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# Fire and its Effects on Mercury and Methylmercury Dynamics for Two Watersheds in Acadia National Park, Maine

Kenneth B. Johnson

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**FIRE AND ITS EFFECTS ON MERCURY AND METHYLMERCURY  
DYNAMICS FOR TWO WATERSHEDS IN  
ACADIA NATIONAL PARK, MAINE**

By

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B. A. Ferrum College, 1998

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Ecology and Environmental Sciences)

The Graduate School

The University of Maine

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cross-continental movement of contaminated air masses and prevailing wind direction. Sites covered with softwood vegetation also received higher Hg deposition than other vegetation types because of the higher scavenging efficiency of the canopy structure. MeHg deposition was not affected by these factors.

Hg deposition was lower in Cadillac Brook watershed (burned) than in Hadlock Brook watershed (unburned) because regeneration after the fire was dominated by mixed hardwood, whereas softwoods dominate the landscape in Hadlock Brook watershed. The lower deposition could also be a result of the watershed aspect; Cadillac Brook watershed faces southeast to east and Hadlock Brook watershed faces south to southwest.

The 1947 fire that burned Cadillac Brook watershed likely removed organic material from the soil through combustion and subsequent erosion. Much of the Hg in the remaining organic material would have been volatilized by the elevated temperature caused by the fire, breaking the chemical bonds between Hg and DOC releasing the Hg, possibly enhancing the soil's ability to sequester Hg more efficiently by. As a result, Cadillac Brook exports less Hg from its watershed than Hadlock Brook, which has unburned soils containing more organic material. Hadlock Brook exports more MeHg, but export cannot be explained by inputs and may be controlled by production in peat and other organic-rich materials in the riparian zone.

Hg and MeHg inputs were weighted by season and vegetation type for budget determination because these two factors had the most influence on

deposition. Hg volatilization from soils, water, and vegetation surfaces was ignored because of the difficulties associated with analyzing gaseous Hg. The Hg budget for Cadillac Brook watershed was  $9.4 \mu\text{g}/\text{m}^2/\text{year}$  (input) –  $0.4 \mu\text{g}/\text{m}^2/\text{year}$  (export) =  $9.0 \mu\text{g}/\text{m}^2/\text{year}$ , or 95% of the total Hg deposited on Cadillac Brook watershed was retained by the watershed. The Hg budget for Hadlock Brook watershed was  $10.2 \mu\text{g}/\text{m}^2/\text{year}$  (input) –  $1.3 \mu\text{g}/\text{m}^2/\text{year}$  (output) =  $8.9 \mu\text{g}/\text{m}^2/\text{year}$ , or 87% of the total Hg deposited on Hadlock Brook watershed was retained by the watershed.

Litter contributed two to five times the Hg to the forest floor as precipitation. Cadillac Brook watershed received  $57.1 \mu\text{g}/\text{m}^2/\text{year}$  of Hg from litter while Hadlock received  $29.0 \mu\text{g}/\text{m}^2/\text{year}$  of Hg, demonstrating that litterfall is a major Hg pathway to the forest floor. The residence time of the Hg from litter and the ultimate fate of the litter itself are unknown.

The MeHg budget for Cadillac Brook watershed was  $0.05 \mu\text{g}/\text{m}^2/\text{year}$  (input) –  $0.04 \mu\text{g}/\text{m}^2/\text{year}$  (output) =  $0.01 \mu\text{g}/\text{m}^2/\text{year}$ , or 25% of the MeHg deposited was not released by the watershed. The MeHg budget for Hadlock Brook watershed was  $0.10 \mu\text{g}/\text{m}^2/\text{year}$  (in) –  $0.06 \mu\text{g}/\text{m}^2/\text{year}$  (out) =  $0.04 \mu\text{g}/\text{m}^2/\text{year}$ , 39% of MeHg deposited was not released by the watershed. MeHg export appears to be controlled by soil processes in the riparian zone rendering a “MeHg budget” an inaccurate portrayal of MeHg dynamics in these watersheds.

## **ACKNOWLEDGMENTS**

I would like to thank my committee for their help and guidance, especially Terry for his patience. I would also like to thank Dave, Bob, and Bill of the National Park Service at Acadia National Park, without whose help I could never have finished. Thanks to Sarah Nelson and Heather Good for everything. And thanks to everyone at the George Mitchell Center for their help.

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## Chapter 1

### INTRODUCTION

#### Background

Mercury (Hg) is of environmental concern because of its health effects on terrestrial and aquatic biota. Both mono- and dimethyl mercury (MeHg) are extremely toxic species of mercury that are absorbed through the skin and membranes of aquatic animals and accumulate in tissue over time. Dimethyl mercury is very volatile and rarely found in environmental or biological matrices. Consumption of contaminated animals by humans, and other organisms, incorporates the accumulated Hg into the consumer's tissues, which can cause nerve and brain damage, and even death. Current health advisories discourage fish consumption for pregnant women and children, and recommend limits for adults, based on Hg concentrations in the fish (EPA, 1997).

Mercury is released to the environment by natural and anthropogenic processes, including volcanism and the combustion of fossil fuels. Pre-industrial levels of Hg deposition to lakes in Maine, as shown by lake sediment cores, were 50 to 65% less than current levels, indicating substantial anthropogenic input to Maine's ecosystems (Norton *et al.*, 1997).

Mercury is typically released to the atmosphere in gaseous or ionic/particulate form and can remain in the atmosphere for one year or more (EPA, 1997). Approximately half of the total Hg emitted is deposited in the immediate proximity of the source as particulates, while the gaseous fraction and

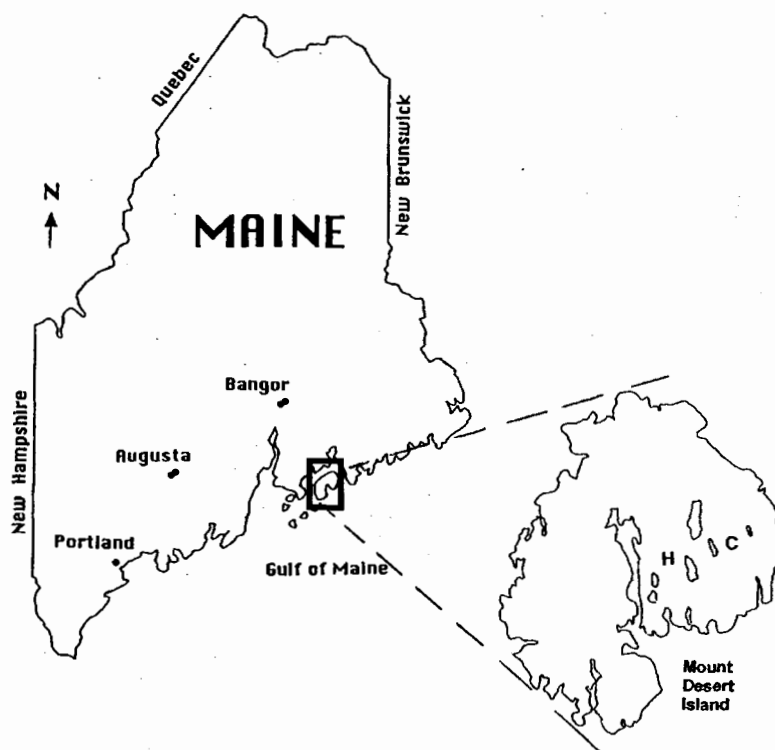
the lightest particles are transported long distances (Mason *et al.*, 1994). As the Hg travels with air currents it falls to earth, or is raked from the atmosphere by vegetation or other exposed structures, accumulating on their surfaces as dry deposition.

Mercury has a high vapor pressure (0.0017 mm of Hg), causing it to exist primarily in the vapor phase in the atmosphere, which is its major global transport mechanism (Mason *et al.*, 1994). This characteristic results in long-range transport of Hg from points of release to areas remote from human activity. New England receives 30% or more of its Hg from long range sources outside the region (EPA, 1997), prompting the U.S. Environmental Protection Agency to initiate a program to investigate what factors control biogeochemical cycling of nitrogen and Hg at the watershed scale.

### **PRIMENet Paired Watershed Project**

Two watersheds were delineated in Acadia National Park for a paired watershed project to determine differences in nutrient and metal deposition, internal cycling, and export at a burned versus an unburned watershed (Figure 1). This study was part of the EPA's PRIMENet (Park Research and Intensive Monitoring of Ecosystems Network) project, in conjunction with the USGS (United States Geological Survey), the NPS (National Park Service), and the University of Maine. Cadillac Brook watershed, which is dominated by hardwoods with patches of softwood, burned in 1947. Due to thin soils and harsh exposure, the period of regeneration that continues today probably began

**Figure 1.** Location of Mount Desert Island and the study watersheds.  
 C = Cadillac Brook watershed,  
 H = Hadlock Brook watershed.



slowly after 1947 (Schauffler *et al.*, in review). Much of the soil organic layer was probably removed through combustion and the subsequent erosion following the fire, and Hg is hypothesized to have volatilized from the upper mineral soil layers.

Hadlock Brook watershed, the reference watershed, is forested primarily by softwood species and has not burned in recent history (Schauffler *et al.*, in review). The canopy is more continuous and the soil organic layer is thicker than at Cadillac Brook watershed. These two watersheds provide a natural experimental design for the study of Hg deposition and transport because of their proximity and similarities in topography and climate and their differences in disturbance history and modern dominant vegetation type.

## **Hypothesis**

The hypothesis for this project was that total Hg export from Cadillac Brook watershed would be lower than the reference watershed (Hadlock Brook) because:

- The soil pool of Hg was depleted at Cadillac Brook watershed due to fire history;
- Landscape characteristics (vegetation type, watershed aspect) result in lower Hg deposition.

## **Objectives**

Our objectives were:

- To develop Hg and methylmercury (MeHg) input/output mass balances for each watershed, through determination of the volume and Hg concentration of streamwater, bulk and throughfall precipitation, and litterfall.
- To identify landscape characteristics governing Hg deposition and integrate the effects of these characteristics into the development of Hg and MeHg mass balances.

Hg and MeHg mass balances are one component in determining the compartmentalization of Hg and MeHg in forested watersheds. This study provides a baseline of information about fire's effects on factors that influence Hg and MeHg cycling in forested catchments to support future research at these sites.

## Chapter 2

### MATERIALS AND METHODS

#### Site Description

Cadillac Brook watershed is on the east side of Mount Desert Island in Acadia National Park, Maine, covers 31.6 ha, and has an average slope of 28%. The watershed is drained by a headwater stream, which originates in a mixed softwood valley at the summit of Cadillac Mountain. Soils are thinner, with a lower content of organic material, than at Hadlock Brook watershed.

The Hadlock Brook watershed is 5.3 km southwest of Cadillac Brook and covers 47.2 ha with an average slope of 20%. It is drained by a headwater stream, Hadlock Brook, which flows south-southwest, and is fed by a large wooded, poor fen at the northern end of the watershed and seasonally by a smaller fen in the southeast end of the watershed. The bedrock is Cadillac Granite with shallow, Haplorthod and Folist soils (Schauffler *et al.*, in review).

The US Geological Survey, in Augusta, Maine, monitors stream stage at the outflow of each watershed with a pressure transducer linked to the World Wide Web via satellite. The gauge at Hadlock Brook is located at Latitude N 44°19'54", Longitude W 68°16'47", at an elevation of 189 meters above sea level. The Cadillac Brook gauge coordinates are Latitude N 44°20'43", Longitude W 68°13'01". It is gauged at an elevation of 195 meters above sea level.



## Vegetation

The Cadillac Brook watershed vegetation is dominated by hardwood species with some mixed soft and hardwood stands. Hardwood species include American beech (*Fagus grandifolia*), paper birch (*Betula papyrifera*), white birch (*Betula populifolia*), sugar maple (*Acer saccharum*), and quaking and big-toothed aspen (*Populus tremuloides* and *P. grandidentata*). Softwood species are the same as in Hadlock Brook watershed. The understory is composed of young individuals of dominant canopy species and striped maple (*Acer pensylvanicum*). The forested landscape is interrupted by exposed bedrock on which grow assorted moss (*Sphagnum*), lichens, and grass: three-seeded sedge (*Carex trisperma*), common hairgrass (*Deschampsia flexuosa*), and little bluestem (*Schizachyrium scoparium*). Late-low blueberry (*Vaccinium angustifolium*) occurs in the understory and along open bedrock areas.

The Hadlock Brook watershed forest vegetation is dominated by softwood species including red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and white spruce (*Picea glauca*). The two wooded poor fens also have mountain holly (*Nemopanthus collinus*), black spruce (*Picea mariana*), and northern white cedar (*Thuja occidentalis*). The majority of the understory is composed of young individuals of the above species.

Vegetation maps, created by Nelson (2002), were used to determine percent and square area of vegetation coverage for each watershed (Table 1). The softwood category includes all conifers. The Hardwood category includes all broadleaf vegetation taller than the throughfall collector.

**Table 1.** Vegetation type and area covered for each watershed.

Vegetation Type	Cadillac Brook watershed		Hadlock Brook watershed	
	Area (m <sup>2</sup> )	Percent (%)	Area (m <sup>2</sup> )	Percent (%)
Softwood	89140	28.2	245460	52.0
Hardwood	96280	30.5	9380	2.0
Open	130600	41.3	217200	46.0
<b>Total</b>	<b>316020</b>	<b>100.0</b>	<b>472040</b>	<b>100.0</b>

The open category includes all un-vegetated areas as well as scrub areas, covered with vegetation that is lower than the throughfall collector.

### **Climate**

Compared to inland Maine, Mount Desert Island experiences cooler summers, and warmer, wetter winters with less snowfall. The average annual precipitation is ~141 cm (NADP 1990-98, website). Typical temperatures range from minus 10°C in the winter to 35°C in the summer (17°F - 95°F). Snowfall depths vary greatly, with a ten-year average of 24.9 cm (NOAA 1991-2000, website).

## **Precipitation and Throughfall Collection and Analysis**

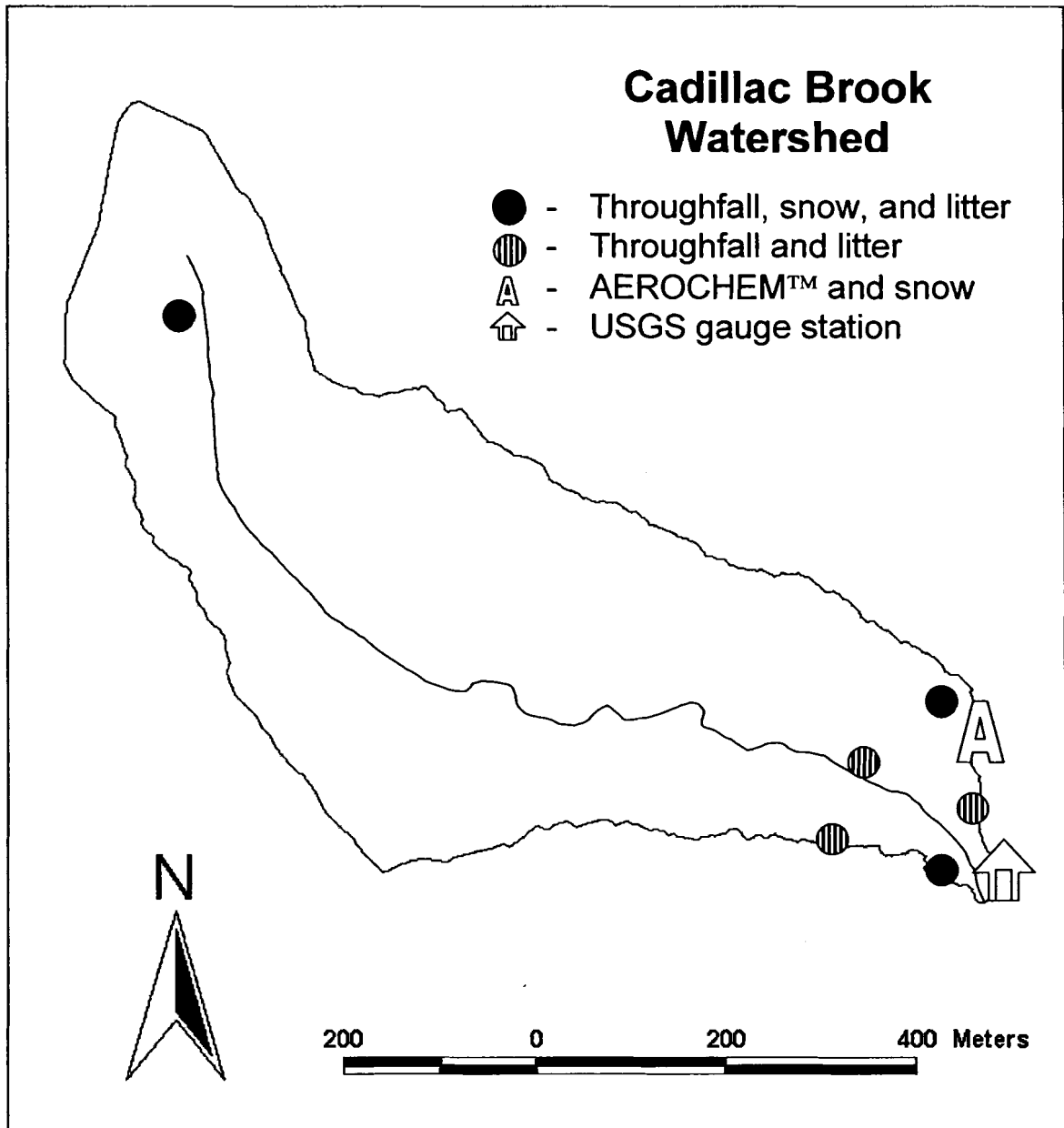
### **Collector Layout**

Six soil plots in Cadillac Brook watershed were chosen in areas where enough soil existed to establish soil plots (Figure 2). Five of the plots were located in the lower reaches of the watershed where slopes are shallower and there is more vegetation. One plot was located at the top of the watershed, near the headwaters of the brook. Between the two soil plots the watershed surface is primarily loose boulders and exposed bedrock with little vegetation, or very

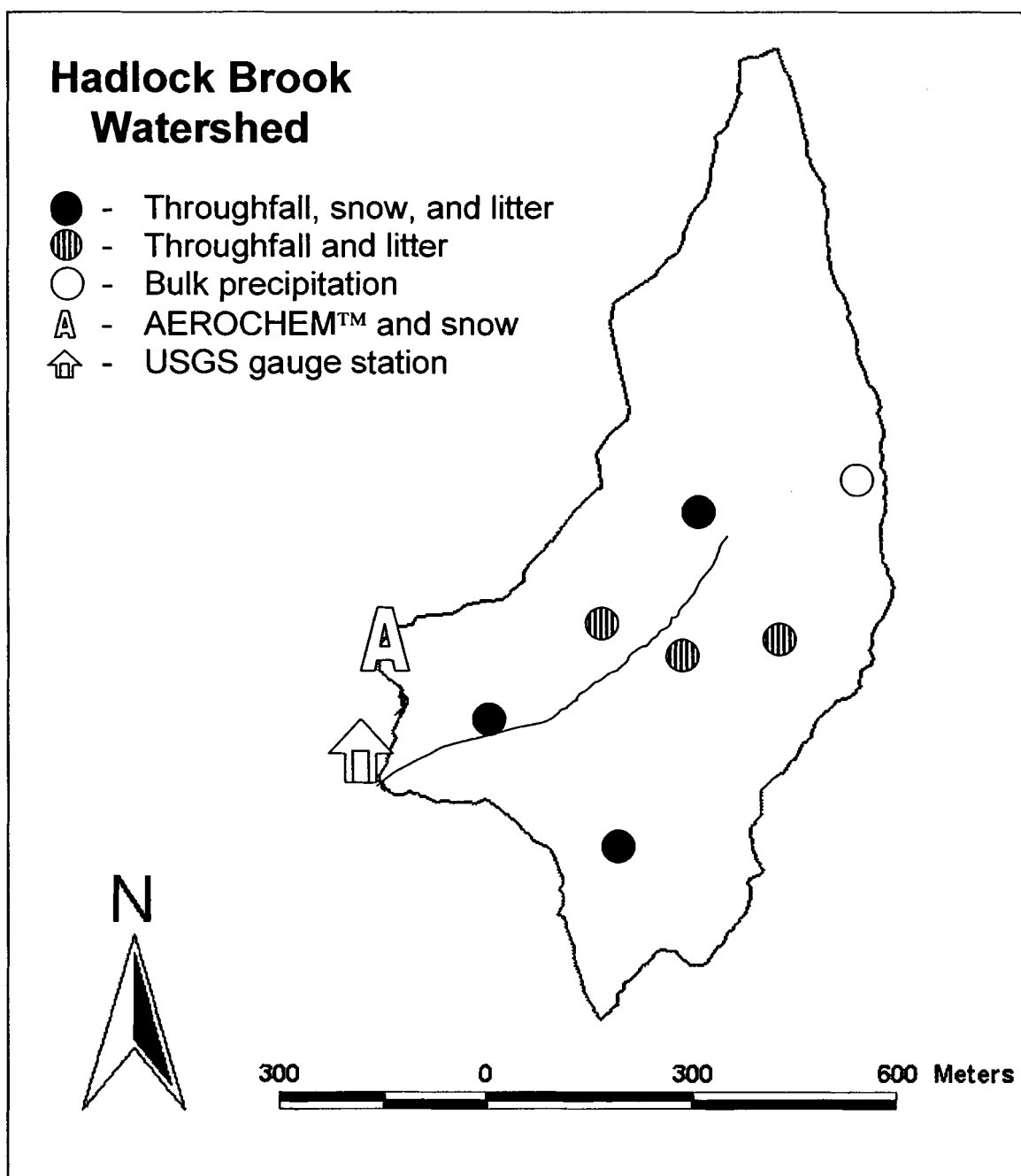
patchy areas of extremely thin soils. The six soil plots at the Hadlock Brook watershed were chosen to spatially represent the watershed (Figure 3). Three were at lower elevations near the brook and three at higher elevations. Two of the plots were level and the others were on slopes; all were fully forested.

Forty-eight of the fifty-two throughfall collectors were located in these plots, four per plot, one throughfall collector per quadrant (Figures 2 and 3). Hadlock Brook watershed had an open precipitation collector, not influenced by vegetation, at the top of the watershed boundary. Bulk precipitation collectors were co-located with one Aerochem™ wet-only collector in each watershed.

**Figure 2.** Map of Cadillac Brook watershed with sample sites marked by sample type.



**Figure 3.** Map of Hadlock Brook watershed with sample sites marked by sample type.



The fourth bulk precipitation collector was located next to the MDN (Mercury Deposition Network) collector on McFarland Hill at Acadia National Park.

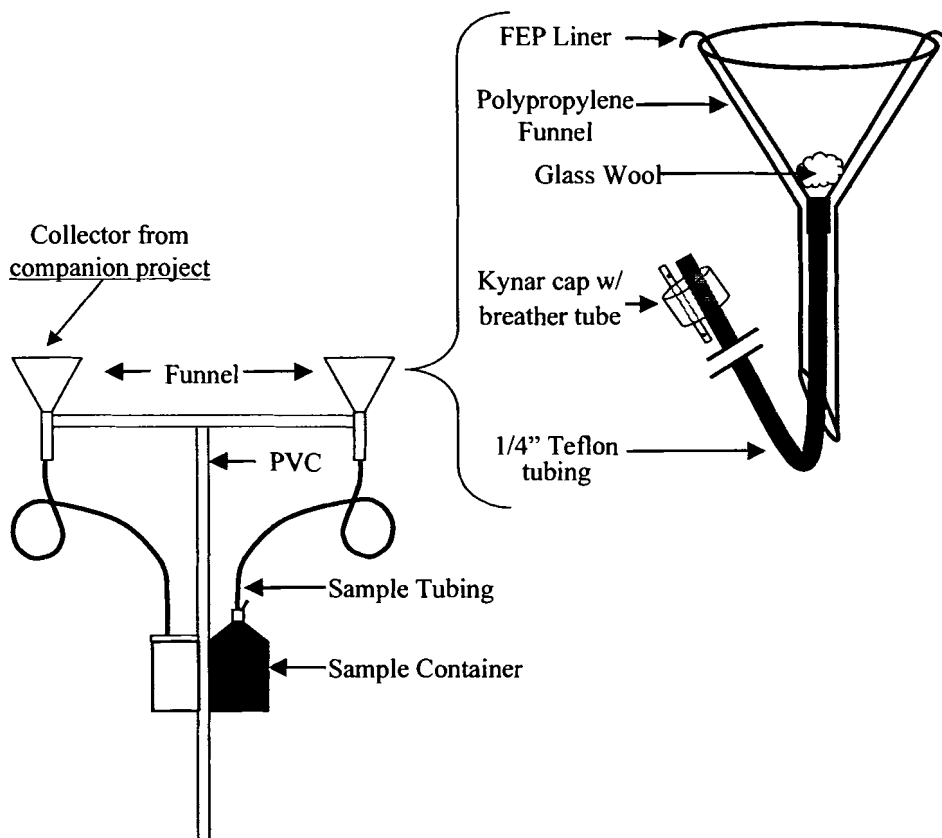
The vegetation type and aspect were recorded for each collector, as well as any abnormal features over or around any of the collectors. The tree type directly over the collector was identified to species and separated into over- or understory. Aspect was determined with a compass, was reported relative to true north, and referred to the main direction that the slope of the soil plot faces.

### **Throughfall Collector Design**

Throughfall collectors (Figure 4) were based on the Swedish IVL design, with structural modifications from Nelson (2002), Lawrence and Fernandez (1993), and Iverfeldt (1991). The precipitation was collected in a funnel and transported to a sample container using tubing. The funnel consisted of a polyethylene support funnel and a Teflon™ liner. The liner was 0.51 mm thick and had a deposition area of 197.93 cm<sup>2</sup>. A 1 m piece of 6 mm FEP Teflon™ tubing was threaded through the neck of the liner and the funnel/tubing set was inserted in the polyethylene funnel for support. The sample containers were 1L borosilicate glass, narrow mouth Boston bottles, with polyethylene screw caps.

Each cap was drilled and fitted with an 8 mm Kynar™ compression fitting and an air vent. The vent was a 5 cm piece of FEP Teflon™ tubing with the ends sealed and 0.2 mm holes drilled in each end to allow pressure release, yet minimize gaseous diffusion from the sample container. The sample container was joined to the funnel/tubing apparatus by the Kynar™ fitting. A one-inch electrical PVC pipe frame supported the assembly. The sample container was

**Figure 4.** Diagram of throughfall collector with exploded view of funnel assembly. Note adjacent throughfall collector from co-located project.



suspended in a two-liter soda bottle in such a way that a loop would form in the tubing. This loop retained a small amount of sample and formed an air lock over the sample container, preventing evaporation.

Special modifications were made to seven collectors in each watershed to collect samples for MeHg determination. During deployment, the MeHg sample containers received dilute acid, 300  $\mu$ L Optima HCl in 30 mL of deionized water to preserve speciation. A one-way duckbill valve on the sample container end of the tubing prevented diffusion of chlorine gas, and cross contamination of the adjacent collector, in the event that the sample tube dried out. Valves were changed after each collection.

### **Equipment Cleaning**

The cleaning and collection regime used in this study termed “semi-clean”, differed from the EPA’s “Ultra-Clean” collection method in three major ways. First, each technician wore a single pair of gloves, instead of two. Second, Tyvek suits, head covers, and booties were not utilized while sampling. Third, the sample container cleaning method did not employ a hot HCl bath. The “semi-clean” and “Ultra-clean” procedures were compared on four sets of paired water samples collected from each stream. For each pair of samples, one was collected using the ultra-clean sampling method and the other using the modified semi-clean method. The mean Hg concentration for water collected by the ultra-clean method was 0.3 ng/L for Cadillac Brook and 0.7 ng/L for Hadlock Brook, and comparable results for the semi-clean method were 0.3 ng/L for Cadillac Brook and 0.8 ng/L for Hadlock Brook. The results were not significantly different (paired t-test,  $\alpha=0.05$ ), and therefore subsequent samples were collected following the semi-clean method.

### **Throughfall Sample Collection**

Throughfall collectors were deployed from 3 May to 16 November 2000. Samples were collected after the accumulation of approximately 1 L of precipitation. Overflow volumes were inferred from adjacent non-Hg collectors that were equipped with overflow containers. The samples were collected ten times at varying intervals in the following manner. Fifty-two, double bagged, 1L sample bottles, and field equipment, were carried into the field in large backpacks. The old bottle was removed from the collector, capped with the lid



from the new bottle, and placed in a labeled polyethylene bag. The old sialized glass wool, used as a strainer for debris, was removed from the funnel and discarded. The 1L of deionized water (DI), which has very low metal concentrations, in the new sample bottle was used to rinse the collector funnel and tubing. On randomly selected collectors, the last 250 mL of DI rinse was retained in a 250 mL Teflon bottle as an equipment field blank. A small amount of DI (~2 mL) was left in the tubing to form the vapor lock over the sample container.

After rinsing, the new sample container was attached to the collector. If the collector was designated as a MeHg collector, a new valve was installed and the preservative was added to the sample container before it was reattached. New sialized glass wool was placed in the funnel to strain debris. Upon return to the laboratory, the throughfall sample and blank containers were removed from their bags, weighed, and a sufficient volume of BrCl added to produce a 1.0% preservative concentration.

### **Precipitation and Throughfall Analysis**

The samples were analyzed on a Tekran model 2600 cold-vapor atomic fluorescence spectrometer, adhering to EPA method 1631 (EPA, 1999) for the analysis of Hg in water. Purge techniques used in this study differed from those specified in the method, namely that a phase-separator tube was used in place of the bubblers, eliminating foaming in samples with a high organic concentration.

Specially collected throughfall samples were analyzed for MeHg using EPA Method 1630 (1998). A custom-built automated-valve system was utilized

to control gas flow and heater timing. Otherwise, protocols followed the EPA method.

Quality control (QC) methods for total Hg analysis in water were as recommended in Method 1631. For every 10 throughfall or stream samples, one replicate of that sample, two spiked samples, and two QC standards were analyzed. The QC standards were constructed in parallel with the calibration standards, but starting with a different stock solution. Known standard analysis was also tracked over time to detect long-term bias. MeHg QC methods were as recommended in EPA Method 1630, and were similar to total Hg QC methods.

### **Precipitation and Throughfall Data Analysis**

Samples collected on 27 July and 19 September 2000 represented more than 6.3 cm of precipitation, which exceeded the capacity of the container. Collectors from another project were located on the same structure, utilized the same size collection funnel, and had overflow bottles. All the non-overflow sample volumes of the adjacent collector were correlated with the non-overflow sample volumes from the Hg collectors and a linear relationship was derived:  $\text{Hg sample volume} = (0.8949 * \text{Co-located collector volume}) + 77.169$ ,  $R^2 = 0.79$ . The paired samples were collected on the same day at the same time. The total volume of each Hg sample that overflowed was calculated from the corresponding volumes from the co-located collectors.

The data from Hg and MeHg analysis were given as ng/L, which were multiplied by the sample volume, then divided by the area of the opening of the funnel,  $197.93 \text{ cm}^2$  and the number of days the sampler collected, then divided by

$10^7$  to get total Hg or MeHg deposition in  $\text{ng/m}^2/\text{day}$ . Data from the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (MDN) were used for Hg deposition from 17 November 1999 to 2 May 2000, because snow data were unreliable and collections were discontinued. Hg deposition calculated from snow fall was less than wet-only MDN deposition estimates. MeHg deposition for 17 November 1999 to 19 June 2000 was estimated from throughfall deposition by extrapolating the average deposition from the period 20 June to 16 November 2000, because no other source of MeHg data for that area was available at that time. The sampling period for Hg and MeHg was extrapolated to one year for comparison with continuous streamwater chemistry data.

Deposition was stratified by vegetation type and season, weighted by the vegetation area in the watershed, and summed to obtain the total input for the sampling period. Un-weighted deposition totals were also calculated by averaging the deposition from all collections, separated by watershed only. These totals were compared to the weighted deposition totals.

Single factor ANOVA tests were conducted on total Hg deposition and MeHg deposition as dependent variables, with watershed, vegetation, season, and aspect as the factors of comparison. These tests grouped all the data from both watersheds together in one data set to determine general relationships between deposition and landscape characteristics or other factors. The analyses were also calculated by watershed.

## **Streamwater Sample Collection and Analysis**

The stream stage was measured by a pressure transducer and relayed, via satellite, to the field office, where stream flow was calculated by the USGS in Augusta, Maine. Stream stage measurements were taken at five-minute intervals from 17 November 1999 to 16 November 2000. These data were averaged by hour for use in calculating Hg and MeHg export. ISCO™ auto-samplers were also located at these sites, to collect stream samples automatically during high flow events ( $Q > \sim 28.3$  Lps) from winter 1999 through November 2000.

All stream samples were taken from small pools just upstream from the USGS gauging stations for each watershed, using semi-clean collection methods. Streamwater samples were collected weekly in the summer and bi-weekly in the winter from 17 November 1999 to 16 November 2000 and consisted of two Teflon bottles for each stream, one for Hg (500 mL), and one for MeHg (250 mL). Duplicate samples were collected on an alternating watershed schedule. Event sampling occurred when flow exceeded approximately 28.3 L per second (Lps), then ISCO™ auto samplers collected one sample every four hours until stream flow decreased to below 28.3 Lps. Event samples were not taken for MeHg analysis. Temperature and weather conditions were recorded at the site.

At the laboratory, sufficient BrCl was added to the streamwater samples to produce a 0.5% preservative concentration. The bottle was capped, and left to stand overnight. Samples to be analyzed for MeHg were acidified with HCl to

preserve speciation. Streamwater samples were analyzed for Hg and MeHg in the same manner as throughfall and precipitation.

The Mitchell Center Laboratory at the University of Maine analyzed streamwater samples for major analytes in a parallel study (Nelson *et al.*, 2002).

Export of Hg from the watersheds was determined by multiplying stream discharge by Hg concentration and integrating for the collection interval. A SAS program interpolated values between measured data. The program used measured datum points for the initial and final concentrations for the collection period as starting and ending points for the interpolation, then assigned a linearly interpolated Hg concentration to each of the hourly stream flow averages between sample concentrations. The results were reported as hourly discharge of Hg in ng/hour. Discharge was calculated for each hour for the entire year and summed to give the yearly export of Hg via streamwater for the watershed, then divided by the area of the watershed to give Hg export as ng/m<sup>2</sup>/year. MeHg export from each watershed was calculated using the same technique. Linear regression was used to relate DOC, Hg, and MeHg concentrations in streamwater, and correlate DOC and stream flow.

### **Litterfall Sample Collection and Analysis**

Litterfall collectors were 43.8 cm x 33.6 cm x 12.7 cm deep polyethylene bus tubs with 5 mm holes drilled in the bottom for drainage. The collection area was 0.15 m<sup>2</sup>. Collectors were placed at the center of each of 12 soil plots during

the autumn of 2000 to collect litter (Figures 2 and 3). The tubs maintained their position throughout the sampling season.

The litterfall collectors were deployed from 26 September 2000 to 14 November 2000. Samples were collected by pouring the contents of the collector into a clean Teflon™ bag. The bag was rolled closed and sealed in a polyethylene bag. In the laboratory, the bulk litter was dried, ground in a Wiley mill, and weighed. The pulverized sample was double bagged and frozen until analysis.

Sub-samples, ~0.1 g of each litterfall sample, were placed in a Teflon™ digestion vessel with 10.0 mL of Optima HNO<sub>3</sub>, covered, and digested in a fume hood overnight. Then the sample containers were capped and microwave digested in a MARS 5, on a three-stage ramp and hold program. Afterwards 5.0 mL of 5% potassium permanganate and 8.0 mL of 5% potassium persulfate were added to the sample vessels and they sat in the fume hood, overnight. Then 10.0 mL 12% hydroxylamine HCl were added, the samples were diluted to 100.00 mL, filtered through a sialized 0.45 µm glass filter, and analyzed for Hg content on a Hewlett-Packard Flow Injection Mercury System model 400 (FIMS) with a model AS90 auto-sampler.

Litterfall digestion QC consisted of a duplicate sample, a spiked sample, a standard reference material (SRM) of known concentration, and a blank. The SRM for this digestion was NIST #1575, pine needles (*Pinus virginias*) with a Hg concentration of 150 µg/g. FIMS QC for litterfall digestion analysis consisted of a

0.05  $\mu\text{g/g}$  QC sample that was analyzed once for every ten samples, and a calibration blank.

### **Mercury Deposition Network (MDN) Wet-only Precipitation**

The National Atmospheric Deposition Program operates a modified AEROChem precipitation collector for Hg analysis of wet-only precipitation in Acadia National Park. The collector (ME98) is located on McFarland Hill adjacent to the Park Service's air monitoring site (Latitude N 44° 22' 26", Longitude W 68° 15' 38"). Samples are collected weekly and sent to a contract laboratory for analysis following EPA Method 1631 protocols. MDN Hg deposition estimates were used as Hg input data for both watersheds for the period 17 November 1999 to 2 May 2000. The analysis methods, quality control procedures, and Hg deposition data for this collector are available from the NADP website at <http://nadp.sws.uiuc.edu/nadpdata/mdnRequest>.

### **Hg and MeHg Mass balance Calculation**

The simple water budget for a watershed is input – output = change in storage (Serrano, 1997), and a similar scheme was applied to Hg and MeHg deposition and transport. Mercury input is the sum of deposition from four processes: 1) Bulk precipitation in areas of no canopy, 2) throughfall precipitation, 3) frozen precipitation, and 4) dry deposition, which may be included in litter and throughfall. MDN deposition data from 17 November 1999 to 2 May 2000 was used instead of Hg data derived from the snow analysis for

this project because data from snow analysis was inaccurate. MeHg data from throughfall were used to estimate winter deposition of MeHg because no other source of MeHg data was available.

Two deposition estimates were calculated for each watershed, weighted and un-weighted, to determine if Hg and MeHg deposition, weighted by season and vegetation type, was different from the numerical average deposition. Weighted deposition was calculated as the average deposition under specific vegetation type multiplied by the area that vegetation type covered in the watershed and summed for the entire watershed. Un-weighted deposition was calculated as the numerical average of all deposition amounts for a specific collection period. The ten throughfall collections were separated into seasons: spring = 3 May to 31 May 2000 (28 days); summer = 1 June to 17 August 2000 (79 days); fall = 18 August to 16 November 2000 (91 days).

Hg output was export from watershed via streamwater. Volatilization of Hg to the atmosphere was not quantified nor was deep groundwater storage or loss because of the difficulties in field measurement (Grigal *et al.*, 2000). Stemflow measurements were not made because it is difficult to sample non-destructively. The subtraction of output from input yields the amount of Hg or MeHg retained by watershed soils and lost to volatilization and are the mass balances for the watersheds.



## Chapter 3

### RESULTS

#### Inputs

##### Hg in Bulk and Throughfall Precipitation

Of 520 throughfall samples collected from 3 May to 16 November, 2000, 494 were used to construct the Hg throughfall and bulk precipitation input portion of the mass balance. Twenty-six samples were lost for various reasons (Table 2). The ten samples from the open throughfall precipitation collector co-located with the MDN total Hg collector at McFarland Hill were not used to create the input portion of the mass balance because the collector was not inside the Cadillac Brook watershed boundary.

**Table 2. Destroyed and discarded throughfall samples.**

Sample Date	Sample ID	Reason for Exclusion
5/17/00	C6A	Contaminated in lab (10x too much BrCl)
5/17/00	CAREO	Bottle broken in field
6/14/00	C1A	Kinked sample tube, sample backed up in funnel
6/14/00	C2B	Negative concentration from analysis (-0.18 ng/L)
7/5/00	H6C	Bottle broken in field
7/5/00	H6D	Bottle broken in field
7/5/00	C5A	Contaminated, Hg = 99.5 ng/L with high P and NH <sub>3</sub>
7/5/00	C5B	Clogged sample tube, sample backed up in funnel
7/5/00	C6D	Negative concentration from analysis (-0.48 ng/L)
9/19/00	C3C	Bottle broken in field
9/19/00	C4C	Accidentally discarded in lab
10/12/00	H3D	Bottle broken in transit
11/1/00	H6A & H6C	Had same labels, discarded both
5/3 – 6/14/00	HT4F	Not deployed during collections 1 and 2
Entire Season	CPARKB	Totally excluded because it is located outside watershed boundary

The mean volume of throughfall precipitation collected on an individual sample basis during the collection period was 985 mL in Cadillac Brook watershed and 991 mL in Hadlock watershed (Table 3), and the volumes in the two watersheds were not significantly different (ANOVA,  $p=0.94$ ) for each event. Equipment blank Hg concentrations ranged from the detection limit to 1.46 ng/L, averaging 0.35 ng/L, and the value of the blank was always less than 10% of the time-equivalent sample Hg concentration. The average total Hg concentration ( $\pm$  SD) in throughfall precipitation over the duration of this study was 14.2 ng/L ( $\pm$  1.5) in the Cadillac Brook watershed and 18.8 ng/L  $\pm$  (1.4) in the Hadlock Brook watershed. The comparable, average, non-weighted total Hg deposition was 30.8 ng/m<sup>2</sup>/day ( $\pm$  2.7) in Cadillac Brook watershed and 41.1 ng/m<sup>2</sup>/day ( $\pm$  2.6) in Hadlock Brook watershed. Hg deposition via throughfall was significantly different between watersheds (ANOVA,  $p<0.001$ ) with Hadlock Brook watershed receiving more Hg deposition (Table 3).

**Table 3.** Throughfall total Hg concentration, non-weighted deposition, and sample volume for Cadillac and Hadlock Brook watersheds for the period during 3 May to 16 November 2000. Matched letters indicate that means are not significantly different (ANOVA,  $p>0.01$ ).

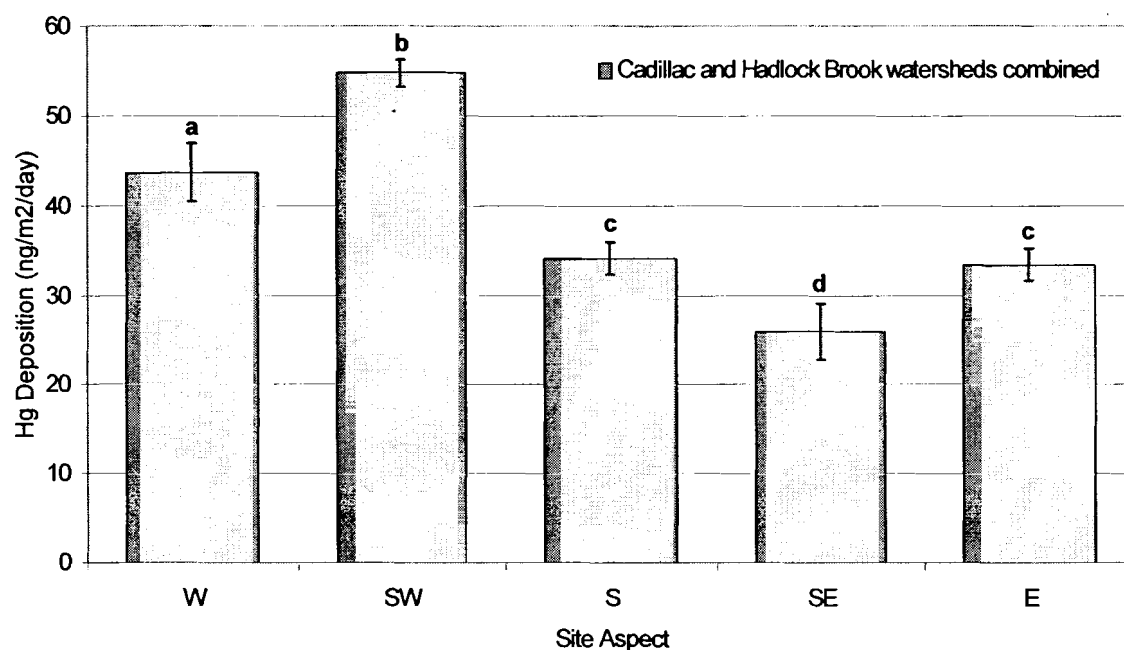
Statistics	Hg Concentration ng/L		Hg Deposition ng/m <sup>2</sup> /day		Sample Volume mL	
	Cadillac	Hadlock	Cadillac	Hadlock	Cadillac	Hadlock
n	241	253	241	253	249	255
Min	2.1	2.2	4.9	1.0	117.0	103.1
Max	68.4	55.9	151.0	116.8	3174.3	3449.6
Median	10.0	15.1	29.2	33.9	870.1	897.6
Mean	14.2 <sup>a</sup>	18.8 <sup>b</sup>	30.8 <sup>c</sup>	41.1 <sup>d</sup>	985.3 <sup>e</sup>	991.3 <sup>e</sup>
Std Dev	11.7	11.3	21.0	20.7	549.2	553.4

Total Hg deposition varied significantly with aspect (Figure 5). Average deposition (mean ng/m<sup>2</sup>/day  $\pm$  SE), in descending order by site aspect, was southwest ( $54.8 \pm 3.1$ ) > west ( $43.7 \pm 1.8$ ) > south ( $34.1 \pm 1.5$ ) = east ( $33.4 \pm 3.2$ ) > southeast ( $25.8 \pm 1.8$ ). Hg deposition on east and south facing sites were not significantly different (ANOVA,  $p = 0.64$ ). Southwest, west, and southeast were significantly different from each other and from south and east facing sites (ANOVA,  $p \leq 0.001$ ). There were no sites, in either watershed that faced northwest, north, or northeast.

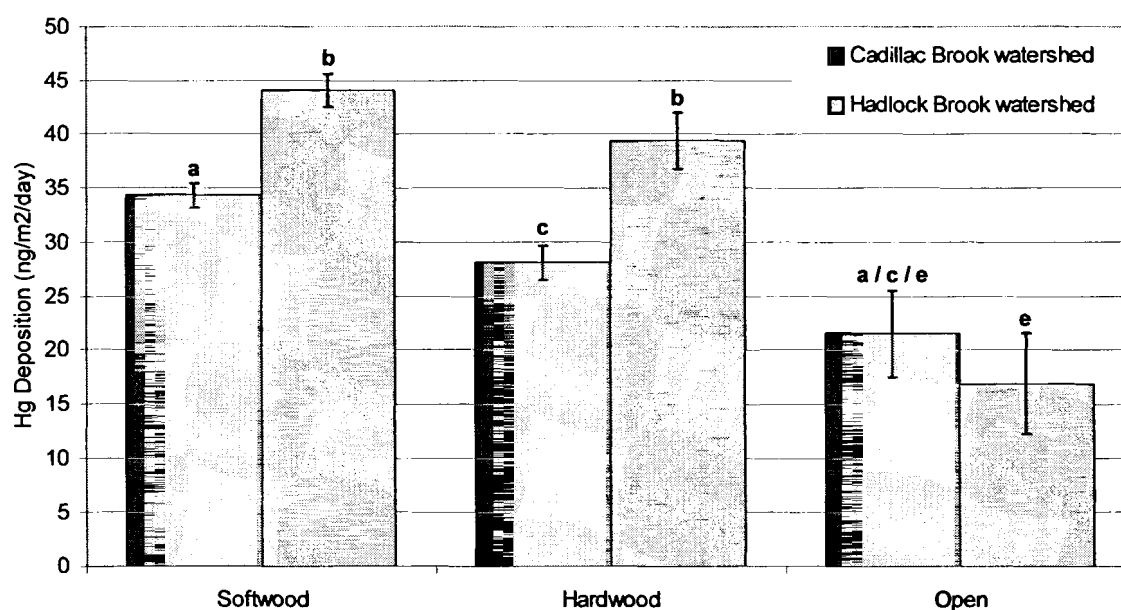
Average Hg deposition ( $\pm$ SE) was highest under softwoods with  $40.2 (\pm 1.2)$  ng/m<sup>2</sup>/day, followed by hardwood with  $31.9 (\pm 1.6)$  ng/m<sup>2</sup>/day, then open sites with  $18.4 (\pm 4.0)$  ng/m<sup>2</sup>/day, when all sites from both watersheds were combined (ANOVA,  $p < 0.001$ ). At Cadillac Brook watershed, Hg deposition under softwood was higher than hardwood sites (ANOVA,  $p = 0.03$ ) but not open sites (ANOVA,  $p = 0.09$ ; Figure 6). Hg deposition did not differ significantly between hardwood and the open site at Cadillac Brook watershed (ANOVA,  $p = 0.33$ ). At Hadlock Brook watershed, Hg deposition was lower in open sites than in softwood or hardwood sites (ANOVA,  $p < 0.001$ ), but Hg deposition in softwood sites did not differ significantly from hardwood sites (ANOVA,  $p = 0.12$ ; Figure 6).

Hg deposition under softwoods at Cadillac Brook watershed was lower than under softwoods at Hadlock Brook watershed (ANOVA,  $p < 0.001$ ) and deposition under hardwoods was also lower at Cadillac Brook watershed than at Hadlock Brook watershed (ANOVA,  $p < 0.001$ ). There was no significant

**Figure 5.** Hg deposition stratified by site aspect for the period during 3 May 2000 to 16 November 2000. Matched letters are not significantly different (ANOVA,  $p > 0.05$ ). Error bars represent standard error.



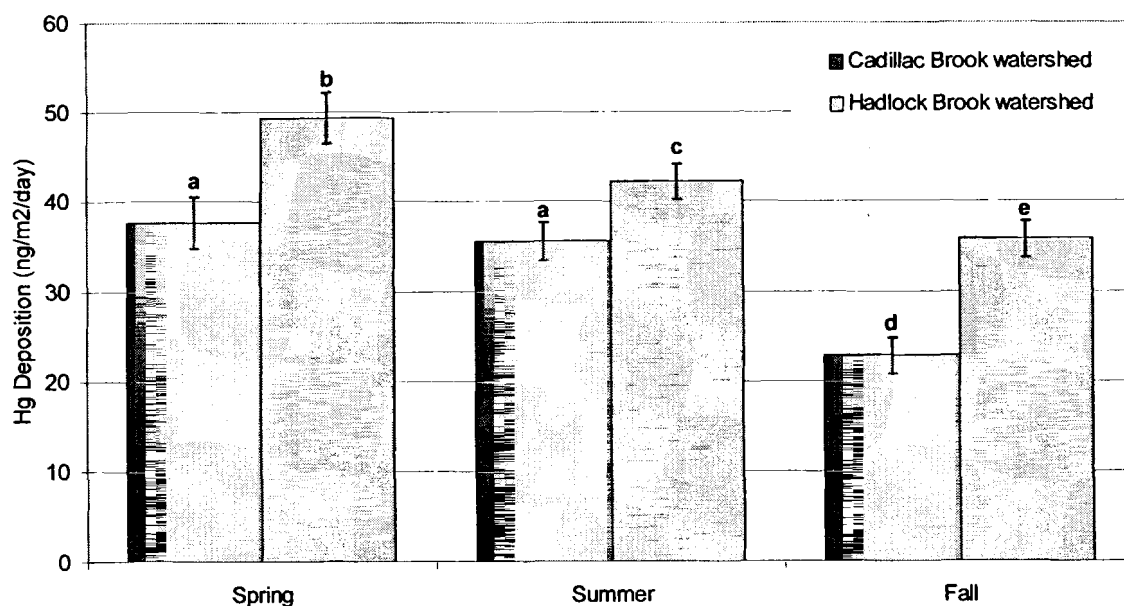
**Figure 6.** Hg deposition stratified by vegetation and watershed for the period during 3 May 2000 to 16 November 2000. Matched letters are not significantly different (ANOVA,  $p > 0.05$ ). Error bars represent standard error.



difference in Hg deposition between watersheds in open sites (ANOVA,  $p=0.48$ ; Table 4).

Hg deposition differed significantly between seasons, both intra - and inter-watershed, for most combinations (Figure 7). Spring Hg deposition at Cadillac Brook watershed was not significantly different from summer deposition (ANOVA,  $p=0.50$ ), but both were higher than fall (ANOVA,  $p<0.0001$ ). Hg deposition at Hadlock Brook watershed was different between all seasons, decreasing from spring to winter (ANOVA,  $p<0.03$ ). Hadlock Brook watershed received more Hg than Cadillac Brook watershed, for each season (ANOVA,  $p<0.02$ ; Figure 7).

**Figure 7.** Hg deposition stratified by season and watershed for the period during 3 May 2000 to 16 November 2000. Matched letters are not significantly different (ANOVA,  $p>0.001$ ). Error bars represent standard error.



**Table 4.** Hg and MeHg average deposition ( $\pm$  standard deviation) stratified by season and vegetation type for Cadillac and Hadlock Brook watersheds for the period during 3 May to 16 November 2000. Matched letters indicate that means are not significantly different (ANOVA,  $p > 0.05$ ).

Separated by		Hg Deposition ng/m <sup>2</sup> /day		MeHg Deposition ng/m <sup>2</sup> /day	
		Cadillac	Hadlock	Cadillac	Hadlock
Season					
	Spring	37.7 (11.6) <sup>a</sup>	49.4 (17.2)	0.28 (0.23) <sup>e</sup>	0.85 (0.68)
	Summer	35.6 (19.5) <sup>a</sup>	42.3 (20.1)	0.11 (0.10) <sup>e</sup>	0.15 (0.10) <sup>e</sup>
	Fall	22.8 (23.3)	35.8 (21.3)	0.16 (0.14) <sup>e</sup>	0.21 (0.19) <sup>e</sup>
Vegetation type					
	Softwood	34.3 (22.2) <sup>b</sup>	44.1 (20.6) <sup>c</sup>	0.14 (0.16) <sup>f</sup>	0.29 (0.39) <sup>g</sup>
	Hardwood	28.1 (19.5)	39.4 (17.1) <sup>c</sup>	0.19 (0.15) <sup>f,g</sup>	0.29 (0.29) <sup>f,g</sup>
	Open	21.5 (17.1) <sup>b,d</sup>	16.9 (15.5) <sup>d</sup>	0.12 (0.15) <sup>f,g</sup>	0.34 (0.63) <sup>f,g</sup>

### MeHg in Open and Throughfall Precipitation

A subset of precipitation samples collected from 3 May to 16 November 2000, were analyzed for MeHg. These data were used to estimate MeHg deposition for the collection period from 17 November, 1999, to 2 May, 2000, by applying the per day deposition amounts to this period.

A total of 131 open ( $n=18$ ) and throughfall ( $n=113$ ) samples were analyzed for MeHg. The average concentration of MeHg in precipitation ( $\pm$  SD) was 0.07 ng/L ( $\pm$  0.06) for Cadillac Brook watershed and 0.10 ng/L ( $\pm$  0.11) for Hadlock Brook watershed. Non-vegetation weighted MeHg deposition for the watershed averaged 0.16 ng/m<sup>2</sup>/day ( $\pm$  0.20) for Cadillac Brook watershed and 0.30 ng/m<sup>2</sup>/day ( $\pm$  0.40) for Hadlock Brook watershed, which also received more MeHg during the collection period (ANOVA,  $p=0.013$ ; Table 5).

MeHg deposition, weighted by vegetation and season, for the collection period of 3 May to 16 November 2000 was  $0.04 \mu\text{g}/\text{m}^2/\text{collection period}$  for Cadillac Brook watershed and  $0.08 \mu\text{g}/\text{m}^2/\text{collection period}$  for Hadlock Brook watershed,

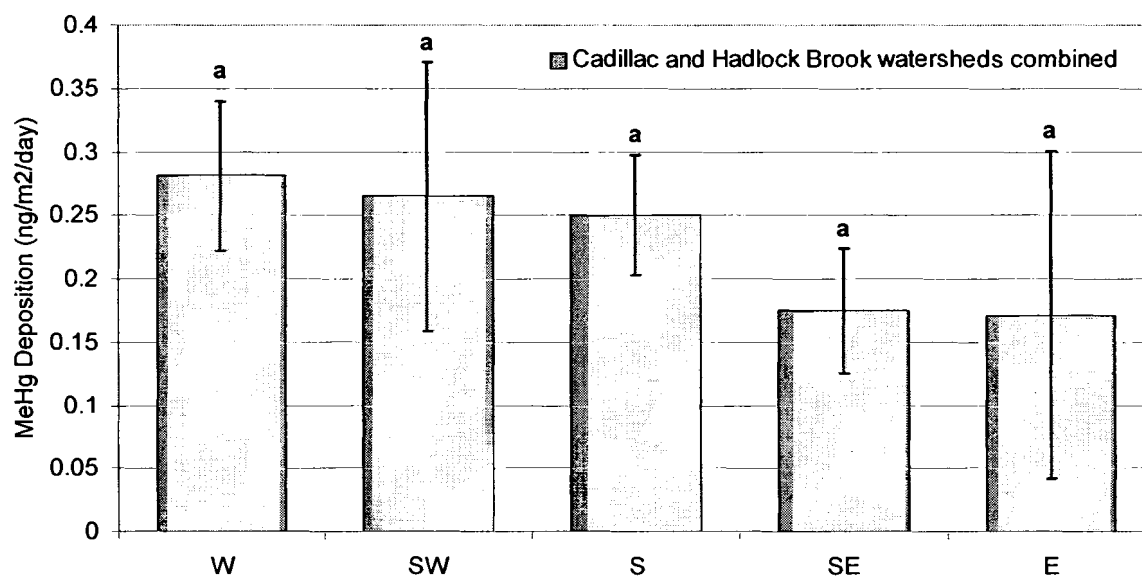
**Table 5.** Throughfall MeHg concentration, non-weighted deposition, and sample volume for Cadillac and Hadlock Brook watersheds 3 May to 16 November 2000. Matched letters indicate that means are not significantly different (ANOVA,  $p>0.05$ ).

Statistics	MeHg Concentration ng/L		MeHg Deposition ng/m <sup>2</sup> /day		Sample Volume mL	
	Cadillac	Hadlock	Cadillac	Hadlock	Cadillac	Hadlock
n	63	68	63	68	63	68
Min	0.025	0.025	0.02	0.03	117	233.4
Max	0.28	0.63	0.70	2.11	2126.1	3449.6
Median	0.05	0.06	0.10	0.18	804.4	909.6
Mean	0.07 <sup>a</sup>	0.10 <sup>b</sup>	0.16 <sup>c</sup>	0.30 <sup>d</sup>	964.7 <sup>e</sup>	1135.9 <sup>f</sup>
Std Dev	0.06	0.11	0.20	0.40	523.1	681.4

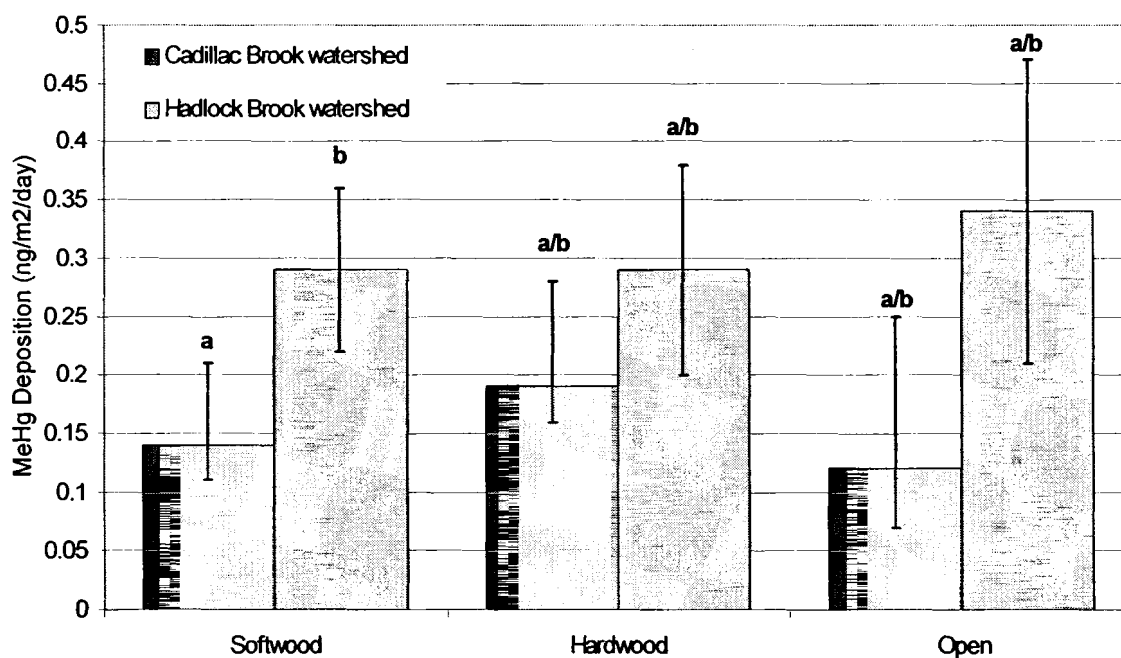
extrapolating to the entire watershed from throughfall data. MeHg deposition for 17 November 1999 to 2 May 2000 was estimated to have been  $0.03 \mu\text{g}/\text{m}^2/\text{collection period}$  for Cadillac Brook watershed and  $0.07 \mu\text{g}/\text{m}^2/\text{collection period}$  for Hadlock Brook watershed, using throughfall data from 3 May to 16 November 2000. The annual weighted MeHg deposition totals, the sum of measured and extrapolated data, for Cadillac Brook watershed was  $9.4 \mu\text{g}/\text{m}^2/\text{yr}$  and  $10.2 \mu\text{g}/\text{m}^2/\text{yr}$  for Hadlock Brook watershed.

Average MeHg deposition was not different among site aspects (ANOVA,  $p=0.65$ ; Figure 8), nor was average MeHg deposition different among vegetation types in Cadillac Brook watershed (ANOVA,  $p=0.43$ ) or in Hadlock Brook watershed (ANOVA,  $p=0.92$ ; Figure 9).

**Figure 8.** MeHg deposition stratified by site aspect for the period during 3 May 2000 to 16 November 2000. Matched letters are not significantly different (ANOVA,  $p > 0.05$ ). Error bars represent standard error.



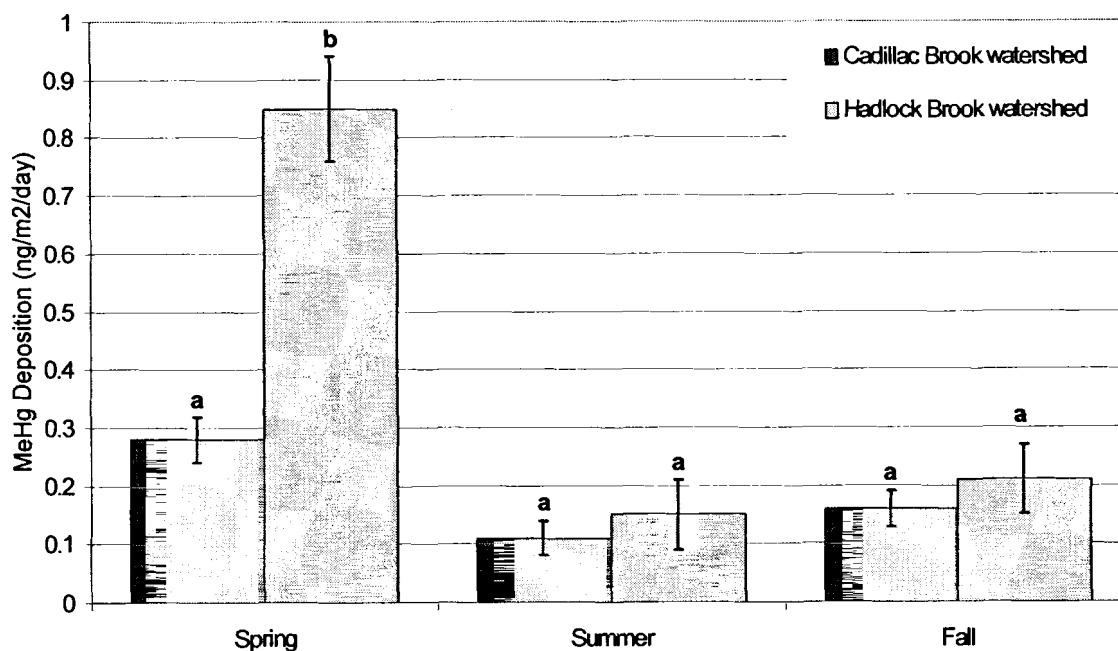
**Figure 9.** MeHg deposition stratified by vegetation and watershed for the period during 3 May 2000 to 16 November 2000. Matched letters are not significantly different (ANOVA,  $p > 0.05$ ). Error bars represent standard error.





Average MeHg deposition in spring was higher than average MeHg deposition in summer or fall for both Cadillac Brook watershed (ANOVA,  $p < 0.05$ ) and Hadlock Brook watershed (ANOVA,  $p < 0.0001$ ). Spring MeHg deposition at Hadlock Brook watershed was higher than MeHg deposition during any other season in either watershed (ANOVA,  $p < 0.0001$ ). Otherwise, MeHg deposition was not different between seasons or watersheds (Figure 10).

**Figure 10.** MeHg deposition stratified by season and watershed for the period during 3 May 2000 to 16 November 2000. Matched letters are not significantly different (ANOVA,  $p > 0.05$ ). Error bars represent standard error.



### **Hg in Litter**

Ten litter samples were collected after the period of 26 September 2000 to 14 November 2000. Litter sample dry weight averaged ( $\pm$  SD) 29.7 g ( $\pm$ 7.7), per collector, at Cadillac Brook watershed (n=4) and 11.8 g ( $\pm$  3.6) at Hadlock Brook watershed (n=6). The average ( $\pm$  SD) Hg concentration in litter samples was 39.7  $\mu$ g/kg ( $\pm$ 3.1) for Cadillac Brook watershed and 51.3  $\mu$ g/kg ( $\pm$ 6.3) for Hadlock Brook watershed.

Total Hg deposition associated with litterfall ranged from 101.6 to 185.2 ng/m<sup>2</sup>/day for collectors in the Cadillac Brook watershed and 49.6 to 113.0 ng/m<sup>2</sup>/day for collectors in the Hadlock Brook watershed. Cadillac Brook watershed Hg deposition, as litterfall, averaged ( $\pm$  SD) 155.9 ng/m<sup>2</sup>/day ( $\pm$  37.2) and Hadlock Brook watershed averaged 79.2 ng/m<sup>2</sup>/day ( $\pm$  22.0). Cadillac Brook watershed received more Hg from litterfall than Hadlock Brook watershed, for the collection period (ANOVA, p=0.001).

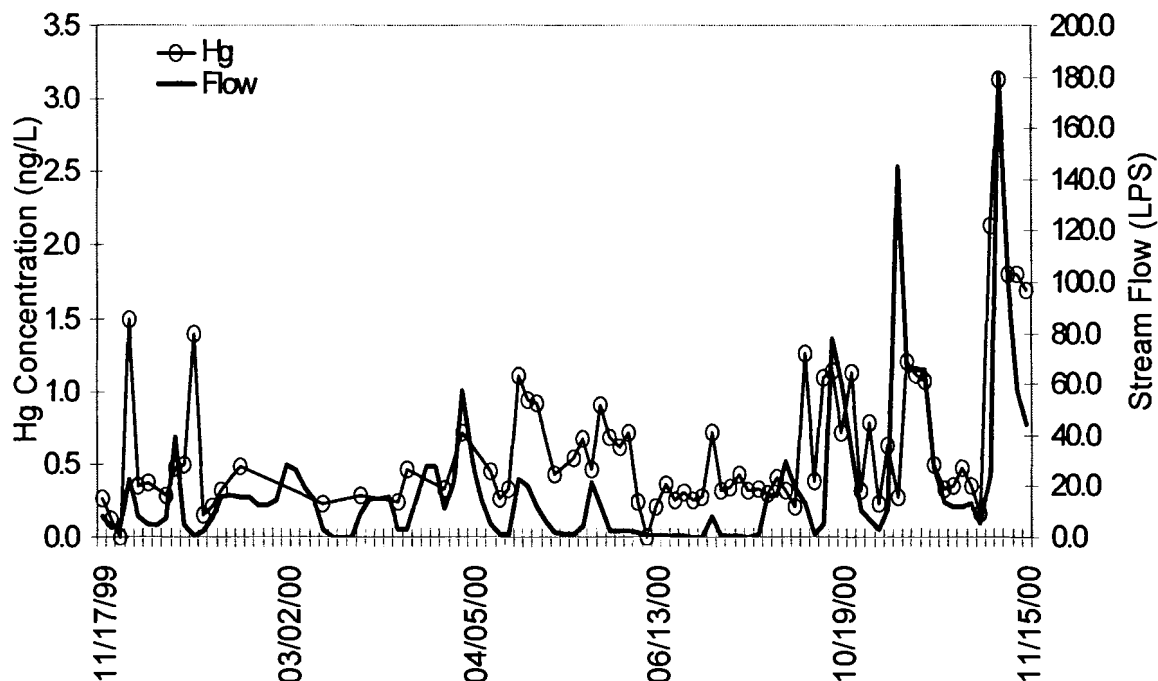
## **Export**

### **Stream Export of Hg**

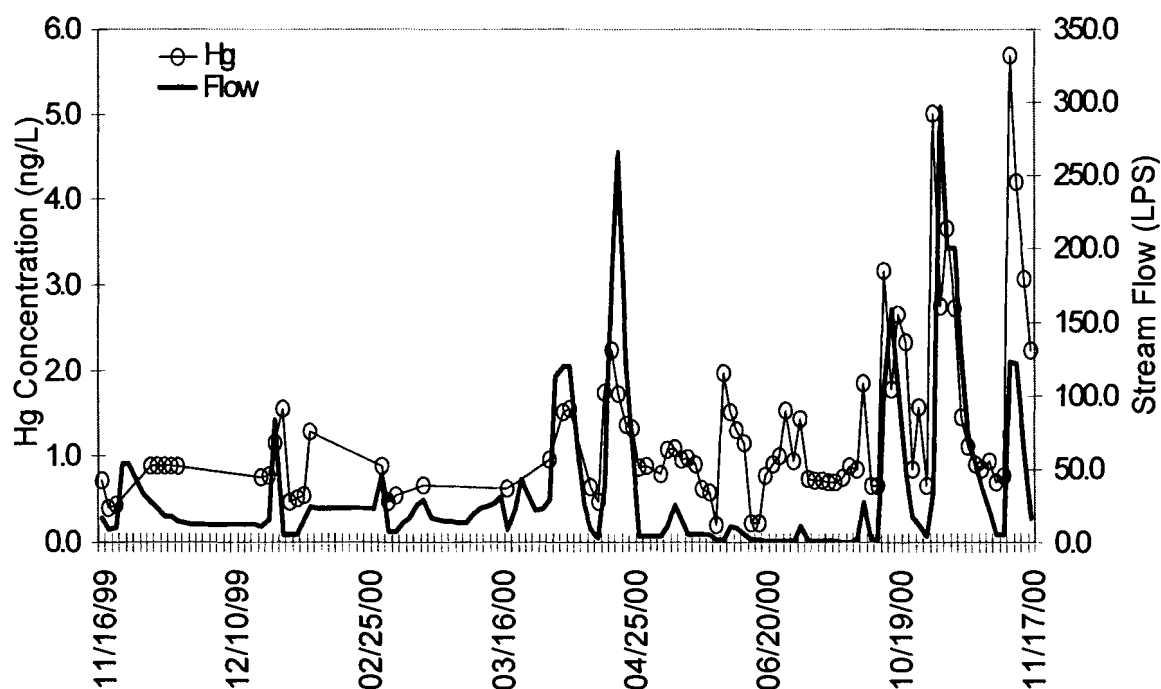
Both Cadillac and Hadlock Brooks were gauged by the USGS and sampled during the period from 17 November 1999 to 16 November 2000. The average flow, discharge, and water yield are shown in Table 6.

Stream Hg concentration generally increased when discharge increased in both streams (Figures 11 and 12). Visual inspection of Figures 11 and 12

**Figure 11.** Hg concentration vs. stream flow in Cadillac Brook during the period 17 November 1999 to 16 November 2000.



**Figure 12.** Hg concentration vs. stream flow in Hadlock Brook during the period 17 November 1999 to 16 November 2000.



**Table 6.** Stream flow, discharge, and water yield for both streams for the period during 17 November 1999 to 16 November 2000. Standard deviation in parenthesis.

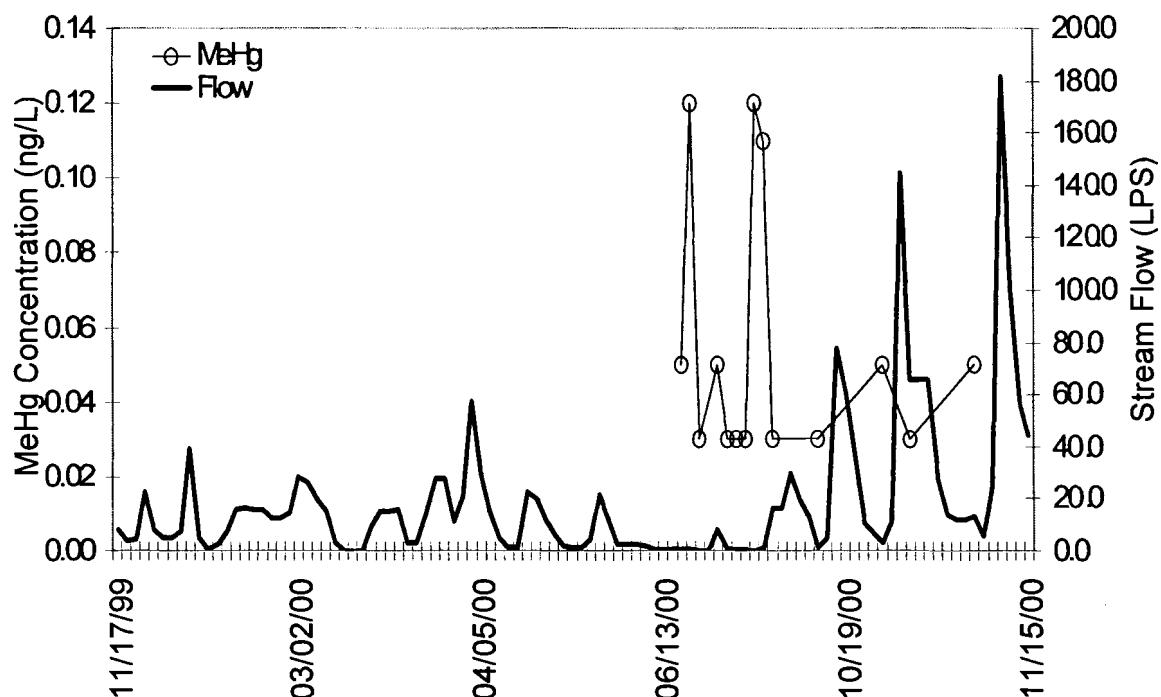
	Mean Flow (LPS)	Discharge (L/yr)	Water Yield (L/m <sup>2</sup> /yr)
<b>Cadillac</b>	7.7 (21.2)	$2.4 \times 10^8$	760
<b>Hadlock</b>	16.3 (42.5)	$5.1 \times 10^8$	1080

indicates that discharge events (flow > ~28.3 LPS) had been adequately represented, with only two discharge events not sampled, one on 4 March 2000 and one on 20 March 2000. Similar comparisons were done for MeHg concentrations in streamwater and flow (Figures 13 and 14).

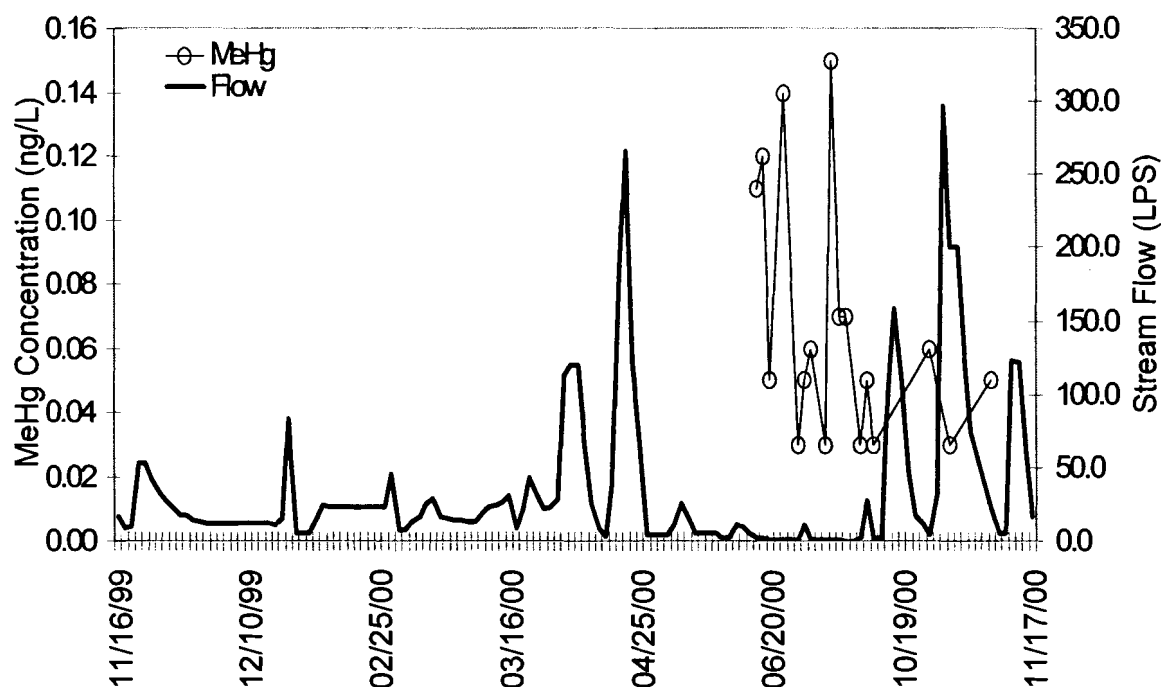
Two hundred and forty-four stream samples were collected and analyzed for total Hg during the period from 17 November 1999 to 16 November 2000, 105 from Cadillac Brook, and 139 from Hadlock Brook. The mean ( $\pm$  SD) Hg concentration of streamwater in Cadillac Brook was 0.6 ng/L ( $\pm$  0.5), and 1.5 ng/L ( $\pm$  1.1) for Hadlock Brook. Hg concentration in streamwater was markedly higher during periods of high stream flow, reaching a maximum of 5.7 ng/L (Table 7).

Kahl's (1999) program's interpolated values, in addition to measured data, were used to estimate average Hg concentrations, to compensate for the disproportionate number of samples taken during periods of high flow, for comparison with averages using measured data only. This method was used because the program assigns a specific Hg concentration to each flow value, effectively volume weighting each Hg value, interpolated or measured, equally. Using this method, the average volume weighted ( $\pm$  SD) Hg concentration in

**Figure 13.** MeHg concentration vs. stream flow in Cadillac Brook during the period 17 November 1999 to 16 November 2000. Samples taken during 20 June to 16 November 2000 analyzed for MeHg.



**Figure 14.** MeHg concentration vs. stream flow in Hadlock Brook during the period 17 November 1999 to 16 November 2000. Samples taken during 20 June to 16 November 2000 analyzed for MeHg.



**Table 7.** Hg (measured and interpolated) and DOC concentrations in Cadillac Brook for the period during 17 November 1999 to 16 November 2000. Matched letters indicate that means are not significantly different (ANOVA,  $p > 0.05$ )

Statistics	Hg Concentration (measured only) ng/L		Hg Concentration (measured and interp.) ng/L		DOC Concentration (measured) mg/L	
	Cadillac	Hadlock	Cadillac	Hadlock	Cadillac	Hadlock
n	105	139	8784	8784	96	130
Min	0.0	0.2	0	0.2	0.6	1.3
Max	3.1	5.7	3.1	5.7	3.8	6.7
Median	0.4	1.1	0.3	0.9	1.6	2.4
Mean	0.6 <sup>a</sup>	1.5 <sup>b</sup>	0.4 <sup>a</sup>	1.0 <sup>c</sup>	1.6 <sup>d</sup>	2.7 <sup>e</sup>
Std Dev	0.5	1.1	0.2	0.5	0.7	1.2

**Table 8.** Hg and MeHg mass balances using weighted precipitation data, MDN data, and both measured and interpolated stream chemistry data. All data are in  $\mu\text{g}/\text{m}^2/\text{year}$ .

	Input	Export	Change	% Retention
<b>Hg</b>				
Cadillac	9.4	0.4	8.9	95.4
Hadlock	10.2	1.3	8.9	87.0
<b>MeHg</b>				
Cadillac	0.05	0.04	0.01	25.8
Hadlock	0.10	0.06	0.04	39.6

Cadillac Brook was 0.4 ng/L ( $\pm 0.2$ ) and 1.0 ng/L ( $\pm 0.5$ ) in Hadlock Brook.

The interpolated plus measured Hg concentrations were also used to estimate Cadillac Brook export as 0.4  $\mu\text{g}/\text{m}^2/\text{yr}$  of Hg and Hadlock Brook export as 1.3  $\mu\text{g}/\text{m}^2/\text{yr}$  of Hg for the period during 17 November 1999 to 16 November 2000 (Table 8).

### Stream Export of MeHg

Thirty-one stream samples were collected and analyzed for MeHg from 20 June 2000 to 16 November 2000, 14 samples from Cadillac Brook, and 17 samples from Hadlock Brook. The un-weighted numerical mean ( $\pm$  SD) MeHg concentration for Cadillac Brook was 0.05 ng/L ( $\pm$  0.04) and 0.07 ng/L ( $\pm$  0.04) for Hadlock Brook. Stream MeHg concentrations were calculated in the same manner as Hg concentrations, using 'volume-weighted' values and measured data. The volume-weighted average ( $\pm$  SD) MeHg concentration in Cadillac Brook was 0.06 ng/L ( $\pm$  0.02) and 0.08 ng/L ( $\pm$  0.03) for Hadlock Brook, using the interpolated values (Table 9). MeHg concentrations less than the detection limit of 0.05 ng/L were recorded as 0.025 ng/L.

**Table 9.** MeHg (measured and interpolated) concentrations for Cadillac Brook for the period during 20 June to 16 November 2000. Matched letters indicate that means are not significantly different (ANOVA,  $p > 0.05$ ).

Statistics	MeHg Concentration (measured only) ng/L		MeHg Concentration (measured and interp.) ng/L	
	Cadillac	Hadlock	Cadillac	Hadlock
n	14	17	8784	8784
Min	0.0	0.0	0.0	0.0
Max	0.12	0.15	0.12	0.15
Median	0.04	0.05	0.05	0.08
Mean	0.05 <sup>a</sup>	0.07 <sup>a</sup>	0.06 <sup>a</sup>	0.08 <sup>a</sup>
Std Dev	0.04	0.04	0.02	0.03

MeHg export was calculated in the same manner as Hg export. MeHg export was  $0.04 \mu\text{g}/\text{m}^2/\text{year}$  of MeHg from Cadillac Brook watershed and  $0.06 \mu\text{g}/\text{m}^2/\text{year}$  of MeHg from Hadlock Brook watershed (Table 8). The MeHg export estimates were based on data from 20 June 2000 to 16 November 2000; the remainder of the year (17 November 1999 to 19 June 2000) was extrapolated for comparison with Hg export.

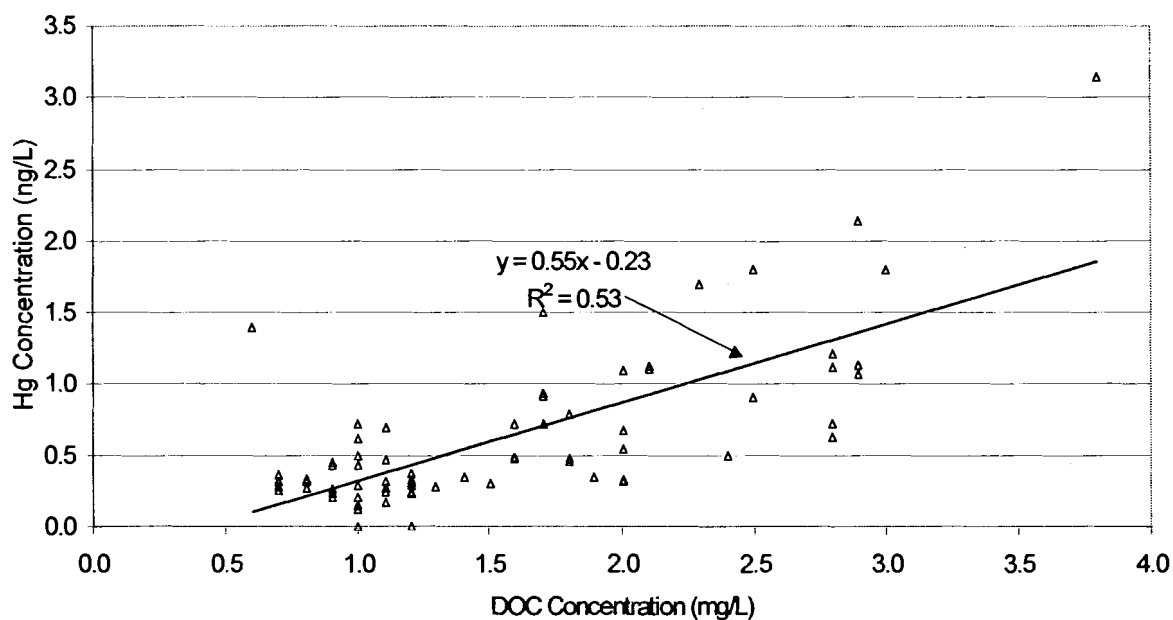
### **DOC vs. Hg and MeHg in Streamwater**

Two hundred and twenty-six streamwater samples were analyzed for DOC, 96 from Cadillac Brook and 130 from Hadlock Brook. The mean ( $\pm$  SD) DOC concentration was  $1.6 \text{ mg}/\text{L}$  ( $\pm 0.4$ ) in Cadillac Brook and  $2.7 \text{ mg}/\text{L}$  ( $\pm 1.2$ ) for Hadlock for the period during 17 November 1999 to 16 November 2000 (Table 7).

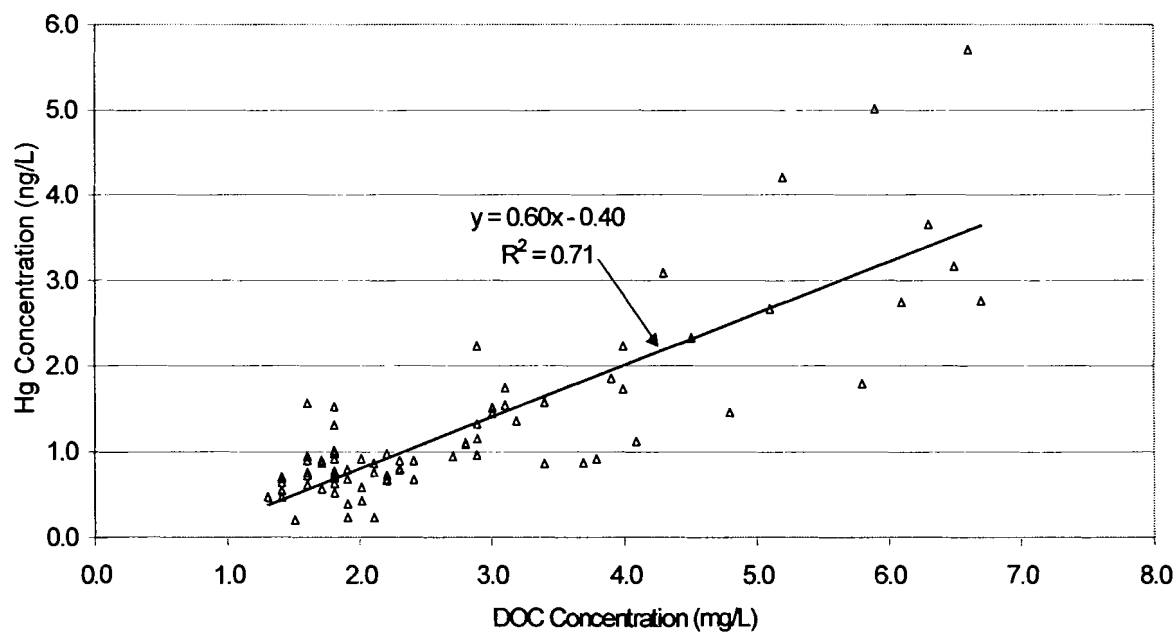
DOC and Hg were positively linearly correlated in streamwater samples in Cadillac Brook ( $R^2 = 0.53$ ,  $p < 0.05$ ), and in Hadlock Brook ( $R^2 = 0.71$ ,  $p < 0.01$ ; Figures 15 and 16). There is no correlation between MeHg and DOC concentrations in either Cadillac ( $R^2 = 0.03$ ,  $p = 0.57$ ) or Hadlock Brooks ( $R^2 = 0.12$ ,  $p = 0.18$ ; Figures 17 and 18).



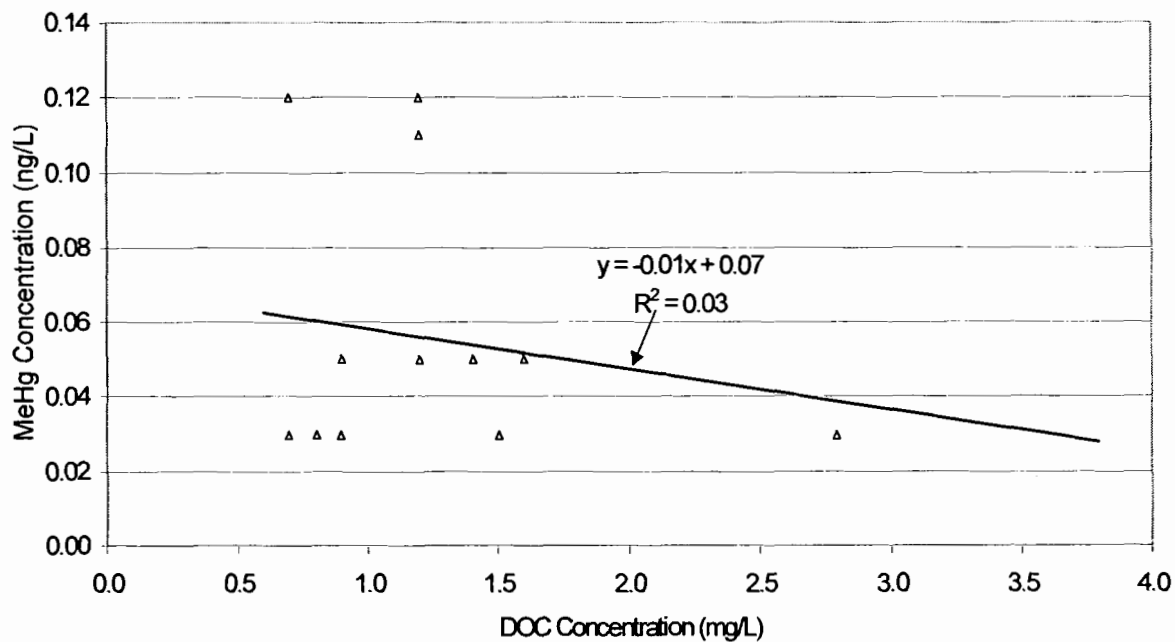
**Figure 15.** Hg vs. DOC concentration in Cadillac Brook for the period during 17 November 1999 to 16 November 2000 (Linear regression  $p < 0.05$ ).



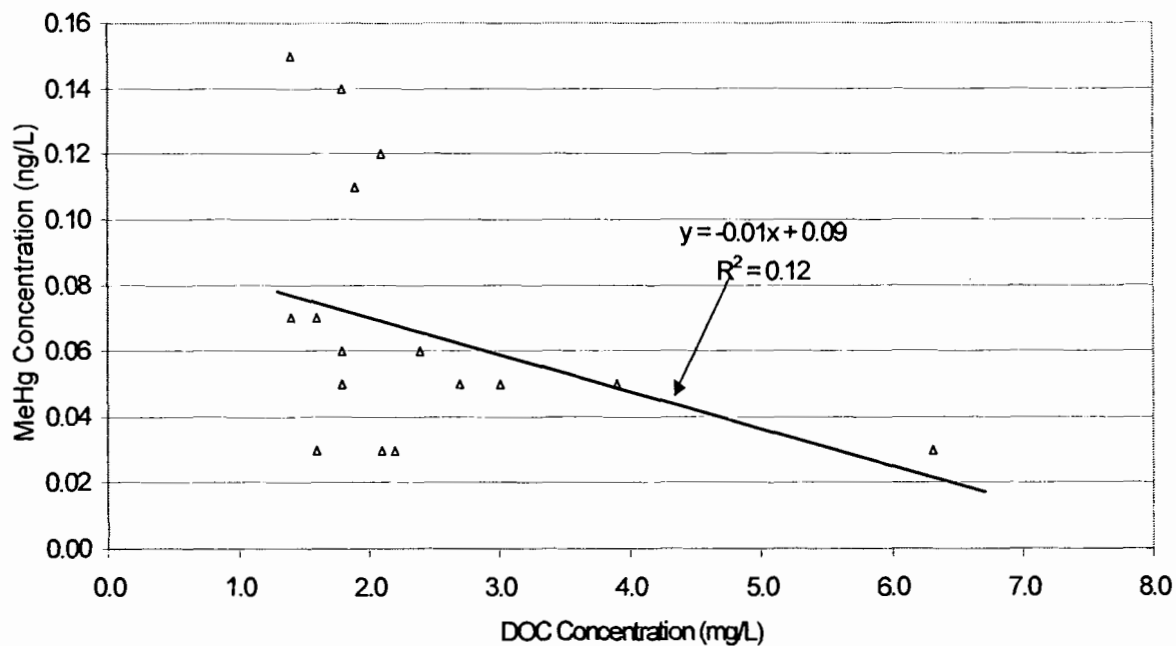
**Figure 16.** Hg vs. DOC concentration in Hadlock Brook for the period during 17 November 1999 to 16 November 2000 (Linear regression  $p < 0.01$ ).



**Figure 17.** MeHg vs. DOC concentration in Cadillac Brook for the period during 20 June to 16 November 2000 (Linear regression  $p=0.57$ ).



**Figure 18.** MeHg vs. DOC concentration in Hadlock Brook for the period during 20 June to 16 November 2000 (Linear regression  $p=0.12$ ).



### Hg and MeHg Mass balance Determination

Hg deposition calculated from MDN deposition amounts, during the period 17 November 1999 to 2 May 2000 were added to throughfall deposition, during the period 3 May to 16 November 2000, to estimate yearly Hg mass balances. MDN deposition was  $4.1 \mu\text{g}/\text{m}^2/\text{yr}$ , while two deposition estimates were calculated for each watershed, weighted and un-weighted, each of which were separately added to the MDN data for two estimates of yearly deposition per watershed (Table 10).

**Table 10.** Throughfall Hg and MeHg deposition, non-weighted and weighted by vegetation and season. Totals include MDN data (Hg) or extrapolated throughfall data (MeHg). Matched letters indicate that means are not significantly different (ANOVA,  $p > 0.05$ )

	Hg Deposition ( $\mu\text{g}/\text{m}^2/\text{yr}$ )		MeHg Deposition ( $\mu\text{g}/\text{m}^2/\text{yr}$ )	
	Cadillac	Hadlock	Cadillac	Hadlock
Non-weighted	10.5	12.3	0.07 <sup>a</sup>	0.15
Weighted	9.4	10.2	0.05 <sup>a</sup>	0.10

The two yearly Hg deposition estimates for Cadillac Brook watershed were  $9.4 \mu\text{g}/\text{m}^2/\text{yr}$  (weighted by season and vegetation) and  $10.5 \mu\text{g}/\text{m}^2/\text{yr}$  (un-weighted) for the period during 17 November 1999 to 16 November 2000. The two yearly deposition estimates for Hadlock Brook watershed for the same time period were  $10.2 \mu\text{g}/\text{m}^2/\text{yr}$  (weighted by season and vegetation) and  $12.3 \mu\text{g}/\text{m}^2/\text{yr}$  (un-weighted).

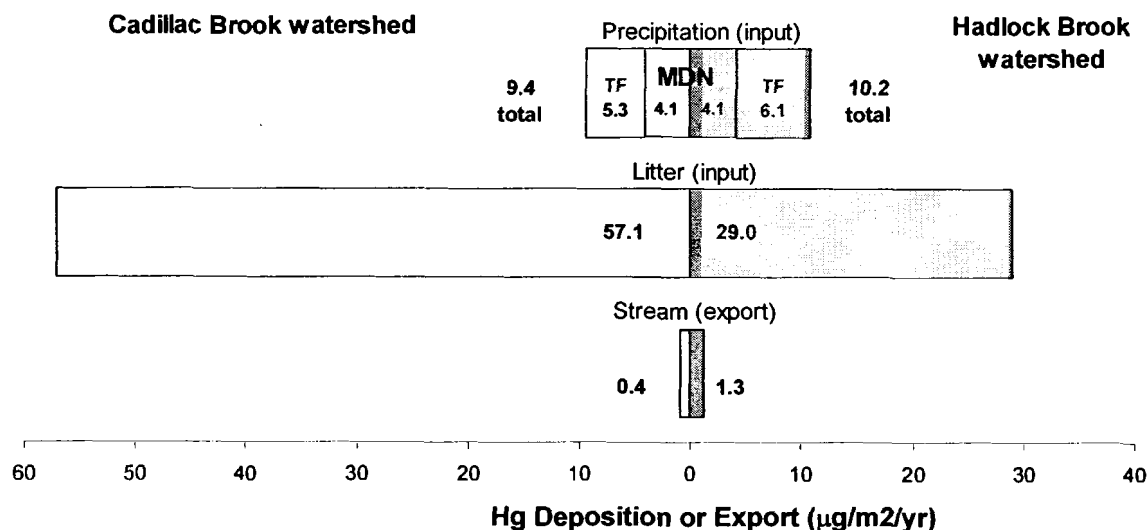
MeHg deposition was also stratified by vegetation and season for inter-comparison with Hg deposition data (Table 10). The two yearly MeHg deposition

estimates for Cadillac Brook watershed were  $0.05 \mu\text{g}/\text{m}^2/\text{yr}$  (weighted by season and vegetation) and  $0.07 \mu\text{g}/\text{m}^2/\text{yr}$  (un-weighted) for the period during 17 November 1999 to 16 November 2000. The two yearly MeHg deposition estimates for Hadlock Brook watershed for the same time period were  $0.10 \mu\text{g}/\text{m}^2/\text{yr}$  (weighted by season and vegetation) and  $0.15 \mu\text{g}/\text{m}^2/\text{yr}$  (un-weighted).

Hg export from Cadillac Brook watershed, via streamwater, was  $0.43 \mu\text{g}/\text{m}^2/\text{year}$ , from Hadlock it was  $1.33 \mu\text{g}/\text{m}^2/\text{year}$ . Hg concentration in streamwater was measured from 17 November 1999 to 16 November 2000. MeHg export was  $0.04 \mu\text{g}/\text{m}^2/\text{year}$  for Cadillac Brook and  $0.06 \mu\text{g}/\text{m}^2/\text{year}$  for Hadlock Brook (Table 8). MeHg concentration in streamwater was measured for the period during 13 June to 16 November 2000. MeHg streamwater data for the period during 7 November 1999 to 19 June 2000 were extrapolated from measured data.

The Hg mass balance for Cadillac Brook watershed was  $9.4 \mu\text{g}/\text{m}^2/\text{year}$  (in) –  $0.4 \mu\text{g}/\text{m}^2/\text{year}$  (out) =  $8.9 \mu\text{g}/\text{m}^2/\text{year}$ , or 95.4% of the total Hg deposited on Cadillac Brook was retained by the watershed, ignoring volatilization losses. The Hg mass balance for Hadlock Brook watershed was  $10.2 \mu\text{g}/\text{m}^2/\text{year}$  (in) –  $1.3 \mu\text{g}/\text{m}^2/\text{year}$  (out) =  $8.9 \mu\text{g}/\text{m}^2/\text{year}$ , or 87.0% of the total Hg deposited on Hadlock Brook was retained by the watershed (Table 8). Litter contributed  $57.1 \mu\text{g}/\text{m}^2/\text{yr}$  of Hg to the forest floor in Cadillac Brook watershed and  $29.0 \mu\text{g}/\text{m}^2/\text{yr}$  of Hg in Hadlock Brook watershed. This deposition vector is not included in the mass balance calculations because the partitioning and residence time of that Hg is

**Figure 19.** Hg inputs and export, separated by vector. Volatilization and stemflow were not measured.



unknown, but it is the largest contributor of Hg to the forest floor in this study and is included in Figure 19.

The MeHg mass balance for Cadillac Brook watershed was  $0.05 \mu\text{g}/\text{m}^2/\text{year}$  (in) –  $0.04 \mu\text{g}/\text{m}^2/\text{year}$  (out) =  $0.01 \mu\text{g}/\text{m}^2/\text{year}$ , or 25.8% of the MeHg deposited on Cadillac Brook was not released by the watershed. The MeHg mass balance for Hadlock Brook watershed was  $0.10 \mu\text{g}/\text{m}^2/\text{year}$  (in) –  $0.06 \mu\text{g}/\text{m}^2/\text{year}$  (out) =  $0.04 \mu\text{g}/\text{m}^2/\text{year}$ , 39.6% of the amount of MeHg deposited on Hadlock watershed was not released by the watershed (Table 8).

## **Chapter 4**

### **DISCUSSION**

#### **Inputs**

##### **Hg in Precipitation**

The data show differences in Hg deposition based on site aspect that are similar to results in Sweden (Iverfeldt, 1991). Iverfeldt noted higher Hg deposition in sites with a southwest aspect due to the increased interception of polluted air, implying that there are more Hg sources in that direction. Southwest facing sites in my watersheds also receive the highest Hg deposition, implying that air masses from the southwest contain more Hg than air masses originating in other areas. Hg sources may lie to the northwest of my watersheds, but no sample sites face that direction. Site aspect analysis encompasses multiple Hg collections, presumably minimizing the affect of varying local wind direction and representing larger transport trends.

Mean Hg concentrations in open precipitation for the period during 3 May to 16 November were similar to those found in a Vermont study (7.4 ng/L, 17 August to 23 September 1994; Rea and Keeler, 1996), but lower than found in Sweden (30.8 ng/L, November 1987 to September 1988; Iverfeldt, 1991). This difference may be attributed to source proximity instead of small-scale deposition variability, because Hg concentrations and volumes in open precipitation were not different between the PRIMENet watersheds, indicating that Hg deposition in these open sites was fairly uniform on a small scale.

Average Hg concentrations in throughfall were similar to those found in a mixed hardwood forest in Vermont (12 ng/L; Rea and Keeler, 1996) and a mature, coniferous forest in Sweden (48 ng/L; Iverfeldt, 1991). The pattern was similar in my study: Hg concentrations in throughfall at Cadillac Brook watershed, covered with mixed hardwood, were lower than Hadlock Brook watershed, which is primarily coniferous. Other studies have attributed this difference in Hg concentration to vegetation type, estimating conifer Hg scavenging efficiency to be two to five times that of deciduous trees (Kolka, 1996; Grigal *et al.*, 2000). The difference between Hg concentrations in open versus forested sites may be attributed to dry-deposition of Hg on vegetation (Iverfeldt, 1991; Rea and Keeler, 1996; Grigal *et al.*, 2000). Coniferous vegetation seems to collect more dry deposition than other vegetation types, resulting in higher Hg concentrations in throughfall precipitation in both watersheds (Rea and Keeler, 1996; Grigal *et al.*, 2000).

Higher Hg concentration in throughfall precipitation at Hadlock Brook watershed resulted in higher Hg deposition, because average throughfall sample volumes between watersheds were not significantly different. Higher Hg deposition in Hadlock Brook watershed may indicate that softwood vegetation was a more efficient scavenger of Hg from the atmosphere. The 1947 fire that burned the majority of Cadillac Brook watershed, resulting in regeneration of a patchy hardwood-dominated forest, may have contributed to lower Hg deposition in the watershed.

Seasonal Hg deposition differences may have been a result of changing Hg concentration in air masses. As Hg deposition in open sites decreased from spring to fall, deposition amounts in the forested areas also decreased. This trend suggests that as the available Hg in the atmosphere decreased, less Hg was scavenged by vegetation.

### **MeHg in Precipitation**

MeHg concentrations in throughfall and open precipitation were not different in my watersheds, and the same result was obtained in the Gårdsjön roof project in Sweden (Munthe *et al.*, 1998). In contrast, at the Svartberget watershed in Sweden, MeHg concentrations in throughfall precipitation were twice as high as in open field samples, suggesting either dry deposition of MeHg to the canopy (Lee *et al.*, 2000), methylation of Hg in the canopy, or emission of MeHg from soils (Hultberg *et al.*, 1994) at this watershed. The varied ratios of MeHg deposition via open and throughfall precipitation might be explained by the difference in length of the studies (Svartberget = 4 years, Gårdsjön = 2 years, present study = 1 year). The Svartberget study may have lasted long enough for the slightly higher MeHg deposition rate under the canopy to produce a significant long-term difference between MeHg deposition in open and forested areas.

The data suggest that neither site aspect nor vegetation type influenced annual MeHg deposition in either watershed. Hultberg *et al.* (1994) reported higher MeHg deposition in spring than in other seasons at Gårdsjön watershed, and attributed this increase to an increase in MeHg concentration in the air and in



precipitation. Higher MeHg deposition values were also recorded during the spring in Hadlock Brook watershed, but not in Cadillac Brook watershed, perhaps due to MeHg emission from the Hadlock soils, a potential source also suggested by Hultberg (Hultberg *et al*, 1994). Hadlock has 77% soil coverage, while Cadillac watershed is only 40% covered (Ruck, 2002), presumably due partially to disturbance history and surficial geology. The difference in soil coverage might explain the difference in MeHg deposition during the spring, which was the wettest period during the study, and therefore had the greatest potential for MeHg production in organic soils (Bishop *et al.*, 1995). Wet organic soils may be facilitating the production of MeHg, which could be degassed from these soils and collected in the throughfall collectors.

### **Hg in Litter**

The contribution of Hg via litter to the forest floor was significant; contributing 2 to 5 times more Hg to each watershed than throughfall precipitation. Many other studies have found the contribution of Hg by litter and throughfall to be approximately equal (Lee *et al*, 2000, Grigal *et al.*, 2000, Rea *et al.*, 1996, Iverfeldt, 1991). Variability in the ratios of Hg input by litter versus throughfall may be the result of differences between collection methods. The bulk of the litterfall from my watersheds was collected in autumn. This method would bias the Hg deposition estimates too high because of the increased volume of litter during that season and/or fall litter may have accumulated more Hg than spring litter. Hardwood leaf surfaces are presumably relatively Hg free when they form in the spring and collect dryly deposited Hg throughout the

growing season. Therefore, sampling litter in the fall would collect greater than average volumes of litter that may have higher than average concentrations of Hg. Rea *et al.* (1996) also sampled litterfall only during the fall, but the mean Hg throughfall deposition they report was more than twice that at Acadia, resulting in nearly equal contributions of Hg to the forest floor. In contrast, litterfall was sampled year-round in the Swedish study resulting in a lower estimate of Hg deposition (Lee *et al.*, 2000). Lower Hg deposition via softwood litter, in spite of higher bulk deposition, may also be a result of a seasonal litterfall collection period. If litter was collected for the entire year then the Hg associated with hardwood leaf-off in the fall would be distributed throughout the season resulting in lower Hg deposition per unit time.

Hg input via litterfall is important in determining total Hg loads to watershed systems, but the residence time and fate of Hg from that input vector is not known. Long-term litter sampling should give a more accurate portrayal of Hg dry deposition because it would incorporate year-round litter from conifers. Year-round litter sampling would also give a better estimate of the terrestrial Hg pool that exists in the forest floor. Mass transport of Hg on litter, from the canopy to the forest floor, may be the most important deposition mechanism for Hg in these systems.

## Export

### Stream Export of Hg

The annual export of total Hg from Hadlock Brook watershed in this study was in the same range as reported for other similar studies. For example, Lee *et al.* (1998) reported a value of  $1.3 \mu\text{g}/\text{m}^2/\text{yr}$  for a coniferous watershed, and Grigal *et al.* found  $2.2 \mu\text{g}/\text{m}^2/\text{yr}$  for a watershed dominated by mature aspen (*Populus tremuloides* Michx.) in Minnesota. However, the annual export of Hg from Cadillac Brook watershed was much lower, being only about 1/3 of that for the other watersheds. Inasmuch as Hg input (from throughfall and litterfall) was in the same range as that for Hadlock Brook watershed, the reduced output of Hg from Cadillac Brook watershed was probably a result of increased Hg retention in the watershed. The increased Hg retention in soils at Cadillac Brook watershed may be a result of the effects that the 1947 fire had on soil characteristics; the decrease in Hg content in upper soil layers due to volatilization and the increased erosion after the fire, which potentially removed organic material, instrumental in Hg sequestering.

The high Hg concentration in streamwater during high discharge episodes may have been caused by DOC mobilization due to increased sub-surface and overland flow. DOC and Hg concentrations in streamwater correlated well, suggesting that Hg and DOC are complexed (Kolka, 1996; Lee *et al.*, 2000). This association and transport mechanism could help explain the lower Hg export by Cadillac Brook, because it was hypothesized that a large portion of the organic matter was destroyed by the 1947 fire in Cadillac Brook watershed and

more was removed by subsequent erosion. DOC concentrations in Cadillac Brook were lower than in Hadlock Brook, resulting in less DOC available in the watershed to facilitate Hg transport, which may be the main transport mechanism of Hg in water (Pettersson *et al.*, 1995; Kolka, 1996; Vaithiyanathan *et al.*, 1996; Lee *et al.*, 1998; Lee *et al.*, 2000).

### **Stream Export of MeHg**

Average MeHg concentrations in my streams were less than reported by Lee (~0.2 ng/L; Lee *et al.*, 2000), but output fluxes fell within the wide range of other watersheds, from 0.03 to 3.4  $\mu\text{g}/\text{m}^2/\text{yr}$  (Hultberg *et al.*, 1994; Lee *et al.*, 1998; Lee *et al.*, 2000). The highest export of MeHg from my watersheds occurred during the periods of lowest flow and in November, which agrees with observations by Lee (2000). These higher levels of MeHg may be the result of accumulation of MeHg in soils and leaching to the stream (Bishop *et al.*, 1995). This hypothesis applies well to Hadlock Brook, which had flow, albeit low, year round, keeping riparian soils continuously moist. In contrast, Cadillac Brook dried completely in the summer but had the same pattern of MeHg production during the rest of the year.

MeHg and DOC concentrations in streamwater do not correlate well. Therefore, other mechanisms must have been influencing MeHg concentrations in streamwater. Bishop and Lee (1997) indicate that the riparian zone along streams may play an important role in the production of MeHg in forested catchments, through a combination of hydrologic flow paths and thick, highly organic soils. The higher MeHg export by Hadlock Brook may be consistent with

their hypothesis, as Hadlock Brook watershed has nearly twice the soil coverage of Cadillac Brook watershed and greater organic content in these soils. The riparian zone of Cadillac Brook is relatively rocky, whereas Hadlock Brook watershed more commonly has forest floor that extends to the edge of the stream channel.

### **Hg and MeHg Mass Balances**

Calculating annual Hg mass balances using deposition weighted by season and vegetation type yielded input estimates that were lower than estimates made with un-weighted averages. Both watersheds are composed of a combination of bare and vegetated areas, each with a unique set of deposition characteristics. Seasonal deposition differences may be a result of canopy differences or changing Hg concentrations in air masses, and can be incorporated into deposition estimates (Iverfeldt, 1991; Grigal *et al.*, 2000). Hg inputs may be more accurately estimated by integrating the influence of vegetation type and season on deposition.

Even though the input fluxes of Hg to these watersheds were different the Hg retention by each watershed was nearly identical on a per unit area basis. The similar retention amounts resulted from differing export amounts, probably because of different soil characteristics in the two watersheds. The fire that burned Cadillac Brook watershed destroyed much of the organic material in the soil through a combination of combustion and erosion. The organic material that was left was hypothesized to have lost most of the associated mercury through

volatilization by the fire. These events left the Cadillac Brook watershed soils depleted of Hg, and therefore capable of retaining a larger portion of deposited Hg than the Hadlock Brook watershed soils.

The higher MeHg-retention percentage that was calculated for Hadlock watershed could not be explained by differences in hydrologic export, because the MeHg concentration in the streams was not dependent on flow. Riparian peat in these watersheds may moderate MeHg concentrations in streams. Increasing MeHg concentrations have been found with increasing peat depth, resulting in MeHg release over a wide range of flow rates from a watershed in Sweden (Bishop *et al.*, 1995).

Higher MeHg export in streams fed by bogs or fens also suggests that organic and humic substances may play a strong role in MeHg production (Kolka, 1996; Grigal *et al.*, 2000). Grigal found that bog areas contribute two times the MeHg to the stream as do upland areas, and Hadlock Brook watershed, which has ~66% more (production or export) of MeHg than Cadillac Brook watershed, is fed by two upland wooded wetlands.

## Chapter 5

### SUMMARY AND CONCLUSIONS

Hg deposition in Cadillac Brook watershed was lower than in Hadlock Brook watershed, because of both the type of vegetation coverage and the site aspect. Cadillac watershed is partially forested by mixed hardwoods and faces east/southeast, whereas Hadlock forest faces southwest and is dominated by conifers. The 1947 fire destroyed the majority of the vegetation in Cadillac Brook watershed and the patchy mixed-hardwood canopy that has resulted was less efficient at scavenging Hg from the atmosphere than the coniferous vegetation that covers the unburned Hadlock Brook watershed.

Hg export, as a percentage of input, from Cadillac Brook watershed was lower than from Hadlock Brook watershed because of the soil thickness and coverage, as well as composition. The 1947 fire that consumed the vegetation in Cadillac Brook watershed also consumed significant quantities of soil organic matter, and the subsequent erosion reduced the amount of soil in the watershed. The fire also volatilized Hg from mineral soils not consumed by the fire. These processes removed Hg from Cadillac Brook watershed and prepared the soils to retain a larger percentage of Hg input than Hadlock Brook watershed, which has been accumulating Hg in its soils for thousands of years.

Litter was determined to contribute the most Hg to the forest floor during the sampling period; two to five times as much as precipitation. The residence time and ultimate fate of the litter and its associated Hg are unknown, making it

difficult to determine if Hg from litter is retained or released by the watersheds. Although this study definitely identifies litter as a major pathway for Hg deposition.

The factors affecting Hg deposition did not seem to affect MeHg deposition. The higher MeHg deposition in the spring at Hadlock Brook watershed might be explained by volatilization of MeHg from soils as suggested by Hultberg et al. (1994). This is a rather tight cycle, which involves emission of MeHg from the soil and entrainment in precipitation or interception by vegetation before it can escape from the site. If this theory is valid then it would follow that the lower MeHg deposition at Cadillac Brook watershed would be a result of lower soil coverage and organic content, which is a result, at least in part, of disturbance history.

Riparian zone processing of overland and sub-surface flow may control MeHg concentrations in streams, as there were no differences in either deposition or discharge of MeHg at the two watersheds. Studies have reported elevated MeHg concentrations in riparian peat throughout its depth, suggesting that these areas may actually control MeHg production and release to streams (Lee and Bishop, 2000).

Fire disturbance had profound effects on the deposition and export of Hg and MeHg at Acadia National Park. The fire encouraged mixed-hardwood regeneration to control the vegetation type in Cadillac Brook watershed, which resulted in decreased Hg deposition to that watershed compared to Hadlock Brook watershed. The fire also destroyed soil organic material, and resulted in



the removal of Hg-laden soil from Cadillac Brook watershed through erosion. Hg also was volatilized from the soil by the heat of the fire, resulting in soils that had an increased ability to sequester Hg. These changes caused a decrease in the amount of Hg export from Cadillac Brook watershed relative to Hadlock Brook watershed.

Through understanding factors that control Hg deposition and transport we can identify areas that may be susceptible to higher Hg loading because of landscape characteristics. MeHg concentrations in streams may be related to the amount of organic material and peat in their watersheds. Wetland inventories may be helpful in targeting watersheds that could have elevated levels of MeHg in their streams.

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## **BIOGRAPHY OF THE AUTHOR**

Ken Johnson was born in Elizabeth, NJ on September 24, 1969. He was raised in many areas of the country as his was a military family. He graduated from Patrick Henry High School in Roanoke, VA. After pursuing a career in management, he enrolled in Ferrum College and graduated in 1998, Summa cum laude in Environmental Science. In 1999, Ken enrolled in a master's program at The University of Maine.

After receiving his degree, Ken plans to continue his research at The University of Maine. Ken is a candidate for the Master of Science degree in Ecology and Environmental Sciences, Water Resources Concentration from The University of Maine in May, 2002.