Biogeochemistry **52:** 13–40, 2001.

Spatial and temporal dynamics of mercury in Precambrian Shield upland runoff

C.J. ALLAN[1], A. HEYES[2], N.T. ROULET[2], V.L. ST. LOUIS[3] & J.W.M. RUDD[4]

[1]*Dept. of Geography and Earth Sciences, University of North Carolina at Charlotte, Charlotte, NC 28227, U.S.A.;* [2]*Dept. of Geography, McGill University, 805 Sherbrooke St. W., Montreal, Quebec, H3A 2K6, Canada;* [3]*Dept. of Microbiology, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada;* [4]*Dept. of Fisheries and Oceans, Freshwater Institute, Winnipeg, Manitoba, R3T 2N6, Canada*

Key words: dissolved organic carbon, episodic runoff, methyl mercury

Abstract. Methylated and total Hg, and TOC concentrations were measured in precipitation and runoff in a first order Precambrian Shield watershed, and in precipitation, throughfall, shallow groundwater and runoff in a zero Precambrian Shield watershed. Plots dominated by open lichen-covered bedrock and another containing small patches of conifer forest and thin discontinuous surficial deposits were monitored within the zero order catchment. Methyl (3–10 fold) and non-methyl (1.4–2.8 fold) Hg concentrations changed irregularly during rainfall and snowmelt runoff events in all catchments. Temporal patterns of Hg concentration in runoff included flushing and subsequent dilution as well as peak concentrations coinciding with peak or recession flow. Mercury export was highest from lichen-covered bedrock surfaces as a result of high runoff yields and minimal opportunity for physical retention and in the case of MeHg demethylation. Forest canopy and lichen/bedrock surfaces were often net sources for Hg while forest soils were mostly sinks. However, upland soils undergoing periodic reducing conditions appear to be sites for the *in situ* production of MeHg.

Introduction

Elevated concentrations of methylmercury (MeHg) in people, fish and other wildlife is of concern in many areas of N. America and Europe (e.g. Hakanson et al. 1990; Facemire et al. 1995; Fleming et al. 1995; Wheatly & Paridis 1995). The direct deposition of atmospheric Hg (Sorenson et al. 1990; Iverfeldt 1991; St. Louis et al. 1995) combined with the waterborne transport of Hg in surface and groundwater draining upland hillslopes (Aastrup et al. 1991; Meili et al. 1991; Allan & Heyes 1998) as well as wetlands (Bishop et al. 1995b; Branfireun et al. 1996; Krabenhoft et al. 1995; St. Louis et al. 1994, 1996), have been identified as the primary transport vectors of Hg to aquatic ecosystems. Limited data from catchments in the SE Blue Ridge,

U.S.A. (Allan & Heyes 1998), N Sweden (Bishop et al. 1995a, c) and NW Ontario, Canada (Branfireun et al. 1996) indicate significant changes in Hg runoff concentrations can occur during episodic hydrologic events. Temporal variations in Hg concentration observed in these and other studies is thought to result from foliar washoff and temporal changes in hydrologic contributing area (Allan & Heyes 1998; Bishop et al. 1995a, b) as well as the depletion of labile pools of Hg during prolonged runoff periods (Bishop et al. 1995c). Other factors which may influence the transport of Hg and other trace metals during episodic events include the character, availability and transportability of binding ligands such as organic and/or particulate material. Significant, but variable positive correlations between Hg and dissolved and particulate organic carbon in surface, soil and groundwaters have been noted in several studies (Mierle & Ingram 1991; Bishop et al. 1995b; Krabenhoft et al. 1995). Positive correlations have also been found between total Hg (THg) and to some degree unfltered methyl mercury (MeHg) and discharge in larger river systems, mainly because of the strong correlation between flow and particulate load (Hurley et al. 1998). Filtered Hg concentrations did not respond of changes in discharge (Hurley et al. 1998). Studies examining the temporal and spatial variability of Hg transport from and within catchments during episodic hydrologic events are needed to further our understanding of the biogeochemical cycling of mercury in terrestrial systems and refine our estimates of terrestrial Hg fluxes to aquatic systems.

In this paper, we examine the spatial and temporal transport of methyl and non methylated Hg in precipitation, throughfall, soil and groundwater and runoff during rapidly changing hydrologic conditions and asses the importance of considering temporal changes in Hg concentration in estimating the mass flux of Hg from upland catchments. By using within event concentration data and directly measured hydrologic fluxes, we examine how different landscape units within upland Precambrian Shield catchments affect Hg speciation and transport in runoff. Finally, we examine the relationship between organic carbon and Hg with regard to waterborne transport within upland Precambrian Shield environments.

Study area

The study was conducted in the zero order U1 catchment (Zero Order), and the first-order 114IF catchment (First Order), located in the Experimental Lakes Area (ELA) of north-western Ontario (49°40′ N, 93°43′ W) (Figure 1, Table 1). A plot (Bedrock Plot) consisting of lichen-covered granitic bedrock and another mixed plot (Forest Plot) containing lichen-covered bedrock (62%) and forested soil deposits (38%) were isolated with small

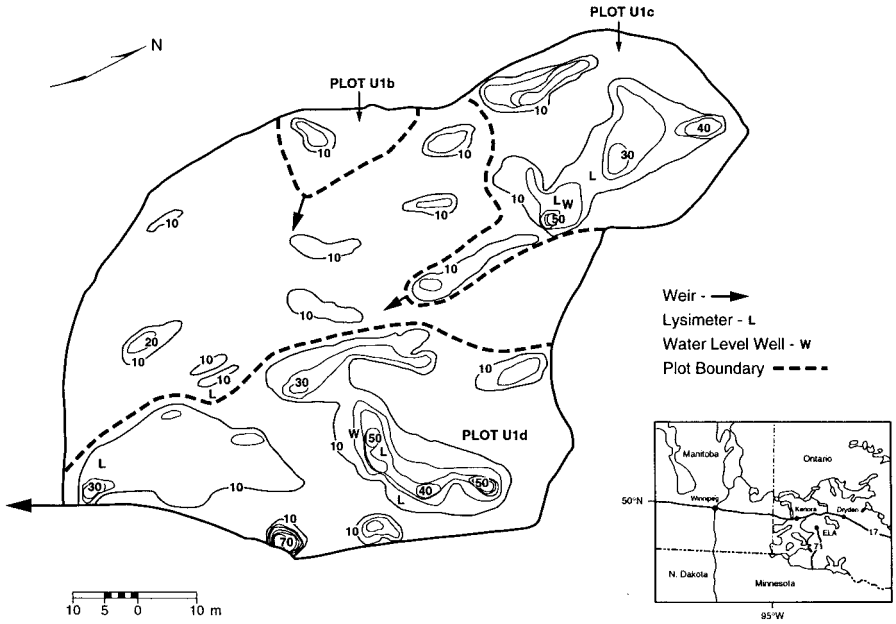

Figure 1. Zero Order Watershed outline map and study area location.

Table 1. Physiography of the study catchments and plots.

Site	Area(ha)	Slope[1]	Bedrock (%)	Forest[2] (%)	Soil Depth (cm)
Zero Order	0.5553	0.177	73	27	8
Bedrock Plot (U1b)	0.0172	0.205	95	5	3
Forest Plot (U1c)	0.1102	0.093	62	38	11
First Order	5.73	0.152	na[3]	na	na

[1]Mean slope of the basin = $oh/A_c^{-\frac{1}{2}}$, where A_c is the Area of the catchment in m^2 and oh is the maximum altitude difference in m. An average slope is calculated as there is no true channelized drainage in the basin to calculate a stream slope (Wells et al. 1990).
[2]Forested areas were assumed to occupy areas with soil deposits $\geq$ 10 cm in thickness. All soil deposits were manually mapped and soil depth determined along multiple transects by auguring. No trees were found where soil depth was $<$ 10 cm.
[3]Not available.

diversion walls and monitored separately within the Zero Order catchment (Figure 1). Soil is absent from the Bedrock Plot while discontinuous silt loam surficial deposits of up to 60 cm in depth are found in the Forest Plot. Over ninety per cent of the annual runoff from the Zero Order catchment and plots occurs as brief episodic events in response to snowmelt and rainfall and runoff yields can approach 100% of precipitation during large or intense rain

events (Allan & Roulet 1994). Runoff is generated as Hortonian overland flow (HOLF) from bedrock surfaces and saturation overland flow (SOLF) and subsurface stormflow (SSSF) contribute later from the discontinuous soil deposits which drain as unchannelized flow.

The Zero Order catchment is underlain by leucocratic coarse-grained metagranites, which form a watertight seal beneath the catchment (Allan et al. 1993). Vegetation on the Zero Order catchment soil deposits consists of an overstorey of *Pinus banksiana*, *Picea mariana* and a few scattered *Pinus strobus*. The bedrock outcrops are colonised by lichens (both crustose and fruticose forms), *Juniperus virginiana* and mosses, *Racomitrium* sp. The Zero Order catchment has never been logged and the last forest fire in the study area occurred more than 115 years ago (Schindler et al. 1980).

A small intermittent stream drains the First Order catchment. The catchment was logged in 1976 and scarified in 1979 as part of a long-term hydrologic investigation. Soils are classified as immature Brunisols developed on thin glacial drift and are underlain by a granodiorite bedrock (Brunskill & Schindler 1971). The catchment today supports a dense, regenerating stand of 20-year-old *Pinus banksiana* and *Betula papyrifera*.

The climate of the study area is classified as boreal cold temperate with monthly air temperatures ranging from –16.5 °C for January to 19.0 °C for July during 1969–1995 (K. Beaty unpublished data). Total annual precipitation averaged 678mm, of which 36% fell as snow during this same period.

Methods

Hydrology

Rainfall for the August, 1993 and September, 1994 events were measured with standard Atmospheric Environment (AES) rain gauges and tipping bucket recorders either located in the Zero Order catchment or within 1 km of this catchment. Throughfall volumes were collected from an eavestrough collector located in the Zero Order catchment. Rainfall totals for the First Order catchment were recorded at the main ELA meteorological station < 2 km from that catchment.

Discharge at the catchment and plot outlets was calculated from continuous water level measurements behind v-notch weirs calibrated independently over a range of flow conditions. Water levels for the stations were measured with potentiometric level recorders connected to a common data logger or with float activated recorders. During the August rain event the weir monitoring system for the Zero Order catchment was disabled by light-

ning. Discharges for the Zero Order catchment and plot outlets during this event were estimated using the SCS dimensionless unit hydrograph technique (Veissman et al. 1989) utilising event recording rain gauge data and checked against several manual stage readings. Runoff totals and hydrograph characteristics from this and the directly monitored September event were similar to those directly measured in previous studies (Allan & Roulet 1994).

During the September runoff event water samples were collected for stable isotope analysis to assess the relative contributions of event and pre-event water to runoff from the various components of the Zero Order catchment. Water samples for stable isotope analysis were collected in clean polyethylene bottles with air displacement caps. Samples were analysed for 18-oxygen (^{18}O) at the University of Waterloo Environmental Isotope Laboratory and are reported relative to standard mean ocean water (SMOW). The accuracy of the ^{18}O determination is $\pm$ 0.2‰. A two-component mixing model was used to separate runoff waters into pre-event and event components;

$$C_tQ_t = C_pQ_p + C_eQ_e$$

where C equals the isotope concentration, Q is the discharge (m^3 s^{-1}), and t, p, and e are the total outlet discharge, pre-event component and event component, respectively (Sklash 1990). The assumptions critical to performing the separation for this study are that storm runoff is from two water sources, pre-event and event water, and that each source has a spatially and temporally uniform isotopic value (C_p and C_e).

The incremental mean approach (McDonnel et al. 1990) was used to assess temporal changes in the event isotopic signature from sequentially collected throughfall samples. The spatial uniformity of the isotopic signature for pre-event soil and groundwater was determined from samples withdrawn from shallow groundwater wells within the forest soils at the crest (one well) and base (two wells) of the Zero Order catchment (Figure 1). Pre-event isotopic signatures for the Forest Plot were determined from the well samples at the slope crest and values for the Zero Order catchment as a whole determined as areally weighted averages of all three sample wells.

Water Chemistry

An ultraclean trace element sampling protocol was employed to collect all samples to be analysed for Hg throughout this study (St. Louis et al. 1994). Precipitation samples were collected at the main ELA meteorological station in pre-washed wide-mouthed Teflon® containers on acid-washed Plexiglas trays 1.5 metres above the ground surface (St. Louis et al. 1995). Containers

were installed just after the initiation of rain events and removed immediately after the event. Throughfall samples were manually collected from an acid-washed Teflon lined eavestrough style collector in prewashed Teflon bottles.

Runoff samples were collected in prewashed Teflon bottles immediately upstream of each weir. Groundwater samples were pumped from wells using prewashed Teflon tubing and a Teflon transfer case whereupon they were transferred to Teflon bottles. Samples to be analysed for THg were acidified with low Hg HCI, and analysed by cold vapour atomic fluorescence (CVAF) (Bloom & Fitzgerald 1988). Samples to be analysed for MeHg were frozen upon collection and later analysed in the trace metal laboratory at the ELA. Methyl Hg was measured using CVAF following the methods of Bloom (1989) and Horvat et al. (1993). The limit of detection and analytic error, for THg is 0.16 $ng \cdot L^{-1}$ and for MeHg is 0.013 $ng \cdot L^{-1}$, calculated as two standard deviations around the mean of the blank. Non methylated Hg (NMHg) was calculated as THg – MeHg.

All water samples to be analysed for organic carbon were collected in clean polyethylene bottles and taken to the ELA analytical laboratory within a few hours of collection for sample processing. Organic carbon analyses were performed either at the DFO, Freshwater Institute Analytical Laboratory, using standard DFO procedures (Stainton et al. 1974), or by high temperature combustion with a Shimadzu TOC 5000 at McGill University. Water and chemical fluxes were determined as follows. Atmospheric deposition and throughfall fluxes were calculated by multiplying concentrations from bulk precipitation and throughfall samples by the recorded depth of precipitation and throughfall, respectively. Runoff fluxes were determined by multiplying the concentration of Hg or TOC by the volume of discharge measured at each outlet weir. The runoff volume assigned to each sample corresponded to the sum of the discharge recorded from the midpoint between the collection of the previous water sample to the mid point in time prior to the subsequent sample. Calculated fluxes were then divided by the area of discharge to express the flux on a unit area basis. The errors reported for the hydrologic and chemical flux terms equal the confidence limits, or one standard deviation around the measured values. Confidence limits for the hydrologic fluxes were estimated by multiplying flux terms by percentage errors derived from the literature and individual rating equations (LaBaugh & Winter 1984). Confidence limits for the chemical fluxes were estimated by summing the individual error terms for the chemical and hydrologic fluxes (Devito et al. 1990).

Table 2. Hydrologic totals and Hg concentrations for the Zero Order catchment and the Bedrock and Forest plots resulting from a 20 mm rainfall August 8, 1993. Uncertainty reported as ± 1 SD hydrological, analytical and sampling uncertainties.

Precipitation			
Total 20 ± 3 mm			
	MeHg	**Non MeHg**	
[1]VWC ngL^{-1}	0.08 ± 0.02	2.14 ± 0.11	
Wet Deposition Flux	16.00 ± 4.03 μg ha^{-1}	0.43 ± 0.07 mg ha^{-1}	
Throughfall			
Total 16 ± 2.4 mm			
	MeHg	**Non MeHg**	
VWC ng L^{-1}	0.09 ± 0.02	15.78 ± 0.79	
Throughfall Flux	14.40 ± 3.63 μg ha^{-1}	2.52 ± 0.40 mg ha^{-1}	
	Bedrock Plot	**Forest Plot**	**Zero Order**
Runoff mm	17.00 ± 1.4 (85)[2]	3.80 ± 0.3 (19)	6.40 ± 0.4 (32)
MeHg			
VWC ng L^{-1}	0.07 ± 0.01	0.11 ± 0.02	0.10 ± 0.02
Max. ng L^{-1}	0.15 ± 0.03	0.29 ± 0.06	0.15 ± 0.03
Min. ng L^{-1}	0.04 ± 0.01	0.04 ± 0.01	0.02 ± 0.004
NMHg			
VMC ng L^{-1}	6.69 ± 0.33	11.08 ± 0.55	9.76 ± 0.49
Max. ng L^{-1}	9.20 ± 0.46	25.20 ± 1.26	11.70 ± 0.59
Min. ng L^{-1}	6.15 ± 0.31	8.90 ± 0.45	8.80 ± 0.44

[1]VMC = volume weighted concentration.
[2]Values in parentheses represent runoff depth as a percentage of precipitation, runoff/precipitation × 100.

Results and discussion

Hydrology

20 mm Rainfall August 8, 1993

Antecedent moisture conditions before this event were dry. A sporadic drizzle totaling 17.8 mm had occurred over the previous eight days, and no rain occurred for three days prior to August 8. All weirs in the Zero Order catchment were dry and groundwater was not detectable in any soil deposits. The runoff yields (runoff m^3/precipitation m^3*100) for this event were 85%, 19%, and 32% for the Bedrock and Forest Plots and Zero Order catchment, respectively (Table 2, Figure 2(a)).

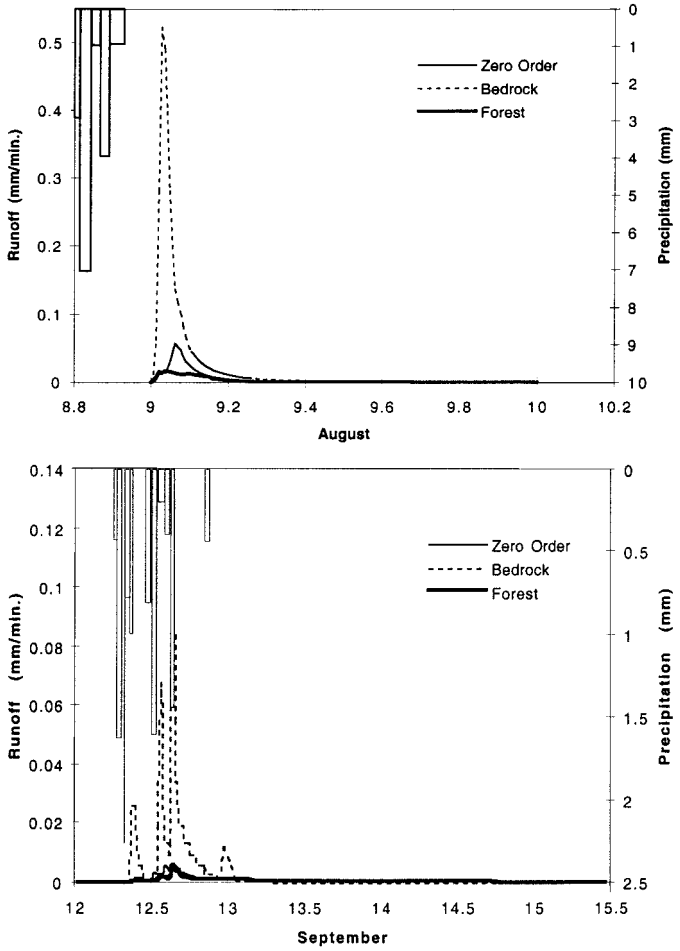

Figure 2(a)–(b). Hydrologic response of the Zero Order catchment and Forest and Bedrock Plots to the August 8, 1993 rain event (1(a)) and the September 12, 1994 rain event (1(b)).

15.4 mm Rainfall September 12, 1994

Prior to this rainfall event no rainfall had occurred in the previous five days. However, small amounts of runoff were still occurring from the Forest Plot and Zero Order catchment as a result of 61.8 mm of rainfall, which occurred on September 4, and 5. The groundwater table was measured at 10 cm below the soil surface in the Forest Plot. The hydrologic yields for this event were 57%, 12%, and 15% for the Bedrock and Forest Plots and the Zero Order catchment, respectively (Table 3, Figure 2(b)). Results from the September 12 hydrograph separation using ^{18}O indicate the following proportions of pre-event water in runoff: $56.8 \pm 5\%$; $74 \pm 5\%$; and $91 \pm 5\%$ for the Bedrock and

Table 3. Hydrologic totals and Hg concentrations for the Zero Order catchment and the Bedrock and Forest plot resulting from a 15.7 mm rainfall September 12, 1994. Uncertainty reported as ± 1 SD hydrological, analytical and sampling uncertainties.

Precipitation			
Total 15.7 ± 2.34 mm	**MeHg**	**Non MeHg**	
VWC ng L^{-1}	0.03 ± 0.01	14.33 ± 0.72	
Wet Deposition Flux	4.71 ± 1.19 μg ha^{-1}	2.25 ± 0.36 mg ha^{-1}	
Throughfall			
Total 10.0 mm	**MeHg**	**Non MeHg**	
VWC ng L^{-1}	0.20 ± 0.04	23.64 ± 1.18	
Throughfall Flux	20.00 ± 5.04 μ ha^{-1}	2.36 ± 0.37 mg ha^{-1}	
	Bedrock Plot	**Forest Plot**	**Zero Order**
Runoff mm	9.10 ± 0.8 (57)[2]	1.90 ± 0.2 (12)	2.40 ± 0.14 (15)
MeHg			
VWC ng L^{-1}	0.06 ± 0.01	0.37 ± 0.07	0.02 ± 0.00
Max. ng L^{-1}	0.10 ± 0.02	2.34 ± 0.47	0.07 ± 0.00
Min. ng L^{-1}	0.01 ± 0.01	0.12 ± 0.02	0.01 ± 0.00
[3]Groundwater (pre)		0.23 ± 0.05	0.25 ± 0.05, 0.07 ± 0.01
[4]Groundwater (post)		0.05 ± 0.01	0.16 ± 0.03, 0.06 ± 0.01
NMHg			
VWC ng L^{-1}	6.04 ± 0.30	6.93 ± 0.35	7.15 ± 0.36
Max. ng L^{-1}	7.60 ± 0.38	26.00 ± 1.30	8.80 ± 0.44
Min. ng L^{-1}	5.60 ± 0.28	9.00 ± 0.45	6.40 ± 0.32
[3]Groundwater (pre) ng L^{-1}		2.44 ± 0.12	1.75 ± 0.09, 4.01 ± 0.20
[4]Groundwater (post) ng L^{-1}		2.47 ± 0.12	1.90 ± 0.10, 3.78 ± 0.19

[1]VWC = volume weighted concentration.
[2]Values in parentheses represent runoff depth as a percentage of precipitation, runoff/precipitation × 100.
[3,4]The two concentrations given for groundwater in the Zero Order catchment refer to the Hg concentrations recorded for the Forest plot groundwater (first value) at the catchment crest while the later two values refer to groundwater concentrations measured in two groundwater wells located in downslope soil deposits above the Zero Order catchment outlet weir. The 'pre' samples refer to samples collected prior to the September event, while the 'post' samples refer to those collected immediately after the event.

Table 4. Precipitation and runoff totals and Hg concentration and export for the First Order catchment resulting from a 89 ± 13.4 mm rainfall June 27–30, 1992. Runoff from the event was 27.4 ± 1.8 mm or 33% of precipitation. Uncertainty reported as ± 1 SD hydrological, analytical and sampling uncertainties.

	MeHg	**NMHg**
[1]VMC ng L^{-1}	0.05 ± 0.01	10.80 ± 0.54
Max. ng L^{-1}	0.06 ± 0.01	12.21 ± 0.61
Min. ng L^{-1}	0.02 ± 0.004	8.23 ± 0.41
Yield μg ha^{-1}, mg ha^{-1}	14.87 ± 3.14	3.15 ± 0.25

[1]VMC = volume weighted concentration.

Forest Plots and First Order catchment, respectively. Runoff yields from each catchment and plot for the two events above as well as proportions of event and pre event water from the September event fall within the ranges observed in earlier longer duration hydrochemical investigations of these catchments (Allan & Roulet 1994). On average eight to twenty one rain events of this magnitude or greater could be expected during each growing season at the ELA (Beaty 1984; Beaty & Lying 1989). Events of this magnitude or greater comprise 40.5% to 68% of the annual rainfall at the ELA.

89 mm Rainfall June 27, 1992 and April Snowmelt, 1992 First Order Catchment

An 89 mm rainstorm June 27, 1992 and the April 1992 snowmelt period represent our most intense sampling efforts for the First Order catchment (Figures 5(a) and 5(b), p. 25). Moisture conditions prior to the June 27 storm were relatively dry with no significant rainfall occurring during the previous week and no runoff occurring at the catchment outlet. Runoff attributable to the June event was 33% of precipitation (Table 4). Precipitation events of this magnitude are unusual at the ELA with only four events of this magnitude or greater recorded for the period 1979–1987 (Beaty 1984; Beaty & Lyng 1989). The 1992 snowmelt period reflects runoff from a 64 cm snowpack accumulation which is 39% above the average snow accumulation recorded for the 1970–1999 period (Beaty unpublished data).

Spatial and temporal dynamics of Hg during episodic runoff events

Temporal trends of Hg concentration in runoff

Temporal changes of runoff Hg concentrations during episodic hydrologic events were inconsistent between catchments and between events (Figures 3–5). NMHg concentrations in Bedrock Plot (Figures 3(a) and 4(a)), Zero Order

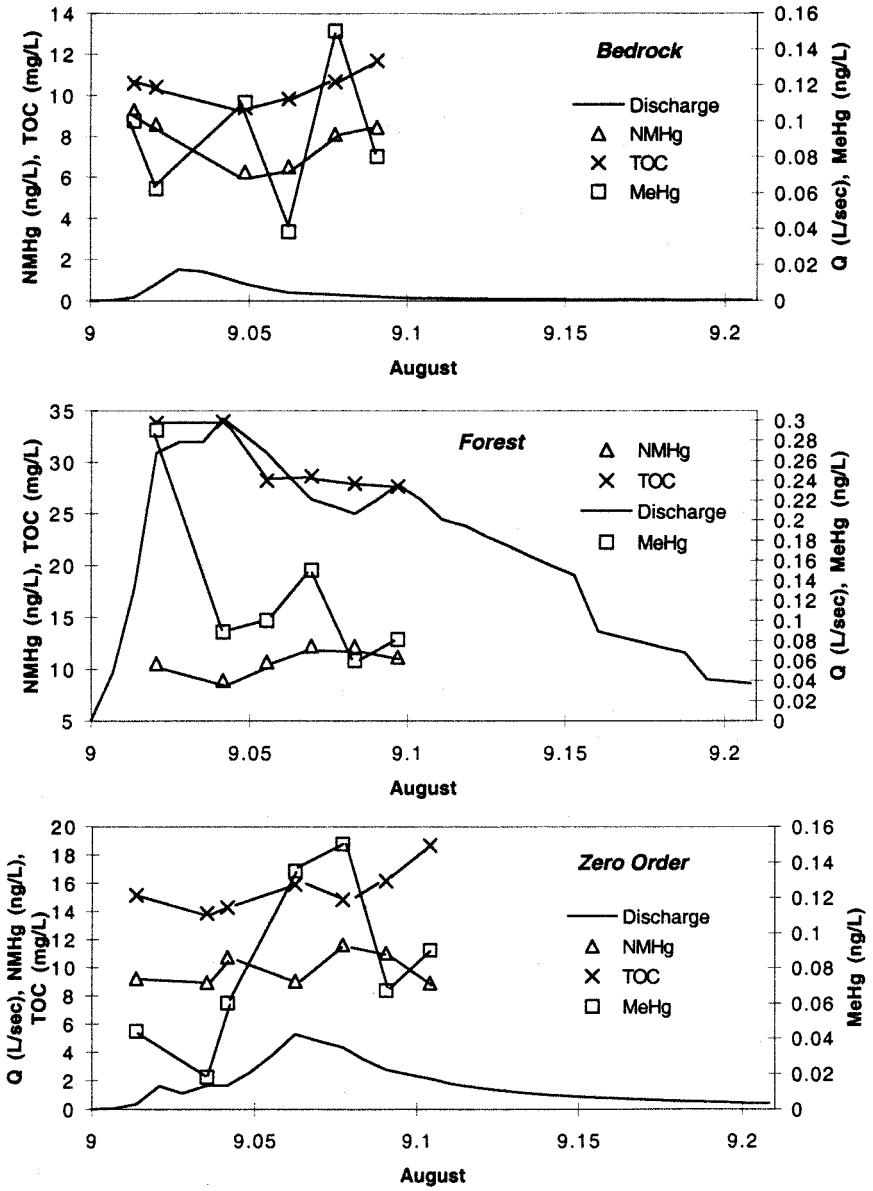

Figure 3(a)–(c). Temporal changes in discharge, MeHg, NMHg and TOC concentrations over time in Bedrock Plot runoff 2(a), Forest Plot runoff 2(b), and Zero Order runoff 2(c), August 8, 1993.

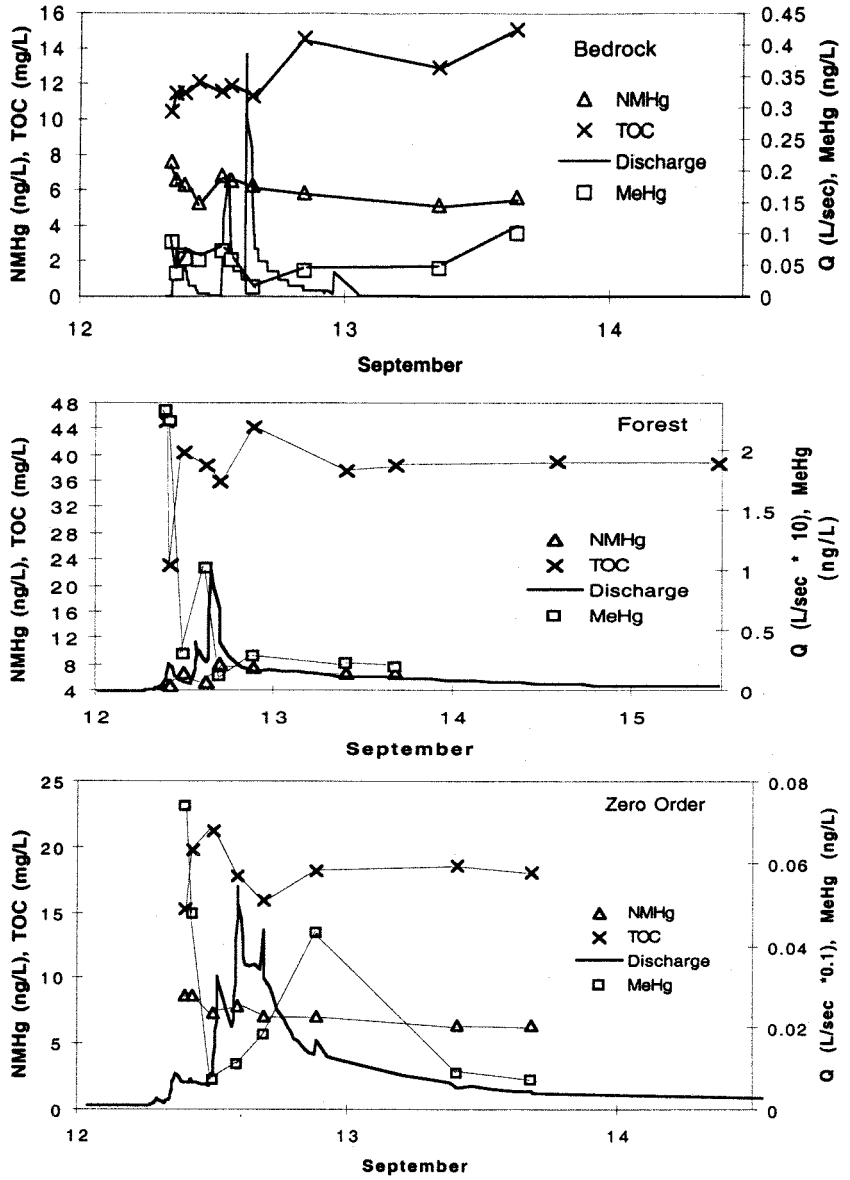

Figure 4(a)–(c). Temporal changes in discharge, MeHg, NMHg and TOC concentrations over time in Bedrock Plot runoff 3(a), Forest Plot runoff 3(b), and Zero Order runoff 3(c), September 12, 1994.

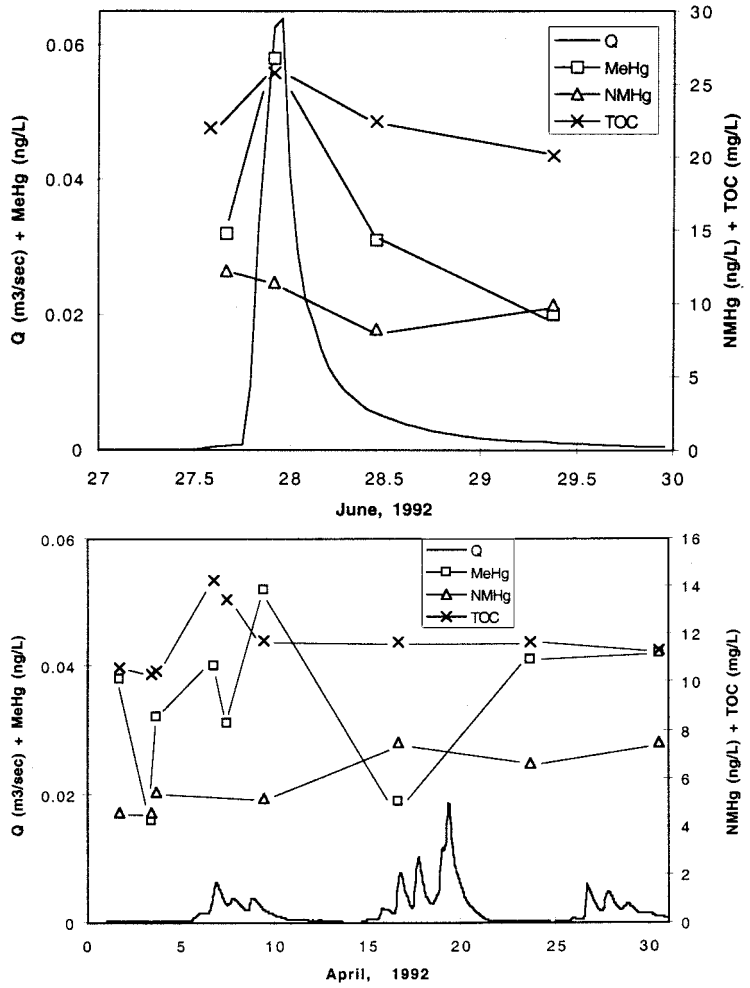

Figure 5(a)–(b). Temporal changes in discharge (Q) an MeHg, NMHg, and TOC concentrations over time in First Order catchment runoff during snowmelt, April, 1993 (4(b)) and storm runoff June 27–29, 1992 (4(a)).

catchment (Figure 4(c)), and First Order catchment runoff (Figure 5(a)), were all highest initially but declined later in the event. Later in the August event, NMHg Bedrock Plot concentrations returned to near initial values. At the Forest Plot, in both events (Figures 3(b) and 4(b)), NMHg concentrations were low initially, fluctuated at peak discharge and then increased to a relatively constant higher value after peak discharge. Finally, during the August event (Figure 3(c)), no temporal trend in NMHg concentrations was evident in Zero Order catchment runoff.

The most common temporal pattern observed for MeHg appeared to be a strong decline in MeHg concentrations early in the event, followed by lower MeHg concentrations during peak and recession flows (Figures 3(b), 4(b) and 4(c)). No pattern was evident for the Bedrock Plot runoff during either event (Figures 3(a) and 4(a)) and peak concentrations coincided with peak discharge for the Zero Order and possibly First Order catchments during the August and June events (Figures 3(c) and 5(b)). No relationship between runoff concentrations for either Hg species and the proportion of event and pre-event water as determined from the isotopic separation was found.

The high initial NMHg and MeHg concentrations observed in several instances suggests an initial wash off of dry deposited NMHg and MeHg and/or in situ methylated Hg produced during intrastorm periods. The subsequent decline in Hg concentrations may stem from precipitation dilution as the catchment pool of mobile Hg becomes exhausted and/or from kinetic constraints as water contact with soil and lichen/bedrock surfaces decrease during higher flows. Where Hg concentrations recover during recession flows, either the kinetic constraints on NMHg desorption are removed and/or evaporative concentration occurs. For the Forest Plot low NMHg concentrations likely reflect overland flow contributions from lichen/bedrock areas, followed by higher NMHg concentration runoff from forest soil deposits which contribute later in the event. In only two instances did peak flow and MeHg concentrations coincide (Figures 3(c) and 5(a)). However, the change in concentrations exhibited in the First Order catchment runoff during this event is near the analytical uncertainty. Allan and Heyes (1998) attributed high THg concentrations coincident with peak discharge inputs of high Hg throughfall onto saturated near stream zones during rain events in headwater Blue Ridge watersheds in SE USA Similar hydrologic conditions could be expected in larger and prolonged rainfall events at the ELA.

The only discernible temporal pattern in Hg concentration observed during spring runoff was a general increase in NMHg concentrations after the first few days of flow which was maintained despite several fold fluctuations in discharge (Figure 5(b)). A similar pattern was reported by Bishop et al. 1995c for the Svartberget catchment in N. Sweden. Unlike Bishop et al. we observed no detectable decrease in MeHg concentration with increasing discharge indicating the mobile pool of MeHg was not limiting to MeHg transport during the 1992 spring runoff. Branfireun et al. (1996) reported a similar stable temporal MeHg pattern for rain driven events in a nearby low order wetland catchment but with higher MeHg concentrations.

MeHg displayed the greatest variability during runoff events with changes as large as an order of magnitude being observed during an event. The range of MeHg concentrations in runoff was similar for the Bedrock Plot and the

Table 5. Summary statistics for First Order catchment Hg concentrations 1991–1994.

	N	Mean Concentration[1] (ng L^{-1})	Concentration Range (ng L^{-1})	Median Concentration (ng L^{-1})
Snowmelt				
MeHg	16	0.05 ± 0.03[2]	0.02–0.13	0.04
NMHg	16	7.82 ± 0.39	4.57–14.58	7.63
Growing Season				
Rising Discharge				
MeHg	21	0.05 ± 0.03	0.02–0.14	0.04
NMHg	21	9.37 ± 0.47	6.14–13.16	8.86
Declining Discharge				
MeHg	12	0.03 ± 0.03	0.02–0.07	0.03
NMHg	12	12.57 ± 0.63	7.50–16.29	12.37

[1]Arithmetic Mean Concentration.
[2]$\pm$ values represent one standard deviation of the mean.

Zero Order and First Order catchments 0.02 ± 0.004 ng L^{-1} to 0.15 ± 0.03 ng L^{-1} (Tables 2–5). Runoff from the Forest Plot typically had higher MeHg concentrations, 0.09 ± 0.02 ng L^{-1} to 2.34 ± 0.47 ng L^{-1} (Tables 2 and 3). NMHG concentrations were generally less variable than MeHg concentrations during runoff events exhibiting changes of less than three fold (Figures 3–5 and Tables 2–5). A summary of the Hg runoff data collected from 1991 through 1994 for the First Order catchment is presented in Table 5. No significant difference in average MeHg concentration is evident in the three groupings of discharge although the maximum concentrations measured during declining discharges are lower than those measured either during snowmelt or rising discharges during the growing season. NMHg concentrations tended to be their lowest during snowmelt and highest during growing season recession flows with the concentration ranges overlapping for all three periods.

Hydrochemical export and sources of Hg in upland precambrian shield landscapes

The measurement of internal hydrochemical fluxes within the Zero order catchment allows us to perform detailed mass balance estimates to identify the sources and sinks of Hg within this landscape (Table 6). Wet deposition accounted for the largest positive flux of MeHg during the August.

Table 6. Catchment and Internal Mass Balance Analysis of Zero Order Catchment Sources and Sinks of NMHg and MeHg, (mg or μg ha^{-1}) ($\pm$ 1 SD hydrological, analytical and sampling uncertainties).

Catchment and Plot Mass Balances				
	August 8		**September 12**	
	MeHg μ**g ha**$^{-1}$	**NMHg** **mg ha**$^{-1}$	**MeHg** μ**g ha**$^{(-1)}$	**NMHg** **mg ha**$^{-1}$
Input[1]	16.00 ± 4.03	0.43 ± 0.06	4.71 ± 1.19	2.25 ± 0.36
Bedrock Plot Export	11.90 ± 2.51	1.14 ± 0.11	5.46 ± 1.15	0.55 ± 0.05
(% Retention)[2]	26 ± 30	-166 ± 29	-16 ± 35	76 ± 16
Input[3]	15.39 ± 3.88	1.22 ± 0.19	10.81 ± 2.72	2.29 ± 0.36
Forest Plot Export	4.18 ± 0.88	0.42 ± 0.04	7.03 ± 1.48	0.13 ± 0.01
(%Retention)	73 ± 26	66 ± 16	35 ± 29	94 ± 16
Input[4]	15.57 ± 3.92	0.99 ± 0.16	9.04 ± 2.28	2.28 ± 0.36
Zero Order				
Catchment Export	6.40 ± 1.35	0.62 ± 0.05	0.48 ± 0.10	0.17 ± 0.01
(%Retention)	59 ± 27	37 ± 17	95 ± 25	92 ± 16
Internal Catchment Fluxes				
Forest Canopy[5]				
Inputs	16.00 ± 4.03	0.43 ± 0.07	4.71 ± 1.19	2.25 ± 0.36
Outputs	14.40 ± 3.63	2.52 ± 0.40	20.00 ± 5.04	2.36 ± 0.37
Net Flux	-1.60 ± 5.42	2.09 ± 0.41	15.29 ± 5.17	0.11 ± 0.52
Bedrock Surfaces[6]				
Inputs	16.00 ± 4.03	0.43 ± 0.07	4.71 ± 1.19	2.25 ± 0.36
Outputs	11.90 ± 2.51	1.37 ± 0.13	5.46 ± 1.15	0.55 ± 0.05
Net Flux	-4.10 ± 4.75	0.71 ± 0.15	0.75 ± 1.65	-1.70 ± 0.36

[1]Inputs to the Bedrock Plot are the Wet Deposition Fluxes Reported in Table 2 and 3.
[2]%Retention = (Input-Yield/Input)*100. Negative values equal net export of Hg.
[3]Inputs to the Forest Plot are Wet Deposition Flux * 0.62 + Throughfall Flux * 0.38. Throughfall Fluxes are reported in Tables 2 and 3. The weighting used to calculate the inputs is the percentage of surface area in the Forest Plot mapped as open bedrock (62%) and treed soil island (38%) (Table 1).
[4]Inputs to the Zero Order Catchment are Wet Deposition Flux * 0.73 + Throughfall Flux * 0.27. The weighting used to calculate the inputs is the percentage of surface area in the Zero Order Catchment mapped as open bedrock (73%) and treed soil island (27%) (Table 1).
[5]Canopy Flux = Wet Deposition Flux – Throughfall Flux.
[6]Bedrock Surface Flux = Wet Deposition Flux – Bedrock Plot Export.

Table 6. Continued

Catchment and Plot Mass Balances				
	August 8		**September 12**	
	MeHg μ**g ha**$^{-1}$	**NMHg** **mg ha**$^{-1}$	**MeHg** μ**g ha**$^{(}-1)$	**NMHg** **mg ha**$^{-1}$
Forest Plot Soils[7]				
Inputs	12.85 ± 2.91	1.66 ± 0.38	10.99 ± 2.49	1.24 ± 0.28
Outputs	4.18 ± 0.88	0.42 ± 0.04	7.03 ± 1.48	0.13 ± 0.01
Net Flux	-8.67 ± 3.04	-1.24 ± 0.38	-3.96 ± 2.90	-1.11 ± 0.28
Zero Order Soils[8]				
Inputs	10.85 ± 2.38	1.26 ± 0.28	8.60 ± 1.88	0.82 ± 0.18
Outputs	6.40 ± 1.35	0.62 ± 0.05	0.48 ± 0.10	0.17 ± 0.01
Net Flux	-4.45 ± 2.74	-0.64 ± 0.28	-8.12 ± 1.88	-0.65 ± 0.18

[7]Forest Plot Soil Flux = Inputs (Bedrock Flux * 0.62 + Throughfall Flux * 0.38) – Outputs (Forest Plot Export). The weighting used to calculate the inputs to the soils of the Forest Plot is the percentage of the Forest Plot represented by open bedrock surface draining into these soils (62%) and the percentage of the plot occupied by the vegetated soil deposit (38%) (Table 1).

[8]Zero Order Soil Flux = Inputs (Bedrock Flux * 0.61 + Throughfall Flux * 0.19 + Forest Plot Export * 0.20) – Outputs (Zero Order catchment Export). The weighting used to calculate the inputs to the soils of the Zero Order Catchment is the percentage of the Zero Order Catchment represented by open bedrock surface (61%) and upslope treed soil island (20%) draining into these soils sand the percentage of the catchment occupied by the vegetated soil deposit (19%) (Table 1).

Washoff from the forest canopy was the largest positive flux of NMHg during both events and for MeHg during the September event. During both events NMHg concentrations increased significantly as rain passed through the forest canopy. Similar increases in THg concentrations have been reported for throughfall passing through a mixed hardwood stand in upstate Vermont (Rea et al. 1996). Throughfall MeHg concentrations in the September event were 10 fold higher than in open areas indicating the presence of a significant pool of mobile MeHg on forest canopy surfaces during this period (Table 3). Precipitation and throughfall MeHg concentrations were essentially the same during the August event.

The degree of Hg retention in the bedrock plot was variable between events (Table 6). Estimates for net retention of MeHg are within the budget uncertainties during both events. NMHg was strongly retained the September event with a net export occurring during the August event. The Bedrock Plot had the highest export of both Hg species, with the exception of MeHg for the Forest Plot during the September event (Table 6). The relatively high

Hg fluxes from this plot are attributed to high runoff yields resulting from minimal storage capacity and the widespread generation of HOLF (Allan & Roulet 1994). The rapid production and cessation of HOLF limits runoff contact with sparse, patchy soil deposits and minimizes potential adsorption and/or demethylation of atmospherically deposited MeHg. The positive flux of NMHg during the August event indicate the washoff and mobilization of residual Hg left from previous rain events or dry deposited Hg during intrastorm periods may exceed Hg immobilization during some runoff events.

Soil deposits within the Forest Plot and the Zero Order catchment were significant sinks for Hg during both events (Table 6). However, the Forest Plot consistently demonstrated the highest MeHg runoff concentrations within the Zero Order catchment. During the September event Forest Plot runoff volume weighted and maximum MeHg concentrations were one to two orders of magnitude greater than MeHg concentrations in wet deposition, throughfall, or Bedrock Plot or Zero Order catchment runoff (Table 3). The only other waters where we have measured MeHg concentrations at this level in the ELA are in peat porewaters or runoff form wetland areas (Branfireun et al. 1996; St. Louis et al. 1996). Upland forest soils in this area are largely covered by moss mats, which have been shown to contain high concentrations of MeHg (Moore et al. 1995). Perhaps more importantly, the Forest Plot behaves hydrologically much like a depression wetland with drainage controlled by a bedrock sill. As a result, saturated soil conditions, as exhibited by gleying, are maintained longer than other forested soil deposits, which drain freely (Allan & Roulet 1994). High MeHg concentrations have been observed in saturated soils (Gilmore et al. 1998; Heyes et al. 1998) and increasing proportions of wetland are associated with higher MeHg fluxes in Wisconsin, ELA and Adirondack watersheds (Babiarz et al. 1998; Driscoll et al. 1994; Hurley et al. 1995; Krabbenhoft et al. 1995; St. Louis et al. 1994). We propose that soil deposits in this landscape which are characterized by periodic saturated, reducing conditions with a high organic content can be areas of active methylation and the *in situ* production of MeHg can occur. The export of MeHg from these saturated soil deposits mimics the same patterns observed in larger watersheds and may contribute to the temporal variations in runoff concentrations observed in this landscape.

The separation of the pre-event and event component in runoff the forest Plot during the September event further supports our contention of an *in situ* source of MeHg production in this upland environment. Without a suitable second conservative tracer we cannot determine the relative proportions of pre-event ground/soil water and throughfall event water from upslope runoff to Forest Plot soils, but we are able to place some constraints as to the source of MeHg in Forest Plot runoff from the relative proportions of pre-event

and event waters and their associated concentrations. If we assume initially that MeHg is a conservative tracer, we find that it is impossible to produce the average MeHg VMC for Forest Plot runoff. During the September event approximately 71 ± 5% of the total Forest Plot runoff was pre-event water with a MeHg concentration of 0.23 ± 0.05 ng L^{-1} as determined from pre-event well samples. During the event groundwater MeHg concentrations declined to 0.05 ± 0.01 ng L^{-1}. The event contribution (29%) could have a maximum concentration of 0.20 ± 0.04 ng L^{-1}, that assigned to throughfall. Upslope runoff to the treed soil deposits is the Forest Plot comprises both pre-event and event water and has a volume weighted concentration of 0.06 ± 0.01 ng L^{-1} and a maximum concentration of 0.10 ± 0.02 ng L^{-1}, as determined from Bedrock Plot runoff. Therefore, the simple mixing of event and pre-event water would produce Forest Plot runoff concentrations substantially lower than the measured MeHg VMC of 0.37 ± 0.07 ng L^{-1} or maximum concentration of 2.34 ± 0.47 ng L^{-1}. The *in situ* production of MeHg within the surface soils or vegetation of this plot may explain the significantly lower MeHg retention despite a smaller runoff flux during the September event which had higher antecedent moisture conditions as compared to the August event (Table 6). We cannot yet quantify the importance of any such MeHg production until the catchment is monitored for an annual cycle.

Significant retention and/or demethylation of MeHg and retention of NMHg also occurred in soils at the base of the Zero Order catchment during both monitored events (Table 6). A relatively large soil volume through which runoff from upslope areas must drain before exiting the catchment occupies the lower portion of the Zero Order catchment. Unlike the Forest Plot, soils in this lower deposit drain rapidly and saturated conditions are short-lived (Allan & Roulet 1994). MeHg retention was substantially higher in these downslope soils in the September event when compared to the August event and may be related to lower runoff fluxes. NMHg retention was almost double in Forest Plot soils as compared to Zero Order catchment soils. The higher NMHg retention may be related to the significantly higher organic content of Forest Plot soils (Allan et al. 1993). Relatively high NMHg retention is a trend observed for other catchments containing saturated organic soils in this area of the Precambrian Shield (St. Louis et al. 1996).

St. Louis et al. (1996) report the annual 1992–1994 retention of atmospherically deposited Hg in the First Order catchment as 99% and 65% for MeHg and THg, respectively. The retention of MeHg for the Bedrock Plot (26 ± 30% August; –16 ± 35%, September), Forest Plot (35 ± 29%, September) and Zero Order catchment (59 ± 27%, August) during our monitored events are lower than that reported for the larger First Order catchment. If the results from our storm driven events are considered as typical, then one can assume

that MeHg transport will be higher from smaller unchannelized drainage areas than larger upland watersheds on the Canadian Shield. Smaller subunits will be 'leakier' with regard to MeHg export both because of high runoff yields and in some instances because of *in situ* production and export of MeHg where conditions favorable for methylation exist. Deeper and more extensive soil deposits in larger watersheds will presents increased opportunities for the adsorption and/or demethylation of MeHg along longer and deeper runoff pathways.

The net retention of NMHg for the Zero Order catchment, Bedrock and Forest Plot (37–94%) is in the same range of values reported for the First Order catchment by St. Louis et al. (1996). However, a net export of NMHg occurred from the Bedrock Plot (–166% retention) during the August event.

Relationship between TOC and Hg in an upland precambrian shield landscape

The transport of atmospherically deposited and *in situ* mehtylated Hg from terrestrial systems has been found to be closely related to the transport of dissolved organic material (Lee & Hultberg 1990; Aastrup et al. 1991; Mierle & Ingram 1991; Petterson et al. 1995; Allan & Heyes 1998). Mercury tends to form strong complexes with organic matter in soils (Schuster 1991) and Petterson et al. (1995) demonstrated the transport of MeHg and the dissolved humic fraction of DOC was strongly correlated in runoff waters. Similar organic/metal complexation behavior has been observed for Cd (Rasmussen 1986) and Pb (Driscoll et al. 1998) and Cu and Pb (LaZerte et al. 1989) in other forested systems.

Temporal trends in TOC concentrations did not follow Hg concentrations during most individual runoff events examined in this study (Figures 3–5). Exceptions to this occurred for MeHg in First Order catchment runoff (June event, Figure 5(a)) and Bedrock Plot runoff (August event, Figure 3(a)). A relatively wide range of TOC concentrations (10–45 mg L^{-1}) exist in runoff waters from low order watersheds at this study site (Figure 6). TOC concentrations for the Zero Order and First Order catchments and the Bedrock Plot overlapped (9 to 32 mg L^{-1}) with the Bedrock Plot consistently at the low end of this range (9 to 15 mg L^{-1}). TOC runoff concentrations for the Forest Plot are generally higher than the other sites (28–45 mg L^{-1}). The low TOC concentrations in Bedrock Plot runoff are attributed to the high runoff volumes and lack of significant accumulations of organic material at this site. The periodic presence of a shallow water table in the Forest Plot routes a significant portion of the annual runoff through surface organic rich soil horizons resulting in high concentrations of TOC ($>$ 90% dissolved) in runoff. Runoff from the Zero Order and First Order catchments must pass through

significant amounts of mineral soil before exiting each site, presenting significantly greater opportunities for biotic and abiotic retention of organic carbon (Allan et al. 1993).

In large Wisconsin rivers a positive relationship is observed between particulate organic carbon (POC) and THg (Babiarz et al. 1998; Hurley et al. 1998). In the ELA upland system the dissolved carbon fraction dominates the net carbon export, accounting for $>$ 94% of the total carbon export in forest plot and whole catchment runoff and 75% of the total for bedrock plot runoff (Allan et al. 1993). Krabbenhoft et al. 1995 report positive correlations between DOC and THg in the Allequash Creek Watershed, Wisconsin. There is a significant but weak positive exponential relationship (MeHg ng L^{-1} = 0.181 e $^{(0.0626^{*}\mathrm{TOCmgL}-1)}$, r^2 0.30, N = 95) between MeHg concentrations and TOC in this Precambrian Shield terrain (Figure 6(a)). Within each of the individual catchments this positive relationship is not evident (data not shown). The elevated TOC and MeHg concentrations, which define the exponential character of this relationship, are all associated with Forest Plot runoff. No significant positive relationship was found between NMHg and TOC (Figure 6(b)). Unlike for MeHg several of the high TOC Forest Plot runoff samples are associated with relatively low NMHg concentrations. The TOC:NMHg ratio is 3.5 times more variable and on average 30% higher for this Forest Plot when compared to the other catchments. This may indicate an over supply of carbon in relation to Hg in some instances or the character of the Forest Plot organic carbon differs from other sites and has a lower affinity for NMHg. Mierle and Ingram (1991) reported that Hg/DOC relationships changed seasonally in Precambrian Shield catchments in south central Ontario as the character of DOC changed. Low TOC groundwater samples from both the Forest Plot and the Zero Order catchment were also significantly depleted in NMHg in relation to runoff waters (Figure 6(b)). Low NMHg concentrations in shallow groundwaters likely reflect the adsorption of Hg derived from atmospheric deposition and upslope runoff within organic and mineral soils.

Hg transport in low order precambrian shield terrain

To put the results of this study into a regional landscape perspective, Hg concentrations for Zero Order catchment and plot runoff form this study are compared to the runoff concentrations from the First Order catchment and several larger Precambrian Shield catchments containing wetlands and lakes (Figure 7). The Zero and First Order catchments and Bedrock Plot runoff exhibit low average MeHg concentrations, similar to the average concentration in wet deposition at the ELA (0.05 $\pm$ 0.013 ng L^{-1}) and runoff from the much larger Lake Outflow catchment. Average Forest Plot MeHg concen-

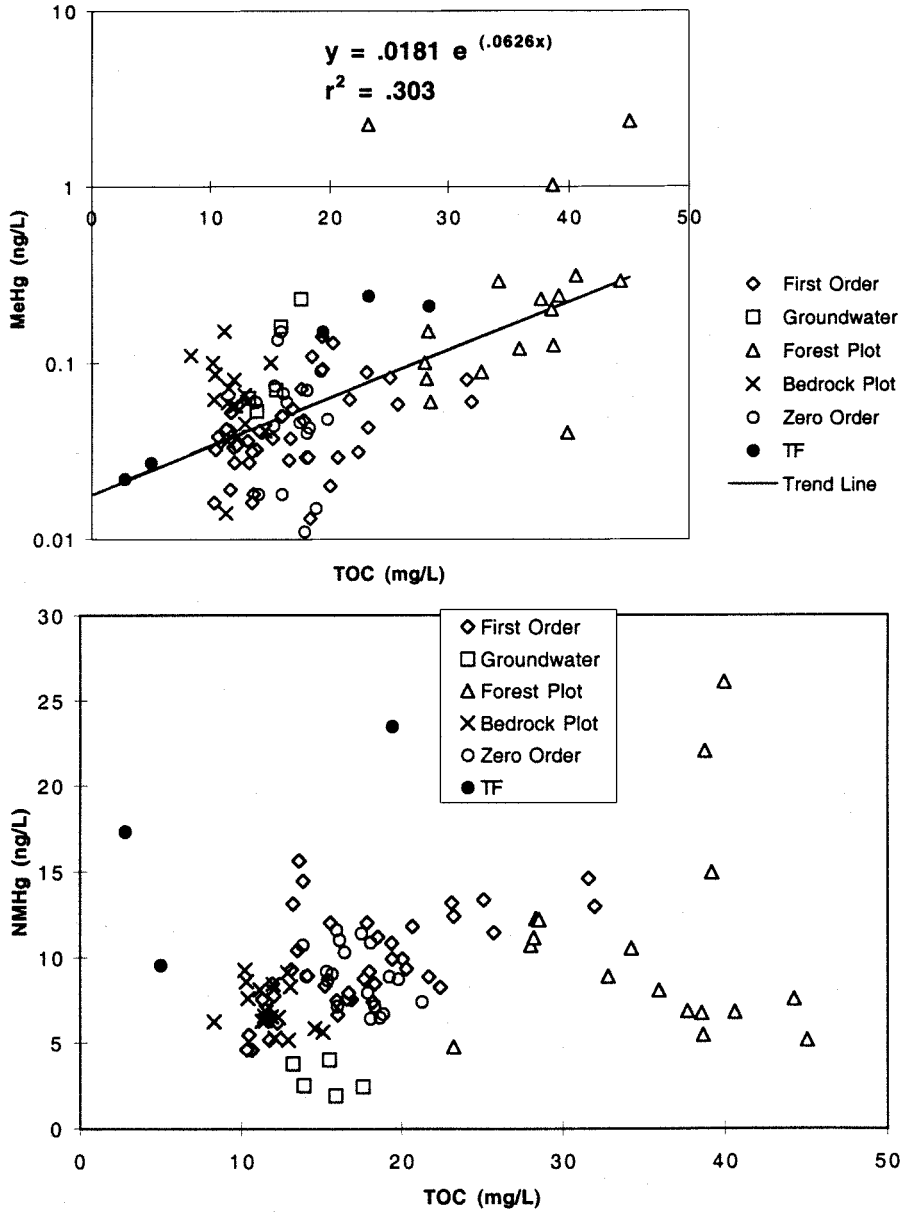

Figure 6(a)–(b). Relationship between TOC and MeHg (6(a)) and TOC and NMHg (6(b)) in Bedrock Plot, Forest Plot, Zero Order and First Order catchment runoff waters, Zero Order catchment groundwater (Groundwater) and Throughfall (TF).

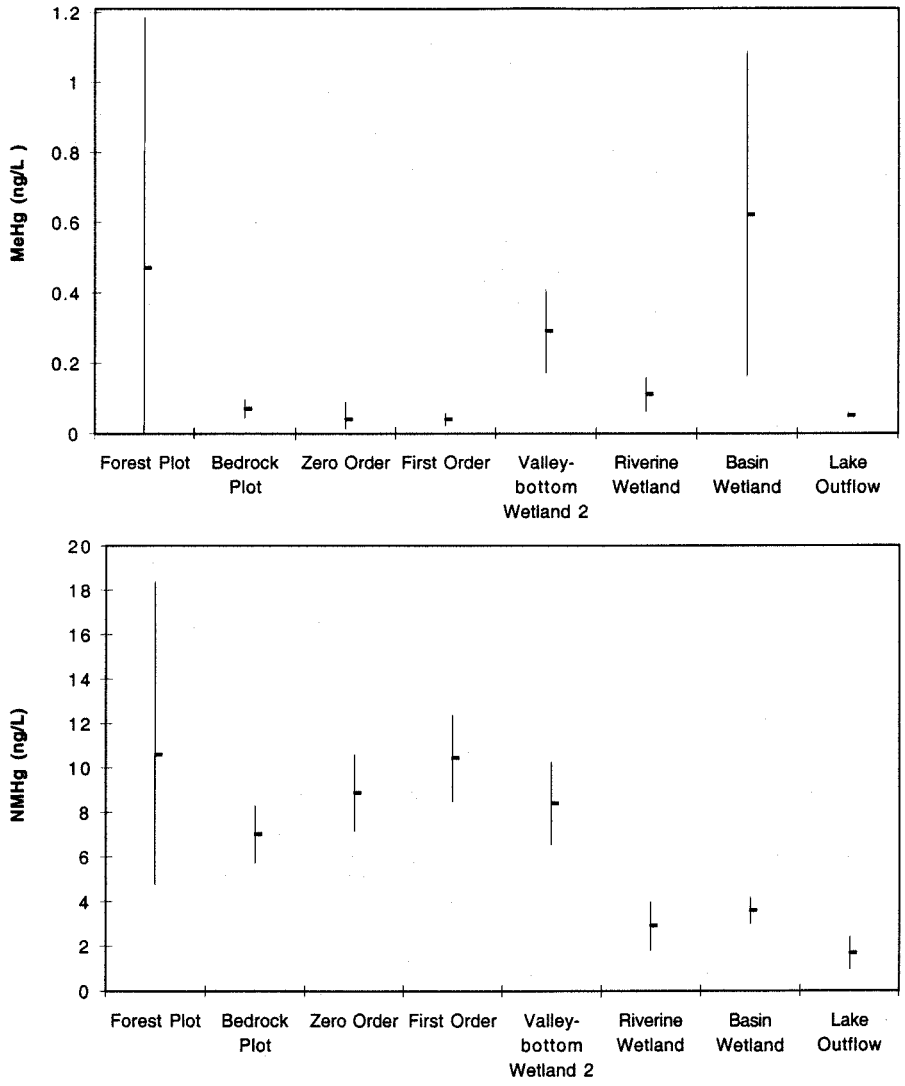

Figure 7(a)–(b). Average and standard deviation of MeHg concentrations (7(a)) and NMHg concentrations (7(b)) in runoff waters from various Precambrian Shield watersheds at the ELA. Data for the First Order Watershed, Valley Bottom Wetland 2 (55.3 ha), Riverine Wetland (98.1 ha), Basin Wetland (40.2 ha) and Lake Outflow (723 ha) are taken from the study of St. Louis et al. (1996).

trations are similar to the Basin and the Valley-bottom Wetland catchments, both of which are identified as sources of MeHg (St. Louis et al. 1996). The Riverine Wetland is also reported to be a net source of MeHg but its runoff concentrations are diluted by runoff from the Lake Outflow catchment. The variability in MeHg concentrations in Forest Plot runoff is of similar magnitude to the Basin Wetland runoff and much higher than that exhibited by the other watersheds. Possible explanations for this high variability include a combination of spatial and temporal variability in the rates of MeHg production and the mobilization of MeHg by changing hydrologic flow paths and contributing areas during episodic runoff events (Branfireun et al. 1996). Average NMHg concentrations were similar between the upland catchments and the Valley-bottom Wetland (which is dominated by upland runoff), with the Forest Plot again exhibiting the greatest variability in runoff concentrations. NMHg concentrations in Riverine and Basin Wetland and Lake Outflow runoff were significantly lower.

An annual waterborne export of Hg from the Precambrian Shield upland terrain may be estimated by multiplying the annual zero order runoff coefficients reported by Allan and Roulet (1994), 0.3 to 0.66, with the annual precipitation at the ELA 678 mm, and the mean volume weighted Hg concentrations from this study. This results in annual MeHg yields of 132 μg ha^{-1} to 291 μg ha^{-1} (Bedrock Plot), 488 μg ha^{-1} to 1,074 μg ha^{-1} (Forest Plot) and 122 μg ha^{-1} to 268 μg ha^{-1} (Zero Order catchment). Repeating this calculation for NMHg results in annual yields of 12.9 mg ha^{-1} to 28.5 mg ha^{-1}, 18.3 mg ha^{-1} to 40.3 mg ha^{-1} and 17.2 mg ha^{-1} to 37.8 mg ha^{-1}, for the same catchments. This compares to reported annual MeHg yields of 70 μg ha^{-1} to 90 μg ha^{-1} for the First Order catchment and 110 ug ha^{-1} to 2,500 μg ha^{-1} for Precambrian Shield catchments containing wetlands (St. Louis et al. 1996). NMHg runoff fluxes of 9.93 mg ha^{-1} to 19.9 mg ha^{-1} for the upland First Order catchment and 3.39 mg ha^{-1} to 33.1 mg ha^{-1} for larger catchments containing wetlands are reported. Clearly, areas of non channelized Precambrian Shield drainage can provide significant inputs of both MeHg and NMHg to wetland and aquatic systems where these areas comprise a significant portion of the upland terrain.

Conclusions

Considerable variability exists in the net export of Hg from small areas of unchannelized drainage in the upland Precambrian Shield terrain. Wet deposition and the washoff of Hg from forest canopy and lichen-bedrock surfaces are net sources of Hg appearing in runoff during episodic hydrologic events. Both MeHg and NMHg are strongly retained in forest soils although

in situ production of MeHg may occur in upland soils prone to periodic reducing conditions, thus allowing the establishment of the anoxic conditions conductive to Hg methylation. In general, MeHg concentrations are more variable than NMHg concentrations in episodic runoff and this variability should be taken into account in the construction of annual mass balance estimates. Most often concentrations of both Hg species declined after the first period of flow, although maximum concentration coincident with peak flow (MeHg) and recession flows (NMHg), were also observed. Much of the temporal variability in Hg concentrations observed in this study is likely the result of temporal variations in the contribution of runoff from different landscape units within these low order catchments. A positive exponential correlation was found between TOC and MeHg concentrations, but this relationship is not evident when low order catchments are considered on their own, only becoming apparent when several catchments encompassing a range of TOC concentrations are examined. We do not observe a strong relationship between NMHg runoff concentrations and organic carbon that has been reported in previous studies in Precambrian Shield terrain (Mierle 1985). A more significant relationship between Hg and organic carbon transport may exist if DOC or some fraction of DOC and Hg concentrations is compared rather than total values (Benoit 1995; Petterson et al. 1995). Given the high runoff fluxes and possible *in situ* production of MeHg, unchannelized runoff from upland Precambrian Shield terrain can represent a significant source of both MeHg and NMHg to downstream aquatic and wetland systems.

Acknowledgments

The authors wish to thank S. Majewski, E. Mewhinney, B. Branfireun, J-J. Dogoua and K. Savage for assisting with the ultra clean field sampling procedures. Funding for the project was provided by a University of North Carolina at Charlotte Faculty Research Grant to C. Allan; a National Science and Engineering Research Council (NSERC) grant to N. Roulet; and research grants from Manitoba, Quebec and Ontario Hydro to J. Rudd. R. Flett and B. Gooding of Flett Research, Winnipeg, Manitoba, provided analytic and technical support. K. Beaty and M. Lyng, DFO, Winnipeg provided hydrologic data from the First Order catchment. Logistics support was provided by the Dept. of Fisheries and Oceans through the Freshwater Institute and Experimental Lakes Area. This manuscript is number 35 in the Experimental Lakes Area Reservoir Project (ELARP) series.

References

Aastrup M, Johnson J, Bringmark E, Bringmark I & Iverfeldt A (1991) Occurrence and transport of mercury within a small catchment area. Water, Air Soil Pollut. 56: 155–167

Allan CJ & Heyes A (1998) A preliminary assessment of wet deposition and episodic transport of total and methyl mercury from low order Blue Ridge watersheds S.E. USA. Water, Air and Soil Pollut. 105: 573–592

Allan CJ & Roulet NT (1994) Runoff generation in zero-order Precambrian Shield catchments: the stormflow response of a heterogeneous landscape. Hydrol. Proc. 8: 369–388

Allan CJ, Roulet NT & Hill AR (1993) The biogeochemistry of pristine, headwater Precambrian shield watersheds: an analysis of material transport within a heterogeneous landscape. Biogeochem. 22: 37–79

Babiarz CL, Hurly JP, Benoit JM, Shafer MM, Anden AW & Webb DA (1998) Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds. Biogeochem. 41: 237–257

Beaty KG (1984) Hydrometeorological Data for the Experimental Lakes Area, Nothrwestern Ontario, 1979 to 1981. Can. Data Rept. Fish. Aquat. Sci. 480: v + 146 p

Beaty KG & Lyng ME (1989) Hydrometeoiological Data for the Experimental Lakes Area, Northwestern Ontario, 1982 to 1987. Can. Data Rept. Fish. Aquat. Sci. 759: v + 280 p

Benoit G (1995) Evidence of the particle concentration effect for lead and other metals in fresh waters based on ultraclean technique analyses. Geochem. Cosmo. Acta, 59(13): 2677–2687

Bishop K, Lee Y-H, Petterson C & Allard B (1995a) Methlmercury in runoff from the Svarhberget catchment in northern Sweden during stormfolw. Water, Air Soil Pollut. 80: 221–224

Bishop K, Lee Y-H, Petterson C & Allard B (1995b) Terrestrial sources of methylmercury in surface waters the importance of the riparian zone on the Svartberget catchment. Water, Air Soil Pollut. 80: 435–444

Bishop K, Lee Y-H, Petterson C & Allard B (1995c) Methylmercury output from the Svartberget catchment in northern Sweden during the spring flood. Water, Air Soil Pollut. 80: 445–454

Bloom NS (1989) Determination of picogram levels of mehtyl mercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. Can. J. Fish. Aquat. Sci. 46: 1131–1140

Bloom NS & Fitzgerald WF (1988) Determination of volatile of mercury species at the picogram levels by low temperature gas chromatography with cold vapour atomic fluorescence detection. Anal. Chimica Acta 208: 151–161

Branfireun BA, Heyes A & Roulet NT (1996) The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland. Water Resour. Res. 32(6): 1785–1794

Brunskill GJ & Schindler DW (1971) Geography and bathymetry of selected lake basins, Experimental Lakes area, norhtwestern Ontario. J. Fish. Res. Board Can. 28: 139–155

Devito KJ, Dillon PJ & LaZerte BD (1989) Phosphorus and nitrogen retention in five Precambrian shield watersheds. Biogeochem. 8: 185–204

Driscoll CT. Yan C, Schofield CL, Munson R & Hopsapple J (1994) The chemistry and bioavailability of mercury in remote Adirondack lakes. Environ. Sci. Technol. 28: 136–143

Driscoll CT, Fuller RD & Simone DM (1998) Longitudinal variations in trace metal concentrations in a northern forested ecosystem. J. Environ. Qual. 17: 101–107

Facemire C, Augspuger T, Bateman D, Brim M, Conzelmann P, Delchamps S, Douglas E, Inmon L, Looney K, Lopez F., Masson G, Morrison D., Morse N & Roninson A (1995)

Impacts of mercury contamination in the southeastern United States. Water, Air Soil Pollut. 80: 923–926

Fleming LE, Watkins S, Kaderman R, Levin B, Ayyar DR, Bizzio M, Stephens D & Bean Ja (1995) Mercury exposure in humans through food consumption in the Florida everglades. Water, Air Soil Pollut. 80: 41–48

Gilmour CC, Riedel GS, Ederington MC, Bell JT, Benoit JM, Gill GA & Stordal MC (1998) Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochem. 40: 227–247

Hakanson L. Anderson T & Nilsson A (1990) Mercury in fish in Swedish lakes – Linkages to domestic and European sources of emission. Water, Air Soil Pollut. 50: 171–191

Heyes A., Moore TR & Rudd JWM (1998) Mercury and Methylmercury in decomposing vegetation of a pristine and impounded wetland. J. of Environ. Qual. 27: 591–599

Horvat M, Bloom NS & Liang L (1993) Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Anal. Chimica Acta, 281: 135–152

Hurley JP, Benoit JM, Babiarz CL, Shafer MM, Andren AW, Sullivan JR, Hammond R & Webb DA (1995) Influences of watershed characteristics on mercury levels in Wisconsin rivers. Environ. Sci. Technol. 29: 1867–1873

Hurley JP, Cowell SE, Shafer MM & Hughes PE (1998) Partitioning and transport of total and methyl mercury in the lower Fox River, Wisconsin. Environ. Sci. Technol. 32: 1424–1432

Krabbenhoft DP & Babiarz CL (1992) The role of groundwater transport in aquatic mercury cycling. Wat. Resour. Res. 28(12): 3119–3128

Krabbenhoft DP, Benoit JM, Babiarz CL, Hurley JP & Andren AW (1995) Mercury cycling in the Allequash Creek watershed, northern Wisconsin. Water, Air Soil Pollut. 80: 425–433

LaBaugh JW & Winter TC (1984) The impact of uncertainties in hydrologic measurements in phosphorus budgets and empirical models for two Colorado reservoirs. Limnol. Oceabogr. 29: 322–339

LaZerte B, Evans D & Grauds P (1989) Deposition and transport of trace metals in an acidified catchment of central Ontario. Sci. Tot. Envir. 87/88: 209–221

Lee Y-H & Hultberg H (1990) Methylmercury in some Swedish surface waters. Environ Toxicol. Chem. 9: 833–841

Lee Y-H & Iverfeldt A (1991) Measurement of methylmercury and mercury in runoff, lake and rain waters. Water, Air Soil Pollut. 56: 309–321

Lee, Y-H, Bishop K, Pettersson C, Iverfeldt A & Allard B (1995) Subcatchment output of mercury and methylmercury at Svartberget in northern Sweden. Water, Air Soil Pollut. 80: 455–465

McDonnell,JJ, Bonell M, Stewart MK & Pearce AJ (1990) Deuterium variations in storm rainfall: implications for stream hydrograph separation. Wat. Resour. Res. 26(3): 455–458

Meili M (1991) The coupling of mercury and organic matter in the biogeochemical cycle – towards a mechanistic model for the boreal forest zone. Water, Air Soil Pollut.: 1–15

Mierle G (1990) Aqueous inputs of mercury of Precambrian shield lakes in Ontario. Environ. Toxicol. Chem. 9: 843–851

Mierle G & Ingram R (1991) The role of humic substances in the mobilization of mercury from watersheds. Water, Air Soil Pollut. 56: 309–317

Moore TR, Bubier JL, Heyes A & Flett RJ (1995) Methyl and total mercury in boreal wetland plants, Experimental Lakes Area Northwestern Ontario. J. Environ. Qual. 24: 845–850

Pettersson C, Bishop K, Lee Y-H & Allard B (1995) Relation between organic carbon and methylmercury in humic rich surface waters from Svartberget catchment in northern Sweden. Water, Air Soil Pollut. 80: 971–979

Rea AW, Keeler GJ & Scherbatskoy T (1996) the deposition of mercury in throughfall and litterfall in the Lake Champlain watershed: a short term study. Atmos. Environ. 30(19): 3257–3263

Rasmussen L (1986) Potential leaching of elements in three Danish spruce forest soils. Water Air Soil Pollut. 31: 377–383

Schindler DW, Newbury RW, Beaty KG, Prokopwhich J, Ruszynski T & Dalton JA (1980) Effects of windstorm and forest fire on chemical losses from forested watersheds and on the quality of receiving streams. Can. J. Fish. Aquat. Sci. 37: 328–334

Schuster E (1991) The behavior of mercury in the soil with special emphasis on complexation and adsorption processes – a review of the literature. Water, Air Soil Pollut. 56: 667–680

Sklash MG (1990) Environmental isotope studies of storm and snowmelt runoff generation. In Anderson MG & Burt TP (Eds) Process Studies in Hillslope Hydrology (pp 401–435). John Wiley & Sons Ltd. NY, NY

Sorenson JA, Glass GE, Schmidt RW, Huber JK & Rap GR (1990) Air borne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediment, plankton and fish of eight northern Minnesota lakes. Environ. Sci. Technol. 24: 1716–1724

St. Louis VL, Rudd JWM, Kelly CA, Beaty KG. Bloom NS & Flett RJ (1994) Importance of wetlands as sources of methylmercury to boreal forest ecosystems. Can. Fish. Aquat. Sci. 51: 1065–1076

St. Louis VL, Rudd JWM, Kelly CA & Barrie LA (1995) Wet deposition of methyl mercury in northwestern Ontario compared to other geographic locations. Wat. Air Soil Pollut. 80: 405–414

St. Louis VL, Rudd JWM, Kelly CA, Beaty KG, Flett RJ & Roulet NT (1996) Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. Environ. Sci. Technol. 30: 2719–2729

Stainton MP, Capel MJ & Bauman FAJ (1974) The chemical analysis of freshwater. Fish. Res. Board Can. Spec. Publ. 25: 125 p

Veissman W Jr, Lewis GL & Knapp JW (1989) Introduction to Hydrology. 3rd Ed., Harper and Row Publ., N.Y., N.Y. 780 p

Wells C, Cornett RJ & LaZerte BD (1990) Groundwater and wetland contribution to stream acidification: an isotopic analysis. Wat. Resour. Res. 26(12): 2993–3003

Wheatly B & Paradis S (1995) Exposure of Canadian Aboriginal people to methylmercury. Water, Air Soil Pollut. 8: 3–11