

## MERCURY TRANSPORT IN A HIGH-ELEVATION WATERSHED IN ROCKY MOUNTAIN NATIONAL PARK, COLORADO

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**Abstract.** Mercury (Hg) was measured in stream water and precipitation in the Loch Vale watershed in Rocky Mountain National Park, Colorado, during 2001–2002 to investigate processes controlling Hg transport in high-elevation ecosystems. Total Hg concentrations in precipitation ranged from 2.6 to 36.2 ng/L and showed a strong seasonal pattern with concentrations that were 3 to 4 times higher during summer months. Annual bulk deposition of Hg was 8.3 to 12.4  $\mu\text{g}/\text{m}^2$  and was similar to deposition rates in the Midwestern and Northeastern U.S. Total Hg concentrations in streams ranged from 0.8 to 13.5 ng/L and were highest in mid-May on the rising limb of the snowmelt hydrograph. Stream-water Hg was positively correlated with dissolved organic carbon suggesting organically complexed Hg was flushed into streams from near-surface soil horizons during the early stages of snowmelt. Methylmercury (MeHg) in stream water peaked at 0.048 ng/L just prior to peak snowmelt but was at or below detection ( $<0.040$  ng/L) for the remainder of the snowmelt season. Annual export of total Hg in Loch Vale streams ranged from 1.2 to 2.3  $\mu\text{g}/\text{m}^2$ , which was less than 20% of wet deposition, indicating the terrestrial environment is a net sink of atmospheric Hg. Concentrations of MeHg in stream water and corresponding watershed fluxes were low, indicating low methylation rates or high demethylation rates or both.

**Keywords:** alpine, atmospheric deposition, dissolved organic carbon, mercury, methylmercury, snowmelt, subalpine, watershed budget

### 1. Introduction

Mercury (Hg) is released to the environment primarily from anthropogenic sources (burning of fossil fuels and wastes) and is transported to most aquatic ecosystems via atmospheric pathways (USEPA, 1997). Investigations in North America have reported high levels of Hg in fish even in remote lakes, implying regional or even global sources for the Hg reaching these lakes (Swain *et al.*, 1992). Long-range transport of Hg also is supported by evidence of elevated Hg concentrations in lake-sediment cores collected from remote areas. In a sub-Arctic region of Canada, Hg concentrations were elevated above preindustrial levels in sediment from lakes located 200 to 1,400 km away from the closest industrial centers (Lucotte *et al.*,

1995). Using age-dated sediment cores from remote lakes in the upper Midwest, Swain *et al.* (1992) estimated that Hg accumulation in lake sediments has increased by a factor of 3.7 compared to preindustrial times due to increased loadings from atmospheric deposition. Similar results were found in eight remote lakes in the Adirondack Mountains where the ratio of modern Hg flux to preindustrial Hg flux to lake sediments averaged 3.5 (Lorey and Driscoll, 1998).

Although atmospheric deposition is the dominant source of Hg to remote lakes, other factors typically are more important in controlling Hg transport and MeHg production within aquatic ecosystems. Recent studies suggest that transport of total Hg in mountainous or high-relief watersheds often occurs during high-flow events and is associated with the movement of organic matter (Bishop *et al.*, 1995; Lee *et al.*, 1995; Branfireun *et al.*, 1996; Allan and Heyes, 1998; Scherbatskoy *et al.*, 1998; Shanley *et al.*, 2002). In a forested headwater stream in Vermont, the dominant mechanism of Hg transport was episodic export of dissolved and particulate Hg during snowmelt (Shanley *et al.*, 2002). The authors attributed the transport to flushing of the soil organic horizon by meltwater and to soil and streambank erosion. A preliminary assessment of Hg budgets at a forested upland watershed in the Blue Ridge Mountains determined that as much as 40% of the annual Hg export occurred during episodic runoff events in summer (Allan and Heyes, 1998). Lee *et al.* (1995) observed increases in total Hg concentrations with flow during spring snowmelt and summer rain events in forested watersheds in Sweden; the largest monthly output of total Hg occurred during spring snowmelt. In contrast, for low-relief watersheds, where high-flow events are less frequent, base-flow conditions regulate Hg fluxes and much lower yield rates are observed (Krabbenhoft *et al.*, 1995).

Methylmercury (MeHg), the most toxic and bio-accumulative form of Hg, is primarily produced within watersheds by bacterial transformation of inorganic Hg to MeHg (Krabbenhoft *et al.*, 2002; Weiner *et al.*, 2003). In remote ecosystems, surface-water concentrations of MeHg appear to be controlled largely by watershed characteristics (Bowles *et al.*, 2003). Greater production of MeHg typically occurs in watersheds with a high percentage of wetlands (St. Louis *et al.*, 1994; Kolka *et al.*, 1999a; Bowles *et al.*, 2003), low pH or low alkalinity (Wiener *et al.*, 2003), and a high ratio of watershed area to lake area (Hurley *et al.*, 1995). Lakes that exhibit anoxic conditions during stratification have been reported to have higher MeHg concentrations than lakes that do not develop anoxic conditions (Driscoll *et al.*, 1995). Oligotrophic surface waters that have low pH and alkalinity also appear to have higher rates of MeHg production (Wiener *et al.*, 2003).

Although Hg contamination has been documented at remote sites in the Eastern U.S. and Canada, relatively little is known about Hg in aquatic ecosystems of the Rocky Mountains, particularly those at high elevations. Mercury deposition may be enhanced in high-elevation areas because of high rates of precipitation in mountainous areas and the process of cold condensation, which causes volatile compounds such as organic contaminants and gaseous elemental Hg to migrate

towards colder areas at high elevation and latitude (Schindler, 1999; Susong *et al.*, 1999; National Park Service, 2002). Two recent studies used paleorecords to show that Hg deposition in the Rocky Mountains is elevated relative to background levels. Sediment cores from several alpine lakes in Colorado indicated that recent Hg accumulation rates in lake sediments were as much as 4 times greater than preindustrial rates (Manthorne, 2002). By using ice cores from a temperate glacier in Wyoming, Schuster *et al.* (2002) determined that Hg deposition in the northern Rocky Mountains peaked in the 1980s and was 20 times greater than during preindustrial times before 1840. Current rates of wet Hg deposition in the Rocky Mountains are measured at Buffalo Pass, Colorado, the only high-elevation station in the Mercury Deposition Network (<http://nadp.sws.uiuc.edu/mdn/>). Deposition at Buffalo Pass is similar in magnitude to areas in the Midwest and Northeast where fish-consumption advisories are common (about  $10.8 \mu\text{g}/\text{m}^2/\text{yr}$ ).

Despite indications that Hg deposition may be elevated in the Rocky Mountains, to date there have been only two studies of Hg in high-elevation aquatic ecosystems. Watras *et al.* (1995b) measured Hg in remote lakes in Glacier National Park in Montana and compared them to remote lakes in northern Wisconsin and in the Adirondack Mountains of New York. The authors found that although total Hg concentrations in Glacier were similar to lakes in the other regions, MeHg concentrations were lower in Glacier because of lower rates of MeHg production. More recently, Hg concentrations were reported for 90 high-elevation lakes in 8 National Parks in the Western U.S. (Krabbenhoft *et al.*, 2002). Although concentrations were low, there was a positive correlation between total Hg and MeHg concentrations suggesting that atmospheric deposition is an important factor controlling Hg concentrations in high-elevation lakes. In the same study, Krabbenhoft *et al.* (2002) studied MeHg dynamics in a small subalpine lake and observed elevated rates of photo-demethylation in the lake because of high water clarity and high incident UV-sunlight exposure.

In 2001, the U.S Geological Survey (USGS) began work in the Loch Vale watershed in Rocky Mountain National Park to investigate Hg cycling in a high-elevation watershed. As well as could be determined, this is the first watershed-scale study of Hg in a mountainous area of the Western U.S. Total Hg concentrations in snowpack and in summer precipitation were measured in 2002, dissolved and particulate Hg concentrations in stream water were measured at Andrews Creek and Glacier Creek in 2001, and total Hg and MeHg concentrations were measured at the outlet of The Loch in 2002 (Figure 1). The objectives of the study were to (1) determine seasonal variations in and the magnitude of Hg deposited from the atmosphere, (2) describe temporal variations in stream-water Hg and MeHg concentrations during snowmelt, (3) investigate processes controlling Hg transport in snowmelt-dominated streams, and (4) calculate preliminary Hg budgets for a high-elevation watershed. A better understanding of the processes that control Hg transport in high-elevation streams is important for assessing the potential for Hg contamination in mountain ecosystems.

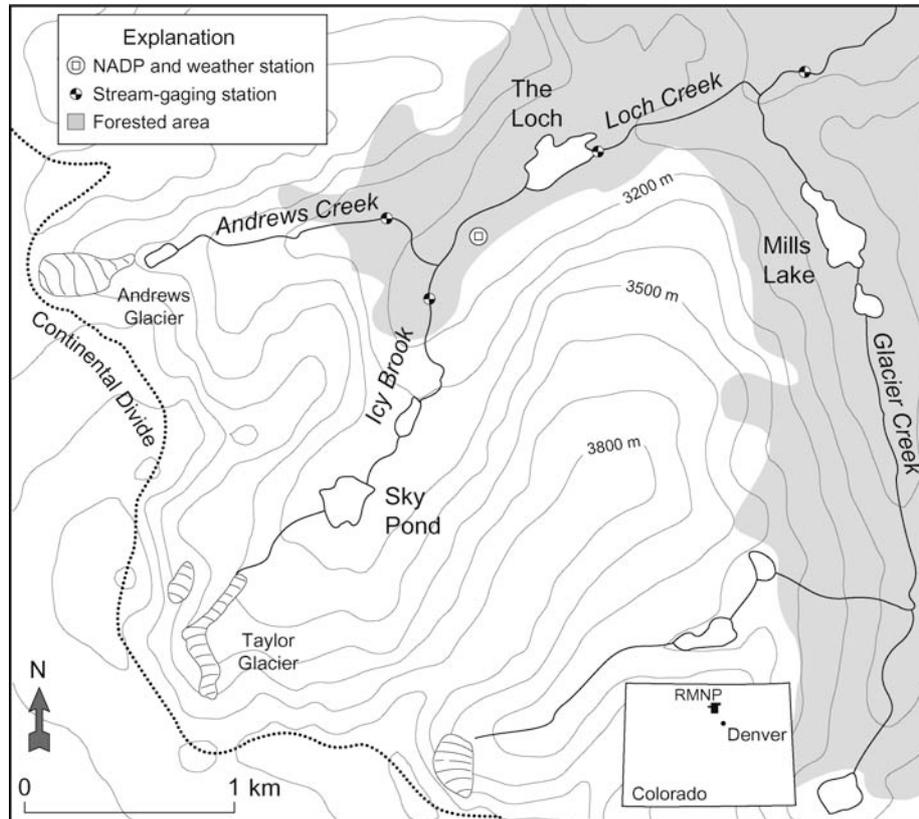


Figure 1. Loch Vale watershed in Rocky Mountain National Park (RMNP) showing location of stream gages, the National Atmospheric Deposition Network (NADP) station, and the main Loch Vale weather station.

## 2. Study Area

The Loch Vale watershed is in Rocky Mountain National Park in the Front Range of Colorado approximately 80 km northwest of Denver, Colorado (Figure 1). Loch Vale watershed has been a site of ecosystem research by the National Park Service since 1981 (<http://www.nrel.colostate.edu/projects/lvws/pages/homepage.htm>) and has been part of the Water Energy and Biogeochemical Budgets program of the USGS since 1992 (<http://water.usgs.gov/webb/>). Climate in Loch Vale is characterized by long, cold winters and a short growing season. Average annual air temperature is 0°C. The watershed is primarily alpine in character and ranges in elevation from 3,000 m to just over 4,000 m along the Continental Divide. Most of the watershed is above treeline and consists of bare rock cliffs, talus and debris slopes, and alpine tundra (Baron, 1992). The lower part of the watershed is covered by an Engelmann spruce-subalpine fir forest with wet-sedge wetlands along the

TABLE I  
 Characteristics of stream sampling sites in Loch Vale

Stream site	Gage elevation (m)	Basin area (ha)	Forest cover (%)	Wetland cover (%)	2001 runoff (cm)	2002 runoff (cm)	Hg sampling period
Andrews Creek	3,215	179	3	1	91	60	2001
The Loch Outlet	3,109	695	12	3	67	44	2002
Glacier Creek	2,969	1,992	22	2	58	— <sup>a</sup>	2001

<sup>a</sup>Not measured in 2002.

stream channels. Bedrock consists of Precambrian gneiss and granite composed of quartz, feldspar, biotite, and sillimanite. Soils in the watershed are formed in till and talus and are primarily Inceptisols and Entisols in alpine areas that grade into Alfisols in forested areas along the valley floor. Soils are thin (20 to 50 cm), have poorly developed soil horizons, and contain high amounts of coarse fragments (Baron, 1992). Stream water at Loch Vale is very dilute and poorly buffered ( $ANC < 50 \mu\text{eq/L}$ ) because of the combination of granitic bedrock and thin, rocky soils.

Precipitation amounts have been measured since 1984 at the Loch Vale National Atmospheric Deposition Network (NADP) station, which is adjacent to the main Loch Vale weather station at an elevation of 3,159 m (Figure 1). The USGS has operated stream gages on Andrews Creek and Icy Brook, the two main tributary streams in the watershed since 1992, and at the outlet of The Loch since 1982. A temporary stream gage was operated on Glacier Creek just downstream from the confluence with Loch Creek in 2000 and 2001. Characteristics of stream sites sampled for this study are summarized in Table I.

For the Loch Vale watershed, runoff from snowmelt constitutes the major hydrologic event each year. Peak flow typically occurs in June, and 70% of the total discharge occurs during May, June, and July. Average annual precipitation at the Loch Vale NADP station was 105 cm from 1984 to 2002, and average annual runoff at The Loch outlet was 75 cm from 1984 to 2002. During the study period, annual precipitation at the Loch Vale NADP station was 97 cm in 2001 and 65 cm in 2002, which was the driest year on record. Annual runoff at the Loch Outlet during the study period was 67 cm in 2001 and 44 cm in 2002. Runoff in 2002 was 59% of the average, reflecting the drought conditions that prevailed in many parts of Colorado during 2002.

### 3. Methods

Bulk deposition was collected in Loch Vale during 2002 to quantify atmospheric deposition of Hg to the watershed. To estimate winter deposition, two full-depth

snowpack samples were collected during April 2002 just prior to the onset of snowmelt. Depth-integrated samples were collected from the freshly exposed face of a snowpit and put into 4-L, precleaned, Teflon bags using polycarbonate shovels according to methods described by Ingersoll *et al.* (2002). The Teflon bags were sealed with plastic ties, wrapped in polyethylene bags for protection, and transported to a freezer where they were stored for as long as 6 weeks prior to processing. During processing, samples were melted at room temperature in the sealed Teflon bags over a 24-hour period. Unfiltered aliquots of the melted samples were pumped from the Teflon bag with Teflon tubing into thermoplastic polyester (PETG) bottles and acidified with 10 mL of ultrapure 6 N hydrochloric acid per liter of sample.

To estimate summer deposition, a bulk collector was operated in an open area near the Loch Vale NADP station from June through October 2002. The collector consisted of a precleaned polycarbonate funnel connected to a PETG collection bottle with Teflon tubing (looped to minimize evaporation) similar to the system described by Landing *et al.* (1998). Prior to installation, all components of the bulk collector were cleaned by soaking in 10% ultrapure hydrochloric acid for 24 hours, rinsed six times with deionized water, and packaged in plastic bags for transport to the field. The polycarbonate funnel and Teflon tubing were replaced monthly with clean equipment, and the PETG collection bottle was replaced weekly whether or not it contained measurable precipitation. Unfiltered weekly composite samples were returned to the laboratory and preserved in the PETG bottles with 10 mL of ultrapure 50% hydrochloric acid per liter of sample within 12 hours. Rain and snow samples were shipped to the USGS Hg laboratory in Madison, Wisconsin (<http://infotrek.er.usgs.gov/Hg/>), where they were analyzed for total Hg according to methods described in Olson and DeWild (1999). The analytical method has a precision of  $\pm 10\%$  and an analytical detection limit of 0.04 ng/L.

Field blanks were collected to assess potential contamination of precipitation samples by collection, processing, and cleaning procedures. Field blanks were collected during the summer months by pouring 1 L of Hg-free blank water through a clean precipitation collector installed at the sampling site. During winter, blank water was poured over the polycarbonate shovel into a Teflon bag. The equipment blanks had Hg concentrations at or below the analytical detection limit indicating the potential for contamination during sample collection and processing was minimal.

During 2001, stream samples were collected at the Andrews Creek and Glacier Creek gaging stations (Figure 1). Grab samples were collected on a weekly schedule during snowmelt and less frequently during low-flow periods of the year. Grab samples were collected rather than integrated (isokinetic) samples to minimize the potential for sample contamination (Lewis *et al.*, 2004). Because the streams in Loch Vale are small and well mixed, grab samples should be representative of the entire stream cross section. Due to the inaccessibility of the sites (4-km foot trail), samples were collected in 1-L Teflon holding bottles and returned to the laboratory for processing, generally within 6 hours of collection. Aliquots for total dissolved Hg were filtered through 0.45- $\mu\text{m}$  polycarbonate filters into acid-washed

glass bottles and preserved with a solution of nitric acid and potassium dichromate. The filter membranes were placed in glass bottles and leached with the dichromate preservative for total particulate Hg. Dissolved and particulate samples were analyzed for total Hg at a USGS research laboratory in Boulder, Colorado, by cold vapor atomic fluorescence spectrophotometry. The method has a precision of  $\pm 10\%$  and a detection limit of 0.4 ng/L (Roth, 1994).

In 2002, stream samples were collected at the outlet of The Loch on a similar sampling schedule to 2001. Unfiltered samples were collected in 1-L PETG bottles and acidified with ultrapure 50% hydrochloric acid within 12 hours of collection. Samples were shipped to the USGS Mercury Laboratory in Madison, Wisconsin, and analyzed for total Hg (discussed above) and MeHg in unfiltered samples. The method for MeHg, which is described in DeWild *et al.* (2002), has a precision of  $\pm 10\text{--}15\%$  and a detection limit of 0.04 ng/L.

Samples for major dissolved constituents and dissolved organic carbon (DOC) also were collected with each Hg sample in 2001 and 2002. Samples were filtered through 0.45- $\mu\text{m}$  capsule filters and analyzed at the Colorado District USGS laboratory according to standard USGS methods (Fishman *et al.*, 1989). In 2001, an additional 1-L aliquot was filtered through a 0.7- $\mu\text{m}$ , prebaked, glass-fiber filter, and the filtrate was retained for particulate organic carbon (POC) analysis at the Chesapeake Biological Laboratory in Solomons, Maryland (<http://www.cbl.umces.edu/nasl/index.htm>).

## 4. Results and Discussion

### 4.1. MERCURY IN ATMOSPHERIC DEPOSITION

Total Hg concentrations and fluxes in precipitation at Loch Vale and the Buffalo Pass Mercury Deposition Network (MDN) station for 2001 and 2002 are summarized in Table II. Data from Buffalo Pass are included for comparison because it is the closest MDN station to Loch Vale (approximately 90 km to the west) and the only station in the network situated at a similar elevation (3,234 m). Concentrations of total Hg in weekly precipitation samples at Loch Vale ranged from 2.6 to 36.2 ng/L and were similar to the range of 1.8 to 26.8 ng/L reported for weekly samples collected at the Buffalo Pass MDN station. Mercury concentrations in precipitation at both these sites had similar seasonal patterns with concentrations that were 3 to 4 times higher during summer months (Table II). Similar seasonality in Hg concentrations in precipitation is observed at many locations throughout the U.S. (Scherbatskoy, *et al.*, 1998; Glass and Sorensen, 1999; Guentzel *et al.*, 2001; Mason *et al.*, 2000). Higher concentrations in summer have been attributed to more efficient scavenging of particulates by rain compared to snow (Glass and Sorensen, 1999) or to seasonal changes in levels of reactive gaseous Hg in the atmosphere (Guentzel *et al.*, 2001). The volume-weighted mean (VWM) summer concentration in Loch

TABLE II

Volume-weighted mean (VWM) concentrations and deposition rates of total Hg in precipitation at Loch Vale and Buffalo Pass during 2001 and 2002. Winter defined as November through April and summer as May through October

Site	Year	Season	VWM concentration (ng/L)	Precipitation amount (cm)	Mercury deposition ( $\mu\text{g}/\text{m}^2$ )	Deposition in summer (%)
Loch Vale	2001	Winter	–	54	–	
	2001	Summer	–	43	–	
	2001	Annual	12.8 <sup>a</sup>	97	12.4	
Loch Vale	2002	Winter	4.6	34	1.6	
	2002	Summer	21.6	31	6.7	
	2002	Annual	12.8	65	8.3	81
Buffalo Pass	2001	Winter	5.0	69	3.5	
	2001	Summer	11.9	30	3.6	
	2001	Annual	7.1	99	7.1	50
Buffalo Pass	2002	Winter	4.5	55	2.5	
	2002	Summer	10.7	33	3.5	
	2002	Annual	6.8	88	6.0	58

<sup>a</sup>Estimated from Hg concentrations measured in Loch Vale in 2002.

Vale in 2002 was 21.6 ng/L (May through October). Snowpack samples collected in Loch Vale during April 2002 had an average concentration of 4.6 ng/L. Because the snowpack was sampled just prior to the onset of snowmelt, the samples should represent net Hg deposition to the watershed during the winter period (November through April). VWM concentrations of Hg at Buffalo Pass in 2002 were 10.7 ng/L during summer and 4.5 ng/L during winter. Although VWM concentrations were similar during winter, summer concentrations in Loch Vale (21.6 ng/L) were twice as high as at Buffalo Pass (10.7 ng/L). One possible explanation is that the Loch Vale samples represent bulk deposition whereas the MDN collector captures wet deposition only. The higher VWM concentration at the Loch also may result from lower amounts of precipitation in Loch Vale during 2002 because of the drought. For example, summer precipitation amounts were 68% of average at Loch Vale in 2002 compared to 94% of average at Buffalo Pass.

Estimates of atmospheric deposition of total Hg in Loch Vale and Buffalo Pass during 2001 and 2002 are listed in Table II. Multiplying the annual VWM Hg concentration by the annual precipitation amount yields an annual Hg deposition of 12.4  $\mu\text{g}/\text{m}^2$  in 2001 and 8.3  $\mu\text{g}/\text{m}^2$  in 2002 at Loch Vale. Mercury deposition in 2001 was estimated by using the annual VWM Hg concentration from Loch Vale in 2002. Deposition during the summer period (May through October) was 6.7  $\mu\text{g}/\text{m}^2$  in 2002 and accounted for about 80% of the annual Hg deposition in Loch Vale. Annual Hg deposition at Buffalo Pass was slightly lower with 7.1  $\mu\text{g}/\text{m}^2$  in 2001

and  $6.0 \mu\text{g}/\text{m}^2$  in 2002. Compared to Loch Vale, deposition at Buffalo Pass was comparatively uniform during the year because concentrations were not as high as in summer rain and precipitation amount during winter was greater. The estimates of total Hg deposition at Loch Vale and at Buffalo Pass may be somewhat low because they do not account for dry deposition of aerosols (particulate Hg) and reactive gaseous Hg (mostly monomeric, gaseous mercuric chloride) to the canopy or for foliar uptake of Hg vapor from the atmosphere (Lindberg *et al.*, 1991). In forested areas, annual inputs of Hg from dry deposition may be as much as 50–100% of wet deposition (Iverfeldt, 1991, 1995; Kolka *et al.*, 1999b).

Annual Hg deposition at Loch Vale and Buffalo Pass is at the middle of the range of deposition rates reported for other sites across the U.S. Wet-deposition rates measured by the MDN range from  $2.1 \mu\text{g}/\text{m}^2$  on the west coast of California to  $18.7 \mu\text{g}/\text{m}^2$  in south Florida (<http://nadp.sws.uiuc.edu/mdn/>). Mercury deposition in Loch Vale is similar to measurements of wet Hg deposition in the Great Lakes region ( $4.7$  to  $10.4 \mu\text{g}/\text{m}^2$ ) and New England ( $4.1$  to  $8.0 \mu\text{g}/\text{m}^2$ ) where statewide fish-consumption advisories are common. These results suggest that Hg deposition rates in Loch Vale are high enough to be of concern depending on net methylation of Hg after it is deposited into aquatic ecosystems (Hurley *et al.*, 1995). The relatively high rates of deposition at Loch Vale and Buffalo Pass result from moderate Hg concentrations in precipitation combined with high rates of precipitation that are typical of high-elevation areas in the Rocky Mountains.

#### 4.2. TOTAL MERCURY AND ORGANIC CARBON CONCENTRATIONS IN STREAM WATER

Total Hg concentrations in stream water at all three stream sites in Loch Vale showed a peak in mid-May just prior to the peak snowmelt discharge. In Andrews Creek in 2001 (Figure 2), total dissolved Hg concentrations peaked on May 15 at  $5.3 \text{ ng}/\text{L}$  then decreased rapidly to less than  $2.0 \text{ ng}/\text{L}$  during the remainder of the snowmelt season. The seasonal pattern for total particulate Hg was similar to dissolved Hg with the peak concentration of  $8.2 \text{ ng}/\text{L}$  occurring on May 15. Concentrations of dissolved Hg were similar to particulate Hg prior to May 15, but were 2 to 5 times higher for the rest of snowmelt season indicating that most Hg in Andrews Creek is transported in the dissolved phase. The pattern at Glacier Creek in 2001 (Figure 3) was similar to Andrews Creek although peak dissolved and particulate Hg concentrations were slightly lower at  $3.0 \text{ ng}/\text{L}$  and  $3.6 \text{ ng}/\text{L}$ , respectively. At Glacier Creek, the peak particulate Hg concentration occurred 1 week prior to the peak dissolved Hg concentration unlike at Andrews Creek where peak dissolved and particulate Hg concentrations occurred on the same sampling date. Similar to Andrews Creek, dissolved Hg concentrations were 2 to 5 times greater than particulate Hg following the peak Hg concentration in mid-May. At both sites, concentrations were lowest during peak flow (early July) then increased

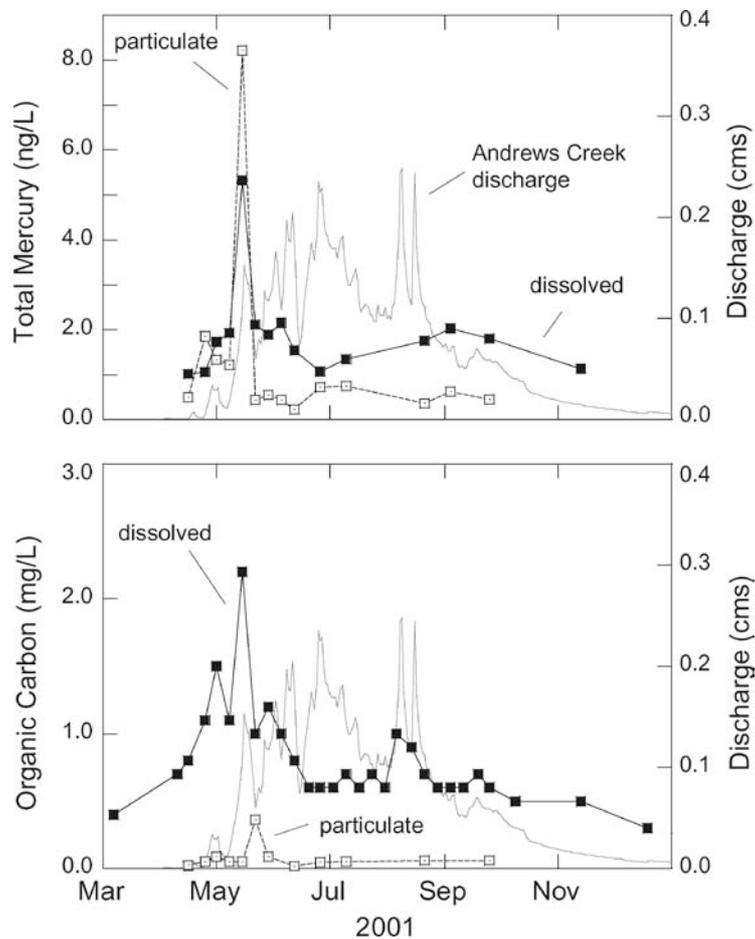


Figure 2. Total Hg and organic carbon concentrations at Andrews Creek, 2001.

gradually through late summer and fall perhaps due to several large rain events that increased discharge in late summer.

Total unfiltered (dissolved plus particulate) Hg at The Loch outlet in 2002 (Figure 4) showed a similar seasonal pattern to stream-water Hg in 2001. Total Hg concentrations peaked on May 21 at 3.5 ng/L then decreased rapidly to about 1.0 ng/L after the beginning of July. The slight increase in total Hg later in the summer in 2001 was not apparent at The Loch outlet in 2002 perhaps because of differences in runoff characteristics between 2001 and 2002. Total Hg concentrations in Loch Vale streams ranged from 0.83 to 13.5 ng/L and were similar to those reported for lower elevation headwater streams dominated by upland forests in the U.S. For example, total (dissolved plus particulate) Hg concentrations in stream water ranged from 1.1 to 80 ng/L at Nettle Brook in Vermont (Sherbatskoy *et al.*, 1998), 0.5 to 5.5 ng/L at Trout Lake in Wisconsin (Krabbenhoft *et al.*, 1995), 1.1

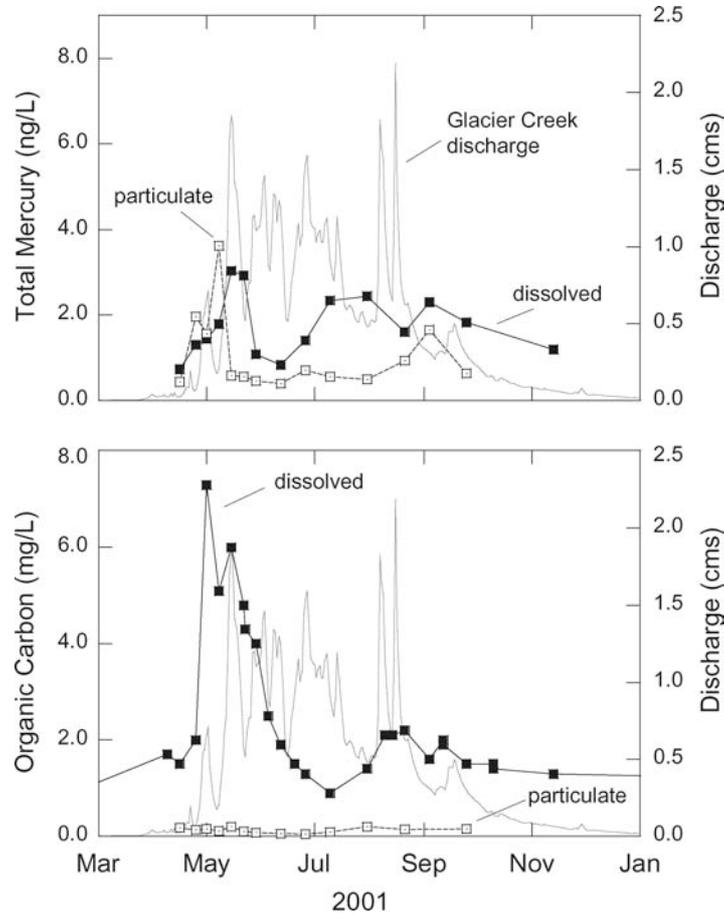


Figure 3. Total Hg and organic carbon concentrations at Glacier Creek, 2001.

to 2.5 ng/L at Coweeta in North Carolina (Allan and Heyes, 1998), and 0.1 to 15.5 ng/L at Sleepers River in Vermont (Shanley *et al.*, 2002).

Dissolved organic carbon (DOC) showed seasonal patterns very similar to those of Hg with concentrations peaking on the rising limb of the hydrograph prior to peak discharge (Figures 2–4). Maximum rising limb concentrations were 2.2 mg/L at Andrews Creek (2001), 7.1 mg/L at Glacier Creek (2001), and 3.4 mg/L at The Loch outlet (2002). After peak discharge in July, average DOC concentrations decreased to stable levels of 0.6 to 0.7 mg/L at Andrews Creek, 1 to 2 mg/L at Glacier Creek, and 0.7 to 1.0 mg/L at The Loch outlet. The difference in DOC among stream sites appears to correspond to the percentage of forest cover (Table I), which is lowest for Andrews Creek (3%) and highest for Glacier Creek (22%). This result is consistent with previous work showing that DOC concentrations in high-elevations streams are strongly related to the areal extent of soil and size of soil organic carbon pools (Hood *et al.*, 2003). Despite the clear differences

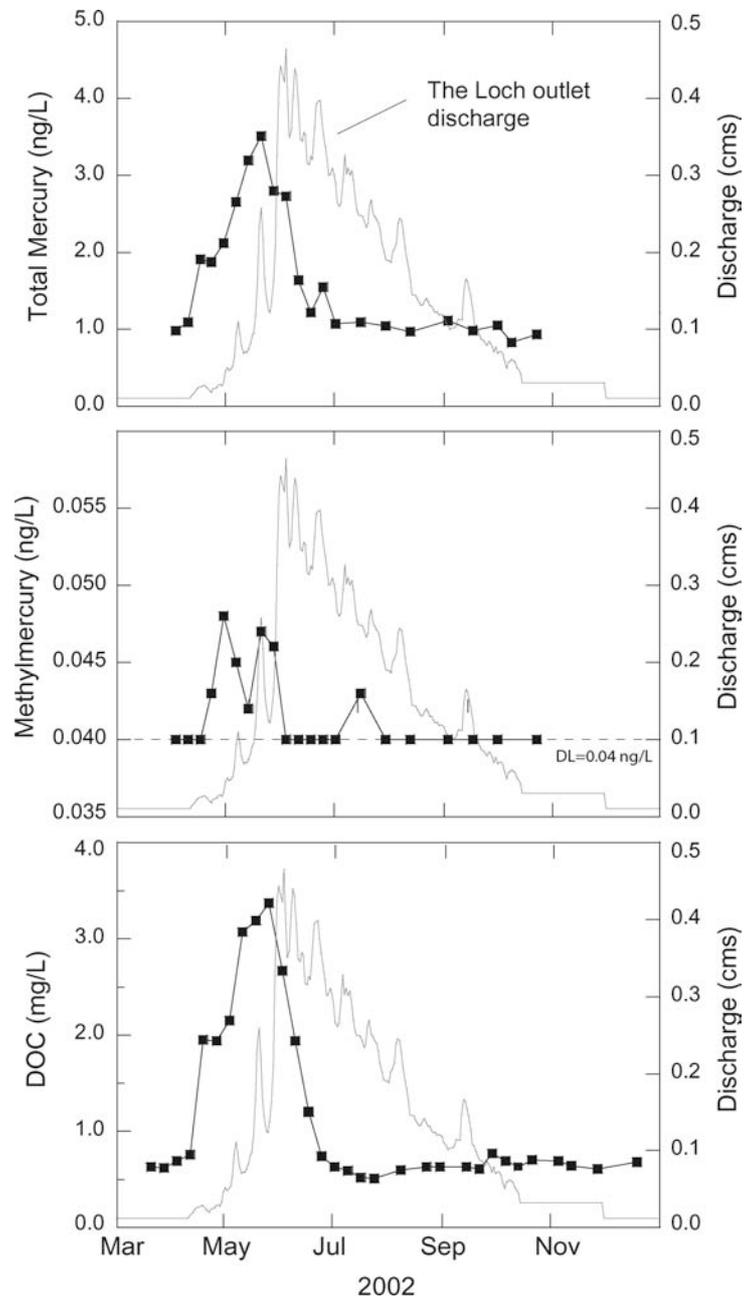


Figure 4. Total unfiltered Hg and MeHg concentrations and dissolved organic carbon (DOC) concentrations at The Loch outlet, 2002.

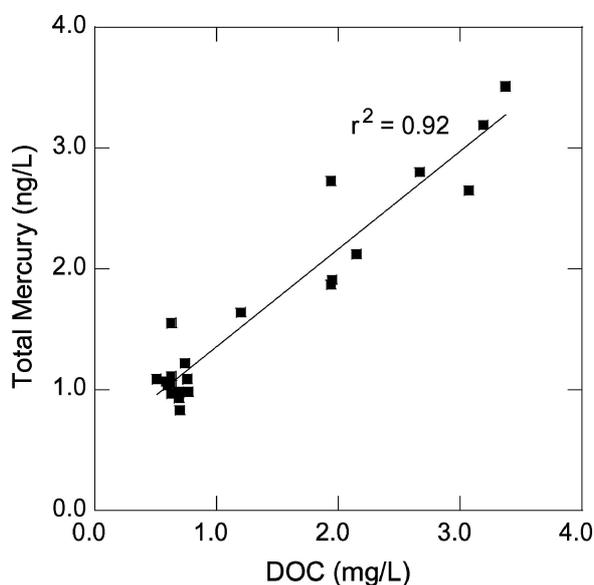


Figure 5. Total Hg concentrations versus dissolved organic carbon (DOC) concentrations at The Loch outlet, 2002.

in DOC concentrations among the sub-watersheds, there was no clear relation between DOC and Hg concentrations among the three stream sites. For example, Glacier Creek had the highest average DOC concentration (2.8 mg/L) and Andrews Creek had the lowest (0.9 mg/L), but Andrews Creek had the highest average Hg concentration (3.2 ng/L) and The Loch outlet had the lowest (1.8 ng/L). By contrast, DOC showed positive correlations with Hg at individual stream sites. The strongest correlation ( $r^2 = 0.92$ ) was for total unfiltered Hg at The Loch outlet in 2002 (Figure 5). The correlations between DOC and total Hg (dissolved plus particulate) were weaker for Andrews Creek ( $r^2 = .41$ ) and Glacier Creek ( $r^2 = 0.20$ ) in 2001. The reason for the weaker correlations, particularly at Glacier Creek, is because the snowmelt flush of Hg was less pronounced in 2001 than 2002. This might be related to differences in the melt pattern between the 2 years. In 2001, the hydrograph was fairly irregular peaking several times in May, June, and July during snowmelt and again in August following two large rain events. By contrast, the 2002 hydrograph reflected a consistent melt pattern with a single snowmelt peak in early June followed by a gradual decline in flow through late summer and fall (Figures 2–4). Differences in sample processing between the 2 years may have played a role as well. In 2001, total Hg was determined by summing the dissolved and particulate Hg whereas in 2002, total Hg was analyzed on whole water samples. The additional sample handling associated with filtering and the error resulting from the calculation may have decreased the precision of the Hg measurements in 2001 thus partially obscuring the Hg-DOC relation in 2001. Finally, differences in watershed

characteristics among the sites also may affect the relation between DOC and Hg. Because Andrews Creek drains primarily alpine tundra with limited soil coverage and smaller soil organic carbon pools, the weaker correlation between Hg and DOC could reflect increasing washout of DOC and decreasing retention of atmospheric Hg by alpine soils as discharge increases. At The Loch, volatilization and perhaps sedimentation or direct uptake of Hg in the lake could effect Hg concentrations at the outlet.

Mercury concentrations were not correlated with other major dissolved constituents at The Loch outlet with the exception of potassium, which showed a positive correlation ( $r^2 = 0.50$ ,  $p = .001$ ). Particulate organic carbon (POC) concentrations in Andrews Creek and Glacier Creek ranged from 0.02 to 0.36 mg/L, which were 10 to 40 times lower than DOC concentrations (Figures 2 and 3). These results suggest that transport of POC in surface waters in Loch Vale is small compared to DOC even during periods of high discharge.

#### 4.3. PROCESSES CONTROLLING MERCURY TRANSPORT

The seasonal patterns of Hg and organic carbon concentrations in streams in Loch Vale suggest that transport of Hg from alpine watersheds is controlled by the movement of organic carbon during snowmelt. The early season peak in DOC at all three sampling sites is consistent with the hypothesis that in high-elevation watersheds, soluble organic carbon accumulates in soils over the winter and is flushed into streams during the early stages of spring snowmelt (Boyer *et al.*, 1997). Studies by Hood *et al.* (2003) in the alpine/subalpine area of Green Lakes Valley just south of Loch Vale determined that DOC on the rising limb of the snowmelt hydrograph had a high fulvic acid component indicating it was primarily derived from flushing of near-surface soil horizons. By inference, the strong correlation between DOC and Hg at the Loch Vale suggests that soluble organic carbon complexes Hg in near-surface soils horizons and transports it to streams during snowmelt (Figure 5). The positive correlation between Hg and potassium (an essential plant nutrient) also provides evidence that Hg is flushed from soils during snowmelt. Moreover, the lack of correlation with constituents derived primarily from atmospheric deposition such as nitrate, sulfate, and chloride suggests that the early season increase in stream-water Hg was not caused by preferential release of Hg stored in the snowpack (Campbell *et al.*, 1998). Many studies have found that wetlands are important for mobilization of Hg to surface waters (Driscoll *et al.*, 1995; Hurley *et al.*, 1995; Kolka *et al.*, 1999a), however, wetlands account for less than 3% of the landscape in Loch Vale. Therefore, organic-rich soil horizons in forested areas and alpine tundra rather than wetlands probably are the primary sources of Hg released to streams in Loch Vale. Interestingly, the majority of Hg in Loch Vale streams appears to be transported in the dissolved phase based on the ratio of dissolved to particulate Hg measured in 2001. This is in contrast to many studies that find Hg is primarily associated with transport of particulate organic matter, particularly during high-flow

events such as snowmelt (Sherbatskoy *et al.*, 1998; Kolka *et al.*, 1999a; Shanley *et al.*, 2002). Despite the steep terrain of Loch Vale, there is relatively little sediment and POC transport by streams even during periods of high discharge, which probably is due to the resistant granitic bedrock and the lack of easily erodible materials in the coarse-grained soils and streambed sediments.

Mercury and DOC concentrations at all three sites peaked before the period of maximum discharge then decreased rapidly to relatively constant levels during the descending limb of the snowmelt hydrograph (Figures 2–4). This type of seasonal pattern in DOC indicates that the pool of soluble organic carbon is limited in shallow soils and quickly becomes depleted during snowmelt (Boyer *et al.*, 1997; Hood *et al.*, 2003). Because Hg shows a similar flushing response to DOC, the mobility of Hg appears to be geochemically linked to organic carbon. Inorganic Hg in soils is strongly sorbed to organic matter and is very immobile especially under low pH conditions (Schwesig *et al.*, 1999), which are characteristic of forest soils in Loch Vale. This is evidenced by the much lower concentrations of Hg in runoff compared to those in rainfall or snow, suggesting that most atmospheric Hg is sorbed to soils, despite their lack of development and sparse coverage in Loch Vale. The transport of Hg from forest soils is dependent on complexation with soluble organic carbon, which is produced by microbial decomposition of plant and soil organic matter. Once the pool of soluble organic carbon is depleted by snowmelt, however, the flux of Hg from soils to surface waters is greatly reduced. In contrast to Loch Vale, a slightly different pattern was reported by Shanley *et al.* (2002) at Sleepers River in Vermont during snowmelt. DOC and Hg concentrations at Sleepers River continued to increase with high-flow events following the initial snowmelt pulse suggesting that pools of Hg and DOC were not depleted by snowmelt. The pattern may be different for Sleepers River because of larger pools of soil organic matter and higher rates of decomposition.

Changes in hydrologic pathways also may be a factor in controlling the flux of Hg to streams after peak snowmelt. Low stream-water DOC concentrations in high-elevation streams in late summer and fall may result from a depletion of soluble organic carbon in near-surface soils and from an increasing component of ground water in streamflow (Hood *et al.*, 2003). Although soluble organic carbon continues to be produced in near-surface soil horizons throughout the summer, the transport of DOC and Hg diminishes as an increasing proportion of stream flow is derived from deeper flowpaths and shallow soil horizons become hydrologically disconnected from the streams. This shift in hydrologic pathways allows soluble organic carbon to accumulate in the upper soil horizons until the following year when it will be flushed into streams along with Hg as meltwater once again infiltrates the unsaturated zone. The notable lower Hg concentrations later in the summer could also be in part related to lower Hg concentrations that are generally observed lower in soil profiles (Schwesig *et al.*, 1999).

The importance of Hg transport during periods of high flow such as snowmelt and heavy rainfall has been recognized in a number of recent studies (Bishop

*et al.*, 1995; Allan and Heyes, 1998; Hurley *et al.*, 1998; Scherbatskoy *et al.*, 1998; Schwesig and Matzner, 2001; Shanley *et al.*, 2002). Bishop *et al.* (1995) observed increases in total Hg and total organic carbon during snowmelt at an upland watershed in Sweden. Similar to Loch Vale, concentrations of total Hg peaked about 6 ng/L during the early part of snowmelt, which was attributed to a predominance of shallow flowpaths during snowmelt. Scherbatskoy *et al.* (1998) investigated movement of Hg in an upland forested watershed in Vermont and observed elevated total Hg concentrations during snowmelt reaching 79.7 ng/L at high flow in 1994 and 20 ng/L at high flow in 1995; at other times of the year concentrations remained below 3 ng/L. In contrast to Loch Vale, transport of Hg during snowmelt in Vermont was not related to DOC but instead was controlled by transport of sediment from riparian areas, streambanks, and bed sediments. A relation between total Hg and POC also was observed by Shanley *et al.* (2002) at Sleepers River, Vermont, during snowmelt, which supports the hypothesis that Hg export in these upland forested watersheds occurs during high-flow events and is associated with large releases of POC. In contrast, at Loch Vale, export of Hg from high-elevation watersheds is controlled primarily by movement of DOC from soils during the early part of snowmelt.

#### 4.4. METHYLMERCURY CONCENTRATIONS IN STREAM WATER

Methylmercury concentrations in stream water were measured at The Loch outlet only in 2002 (Figure 4). The seasonal pattern in MeHg was slightly different than total Hg showing two distinct peaks during the initial stages of melting in contrast to the single peak observed for total Hg. Stream-water concentrations following peak discharge were at or below the detection limit of 0.04 ng/L for the remainder of the snowmelt season. The first pulse of MeHg at The Loch outlet occurred on April 30 and appears to precede the main flush of total Hg and DOC by several weeks. One possible explanation is that the initial pulse represents flushing of MeHg that has accumulated in the hypolimnion of The Loch during winter. Bottom waters in The Loch typically become depleted in dissolved oxygen (<2 mg/L) during mid-winter (Baron, 1992), which could enhance conditions for methylation, which is predominantly driven by microbial sulfate reduction (Wiener *et al.*, 2003). Seasonal buildup of MeHg was observed in the anoxic (dissolved oxygen <0.5 mg/L) bottom waters of Mills Lake (just north of The Loch) in April 1999 while the lake was still under ice (Krabbenhof *et al.*, 2002). This buildup was thought to result in elevated concentrations at the Mills Lake outlet as the lake water was displaced by inflowing snowmelt. Hydrologically this explanation also makes sense for The Loch because the volume of the lake is relatively small (61,000 m<sup>3</sup>) and could be completely displaced by inflowing meltwater during the first several weeks of snowmelt. During 2002, the equivalent of one lake volume was discharged at The Loch outlet between April 12, when flow began to increase, and May 5, which was just after the first peak in MeHg concentrations. The second peak in MeHg,

which occurred on May 21, was concurrent with the peak in DOC and total Hg and probably is related to hydrologic flushing of near-surface soil horizons in the watershed.

Reports of seasonal patterns in stream-water MeHg concentrations particularly during snowmelt are rare. Krabbenhoft *et al.* (2002) reported a monotonic decline in MeHg at Mills Lake between June (0.040 ng/L) and September (0.025 ng/L), which was attributed to flushing of MeHg from the lake in spring and high rates of demethylation during late summer and fall. Bishop *et al.* (1995) measured stream-water MeHg concentrations at the Svartberget watershed in northern Sweden during snowmelt that were 5 to 10 times higher (<0.1 to 0.42 ng/L) than those measured at The Loch outlet (<0.04 to 0.048 ng/L). In contrast to Loch Vale, MeHg concentrations at Svartberget were diluted during snowmelt despite indications that the concentrations in snowmelt were higher than the concentrations in stream runoff. Schwesig and Matzner (2001) measured MeHg in runoff from an upland forested watershed in Germany. Methylmercury concentrations in stream water ranged from <0.01 to 0.40 ng/L with the lowest concentrations occurring during spring snowmelt, which the authors suggest was controlled by seasonal variations in temperature rather than snowmelt dilution.

#### 4.5. MERCURY BUDGETS FOR LOCH VALE

Annual deposition and export of total Hg for the three stream sites in Loch Vale are presented in Table III. Total deposition was estimated by assuming that dry deposition is equal to wet deposition in forest areas (Kolka *et al.*, 1999b) and adjusting wet deposition (Table II) for additional inputs of dry deposition based on the percentage of forested area in each watershed. Export was calculated using the midpoint method by multiplying the concentration of a stream sample by the total discharge between sampling dates centered on the day of sampling. Results

TABLE III  
Annual deposition and export of total Hg and MeHg in Loch Vale for 2001 and 2002

Stream site	Year	Precipitation (cm)	Runoff (cm)	Total Hg deposition <sup>a</sup> ( $\mu\text{g}/\text{m}^2$ )	Total Hg export ( $\mu\text{g}/\text{m}^2$ )	MeHg export ( $\mu\text{g}/\text{m}^2$ )	Total Hg retention (%)
Andrews Creek	2001	97	91	12.8	2.34	– <sup>c</sup>	82
The Loch Outlet <sup>b</sup>	2001	97	67	13.9	1.19	– <sup>c</sup>	92
Glacier Creek	2001	97	58	15.1	1.44	– <sup>c</sup>	90
The Loch Outlet	2002	65	44	9.3	0.65	0.013	93

<sup>a</sup>Total Hg deposition adjusted for dry deposition based on percentage of forest cover in Table I.

<sup>b</sup>Stream-water Hg in 2001 estimated from the equation:  $\text{Hg (ng/L)} = 0.81 * \text{DOC (mg/L)} + 0.55$ .

<sup>c</sup>Not measured.

were normalized for watershed area and reported as  $\mu\text{g}/\text{m}^2/\text{yr}$ . In order to calculate export at The Loch outlet in 2001, Hg concentrations were predicted from DOC based on linear regression of DOC and Hg concentrations in 2002, which yielded the expression: total Hg (ng/L) =  $0.81 * \text{DOC (mg/L)} + 0.55$  (Figure 5). For the purposes of calculating export, all MeHg concentrations reported below detection were set to 0.02 ng/L or one-half the method detection limit of 0.04 ng/L.

Total Hg export at the three stream sites in Loch Vale in 2001 ranged from 1.19 to  $2.34 \mu\text{g}/\text{m}^2$ , which falls in the range of 0.3 to  $3.5 \mu\text{g}/\text{m}^2$  reported for forested watersheds in the literature (see Table IV in Allan and Heyes, 1998). Higher export at Andrews Creek in 2001 compared to Glacier Creek primarily is driven by higher amounts of runoff from this predominantly alpine watershed. Export at The Loch outlet in 2002 ( $0.65 \mu\text{g}/\text{m}^2$ ) was considerably lower than in 2001 ( $1.19 \mu\text{g}/\text{m}^2$ ) primarily reflecting the drought conditions that prevailed during 2002. On an annual basis, 82 to 93% of the total Hg deposition in Loch Vale was retained indicating the watersheds primarily act as net sinks for atmospherically deposited Hg. This result is supported by recent studies which used Hg tracers to show that recently deposited Hg is largely retained on plant and soil surfaces (Hintelmann *et al.*, 2002). Some Hg may be revolatilized and lost directly to the atmosphere through emissions from the soil (Lindberg *et al.*, 1995) and snowpack (Lalonde *et al.*, 2002), although the magnitude of this loss is poorly quantified. There appeared to be greater retention of Hg lower down in the hydrologic system (92% at The Loch compared to 82% at Andrews Creek), perhaps because of greater soil coverage and larger pools of soil organic matter at lower elevations in the watershed. The flux of total Hg in stream water was strongly linked to the early snowmelt period when concentrations and discharge were elevated. At The Loch outlet, more than 50% of the annual export occurred during the first 6 weeks of snowmelt in May and early June. These results emphasize the importance of frequent sampling during early snowmelt to accurately characterize Hg concentrations and fluxes for high-elevation streams.

Export of MeHg also was calculated at The Loch outlet in 2002 although there is no estimate of MeHg in deposition at this time (Table III). Nearly one-half of the stream samples were at or below the detection limit for MeHg, which increases error in the estimate of export from the watershed. Estimated MeHg export was  $0.013 \mu\text{g}/\text{m}^2$ , which accounted for just 1% of total Hg export from the watershed in 2002. This value is similar to those reported for upland forested watersheds at Coweeta in North Carolina (0.01 to  $0.05 \mu\text{g}/\text{m}^2$ , Allan and Heyes, 1998) and in the Experimental Lakes Area of Ontario ( $0.007 \mu\text{g}/\text{m}^2$ , St. Louis *et al.*, 1994) but much lower than the export from the Svartberget watershed in Sweden (0.08 to  $0.16 \mu\text{g}/\text{m}^2$ , Lee *et al.*, 1995). The low stream-water flux of MeHg from Loch Vale likely resulted from a combination of low MeHg production rates and high rates of demethylation in the watershed. Many studies have shown that the major sources of MeHg to lakes and streams are riparian wetlands (St. Louis *et al.*, 1994; Driscoll *et al.* 1995; Branfireun *et al.*, 1996; Bowles *et al.*, 2003). The lack of wetlands in Loch Vale, which cover less than 3% of the landscape, is one apparent reason for

low MeHg flux in streams. Cold air temperatures in Loch Vale may be a factor because temperature also has been identified as an important factor governing the rate of MeHg production in terrestrial environments (St. Louis *et al.*, 1994). Low stream-water fluxes also may result from elevated rates of demethylation in lakes and streams. Krabbenhoft *et al.* (2002) demonstrated that high water clarity and sunlight exposure enhanced rates of demethylation in Mills Lake during summer. The authors concluded that the high rate of demethylation was an important reason why MeHg concentrations were low in high-elevation lakes throughout the Rocky Mountain region.

## 5. Conclusions

Our studies of Hg in Loch Vale begin to elucidate some of the processes controlling Hg cycling in high-elevation ecosystems. Atmospheric deposition of Hg in Loch Vale was relatively high because of moderate Hg concentrations in precipitation combined with high rates of precipitation that are typical of high-elevation areas in the Rocky Mountains. Despite the fact that snow accounts for most of the annual precipitation, deposition was higher in summer than winter, which indicates that year-round monitoring is important to accurately quantify Hg deposition. The majority (>80%) of Hg in atmospheric deposition does not leave the watershed via runoff and appears to be limited by DOC generating processes. Based on seasonal patterns of total Hg in streams, transport of Hg from snowmelt-dominated watersheds is controlled by flushing of near-surface soil horizons during the early stages of snowmelt. Because of a lack of wetlands in the watersheds, the major source of Hg released to surface waters appears to be organic-rich soil horizons in forested areas and in the alpine tundra. The positive correlation between Hg and DOC and low export of POC in streams suggest that Hg primarily is transported in the dissolved phase. On an annual basis, less than 20% of atmospherically deposited Hg was exported in streams indicating the terrestrial environment is a net sink of Hg. More than 50% of the annual export in streams occurred during the first 6 weeks of snowmelt emphasizing the importance of frequent sampling during early snowmelt to accurately characterize Hg concentrations and fluxes for snowmelt-dominated streams. Methylmercury concentrations were very low and accounted for 1% of the total Hg export from the watershed. Low MeHg in streams was attributed to a lack of wetlands in the watershed and to high rates of photo-demethylation in surface waters.

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