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James B. Shanley

U.S. Geological Survey, jshanley@usgs.gov

M. Alisa Mast

U.S. Geological Survey, mamast@usgs.gov

Donald H. Campbell

U.S. Geological Survey, dhcampbe@usgs.gov

George R. Aiken

U.S. Geological Survey, graiken@usgs.gov

David P. Krabbenhoft

U.S. Geological Survey, dpkrabbe@usgs.gov

See next page for additional authors

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Authors

James B. Shanley, M. Alisa Mast, Donald H. Campbell, George R. Aiken, David P. Krabbenhoft, Randall J. Hunt, John F. Walker, Paul F. Schuster, Ann Chalmers, Brent T. Aulenbach, Norman E. Peters, Mark Marvin-DiPasquale, David W. Clow, and Martin M. Shafer

Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach

James B. Shanley^{a,*}, M. Alisa Mast^b, Donald H. Campbell^b, George R. Aiken^c,
David P. Krabbenhoft^d, Randall J. Hunt^d, John F. Walker^d, Paul F. Schuster^c,
Ann Chalmers^a, Brent T. Aulenbach^e, Norman E. Peters^e,
Mark Marvin-DiPasquale^f, David W. Clow^b, Martin M. Shafer^g

^a US Geological Survey, PO Box 628, Montpelier, VT 05601, USA

^b US Geological Survey, MS 415 Denver Federal Center, Denver, CO 80225, USA

^c US Geological Survey, 3215 Marine Street, Suite E-127, Boulder, CO 80303, USA

^d US Geological Survey, 8505 Research Way, Middleton, WI 53562, USA

^e US Geological Survey, 3039 Anwiler Road, Suite 130, Atlanta, GA 30360, USA

^f US Geological Survey, 345 Middlefield Rd., MS 480, Menlo Park, CA 94025, USA

^g Environmental Chemistry & Technology and Wisconsin State Laboratory of Hygiene, University of Wisconsin, Madison, WI 53706, USA

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High-flow sampling reveals strong contrasts in total mercury and methylmercury cycling in five diverse USA watersheds.

Abstract

The small watershed approach is well-suited but underutilized in mercury research. We applied the small watershed approach to investigate total mercury (THg) and methylmercury (MeHg) dynamics in streamwater at the five diverse forested headwater catchments of the US Geological Survey Water, Energy, and Biogeochemical Budgets (WEBB) program. At all sites, baseflow THg was generally less than 1 ng L⁻¹ and MeHg was less than 0.2 ng L⁻¹. THg and MeHg concentrations increased with streamflow, so export was primarily episodic. At three sites, THg and MeHg concentration and export were dominated by the particulate fraction in association with POC at high flows, with maximum THg (MeHg) concentrations of 94 (2.56) ng L⁻¹ at Sleepers River, Vermont; 112 (0.75) ng L⁻¹ at Rio Icacos, Puerto Rico; and 55 (0.80) ng L⁻¹ at Panola Mt., Georgia. Filtered (<0.7 μm) THg increased more modestly with flow in association with the hydrophobic acid fraction (HPOA) of DOC, with maximum filtered THg concentrations near 5 ng L⁻¹ at both Sleepers and Icacos. At Andrews Creek, Colorado, THg export was also episodic but was dominated by filtered THg, as POC concentrations were low. MeHg typically tracked THg so that each site had a fairly constant MeHg/THg ratio, which ranged from near zero at Andrews to 15% at the low-relief, groundwater-dominated Allequash Creek, Wisconsin. Allequash was the only site with filtered MeHg consistently above detection, and the filtered fraction dominated both THg and MeHg. Relative to inputs in wet deposition, watershed retention of THg (minus any subsequent volatilization) was 96.6% at Allequash, 60% at Sleepers, and 83% at Andrews. Icacos had a net export of THg, possibly due to historic gold mining or frequent disturbance from landslides. Quantification and interpretation of Hg dynamics was facilitated by the small watershed approach with emphasis on event sampling.

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Keywords: Total mercury; Methylmercury; Episodic transport; Watershed

* Corresponding author. Tel.: +1 802 828 4466; fax: +1 802 828 4465.

E-mail addresses: jshanley@usgs.gov (J.B. Shanley), mamast@usgs.gov (M. Alisa Mast), dhcampbe@usgs.gov (D.H. Campbell), graiken@usgs.gov (G.R. Aiken), dpkrabbe@usgs.gov (D.P. Krabbenhoft), rjhunt@usgs.gov (R.J. Hunt), jfwalker@usgs.gov (J.F. Walker), pschuste@usgs.gov (P.F. Schuster), chalmers@usgs.gov (A. Chalmers), btaulenb@usgs.gov (B.T. Aulenbach), nepeters@usgs.gov (N.E. Peters), mmarvin@usgs.gov (M. Marvin-DiPasquale), dwclow@usgs.gov (D.W. Clow), mmshafer@wisc.edu (M.M. Shafer).

1. Introduction

Much environmental mercury research has focused on lowland lakes and large wetlands (Gilmour et al., 1998; Hurley et al., 1998b; Benoit et al., 2003) and coastal lowlands (Balcom et al., 2004; Hammerschmidt and Fitzgerald, 2004). These environments provide favorable conditions for Hg methylation and bioaccumulation in fish that people consume. Upland landscapes are also sources of mercury and sites of methylmercury production, and research in uplands has often targeted boreal systems (St. Louis et al., 1994, 1996; Branfireun et al., 1996; Allan et al., 2001; Bishop et al., 1995a,b), where wetlands are a major landscape component. Boreal landscapes are rich in organic matter and anoxic conditions that favor Hg methylation and MeHg export. Research in higher-gradient, low-DOC uplands (Allan and Heyes, 1998; Scherbatskoy et al., 1998; Mast et al., 2005) has been more limited. However, scientists have increasingly recognized that these non-boreal headwater terrestrial uplands (which may contain wetlands and wetland-like areas) both produce methylmercury and supply Hg that sustains Hg methylation in low-lying landscapes down-gradient (Munthe et al., 2007).

Much of the world's land surface is covered by forested uplands. Hg research in headwater upland landscapes is important because: (1) Hg deposition is enhanced at higher elevations and by forest canopy (St. Louis et al., 2001; Miller et al., 2005); (2) headwaters harbor a large pool of Hg with uncertain fate; and (3) the bioavailability of this Hg is unclear and needs to be better assessed.

Investigation of Hg cycling in headwater landscapes lends itself to the small watershed approach (Likens and Bormann, 1995), whereby careful mass balance in small, relatively simple ecosystems allows one to infer controlling processes. Application of the small watershed approach to investigations of Hg cycling remains limited (Krabbenhoft et al., 2005), but there are several examples in the literature (Krabbenhoft et al., 1995; Bishop et al., 1995a,b; Lee et al., 1998; Scherbatskoy et al., 1998; Allan and Heyes, 1998; Kolka et al., 1999; Allan et al., 2001; Schwesig and Matzner, 2001; Mast et al., 2005; Nelson et al., 2007; Harris et al., 2007). Event sampling, one of the key elements in small watershed research, is not always part of the design of these watershed studies, and has more often been applied to mesoscale or larger rivers (Hurley et al., 1995, 1998a; Babiarz et al., 1998; Balogh et al., 1997, 1998, 2005). Event sampling of flashy headwater streams is a challenging endeavor because of the unpredictability of high flows, remoteness of the sites, and the need for human presence (automated sampling of Hg is difficult and rare). Yet, to understand the processes and evaluate the magnitude of Hg dynamics in headwaters, event sampling is essential.

In this paper we use the small watershed approach with an emphasis on high-flow sampling to compare and contrast THg and MeHg cycling in five diverse sites across the USA. Unlike most upland Hg studies, these sites are non-boreal, low-DOC landscapes. The five watersheds comprise the USGS Water, Energy, and Biogeochemical Budgets (WEBB) research program, established in 1990 (Lins, 1994). The long-term data

and biogeochemical understanding from nearly two decades of intensive research at these sites provide rich context for the interpretation of Hg behavior. This recent focus on Hg in the WEBB program builds on previous work at three of the sites: Vermont (Shanley et al., 2002; Schuster et al., 2008); Colorado (Mast et al., 2005); and Wisconsin (Krabbenhoft et al., 1995).

2. Site descriptions

The five sites of the WEBB program are Sleepers River, VT; Loch Vale, CO; Trout Lake, WI; Panola Mountain, GA; and Luquillo Experimental Forest, PR (Fig. 1; Table 1). Within each site, we chose a small, undisturbed catchment for our Hg investigations. These catchments are the same as those reported in an intercomparison of water and solute mass budgets at the five sites (Peters et al., 2006). At Sleepers River, VT, Hg was sampled at the 41-ha W-9 catchment (called Sleepers herein) (Shanley et al., 2004), a forested, glaciated, calcareous catchment with mucky histosols in riparian zones and depressions. At Loch Vale, CO, we sampled the 179-ha Andrews Creek (Andrews), an alpine catchment dominated by steep bedrock and talus slopes with 2% coniferous forest cover on lower slopes (Campbell et al., 1995). Trout Lake, WI, is a forested low-relief landscape mantled with sandy till and dotted with numerous lakes and wetlands. We sampled the 1395-ha middle site on Allequash Creek (Allequash) (Walker et al., 2003), a catchment nested within the Allequash Creek site reported in Peters et al. (2006). The 41-ha Panola Mountain, GA site (Panola) (Peters, 1989) is forested except for a 3-ha granodiorite outcrop in the headwaters. At Luquillo, PR, we sampled Rio Icacos, a 326-ha forested catchment on rapidly weathering granodiorite (White et al., 1998). All sites average 1000 ± 300 mm annual precipitation, except Rio Icacos (Icacos), which averages more than 4000 mm.

3. Methods

The frequency and timing of Hg sampling varied among the five sites (Table 2). Each site used a combination of fixed interval and high-flow event sampling to capture Hg dynamics in streamwater at the catchment outlet. Grab samples were taken near the centroid of flow, except occasionally from the streambank at high flow. All sites except Panola had sufficient data to compute annual budgets for at least one year.

Samples for unfiltered THg and MeHg analysis were collected in rigorously cleaned Teflon bottles and acidified with ultra-pure 6N HCl (Olson and DeWiild, 1999). Samples for filtered and particulate THg and MeHg analysis were collected in new polyethylene terephthalate G Copolymer (PETG) bottles and filtered within 24 h with pre-baked 0.7- μ m quartz fiber filters (QFFs) within a closed chamber using clean techniques (Lewis and Brigham, 2004). The filtrate was then acidified as above; the QFFs were stored frozen and later digested for Hg analysis of the particulate fraction. A small number of base flow samples ($n < 10$) were filtered during collection through an in-line filter pack assembly using



Fig. 1. Locator map of the five USGS WEBB watersheds.

a peristaltic pump with Teflon tubing. When not determined on raw samples, unfiltered THg and MeHg concentrations were calculated by summing the filtered and particulate concentrations. We prefer the term “filtered” to “dissolved” based on the finding of Babiarz et al. (2001) that much of the THg and MeHg passing a 0.4- μ m filter is colloidal. All THg and MeHg concentrations were determined by cold vapor atomic

fluorescence spectrometry (CVAFS) at the USGS Mercury Laboratory in Middleton, WI (Olson and DeWild, 1999; DeWild et al., 2002).

With each Hg sample, aliquots were concurrently collected for dissolved organic carbon (DOC) in a 120-mL amber glass bottle by on-site syringe filtration (0.7- μ m glass fiber filter). For select samples, 3 L were filtered in-line by peristaltic

Table 1
Site characteristics of the five USGS WEBB catchments

	USGS WEBB site				
	Loch Vale, CO	Luquillo Forest, PR	Trout Lake, WI	Panola Mountain, GA	Sleepers River, VT
Watershed	Andrews Creek	Rio Icacos	Allequash Creek	Lower Gage	W-9
Ecosystem type	Alpine tundra/boreal forest	Subtropical wet forest	Northern lakes and forests	Southern hardwood forest	Northern hardwood forest
Catchment area (ha)	179	326	1395	41	41
Outlet elevation (m)	3215	616	494	225	524
Highest elevation (m)	3850	844	555	270	679
Mean slope (%)	66	21	0.28	18	22
Climate type	Cold continental	Humid tropical	Humid continental	Humid continental/subtropical	Humid continental
Mean annual temperature ($^{\circ}$ C)	0	21	4.5	16	4.5
Mean annual precipitation (mm)	1230	4210	760	1300	1320
Mean annual runoff (mm)	970	3690	300	490	670
Bedrock	Biotite schist	Quartz diorite	Amphibolite	Granodiorite/amphibolite	Phyllite/granulite
Surficial geology	Thin soil/talus	Colluvium	Glacial drift	Colluvium	Silty calcareous till
Soil type	Spodosols	Inceptisols/ultisols	Spodosols	Inceptisols/ultisols	Inceptisols/spodosols
Forest cover (%)	2	99	84	91	100
Wetland and lake cover (%)	1	2 to 5	16	1	4
Water type	Ca-Mg sulfate nitrate	Na-Ca-Cl-bicarbonate	Ca-Mg bicarbonate	Na-bicarbonate-sulfate	Ca-bicarbonate-sulfate

Table 2
Summary of sample quantities and concentration model regressions for stream flux calculations

	Years	Filtered THg			Filtered MeHg			Particulate THg			Particulate MeHg			Unfiltered THg			Unfiltered MeHg		
		<i>n</i>	<i>r</i> ²	Model	<i>n</i>	<i>r</i> ²	Model	<i>n</i>	<i>r</i> ²	Model	<i>n</i>	<i>r</i> ²	Model	<i>n</i>	<i>r</i> ²	Model	<i>n</i>	<i>r</i> ²	Model
Sleepers	4	19	0.26	Q	<DL									54	0.37	Q	53	0.34	Q
Icacos	1	10	0.83	Q	<DL									18	0.82	Q	17	0.72	Q
Andrews	3							Negligible			Negligible			85			HB		
Allequash	2	34	0.35	Q,S	35	0.15	S	28	0.17	S	22		HB						
Panola	0	6			6									11			9		

Years, number of complete years for flux calculation; *n*, number of analyses used in computation (for Panola, *n* is the number of samples collected); *r*², model *r*²; 'Model' indicates terms present: Q, flow term; S, seasonal term; HB, Hubbard Brook model used because no concentration model was significant; <DL, most or all concentrations below detection limit.

pump and cartridge glass fiber filter into glass amber bottles for analysis of carbon fractions (Aiken et al., 1992). DOC and C fractions were determined at the USGS laboratory in Boulder, CO. Additional aliquots were collected for total suspended solids (TSS) and particulate organic carbon (POC) analysis and filtered with separate glass fiber filters for gravimetric determination at the Chesapeake Biological Laboratory in Solomons, MD.

At three sites, THg input flux in precipitation was measured near (Allequash, Andrews) or a few kilometers away (Icacos) from the stream site. Allequash used site WI36 of the Mercury Deposition Network (MDN). The Icacos site is not in the MDN but is operated under MDN protocols, using the same laboratory for analysis (Frontier Geosciences, Seattle, WA). Deposition flux at Icacos was scaled to the higher precipitation amount at the higher-elevation watershed. At Andrews, weekly bulk deposition was sampled during the non-snow period, and an April snowpack sample represented Hg deposition for the November–April snow accumulation period, recognizing that some revolatilization of Hg may have occurred (Mast et al., 2005). At Sleepers, both wet and dry Hg deposition were estimated from the regional model of Miller et al. (2005), which utilizes regional wet Hg deposition data and models dry deposition considering Hg sources, elevation, and land cover type. Hg dry deposition at the other three sites was estimated assuming that dry deposition is two times wet deposition on the forested parts of the watershed (St. Louis et al., 2001). Hg deposition was not estimated at Panola as no mass balance was computed.

Continuous stream stage was recorded at all sites at one-hour or finer increments, and converted to discharge through empirical ratings. THg and MeHg output fluxes in stream-water were computed by the composite method (Aulenbach and Hooper, 2006), which builds a concentration model based on stream discharge, and sine/cosine terms that simulate seasonality. Modeled concentrations were adjusted to match actual sample concentrations, and adjusted between samples by the model residuals linearly interpolated through time between successive samples. Occasionally, e.g. after a storm, the concentration was forced to the modeled value to avoid carrying a high residual through a long period without samples. Finally, adjusted model THg and MeHg concentrations were multiplied by water flux to compute their respective fluxes.

Streamwater fluxes of unfiltered (or particulate, if measured) and filtered THg and MeHg were calculated independently at each site to the extent possible (Table 2). Icacos had strong concentration-discharge relations with no seasonal component for both THg and MeHg. At Sleepers, concentration-discharge relations were much weaker but still significant ($p < 0.0001$ except for filtered THg, $p < 0.02$). At Allequash, only filtered THg had a significant relation with flow, but filtered THg, filtered MeHg, and particulate THg had seasonal components, resulting in significant concentration models ($p < 0.0005$) for these three fractions. Fluxes computed from these three models were very similar to those computed using the period-weighted approach (also known as the Hubbard Brook approach, where a sample concentration is assigned to all flow between the midpoints of successive samples (Likens and Bormann, 1995)). Due to lack of significant models, we applied the Hubbard Brook approach for particulate MeHg at Allequash and for unfiltered THg at Andrews.

4. Results and discussion

4.1. Hg concentration dynamics

The distribution of samples on the flow duration curves indicates that high flows were effectively captured at all sites (Fig. 2). Low-flow regimes were also adequately represented. The very highest flows (<5% exceedance) were missed at Andrews, but high flow sampling at this site is the least critical because of the low slope on the high-flow end of the flow duration curve.

The five sites can be arranged in two groups with contrasting THg dynamics (Fig. 3). One group included Sleepers, Icacos, and Panola, and had high THg concentrations that ranged above 50 ng L⁻¹, strongly dominated by particulate THg (unfiltered THg minus filtered THg). The higher median and range at Icacos was influenced in part by a relatively greater emphasis on high flow sampling at that site (Fig. 2). The second group included Andrews and Allequash, and had lower THg concentrations dominated by the filtered fraction. The filtered THg fraction accounted for nearly all of the THg at Andrews and most of the THg at Allequash.

Filtered THg concentrations were more uniform than unfiltered THg concentrations across the five sites; median filtered

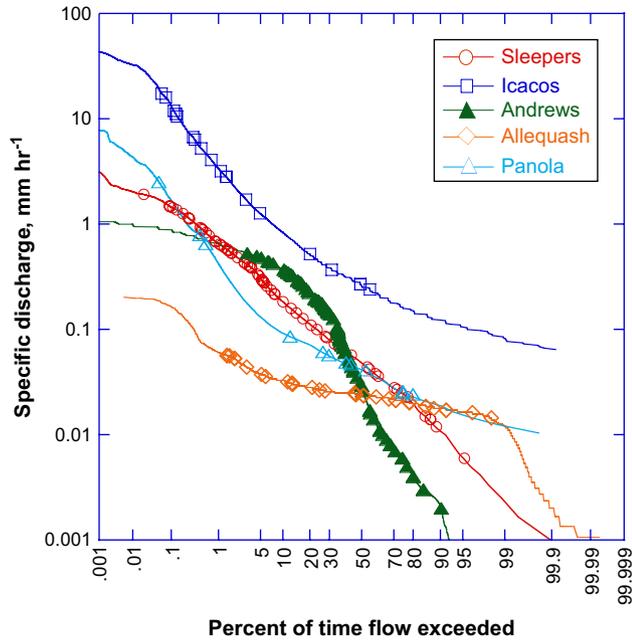


Fig. 2. Mercury samples plotted on flow duration curves for the five WEBB watersheds.

THg concentrations ranged from 1.0 ng L⁻¹ at Allequash and Andrews to 2.0 ng L⁻¹ at Sleepers and Icacos (Fig. 3). Panola had a median filtered THg concentration of 2.4 ng L⁻¹, but this value was based on only 6 storm samples. Sleepers and Icacos each had maximum filtered THg concentrations near 5 ng L⁻¹.

The maximum concentrations for unfiltered THg of 112 ng L⁻¹ at Icacos and 94 ng L⁻¹ at Sleepers are among the highest values reported in the literature for pristine sites. Only two storms were sampled at Panola, and the maximum of 55 ng L⁻¹ occurred during a relatively small storm, suggesting

a potential for even higher concentrations at this site. Scherbatskoy et al. (1998) reported an unfiltered THg concentration of 80 ng L⁻¹ during snowmelt in a small forested Vermont stream. Schwesig and Matzner (2001) reported two values greater than 100 ng L⁻¹ in filtered samples during a year of biweekly sampling in a German catchment. In less pristine environments, Balogh et al. (2005) reported maximum concentrations near 70 ng L⁻¹ in agricultural Minnesota rivers and Hurley et al. (1998a) reported a maximum THg concentration of 182 ng L⁻¹ in an industrially impacted Wisconsin river.

The range of MeHg was somewhat more uniform than THg among sites, with median concentrations for both filtered and unfiltered MeHg fractions ranging from below detection (0.04 ng L⁻¹) to 0.2 ng L⁻¹ (Fig. 3). Unfiltered MeHg values ranged up to 1.1 ng L⁻¹ at Allequash and 2.6 ng L⁻¹ at Sleepers. As with THg, MeHg at Sleepers, Icacos, and Panola was generally greater in the particulate fraction. Only Allequash had MeHg consistently above detection in both fractions, and here most of the MeHg was in the filtered fraction. Andrews consistently had MeHg below detection. Except in some wetland systems, MeHg concentrations reported for forest streams are generally <1 ng L⁻¹ (Branfireun et al., 1996; Allan and Heyes, 1998; Munthe and Hultberg, 2004; Nelson et al., 2007); high MeHg concentrations would not have been detected without high-flow sampling.

4.2. Episodic transport

A marked increase in THg and MeHg concentrations during high-flow events (Fig. 4) was a key feature at most of these sites. At the high-THg sites (Sleepers, Icacos, Panola), this increase was most prevalent for the unfiltered THg and MeHg fractions with a more moderate increase in the filtered fractions. THg concentrations at Andrews did not rise as high as those at these other three sites but increased sharply relative

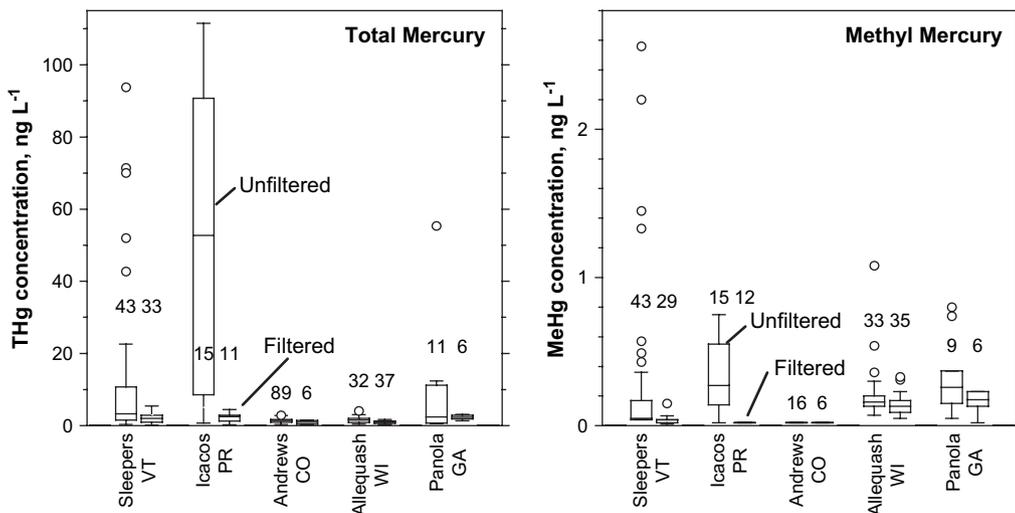


Fig. 3. Boxplots showing ranges of unfiltered (left bar of each pair) and filtered (right bar) THg and MeHg concentrations at the five sites. Horizontal bar within box is median value; top and bottom of box are 25th and 75th percentile values; ticks at end of vertical lines extending from box are 10th and 90th percentile values; and circles represent individual values at the extremes of the range. Numbers on plot show number of samples for each boxplot.

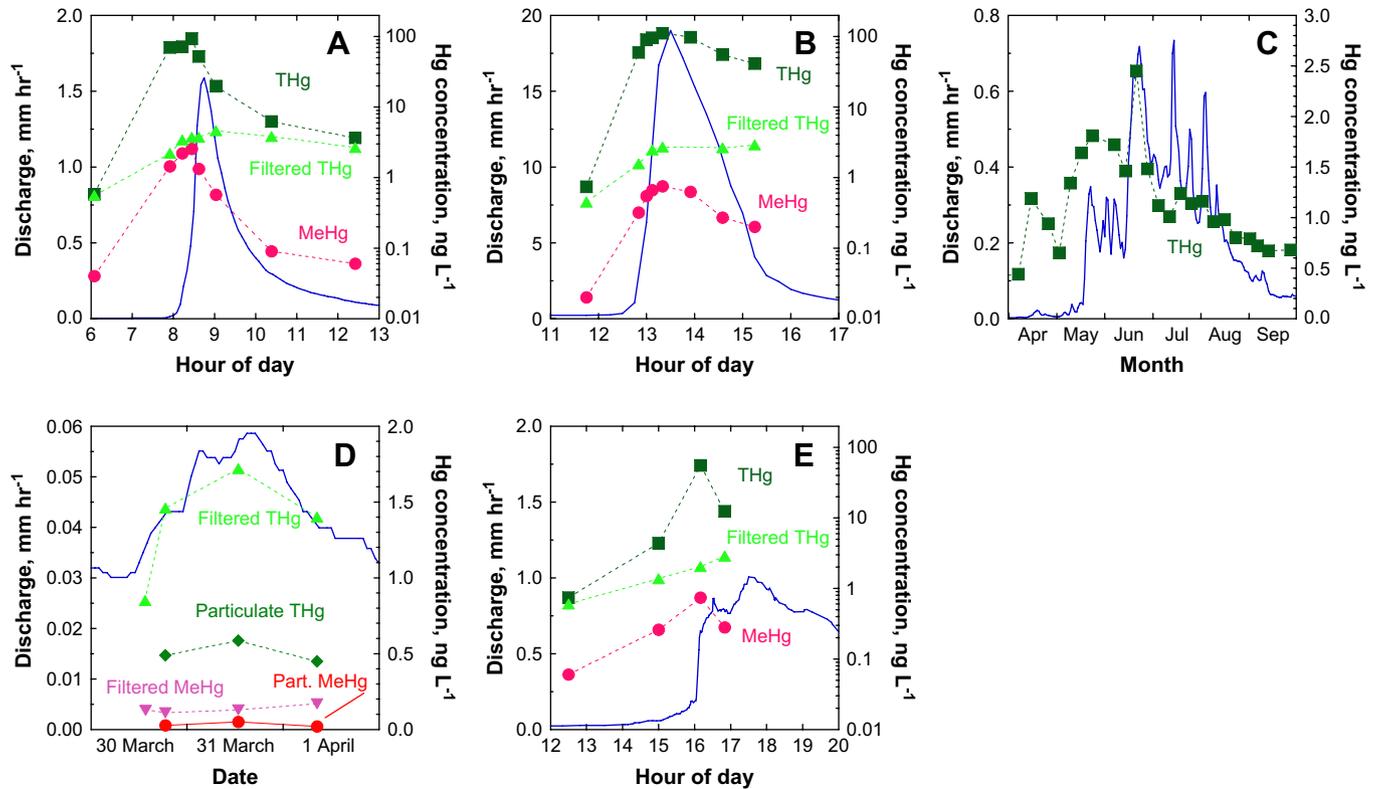


Fig. 4. THg and MeHg concentration patterns during high-flow episodes (with % exceedance time of event peak from flow duration curve (Fig. 2) in parentheses) at (a) Sleepers River, VT (0.07%) 15 Sept. 2002; (b) Rio Icacos, PR (0.05%) 13 Nov 2006; (c) Andrews Creek, CO (0.36%) 2005; (d) Allequash Creek, WI (1.21%) 2006; and (e) Panola Mt., GA (0.23%) 15 Nov 2006. Unless otherwise indicated, concentrations are for unfiltered samples.

to base flow periods. THg and MeHg concentrations at the groundwater-dominated Allequash system were least sensitive of the five sites to changes in flow, though a few elevated values occurred during snowmelt. Sleepers, Andrews, and Panola showed hysteresis, whereby THg and MeHg had higher concentrations on the rising limb of the hydrograph relative to the same discharge on the falling limb. Hysteresis was minimal at Icacos.

THg and MeHg concentrations generally increased in parallel during events (Fig. 4), suggesting common sources for the two species. At Sleepers we have inferred that near-stream or in-stream particulate organic matter, mobilized during storms (Hall and St. Louis, 2004), is the common source for THg and MeHg (Schuster et al., 2008). Mobilization of particulate organic matter is also a plausible mechanism at Panola, where in-stream sediment is high in organic matter, and at Icacos, where bed sediment and suspended sediment are low in organic matter but there is a high correlation of THg and POC (see below).

Episodic transport of THg driven by large concurrent increases in THg concentrations and streamflow has been well documented (Hurley et al., 1998a; Babiarz et al., 1998; Balogh et al., 2005; Scherbatskoy et al., 1998). Episodic transport of MeHg has been less commonly observed but does occur (Branfireun et al., 1996; Babiarz et al., 1998). Our finding of parallel patterns in THg and MeHg concentrations in the

current study contrasts with most published studies that show either scattered or even divergent patterns. Allan et al. (2001), at a small stream in the Canadian Precambrian Shield, found that THg decreased with flow after an initial flush at the start of an event, but that MeHg had a varying response to flow. Allan and Heyes (1998) likewise found that THg and MeHg were decoupled during storm events at Coweeta, NC; THg increased with flow while MeHg changed little. Schwesig and Matzner (2001) found THg and MeHg were decoupled in a German catchment. In Swedish catchments, Bishop et al. (1995a,b) found divergent patterns; THg increased with flow while MeHg decreased. These authors identified organic-rich soils as the source of both THg and MeHg, but attributed the decline in MeHg to a low net methylation rate relative to the hydrologic flushing rate.

4.3. Mercury fluxes

Annual streamwater THg fluxes ranged over two orders of magnitude among the four watersheds quantified (Table 3; Fig. 5), from an average $0.25 \mu\text{g m}^{-2} \text{ year}^{-1}$ at Allequash to $54.4 \mu\text{g m}^{-2} \text{ year}^{-1}$ at Icacos. THg fluxes at Sleepers ($3.26 \mu\text{g m}^{-2} \text{ year}^{-1}$) and Andrews ($1.55 \mu\text{g m}^{-2} \text{ year}^{-1}$) were intermediate, about one order of magnitude from each extreme. Most streamwater THg fluxes reported in the literature for pristine forested catchments are similar to our mid-

Table 3
Water and mercury input and output fluxes at four of the WEBB sites

Site	Full year end date	Water (mm)		Mercury ($\mu\text{g m}^{-2} \text{ year}^{-1}$)							
		In	Out	Atmospheric input		Stream output ^c					
				Wet THg ^a	Dry THg ^b	Filtered THg	Filtered MeHg	Particulate THg	Particulate MeHg	Unfiltered THg	Unfiltered MeHg
Sleepers, VT	9/30/2002	1373	768			1.17				3.03	0.058
	9/30/2003	1174	638			1.19				2.43	0.039
	9/30/2004	1432	941			1.65				4.67	0.077
	9/30/2005	1236	699			0.74				2.92	0.049
	Average	1304	761	8.2	16.9	1.19	0.0152 ^d			3.26	0.056
Icacos, PR	12/31/2006	4362	3692	39.7	79.4	3.48	0.076 ^d			54.38	0.370
Andrews, CO	9/30/2003	1270	1110	9.5	0.4					1.78	
	9/30/2004	1210	790	8.4	0.3					1.50	
	9/30/2005	1170	1010	8.9	0.4					1.38	
	Average	1217	970	8.9	0.4					1.55	0.019 ^d
Allequash, WI	3/31/2005	756	203	7.2	12.1	0.14	0.022	0.064	0.006	0.20	0.028
	3/31/2006	783	221	7.5	12.6	0.20	0.039	0.093	0.006	0.30	0.046
	Average	770	212	7.4	12.3	0.17	0.031	0.078	0.006	0.25	0.037

^a Wet deposition Hg input: Sleepers, annual average from regional model (Miller et al., 2005); Allequash from MDN station WI36; Icacos from lower elevation site using MDN protocols; wet deposition of $26.4 \mu\text{g m}^{-2}$ with 2900 mm precipitation scaled to 4362 mm precipitation at watershed; Andrews from snowpack (winter) or bulk collector (summer).

^b Dry deposition Hg input: Sleepers, annual average from regional model (Miller et al., 2005); other sites assumed that forested areas had dry deposition two times wet deposition.

^c Output assumed to be dissolved at Andrews (negligible suspended sediment); a subset of samples was filtered at Sleepers and Icacos; unfiltered values used in flux calculations were a combination of directly measured values and computed values (filtered + particulate). All samples were filtered at Allequash, unfiltered fluxes were computed as sum of filtered and particulate fluxes. Except at Allequash, filtered MeHg (unfiltered at Andrews) was always or nearly always below detection, so filtered MeHg flux (Unfiltered MeHg flux at Andrews) was calculated assuming concentration was always one half detection limit. These estimated fluxes were not added to the corresponding unfiltered fluxes.

^d Estimated assuming MeHg concentration of 0.02 ng L^{-1} , one-half the detection limit.

range values, including (all values in $\mu\text{g m}^{-2} \text{ year}^{-1}$) 2.3 at Gårdsjön, Sweden (Munthe and Hultberg, 2004); 1.3 at Svartberget, Sweden and 3.2 at Paroninkorpi, Finland (Lee et al., 1998); 1.2–2.1 in Ontario (St. Louis et al., 1994); 0.7–2.8

in Minnesota (Kolka et al., 1999); and 0.4–1.3 at Acadia National Park, Maine (Nelson et al., 2007). Schwesig and Matzner (2001) reported THg export of $15.9 \mu\text{g m}^{-2} \text{ year}^{-1}$ in the forested Lehstenbach catchment in industrialized central Europe.

At Icacos, more than 93% of the THg export was in the particulate fraction, compared to 63% at Sleepers, 31% at Allequash, and $\sim 0\%$ at Andrews. This order of decreasing particulate THg reflects the decreasing importance of episodes to Hg export, except at Andrews, where events dominated THg export but mostly as filtered Hg because the stream had very little suspended sediment (Mast et al., 2005).

Despite the two order of magnitude difference in THg flux, Allequash and Icacos had only a one order of magnitude difference in MeHg flux (0.037 vs. $0.37 \mu\text{g m}^{-2} \text{ year}^{-1}$, respectively). Sleepers MeHg export ($0.056 \mu\text{g m}^{-2} \text{ year}^{-1}$) was similar to that at Allequash, whereas Andrews had no detectable MeHg. Published values of MeHg fluxes are uncommon, but the Sleepers and Allequash MeHg fluxes fall within the range of those reported. Lee et al. (1998) reported 0.03 – $0.16 \mu\text{g m}^{-2} \text{ year}^{-1}$ for four Swedish and Finnish catchments. Schwesig and Matzner (2001) reported $0.089 \mu\text{g m}^{-2} \text{ year}^{-1}$ for filtered MeHg in a German catchment. Balogh et al. (2005) calculated 0.03 – $0.09 \mu\text{g m}^{-2} \text{ year}^{-1}$ MeHg export for five Minnesota rivers. At Allequash, about 80% of the MeHg export was in the filtered fraction, whereas nearly all the MeHg export at Sleepers and Icacos was particulate.

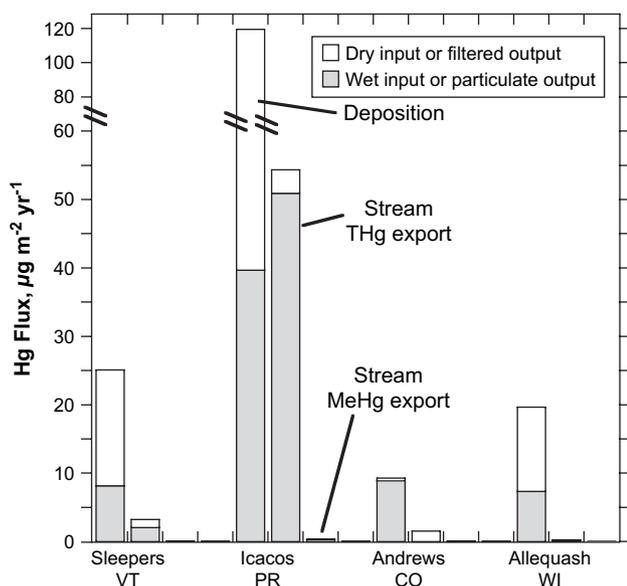


Fig. 5. Mercury fluxes at the four sites quantified for the periods indicated in Table 3. Inputs are measured wet deposition and estimated dry deposition as described in text. Output stream flux calculations for THg and MeHg described in text; apportioned to filtered and particulate load where possible. Fluxes too small to discern are included in Table 3.

These MeHg fluxes in streamwater could potentially be accounted for by wet and dry deposition of MeHg (St. Louis et al., 2001; Hall et al., 2005), with the possible exception of Icacos (where measurements are lacking). However, just as THg newly deposited to uplands is sequestered by soils and vegetation and only slowly (over years) released to surface waters (Harris et al., 2007), atmospheric MeHg inputs to the forest floor are unlikely to enter streamwater rapidly and without transformation. Rather, there is ample evidence that watershed processes exert a stronger control than atmospheric deposition on MeHg concentrations in water and accumulation in fish (Driscoll et al., 2007; Evers et al., 2007; Munthe et al., 2007).

The high THg flux at Icacos is due in part to high wet Hg deposition, which is the highest measured in the USA (Shanley et al., 2006), and high stream runoff, which averages $3610 \text{ mm year}^{-1}$ (Peters et al., 2006). However, the stream THg flux ($55.4 \mu\text{g m}^{-2} \text{ year}^{-1}$) exceeded the Hg input in precipitation (estimated as $39.7 \mu\text{g m}^{-2} \text{ year}^{-1}$ by scaling up from the $26.4 \mu\text{g m}^{-2} \text{ year}^{-1}$ at the deposition station by the difference in precipitation (4362 vs. 2900 mm)). Dry deposition and possibly cloudwater deposition of Hg likely shift the balance to a net Hg retention (subject to unmeasured volatilization losses), but compared to most other sites landscape retention is minimal at Icacos. One explanation could be frequent landslides (Larsen and Torres Sánchez, 1998); disturbance mobilizes THg and MeHg (Porvari et al., 2003; Munthe and Hultberg, 2004). The apparent limited Hg retention may also be an artifact of a geologic source or of Hg used in placer gold mining in this area in the late 19th and early 20th centuries (Wardsworth, 1949; Cardona, 1984).

THg export in excess of wet Hg input is extremely rare; ignoring possible volatilization losses, watersheds typically retain 70–95% of Hg inputs in precipitation (Krabbenhoft et al., 2005; Grigal, 2002; Quémerais et al., 1999; Scherbatskoy et al., 1998; Allan and Heyes, 1998; Mast et al., 2005). Lee et al. (1998) reported lower retention (37%) at a low-lying watershed in southern Finland, and attributed it to the dominance of shallow flow paths through organic-rich soils.

Sleepers retained 60% of THg in wet deposition (Fig. 5). Wet THg deposition was derived from the model of Miller et al. (2005), based on regional measurements. This retention percentage is considerably lower than is typical, and may reflect the focus on event sampling (Fig. 2), whereby we captured a component of export that may often be overlooked. Miller et al. (2005) also modeled dry deposition, considering speciation, elevation, and land cover type. There is increasing recognition that dry deposition may exceed wet deposition in forested landscapes (Kolka et al., 1999; St. Louis et al., 2001; Miller et al., 2005). The modeled dry deposition at Sleepers, including uptake of Hg^0 by foliage, was $16.9 \mu\text{g m}^{-2} \text{ year}^{-1}$ (E. Miller, personal communication). Factoring in dry deposition, watershed THg retention at Sleepers was 87% of atmospheric input.

At Andrews, watershed Hg retention was 83% of bulk Hg input, in close agreement with earlier estimates for this site (Mast et al., 2005). The bulk Hg input measured at Andrews

is likely a reasonable approximation of total Hg deposition, except for a small amount of additional dry input in the 2% of the basin that is forested (Table 3; Mast et al., 2005). Most snowmelt and rainfall in the Andrews basin flows through shallow subsurface flow paths to the alpine stream. These flow paths regulate the export of other chemical constituents (Campbell et al., 1995; Clow et al., 2003), and likely explain why such a high percentage of the Hg input is retained, despite thin, patchy soil cover.

At Allequash, 96.6% of wet Hg input was retained in the basin. Accounting for estimated dry deposition (Table 3), Hg retention increased to 98.7%. About two-thirds of stream THg export was in the filtered fraction. Dominance by the filtered fraction is typical for low-gradient landscapes, although Kolka et al. (2001) found 70% of THg exported in association with POC in a Minnesota bog watershed. Stream THg export at Allequash was about one half that reported from the same watershed in the early 1990s based on analysis of unfiltered samples (Krabbenhoft et al., 1995). The lower export (greater retention) in the present study may be a consequence of dry conditions; runoff at Allequash averaged 210 mm per year compared to 310 mm per year in the previous study.

MeHg flux made up a much higher proportion (14.8%) of the THg flux at Allequash than at the other sites. Despite the lower percent MeHg flux at Sleepers (1.7%) and Icacos (0.7%), the larger THg fluxes at these sites resulted in slightly more (Sleepers) and an order of magnitude more (Icacos) MeHg export compared to Allequash. MeHg export at Icacos and Sleepers, however, was dominated by the particulate fraction (filtered MeHg was generally below detection). Particulate MeHg may be less readily assimilated by aquatic biota, thus low-relief systems like Allequash, despite retaining most of the incoming Hg, may show the most adverse biological effects because of greater MeHg availability.

The export of MeHg from these catchments suggests that upland landscapes have zones and conditions conducive to Hg methylation, and may serve as an entry point for MeHg in the aquatic food web, and/or export MeHg to downgradient ecosystems where it may be taken up. Moreover, the high THg fluxes from these uplands suggest that they are an important source of THg for methylation in lowland streams, wetlands, and lakes (Allan et al., 2001; Munthe et al., 2007). Even if exported in the particulate fraction, THg is available for methylation in downstream receiving waters if desorbed or upon decomposition of the binding organic matter (Hurley et al., 1998a), though questions remain about the bioavailability of this particulate THg (Munthe et al., 2007).

4.4. Controls on THg concentration

At Sleepers, Icacos, and Panola, THg was dominated by the particulate fraction, and the THg-POC relation for Sleepers and Icacos (no POC data were available for Panola) had a strikingly similar slope (Fig. 6), despite their large physical and climatic differences. Allequash had a lower slope. At Andrews, there was little particulate matter so the unfiltered Hg fraction was assumed equal to filtered Hg. The lack of sediment

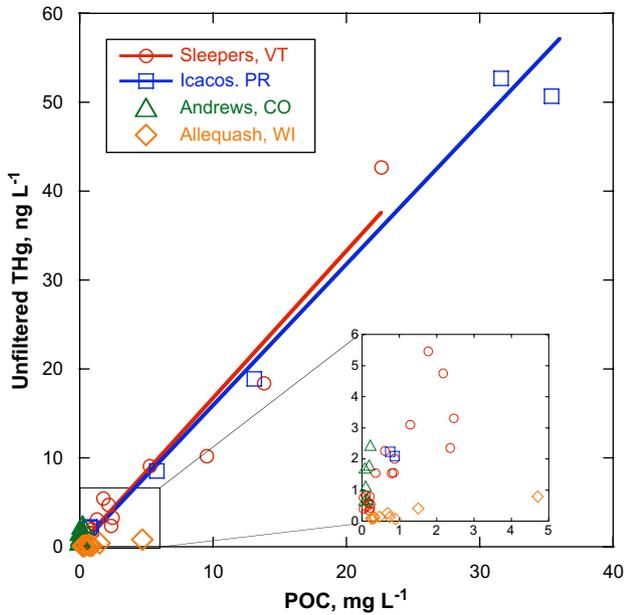


Fig. 6. Unfiltered THg vs. POC at the five WEBB watersheds.

transport at Andrews is one explanation for the low overall THg export.

A similar strong positive relation was evident for filtered THg and DOC (Fig. 7). Sleepers, Icacos, and Allequash had similar slopes, while Andrews had a much steeper slope. The ratio of filtered Hg to DOC in ng Hg/mg DOC was 0.36 ± 0.10 ($n = 26$) at Sleepers; 0.37 ± 0.16 ($n = 4$) at Icacos; 0.24 ± 0.08 ($n = 26$) at Allequash; and 2.94 ± 1.82 ($n = 86$) at Andrews. These ratios are all higher than the ~ 0.2 ng Hg/mg DOC average from the literature reported by Grigal (2002), suggesting that in these low-DOC systems, more Hg is mobilized per unit of DOC. Despite this greater than average “efficiency” of Hg mobilization by DOC, however, mobilization by particles still dominated overwhelmingly

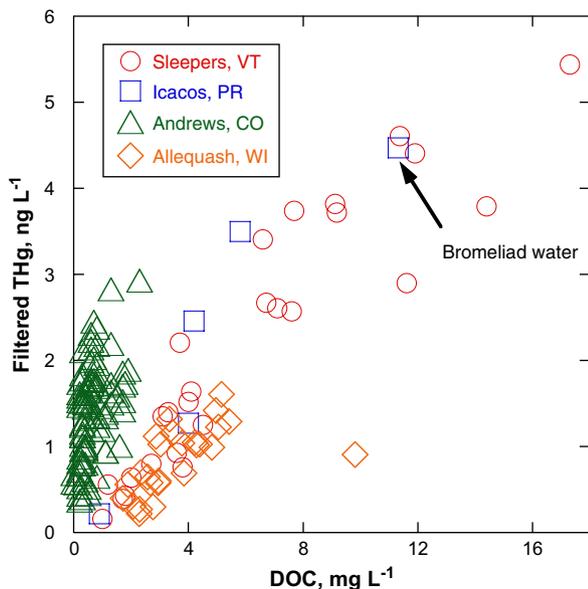


Fig. 7. Filtered THg vs. DOC at the five WEBB watersheds.

at Sleepers, Icacos, and Panola; note that the scale on the filtered THg plot is an order of magnitude lower (Fig. 7).

The hydrophobic acid fraction of the DOC (HPOA) is an even stronger predictor of filtered Hg than bulk DOC, as demonstrated for Sleepers (Fig. 8). HPOA comprises about 50% of the DOC at all sites, and is known to contain the reduced S sites that bind Hg (Haitzer et al., 2002; Ravichandran, 2004). The narrow range of %HPOA in DOC resulted in a strong relation between filtered THg and total DOC, even though HPOA was probably driving this relation.

4.5. Controls on MeHg concentration

As for THg, MeHg was dominated by the particulate fraction at Sleepers, Icacos, and Panola. Unfiltered MeHg was strongly correlated with POC at Sleepers ($r^2 = 0.93$, $p < 0.0001$, $n = 30$) and at Icacos ($r^2 = 0.83$, $p = 0.0004$, $n = 9$) (no data were available from Panola). While the two sites had similar slopes for the unfiltered THg-POC relation, the slope of the unfiltered MeHg-POC relation was more than 2 times greater at Sleepers than at Icacos. Filtered MeHg dominated at Allequash, the only site where it was consistently above the method detection limit. In contrast to the strong unfiltered MeHg-POC relation, filtered MeHg did not correlate with DOC.

Each of the five WEBB catchments had a characteristic streamwater MeHg/THg ratio that remained fairly constant throughout the flow regime at a given site but varied markedly among sites (Fig. 9). These constant ratios suggest that within each site, THg and MeHg have a common source. This source is likely to be hydrologically connected zones within these upland systems—wetlands, riparian areas, in-stream sediments—that sequester THg and provide an environment conducive to methylation. However, THg sources and MeHg

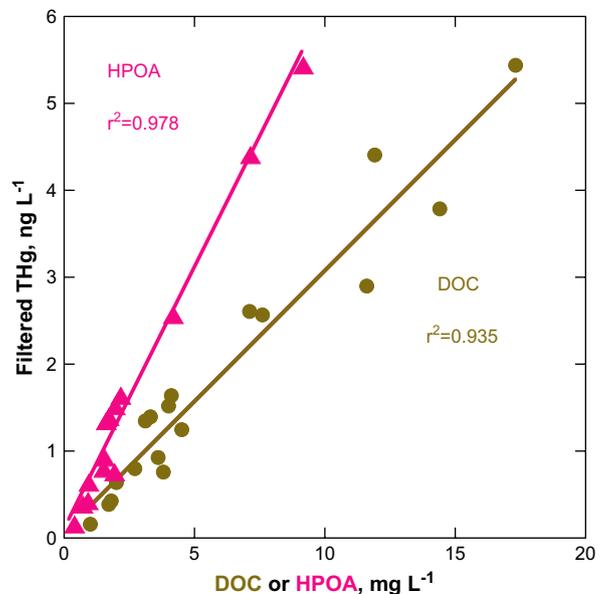


Fig. 8. Concentration of filtered THg vs. DOC and vs. the HPOA fraction of DOC at Sleepers River, VT.

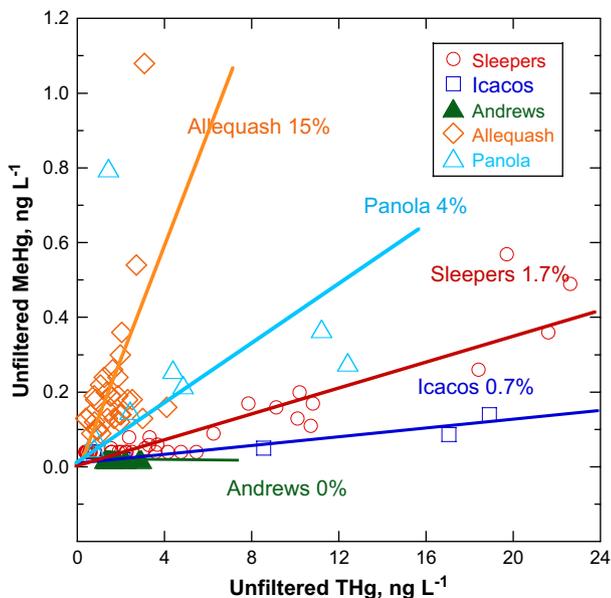


Fig. 9. Unfiltered MeHg vs. unfiltered THg at the five WEBB watersheds. The solid line and percentages for each site are not true regression lines, but are drawn to match the ratios from the calculated fluxes for each site. For Panola, where the relation has a great deal of scatter, the line was fitted approximately and forced through the origin.

production away from water body margins (Stoor et al., 2006) may also contribute to stream fluxes as these areas become hydrologically connected during large storm or snowmelt events. The constant MeHg/THg ratios at each site are surprising given that MeHg concentrations typically vary seasonally (St. Louis et al., 1994; Babiarz et al., 1998; Schwesig and Matzner, 2001; Balogh et al., 2005; Selvendiran et al., 2008).

The percentage of THg as MeHg ranged from near 0% at Andrews to about 15% at Allequash (Fig. 9). These methylated percentages were inversely related to watershed slope; Andrews is the steepest catchment at 67% average slope while Allequash is a low-lying landscape with less than 1% average slope. The other three catchments each have average slopes near 20%, and have intermediate MeHg/THg ratios. Steep slopes tend to limit the amount of soil saturation and anoxia, and thus reduce potential for methylation, but other factors such as rainfall amount, C and S availability, and temperature may also be important factors.

At tropical Icacos, with annual rainfall >4000 mm, and soils at or near saturation year round, the low fraction of MeHg in streamwater (0.7% of THg flux) was surprising. We tested for limitations to methylation by analysis of organic sediment in tank bromeliads. Bromeliads are epiphytes on trees that receive nutrients only from rain and forest debris, often becoming anoxic with high DOC concentrations (Richardson et al., 2000), and thus represent a best-case scenario for methylation. The bromeliad water sample was roughly collinear with stream samples on the filtered THg vs. DOC plot (Fig. 7). Bromeliad sediment had 230 ng THg and 7 ng MeHg per liter of slurry filtered, suggesting that there are no Hg, C, S, or bacterial limitations to methylation in this

ecosystem. One possibility for the low percentage of MeHg in streamwater is that demethylation rates are high.

5. Conclusions

We used the small watershed approach with an emphasis on high-flow sampling to investigate THg and MeHg cycling at the five geographically and climatically diverse USGS WEBB sites. Watershed processing of THg ranged widely, from >96% retention (based on wet deposition and ignoring any subsequent volatilization) at low-relief Allequash Creek, WI, to net export at high-relief wet tropical Rio Icacos, Puerto Rico. At the two sites with greatest export, Icacos and Sleepers River, VT (60% retention) and likely also at Panola Mountain in the Georgia Piedmont (annual fluxes not computed), Hg flux was dominated by episodic transport of particulate THg in association with POC at high flows. These three sites had more modest episodic fluxes of filtered (<0.7 μm) THg. THg export was lower but also episodic at Andrews Creek in the Colorado Rockies (83% retention), but was dominated by filtered THg because POC was low. Filtered THg at these sites was strongly correlated with DOC, particularly the HPOA fraction of DOC.

MeHg behavior paralleled THg behavior to a surprising extent at most of the sites. Like THg flux, the particulate fraction dominated MeHg flux at Sleepers, Icacos, and Panola, and the filtered fraction dominated MeHg flux at Allequash. MeHg was below detection (0.04 ng L^{-1}) at Andrews. The parallel patterns of THg and MeHg resulted in constant MeHg/THg ratios at each site, ranging from near 0% at Andrews to 15% at Allequash. At Icacos, MeHg was only 0.7% of THg, but the high THg flux resulted in MeHg flux that was an order of magnitude greater than that at Allequash.

Capturing THg and MeHg dynamics during high flow, when most of the flux occurs, provides insights into processes and better quantification of watershed retention than can be obtained from fixed interval sampling. Much of the previous upland mercury research has focused on boreal landscapes; we stress that processes in lower-DOC landscapes as represented by these five WEBB watersheds also result in the export of considerable THg and MeHg.

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