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Streamwater fluxes of total mercury and methylmercury into and out of Lake Champlain

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ABSTRACT

From 2000 to 2004, we sampled for total mercury (THg) and methylmercury (MeHg) in inlet streams to Lake Champlain, targeting high flow periods to capture increases in THg and MeHg concentrations with increasing flow. We used these data to model stream THg and MeHg fluxes for Water Years 2001 through 2009. In this mountainous forested basin with a high watershed-to-lake area ratio of 18, fluvial export from the terrestrial watershed was the dominant source of Hg to the lake. Unfiltered THg and MeHg fluxes were dominated by the particulate fraction; about 40% of stream THg was in the filtered (<0.4 μm) phase. THg flux from the watershed to the lake averaged 2.37 μg m^{-2} yr^{-1}, or about 13% of atmospheric Hg wet and dry deposition to the basin. THg export from the lake represented only about 3% of atmospheric Hg input to the basin.

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1. Introduction

All 50 states in the USA have advisories on fish consumption due to mercury (Hg) content. The Northeast is particularly susceptible to Hg contamination for two reasons: (1) it has moderately high atmospheric Hg deposition (Miller et al., 2005), and (2) the landscape is rich in organic matter and sulfate, and has abundant wetlands which promote the conversion of total Hg (THg) to the toxic methylmercury (MeHg) form that transfers up the food chain (Evers and Clair, 2005). Research on the methylation process has long focused on wetlands, for example, the Everglades (Benoit et al., 2001; Reddy and Aiken, 2001; Aiken et al., 2003) and San Francisco Bay delta (Marvin-DiPasquale and Agee, 2003), where anoxic conditions support sulfate reducing bacteria thought to be the primary agent performing the methylation. Runoff from uplands supplies Hg to downstream wetlands. Upland landscapes hold a legacy of stored Hg from past decades of elevated deposition (Engstrom and Swain, 1997; Schuster et al., 2002; Grigal, 2002; Kamman and Engstrom, 2002). We now know that Hg is methylated in uplands as well (Krabbenhoft et al., 2004; Stoor et al., 2006) and enters the terrestrial food chain, for example in mountain songbirds of the northeastern USA (Rimmer et al., 2005).

The Great Lakes and upper Mississippi River basins have been a focal point for Hg research (Hurley et al., 1995, 1998; Balogh et al., 1997, 1998; Babiarz et al., 1998, 2001; Rolfhus et al., 2003), due in part to the importance of these water bodies for fishing and water supply. Much of the Hg research on the Great Lakes was also motivated by their relatively small watershed-to-lake area ratios (e.g., 1.6 for Lake Superior). Such a small ratio makes the Great Lakes uniquely suited to assess the relative importance of direct atmospheric Hg deposition to the lake surface, compared with streamwater Hg input. Lake Champlain has a mountainous watershed and a much higher watershed-to-lake area ratio of 18, posing an interesting contrast to the Great Lakes for Hg cycling research.

Research on Hg in the Lake Champlain basin started in the early 1990s with the establishment in Underhill, Vermont, of what is now the longest continuously operating event-based Hg wet deposition monitoring station in the world (Keeler et al., 2005). Other research has focused on stream dynamics (Scherbatskoy et al., 1998), and throughfall and litterfall (Rea et al., 1996). Some of this earlier work on Hg in the Lake Champlain basin was summarized in Shanley et al. (1999) and used to develop a model of Hg concentration distribution within the lake based on atmospheric and streamwater inputs (Gao et al., 2006). The Gao et al. (2006) model has been updated by Miller et al. (submitted for publication). The research reported here marks the first comprehensive study of streamwater THg and MeHg in the Lake Champlain basin. Our study focused on characterizing THg and MeHg dynamics in streamwater with respect to hydrologic conditions and land cover, and quantifying fluxes into and out of Lake Champlain.

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2. Lake Champlain setting

The Lake Champlain basin occupies 21,150 km^2, including much of western Vermont, northeastern New York, and part of southern Québec. Land cover is 64% forested, 16% agricultural, 14% water/wetlands (nearly half of which, 1136 km^2, is Lake Champlain itself), and 6% urban (Table 1) (Lake Champlain Basin Program, 1999). Land use within the 18 sampled tributaries ranged from 24 to 99% forested, 0–53% agricultural, and 0–4.4% urban, except one small watershed (1.7 km^2) in Burlington, VT that was 71% urban. All land use percentages were derived from the National Land Cover Dataset (http://landcover.usgs.gov) and its Canadian counterpart (http://www.vcgi.org).

3. Methods

3.1. Field sampling

We collected 135 samples from 18 Lake Champlain tributaries, 14 sites within the lake, and the lake outlet (Fig. 1) during a 4-year period from 2000 to 2004. All tributaries in the study had USGS streamflow gages. We sampled either at the gage or as far downstream as possible while remaining above the effect of backwater from Lake Champlain, which fluctuates as much as 2 m annually (Shanley and Denner, 1999). Fourteen streams, representing 68% of the terrestrial basin area, were sampled routinely and four additional streams were sampled for a one-time purpose (Table 1). One round of streamwater samples was collected at the 14 routine sites during summer low flow, and most other sampling was conducted during high flow events, both snowmelt and rainstorms. High-flow sampling focused on a subset of 7 of the 14 sites representing a range of watershed sizes and land uses (Table 1). Five samples were collected from the Richelieu River, the outlet of Lake Champlain, near the Environment Canada gage at St. Jean, Québec. Lake-water epilimnion samples (0.3 m depth) were collected at 14 sites representing diverse sites on Lake Champlain in September 2001. Most water samples were collected for unfiltered THg and MeHg. However, filtered THg and MeHg were also analyzed on one set of base flow samples (THg only), one set of snowmelt samples, and multiple samples at 3 sites during a fall storm.

Mercury samples were collected in precleaned Teflon bottles stored in double ziplock bags, and processed using ultra-clean techniques (Olson and DeWild, 1999). Major tributaries were sampled from the bank at base flow in summer 2000. All subsequent samples were collected near the centroid of flow by grab at wadeable streams, and from bridges using a reel and cable to lower an isokinetic D-95 sampler (Wilde et al., 2005), equipped with a teflon nozzle and sample bottle at non-wadeable streams. The need to sample multiple rivers during high flows of limited duration prevented integrated cross-section sampling, however we assumed streams were relatively well-mixed at high flows. Colman and Breault (2000) reported good agreement in THg concentrations between integrated and single-point sampling for similar size rivers in Massachusetts. Of the 135 total samples, 38 samples were filtered (quartz fiber, 0.4-μm) for determination of filtered THg and MeHg.

3.2. Laboratory analysis

The base flow samples from 2000 were analyzed for THg at the University of Michigan Air Quality Laboratory in Ann Arbor, MI, using methods described in Burke et al. (1995). For the remainder of the study, THg and MeHg were analyzed by cold vapor atomic fluorescence spectrometry (EPA methods 1631 and 1630) at the USGS Mercury Lab in Middleton, Wisconsin (Olson and DeWild, 1999; DeWild et al., 2002). Laboratory quality control procedures at both labs included blank and replicate samples, matrix spikes and certified reference materials. The minimum reporting limit for THg was 0.04 ng/L. Minimum acceptable precision on replicate samples was a relative percent difference of 10% (if THg $>$ 0.2 ng/L) or an absolute difference of 0.02 ng/L (if THg $<$ 0.2 ng/L), and acceptable percent recovery for a matrix spike between 90 and 110%. For methylmercury, the minimum reporting limit was 0.025 ng/L, and the minimum acceptable precision on replicate samples was a relative percent difference of 20%, and acceptable percent recovery for a matrix spike between 80 and 120%.

Total organic carbon (TOC) was analyzed at the USGS Mercury Lab by a carbon analyzer using acidification and persulfate/UV oxidation. Total suspended sediment (TSS) and particulate carbon (PC) (EPA method 440.0, Zimmerman et al., 1997) were analyzed for all stream samples at the Chesapeake Biological Laboratory (CBL). Particulate inorganic carbon (PIC) was determined on four samples from different streams during the 2003 snowmelt. PIC was 0.6%, 2.0%, 3.3%, and 13.8% of PC, low enough that we assumed PC approximated particulate organic carbon (POC) on all samples. Prior to 2003, TSS and loss on ignition (LOI) were determined at the University of Vermont (UVM). LOI was determined gravimetrically on TSS samples after heating to 550 ° C. For converting LOI to POC, we used the common assumption that LOI was 50% C. No direct comparison of TSS analysis was made between labs, but the relations between THg concentration and TSS for each period have identical slopes ($p < .001$). A similar assessment suggests that C content determined from LOI (UVM) was biased slightly low compared to POC (CBL).

3.3. Hg flux calculations

To calculate unfiltered THg flux in the inlet streams, we exploited the strong relation of THg to TSS (Wall et al., 2005; Whyte and Kirchner, 2000; Riscassi et al., 2011) ($r^2 = 0.92$, $n = 135$ in this study, Supplementary Material (SM) Table S1). We made use of the frequent TSS measurements by the Vermont Department of Environmental Conservation – about 12 samples per year at or near our sampling sites on each of the 14 streams we routinely monitored for Hg (www.anr.state.vt.us/

Table 1
Characteristics of sampled watersheds. Sites in bold were priority for high flow sampling. Sites in italics were sampled on a limited or specialized basis, and fluxes were not calculated.

Sampling site[a]	n[b]	Latitude[c]	Longitude[c]	Basin area, km^2[d]	Land use, percent				
					Forested	Agriculture	Urban	Water	Wetlands
Lake Champlain, 14 locations	14	na	na	21150	64.3	16.0	5.6	10.3	3.8
Pike River @ Rt 133, Quebec	5	45°07′25″	−73°04′11″	593	48.6	43.7	4.4	1.9	0.9
Missisquoi River @ Rt 78, Swanton, VT	11	44°55′00″	−73°07′44″	2202	73.2	20.9	3.0	1.0	1.9
Lamoille River @ Rt 2, near Milton, VT	22	44°36′12″	−73°12′16″	1862	77.4	15.8	2.2	1.3	3.4
West Branch Little River near Stowe, VT	3	44°31′29″	−72°46′31″	12	98.0	0.4	1.2	0.0	0.4
Ranch Brook @ Ranch camp, near Stowe, VT	8	44°40′14″	−72°46′56″	10	99.3	0.0	0.0	0.0	0.6
Winooski River @ Rt 127, Colchester, VT	25	44°31′28″	−73°15′23″	2748	79.6	12.5	4.0	1.0	3.0
Englesby Brook @ Burlington, VT	22	44°27′28″	−73°13′11″	1.7	24.2	0.0	71.2	0.0	6.1
Laplatte River @ Falls Rd, Shelburne, VT	24	44°22′12″	−73°13′00″	115	43.9	48.3	2.1	1.2	4.5
Lewis Creek @ old Rt 7, N Ferrisburg, VT	1	44°14′57″	−73°13′44″	198	64.2	29.1	0.6	1.0	5.1
Little Otter Creek @ Ferrisburg, VT	19	44°11′53″	−73°14′58″	151	40.9	52.9	1.6	0.3	4.4
Otter Creek @ Rt 22A, Vergennes, VT	15	44°09′58″	−73°15′23″	2261	67.8	23.7	2.6	1.6	4.3
Poultney River @ East Bay Rd nr Whitehall, NY	4	43°34′12″	−73°23′32″	677	65.7	26.2	2.6	3.0	2.5
Mettawee River @ Saunders St, Whitehall, NY	4	43°33′25″	−73°24′04″	1097	64.2	29.5	3.4	1.4	1.6
LaChute River @ Ticonderoga, NY	1	43°50′59″	−73°24′51″	673	77.2	2.0	1.7	18.1	0.9
Bouquet River @ Rt 22, Willsboro, NY	4	44°21′30″	−73°23′50″	705	90.3	7.5	1.0	1.0	0.2
Ausable River @ Rt 9, NY	5	44°33′32″	−73°26′56″	1330	91.9	3.8	1.3	1.9	1.0
Saranac River @ Saranac St, Plattsburg, NY	5	44°41′32″	−73°27′12″	1586	85.2	4.4	1.5	6.4	2.5
Great Chazy River @ Rt 9B, Coopersville, NY	4	44°56′32″	−73°24′33″	694	68.9	22.2	0.9	1.6	6.2
Richelieu River @ Gouin Bridge, Iberville, Quebec	6	45°18′25″	−73°14′48″	22000	64.3	16.0	5.6	10.3	3.8

[a] Sites presented in same order as Fig. 2, generally clockwise around lake.
[b] n, number of samples collected.
[c] 1927 North American datum.
[d] Basin area at point of sampling.

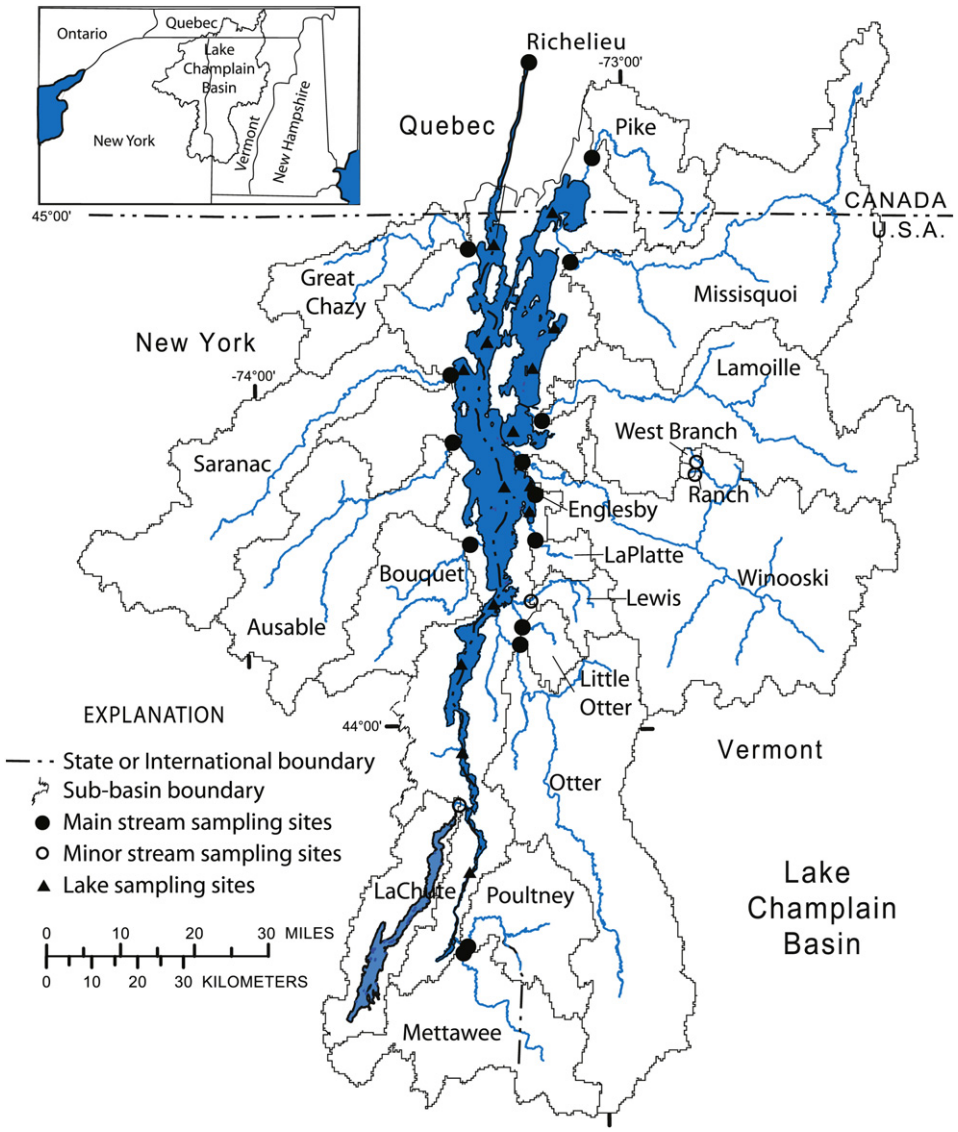

Fig. 1. Map of Lake Champlain basin, showing tributary sampling sites and watershed outlines, lake sampling sites, and lake outlet sampling site (Richelieu River).

dec/waterq/lakes/htm/lp_long-term.htm). We also determined TSS in our study with each Hg analysis, and individual site regressions of TSS vs. discharge indicated no bias between the two sources of TSS values, so we pooled the TSS data. The THg flux was calculated for each 15-min interval stream discharge value by first calculating a TSS concentration from the TSS-discharge relation, then converting to a THg concentration from the THg–TSS relation, and finally multiplying THg concentration by discharge. The 15-min THg fluxes were summed to compute annual THg fluxes on a water-year basis. Annual fluxes were then normalized to basin area.

Keying the flux calculation to the detailed hydrograph captures the exponential increases in THg flux that occur at high flow. Note that the regression equations ultimately allow the calculation of THg concentration from discharge alone, but using TSS as an intermediary helps refine the THg–discharge relation. The large number of TSS analyses helped to build robust models, allowing an improved prediction of THg than if the smaller number of THg analyses were regressed directly on discharge (SM Table S1). However, the underlying TSS-discharge relations had scatter due to hysteresis, precipitation intensity, and other factors, imparting uncertainty to the estimated fluxes. We calculated percent uncertainty in fluxes at each site as standard error of the final concentration model (assessed from residuals) relative to the mean of observed values. Uncertainty in stream discharge, which was typically <10%, was ignored.

For unfiltered MeHg, 4 streams had significant concentration–discharge relations, and we used these to model MeHg fluxes. For the other 10 streams that lacked a relation, we calculated MeHg flux assuming a constant, average MeHg concentration for each stream (SM Table S2). We had many fewer filtered THg and MeHg samples, and none at all for many sites. However, across all sites sampled, filtered THg had a fairly linear relation to specific discharge up to moderate discharges, then plateaued at an average value of 2.2 ng L^{-1} (SM Figure S1), and we applied this single stepwise relation to each stream to estimate filtered THg flux. Filtered MeHg was too often below detection to calculate its flux. For the Richelieu River (Lake Champlain outlet), we had TSS concentrations only from our samples, so we built THg and MeHg concentration models solely from discharge.

Although we sampled only from 2000 to 2004, we calculated stream Hg fluxes for Water Years 2001–2009 (a water year runs from October 1 of the prior year through September 30 of the designated water year), assuming no change in the empirical relations, as the more recent flux values supported other studies (e.g., Miller et al., submitted for publication).

4. Results

4.1. Hydrology

For hydrologic context, we note that the 2001–2004 sample collection period was a somewhat drier than average period that followed a wet decade. For the 7 tributaries with 80–100 years of record, runoff during the 1990s was 110% of average, whereas runoff for each of water years 2001, 2002, and 2003 was from 92 to 96% of the long-term average. However, the rest of the 2000s decade, through which the Hg flux calculations were extended, was quite wet, with runoff for all six water years from 2004 through

2009 ranging from 100 to 151% of the long term average and 135% overall. We assumed that the concentration models calibrated during a relatively dry period did not shift during the following wetter period, but we have no way of testing this assumption.

Snowmelt is the dominant hydrologic event, generating sustained high flow and often the highest annual peak flows from mid-March to mid-May (Shanley and Denner, 1999). Summer and fall storms may also generate high peak flows, but streams quickly return to base flow following these storms. Some of the larger tributaries to Lake Champlain are regulated for hydropower generation, damping and redistributing the natural runoff.

4.2. Lake Champlain

THg concentrations in the Lake Champlain epilimnion were lower than any of the tributaries (Fig. 2). Over the 11 sampling days (August 17–27, 2001) samples from 14 distributed points on the lake showed surprisingly little variation in THg (0.31 ± 0.19 ng L^{-1}). Methylmercury concentrations were below detection (0.04 ng L^{-1}) at all but one site (0.05 ng L^{-1}). THg and MeHg concentrations in the lake epilimnion were typically lower than those in the Richelieu River, the lake outlet.

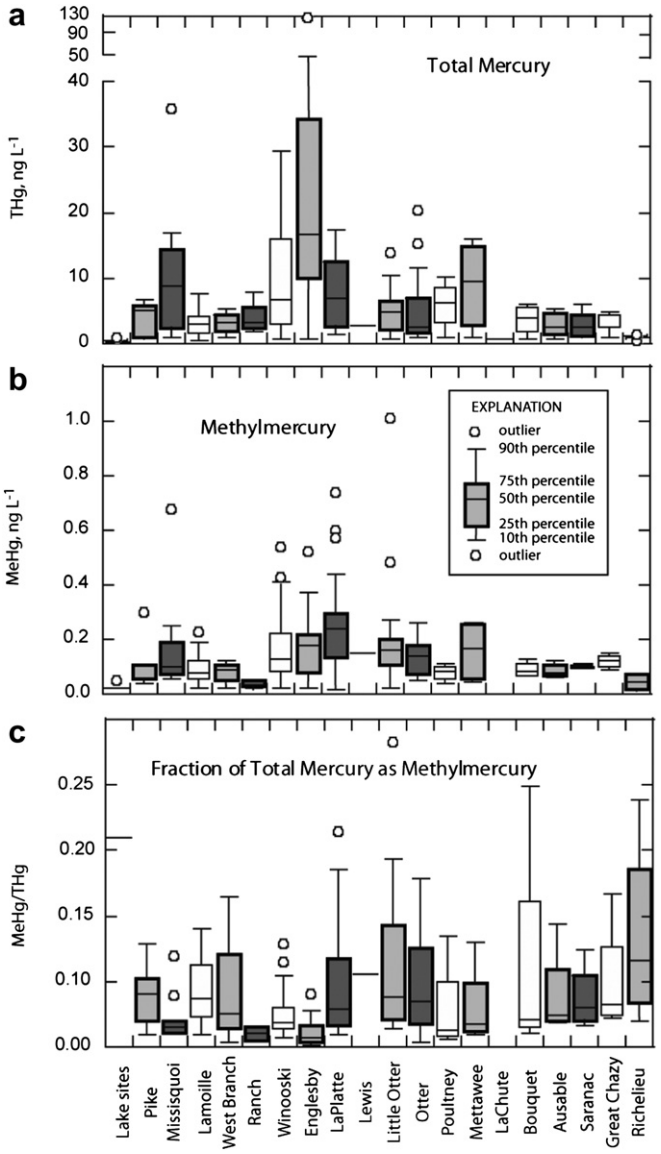

Fig. 2. Boxplots of (a) unfiltered THg, (b) unfiltered MeHg, and (c) fraction of total mercury as methylmercury (MeHg/THg) in Lake Champlain basin streamwater and lake sampling sites, 2001–2004.

4.3. Stream THg and MeHg – Spatial patterns

For the 38 filtered (<0.4 μm) samples analyzed, filtered THg ranged from 0.28 to 0.95 ng L^{-1} at base flow, 0.51–3.0 ng L^{-1} at snowmelt and 0.33–5.6 ng L^{-1} in a fall storm (Table S3). We term the <0.4 μm fraction "filtered THg" rather than "dissolved THg" because colloids are present in this fraction (Babiarz et al., 2003). Filtered MeHg was not analyzed in the 2000 base flow samples. During snowmelt, filtered MeHg concentrations ranged up to 0.09 ng L^{-1}; 9 of 15 samples were below detection (0.04 ng L^{-1}). For the fall storm, all 14 samples had filtered MeHg below detection (SM Table S3). Given that both THg and MeHg in streamwater were primarily in particle form, we usually collected and analyzed only unfiltered samples. Unless noted otherwise, all results reported hereafter are for THg and MeHg concentrations on unfiltered samples.

Total Hg concentrations in most streams varied from <1 to >15 ng L^{-1} (Fig. 2). The median THg concentration was less than 10 ng L^{-1} for all sites except the urban Englesby Brook, but several individual samples had THg greater than 20 ng L^{-1}. Englesby Brook had the highest median (15 ng L^{-1}) and single sample (129 ng L^{-1}) THg concentrations. The Richelieu River, the outlet of Lake Champlain, had consistently lower THg concentrations than any of the inlet streams, with a median of 0.92 ng L^{-1} and a highest measured concentration of 1.4 ng L^{-1}.

MeHg concentrations in streamwater ranged from <0.04 ng L^{-1} – ~1.0 ng L^{-1} (Fig. 2). The relative variation in median concentrations of MeHg was somewhat less than that of THg across sites. LaPlatte River had the greatest median MeHg concentration of 0.25 ng L^{-1}. Seven sites, including LaPlatte, had at least one sample with MeHg concentration less than detection limit. Although THg and MeHg followed a similar dynamic of increasing concentrations with increasing flow, the fraction of THg as MeHg varied considerably both within and across sites (Fig. 2).

Urban Englesby Brook had the highest THg concentrations, but its MeHg concentrations were comparable to the other tributaries (Fig. 2). Conversely, two mesoscale basins, LaPlatte River and Little Otter Creek, showed some of the highest MeHg concentrations while THg was average. These two streams drain primarily agricultural basins that also contain wetlands. Two of the largest tributaries, Winooski River and Missisquoi River, which have a mix of mountainous forested land and low-lying agricultural land, had relatively high THg and MeHg. Another large basin with similar land-use mix, the Lamoille River, had relatively low THg and MeHg, possibly due to impoundments in its lower reaches. Finally, Otter Creek, a large low-gradient tributary with abundant riparian wetlands, had THg and MeHg concentrations slightly below average (Fig. 2).

4.4. Stream THg and MeHg – Temporal patterns and relations to TSS

THg and MeHg concentrations in streamwater varied greatly with season and hydrologic conditions, as exemplified by the Winooski River (Fig. 3). At summer base flow, THg concentrations were typically <2 ng L^{-1} and MeHg concentrations were typically <0.1 ng L^{-1}. Both THg and MeHg concentrations increased by about an order of magnitude under high flow conditions. Excluding the urban Englesby Brook, THg concentrations at the other 13 routine sites strongly correlated with total suspended solids (TSS) ($r^2 = 0.90$) (Fig. 4). This strong relation was the basis for using TSS as a surrogate in the THg flux calculations. At Englesby Brook, the relation had an r^2 of only 0.44 but a slope 4 times steeper, i.e., 4 times more THg export per unit

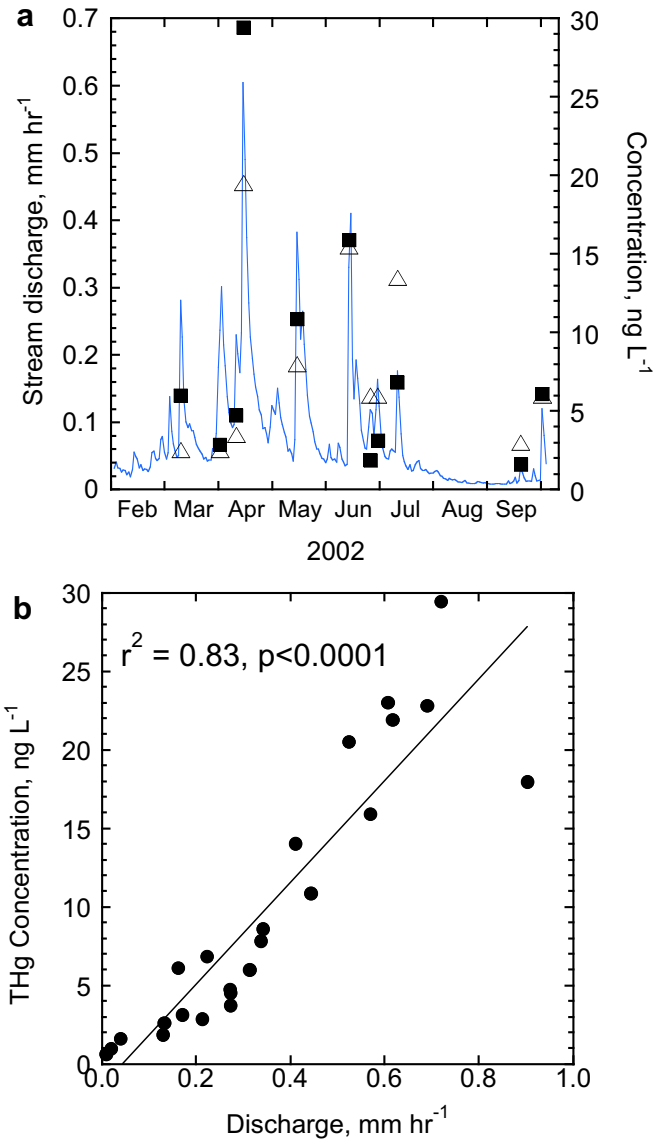

Fig. 3. (a) Unfiltered THg and MeHg concentrations plotted on the Winooski River hydrograph for part of 2002. (b) Relation of unfiltered THg and stream discharge for the Winooski River, all samples, 2001–2004. Unfiltered MeHg vs. stream discharge (not shown) also had a positive correlation with $r^2 = 0.38$, $p<0.05$.

of TSS. TSS at these sites was primarily inorganic; POC positively correlated with TSS ($r^2 = 0.78$, excluding Englesby) with only about 3% of the TSS as POC, indicating that the TSS was about 6% organic matter. The relation of THg concentration to POC had a slightly lower correlation ($r^2 = 0.87$, excluding Englesby) than that to TSS (Fig. 4). The relation at Englesby Brook again had a lower r^2 (0.70) but greater slope. MeHg concentrations correlated more weakly to TSS ($r^2 = 0.43$) and POC ($r^2 = 0.25$).

Based on the tight linear fit of the THg–TSS relation, there appeared to be little seasonal pattern in the amount of THg per unit of TSS. The considerable scatter in the relation between MeHg and TSS, on the other hand, was likely due to seasonality, i.e., the strong temperature dependence of methylation. MeHg concentrations were relatively low during the snowmelt season, but increased as water temperature increased in summer (Fig. 5). Total Hg concentrations generally decreased in summer due to lower flows and lower TSS. Decreasing THg coupled with increasing MeHg led to a sharp increase in percent MeHg, from <1% in the dormant season to as much as 20% in summer (Fig. 5). The greater importance of methylation in summer was also evident in the relative patterns of THg and MeHg in the Winooski River (Fig. 3).

4.5. Hg mass flux in streams

Annual THg flux per unit area varied within a factor of 2 across sites (excluding urban Englesby Brook, which was a high outlier) and by factors of 2–7 across years (Table 2). Annual discharge varied by factors of 1.5–4 (depending on the site) across years, but the positive THg–discharge relations caused disproportionately high THg export in wet years. For water years 2001 through 2009, the grand mean THg flux per unit area was 2.37 ± 1.53 μg m^{-2} yr^{-1} for the 14 inlet streams monitored (Table 2). These stream basins include 68% of the terrestrial Lake Champlain basin area. For the purpose of calculating a mass balance for the lake, we assumed that the THg flux per unit area in the unmonitored area equaled that in the monitored basins. THg output from the lake via the Richelieu River averaged 0.53 μg m^{-2} yr^{-1}, 23% of the tributary THg flux into the lake. The large uncertainty of THg flux out of Lake Champlain is due to limited sampling and a poor THg-discharge model (Table 2). By comparison, the average basinwide atmospheric Hg deposition (wet + dry), calculated from Miller et al. (2005), was 19.2 μg m^{-2} yr^{-1}. Thus the net retention of Hg in the terrestrial basin was 87 ± 8% and the net retention of Hg in the lake/watershed system was 97 ± 4% (Fig. 6).

Relative to unfiltered THg, filtered THg had a subdued response to flow, initially increasing but then leveling off with increasing discharge. At low flow, most of the THg was in the filtered phase, so filtered and unfiltered THg concentrations were about the same. Thus the cumulative filtered THg flux increased incrementally, in contrast to the more episodic unfiltered THg flux, which was strongly dominated by particle THg during events. For the combined tributary input to the lake over the 9 years, the filtered THg flux was 40% of the unfiltered THg flux.

Annual MeHg flux per unit area varied within a factor of just over 2 across sites and by factors of 1.6–4 (depending on the site) across years (Table 2). This range was smaller than that of THg, and similar to that of discharge across years, suggesting that MeHg has a more proportional response to flow than THg. For Water Years 2001 through 2009, the grand mean MeHg flux per unit area was 0.07 ± 0.04 μg m^{-2} yr^{-1} for the 14 inlet streams monitored (Table 2). As with THg, we assumed this areal flux applied to the unmonitored areas as well. For the period, MeHg flux from watershed to lake averaged 2.8% of the THg flux. We estimated MeHg at the lake outlet as 0.025 μg m^{-2} yr^{-1} (Table 2), but due to the poor MeHg-discharge relation this flux has high uncertainty. The lake appears to be a net sink for MeHg.

Typical relative timing of stream outputs of the Hg fractions and flow are illustrated by cumulative flux plots for the Winooski River in Water Year 2001 (Fig. 7). WY2001 was slightly drier than average but had a larger than average snowmelt. The episodic nature of particulate THg flux and its dominance by the particle phase was apparent from the steep increases in cumulative flux relative to flow and filtered THg flux in a large December rainstorm and April snowmelt (Fig. 7a), and the finding that greater than 90% of the THg flux occurred during less than 10% of the total time and with less than 50% of the total flow (Fig. 7b). Cumulative MeHg flux followed a pattern similar to THg, but periods between the large events accounted for a larger fraction (steeper slope in Fig. 7a) of its flux. Filtered THg was a minor fraction of THg during the large events, but made up most of the THg at other times.

4.6. Land cover effects

Mean flow-weighted THg and MeHg concentrations for the 14 streams were back-calculated by dividing annual THg flux (Table 2)

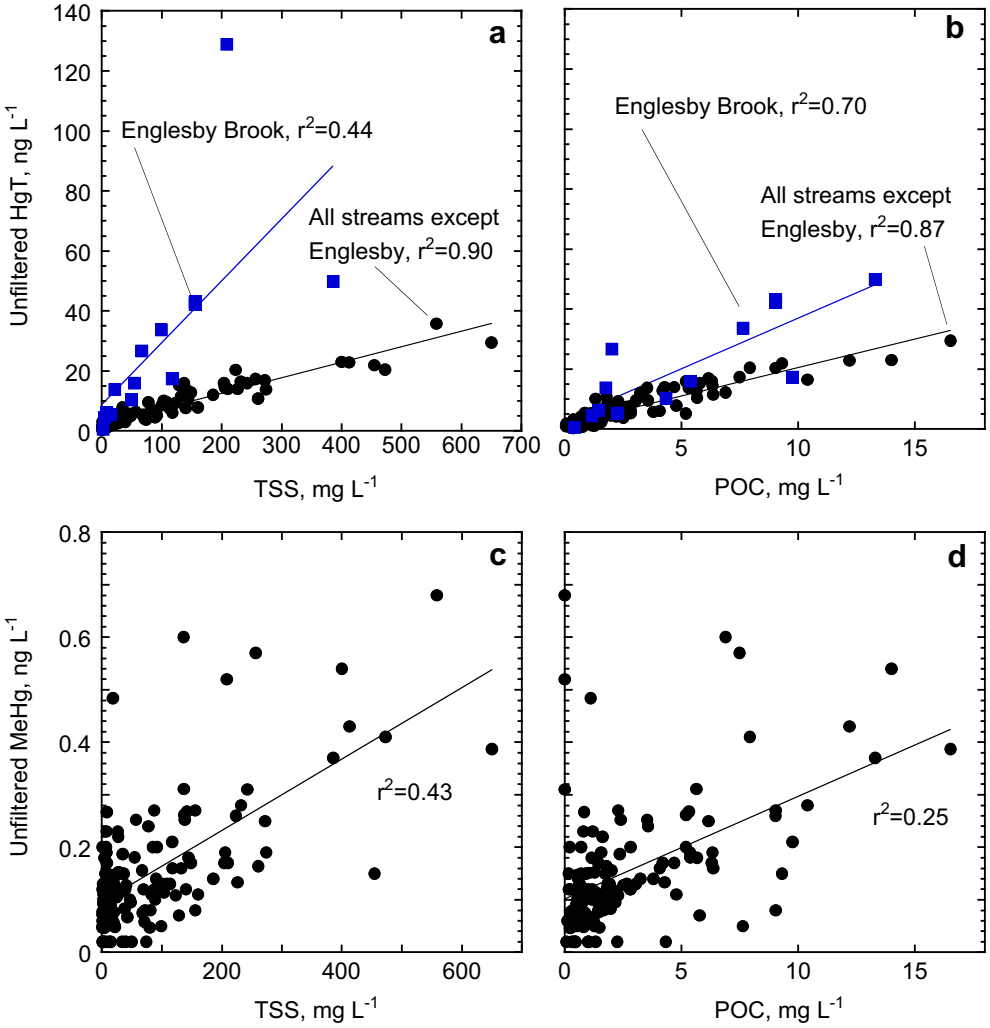

Fig. 4. Relations of (a) THg to TSS, (b) THg to POC, (c) MeHg to TSS, and (d) MeHg to POC, at all 18 tributary sampling sites.

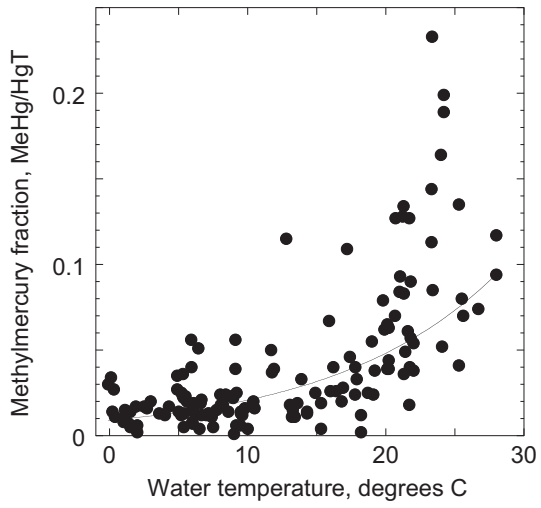

Fig. 5. Fraction of total mercury as methylmercury (MeHg/THg) as a function of water temperature, all 18 tributary sampling sites.

by annual runoff and regressed against percent coverage of the 5 individual land cover categories (Table 1). THg concentration correlated positively with percent agricultural land ($r^2 = 0.66$), as did MeHg ($r^2 = 0.44$). Englesby Brook was excluded from these regressions because it has no agricultural land, and the high urban influence confounds the relation. MeHg concentration also correlated positively with percent wetlands ($r^2 = 0.40$) (SM Figure S2). Because agricultural and forest cover co-dominate, their percent cover values were inversely correlated, thus THg and MeHg concentrations decreased with increasing forest cover. Englesby Brook, with 71% urban cover, had the highest average THg flux per unit area by nearly a factor of three (Table 2). The second most urbanized basin, Pike River, had only 4.4% urban cover, so the effect of urbanization could not be rigorously evaluated.

5. Discussion

5.1. Hg retention in the basin

It is commonly reported that about 90% of mercury deposition is retained in watersheds (Shanley and Bishop, in press), but these retention estimates do not always account for dry deposition, so true retention would be even greater. In this context, our estimate of 87% retention of THg in the terrestrial basin, which does account for dry

Table 2
Annual areal fluxes in μg m^{-2} for unfiltered THg and MeHg for Water Years[a] 2001–2009 for Lake Champlain inlet tributaries and Richelieu River, the lake outlet.

	Area, km^2 [b]	THg										Standard error, %[d]
		WY01	WY02	WY03	WY04	WY05	WY06	WY07	WY08	WY09	Average	
Ausable	1155	1.88	1.53	1.41	2.07	1.93	2.70	2.33	2.23	1.61	1.97	46
Bouquet	705	1.38	0.86	1.06	1.91	1.80	2.28	1.73	1.92	1.32	1.59	23
Chazy	629	1.88	1.94	1.60	2.64	2.00	2.73	2.30	2.31	2.19	2.18	63
Englesby	1.7	7.61	6.44	3.51	24.43	7.26	12.70	7.28	9.53	5.27	9.34	54
Lamoille	1776	1.11	1.58	1.07	2.01	1.13	2.26	1.63	1.83	1.17	1.53	32
Laplatte	115	2.47	0.59	1.40	1.88	1.32	4.19	2.38	2.54	1.00	1.97	68
Little Otter	148	4.09	0.67	1.47	3.40	1.22	4.00	2.94	4.54	1.94	2.69	96
Mettawee	432	4.56	1.39	1.63	3.52	2.13	4.07	2.68	3.71	2.10	2.87	73
Missisquoi	2202	2.29	3.46	1.79	4.93	2.31	5.38	3.76	3.30	1.77	3.22	65
Otter	1626	2.32	1.39	1.92	2.86	1.74	3.08	2.65	3.07	2.75	2.42	119
Pike	89	1.85[c]	2.24	1.47	4.89	1.97	7.49	3.32	3.02	1.23	3.05	112
Poultney	484	2.54	1.37	2.06	3.15	1.65	3.53	3.10	3.44	2.39	2.58	51
Saranac	1574	1.48	1.30	1.12	1.76	1.28	1.99	1.87	2.27	1.42	1.61	109
Winooski	2703	3.28	1.87	1.59	3.23	2.44	4.81	3.60	3.67	1.63	2.90	44
Average[e]		2.24	1.83	1.51	2.95	1.87	3.57	2.73	2.85	1.75	2.37	65
Richelieu	21150[f]	0.41	0.39	0.40	0.62	0.49	0.74	0.60	0.65	0.51	0.53	202
		MeHg										
Ausable	1155	0.042	0.037	0.036	0.049	0.045	0.061	0.052	0.050	0.041	0.046	16
Bouquet	705	0.034	0.028	0.034	0.051	0.046	0.060	0.047	0.051	0.042	0.044	40
Chazy	629	0.048	0.052	0.050	0.072	0.057	0.075	0.063	0.064	0.066	0.061	27
Englesby	1.7	0.053	0.047	0.035	0.132	0.054	0.084	0.058	0.079	0.046	0.065	67
Lamoille	1776	0.047	0.063	0.051	0.076	0.050	0.084	0.067	0.076	0.056	0.063	59
Laplatte	115	0.067	0.041	0.073	0.087	0.068	0.134	0.095	0.120	0.071	0.084	74
Little Otter	148	0.056	0.026	0.044	0.078	0.039	0.094	0.066	0.102	0.062	0.063	109
Mettawee	432	0.089	0.068	0.079	0.121	0.085	0.130	0.100	0.121	0.099	0.099	61
Missisquoi	2202	0.041	0.060	0.042	0.082	0.045	0.086	0.070	0.068	0.047	0.060	106
Otter	1626	0.075	0.060	0.077	0.108	0.077	0.113	0.095	0.113	0.111	0.092	51
Pike	89	0.041[c]	0.047	0.043	0.091	0.046	0.097	0.073	0.070	0.041	0.061	103
Poultney	484	0.037	0.027	0.042	0.055	0.034	0.059	0.051	0.058	0.049	0.046	47
Saranac	1574	0.047	0.051	0.048	0.065	0.051	0.074	0.063	0.067	0.061	0.059	10
Winooski	2703	0.074	0.052	0.048	0.086	0.064	0.120	0.093	0.096	0.057	0.077	63
Average[e]		0.055	0.052	0.050	0.079	0.055	0.091	0.074	0.079	0.062	0.066	55
Richelieu	21150[f]	0.020	0.020	0.021	0.030	0.025	0.035	0.029	0.032	0.026	0.026	200

[a] A Water Year (WY) runs from October 1 of the prior year through September 30 of the indicated year.
[b] Based on area at streamgage for accurate water flux; areas may differ from those in Table 1, which are based on sampling point.
[c] Pike Hg flux estimated for WY01 as gage was established late in year.
[d] Model standard error as percent of mean of observations.
[e] Average for each water year weighted by watershed area; best estimate of overall areal flux from the watershed-to-lake.
[f] Compare to: Total area of basin (minus lake) 20,014 km^2; Total gaged area of sampled streams; 13,639 km^2.

deposition, could be considered relatively low. Another watershed study in Vermont, where dry deposition was also considered, likewise found 87% retention of THg (Shanley et al., 2008). Within the Lake Champlain basin, Scherbatskoy et al. (1998) reported 94% THg retention for a small forested watershed, but dry deposition may have been overestimated in that study. This discussion has not considered revolatilization of Hg from the terrestrial landscape, which would cause overestimation of Hg retention, but its flux is considered small (Shanley and Bishop, in press). Only about one quarter of the THg flux to the lake (streamwater plus direct deposition) left the lake in the Richelieu River, for a 97% overall retention in the lake-watershed system. THg may be lost from the lake by evasion to the atmosphere, deposition to sediment, or net uptake by biota.

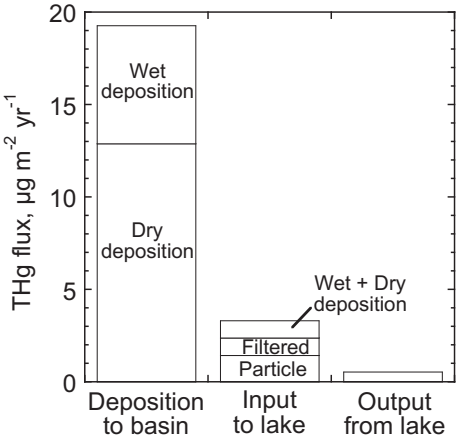

Fig. 6. Mass balance of THg for Lake Champlain and its basin. Wet and dry deposition are modeled estimates from Miller et al. (2005). Output from lake is for unfiltered THg. Uncertainty is not shown to reduce clutter, but is presented in Table 2 and discussed in text.

An earlier review (Shanley et al., 1999) estimated that streamwater inputs of Hg to Lake Champlain roughly equaled direct atmospheric inputs of Hg to the lake surface. Revised estimates of atmospheric deposition (Miller et al., 2005; Gao et al., 2006) and the more rigorous flux calculations presented here, suggest that streamwater Hg input to Lake Champlain is about 2 times direct atmospheric Hg deposition to the lake surface (2.37 vs. 0.94 μg m^{-2} yr^{-1}, normalized to the entire terrestrial basin area). This contrasts with Lake Superior, where tributary loading was only 25–50% of direct atmospheric loading (Rolfhus et al., 2003; Babiarz et al., 2003). The difference is explained by the larger watershed-to-lake area ratio for the Lake Champlain basin (18) compared to the Lake Superior basin (1.6).

5.2. Hg in Lake Champlain

THg and MeHg concentrations in Lake Champlain were quite low. In fact, the frequent MeHg non-detects inspired a subsequent

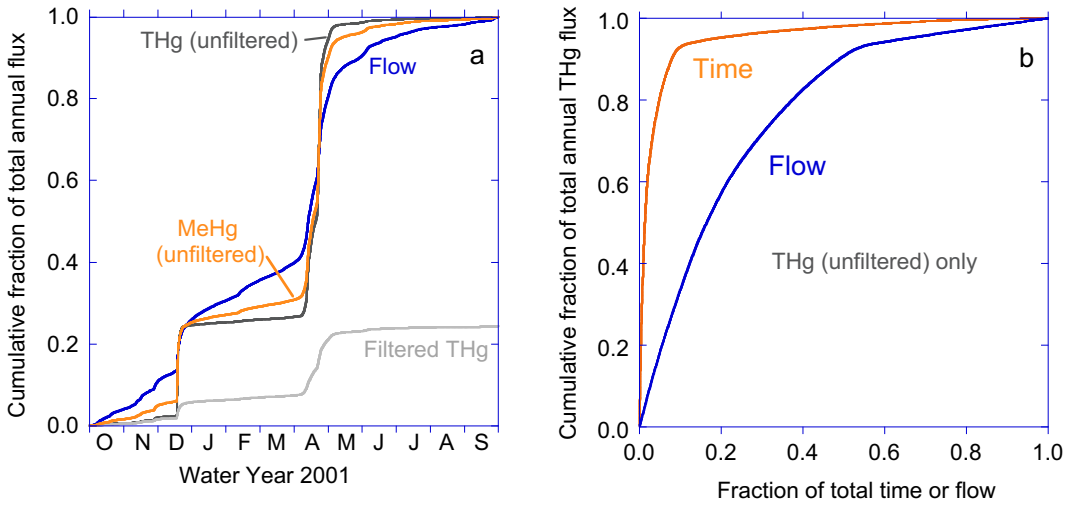

Fig. 7. (a) Relative fluxes of unfiltered THg, unfiltered MeHg, filtered THg, and water for Water Year 2001 in the Winooski River. The filtered THg flux is relative to unfiltered THg flux. (b) Cumulative THg flux as a function of minimum fractions of time and flow needed for transport.

laboratory effort devoted to lowering the MeHg detection limit in Lake Champlain waters (Jackson et al., 2009). The median lake THg of 0.31 ng L^{-1} was similar to that found in Lake Champlain in other recent studies (Miller et al., submitted for publication, Miller et al., in preparation), and to the value of 0.30 ng L^{-1} reported for Lake Michigan (McCarty et al., 2004), but less than the 2.6 ng L^{-1} reported in an earlier study (Cleckner et al., 1995). In a survey of 92 lakes in Vermont and New Hampshire, median epilimnetic concentrations were 1.31 ng L^{-1} for THg and 0.26 ng L^{-1} for MeHg (Kamman et al., 2004). We caution that our low values represent results from one point in time; recent findings by Miller et al. (submitted for publication) indicate high month-to-month variability in THg and MeHg concentrations in epilimnetic Lake Champlain waters.

5.3. Hg dynamics in streamflow

The present study builds on previous studies in the Lake Champlain basin (Scherbatskoy et al., 1998; Rinehart, 2003), and elsewhere in Vermont (Shanley et al., 2008; Dittman et al., 2010), that confirm the importance of high-flow events to streamwater transport of THg. The dominance of THg and MeHg associated with particles was consistent with these earlier studies.

Scherbatskoy et al. (1998) found that the annual THg flux in a small catchment was dominated by a small number of high-flow events in a small catchment, and several other studies have noted the importance of high-flow events to stream THg flux (Hurley et al., 1998; Babiarz et al., 1998; Shanley et al., 2008; Bishop et al., 1995; Quémerais et al., 1999). MeHg was also transported primarily at high flows, and also primarily in the particle phase. Particle MeHg is often a significant and occasionally the dominant phase of MeHg in surface waters (Babiarz et al., 2001). Researchers in Scandinavia (Bishop et al., 1995; Munthe and Hultberg, 2004) and Germany (Schwesig and Matzner, 2001) have shown decoupled behavior of THg and MeHg. In these studies, THg concentration increased but MeHg diluted with flow, most likely because MeHg was supplied in base flow from anoxic sediments, and was diluted by meteoric waters during events while THg was flushed from surficial soils. Unlike the European sites, THg and MeHg concentrations in Lake Champlain tributaries both increased with flow and both were dominated by particles, suggesting they may have sources in common. Because of the known affinity of Hg for organic matter, we propose that these sources are near-stream surficial soils and/or in stream organic sediments. The increasing MeHg/THg through the summer can be accounted for by increased methylation rates with warmer temperatures (Fig. 5), but streamwater MeHg was still primarily particulate.

5.4. Land use effects

Despite varying proportions of agricultural and forested land, the THg-TSS relation was fairly linear across all sites, excluding urban Englesby Brook (Fig. 4), suggesting that forested and agricultural lands delivered similar amounts of Hg per unit of TSS. Thus stream THg concentrations were largely controlled by TSS concentrations. Soil erosion from agricultural areas has been suggested as a major source of THg loading in large rivers of the central U.S. (Balogh et al., 1998). The urban landscape, represented by Englesby Brook, may contribute disproportionately to stream THg flux to Lake Champlain, as it does for phosphorus flux (Smeltzer and Quinn, 1996). Elevated THg concentrations and fluxes as found at Englesby Brook are consistent with findings from other urban landscapes such as Boston (Waldron et al., 2000) and Washington D.C. (Mason and Sullivan, 1998). High urban THg fluxes may result from industrial sources, coupled with the ineffectiveness of urban surfaces to retain Hg. Even in predominately forested areas, watershed disturbance may release stored THg and MeHg (Kamman and Engstrom, 2002; Munthe and Hultberg, 2004; Garcia and Carignan, 2000; Porvari et al., 2003). Thus, regardless of land cover type, control of sediment in runoff is a management tool that can limit Hg movement to Lake Champlain and its tributaries.

Wetlands are important sites for methylation, but MeHg concentration correlated only moderately with percent wetlands ($r^2 = 0.40$) (SM Figure S2). In contrast, MeHg and percent wetlands were not correlated in studies in Wisconsin (Hurley et al., 1998) and New England (Shanley et al., 2005). One explanation for these weak relations is that percent wetland cover does not necessarily reflect the amount of wetland hydrologically connected to stream channels, which is the important control (Grigal, 2002; Kramar et al., 2005). In addition, uplands may be a more important source of MeHg than previously recognized (Rimmer et al., 2005), and MeHg produced in lowlands may be taken up by the food web (Chen and Folt, 2005).

6. Conclusions

Total mercury (THg) and methylmercury (MeHg) fluxes to Lake Champlain from its tributaries were highly episodic and dominated

by the particle phase. Stream THg flux to the lake for Water Years 2001 through 2009 averaged 2.37 ± 1.54 μg m^{-2} yr^{-1}, or about 13% of atmospheric wet and dry THg deposition to the basin. For flux calculations we exploited the strong THg-TSS and TSS-discharge relations. THg uncertainty was primarily due to hysteresis in the latter. Roughly 40% of the lake input THg flux was in the filtered phase. Considering the 2.37 μg m^{-2} yr^{-1} THg flux into the lake from tributaries and an additional 0.94 μg m^{-2} yr^{-1} via direct atmospheric deposition to the lake surface, the stream output from the lake of 0.53 μg m^{-2} yr^{-1} marked a further reduction in THg throughput; overall about 97% of THg deposition was retained in the lake-watershed system (discounting any evasion from the lake surface). Stream MeHg concentrations averaged about 3% of THg, but increased to 10% or more in late summer. The lake was also a net sink for MeHg; tributary input was 0.07 μg m^{-2} yr^{-1} and lake output was 0.025 μg m^{-2} yr^{-1}, but again, confidence in these fluxes is limited due to few measurements. Though forests are thought to receive higher Hg deposition, stream THg and MeHg concentrations correlated positively with percent agricultural land, probably because of greater erosion and particle Hg transport. Urban land represented only 5.6% of the basin, but THg yield from a small urban watershed was about 4 times the average for the basin. Land management measures to reduce soil erosion and street washoff would help to limit Hg loading to Lake Champlain.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2011.07.006.

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