

Mercury on the Move During Snowmelt in Vermont

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Although mercury (Hg) emissions peaked in the United States over the last 20 to 40 years and are now declining, they remain well above natural background levels in soils and sediments. Only a small fraction of the Hg deposited from the atmosphere to the terrestrial landscape runs off in streamflow. However, some of this Hg is methylated in the environment and can potentially bioaccumulate to the top of food webs, posing a hazard to people who eat fish, especially children and pregnant women.

What factors determine the amount of Hg that runs off in streams? During the 2000 snowmelt at Sleepers River in Vermont, strong correlations were found between dissolved and particulate mercury and the respective dissolved and particulate organic carbon fractions, even when data were pooled from 10 streams of diverse watershed size and land cover. Episodic export of particulate Hg during the highest flows appears to be the dominant mechanism of Hg movement.

Evidence for an Hg-organic carbon (OC) association is not new. A long and growing list of studies in temperate and boreal environments in North America and northern Europe have reported Hg-OC associations [e.g., Meili, 1991; Bishop *et al.*, 1995]. Hg and OC are correlated both in stream water and O-horizon soil water at other Vermont sites [Shanley *et al.*, 1999], and DOC appears to play an important role in regulating Hg in Adirondack (New York) lakes [Driscoll *et al.*, 1995]. The present study supports previous research in Vermont that suggests Hg export in stream flow occurs principally in discrete episodes of high flow accompanied by large releases of particulate organic carbon [Scherbatskoy *et al.*, 1998]. The association of Hg export with particulate organic matter implies that activities that disturb the forest floor such as logging, road-building, and residential development may release large amounts of Hg to streams.

Hg is a potent toxin that primarily affects humans' central nervous systems. The risk of Hg toxicity to human health is now recognized by most U.S. states. As of 1999, 41 states had issued Hg-related advisories on fish consumption, up from 27 states in 1993. Hg has long been used in commercial applications. Starting in the 1850s, California miners released Hg to mountain streams by the kilogram as a byproduct of gold mining. Despite increased awareness of the health risks, Hg is

still used in fluorescent bulbs, thermometers, electronic switches, and other products. The primary anthropogenic sources of Hg are coal combustion and waste incineration.

We investigated the dynamics of Hg movement at the Sleepers River Research Watershed in northeastern Vermont during the spring 2000 snowmelt. About one-half of the annual stream flow occurs during a 6-week period from late March to early May. We chose this dynamic time to assure that high flows would be captured. Sampling when Hg movement was expected to be greatest provided the best opportunity to identify the most important biogeochemical controls on Hg movement. The investigation was designed to define the role of both dissolved organic carbon (DOC) and particulate organic carbon (POC) in Hg movement, and to assess whether these relations varied with land cover type. We sampled streams in both agricultural and forested landscapes, including the outlet stream of a small wetland.

Sleepers River Research Watershed

Sleepers River Research Watershed (Figure 1) was established in 1959 by the U.S. Department of Agriculture (Agricultural Research Service) and is currently operated by the U.S. Geological Survey (USGS). It is one of five sites of the USGS Water, Energy and Biogeochemical Budgets (WEBB) Program, which seeks to understand the effects of climatic variation and human influence on watershed processes. Sleepers

River watershed comprises 111 km² in a hilly landscape of mixed forest and agricultural land. Northern hardwood forest at upper elevations (500–750 m) gives way to mixed forest with open dairy farm pasture and fields at lower elevations (200–500 m).

Stream water at Sleepers River is well-buffered by calcite within the quartz/mica phyllite bedrock. An average of 2 m of dense basal till derived from local bedrock covers the watershed. Dominant soils are spodosols and inceptisols developed to a depth of about 75 cm in the till. The region receives more than 1000 mm of precipitation evenly distributed throughout the year, and about 30% of it is snow. The year 2000 was fairly typical; in late March, maximum snowpack water equivalent was 20–25 cm at upper elevations and 12–15 cm at lower elevations. For this study, we sampled 10 streams with drainage areas from ~2 ha to 111 km². Forest cover ranged from 27% to 100%.

Methods

One challenge of this study was to develop protocols for sampling Hg and carbon species with high spatial and temporal intensity within the narrow window of peak discharge. The near-simultaneity of peak flow in the network of mountain streams combined with the possibility of sub-freezing temperatures precluded time-consuming on-site filtration. Instead, we collected all samples in holding bottles (Teflon for Hg; glass amber for C species) (Figure 2) and processed them in a field laboratory within 4 hours of collection. Common field parameters were measured in situ.

Duplicate aliquots for total Hg analysis were filtered (0.4- μ m polycarbonate) into acid-washed glass bottles for dissolved Hg (Hg_d), and the filter membranes were leached in

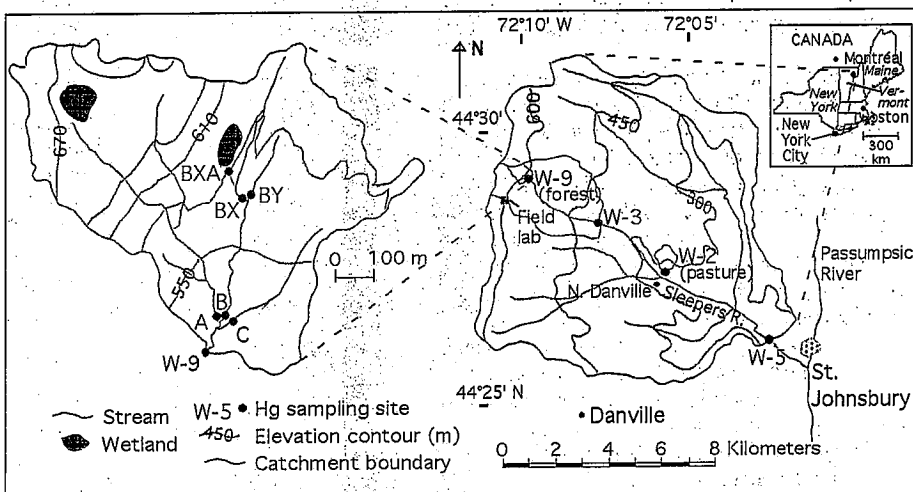


Fig. 1. The Sleepers River Research Watershed and Hg sampling sites are shown.

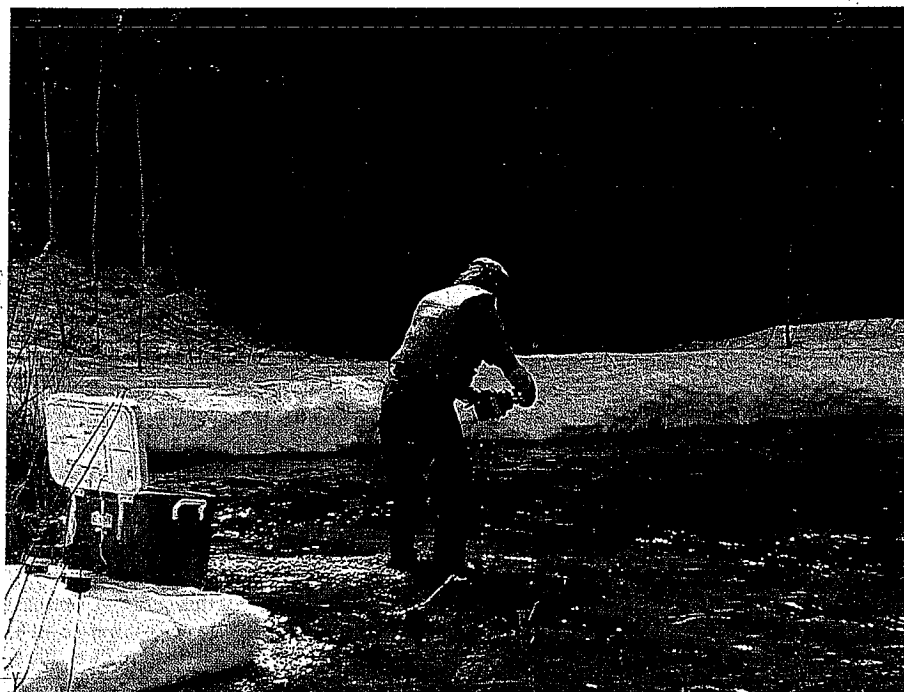


Fig. 2. Researcher is sampling for Hg during moderate snowmelt flow at the mixed land-use catchment W3. Photo courtesy of Paul F. Schuster, USGS.

double-distilled nitric acid and the oxidant potassium dichromate for particulate Hg (Hg_p). Duplicate aliquots for DOC were filtered through a 0.7- μ m glass fiber membrane and POC was analyzed on the retained particles. Additional sample aliquots were reserved for major ion analysis. Researchers wore particle-free latex gloves when performing all field and laboratory procedures for the Hg samples.

Hg and major ion concentrations were determined in triplicate and DOC was determined in duplicate at the USGS National Research Program Laboratory in Boulder, Colorado. Hg was determined by cold-vapor atomic fluorescence spectrophotometry. For this study, the procedure provided a method detection limit of 0.3 ng/L and a precision of $\pm 6\%$ RSD. DOC was analyzed by wet-chemical oxidation with infrared detection. Anions were determined by ion chromatography and cations were determined by inductively coupled plasma emission spectrophotometry. POC was analyzed by elemental analysis at the Chesapeake Biological Laboratory.

Mercury at High Flow

An important contribution of the past 25 years of catchment research is recognition of the chemical dynamics during high flow periods and, thus, the need to sample during these times. High-flow sampling is particularly critical for Hg. Hg is among the minority of solutes whose concentration tends to increase with greater stream flow [Bishop *et al.*, 1995], causing an exponential increase in flux (product of concentration and stream discharge) during high flow. Scherbatskoy *et al.* [1998] calculated that half of the annual Hg flux in stream flow occurred on the single

day of peak snowmelt at a different Vermont site. The sampling strategy in this study was designed to capture this high-flow dynamic.

We obtained 58 samples at 10 different stream sites during the 2000 snowmelt, and an

additional seven seep/groundwater samples near the peak of melt. Samples were collected at winter base flow at each of three rain-on-snow flow peaks and during post-snowmelt recession (Figure 3). Both Hg_p and Hg_d displayed significant positive correlations with stream discharge, suggesting that most stream transport of Hg occurs during high-flow periods. This relation held (Hg_p , $r^2=0.54$, $p<0.00001$; Hg_d , $r^2=0.20$, $p=0.0005$) when data were pooled from all 10 sites and Hg_d concentration was regressed on specific discharge (stream flow per unit area, which normalizes discharge by catchment size), despite sharp contrasts among catchments in percent forest cover.

The Carbon Connection

Despite a general six-order of magnitude difference in absolute concentrations, Hg and organic carbon were consistently associated in stream water throughout the snowmelt period. Hg_p closely tracked DOC and Hg_d closely tracked POC (Figure 4). The Hg_p -DOC and Hg_d -POC relations were remarkably persistent irrespective of catchment size, land use, and hydrologic conditions. Once again pooling samples from all 10 stream sites, as well as the 7 seeps, Hg_p had a strong positive correlation with DOC ($r^2=0.46$, $p<0.0001$), and Hg_d had a strong positive correlation with POC ($r^2=0.84$, $p<0.0001$) (Figure 4). Although sampling at any given site was too sparse to compute Hg fluxes, the occasional very high Hg concentrations (up to 16 ng/L, compared to a

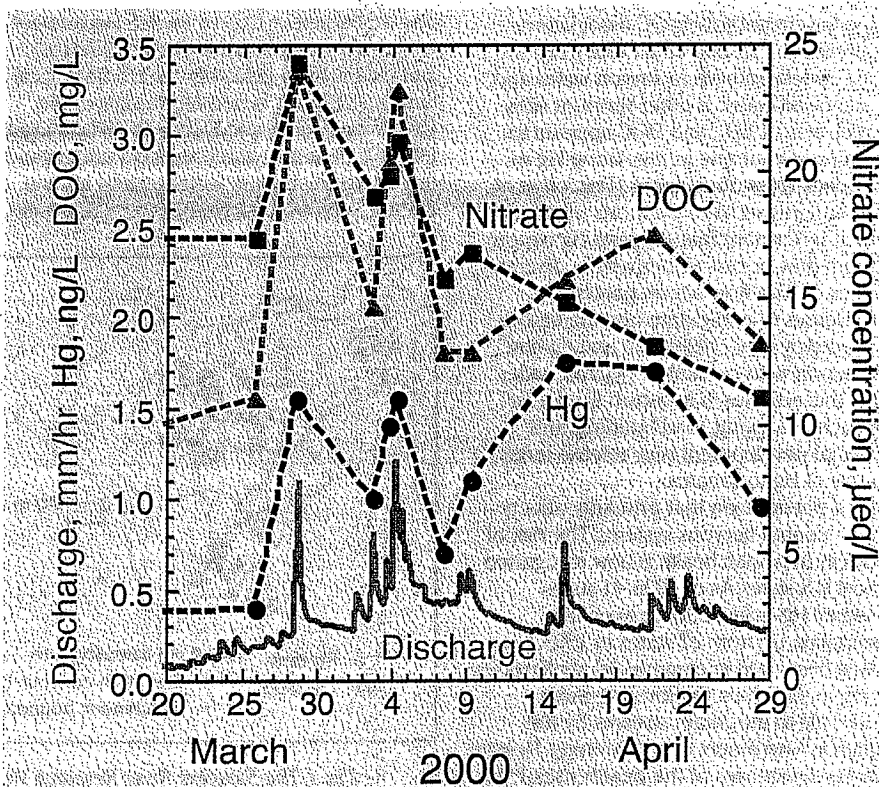


Fig. 3. This hydrograph shows Sleepers River Stream B (13 ha) during the 2000 snowmelt period, with dissolved Hg, DOC, and nitrate concentrations. Note the diurnal snowmelt peaks and larger rain-on-snow event peaks and the emphasis on high-flow sampling.

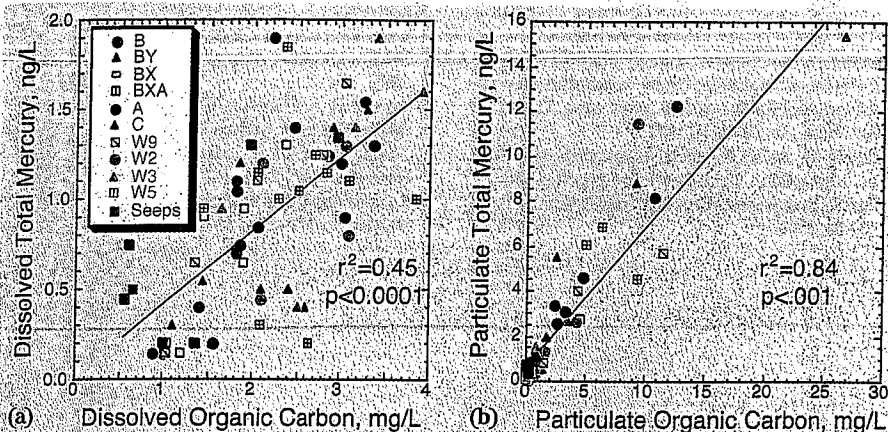


Fig. 4. Graphs depict (a) dissolved total Hg versus DOC and (b) particulate total Hg versus POC, for all 10 stream sites as well as 7 seeps during snowmelt. (p is the probability of false correlation.) Samples for which Hg was not detected were plotted at one-half of detection limit.

maximum of 2 ng/L for Hg_d) suggest that Hg flux is dominated by a small number of high-Hg episodes.

There are two possibilities to explain the strong Hg-OC correlations: (1) Hg in streamwater represents a small fraction of incoming Hg in rain or snowmelt that avoids removal by the soil because it associates with a mobile OC fraction (for example, ion-pair formation with an organic anion or binding to an OC colloid) and thus reaches the stream channel, or (2) Hg and OC are flushed from a common source—the soil organic horizon—by infiltrating meltwater or rising groundwater. While both processes likely operate, our data suggest that the latter may dominate, at least during snowmelt. Hg concentrations in the snowpack just before the onset of snowmelt were near or below the detection limit, suggesting an additional source such as soil organic matter was necessary to account for Hg in stream water. Secondly, the high Hg episodes suggest that erosion of near-stream areas or stream sediment re-suspension may transport Hg previously sequestered in litter fall and soil organic matter [Hurley *et al.*, 1998].

One difficulty in establishing causality in the Hg-OC relation is that Hg in stream water is correlated to constituents other than the OC fractions. For example, Hg_d is negatively correlated with alkalinity ($r^2=0.32$), suggesting an alternative hypothesis that Hg is mobilized under acidic conditions. This negative correlation, however, is most likely an artifact of dilution. Stream water composition at Sleepers River is controlled largely by two-component mixing; pre-event groundwater mixes with incoming meteoric water. The composition of meteoric water is modified by its passage through the soil organic horizon, where it acquires nitrate and DOC (and Hg). As snowmelt progresses, increasing contributions of meltwater enrich stream water in these solutes while diluting the weathering solutes (Si, base cations, and alkalinity). Therefore, Hg, which is positively correlated with DOC and nitrate, will necessarily be negatively correlated with each of the weathering solutes. The inverse correlation of Hg and alkalinity does not

indicate an acid mobilization effect because even at peak flow, the calcite in the bedrock and glacial till buffers stream alkalinity to no less than 400 $\mu\text{eq/L}$ while pH remains near 7.

Hg and OC are not always linked. In subtropical environments, such as the Florida Everglades, correlation of Hg bioaccumulation and DOC is absent. Instead, methyl Hg concentration in sediments (an indicator of the bio-availability of Hg to methylating bacteria) correlates inversely to sulfide concentration [Benoit *et al.*, 1999]. In the Everglades, the formation of Hg-sulfide complexes and their associated redox states, along with the character of the DOC in the sediment and water column, are thought to play an important role in Hg movement and bio-availability [Reddy and Aiken, 2001].

Soil Flushing

A key to understanding Hg behavior in the Sleepers River watershed may lie in the Hg flushing rate relative to DOC and nitrate. Although nitrate, DOC, and Hg each show a positive relation to flow, the dynamics of their release to stream flow during snowmelt differ (Figure 3). Nitrate in stream flow peaks highest during the initial snowmelt pulses, then shows a progressively subdued response to subsequent peaks in flow even if the peaks are larger, which suggests that a limited pool of nitrate is available to be flushed.

DOC, in contrast, tracks the snowmelt discharge curve more closely, continuing to reach high concentrations with successive discharge peaks. Hg behaves similarly to DOC, and the Hg source appears to be even more enduring than DOC; the Hg/DOC ratio in stream water tends to increase as snowmelt progresses. This pattern, which held at most of the sampling sites, suggests that Hg is associated with a particular fraction of DOC that may behave differently than total DOC.

Mercury and the Catchment Approach

The instrumented research catchment, with a long-term record and a history of process

understanding, provides an optimal setting for research on the fate and cycling of atmospheric pollutants such as Hg. Yet there is little overlap between the Hg and catchment research communities. Even those Hg studies that have utilized research catchments [e.g., Krabbenhoft *et al.*, 1995] have seldom focused on high-flow periods [Bishop *et al.*, 1995; Hurley *et al.*, 1998]. From the present study and other recent studies [Scherbatskoy *et al.*, 1998; Babiarz *et al.*, 1998; Hurley *et al.*, 1998], evidence is accumulating that episodic mobilization of particulate Hg may provide effective transfer of Hg from upland to lowland environments. Although Bishop *et al.* [1995] found that MeHg per se diluted with increasing flow during snowmelt in a boreal catchment in Sweden, these episodic fluxes of total Hg may be the dominant source of Hg that is ultimately methylated and assimilated in the food web in downstream receiving waters.

A coordinated effort of intensive high-flow sampling for Hg in research catchments could capitalize on existing process understanding to clarify the nature of this important episodic Hg transport mechanism. Because Hg likely will persist in the environment well into the future, appropriate land management practices may be an effective strategy for controlling the input of Hg to aquatic systems.

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