

Mercury transport in response to storm events from a northern forest landscape

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Abstract:

Concentrations and fluxes of mercury (Hg) species in surface waters of forested watersheds are affected by hydrological events. The mechanisms of Hg transport during these events are poorly understood and yet may influence Hg bioavailability and exposure to aquatic biota. Three storm events with varying magnitude and intensity were investigated (June, September and November 2005) at a forested watershed in the Adirondack region of New York State, USA. Concentrations of Hg species increased during these events, both above and downstream of wetlands in the watershed. While Hg flux was higher from wetland drainage, the Hg flux from the upland site exhibited a greater relative increase to elevated runoff. Hg flux was controlled by discharge; however, Hg species concentrations were not well correlated with discharge, dissolved organic carbon (DOC), or total suspended solids (TSS) through the duration of events. A counter-clockwise hysteresis response of DOC with increasing runoff contrasted with the clockwise response for total Hg, suggesting different contributions from source areas for these solutes. Correspondence with elevated total K and NO₃⁻ ($\alpha < 0.05$) during the rising limb of the hydrograph suggests rapid delivery of throughfall Hg, potentially enhanced by hillslope hollows, to the stream channel. As the watershed saturated, stream Hg appears to be derived from the soil Hg pool. Results suggest that particulate Hg did not contribute substantially to total Hg flux during events (<25%). These results emphasize the role of watershed attributes and storm characteristics in Hg transport and bioavailability. Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

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INTRODUCTION

Mercury (Hg) has the potential for bioaccumulation and subsequent toxicity in both aquatic and terrestrial environments. Organic species (i.e. methylmercury, MeHg) are of particular concern and strongly bioaccumulate within aquatic food chains (Munthe *et al.*, 2007). Such bio-magnification places fish, wildlife, and humans at risk from Hg exposure. Due to atmospheric transport and deposition, Hg contamination has been shown to affect otherwise pristine ecosystems (Dennis *et al.*, 2005; Driscoll *et al.*, 2007). Many investigations have focused on forested ecosystems (Driscoll *et al.*, 1995; Hurley *et al.*, 1995; St. Louis *et al.*, 1996; Babiarz *et al.*, 1998), demonstrating variability in total Hg (THg) loading and speciation due to watershed characteristics. Wetland area (Bishop and Lee, 1997; Driscoll *et al.*, 1998), type of wetland (Branfireun *et al.*, 1996), and hydrologic conditions (Branfireun *et al.*, 1996; St. Louis *et al.*, 1996) can all influence Hg dynamics. Within forested watersheds, dissolved organic carbon (DOC) concentrations have been linked to the mobility of Hg (Driscoll *et al.*,

1995, 1998; Pettersson *et al.*, 1995). In contrast, MeHg concentrations are negatively correlated with SO₄²⁻ due to the production of MeHg by sulfate-reducing bacteria (Gilmour *et al.*, 1998; Jeremiason *et al.*, 2006; Selvendiran *et al.*, 2008).

Elevated discharge influences annual Hg flux (Babiarz *et al.*, 1998), particularly within developed watersheds (Babiarz *et al.*, 1998; Hurley *et al.*, 1998; Mason and Sullivan, 1998) due to THg associated with particulate matter (Hurley *et al.*, 1998). Chemical and hydrologic responses during precipitation events are less varied for forested watersheds (Hurley *et al.*, 1998). Babiarz *et al.* (1998) reported no change in Hg concentrations with discharge during monthly sampling of forested ecosystems in Wisconsin, suggesting that Hg flux was largely a function of discharge. However, increases in Hg flux and changes in stream Hg chemistry during high flow events in forested watersheds have been reported elsewhere (Allan and Heyes, 1998; Scherbatskoy *et al.*, 1998; Shanley *et al.*, 2002; Mast *et al.*, 2005). Hg flux was related to particulate organic matter during snowmelt in Vermont (Scherbatskoy *et al.*, 1998; Shanley *et al.*, 2002). The dissolved fraction of Hg, particularly in relation to DOC, also contributes to Hg mobilization during elevated discharge events, including snowmelt

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(Shanley *et al.*, 2002; Mast *et al.*, 2005) and summer storms (Allan and Heyes, 1998; Balogh *et al.*, 1998). Hurley *et al.* (1998) observed that the dissolved fraction of Hg increases during summer storm events, with these events accounting for 80% of the annual THg flux. Allan and Heyes (1998) reported increases in dissolved THg concentrations during a storm from 2 to 10 ng L⁻¹, with a significant correlation between dissolved THg and DOC.

Previous studies largely have examined the effects of elevated discharge on Hg species flux using time-series sampling (Babiarz *et al.*, 1998; Balogh *et al.*, 1998), with weekly–monthly collections predominantly from a single site (Hurley *et al.*, 1995, 1998; Babiarz *et al.*, 1998; Lawson and Mason, 2001; Dennis *et al.*, 2005; Hamerschmidt *et al.*, 2006). Some studies have focused on a single event, typically at peak discharge (Hurley *et al.*, 1995; 1998), or during snowmelt (Scherbatskoy *et al.*, 1998; Shanley *et al.*, 2002; Mast *et al.*, 2005). Few investigations have collected samples across a hydrograph to assess changes in Hg dynamics during a storm event (Allan and Heyes, 1998; Lawson and Mason, 2001). Detailed event sampling provides insight into the potential hydrologic sources of Hg, including throughfall, near-stream/riparian water, deep soil water, and surface soil water (McHale *et al.*, 2002), that contribute to Hg transport and bioavailability during high flow periods. Atmospherically deposited Hg largely is retained within watersheds (Hurley *et al.*, 1995; Lawson and Mason, 2001; Mast *et al.*, 2005). However, during storm events there is the potential for rapid delivery of atmospherically deposited Hg to surface waters due to direct throughfall inputs to the stream channel or supply from the near

stream environment. It is likely that this ‘new’ Hg is more bioavailable than Hg that has been processed through a watershed (Driscoll *et al.*, 2007; Harris *et al.*, 2007).

The objective of the present study was to investigate the effects of elevated runoff on the concentrations and fluxes of Hg species at nested sites within a forested watershed in the Adirondack region of New York. Samples were collected during three summer/fall events along Archer Creek, the primary inlet to Arbutus Lake. The specific objectives were to: (1) examine Hg species concentrations during individual events in relation to water chemistry parameters associated with Hg mobility (i.e. DOC, TSS, SO₄²⁻); (2) evaluate changes in Hg species in relationship to discharge and storm hydrographs; and (3) assess the potential sources of Hg to stream water during events. The effects of land cover and seasonality on Hg mobility and potential bioavailability were also evaluated.

STUDY SITE

Event samples were collected along Archer Creek within the Huntington Wildlife Forest (HFNY; Figure 1) of the central Adirondack Mountains of New York State, USA (43°59'N, 74°14'W). The 135 ha watershed is the primary inlet to Arbutus Lake. Extensive biogeochemical research, including studies on Hg cycling, has been conducted at the HFNY, a site administered by the Adirondack Ecological Center and State University of New York College of Environmental Science and Forestry (http://www.esf.edu/hss/huntington_forest_research_over-

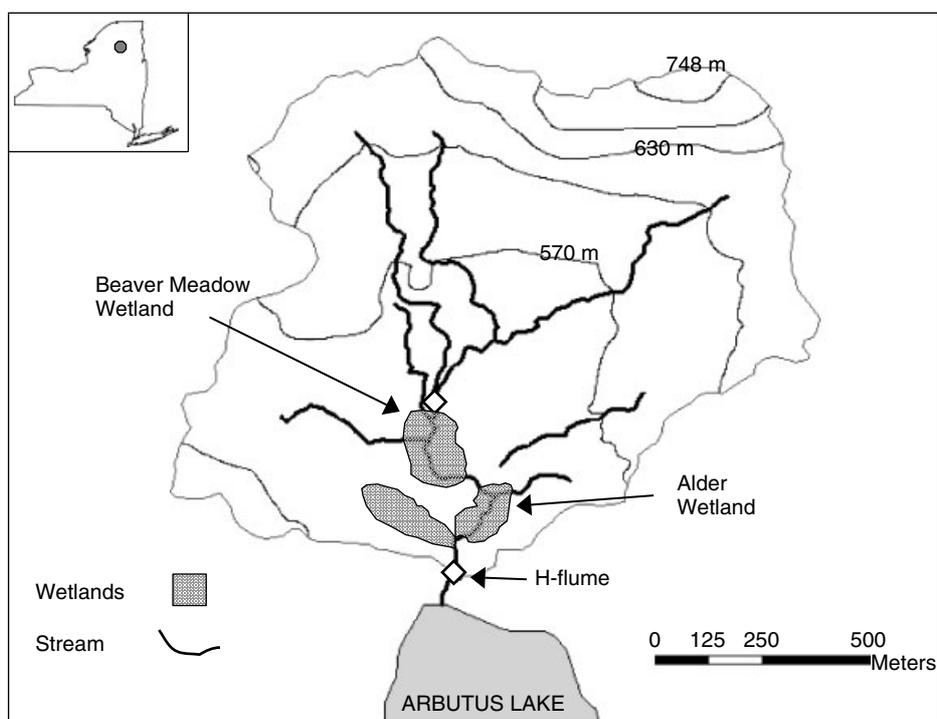


Figure 1. Intensive study areas (adapted from McHale *et al.*, 2002) for Hg transport during elevated flow events within the Archer Creek, New York watershed. Sampling locations (○) are the upstream and Archer Creek outlet. Note the position of the wetlands relative to the sampling locations. An additional beaver pond is located between the alder wetland outlet and the Archer Creek outlet sampling location

view.htm, (29/10/07); Mitchell *et al.*, 2006). The climate is cool, moist, and continental, with an average annual temperature of 4.4 °C and average annual precipitation of 1010 mm for the period 1951–1980 (Shepard *et al.*, 1989).

Upland ecosystems dominate the watershed, with wetlands comprising only 4% by area and forming the transition between upland areas and the watershed outlet into Arbutus Lake. Upland areas, with an average slope of 11%, are covered by mixed hardwood forests with few, relatively-minor, wetland areas, and are characterized by coarse, loamy, mixed frigid Typic Haplorthods soils typically <1 m thick underlain by a thin layer of bouldery glacial till derived from local bedrock. As in many Adirondack watersheds, hillslope hollows influence runoff from the upland areas. Although a stream channel does not exist, running water is audible during events or high saturation conditions below the forest floor within these low spots in the topography which are lined with rocks and boulders that have high hydraulic conductivity. For Archer Creek, McHale *et al.* (2002) and Inamdar *et al.* (2004) hypothesized that soil water in and near the hollows was mobilized with infiltration and/or the rising water table in the surrounding surface soil.

The influence of two wetlands along Archer Creek (Figure 1) on the concentrations and fluxes of Hg species was examined. The upstream wetland is an abandoned beaver meadow covered by grasses, sedges, and some *Sphagnum* spp. with soils that are a mixture of Greenwood Mucky peats and hydric soils with a high sand content. The downstream wetland is a riparian peatland with an overstory consisting primarily of *Alnus incana* (L.) Moench. (speckled alder) and an understory dominated by *Sphagnum* spp., *Osmunda cinnamomea*, and a variety of sedges. Riparian wetland soils are Greenwood Mucky peats ranging from 1–5 m in depth with some coarse sand layers at 0.5–1.5 m (Bischoff *et al.*, 2001; McHale *et al.*, 2004).

METHODS

Three hydrologic events were sampled from June through November 2005. These three events differed in total precipitation amount and intensity as well as pre-event moisture conditions (Table I). The early summer event (29 June–1 July) resulted from a series of afternoon thunderstorms of moderate intensity (total precipitation = 10.2 mm; yield = 20%; yield = discharge/precipitation for the event); the late summer event (16–18 September) followed a short, intense nighttime thunderstorm (3.5 mm; yield = 23%); the fall event (9–12 November) was the consequence of prolonged, day-long heavy rain with a few thunderstorms (32.8 mm; yield = 59%). Wet-only precipitation amount (hourly; EPA, 2007) and solute chemistry (weekly; NADP, 2007) were obtained from the NADP/NTN long-term monitoring site located at the HFNY.

For each event, samples were collected at two locations within the Archer Creek watershed to assess the effects

Table I. Precipitation event characteristics and pre-event watershed conditions as assessed by the Antecedent Precipitation Index (API; McHale *et al.*, 2002) and the average discharge at the Archer Creek outlet weir for the 7 and 28 day periods preceding the 29 June–1 July, 16–18 September, and 9–12 November elevated discharge events in 2005

	June	September	November	
Precipitation (mm) ^a	10.2	3.5	32.8	
Discharge (mm)	2.07	0.82	19.3	
Water yield (%)	20	23	59	
Antecedent conditions:				
API (mm)	7-day	3.6	1.7	18
	28-day	33	55	26
Average discharge (mm day ⁻¹)	7-day	0.34	0.15	1.99
	28-day	1.13	0.72	3.54

^a EPA (2007)

of sub-catchment attributes (Figure 1). Sampling efforts focused on the inlet to the beaver meadow wetland (upstream, 64.3 ha) and the Archer Creek outlet (135 ha), reflecting the upland input to and the effect of wetlands along Archer Creek. Hydrologic response was monitored at 15-min intervals at an H-flume installed near the inlet of Archer Creek to Arbutus Lake (Figure 2). Flow at the upstream site was estimated by scaling event discharge at the H-flume using the watershed area ratio and adjusting the hydrograph observations of stream stage. Samples were collected to span various flow stages within the hydrograph including the rising limb, peak discharge, the falling limb, and the return to base flow of each event. Six to nine samples were collected for chemical analysis during each event, with base flow samples collected prior to each event. The beginning of each event was characterized by the onset of precipitation with sampling concluding as the hydrograph returned to baseline conditions. Note that Selvendiran *et al.* (2008) provides a detailed analysis of seasonal Hg dynamics under base flow (non-event) for Archer Creek.

Samples were collected in Teflon[®] bottles and analysed unfiltered for THg and MeHg concentrations. Two additional samples were collected in November during base and peak conditions at the upstream and Archer Creek outlet, filtered (0.45 µm), and analysed for dissolved Hg. THg was analysed via oxidation, purge and trap, and cold vapour atomic fluorescence spectroscopy (CVAFS; Method 1631, revision E—EPA, 2002). MeHg was analysed via distillation, aqueous ethylation, purge and trap, and CVAFS (Method 1630, modified to 90 mL—EPA, 2001). Additional water chemistry samples were collected and analysed via Standard Methods (APHA/AWWA/WEF, 1998): dissolved organic carbon (DOC)—the persulfate-ultraviolet oxidation method (5310C); anions (sulfate—SO₄²⁻, nitrate—NO₃⁻)—ion chromatography with chemical suppression of eluent conductivity (4110 B); and acid neutralizing capacity (ANC/pH, 2320). Cations (total potassium—K_T, total magnesium—Mg_T, total calcium—Ca_T, and total silica—Si_T) were analysed

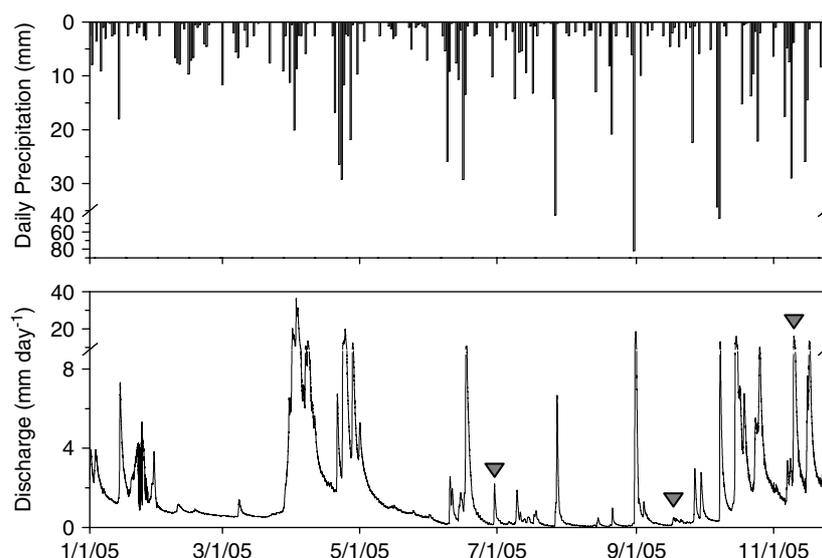


Figure 2. Daily precipitation as measured at the Huntington Forest (NY) meteorological site (EPA, 2007) and Archer Creek discharge measured at the Archer Creek outlet for January–November 2005. The individual events that were investigated in this study are shown (▼). Note the break in the axis

via inductively-coupled plasma mass spectrometry (EPA method 200.8 ICP/MS; EPA, 1994). For the September and November events, a complete set of samples was collected at the Archer Creek outlet and a few samples were collected at the upstream site for analysis of total suspended solids (TSS, 2540D) and particulate organic carbon via flash combustion/chromatographic separation and multi-detector techniques (POC, Nelson and Sommers, 1996). Quality assurance was maintained through duplicate sampling, trip/process blanks, and matrix spike duplicates with recoveries of THg for spikes and standards $\pm 10\%$ ($\pm 20\%$ for MeHg).

Chemical concentrations and area-normalized fluxes were compared with runoff for Hg species, DOC, and TSS to assess potential relationships within and between events. Discharge-weighted concentrations were calculated for each event at both sites to assess the effect of elevated runoff on Hg species mobility. Mass fluxes also were calculated for Hg species, DOC, SO_4^{2-} , and NO_3^- by integrating area-normalized flux values over each event. The effect of the wetlands on chemical transport was assessed by comparing mass fluxes between the sites. Net Hg transported was estimated as the percentage of Hg entering in precipitation relative to that transported in streamwater during an event. Statistical analyses, including correlations between Hg species and other solutes, were conducted using JMP™ (SAS Institute Inc., Cary, North Carolina).

Principal component analysis (PCA, McHale *et al.*, 2002) focusing on NO_3^- sources and isotopic assessments of NO_3^- and SO_4^{2-} (Piatek *et al.*, 2005; Campbell *et al.*, 2006; Mitchell *et al.*, 2006) has been conducted previously at Archer Creek. In addition to multiple stream sampling locations, McHale *et al.* (2002) evaluated the contribution of shallow/deep soil water, shallow/deep wetland pore water, groundwater, and through-fall as potential runoff sources using end-member mixing

analysis (EMMA). A suite of water chemistry parameters was analysed for potential end members as part of the current analyses with end member chemistry similar to that from previous investigations (McHale *et al.*, 2002; Inamdar *et al.*, 2004; Mitchell *et al.*, 2006). This stream chemistry was compared with that from the previous PCA/EMMA analysis, demonstrating the value of long-term ecosystem study sites.

RESULTS

Discharge reflected the magnitude, intensity, and pattern of the precipitation events (Figure 3) as well as the antecedent moisture conditions (Table I). Discharge at the H-flume ranged from 0.34–1.94, 0.13–0.47, and 2.34–14.6 mm day^{-1} for the June, September, and November events, respectively. Discharge increased quickly for the intense June thunderstorm, while there was a delayed increase in flow for the November event. Flow increased slowly during the September event coinciding with minor rain events leading up to the quick, intense thunderstorm (1.5 mm in 15 min). During all three events, discharge at the site upstream of the wetlands responded more quickly and exhibited a sharper peak indicative of the difference in hydrologic attenuation between headwater upland and wetland dominated watersheds. Water levels were above the surface of the wetlands only during the November event. This high water may have been influenced by beaver activity immediately upstream of the Archer Creek outlet sampling location on this date.

Concentrations of Hg species increased with increasing discharge, reaching a maximum value prior to the peak runoff before decreasing slowly over the remainder of the hydrograph for all of the events studied (Figure 4). Temporal patterns in Hg concentrations for the June event at the upstream site and for the September and

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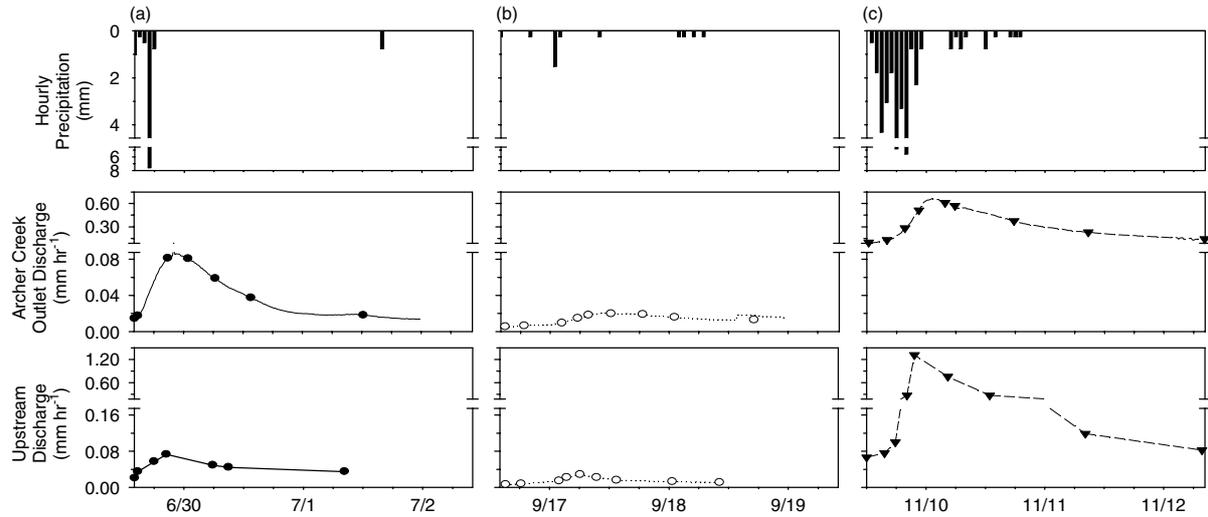


Figure 3. Hourly precipitation as measured at the Huntington Forest (NY) meteorological site (EPA, 2007) and discharge at the Archer Creek outlet and upstream sites during each 2005 hydrologic event: 29 June–1 July (a), 16–18 September (b), and 9–12 November (c). Symbols represent sample collection. Lines for discharge at the Archer Creek outlet reflect 15-min data collected at an H-flume. Discharge at the upstream site was estimated using the total event runoff at the H-flume and upstream site stream stage measurements. Lines for the upstream site are not reflective of trends between data. Note the breaks in the axis for precipitation and discharge. Dates reflect the beginning (12 am) of the day indicated

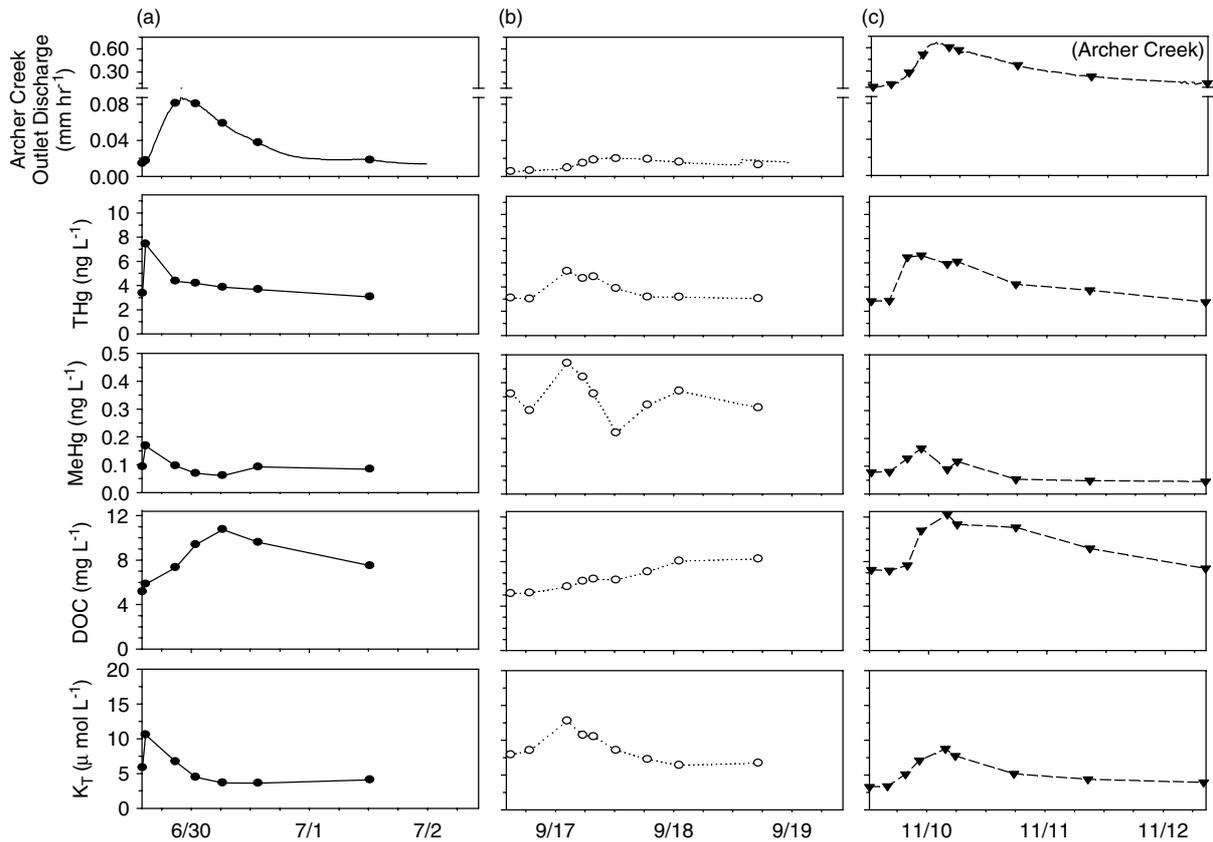


Figure 4. Total Hg (THg), methyl mercury (MeHg), dissolved organic carbon (DOC), and total suspended solid (TSS) concentrations over time at the Archer Creek outlet (i) and upstream (ii) sampling sites during each 2005 hydrologic event for 29 June–1 July (a), 16–18 September (b), and 9–12 November (c). Symbols represent sample collection. Runoff included from Figure 3 to facilitate water chemistry dynamic comparison. Lines are not reflective of trends between data. TSS was not analysed during the June event and was not analysed on every sample for the upstream site. Dates reflect the beginning (12 am) of the day indicated

November events at the Archer Creek outlet experienced fluctuations during the rising limb. Upstream streamwater concentrations of THg ranged from 1.07–5.04, 1.51–5.66, and 1.25–4.59 ng L⁻¹, while MeHg ranged from 0.01–0.03, 0.03–0.14, and 0.01–0.06 ng L⁻¹ for

the June, September, and November events, respectively. Archer Creek outlet concentrations of THg varied from 3.06–7.43, 3.02–5.30, and 2.76–6.61 ng L⁻¹, with MeHg ranging from 0.06–0.17, 0.30–0.47, and 0.05–0.16 ng L⁻¹ for the June, September, and

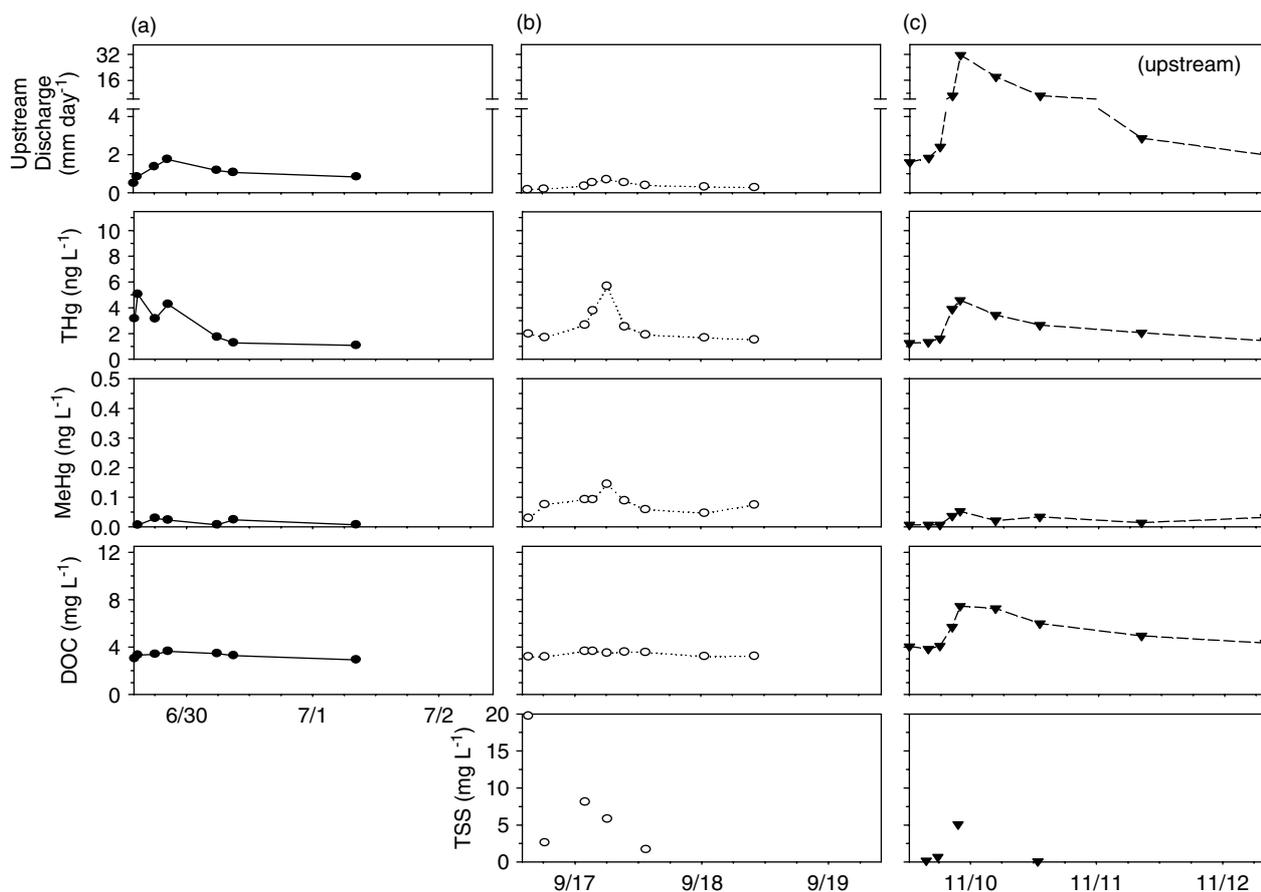


Figure 4. (Continued)

November events, respectively. Hg concentrations at the Archer Creek outlet were greater than values at the upstream site, with the concentration increase likely due to the influence of wetlands in the lower reaches of the catchment (Selvendiran *et al.*, 2008).

DOC concentrations peaked at or after peak discharge (Figure 4). Concentrations decreased on the receding limb for the June and November events at both sites and at the upstream site during the September event. For the September event, with its relatively dry antecedent conditions (Table I, Figure 2) and focused precipitation period (Figure 3), DOC concentrations at the Archer Creek outlet increased slowly as the watershed saturation increased. Upstream DOC concentrations ranged from 2.9–3.6, 3.2–3.6, and 3.8–7.5 mg L⁻¹, while values for the Archer Creek outlet ranged from 5.2–10.7, 5.1–8.2, and 7.2–12.2 mg L⁻¹ for the June, September, and November events, respectively. As with Hg, DOC concentrations consistently were higher at the Archer Creek outlet site relative to the upstream site.

TSS were analysed only for the September and November events, mostly for the Archer Creek outlet site (Figure 4). Highest TSS concentrations (~10.5 mg L⁻¹) occurred just prior to peak November discharge at the Archer Creek outlet and subsequently declined to ~0.2 mg L⁻¹. At the upstream site, TSS concentrations ranged from 0.1–8.1 mg L⁻¹, following a similar temporal pattern to that observed at the Archer Creek outlet.

Changes in concentrations of SO₄²⁻, NO₃⁻, K_T, and Si_T during the events are shown in Figure 5. Interest in these solutes is due to the linkages with Hg cycling (SO₄²⁻; Gilmour *et al.*, 1998; Jeremiason *et al.*, 2006), correlation with Hg for source assessment (NO₃⁻ and K_T), and hydrologic flow path consideration (Si_T; Peters and Driscoll, 1987). SO₄²⁻ (ranging from 55–65 μmol L⁻¹ at the Archer Creek outlet and 51–73 μmol L⁻¹ at the upstream site) is the dominant anion in Archer Creek (McHale *et al.*, 2002; Mitchell *et al.*, 2006) and generally decreased with increasing discharge at both sites. However, SO₄²⁻ concentrations increased in response to the intense precipitation following dry pre-event conditions during the June and September events and remained elevated throughout these events at the upstream site (Mitchell *et al.*, 2006). Si_T (ranging from 137–226 μmol L⁻¹ at the Archer Creek outlet and 154–247 μmol L⁻¹ at the upstream site) generally decreased with increasing discharge at both sites, particularly in response to the more intense precipitation events. NO₃⁻ and K_T concentration patterns were similar to those for Hg, increasing during the rising limb, peaking before the hydrograph peak and decreasing during the recession (Evans and Davies, 1998) for the intense June and September events during the forest canopy cover period. NO₃⁻ and K_T concentrations ranged from 6–29 μmol L⁻¹ and 3.3–13 μmol L⁻¹, respectively, at the Archer Creek outlet and 10–25 μmol L⁻¹ and

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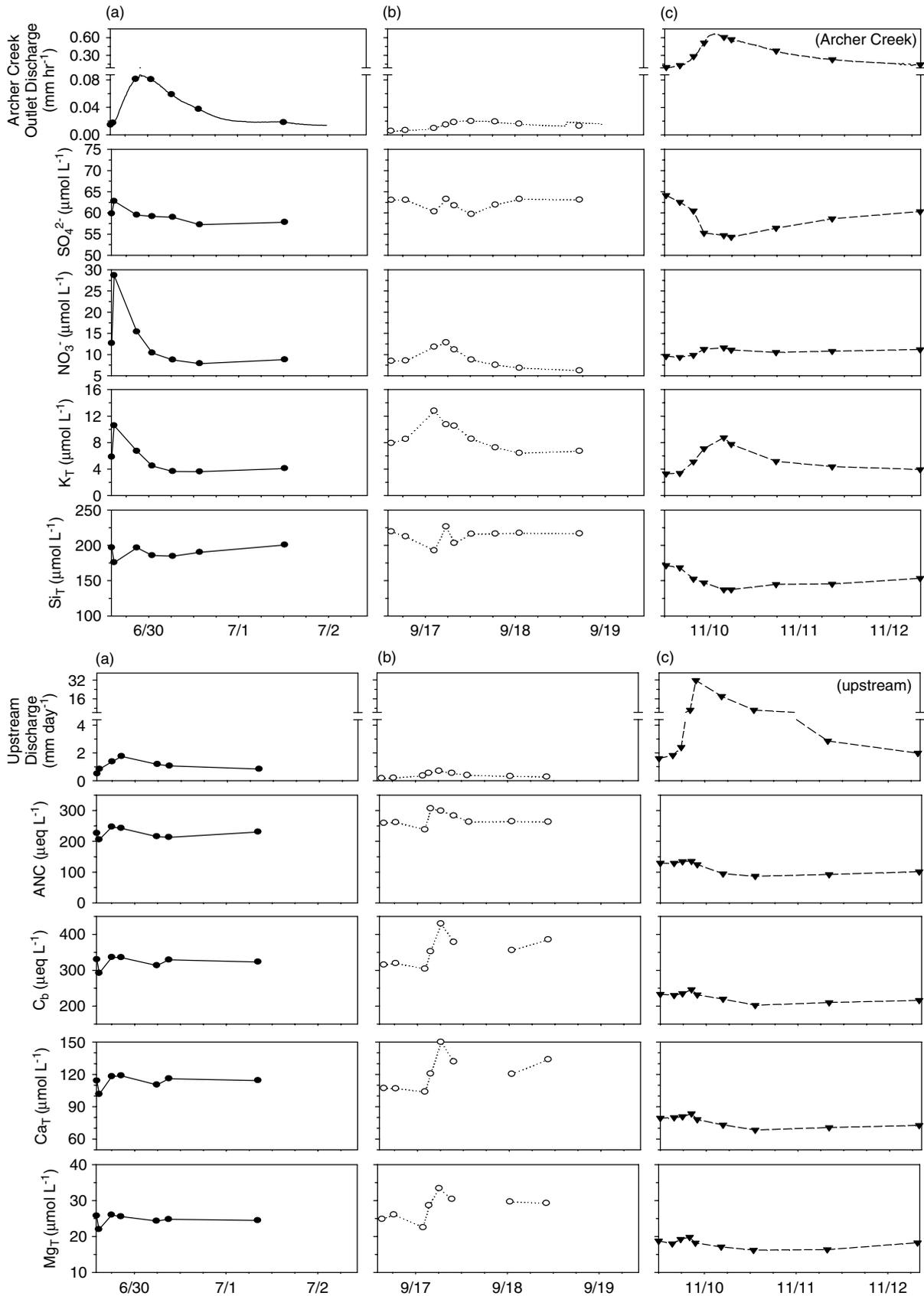


Figure 5. Nitrate (NO_3^-), sulfate (SO_4^{2-}), total potassium (K_T), and total silica (Si_T) concentrations over time at the Archer Creek outlet (i) and upstream (ii) sampling sites during each hydrologic event for 29 June–1 July (a), 16–18 September (b), and 9–12 November (c). Symbols represent sample collection. Runoff included from Figure 3 to facilitate water chemistry dynamic comparison. Lines are not reflective of trends between data. Dates reflect the beginning (12 am) of the day indicated

2.2–7.4 $\mu\text{mol L}^{-1}$, respectively, at the upstream site. SO_4^{2-} , NO_3^- , and Si_T concentrations were lower at the Archer Creek outlet site relative to the upstream site, probably due to wetland retention (Selvendiran *et al.*, 2008). In contrast, higher K_T concentrations at the Archer Creek outlet site relative to the upstream site probably reflected a greater response to the intense June and September events.

ANC and the sum of the base cations (C_B) remained relatively constant at both sites during all events, with Ca_T the dominant cation (Figure 1, Supporting Information). Values reflected the pre-event watershed saturation conditions (Table I), with stream concentrations decreasing in the order September, June, and November sample collections, respectively. Within each event, concentrations generally exhibited a slight dilution or remained relatively constant throughout the events with potential for episodic acidification under wet antecedent watershed conditions (i.e. short-term ANC decreases; Wellington and Driscoll, 2004) as observed for the November event at the Archer Creek outlet.

DISCUSSION

THg concentrations observed for Archer Creek were similar to values previously reported for other forested upland and wetland sites (Hurley *et al.*, 1995; Babiarz *et al.*, 1998), but varied over a relatively narrow range (Figure 4, $<7.5 \text{ ng L}^{-1}$) in comparison with previous event studies (up to 80 ng L^{-1} ; Allan and Heyes, 1998; Scherbatskoy *et al.*, 1999; Lawson and Mason, 2001). MeHg concentrations (Figure 4) were also similar to values observed in other studies (Allan and Heyes, 1998; Mast *et al.*, 2005), but were less responsive to increases in flow than reported previously (e.g. ~ 10 -fold increase; Lawson and Mason, 2001). In the current study, MeHg concentrations were elevated during the September event relative to the June and November events, probably due to increased biological activity. Higher substrate availability and temperatures are both associated with increased methylation rates (Babiarz *et al.*, 1998; Selvendiran *et al.*, 2008). The relatively narrow concentration range of Hg species suggests that for relatively undisturbed watersheds, including the current study site, there is less temporal variation associated with hydrologic events than for disturbed watersheds with high particulate Hg concentrations (Hurley *et al.*, 1995; Mason and Sullivan, 1998). However, while particulate transport of Hg has been previously demonstrated for the forested portion of the Sleepers River watershed in Vermont (Shanley *et al.*, 2002), a watershed encompassing varied levels of disturbance, no such effect of elevated discharge and in-stream mobilization of TSS occurred at Archer Creek.

Increases in Hg species concentrations during elevated discharge have been linked with hydraulic flushing (Branfireun *et al.*, 1996) and water chemistry parameters, including DOC (Allan and Heyes, 1998; Shanley *et al.*, 2002) and TSS (Scherbatskoy *et al.*, 1998;

Lawson and Mason, 2001; Shanley *et al.*, 2002). To help evaluate the mechanisms affecting changes in Hg species during events, concentrations of Hg species and other constituents were evaluated as a function of discharge (Figure 6). Only DOC concentration increased significantly ($\alpha = 0.05$) between storms, possibly due to the role of wetlands increasing DOC mobility (Mitchell *et al.*, 2006), particularly for the November event. Litter inputs and beaver activity also could have contributed to these higher DOC, and potentially Hg (Balogh *et al.*, 2002), concentrations during autumn. While THg concentrations generally increased during events with increasing discharge, the response did not reflect differences in discharge among events (Figure 6; Figure S2, Supporting Information) and was not correlated significantly with DOC ($\alpha = 0.05$; Figure 7). MeHg concentrations remained relatively constant within storms and between the June and November events, with the increased concentration for the September event reflecting the seasonality of the methylation process (Selvendiran *et al.*, 2008). The lack of a relationship between THg concentrations and discharge demonstrates that discharge at Archer Creek cannot be used to predict THg concentrations.

Hg species flux

The area-normalized instantaneous watershed Hg fluxes at the Archer Creek outlet (Figure 6) for THg ($0.3\text{--}60 \times 10^{-3} \text{ ng m}^{-2} \text{ min}^{-1}$) and MeHg ($0.02\text{--}1.4 \times 10^{-3} \text{ ng m}^{-2} \text{ min}^{-1}$) were similar to values observed in other forested watersheds during high flow ($0\text{--}57 \times 10^{-3} \text{ ng m}^{-2} \text{ min}^{-1}$; $0\text{--}1.7 \times 10^{-4} \text{ ng m}^{-2} \text{ min}^{-1}$, respectively; Allan and Heyes, 1998; Lawson and Mason, 2001). Fluxes at the upstream site (Figure S2, Supporting Information) were similar, yet consistently lower, than at the Archer Creek outlet. THg, DOC, and TSS area-normalized instantaneous fluxes were correlated significantly with discharge ($\alpha = 0.05$). The significant positive relationship for THg instantaneous flux with discharge suggests a predictive relationship could be developed, if additional sampling is conducted to better quantify this relationship. Seasonal effects, moreover, would also need to be considered (Selvendiran *et al.*, 2008), particularly for MeHg. As instantaneous flux is correlated with discharge, annual watershed flux estimates using average THg concentration values and the instantaneous flux relationship are similar.

Volume-weighted concentrations were estimated to compare Hg mobilization across events for each site, supplementing instantaneous flux measurements. During events, volume-weighted THg concentrations increased relative to base flow concentrations (Table II; Figure 4). The exception for the June event at the upstream site results from the timing of the THg peak relative to the discharge pattern (Figure 4). The relative increase in THg transport was greater at the upstream site, with increases in peak instantaneous flux relative to base instantaneous flux of 4.8 to 73 times (Figure S2, Supporting Information) compared with only 5.3 to 13

Table II. Volume-weighted stream event concentrations (C_{Vol-Wt}), throughfall (Choi *et al.*, 2008), event mass flux per unit area, and net transported or total Hg (THg) and methyl Hg (MeHg) for the 29 June–1 July, 16–18 September and 9–12 November elevated discharge events in 2005. Split values represent the upstream/Archer Creek outlet sites, respectively. For throughfall, MeHg (0.07 ng L⁻¹; data not shown) is assumed to be constant. Net transported is the percentage of throughfall mass THg or MeHg input transported from the watershed in stream water. Flux and net transport for DOC, SO₄²⁻, and NO₃⁻ are provided in Supporting Information

		June	September	November
THg	Stream C_{Vol-Wt} (ng L ⁻¹)	2.90/4.18	3.06/3.83	3.64/5.33
	Throughfall (ng L ⁻¹)	18.6	25.4	3.55
	Mass flux (ng m ⁻²)	4.9/8.6	1.8/2.9	65.5/78.5
	Net transported (%)	3.1/5.5	2.8/4.5	71.3/85.4
MeHg	Stream C_{Vol-Wt} (ng L ⁻¹)	0.02/0.08	0.09/0.34	0.04/0.10
	Mass flux (ng m ⁻²)	0.04/0.18	0.05/0.27	0.67/1.79
	Net transported (%)	5.3/25.7	10.3/50.1	29.3/78.0

times for the Archer Creek outlet site (Figure 6). MeHg volume-weighted concentrations also increased relative to pre-event base flow conditions for the upstream site, but not the wetland-influenced Archer Creek outlet site. Although base flow MeHg concentrations were low, particularly for June and November, the volume-weighted MeHg concentrations at the upstream site responded to

increased wetness and discharge to a greater extent than the Archer Creek outlet site (Table II), with increases in peak instantaneous MeHg flux relative to base flow conditions at the upstream site (11 to 140 times) versus that at the Archer Creek outlet site (3.4 to 11 times).

While the upstream site exhibited a greater relative hydrological and chemical response to precipitation

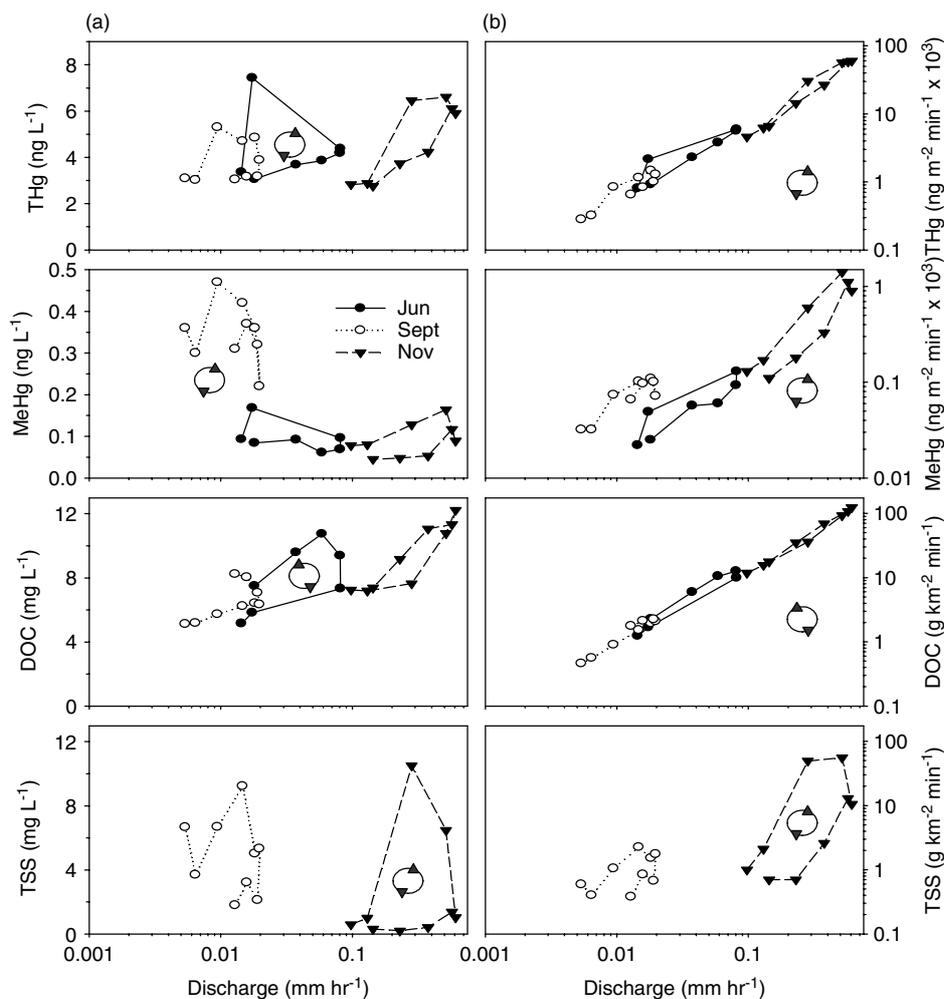


Figure 6. Concentration (a) and flux (b) as a function of discharge for total Hg (THg), methyl Hg (MeHg), dissolved organic carbon (DOC), and total suspended solids (TSS) at the Archer Creek outlet site. Note the log scale for runoff and flux. For concentration and flux relationships, Hg species and TSS exhibit a clockwise hysteresis pattern, while DOC is counter-clockwise as shown by the circular arrows. Samples represent 2005 precipitation events of 29 June–1 July (●), 16–18 September (○), and 9–12 November (▼). Symbols represent sample collection and correspond to the discharge provided in Figure 3. Lines are not reflective of trends between data

events, the wetlands were a net source of Hg species (Table II) and DOC (Table S1, Supporting Information), a finding in agreement with previous studies (Branfireun *et al.*, 1996; Selvendiran *et al.*, 2008). THg mass transported per unit watershed area during the events increased between the upstream and Archer Creek outlet sites, with mass per area similar to values previously reported for an upland watershed (2.8–5.7 ng m⁻²; Allan and Heyes, 1998). The values of net THg transported (the percentage of precipitation input transported in streamwater during an event) were similar for the June and September events (2.8–5.5%). While evasive losses of Hg are important (H.D. Choi and T. Holsen, Clarkson University, unpublished data), such low net transport values during high flow suggest strong retention of Hg species within the watershed. However, the values of net MeHg transported were greater than those reported by Allan and Heyes (1998), possibly due to the higher average watershed slope (52%) and lower wetland watershed area in that study. In the current study, the values of net percentage THg transported were 2–10 times lower than those for MeHg during the June and September events before increasing to 71–85% for THg and 29–78% for MeHg in November, when the watershed saturation was greater.

Hg hydrologic flowpaths

Water chemistry exhibited hysteresis, varying between the rising and falling limbs of the hydrograph (Figure 6; Figure S2, Supporting Information), suggesting significant contributions from multiple sources of runoff (Evans and Davies, 1998). A discrepancy in the hysteresis patterns existed between relationships of Hg species with discharge and those for water chemical parameters linked with Hg mobilization (i.e. DOC, TSS). The difference in chemical response, as demonstrated by the hysteresis, among the three events demonstrates the potential variability in the Hg mobilization pathways and timing, including the direct influence of event throughfall.

Previous studies have hypothesized that increases in Hg during events are due to the influence of TSS (Shanley *et al.*, 2002) or mobilization with DOC (Driscoll *et al.*, 1995, 1998). However, elevated concentrations of THg at the start of the June and September storm events were significantly correlated with K_T and NO_3^- ($\alpha = 0.05$) rather than DOC values (Figure 7). The coincidence of elevated THg with K_T and NO_3^- on the rising limb of the hydrograph without increasing DOC suggests rapid delivery of Hg to the stream channel from direct throughfall inputs during these intense events (Table S2, Supporting Information), and via preferential flow paths (McHale *et al.*, 2002; Inamdar *et al.*, 2004). Other end members did not coincide with the initial increase in Hg species, with SO_4^{2-} , Si_T , and C_B exhibiting a dilution response consistent with an initial increase in flow due to throughfall delivery to the stream (Figure 5; Figure S2, Supporting Information). Given the throughfall THg concentration (Table II), an increase in the Archer Creek saturated watershed area directly connected via surface flow to the

stream channel (i.e. 'connectivity') of 2% could account for the initial THg stream water concentration increase during the events, consistent with a pathway suggested by Allan and Heyes (1998). During both the June and particularly the September events, the initial response of THg at the Archer Creek outlet was greater than the upstream site, possibly due to increased surface water area and connectivity to the stream channel. Watershed wetness and event size were likely factors in the relative contribution from throughfall to stream water THg. For example, throughfall contributions would have been negligible compared with soil water contributions during the larger, less intense, November event when the watershed was saturated. Conversely, should the watershed saturation have been higher during the September storm, the Hg species response may have been more pronounced due to the increased biological activity.

After the initial effects of throughfall inputs, especially during the June and September events, the pattern of solute concentrations was consistent with a soil flushing mechanism (Creed and Band, 1998). Cations, anions, and ANC at the Archer Creek outlet exhibited dilution, decreasing to minimum values just after peak flow before slowly returning to base conditions on the recession limb. While a similar pattern of dilution was evident at the upstream site, a notable difference was the increase in SO_4^{2-} during September. This increase in SO_4^{2-} was probably due to dry watershed conditions prior to the relatively minor precipitation event, leading to oxidation and subsequent flushing of previously reduced sulfide as SO_4^{2-} from saturated areas within the uplands undergoing rewetting (Mitchell *et al.*, 2006). Following the dry pre-event conditions, SO_4^{2-} and ANC increased with the rising stream stage and remained elevated during the falling limb, while DOC increased over the entire event as the watershed re-wetted. Generally, DOC values increased with watershed saturation. As with the cation and anion response, the temporal DOC patterns reflected a flushing mechanism, consistent with runoff generation from shallower soil layers (Table S2, Supporting Information).

The mobilization of Hg via preferential flowpaths, prior to and in addition to flushing, as watershed wetness increases (Branfireun *et al.*, 1996), supports the importance of the uplands in the supply of Hg and the potential for rapid delivery of Hg species to waterways within both upland and wetland watersheds (B. Branfireun, University of Toronto at Mississauga, personal communication), particularly during intense events. Similar to previous investigations of Hg mobilization at other locations (Branfireun and Roulet, 1998), the relative contributions of various water sources varied between events (McHale *et al.*, 2002; Inamdar *et al.*, 2004; Mitchell *et al.*, 2006), demonstrating the importance of storm magnitude, season, and watershed wetness on runoff response and Hg supply mechanisms. During the short, intense thunderstorms in June and September while the deciduous canopy was present, rapidly delivered throughfall contributed an average of approximately 3% of the Hg mass flux during

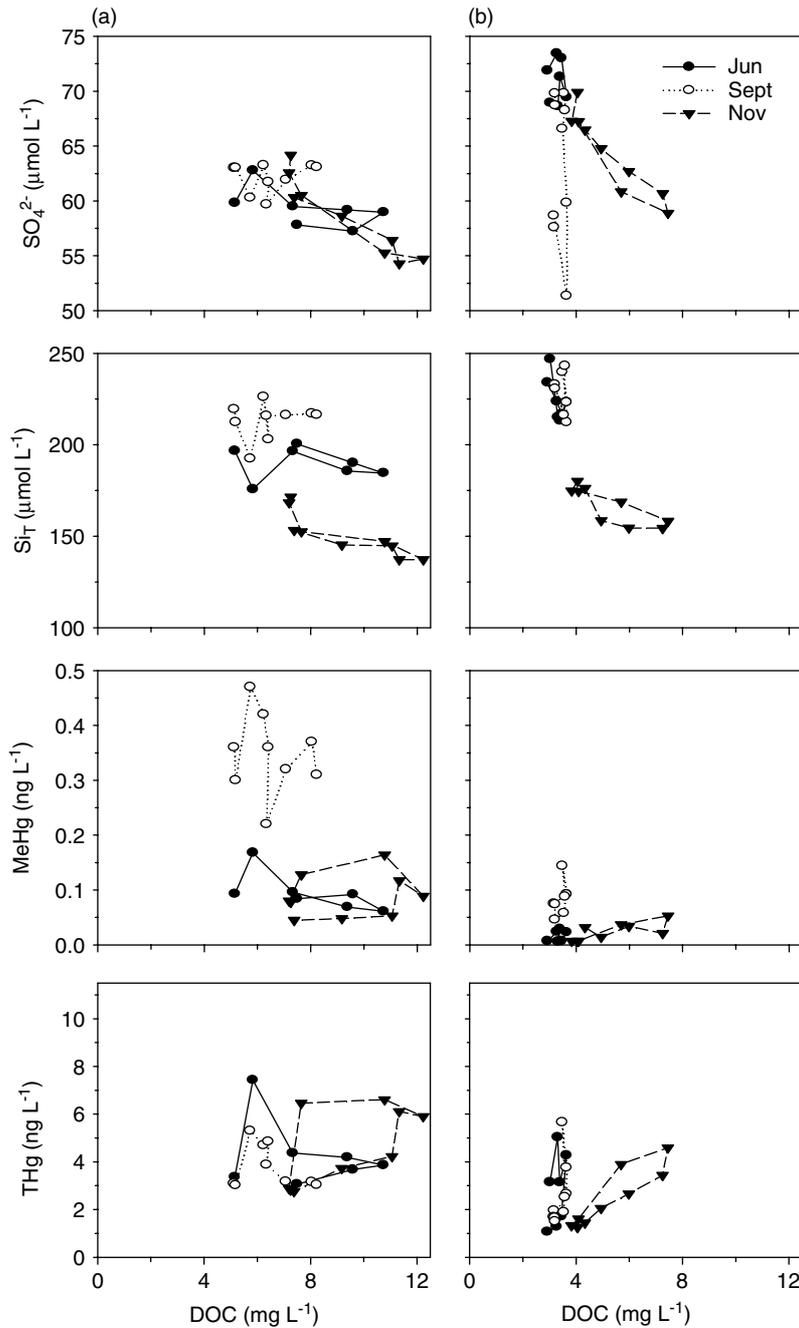


Figure 7. Sulfate (SO_4^{2-}), total silica (Si_T), methyl Hg (MeHg), and total Hg (THg) relationships with respect to dissolved organic carbon (DOC) for the Archer Creek outlet (a) and upstream (b) sampling locations. Samples represent 2005 precipitation events of 29 June–1 July (●), 16–18 September (○), and 9–12 November (▼). Symbols represent sample collection and correspond to the runoff at each site provided in Figure 3. Lines are not reflective of trends between data

the June storm at both sites and the September event at the Archer Creek outlet. While small relative to total flux, this ‘new’ Hg may be more bioavailable than soil-derived Hg in downstream Arbutus Lake. Harris *et al.* (2007) documented fish bioaccumulation of ‘new’ Hg as determined by isotopic watershed spikes in association with the METAALICUS study. However, ‘new’ Hg within lake fish resulted almost exclusively from that applied directly to the lake, with <1% of the watershed spike being transported to the lake. The high watershed retention may reflect the association of spike Hg with plants and soil due to application during dry periods.

Hg delivery with precipitation, as documented by the results at Archer Creek, may result in higher mobilization, demonstrating the importance of event mobilization mechanisms.

Water chemical influence on Hg species flux

The concentration patterns of MeHg and THg suggest similar mobilization mechanisms (Figure 4), with each demonstrating the potential for rapid mobilization at the beginning of events due to throughfall followed by flushing of near-channel surface soils. The MeHg levels relative to those for THg depended on the site and season,

with significantly correlated ($\alpha = 0.05$) responses during September for the upstream site and during June and November for the Archer Creek outlet site. The percentage of THg occurring as MeHg for each site was similar for the June and November events ($\sim 2\%$ and 1% for the Archer Creek outlet and upstream sites, respectively), but values increased during the warmer low-flow period in mid-September when a larger pool of MeHg is available for transport (Selvendiran *et al.*, 2008). The fraction of THg as MeHg increased for the September event by a factor of 4.5 at the Archer Creek outlet site. While the lower percentage at the upstream site (3.0 times) reflects the influence of wetlands on streamwater MeHg concentrations, the MeHg increase demonstrates the potential importance of upland ecosystems on MeHg transport to downstream aquatic ecosystems.

Excluding September, MeHg significantly ($\alpha = 0.05$) increased with DOC and decreased with SO_4^{2-} (Figure 7) at the upstream site, consistent with a mobilization mechanism from saturated watershed soils. Surprisingly, correlations did not exist between DOC and SO_4^{2-} with MeHg at the wetland-influenced Archer Creek outlet site (Selvendiran *et al.*, 2008), suggesting that flushing of MeHg-rich wetland water is not occurring during events, an observation consistent with previous results showing that during baseflow the contribution of solutes from wetland soils was low due to low hydrologic conductivity (McHale *et al.*, 2002). The significant relationships for the upstream site are consistent with increases in watershed connectivity leading to Hg mobilization and with the increased responsiveness relative to the Archer Creek outlet site. DOC was significantly negatively correlated ($\alpha = 0.05$) with both SO_4^{2-} and Si_T (Figure 7), a result consistent with a flushing mechanism, particularly from wetlands. DOC concentrations increased as shallower soil layers became saturated, while SO_4^{2-} and Si_T were elevated in deep soil water and groundwater (Table S2, Supporting Information; Mitchell *et al.*, 2006). While these patterns suggest flushing mechanisms for watershed runoff, relationships between solutes as assessed across all events are dominated by the November event, particularly for the upstream site. When examining individual events, DOC correlations with SO_4^{2-} and Si_T were only significant for the November event, suggesting that soil flushing was the dominant mechanism, with runoff generation during June and September resulting from a combination of mechanisms.

Particulate matter has been shown to be an important mechanism of Hg transport within some forested watersheds during hydrologic events (Scherbatskoy *et al.*, 1998; Lawson and Mason, 2001; Shanley *et al.*, 2002). However, Hg species flux at Archer Creek was largely in the dissolved form. Particulate transport contributed only during the hydrograph rise at the Archer Creek outlet during the November event with particulate organic carbon content remaining relatively constant during events (Figure S3, Supporting Information). Limited analysis of

two particulate Hg samples collected during the November event is supported by additional sampling comparing filtered and unfiltered samples at both locations for other events (J. Dittman, Syracuse University, unpublished data) which suggest that only 25% of the peak THg content is associated with particulates. Based upon this value, we approximate that $0.8 \text{ ng THg L}^{-1}$ was associated with the 9 mg L^{-1} increase in TSS associated with the November Archer Creek outlet hydrograph rise. The THg concentration on particulates required for such a response (90 ng g^{-1}) is comparable with values of upland forest floor in the Archer Creek watershed (J. T. Bushey, unpublished data).

Event results for Archer Creek suggest that the role of particulates in Hg species flux is site specific, with ecosystems delivering a high fraction of THg as dissolved potentially increasing Hg bioavailability downstream in lakes. TSS concentrations at Archer Creek were $< 11 \text{ mg L}^{-1}$, significantly less than those measured ($> 100 \text{ mg L}^{-1}$) in other event studies within forested watersheds (Allan and Heyes, 1998; Scherbatskoy *et al.*, 1998; Lawson and Mason, 2001). The greater THg concentrations reported in these studies (i.e. $5\text{--}20 \text{ ng L}^{-1}$) are consistent with estimates based upon the elevated particulate loading, assuming a THg content in particulate matter of 100 ng g^{-1} . Additionally, TSS was highest during the rising limb of the hydrograph at Archer Creek, demonstrating the importance of sampling intensity and timing in assessing mobilization mechanisms of particulate Hg (Lawson and Mason, 2001).

CONCLUSIONS

Concentrations of Hg species increased during storm events at both the upstream and the Archer Creek outlet sites. While the relative response of Hg species flux to elevated discharge was more dynamic in the upstream reach, the absolute increase in Hg flux was greater at the Archer Creek outlet site. THg and MeHg concentrations were not significantly correlated with discharge across all storms. Hg species flux was more controlled by discharge, rather than concentration, with the significant flux–discharge correlation demonstrating predictive potential in estimating annual THg delivery to Arbutus Lake. Unlike previous investigations, Hg species concentrations were not correlated significantly with discharge, DOC, or TSS. The rapid response of Hg species produced a clockwise hysteresis in the concentration–discharge relationships, with a larger hysteresis pattern for the wetland-dominated reach. Unlike Hg species, DOC concentrations peaked at or after discharge, suggesting that the sources of these solutes vary over the hydrograph.

The initial response of Hg species during intense events in which there is canopy cover demonstrates the potential for rapid delivery from watersheds, particularly upland sections. THg relationships with K_T and NO_3^- suggest an important contribution of throughfall during the hydrograph rise and probably emphasize the importance

of hillslope hollows in generating runoff, in agreement with previous investigations at Archer Creek. Preferential flowpaths such as hollows exhibit a greater impact on Hg supply for the upland ecosystem as the watershed re-wets and source areas hydrologically connect. The timing of the DOC peak signifies a shift in runoff contribution from throughfall to the flushing of water from the surface soil, including riparian areas and those surrounding hollows. Particulate Hg is generally a minor contribution to stream Hg during events at Archer Creek. A lack of particulate Hg contribution differs from previous investigations and, coupled with the rapid Hg runoff response and the lack of a Hg–discharge relationship, emphasizes that an understanding of mechanisms associated with individual watersheds is necessary to assess Hg transport during elevated discharge events and the associated effects on bioavailability.

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