revolatilized from soils back to the atmosphere.

The percent of THg retained varied from a 3-year average of 65 percent at the Experimental Lakes Area in Canada (St. Louis, et al., 1996) to 60-90 percent in a Vermont study (Scherbatskoy et al., 1998). Watershed THg retention has been shown to have seasonal differences with high retention in the fall and a much lower retention in the spring (Hurley, et al., 1995). In one study, there were similar exports of THg from several types of watersheds and the presence or absence of wetlands did not have an effect on the THg retention (St. Louis, et al., 1996). However, in another study, the presence of wetlands was accompanied by a decrease in THg retention (Hurley, et al., 1995). Our study lakes have a varied amount of wetlands, as there are a few lakes with no wetlands in their watershed, and one with as much as 40 percent wetlands.

While changes in the watershed could explain the apparent decreased watershed retention of THg for these lakes, there is no evidence to support such hypotheses. Both MeHg and THg are bound to soil organic matter in the upper soil horizons (Lee, et al., 1994; Lodenius 1994). The soil organic matter may have simply become saturated with Hg and thus no longer retain as much of the atmospherically deposited Hg. Although acidic deposition is thought to mobilize many metals in the soil, the effects of a decreased pH on soil Hg sorption are not clear (Lodenius 1994). Another possible factor is a decrease of soil Hg sorption due to an increase in chloride (Lodenius, 1994). However, the concentration of Cl^- has been decreasing in precipitation in the Adirondacks over the past 20 years (National Atmospheric Deposition Program, 2001) and in lake water (Driscoll, et al. 2003a, b).

An alternative hypothesis was investigated previously by Kamman and Engstrom (2002). They note that: "Viewed from the perspective of Hg retained in the watersheds, our results appear to suggest that watershed retention of atmospherically deposited Hg has declined progressively from the 1950s to the present." In reality, this trend is more likely a function of declining atmospheric Hg deposition to lake surfaces than an actual increase in export of Hg from watershed soils. A decrease in atmospheric Hg deposition should be reflected most immediately in the sediments of lakes with very small watersheds, while lakes with relatively large watersheds should continue to receive large Hg inputs (relative to direct Hg deposition to the lake surface), owing simply to a greater quantity of runoff from soils that have become saturated with anthropogenic Hg. The effect of this lag between declines in direct Hg deposition and watershed delivery is that watershed Hg loading as a percent of atmospheric deposition will increase, especially for lakes with large watershed: lake area ratios. This point was first proposed by Mielli (1995). The Adirondack data provide confirmation that there is a lag between reduced Hg deposition and Hg inputs to lakes (and by inference food chain contamination).

11.4 Conclusions

Sediment cores from eight Adirondack lakes have shown decreasing Hg accumulation rates in recent years. These accumulation rates show a direct relationship with the ratio of the watershed area to the lake surface area. The continued contribution of mercury from watershed soils derived from past atmospheric deposition at a higher rate than current atmospheric deposition leads to greater transport of Hg to lake sediments. This will slow the recovery of remote lake ecosystems even with declines in atmospheric Hg deposition.

12 The Mercury Cycling Model for Headwater Drainage Lakes (MCM-HD): Model Formulations and Application

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12.1 INTRODUCTION

Terrestrial and wetland processes play a vital role in determining the aqueous chemical characteristics and fish tissue mercury concentrations in drainage lake systems (Driscoll, et al. 1994b). Because drainage lake-watershed systems comprise over 85 percent of the lakes in the Adirondacks (Kretser, et al. 1989), the development of an analysis tool for use in headwater drainage lake systems was necessary. In this section of the report, we present the Mercury Cycling Model for Headwater Drainage Lake Systems (MCM-HD) which integrates mercury cycling in headwater uplands, wetlands and a lake in a single modeling framework. Figure 12-1 represents the conceptualization of the MCM-HD model. The upper panel shows a cut-away representation of a watershed that includes upland areas, riparian wetlands, and a stream that drains into a lake. As indicated in the lower panel, the model segments each of these watershed components into compartments that are further subdivided into vegetation, multiple soil layers, surface waters, and sediment layers. Precipitation enters all of the compartments directly. Water is then routed through the soil layers of the upland into the riparian wetland and then into the stream and lake. Biogeochemical processes that impact mercury concentration and speciation are simulated in each of the compartments and subcompartments in order to track the changes in mercury characteristics as water moves through the lake-watershed system.

MCM-HD evolved from three previous models and the scientific results of mercury cycling in the Sunday Lake watershed presented elsewhere in this report. Earlier mercury studies in the Adirondacks in the 1990s led to the Mercury in Adirondack Wetlands and Watersheds Model (MAWWM). This model simulated mercury biogeochemistry within wetland and terrestrial systems. The model simulated hydrology and the behavior of three major mercury species (Hg(0), Hg(II), and MeHg) in up to five soil layers and in wetland surface waters, but is not designed for lakes. The Dynamic Mercury Cycling Model (D-MCM, Hudson, et al. 1994, EPRI 2002) simulates mercury cycling and bioaccumulation in lakes, but it does not predict terrestrial runoff loads to the lake being simulated. D-MCM was also adapted to represent conditions in Florida Everglades marshes, resulting in the development of the Everglades Mercury Cycling Model (E-MCM, Harris, et al. 2003, Tetra Tech 1999). The MCM models also included food webs and bioaccumulation in fish, which were not included in MAWWM. Components of MAWWM, D-MCM and E-MCM were combined in a single framework to simulate mercury cycling and bioaccumulation in headwater uplands, wetlands, and lakes.

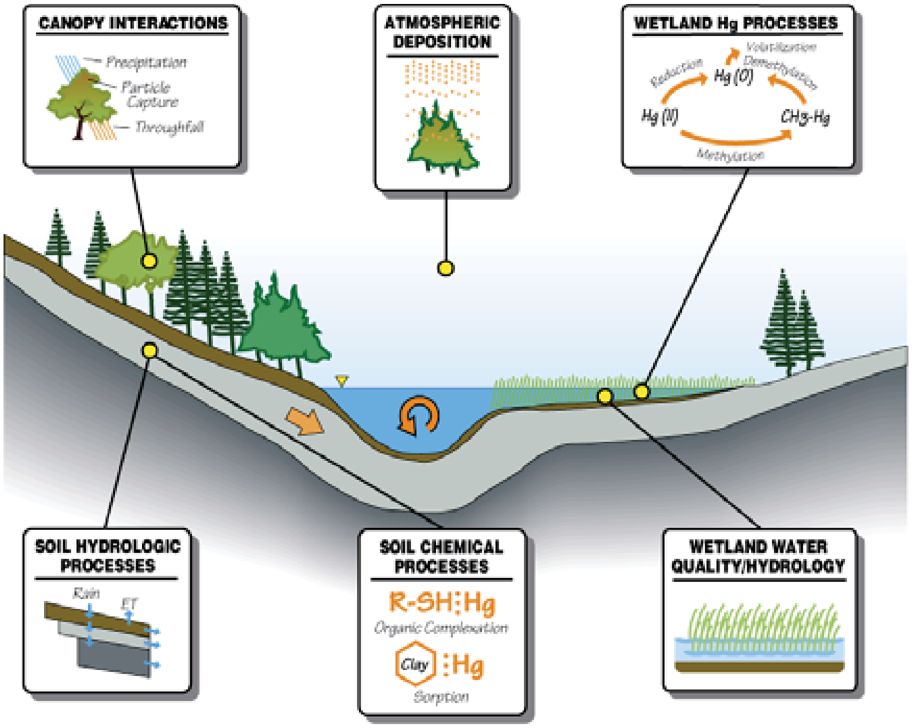


Figure 12-1. The Mercury Cycling Model for Headwater Drainage Lakes (MCM-HD): Model Formulations and Application

The model was calibrated using results of the Sunday Lake watershed studies presented elsewhere in this report. Finally, hypothetical scenarios were simulated with the model to examine the potential response of fish mercury concentrations in Sunday Lake to reduced atmospheric deposition. The remainder of this section of the report presents information on the treatment of hydrology and mercury cycling in MCM-HD, followed by the model calibration and load reduction scenarios.

12.2 MCM-HD Hydrology

The MAWWM routines used to route water in the MCM-HD model are similar to those used in the ILWAS model (Gherini, et al., 1985). The specific hydrologic equations are included in Appendix A, and are described in Chen, et al. (1982.)

12.2.1 Rainfall and Snowfall

The model can accept precipitation in the form of rainfall, snowfall, or a mixture of both. The model determines what type of precipitation is incoming and whether or not there is any mixed precipitation by using a snow formation temperature. The snow formation temperature is an input parameter that generally has a value near 0°C. If the maximum air temperature is below the snow formation temperature, then all of the precipitation is snow. If the minimum air temperature is above the snow formation temperature, then all of the precipitation is rain. If the air temperatures bracket the snow formation temperature, then there is a mixture of rain and snow in the precipitation. The equations used to represent rainfall and snowfall in the model are included in Appendix A.

12.2.2 Evapotranspiration

Evapotranspiration includes direct evaporation and the movement of water through plants and into the atmosphere. Evapotranspiration removes water from the system. Potential evapotranspiration is defined as the maximum evapotranspiration possible for a given timestep under the prevailing meteorological conditions. Evapotranspiration of water from the upper soil horizons is an important hydrologic process, and concentrates mercury in solution. When there is adequate soil moisture, the actual evapotranspiration will be bound by the potential evapotranspiration for each soil layer. All moisture above the field capacity (the moisture content above which gravity drainage of soil moisture occurs) is available for the process of evapotranspiration. When the moisture content of the soil is below field capacity the actual amount of evapotranspiration is reduced exponentially between field capacity and zero moisture content. The equations used to represent evapotranspiration are included in Appendix A.

12.2.3 Advection/Runoff

Downward advection of solutes from the soil surface can occur when precipitation percolates through the soil profile. Lateral flow from a soil horizon, which occurs when the horizon becomes saturated, can carry solutes from watershed soils to surface waters. The extent to which kinetically controlled reactions take place is affected by the amount of time that water stays in contact with a particular component of the solid phase. The extent of these reactions can influence the concentration and speciation of mercury in soil solution and surface waters.

The model allows for multiple separate soil layers of varying areal extent. Hydraulic routing is simulated for each soil layer based upon volumetric soil moisture content, field capacity, saturated soil moisture content, and hydraulic conductivity. Water that flows into the soil layers can contribute to the soil moisture, become lateral flow, percolate to the next layer below, or be lost to evapotranspiration. For a given soil layer, conservation of mass requires that the change in the moisture content of a layer is equal to the amount of water percolating in from the layer above minus the outflow from the layer. The percolation rate is assumed to be zero at and below field capacity, and it increases with soil moisture content to the hydraulic conductivity at saturation.

As a general rule, lateral flow from a layer should not occur when its soil moisture content is below saturation. There are times, however, when that rule is not applicable. This can occur because the soil moisture content for a layer is represented by its average value. However, it is possible for the soil moisture to be distributed nonuniformly with depth in the soil layer. This would be especially true where there is a large reduction of surface area between layers and a saturated condition in the next lower layer. A temporary saturated zone may then be formed to produce lateral flow. Surface runoff can occur if the top layer of soil becomes frozen or saturated. These occurrences impede infiltration. The equations used for surface runoff are described in the appendix.

12.2.4 Snowpack

The formation of a snowpack can affect the mercury concentration of the soil solution. The snowpack slows the infiltration of water into the soil system. Abiotic and microbial reactions take place in the soil under the snowpack, but since the flow of water through the soil is limited, the concentrations of the products of these reactions can increase. These products are rapidly leached from the soil when snowmelt occurs. Increasing air temperature and/or the occurrence of rainfall can cause the snow to melt.

12.3 MCM-HD MERCURY FORMULATIONS

This section describes the treatment of wetland, upland and lake Hg cycling, and bioaccumulation in MCM-HD.

12.3.1 Atmospheric Deposition

Atmospheric methylmercury and HgII can enter a modeled compartment directly via wet deposition, dry deposition of particles, and deposition of reactive gaseous mercury. In vegetated areas, wet, dry, and RGM deposition can occur onto plant surfaces where interactions can occur, reflected in throughfall and litterfall. Wet and dry deposition of elemental mercury is assumed insignificant and is not included in the model.

Wet Deposition

Wet deposition of mercury is calculated as the product of the precipitation rate, surface area, and concentration of Hg(II) or methylmercury in precipitation. These parameters are entered as time-series inputs, not modeled.

Dry Deposition Direct to the Water Surface

Dry deposition of mercury in this model is the flux of atmospheric particles directly to the water surface. In vegetated areas, dry mercury deposited onto leaves is handled via throughfall and litterfall. Dry deposition rates are directly input by the user as time series data on a per square meter basis.

Deposition of Reactive Gaseous Mercury Directly to the Water Surface

Deposition of atmospheric reactive gaseous mercury (RGM) may be a significant pathway for atmospheric loading of mercury (J. Keeler, pers. comm.). RGM deposition is directly input by the user on the basis of atmospheric concentrations of RGM and a deposition velocity. RGM deposited to the water surface is assumed to be a component of the pool of readily exchangeable Hg(II).

12.3.2 Vegetation Mediated Mercury Fluxes

Throughfall

Throughfall occurs when dry deposition of particles and RGM deposition on vegetation is purged by wet deposition. This process is accommodated by monitoring the accumulation of dry deposition and RGM deposition on vegetation between precipitation events, and purging some or this entire amount during precipitation. The remainder is carried with litter to the soil surface. A leaf area index is used to accommodate the increased surface collection area of vegetation. Throughfall is calculated as the incremental loading in addition to wet deposition, rather the combination of the two. Stemflow is not estimated separately from throughfall.

Litterfall

Litterfall has two components: (1) Hg within the leaf, and (2) Hg which has collected on the leaf surface via dry deposition and RGM deposition, but which has not been purged as throughfall during precipitation events. Litterfall is expressed by combining the vegetation litterfall rate with the HgII and methylmercury concentrations within and on vegetation. Mercury in litter is assumed to be readily available to exchange with the mercury pool in soils/sediments. The biomasses and litterfall rates are input directly as time series by the user.

Transpiration of Elemental Mercury

Transpiration of elemental mercury constitutes the exchange of mercury between the vegetation and atmosphere. Transpiration of elemental mercury is calculated on the basis of the water transpiration rate and the concentration of elemental mercury in the water being transpired. Elemental mercury in vegetation is derived from the uptake of elemental mercury from each of the soil/sediment layers, and from the reduction of Hg(II) within the plant (or at the root surface).

12.4 Wetland and Upland Hg Cycling in MCM-HD

A conceptual diagram showing the representation of Hg cycling in wetlands is shown in Figure 12-2. The deepest layer of sediment has similar processes, but is not shown in this figure. Using a mass balance approach, the model predicts time-dependent mercury concentrations in several compartments. Three primary mercury forms in freshwaters are simulated: Methylmercury, Hg(II) and elemental mercury. Hg(II) is defined here as mercury which is neither methylmercury nor elemental mercury.

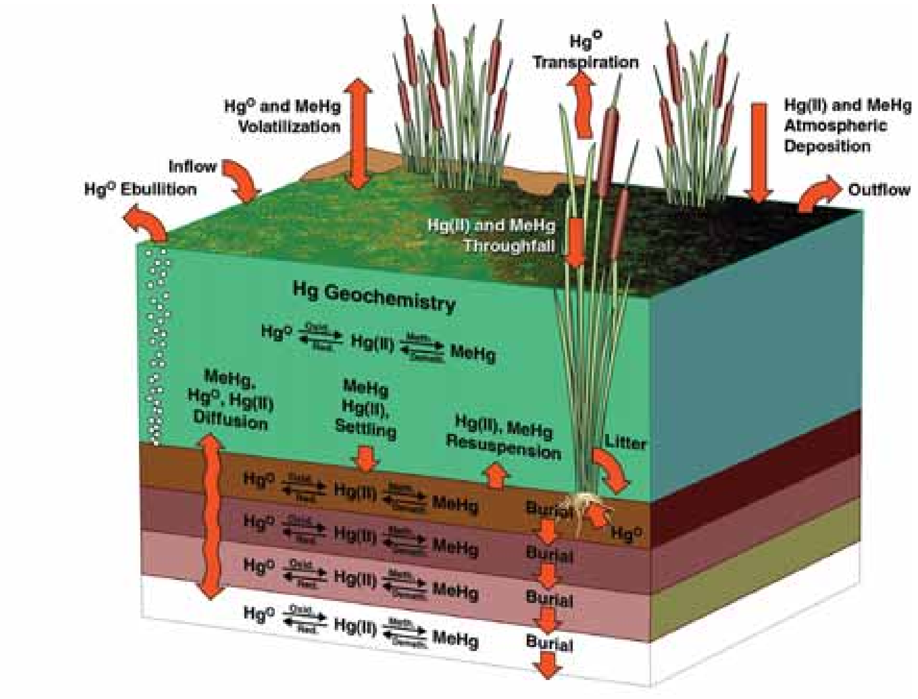


Figure 12-2. Conceptual representation of wetland Hg geochemical cycling in MCM-HD (Tetra Tech 1999)

Model compartments include the wetland water column, up to three macrophyte species and up to five sediment layers. Thermal stratification in the water column can be invoked if desired, resulting in upper and lower water column compartments. The model has two types of "non-living" particles in the water column: detritus and other suspended solids. For both detritus and other suspended solids, compartments have been set up for two types of Hg(II) exchange: (1) instantaneous and (2) slow exchange governed by the kinetics of adsorption/desorption.

The wetland Hg(II) cycle in MCM-HD includes loading from the atmosphere and inflow, followed by a series of fluxes and pathways ultimately leading to storage or removal of Hg(II). Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry deposition, deposition of reactive gaseous mercury). Removal mechanisms include Hg(II) reduction, burial, and outflow. Vegetation plays a role in the Hg(II) cycle via transpiration, throughfall and litterfall, as described previously. Water column Hg(II) processes include atmospheric deposition, surface inflows and outflows, vertical groundwater flow, settling of non-living particles and detritus into sediments, Hg(II) diffusion across the sediment/water column interface, sediment resuspension, Hg(II) photoreduction, oxidation of elemental Hg to Hg(II), methylation, transpiration, throughfall, and litterfall. Litter is assumed to settle directly to the sediment water interface.

The methylmercury cycle in MCM-HD includes loading from the atmosphere and inflow, but unlike Hg(II), also includes a third source: in-situ production. Methylmercury in the wetland then follows a series of fluxes and pathways ultimately leading to its removal or storage. Removal mechanisms include photodegradation, biological demethylation, burial and outflow. As is the case for Hg(II), vegetation plays a role in the methylmercury cycle via transpiration, throughfall and litterfall. Methylmercury processes in the water column include atmospheric deposition, surface inflows and outflows, groundwater flow, settling of non-living particles and detritus into sediments, transpiration, throughfall, litterfall, diffusion across the sediment/water column interface, sediment resuspension, methylation (if anoxic conditions exist), and photodegradation . Methylmercury processes in sediments include diffusion, groundwater flow, burial/erosion, resuspension, methylation, and biological demethylation. Demethylation can produce Hg(II) and Hg(0) in proportions set by the user.

Thermodynamic equilibria are used in MCM-HD to calculate concentrations of dissolved Hg(II) and MeHg complexes in solution in the water column and sediment porewater (see example for Hg(II) in Figure 12-3). This component of the model is required because Hg speciation in solution can affect its availability for reactions such as methylation.

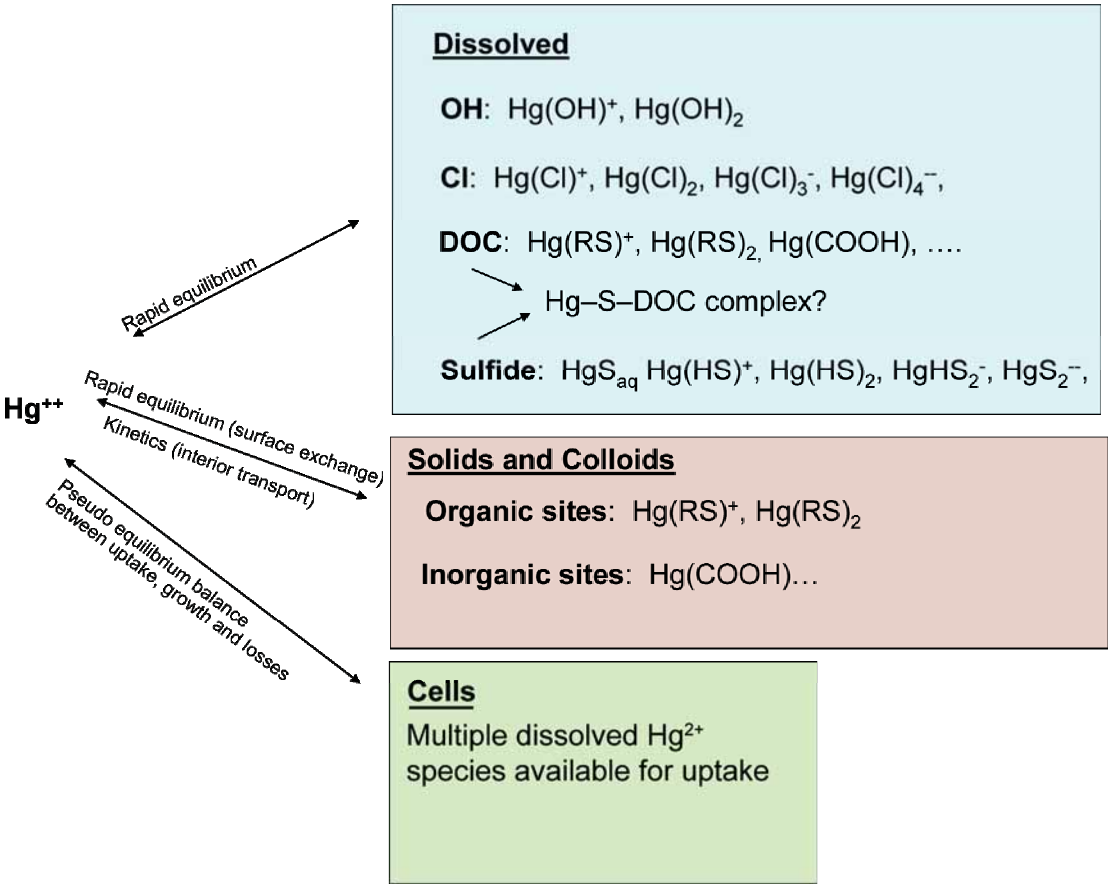


Figure 12-3. Conceptual diagram of competition for inorganic Hg(II) in MCM-HD; Rapid equilibrium estimated with thermodynamics; Slower exchange on solids represented with adsorption/desorption kinetics; Cell exchange represented as pseudo steady-state balance of uptake and losses

12.5 Lake Hg Cycling in MCM-HD

Lake mercury cycling and bioaccumulation in MCM-HD is based on the Mercury Cycling Model (Hudson et al. 1994) and the subsequent Dynamic Mercury Cycling Model (D-MCM, EPRI 2002). The model predicts time-dependent mercury concentrations in several abiotic lake compartments, as well as a food web. Similar to uplands and wetlands, three primary mercury forms in lakes are simulated: methylmercury, Hg(II), and elemental mercury (Table 12-1).

Lake compartments include the water column (epilimnion and hypolimnion), sediments, and a food web that includes three fish populations. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry deposition). Similarly, watershed/upstream loadings of inorganic Hg(II), and methylmercury are input directly as time-series data, not modeled. The user provides inputs for flow rates (surface and groundwater) and associated mercury concentrations, which are combined to determine the watershed mercury loads.

Table 12-1.
Compartments and mercury forms in lake module in MCM-HD

Compartment	Mercury Form		
	MeHg	Hg(II)	Elemental Hg
Water Column (abiotic)			
Dissolved	●	●	●
Non-living suspended particles*	●	●	
Sediments			
Sediment Porewater	●	●	●
Sediment Solids*	●	●	
Food Web			
Phytoplankton	●	●	
Zooplankton	●	●	
Benthos	●	●	
Non-Piscivore Fish Cohorts (up to 20)	●		
Omnivore Fish Cohorts (up to 20)	●		
Piscivore Fish Cohorts (up to 20)	●		

**Includes slowly and rapidly exchanging components for Hg(II).*

The food web consists of six trophic levels (phytoplankton, Zooplankton, benthos, piscivore fish, omnivore fish, and non-piscivore fish). Specific fish species can be selected. Fish mercury concentrations tend to increase with age, and are therefore followed in each year class.

Major processes in the lake module of MCM-HD include surface inflows and outflows, vertical groundwater flow, instantaneous methylmercury partitioning between abiotic solids and dissolved complexes, instantaneous and slower adsorption/desorption kinetics for Hg(II) on abiotic solids, particulate settling, resuspension and burial, atmospheric deposition, air/water gaseous exchange, in-situ transformations (methylation, demethylation, MeHg photodegradation, Hg(II) photoreduction), mercury kinetics in plankton, and methylmercury fluxes in fish populations. The same thermodynamic routines used to speciate Hg(II) and MeHg dissolved complexes in wetland and upland porewaters are used to speciate mercury in lake waters and sediments (Figure 12-3).

Hg(II) and methylmercury concentrations in phytoplankton are determined by rates of uptake and losses. Uptake includes passive diffusion and facilitated uptake. Losses are represented by cell growth/division and possibly depuration. Although this is a dynamic model, the kinetics of Hg uptake and losses in phytoplankton are assumed to be sufficiently rapid that a steady state concentration is reached during the period of the model time step (e.g. one day). The model therefore uses uptake and loss kinetics to calculate apparent partitioning constants for Hg(II) and methylmercury into phytoplankton each timestep. By default, the model assumes that uptake of methylmercury into phytoplankton is via facilitated transport of inorganic complexes (those not associated with DOC).

Methylmercury concentrations in Zooplankton are calculated by multiplying the concentrations in phytoplankton by a scaling factor. This approach is based on the concept that Zooplankton obtain the majority of their mercury from food, assumed to be phytoplankton. Benthic organisms are assumed to concentrate both methylmercury and Hg(II) in direct proportion to the solid phase concentration of mercury on sediment solids. This approach assumes that benthos mercury uptake is governed by dietary Hg exposure, and that most of this mercury exposure occurs via ingested sediment matter.

Methylmercury fluxes for individual fish are estimated by coupling MeHg concentrations with fish bioenergetics equations from Hewett and Johnson (1992) as described by Harris and Bodaly (1998) (Figure 12-4). Fluxes are then scaled up to estimate MeHg uptake via food and water, excretion, egestion, mortality, fishing for classes, and entire populations (Figure 12-5).

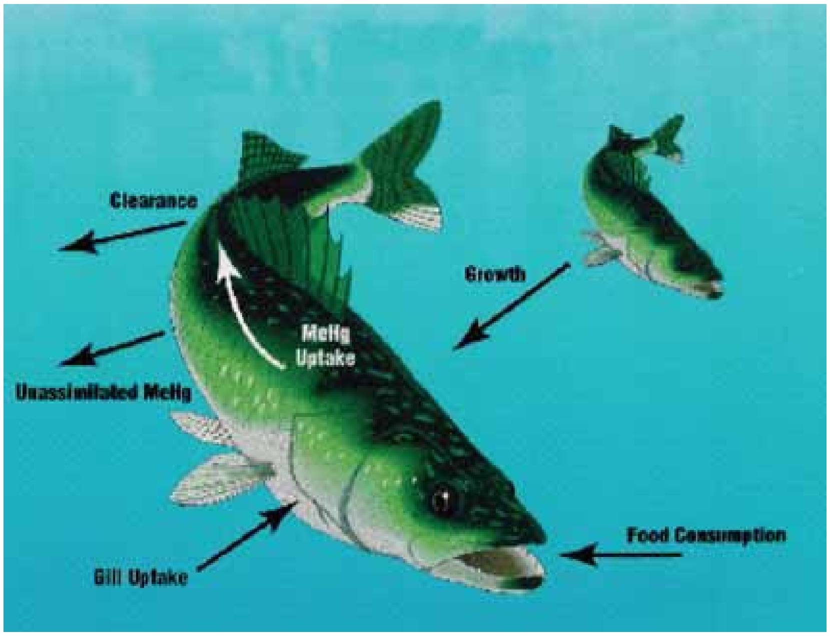
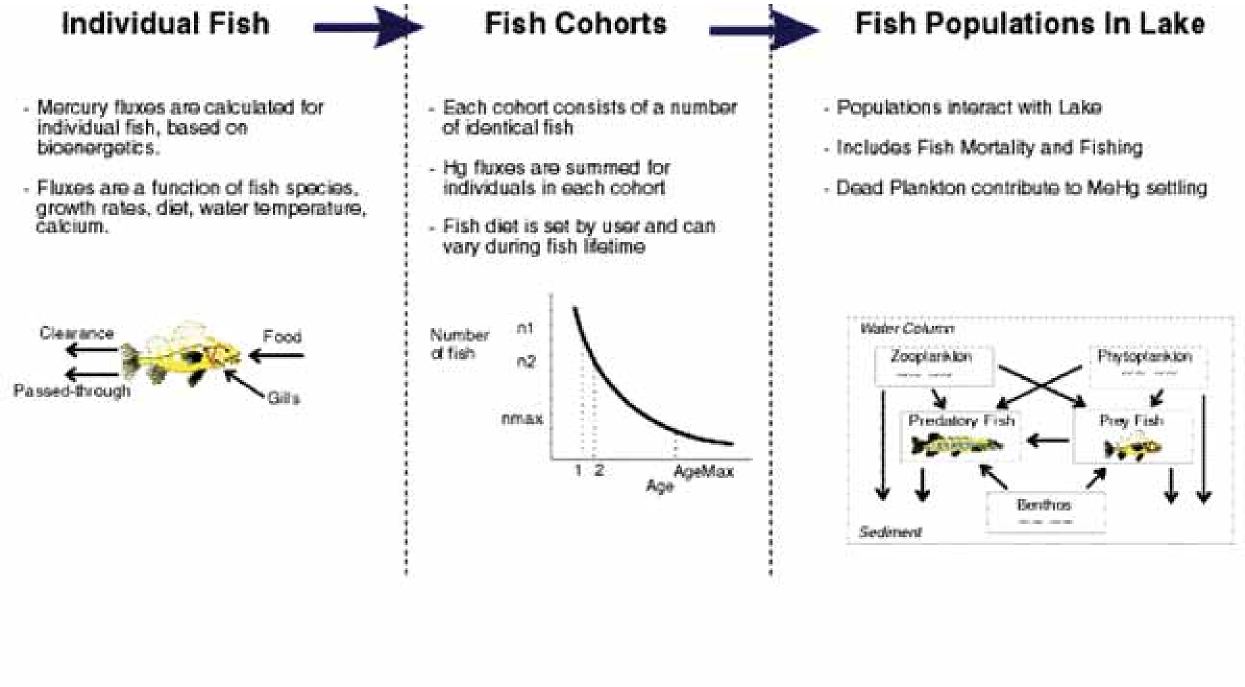


Figure 12-4. **MCM-HD's bioenergetic representation of fish methylmercury dynamics**



Individual Fish

- Mercury fluxes are calculated for individual fish, based on bioenergetics.
- Fluxes are a function of fish species, growth rates, diet, water temperature, calcium.

Fish Cohorts

- Each cohort consists of a number of identical fish
- Hg fluxes are summed for individuals in each cohort
- Fish diet is set by user and can vary during fish lifetime

Fish Populations In Lake

- Populations interact with Lake
- Includes Fish Mortality and Fishing
- Dead Plankton contribute to MeHg settling

Figure 12-5 **Approach to representing MeHg dynamics in fish populations in MCM-HD**

12.5.1 MCM-HD representation of methylation

Methylation is a key step in the methylmercury cycle, strongly influencing concentrations in fish. Methylation occurs in MCM-HD where the transition to anoxia occurs and sulfate reducers are expected to be active. This may be in soil or peat porewater, sediments, or in the water column. Bacterial methylation rates depend on the concentration of available dissolved Hg(II) and the activity of methylating microbes.

Available Hg(II)

It is assumed that methylating bacteria only use dissolved Hg(II) (operationally determined as filtered Hg(II)) or some fraction of it. The available fraction of Hg(II) for methylation is unresolved, so a user switch is included to allow different options to be selected, including the following:

- free Hg^{++} ion
- $HgCl_2$
- all neutral complexes, including neutral dissolved HgS
- all neutral complexes, but excluding all DOC complexes
- non-DOC bound Hg(II)
- all dissolved Hg(II)

Currently the model is calibrated to methylate all dissolved Hg(II). It is recognized that additional work and model testing is needed on this topic.

Activity of Methylating Bacteria

Much attention has been given to the role of sulfate-reducing bacteria (SRB) in methylation (e.g. Gilmour et al., 1996). While sulfate-reducing bacteria have been identified as having the ability to methylate Hg(II), there are several complicating factors when trying to simulate the activity of methylating bacteria:

- Sulfate reducers may methylate when consuming sulfate, or when sulfate is absent they may use other energy pathways (Benoit, 1999a).
- There are many strains of sulfate-reducing bacteria, and multiple strains are capable of methylating Hg(II). How the distribution of different strains changes with different environmental conditions is unknown.
- Sulfate additions have been shown to increase the rate of methylation in some sediment cores spiked with ^{203}Hg, but not others (Gilmour and Riedel 1995). One hypothesis for the variable effects of sulfate additions is that SRBs may be limited by either carbon or sulfate depending on the relative abundance.
- High levels of sulfate reduction can produce sufficient levels of sulfide to reduce the bioavailability of Hg(II) for methylation, and reduce methylation rates (Marvin-DiPasquale, et al, 2001).

Given the above uncertainties, MCM-HD is currently set up to depend partly on the overall rate of decomposition. It is assumed that changes in carbon decomposition rates reflect proportional changes in overall sulfate-reducing bacteria activity and methylation. For example, a 50 percent reduction in the carbon decomposition rate would result in a 50 percent reduction in methylation, with other factors being equal. The methylation equation also considers whether sulfate is limiting the activity of SRBs under some circumstances. When sulfate supply is plentiful and carbon is limiting SRB activity, changes in sulfate loads will not change the SRB activity or methylation. In sediments where sulfate is limiting the overall activity of SRBs, changes in sulfate loads will affect methylation rates. In situations where sulfate is effectively absent, methylation will still proceed at a rate based on the activity of sulfate-reducing bacteria in the absence of sulfate.

12.6 Model Calibration to Sunday Lake Watershed

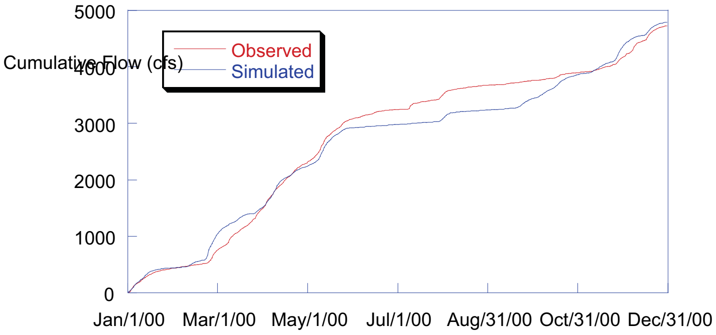
The MCM-HD model was applied to the Sunday Lake watershed in the Adirondack region of New York. Sunday Lake is a drainage lake, with extensive wetlands (20 percent of the watershed) and a relatively large watershed to lake area ratio (~175). From 1999 through 2000, the lake had an average pH of 5.5, Total Hg 3 ng/L, MeHg 0.7 ng/l, ANC 20 µeq/L, and DOC 10mg C/L. Current Hg concentrations in three to five year old Yellow Perch average 0.88 µg/g wet weight. As a result of the physical and chemical characteristics of the lake and watershed, Sunday Lake is very sensitive to atmospheric Hg deposition. The MCM-HD model was calibrated using the Sunday Lake watershed data collected during this study and described in the preceding sections. Concentrations of total and methylmercury observed from July 1999 through December 2000 in Sunday Lake were compared to model estimates. The model was parameterized using observed lake-watershed physical characteristics and precipitation quantity and quality as driving variables. Calibration parameters were adjusted until simulated flows and concentrations matched those observed.

12.6.1 Model Results for Sunday Lake

The first step in the calibration process is to show that the total hydrologic inputs and outputs to the lake are closely matched, as seen in Figure 12-6a that shows simulated and observed cumulative flows at the outlet gage for Sunday Lake for the period from January through December 2000. Simulated and observed values match well through the winter and spring, deviate slightly during the summer, and then match well again through the fall. Next, the seasonal timing of the flows is compared, as shown in Figure 12-6b. This plot shows that the majority of the storm events were captured, but not all, particularly the short duration rain storms such as in July 2000. In addition, the simulated flows in the fall were slightly higher than observed flows.

The simulated and observed total and methylmercury concentrations in Inlet 2 are shown in Figure 12-7. While the model has a similar seasonal variation between low concentrations in the winter and high concentrations in the summer, the simulated concentrations are dampened, compared to the observed data. The seasonal variation is more pronounced for total mercury than methylmercury for Inlet 2. The simulated peaks for total and methylmercury were close to the observed data for the years 2000 and 2001, but not 2001, perhaps due to higher simulated flows.

Figure 12-8 shows simulated and observed aqueous total and methylmercury concentrations at the Sunday Lake surface station. The calibration resulted in a reasonable fit between observed and simulated total and methylmercury concentrations. The model simulation follows the seasonal changes in total mercury concentrations, but the magnitude of the summer maximum concentration in July 2000 and 2001 is low. For methylmercury, the simulated concentrations match the general pattern of observations, that is lowest in the winter and highest in the summer, but the range of observed concentrations is slightly larger than the simulated range. Both summer peaks in 2000 and 2001 were also low. The seasonal peaks and lows observed for THg and MeHg were governed by the relative contributions of upland and wetland areas to the lake inflows.



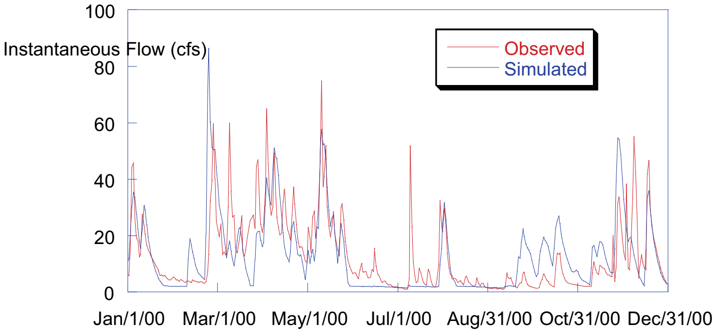
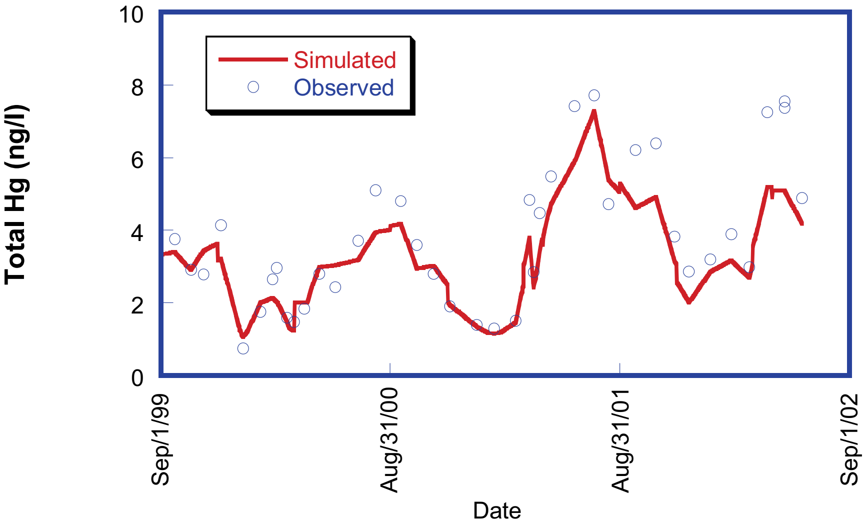


Figure 12-6. Hydrologic calibration for Sunday Lake, comparison of simulated and observed cumulative flows (a), and comparison of simulated and observed flows (b) from January to December 2000



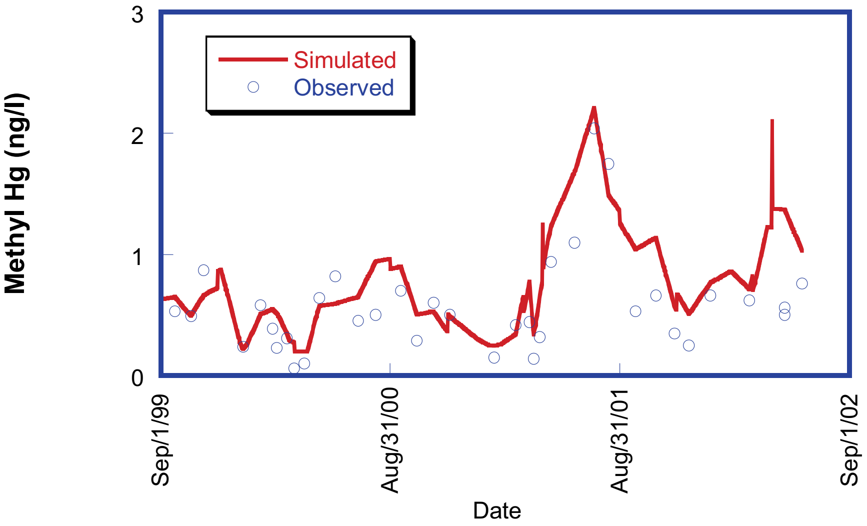


Figure 12-7. **Simulated versus observed total Hg and MeHg at Inlet 2 to Sunday Lake**

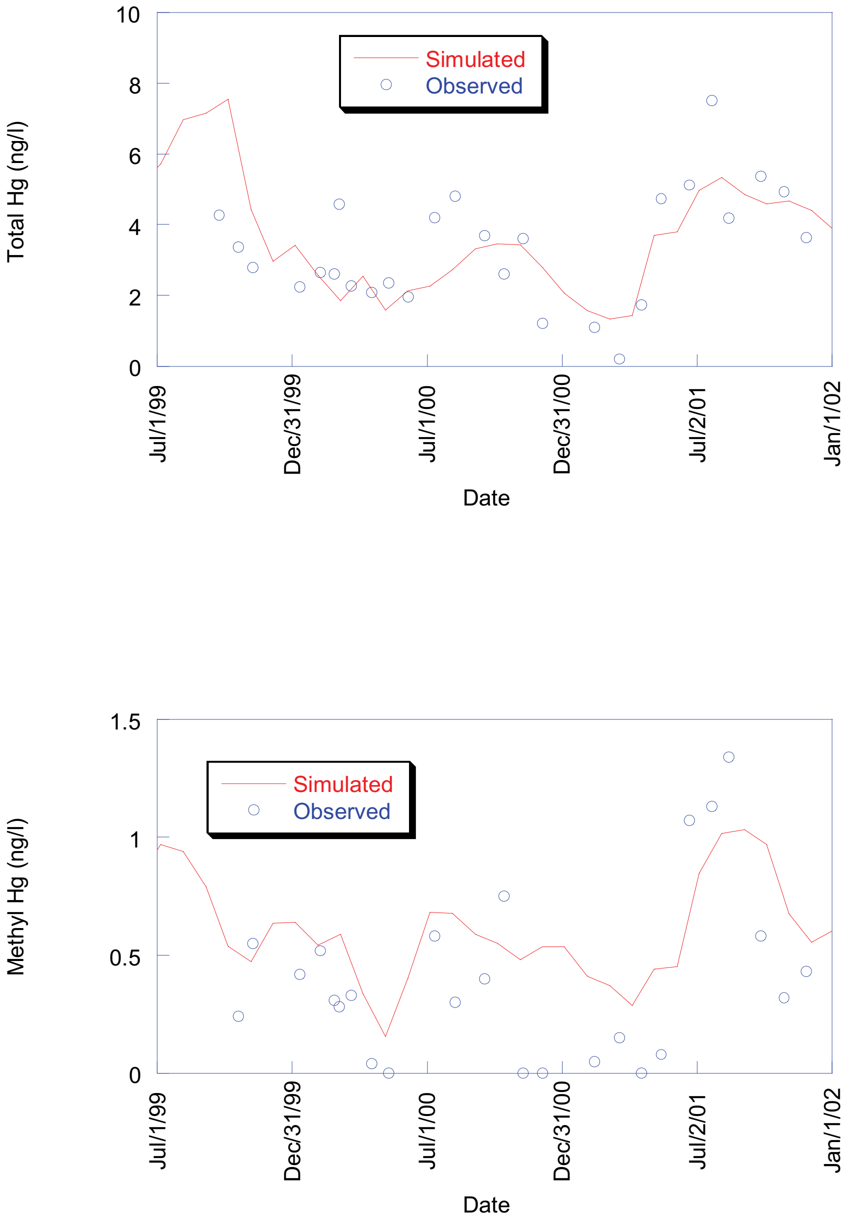


Figure 12-8. Simulated versus observed MeHg and total Hg for the surface sample from Sunday Lake

Model results are in agreement with mass balance calculations indicating that both the watershed and the lake are sinks for Hg_T. Wetlands are a significant source of CH_3Hg^+ to the surface waters in the Sunday Lake watershed. These wetlands represent the dominant source of CH_3Hg^+ to Sunday Lake. For this lake, the in-lake contribution of CH_3Hg^+ is small.

12.6.2 Load Reduction Scenarios

Based upon the previous calibration, scenario analyses were conducted to determine the response of simulated fish mercury and aqueous methylmercury concentrations to a reduction in atmospheric loading of mercury. First, a five-year simulation was run to show the initial response and to the load reduction and the seasonal changes. Results of this analysis are presented in Figure 12-9. As indicated, the simulated response is nearly linear over the 5-year simulation period.

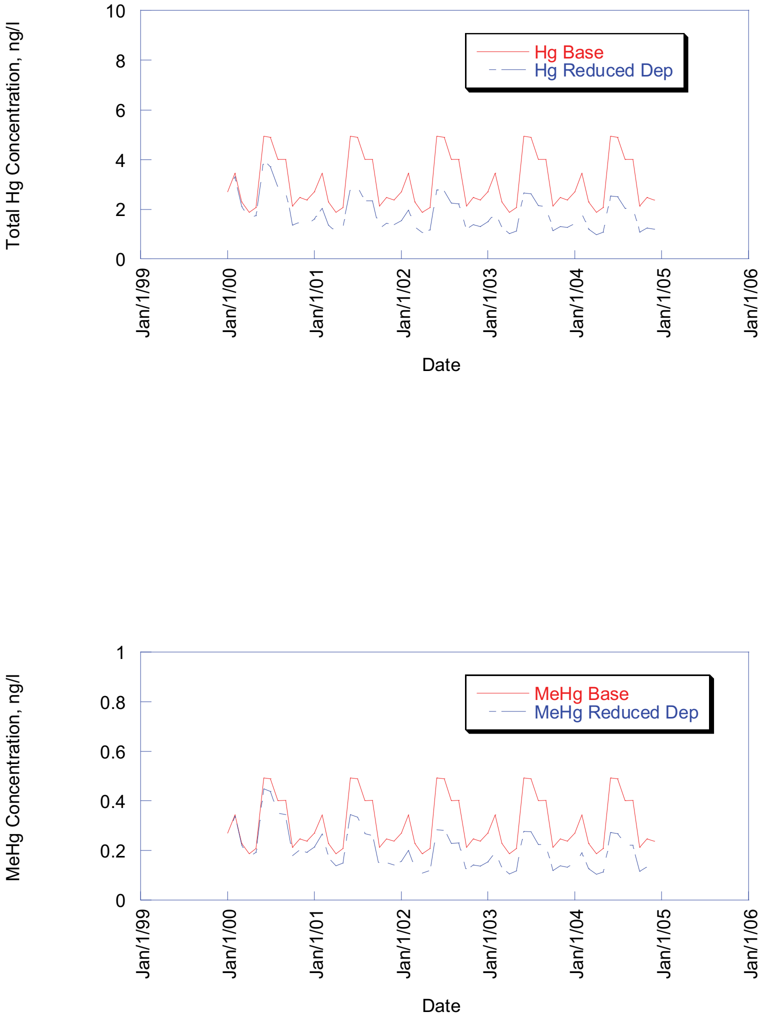


Figure 12-9. Simulated response to a 50 % reduction in Hg deposition showing seasonal variations

Next, two long-term scenarios were evaluated for Sunday Lake - step reductions of total atmospheric Hg deposition by 15 percent and 50 percent. The results for these two scenarios were compared to base case conditions, which assume emissions and deposition will continue at the current level (Figure 12-10).

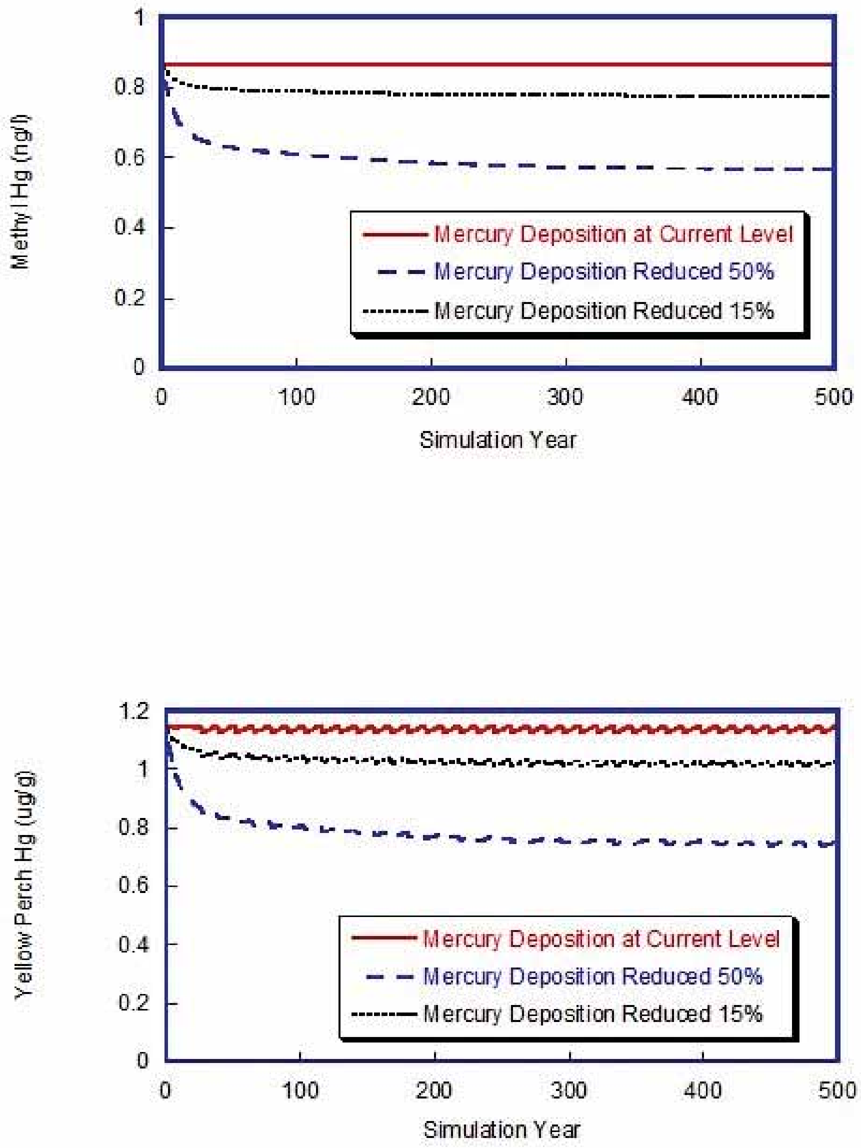


Figure 12-10. Simulated response to 15 and 50 % decreases in mercury deposition

The results show that simulated Hg concentrations in water and fish decline relatively rapidly over the first 35 years of the simulation and then decline slowly over the remainder of the simulation period. After 50 years, the water and fish Hg concentrations remain high under both scenarios, with fish concentrations at 0.64 µg/g in 2050 with a 50 percent decline in Hg deposition beginning in 2005 (Table 12-2). The decrease in fish mercury after 50 years (27 percent) is less than the reduction in deposition due to retention in soil layers in the watershed. The model results indicate that fish Hg concentrations may remain above the USEPA criterion of 0.3 μg/g under all scenarios. However, the actual timing of the simulated decrease is highly uncertain due to interannual hydrologic variations as well as other factors discussed below.

One reason for the uncertainty is the timing of the response of Hg concentrations in runoff and groundwater from terrestrial ecosystems to changes in atmospheric Hg deposition. If Hg deposition is permanently sequestered in soil, it is anticipated that concentrations in surface waters will decrease relatively rapidly following decreases in atmospheric Hg deposition. Conversely, if soil Hg is reversibly desorbed from soil in response to decreases in atmospheric Hg deposition the response time of watersheds to controls of Hg emissions will be greatly delayed. Data from paleoecological studies in the Northeast indicate that apparent retention of atmospheric Hg deposition in lake-watersheds has declined over recent decades (Lorey and Driscoll 1999, Kamman and Engstrom 2003). Possible reasons for the apparent decrease in retention are discussed in Section 11 of this report.

Another reason for uncertainty is the relative contribution of direct deposition to the lake versus indirect deposition to the watershed, which can then be transported by rapid, shallow flowpaths or slower, deeper flowpaths to the lake. In the Sunday Lake watershed, the direct deposition is small, and much of the mercury from deposition is retained in the soil layers, which would delay the change in mercury concentrations in the lake and hence, fish mercury concentrations. However, the retention time of inflows in this lake is short, suggesting that the response might be sooner than would be expected otherwise. Predictions of fish response times for ecosystems receiving most of their Hg from terrestrial runoff also strongly depend on assumptions made regarding the bioavailability for methylation of this Hg source. If newly added Hg (i.e. direct deposition to the lake and rapid runoff) is more available for methylation, the response times would be expected to shorten compared to current simulations. The timing of the response to changes in deposition is highly uncertain and the subject of continuing research.

Table 12-2.
Results of MCM-HD simulations for Sunday Lake Watershed for the base case and 15 percent and 50 percent decreases in total Hg deposition

Media	Mercury for base conditions* Mercury	Simulation period	15% decrease in total Hg deposition	50% decrease in total Hg deposition
Total Hg in Water (ng/L)	0.7	10 years	0.67	0.58
		50 years	0.64	0.51
Fish (μg/g)	0.88	10 years	0.83	0.73
		50 years	0.80	0.64

**Base conditions for water and fish represent average lake concentrations and average 3-5 year old Yellow Perch concentrations from the observed data for 1999-2000.*

Another analysis was conducted using the model to evaluate the impact of reductions in atmospheric sulfur and nitrogen inputs on lake and fish Hg concentrations. Reductions in sulfur emissions related to the requirements of the Clean Air Act Amendments have resulted in statistically significant decreases in the sulfate concentrations of Adirondack Lakes. Some of these lakes have also experienced increases in ANC and pH. Mercury uptake by biota is influenced by aqueous pH, and this influence is reflected in the model. Further reductions in sulfur emissions, as well as nitrogen emissions, have been proposed, and may result in further increases in lake water pH. In addition, experimental studies have shown that methylation rate may be a function of aqueous sulfate concentration. If the sulfate concentrations of surface waters and porewaters are reduced as a result of decreases in sulfur deposition, net methylation may decrease, potentially resulting in lower lake and fish MeHg concentrations.

The analysis was conducted assuming a 50 percent reduction in lake and porewater sulfate concentrations and a one-unit change in lake water pH. The simulated response to these changes was smaller than the simulated response to a 50 percent decrease in atmospheric THg deposition. This result is consistent with the fact that the major mercury input to the watershed and lake system is from deposition, while pH and sulfate concentrations are influences on methylation. There is uncertainty in the model results, however, associated with the current functional dependency of methylation on aqueous sulfate concentration. This dependency was developed based on data for lakes, and is a weak dependency that generates a less-than-linear response. Experiments in which sulfate has been added to wetland porewaters with low sulfate concentrations where active methylation is occurring have shown a greater-than-linear response to the sulfate additions. Further evaluation of methylation rates under varying sulfate concentrations in a wetland environment is a high-priority research need for the future.

13 Summary and Conclusions

13.1 Description of Sunday Lake Watershed

The lake-watershed system selected for mass balance analysis was Sunday Lake. It is a 1,340 ha, third order, catchment lying within the larger, Oswegatchie-Black watershed. The watershed has 202 m of relief, with elevations ranging from 488 m at the outlet gage station to 690 m at Stillwater Mountain on the eastern edge of the watershed. There are nine small lakes and ponds within the watershed with a total surface area of 23.2 ha. Sunday Lake (7.8 hectares) is located at the outlet of the catchment and is second in size to Fifth Creek Pond (10.6 ha) located near the southern watershed divide.

Wetlands cover approximately 20 percent of the Sunday Lake watershed (274 ha) with most located adjacent to lakes and streams. Wetland cover types fall mainly into the needle-leaved evergreen forested class (52 percent) and the broad-leaved deciduous scrub shrub class (37 percent). Hydrologically, saturated wetlands dominate (69 percent) together with semi-permanently flooded areas (27 percent). Wetlands border 66 percent of all the stream channels and much of the lake shorelines.

13.2 Hydrology

Daily total precipitation was compared to total daily flow at the outlet gage station for the period 1999 through 2001. The locations of hydrologic monitoring locations in the watershed were shown in Figure 5-1. During the period of study, precipitation averaged 127.1cm compared to an average of 77.4cm of stream flow (See Table 5-3). Total stream runoff was thus 61 percent of precipitation and the remaining 39 percent was assumed lost to evapotranspiration (ET).

Most of the soils in the Sunday Lake watershed have relatively high infiltration capacities so that the amount of infiltration is only limited by areas where bedrock is exposed at or near the surface and by areas where the water table is at or near the surface. One uncertainty with respect to flow paths is the depth of the shallow riparian wetland zone where higher MeHg concentrations were observed. Additional piezometers would be needed below a depth of 1 m to define this zone.

Sunday Lake is small relative to the size of the watershed and is thus greatly impacted by high flow events. The location of the major inlet at the same end of the lake as the outlet suggests that the lake may undergo uneven mixing. Although the lake is shallow, a thermocline develops both in the summer when surface waters are warmer than bottom waters and in the winter when surface waters are colder than bottom waters. During high flow events the lake becomes isothermal indicating that it is completely mixed. At these times the lake is simply acting as a wide spot in the river.

13.3 The Transport, Transformations, and Fate of Mercury in Sunday Lake Watershed

A wet Hg deposition collector was deployed at Huntington Forest in the central Adirondacks as part of the Mercury Deposition Network (MDN). Precipitation concentrations of total Hg (THg) were highly variable during the study period, but concentrations were similar to values for other sites in eastern North America (Figure 13-1).

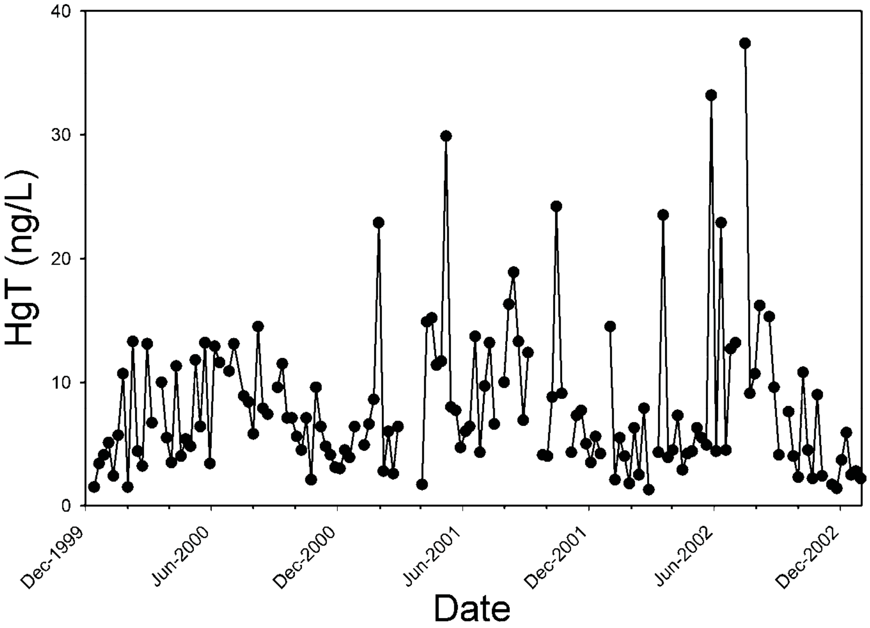


Figure 13-1. Time series of total Hg concentrations collected in precipitation at the Huntington Forest

The dynamics of Hg were studied within upland coniferous and deciduous forest plots at Sunday Lake watershed (See Figure 8-1). Higher concentrations of THg occurred in throughfall at the coniferous plot (3.0-38.2 ng/L, mean 23.7 ng/L THg) than at the deciduous plot (1.0-3.8 ng/L, mean 2.0 ng/L THg). Leaf litter concentrations of THg differed among individual tree species, but not significantly among plots (coniferous mean 58 ± 18.4 ng/g, deciduous mean 50.6 ± 11.6 ng/g). The flux of Hg to the forest ecosystem was dominated by dry deposition (estimated as throughfall plus litter fall; 70 percent of total deposition). THg fluxes via throughfall and litter were 32 and 6 $\mu g/m^2$-yr, respectively, at the coniferous plot, and 7 and 15 $\mu g/m^2$-yr, respectively, at the deciduous plot.

Total Hg concentrations in soil varied with horizon but were similar among plots with highest concentrations in the Oa horizon (13.2-188.9 ng/g), lowest in the E horizon (3.9-25.2 ng/g), a peak in the Bh horizon (3.7-67.5 ng/g) and lower values in the Bs horizon (2.7-47.5 ng/g). Concentrations of THg in the soil solutions were highest in waters draining the forest floor (9.8-41.8 ng/L) and decreased through the Bh (0.9-13.9 ng/L) and Bs (0.9-11.0 ng/L) horizons at both plots. MeHg concentrations in the soil were relatively uniform throughout both forest soil profiles (1.0-2.2 ng/g), whereas soil solutions were highly variable (below detection limit (<0.02)-1.4 ng/L). Mass balance calculations show that the soil was a net sink for inputs of THg and MeHg at both the coniferous and deciduous plots.

Vegetation is known to play an important role in Hg cycling in forested watersheds. Hg concentrations in upland and riparian wetland vegetation were studied over one growing season in the Sunday Lake watershed. Both *Fagus grandifolia* and *Abies balsamea* foliage was collected from an upland forest. *Sphagnum spp.*, *Carex spp.*, and *Alnus rugosa* were sampled in a riparian wetland along the main tributary to Sunday Lake. Conifers growing in a large wetland adjacent to Sunday Lake were also sampled. *Sphagnum spp.* THg was strongly correlated with riparian wetland groundwater THg over the growing season.

The amount of MeHg in remote lakes shows a positive correlation with wetland area in the watershed. Solution chemistry and soil in four wetlands located within the Sunday Lake watershed were characterized. All four soils were organic rich (peat) with low pH. Water flowed rapidly through the top 50cm of the peat in each site, with much lower flux rates in deeper peat. The riparian wetland had higher concentrations of THg and MeHg and presumably, was a site for in-situ methylation (Figure 13-2).

The trophic transfer of MeHg was analyzed in Sunday Lake. Mercury concentrations in water, Zooplankton, Forage fish, and Yellow Perch samples were used for this analysis. MeHg concentrations in the lake epilimnion were most strongly correlated with MeHg in the main tributary to Sunday Lake, which is consistent with the short retention time in this lake. Zooplankton MeHg concentrations were lower than values observed in Wisconsin lakes, and differed between species. Mercury concentrations in Yellow Perch of Sunday Lake averaged 1.0 + 0.47 ng/g THg (ww), and were higher than values observed in many remote regions. However, log bioconcentration factors were generally lower than values reported for Yellow Perch in other Adirondack lakes, suggesting that MeHg in Sunday Lake is less bioavailable due to binding associated with high concentrations of dissolved organic carbon from the riparian wetlands (see Figure 10-6).

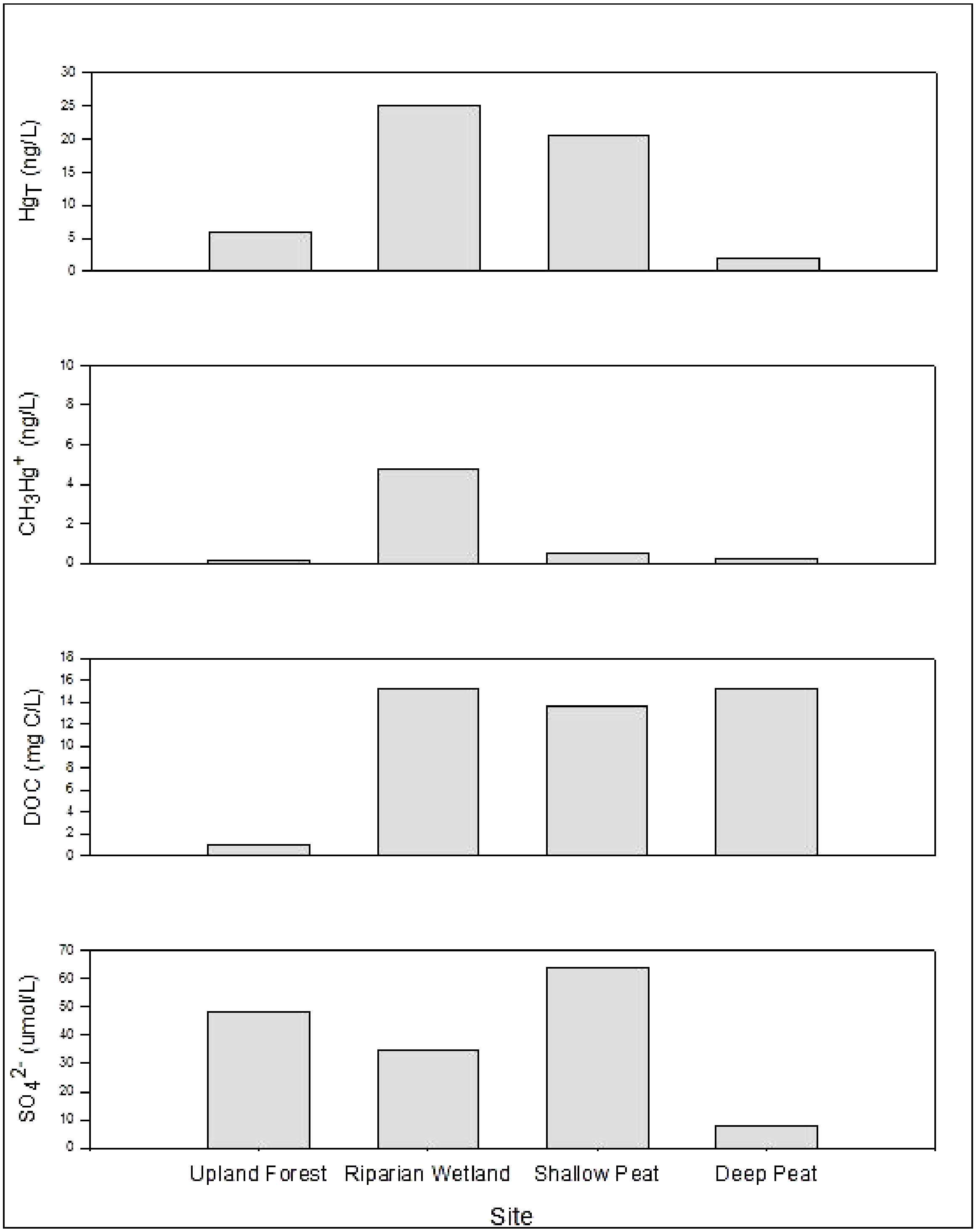


Figure 13-2. Mean aqueous concentrations of total Hg, MeHg, DOC, and sulfate in porewaters associated with different wetland types in the Sunday Lake Watershed

13.4 Mass Balance for Sunday Lake Watershed

Precipitation to the Sunday Lake watershed averaged 127.1cm for 1999-2001, of which about 77.4cm or 61 percent was lost as streamflow. The remainder was considered to be lost through evapotranspiration. Streamflow was divided into three components: surface stormflow, riparian wetland groundwater flow, and deeper groundwater flowing beneath the one-meter riparian wetland zone. Flow through wetlands is important in this watershed, because 70 percent of the streamflow comes from runoff from wetland areas or groundwater through the riparian wetlands. Because the lakes are only two percent of the watershed, direct precipitation is a small percent of the total precipitation to the watershed.

The measured wet deposition of mercury from the Huntington NADP/MDN Station was used to quantify the direct wet deposition to Sunday Lake and the upland and wetland areas of the watershed. The total mercury wet deposition flux was calculated as 9.4 µg/m2/yr and the methylmercury flux as 0.05 µg/m2/yr. The estimated quantities of total and methylmercury input to the watershed and lake are shown in Figure 13-3. The wet deposition of total mercury to the upland and wetland areas is greater than the estimated total mercury flux reaching the lake, indicating that much of the mercury is retained in the watershed. The Sunday Lake watershed is largely forested with 75 percent deciduous and 15 percent coniferous forests in the upland areas and partially forested wetland areas. Thus, dry deposition is a significant input to the watershed. The total and methylmercury flux rates for throughfall and litter fall were measured for both coniferous and deciduous plots (See Figure 8-11), and used to estimate the contribution from dry deposition based on the percent cover by coniferous or deciduous forests. Dry deposition was a greater flux to the watershed than wet deposition for both total and methylmercury.

The pools of total and methylmercury present in the soil layers and estimated drainage fluxes to underlying layers are also shown in Figure 13-3. Mass balance calculations show that the soil was a net sink for inputs of HgT and CH3Hg+ at both the coniferous and deciduous plots. Most of the mercury is retained in the deeper soil layer, the Bs horizon. The pool of total mercury retained in all the soil layers is over 500 times the annual flux to the watershed. The primary flux out of the soil plots in the forested areas was considered to be the flux from the Bs horizon, which was small for total mercury (30.8 g/yr), representing about 12 percent of the total flux to the forest floor. The methylmercury flux from the Bs soil horizon was 1.2 g/yr, representing about five percent of the total flux to the forest floor.

For the coniferous plot, the average residence time of total mercury in the forest floor (mean depth of 15cm) was 50 years and for the total soil profile (mean depth of 75cm) it was 210 years. For the deciduous plot, the average residence time of total mercury in the forest floor (mean depth of 15cm) was 210 years and for the total soil profile (mean depth of 75cm) it was 810 years. Due to the large pool of mercury already present in the soil horizons, changes in the flux out of the deeper soil horizons are expected to be slow in response to changes in mercury concentrations of the precipitation. In the Sunday Lake watershed, surface flow was about 37 percent of total streamflow to the lake, which is the component of flow that would be expected to change faster in response to changes in precipitation quality. However, this flow was found to pass through the riparian wetlands before entering the lake, which can modify the mercury concentrations. Piezometers in the riparian wetlands indicated that both total and methylmercury were higher in the wetlands than in deeper groundwater. The average total mercury in the riparian groundwater, defined as water flowing within the upper 1 meter of the wetland, was 21.15 ng/L and the average methylmercury concentration was 2.96 ng/L. The flow through the riparian wetland represents 70 percent of all the streamflow as both surface stormflow and riparian groundwater in the top 1 meter also pass through wetlands prior to entering the lake.

The total mercury flux from the watershed to the lake was estimated as 40.7 g/yr based on the total lake inflow of 77.4cm and the average total mercury concentration of 3.95 ng/L. This total inflow represents the combination of surface stormflow, riparian groundwater in the top one meter, and deeper non-wetland groundwater. The average total and methylmercury concentrations in Inlet 2, the major tributary to the lake, were used to compute the fluxes, since data to estimate each component individually were not available. The methylmercury flux to the lake from the watershed was 7.7 g/yr based on the above flow rate and had an average methylmercury concentration of 0.75 ng/L. The major contribution of methylmercury to the lake is thought to be from the riparian wetlands. Uncertainties in the mass balance include the flux from the riparian wetlands. Additional peizometers are needed to define the depth of this flowpath. More frequent mercury measurements are also needed to determine seasonal variability.

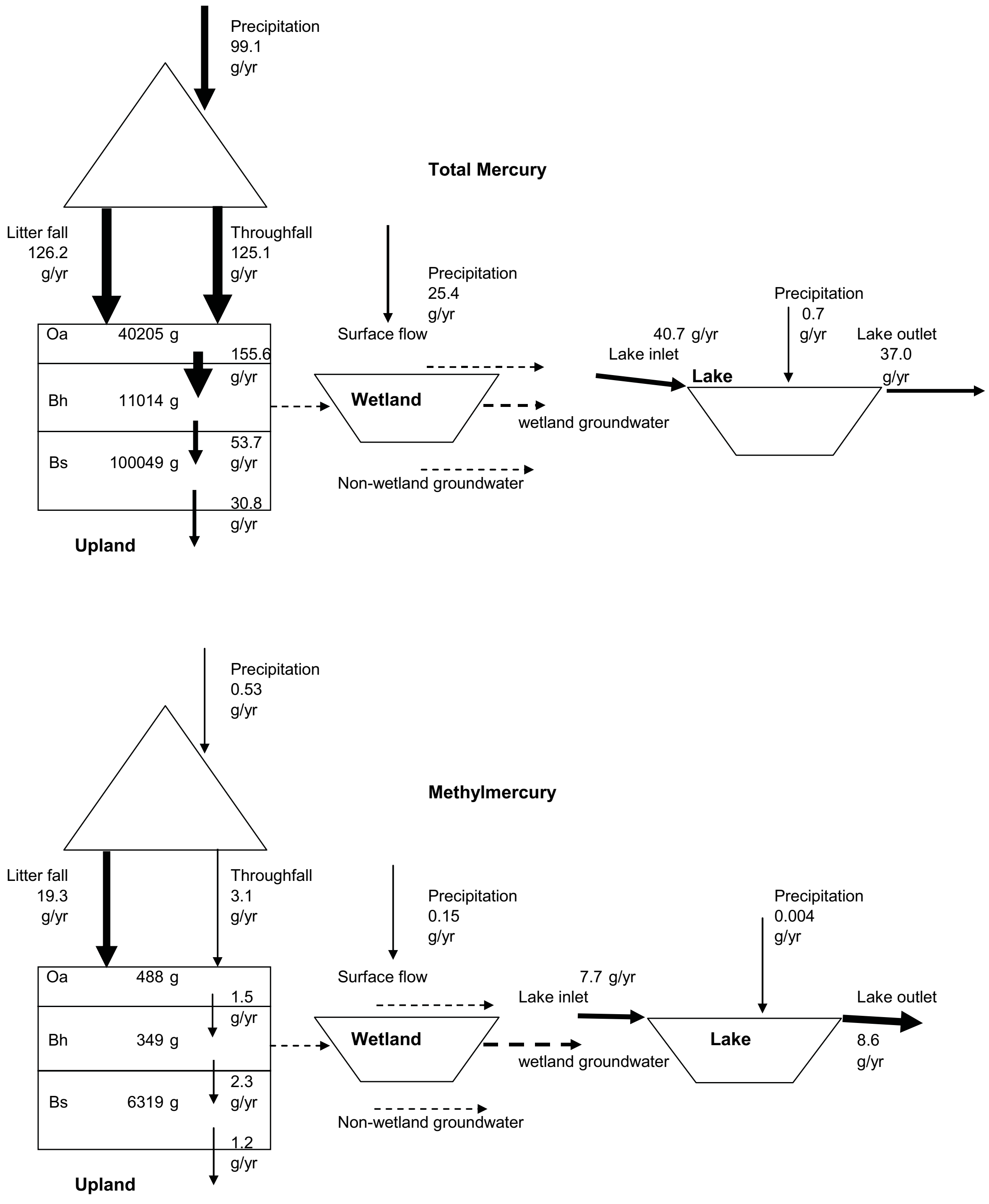


Figure 13-4. Total and Methylmercury Mass Balances for Sunday Lake and Watershed

Mercury pools in soils ranged from ~8000 – 18000 μg/m^2, roughly three orders of magnitude greater than annual atmospheric deposition or runoff mercury fluxes. The quantities of total mercury and methylmercury in the organic and deeper soil horizons are shown in Table 13-1. Using these mercury pool sizes, the retention time of mercury in soils in the Sunday Lake watershed was estimated to be on the order of decades to centuries. Most of the mercury in terrestrial runoff is probably not based on deposition from the same year unless significant hydrologic shortcuts allow recent atmospheric Hg deposition to pass quickly through the watershed. Ratios of mercury loading to export in runoff should therefore be viewed as snapshots at a given point in time rather than long-term stable ratios.

Table 13-1.
Pools of THg and MeHg by soil horizons at Sunday Lake Watershed

	Pools (g/ha)			
	Coniferous		Deciduous	
Soil Horizon	THg	MeHg	THg	MeHg
Oa	17.53	0.40	46.97	0.49
E	1.67	0.45	7.19	0.77
Bh	1.95	0.10	14.09	0.43
Bs1	14.48	1.52	25.94	1.4
Bs2	43.78	3.06	84.67	5.2
Total	**79.4**	**5.53**	**178**	**8.29**

Concentrations of total Hg were measured in sections of sediment cores collected from eight lakes in the Adirondack region, but not in Sunday Lake. By ^{210}Pb dating, historical profiles were determined for each lake showing changes in sediment Hg deposition over the past 200 years. Although there were lake-to-lake variations, on average sites showed a 5.8-fold increase in sediment Hg deposition from background values (before 1900) to peak values. Mercury deposition peaked (from 1973 to 1995) and decreased in recent years. Current sediment Hg deposition is 3.5 times background values. Measurement of the mercury concentrations and sedimentation rate in Sunday Lake would provide additional data for model calibration and help estimate how quickly a lake will respond to changes in mercury deposition.

13.5 Application of the Mercury Cycling Model for Headwater Drainage Lakes (MCM-HD)

The Mercury Cycling Model for Headwater Drainage Lake Systems (MCM-HD) was developed and applied to simulate Hg interactions in headwater drainage lakes and the adjacent watersheds, including wetlands. The model was parameterized using observed lake-watershed physical characteristics and precipitation quantity and quality as driving variables. Calibration parameters were adjusted until simulated flows and concentrations matched those observed.

Model results indicate that both the watershed and the lake are sinks for THg. Wetlands are a significant source of MeHg to the surface waters in the Sunday Lake watershed. These wetlands represent the dominant source of MeHg to Sunday Lake. The lake itself may be a source of MeHg, but the watershed inputs are much larger than the lake inputs of MeHg.

Following calibration, a scenario analysis was conducted to evaluate the response of the lake water and Yellow Perch to 15 and 50 percent decreases in atmospheric inputs of THg (See Figure 12-10). The simulated concentrations of both water and fish decrease relatively rapidly in the first 35-40 years following deposition decreases, and then decline slowly over the remainder of the simulation period. The timing of the response to changes in deposition is dependent on the relative fraction of direct deposition to the lake compared to the total deposition over the entire watershed, the percent retained in the soil layers; and the efficiency of wetland areas and lake in methylating mercury. Additional work is needed to refine estimates of the timing of the response such as on methylating efficiency and quantification of wetland input to the lake.

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APPENDIX A. MCM-HD MODEL EQUATIONS

Rainfall and Snowfall

The amount of rainfall in mixed precipitation is determined as follows:

$$R = P_t\{(T_{max} - T_{sn})/(T_{max} - T_{min})\}$$

where

R = the amount of rainfall in centimeters/time

P_t = the total amount of precipitation in centimeters/time

T_{max} = the maximum temperature

T_{min} = the minimum temperature and

T_{sn} = the snow formation temperature (all temperatures in °C)

The amount of snow in mixed precipitation is calculated as the difference between the total precipitation and the amount of rain as follows:

$$S = P_t - R$$

where

S = the amount of snowfall in centimeters/time

Potential Evapotranspiration

The equation to calculate daily potential evapotranspiration is the following:

$$ET_p = (F_{et}/n)(T_m C_e H_c)$$

where

ET_p = the daily potential evapotranspiration in mm/day

F_{et} = the evapotranspiration factor for the month in mm/°F-month

n = the number of days in the month

T_m = the mean ambient temperature of the day in °F

C_e = a calibration parameter which accounts for local microclimatological characteristics (e.g. elevation, wind exposure) which may differ from the average of the region

H_c = the humidity correction factor (unitless)

The humidity correction factor, H_c, is determined by the following equation:

$$H_c = 0.166\ (100\text{-}H)^{1/2}\ (\text{for } H > 64\%)$$

and

$$H_c = 1\ (\text{for } H < 64\%)$$

where

H = the mean monthly relative humidity in percent

F_{et} is a function of latitude and the season of the year. According to Hargreaves (1974), the mean annual value of F_{et} can be represented by the following relationships.

$$F_{et} = 2.322 - 0.0115\ r,\ r < 35°\text{N}$$

and

$$F_{et} = 3.434 - 0.0434\ r,\ r > 35°\text{N}$$

where

F_{et} = the mean annual evapotranspiration factor in mm/°F-month

r = the latitude of the site location in degree

F_{et} can be calculated for each month by using a Fourier model

$$F_{et} = \overline{F}_{et} + \sum_{K=1}^{2}\left[A(K)\cos\left(\frac{\pi MK}{P}\right) + B(K)\sin\left(\frac{\pi MK}{P}\right)\right]$$

where

K = the harmonic number (only two are used)

A(K) = Fourier coefficient

B(K) = Fourier coefficient

M = the month of the year and

P = the total number of periods

The Fourier coefficients are a function of latitude and are determined using the following relationships.

$$A(1) = 0.037 - 0.0328\ r,\ r < 35°\text{N}$$

$$A(1) = 0.8235 - 0.0034\ r,\ 35°\text{N} < r < 45°\text{N}$$

$$A(1) = -1.741 + 0.0118\ r,\ r > 45°\text{N}$$

$A(2) = -0.1042 + 0.0033\ r,\ r < 29°N$

$A(2) = -0.2332 + 0.0077\ r,\ r > 29°N$

$B(1) = -0.57 - 0.0015\ r$

$B(2) = -0.045 + 0.0017\ r$

Actual Evapotranspiration

When the moisture content of the soil is below field capacity the actual amount of evapotranspiration is reduced exponentially between field capacity (θ_{fc}) and zero moisture content and is represented by the following equation:

$$d\theta/dt = -k\theta, \text{ for } \theta < \theta_{fc}$$

where

θ = the volumetric soil moisture content (decimal fraction of the bulk soil volume)

$$k = \theta d/(\theta fc \Delta t)$$

where

θd = the actual evapotranspiration demand and

Δt = the time step

Advection/Runoff

Downward advection of solutes from the soil surface can occur when precipitation percolates through the soil profile. Lateral flow from a soil horizon, which occurs when the horizon becomes saturated, can carry solutes from watershed soils to surface waters. The extent to which kinetically controlled reactions take place is affected by the amount of time that water stays in contact with a particular component of the solid phase. The extent of these reactions can influence the concentration and speciation of mercury in soil solution and surface waters.

The model allows for multiple separate soil layers of varying areal extent. Hydraulic routing is simulated for each soil layer based upon volumetric soil moisture content, field capacity, saturated soil moisture content, and hydraulic conductivity. Water that flows into the soil layers can contribute to the soil moisture, become lateral flow, percolate to the next layer below, or be lost to evapotranspiration. For the jth layer, conservation of mass requires the following:

$$A_j\ Z_j\ d\theta_{d\ j}/dt = A_{j-1}\ P_{j-1} - A_j\ (ET_{pj} + P_j) - L_j$$

where A_j is the area of layer j in cm^2, Z_j is the thickness of layer j in cm, θ_j is the average volumetric water content of layer j, A_{j-1} is the surface area of the soil layer immediately above (layer j-1) in cm^2, P_{j-1} is the percolation from layer j -1 in cm/sec, P_j is the percolation from layer j to the next lower layer in cm/sec and L_j is the lateral flow from layer j in cm^3/sec. This means that the change in the moisture content of layer j is equal to the amount of water percolating in from the layer above minus the outflow from the layer.

The percolation rate is assumed to be zero at and below field capacity, and it increases with soil moisture content to the hydraulic conductivity at saturation.

$$P_j = K_j ((\theta_j - \theta_{cj})/(\theta_s - \theta_{cj}))$$

where K_j is the saturated hydraulic conductivity of layer j in cm/sec, θ_{cj} is the field capacity of layer j and θ_s is the saturated moisture content of layer j.

As a general rule, lateral flow from a layer should not occur when its soil moisture content is below saturation. There are times, however, when that rule is not applicable. This can occur because the soil moisture content for a layer is represented by its average value, θ_j. However, it is possible for the soil moisture to be distributed nonuniformly with depth in the soil layer. This would be especially true where there is a large reduction of surface area between layers and a saturated condition in the next lower layer. A temporary saturated zone may then be formed to produce lateral flow. For example,

$$L_j = K_j W_s F_r Z_s$$

in which L_j is lateral flow in cm^3/sec, K_j is saturated hydraulic conductivity in cm/sec, W_s is the width of the stand in cm, F_r is the vertical depth over the horizontal distance for flow and Z_s is the equivalent saturation depth. Z_s is approximated by:

$$Z_s = Z_j ((\theta_j - \theta_{cj})/(\theta_s - \theta_{cj}))$$

where Z_j is the thickness of the soil layer j in cm, θ_{cj} is the field capacity of layer j, and θ_s is the saturated moisture content of layer j.

In the model, the preceding equation is established for each soil layer. P_{j-1} is the infiltration rate for the very top soil layer. If the bedrock is assumed to be impermeable then the value for P_j in the bottom layer is zero. If P_j is higher than the potential for the next lower layer to receive water, iterative corrections need to be made in overlying layers since the conservation of mass equation presented above is not coupled between soil layers.

Surface runoff can occur if the top layer of soil becomes frozen or saturated. These occurrences impede infiltration. The mass balance equation for surface runoff is:

$$T_m - R_s = A(dD/dt)$$

in which T_m is the amount of rainfall plus snowmelt in cm^3/sec, R_s is the surface runoff in cm^3/sec, A is the surface area in cm2, and D is the depth of the water on the surface in cm. R_s is calculated using the Manning equation:

$$R_s = (W_s(D-D_o)^{5/3} S^{1/2})/n \text{ for } D > Do$$

$$R_s = 0 \text{ for } D < D_o$$

where D_o is the maximum detention storage on the land surface in cm and n is the Manning coefficient. In this formulation, the hydraulic radius is the depth of the sheet flow (Crawford and Linsley, 1966; Chen and Shubinski, 1971).

Snowpack

The following equation is used to calculate the rate of air temperature induced snowmelt:

$$M_o = \alpha_o (T - T_{sn}) (0.4 + \sin(0.0087\beta))$$

where

M_o = the melting rate for snow

αo = a calibration coefficients with units of cm/day°C

T = the mean stand air temperature in °C

T_{sn} = the incipient snow formation temperature in °C

β = the aspect of the watershed in degrees measured clockwise from north

The value of 0.0087 is used to give the sine function a maximum when evaluated in radians for the case when β is 180°. Relationships for melting rates without the aspect correction are found in Chow (1964).

Rain-induced melting is determined by the following (Corps of Engineers, 1960):

$$M_r = 0.0039 (T - T_{sn}) T_l$$

where

M_r = the rain-induced melting rate in cm/day

T_l = the rainfall rate in cm/day

The water equivalent depth of the snowpack is calculated using the following equation:

$$D_s = S_e + S - (S_s + S_m) \Delta t$$

where

D_s = the water equivalent snowpack depth in cm of water

S_e = the water equivalent snowpack depth at the end of the previous time step in cm of water

S = the snowfall during the time step in cm of water

S_s = the snow sublimation rate in cm/day

S_m = the rate of snowmelt in cm/day

Δt = the time step in day

Not all the water that is produced from the melting snow is drained from the snowpack. The ‘field capacity’ of the snowpack must be satisfied before the water can be drained from the snowpack. The effective snowmelt rate is determined by:

$S_m = (M_o + M_r) - ((\theta fc - \theta)/\Delta t)\ S_e$

where

θfc = the field capacity of snow in a decimal fraction of the total volume

θ = the liquid water content of the snow in a decimal fraction of the total volume

Wet Deposition of Mercury

The general equation for wet deposition of mercury is:

$$\text{WetDepHg} = \text{Area} * V_{precip} * [\text{Hg}]_{precip}$$

where

WetDepHg = wet deposition of Hg(II) or MeHg (μg day^{-1})

Area = water surface area (m^2)

V_{precip} = precipitation rate (m day^{-1})

$[\text{Hg}]_{precip}$ = concentration of Hg(II) or methylmercury in precipitation (μg m^{-3})

Particle Deposition of Mercury Direct to the Water Surface

The general equation for dry deposition of mercury on particles to the water surface is:

$$\text{DryDepHg} = \text{DryHg} * \text{Area}$$

where

DryDepHg = dry deposition rate of Hg(II) or MeHg directly to water surface (μg day^{-1})

DryHg = dry deposition of Hg(II) or MeHg per m^2 (μg m^{-2} day^{-1})

Area = total water surface area (m^2)

Deposition of Reactive Gaseous Mercury Directly to the Water Surface

The general equation for deposition of RGM directly to the water surface is:

$$\text{RGMdep} = \text{RGM}_{atm} * \text{Vel}_{RGM} * \text{Area}$$

where

RGMdep = RGM flux directly to water surface (µg Hg(II) day-1)

RGM_{atm} = concentration of RGM in air (µg m-3 , input as pg m-3)

Vel_{RGM} = RGM deposition velocity (m day-1, input as cm s-1)

Area = total water surface area (m2)

Mercury Throughfall

$$\text{ThroughfallHg} = \{\text{HgLeafSurface}_i) * K_{throughi} * \text{Precip} * \text{Area}$$

where:

ThroughfallHg = quantity of HgII or MeHg purged from leaf surfaces during precipitation (ug/timestep)

HgLeafSurface = pool of HgII or MeHg on leaf surfaces, accumulated via dry deposition and RGM deposition (ug Hg)

$K_{through}$ = Throughfall rate constant (fraction purged per mm precip)

Precip = Precipitation during timestep (mm/timestep)

Area = vegetated area

Litterfall Mercury

The general equation for mercury in litterfall is:

$$\text{LitterfallHg} = \{([\text{Hg}]_i * \text{Biomass}_I) + \text{HgLeafSurface}_I\} * k_{biomass} * \text{Area}) + \text{RGM}_{litter}$$

where:

LitterfallHg = litterfall flux of HgII or MeHg to sediments (ug day^{-1})

$[\text{Hg}]_i$ = concentration of HgII or MeHg in vegetation (ug g^{-1})

Biomass_i = vegetation biomass (g m^{-2})

$k_{biomass}$ = litterfall rate (day^{-1})

Area = vegetated surface area (m^2)

RGM_{litter} = RGM accumulation which is associated with litter flux rather than being purged by rain (ug day^{-1})

Hg Inflows and Outflows with Water

The general equation for mercury surface water is:

HgInflow = Qin * $[\text{HgxIn}]_{\text{unfiltered}}$

where

HgInflow = inflow of readily exchangeable Hg(II) or MeHg (µg Hg day^{-1})

Qin = surface inflow rate (m^{3} day^{-1})

$[\text{HgxIn}]_{\text{unfiltered}}$ = unfiltered concentration of readily exchangeable Hg(II) or MeHg in inflowing water (µg Hg m-3).

An analogous expression is used for groundwater inflow.

Settling

The equation for settling of Hg(II) or methylmercury is:

SettlingHg_{j} = Vsettle_{j} * SS_{j} * $[\text{Hg}_{p}]_{i}$ * Area

where

j = Particle type (detritus or other suspended solids)

SettlingHg_{j} = Settling of Hg(II) or methylmercury on particle type j (µg Hg day^{-1})

Vsettle_{j} = Settling velocity of particle type j (m day^{-1})

SS_{j} = Concentration of particle type j suspended in water (g m^{-3})

$[\text{Hg}_{p}]_{i}$ = Concentration of Hg(II) or MeHg on particle type j in water (µg g^{-1})

Area = Area (m^{2})

Sediment Burial/Erosion

The general equation for burial of Hg(II) or methylmercury is:

Burial_{i} = Area_{i} * Vburial_{i}, * ϕ_{i} * $[\text{Hg}_{p}]_{i}$, * SedDensity_{i}

where

i = sediment layer number, increasing downward

Burial_{i} = burial rate of Hg(II) or methylmercury out of layer i (µg Hg day^{-1})

Area_{i} = sediment area of layer i (m^{2})

Vburial_{i} = bulk burial velocity out of layer i (m day^{-1})

ϕ_{i} = volume fraction in layer i

$[\text{Hg}_{p}]_{i}$ = particle concentration of Hg(II) or MeHg in sediment layer i (µg g^{-1})

SedDensity$_i$ = sediment density in layer i (g m^{-3})

If erosion is occurring, the equation is:

Erosion$_i$ = Area$_i$ * Verode$_i$ * ϕ_{i+1} * [Hg$_p$]$_{i+1}$ * SedDensity$_i$

where

i = sediment layer number, increasing downward

Erosion$_i$ = erosion rate of Hg(II) or methylmercury on particle type j into sediment layer i, out of layer i + 1 (µg Hg day^{-1})

Verode$_i$ = bulk erosion velocity for layer i into layer i + 1 (m day^{-1}) ϕ_{i+1} = volume fraction of particle type j in layer i +1

[Hg$_p$]$_{i+1}$ = particle concentration of Hg(II) or MeHg on particle type j, in sediment layer i + 1 (µg g^{-1})

SedDensity$_i$ = sediment density of particle type j (g m^{-3})

Area$_i$ = area of sediment layer i (m^2)

Sediment Resuspension

The equation for resuspension of Hg(II) or methylmercury is:

HgResusp = Area$_1$ * Resusp * [Hg$_p$]$_1$

where

HgResusp = Resuspension rate of Hg(II) or MeHg from surface sediment (µg Hg day^{-1})

Resusp = Particle resuspension rate (g m^{-2} d^{-1})

[Hg$_p$]$_1$ = particle concentration of Hg(II) or MeHg in surface sediment layer (µg g^{-1})

Area$_1$ = Sediment area (m^2)

Diffusion

The general equation for diffusion in the dissolved phase is:

Diffusion = ([Hg$_d$]$_i$ - [Hg$_d$]$_j$) * MTC$_{overall}$ * Area

where

Diffusion = diffusion of dissolved Hg(II), MeHg or elemental Hg between compartment i and compartment j (µg Hg day^{-1})

$[Hg_d]_i$ = concentration of Hg(II), MeHg or elemental Hg in compartment i ($\mu g\ m^{-3}$)

$[Hg_d]_j$ = concentration of Hg(II), MeHg or elemental Hg in compartment j ($\mu g\ m^{-3}$)

$MTC_{overall}$ = overall mass transfer velocity between compartments i and j (m day ^{1})

= $\{(MTC_i)^{-1} + (MTC_j)^{-1}\}^{-1}$

MTC_i = mass transfer velocity for compartment i (m day^{-1})

MTC_j = mass transfer velocity for compartment j (m day^{-1})

Area = diffusion area between compartments (m^2)

An analogous expression is used for gas-phase diffusion in partially saturated sediments during periods when water levels drop and expose sediments.

The value of MTC will depend on location. Values of MTC in the water column compartment are greater than in sediments, reflecting more mixing in the water column. Values of MTC for diffusion within given soil/sediment layers account for the tortuosity (the need to travel around particles) and moisture content, are based on Jury, et al., (1990) and Jury, et al., (1983).

For liquid-phase diffusion within a sediment compartment:

$MTC = MTC_L * (\theta 10/3/\phi^2)$

where

MTC_L = Mass transfer constant in pure liquid (m day^{-1})

θ = Volumetric water content (fraction)

ϕ = Soil porosity (fraction)

For gas-phase diffusion within an unsaturated sediment compartment:

$MTC = MTC_g * (a^{10/3}/\phi^2)$ where

MTC_g = Mass transfer constant in pure gas (m day^{-1})

a = Volumetric air content (fraction)

ϕ = Soil porosity (fraction)

Volatilization

The general equation for volatilization of elemental mercury or methylmercury between air and water is:

$\text{Volat}_{air/water}$ = Area * koverall_{air} * { ($[Hg_g]_{air}$ * H^{-1}) - $[Hg_d]_{water}$ }

where

Volatair/water = volatilization rate across air/water interface (µg day^{-1})

Area = area (m^2)

koverall_{air} = overall mass transfer coefficient with respect to air (m day^{-1})

$[Hg_d]_{water}$ = dissolved concentration of Hg^0 or CH_3HgCl in water (µg m^{-3})

$[Hg_g]_{air}$ = gaseous concentration of Hg^0 or CH_3HgCl in air (µg m^{-3})

H = Henry's law constant for Hg^0 or CH_3HgCl (dimensionless)

The overall mass transfer coefficient at the air/water interface is represented by:

koverall_{air} = $\{(MTC_w)^{-1} + (MTC_{air} * H)^{-1}\}^{-1}$

where

MTC_w = Mass transfer coefficient for Hg^0 or CH_3HgCl at water surface (m day^{-1})

MTC_{air} = Mass transfer coefficient for Hg^0 or CH_3HgCl in air (m day^{-1})

Bacterial Methylation

The general equation for methylation is (example for sediments):

M = C_{decomp} * Efficiency * SulfateEffect * $[HgII_{avail}]$ * Area * Porosity

where

M = methylation rate, µg Hg(II) day^{-1}

Efficiency = methylating efficiency of microbes (µg MeHg produced per µg $Hg(II)_{avail}$ per g C decomposed per m^3)

$[HgII_{avail}]$ = concentration of dissolved Hg(II) in water or porewater which is available for methylation (µg Hg(II) m^{-3})

Area = sediment area (m^2)

Porosity = porosity of sediments

C_{decomp} = g carbon decomposed per day per m^2 sediment (for the sediment layer being modeled)

= $(C_{decomp})_{POC} + (C_{decomp})_{DOC}$

$(C_{decomp})_{POC}$ = decomposition of particulate organic carbon in sediment layer (g m^{-2} day^{-1})

= Sedmass * OrgCFrac * k_{POC}

Sedmass = mass of particles in sediment layer (g C m^{-2})

OrgCFrac = Organic Carbon Fraction of sediment particles (fraction)

k_{POC} = Decomposition rate of carbon settling into sediments (day^{-1})

= $(k_{POC})_{base} * Q10_{m}^{(T-Tb/10)}$

$(k_{POC})_{base}$ = Rate constant at a base temperature (e.g. 15 °C) (day^{-1})

$Q10_{CT}$ = Effect of a 10 °C change on the decomposition of POC

T = Temperature (°C)

Tb = Base Temperature for Rate Constant (°C)

$(C_{decomp})_{DOC}$ = Decomposition of DOC in sediment layer (g m^{-2} day^{-1}

= DOC * k_{DOC}

DOC = dissolved organic carbon in water column (g m^{-3})

k_{DOC} = $(k_{DOC})_{base} * Q10_{meth}^{(T-Tb/10)}$ (m day^{-1})

$Q10_{meth}$ = Effect of a 10 °C change on the decomposition of DOC

$(k_{DOC})_{base}$ = Rate constant at a base temperature (e.g. 15 °C) (m day^{-1})

SulfateEffect = $(SO4_{supply}) * (SO4_{supply} + KSO4_{supply})^{-1})$ (dimensionless)

$SO4_{supply}$ = Sulfate concentration (μeq L^{-1})

$KSO4_{supply}$ = Half saturation constant for sulfate effect (μeq L-1)

Bacterial Demethylation

The general equation for demethylation is (example for sediments):

D = $C_{decomp} * Efficiency_{d} * [MeHg_{avail}]$ * Area * Porosity

where

D = demethylation rate, μg Hg(II) day^{-1}

$Efficiency_{d}$ = demethylating efficiency of microbes (μg Hg0 produced per μg $MeHg_{avail}$ per g C decomposed per m^{3})

$[MeHg_{avail}]$ = concentration of dissolved MeHg in water or porewater which is available for demethylation (µg MeHg m^{-3})

Area = sediment area (m^2)

Porosity = porosity of sediments

C_{decomp} = g carbon decomposed per day per m^2 sediment (for the sediment layer being modeled)

Methylmercury Photodegradation

Photodegradation is calculated for a number of horizontal layers in a compartment and then summed to obtain the total photodegradation in the compartment:

$$D_{me} = C_{eMeHg} \cdot \sum_{1}^{n} \left(K_{dlayer} \cdot V_{layer}\right)$$

where

D_{me} = photodegradation rate in the water column, mgHg/day

$\sum_{1}^{n}$ = summation from layer 1 to n

C_{eMeHg} = MeHg dissolved concentration, µgMeHg/m^3

K_{dlayer} = photodegradation rate constant averaged over the volume of the layer, 1/day

V_{layer} = volume of layer, m^3

The photodegradation rate constant is attenuated with depth based on the following expression:

$K_{dz} = K_{ds} * \exp(-K_{Light} \cdot * z)$

where

Z = depth from water surface (m)

K_{dz} = photodegradation rate constant at depth z , 1/day

K_{ds} = photodegradation rate constant at lake surface, 1/day

K_{Light} = light extinction coefficient, 1/m $K_{ds} = L * K_i$

where

K_{ds} = demethylation rate constant at water surface, 1/day

L = light intensity at water surface, µ Einsteins/m^2/s

K_i = demethylation constant normalized to light intensity, m^2/μ Einsteins

Hg(II) Reduction/Hg(0) Oxidation

The photochemical equation for Hg(II) reduction is:

$\text{ReductionHg} = k_{red} * [HgII_d]_{red} * \text{Volume}$

where

ReductionHg = Hg(II) reduction rate (μg day^{-1})

k_{red} = integrated photoreduction rate constant over depth of compartment (day^{-1})

= $(k_{RedSurf} / ke) * (1 - \exp\{-ke * z\}) / z$

z = mean depth (m)

ke = light extinction coefficient (m^{-1}) (for applicable wavelengths)

$k_{RedSurf}$ = photodegradation rate constant at water surface (day^{-1})

L = light intensity at water surface (e.g. PAR or UV, μEinsteins m^{-2} day^{-1})

$[Hg_d]_{red}$ = Concentration in Hg(II) available for photoreduction in surface water ($\mu g\ m^{-3}$)

Volume = Compartment volume (m^3)

Mercury Partitioning in the Water Column: Abiotic Compartments

The general form of the equations used to calculate mercury partitioning is (example given for methylmercury in water column):

$\text{KeMeHg} = K_{eMeHg} * 1/(1 + [H^+]K_c)$

where

K_{eMeHg} = partition constant entered by the user (m^3/g dry particle)

$[H^+]$ = concentration of hydrogen ions (moles/L, the model input is pH))

K_c = half saturation constant for the effect of pH on the partition constant (L/mole)

Mercury Dynamics in Plankton

The partitioning between mercury in phytoplankton and dissolved Hg in solution can be defined as:

K_{pl} = $[Hg]_{pl} / \{[pl] * [Hg]_{dis}\}$

where

Hg = methylmercury or Hg(II)

K_{pl} = partition constant (L/kg dry plankton)

[pl] = phytoplankton biomass (kg dry/L) (Model input is mg dry/L)

$[Hg_{dis}]$ = moles Hg /L water, dissolved

$[Hg]_{pl}$ = moles Hg /L in phytoplankton

K_{pl} is estimated as follows:

K_{pl} = $(F_{ic} * K_{ipl} * K_{di}) / (K_{ipl} + K_{di})$

where

F_{ic} = fraction of dissolved Hg(II) or methylmercury which is in the inorganic (non - DOC) complexes (dimensionless)

K_{ipl} = partition constant between phytoplankton and *inorganic species* in solution, which would occur without diffusion limitation (i.e., due to the balance of uptake (facilitated and passive) and losses (cell growth, depuration)) (L/kg dry).

K_{di} = partition constant between phytoplankton and *inorganic species* in solution, which would occur due solely to diffusion limitation (L/Kg dry).

The result of this formulation is that the partition constant, K_{p1}, between phytoplankton and dissolved Hg in solution is with respect to dissolved Hg(II) or methylmercury

where

$$\mathrm{Kipl} = \{ \sum_{i=1}^{n} a_i \, (\mathrm{Uf} + \mathrm{Dp})\} / \{\mathrm{Fic} * (\mathrm{u} + \mathrm{kd}) * \mathrm{Mcell}\}$$

where

K_{ipl} = partition constant between phytoplankton and inorganic Hg species in solution, without any effects of diffusion limitation (L/Kg dry plankton).

F_{ic} = fraction of dissolved Hg(II) or methylmercury which is not bound to DOC (dimensionless)

u = growth rate of cells (1/day)

kd = mercury depuration constant for cells (1/day)

M_{cell} = mass of cell : (kg/dry cell)

U_f = facilitated uptake constant as defined below (L/cell/day)

D_p = passive diffusion constant as defined below (L/cell/day)

a_i = fraction of dissolved Hg(II) or MeHg as inorganic complex *i*

n = number of inorganic Hg complexes

Passive Diffusion

In the model, passive diffusion is included for HgCl2, CH,HgCl and CH,HgOH. As an example, the expression for the passive diffusion of $HgCl_2$ is:

$F = D_p\ HgCl_2 * [HgCl_2]$ (moles $HgCl_2$/cell/day)

where

F = flux of $HgCl_2$

D_pHgCl_2 = $P_m\ HgCL1_2 * A_{cell}$ (L/cell/day)

$P_m\ HgCl_2$ = dm/day (1dm = 0.1m, $1dm^3$ = 1 L))

A_{cell} = Surface area of cell (dm^2/cell)

Facilitated Uptake

The facilitated uptake rate, when expressed as a function of the free ion concentration, is:

$F_{Hg++} = U_{fHgII} \cdot [Hg{+}{+}]$

where

F_{Hg++} = flux of Hg++, moles Hg/cell/day

U_{fHgII} = $k_x/\{1 + (BetaHX[H+])\}$

[Hg++] = concentration of free ion, moles/L

k_x = facilitated uptake rate constant for Hg++, L/cell/day

BetaHX = half-saturation constant for the effect of pH on facilitated uptake rate, L/Mole H+

[H+] = concentration of hydrogen ions, moles/L

A similar expression can be written for facilitated uptake which is controlled by the sum of the inorganic complexes rather than the free ion:

$U_{fHgII}F_{HgII}$ = U_{fHgII} * [Hg(II) Inorganic]

where

U_{fHgII} = $k_x/\{1 + (BetaHX[H+])\}$, moles Hg/cell/day

[Hg(II) Inorganic] = Moles Hg/cell/day

Analogous expressions are also included for methylmercury.

Diffusion Limited Uptake

The expression for diffusion limitation is (from Hudson et al. 1994):

$$K_{di} = (4 * pi * R_{cell} * D_c) / (u * M_{cell})$$

where

K_{di} = Diffusion limited partition coefficient with respect to inorganic species, L/Kg dry plankton

R_{cell} = Cell Radius, dm

D_c = Diffusion constant, dm2/day

u = cell growth rate, 1/day

M_{cell} = cell mass, kg dry/cell

Mercury Partitioning in Zooplankton and Benthos

The general equation for the mercury concentration in Zooplankton is:

$$[Hg]_z = [Hg]_{pp} * ZooFac$$

where:

$[Hg]_z$ = concentration of HgII or MeHg in invertebrates (ug g^{-1} dry)

$[Hg]_{pp}$ = concentration of HgII or MeHg in phytoplankton (ug g^{-1} dry)

ZooFac = partition constant for HgII or MeHg (dimensionless)

Mercury Partitioning in Soils/Sediments

The general expression for mercury partitioning in soils/sediments is (example given for methylmercury on sediment solids):

$$K_{se} = K_{se} * (1 / (1 + [H^+]*K_c))$$

where

K_{se} = partition constant entered by the user (m^3/g dry particle)

$[H^+]$ = concentration of hydrogen ions in porewater (moles/L, the model input is pH))

K_c = half saturation constant for the effect of pH on the partition constant (L/mole). The model input is the log (base 10) of this constant.

Methylmercury Uptake in Fish

Uptake via food

The amount of methylmercury absorbed via food eaten by a fish is expressed as:

$$Ff_{MeHg} = E_{pf} * MeHg_f * Consumption$$

where

Ff_{MeHg} = Fish uptake of MeHg via food (ug MeHg fish^{-1} day^{-1})

E_{pf} = Uptake efficiency of MeHg from food (fraction)

Consumption = g wet food fish^{-1} day^{-1}

$MeHg_f$ = ug MeHg g^{-1} wet food

Mercury Uptake Across the Gills

$$Fg_{MeHg} = E_{pw} * MeHg_d * (R+S) * W * (E_{OX} * C_{OX} * Q_{OX})^{-1}$$

where

Fg_{MeHg} = Methylmercury flux into fish via gills (ug MeHg fish^{-1} day^{-1})

W = Fish Weight (g)

E_{pw} = Efficiency of uptake of methylmercury from water (dimensionless)

$MeHg_d$ = Methylmercury concentration dissolved in water (ug MeHg m^{-3})

E_{ox} = Efficiency of uptake of oxygen from water (dimensionless)

C_{ox} = Oxygen concentration in water (g O_2 m^{-3})

Q_{ox} = Caloric value of oxygen (kcal g^{-1} O_2)

R = specific respiration rate (kcal * g^{-1} wet fish * d^{-1})

S = energy accounted for by specific dynamic action (kcal * g $^{-1}$ wet fish * d^{-1})

R and S are calculated on the basis of equations developed by Hewett and Johnson (1992).

Methylmercury Excretion

Excretion is treated in the model as follows:

E_{xc} = $C_{fMeHg} * k_{mx} * R_{wf}$ (ug MeHg/day)

where

C_{fMeHg} = concentration of MeHg in fish, ug/g wet (whole body)

K_{mx} = rate of nitrogenous wastte excretion (g metabolic wastes/day)

R_{wf} = Ratio of MeHg concentration in excreted wastes/MeHg concentration in fish (wet, whole body) (dimensionless)

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MERCURY IN ADIRONDACK WETLANDS, LAKES, AND TERRESTRIAL SYSTEMS (MAWLTS)

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