Hydrological Controls on Mercury Mobility and Transport from a Forested Hillslope during Spring Snowmelt

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
Department of Geography
University of Toronto

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Abstract

Upland environments are important sources of mercury (Hg) to downstream wetlands and water bodies. Hydrology is instrumental in facilitating Hg transport within, and export from watersheds. Two complementary studies were conducted to assess the role hydrological processes play in controlling Hg mobility and transport in forested uplands. A field study compared runoff and Hg fluxes from three, replicate hillslope plots during two contrasting spring snowmelt periods, in terms of snowpack depth and timing. Hillslope Hg fluxes were predominately flow-driven. The melting of soil frost significantly delayed a large portion of the Hg flux later into the spring following a winter with minimal snow accumulation. A microcosm laboratory study using a stable Hg isotope tracer applied to intact soil cores investigated the relative controls of soil moisture and precipitation on Hg mobility. Both hydrologic factors control the mobility of contemporary Hg; with greatest Hg flushing from dry soils under high-flow conditions.
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Chapter 1
Introduction

1

1.1 Mercury in the Environment

Mercury (Hg) is a naturally occurring element on Earth. In addition to natural sources such as volcanic activity, anthropogenic activities such as coal and fossil fuel burning and gold mining have contributed to global Hg pools in the atmospheric, terrestrial and aquatic environments (Selin 2009). Mercury exists predominantly in three forms in the environment: elemental Hg (Hg\textsubscript{0}), inorganic divalent Hg (Hg\textsuperscript{2+}) and bioavailable methylmercury (CH\textsubscript{3}Hg\textsuperscript{+}; MeHg) (Zillioux et al. 1993). All forms of Hg pose a severe health risk to both vulnerable human and wildlife populations; particularly MeHg, which is known to bioaccumulate in tissue and biomagnify in higher trophic levels of the food web (Mergler et al. 2007; Scheuhammer et al. 2007). Humans are exposed to MeHg, a potent neurotoxin and teratogen, primarily through the consumption of contaminated fish. The threat of Hg pollution to human health is exemplified by the extent of fish consumption advisories due to high Hg levels (all 50 states in the United States) (Driscoll et al. 2007). The western Great Lakes region, in which my research was conducted, is particularly prone to advisories (Kolka et al. 2001).

Atmospheric deposition represents the major input of Hg pollution to watersheds (Fitzgerald et al. 1998; Driscoll et al. 2007), with a large portion of this deposited Hg being incorporated into the soil and vegetation pools (Hintelmann et al 2002). However, while acting as sinks of Hg, terrestrial watersheds can also serve as important sources of Hg to downstream wetlands and water bodies via runoff (Munthe et al. 2007; Harris et al. 2007). Wetlands, as well as other aquatic environments such as lake sediments, are known to be sites of Hg methylation due to favourable redox and hydrological conditions (Branfireun and Roulet 2002; Gilmour et al. 1992). The microbially-mediated process of MeHg production has been found to be conducted primarily by sulphate-reducing bacteria (Compeau and Bartha 1985) and to a lesser extent by iron-reducing bacteria (Warner et al. 2003). Recent research has also shown that the provision of sulphate and labile carbon to wetland systems from upland environments via runoff stimulates
Hg methylation (Mitchell et al. 2008a); particularly at the upland-peatland interface creating “hot spots” of MeHg production (Mitchell et al. 2009). Given the role of upland environments in the export of Hg to receiving wetlands, and the health risks associated with MeHg, research into the controls on Hg mobility and transport from terrestrial uplands, the important first stage in Hg mobilization, is warranted.

1.2 Hydrology and Mercury Transport

Hydrological processes play an important role in the biogeochemical cycling of chemical constituents in ecosystems through transport between watershed compartments as well as facilitating biogeochemical transformations. Research has demonstrated that hydrology is active in controlling Hg transport in addition to facilitating speciation processes such as Hg methylation. Mercury and methylmercury export from watersheds have been observed to be enhanced as a result of both high-flow events (Bushey et al. 2008; Dittman et al. 2010; Scherbatskoy et al. 1998) as well as spring snowmelt (Mitchell et al. 2008b; Demers et al. 2010; Bishop et al. 1995; Babiarz et al. 1998). Several studies have reported that a significant portion of the annual Hg export from a watershed occurred during the spring melt season (i.e. Bishop et al. 1995; Mitchell et al. 2008b). Given that between 34% (Bishop et al. 1995) and 26-39% (Mitchell et al. 2008b) of the annual total Hg flux has been observed to be exported from watersheds as a result of spring snowmelt, such events represent notable “hot moments” (McClain et al. 2003) in Hg fluxes to downstream wetlands and water bodies. The large pulse of Hg to receiving aquatic systems, in association with such solutes as dissolved organic carbon (DOC) (Dittman et al. 2010; Ågren et al. 2008) and sulphate and other ions (Stottlemyer and Toczydlowski 1991) known to stimulate MeHg production, may contribute to enhanced availability of MeHg and biotic uptake.

In addition to runoff, it has been suggested that other hydrologic factors such as antecedent soil moisture may play a key role in the mobilization of Hg from soil during high-flow events (Babiarz et al. 1998). Mercury fluxes from upland soils may be augmented following dry periods, as has been found in wetland environments (Gustin et al. 2006; Grondin et al. 1995; Zillioux et al. 1993). However, the role of antecedent soil moisture on Hg mobility from upland environments has not been extensively studied and is not fully understood.
Elucidating the relative controls of runoff and soil moisture on Hg mobility and transport from upland systems could aid in modeling the potential response of Hg transport to land use changes as well as global climate change.

1.3 Hillslope Hydrological Processes and Global Climate Change

Global climate change is forecasted to impact the depth and timing of snowpack accumulation. In northern Minnesota, the study area in which this research was conducted, as well as other regions in North America and globally, snow accumulation is predicted to be diminished as air temperatures are expected to increase (Mohseni and Stefan 2001; Moore and McKendry 1996). Despite the forecasted increases in atmospheric temperatures in the western Great Lakes region, reduced snowpack depth and potentially delayed snow accumulation may result in deeper soil frost development (Sinha et al. 2010; Isard et al. 2007); as a result of diminished insulating snow cover (Hardy et al 2001). It is probable that with smaller and potentially later snowpack development the volume of spring runoff will decrease or soil water dynamics and hydrologic flow paths may be altered as a result of soil freezing (Iwata et al. 2010; Hardy et al. 2001). Recent research has observed that reduced snow accumulation greatly enhanced the depth of soil freezing, which subsequently hindered the infiltration of snowmelt waters and augmented the partitioning of melt input into runoff (Iwata et al. 2010); particularly during the early spring melt period (Laudon et al. 2004).

Given that spring snowmelt is an important period for Hg, DOC and other solute export from watersheds (Mitchell et al. 2008b; Bishop et al. 1995; Stottlemyer and Toczydlowski 1991), global climate change and the potential alterations in hydrologic flow paths and the volume of spring runoff may consequently impact chemical transport. Both soil biogeochemical processes (Hardy et al. 2001) as well as the chemistry of streamflow and snow meltwater (Fitzhugh et al. 2003) have been found to be notably impacted as a result of increased soil freezing resulting from diminished insulating snow cover. Due to more frequent, extensive and severe soil freezing episodes, Fitzhugh et al. (2003) found that the loss of nutrients such as nitrate, potassium and calcium was stimulated under conditions of reduced snowpack depth. Few studies, however, have investigated the potential effects of increasing soil frost on Hg mobility and transport in
upland systems during spring snowmelt. My research, therefore, studied how Hg transport from forested upland environments may be impacted by diminished snow accumulation and increased soil frost depth, as expected under predicted changes in global climate (Hardy et al. 2001; Sinha et al. 2010; Isard et al. 2007). Also, other hydrologic factors which may be impacted by climate change, such as antecedent soil moisture, may significantly affect Hg mobility and enhance Hg transport to downstream wetlands. Research investigating the relative controls of hydrologic variables such as precipitation input and soil moisture is warranted in order to potentially predict the effect of climate and other land use changes on Hg mobility from upland environments.

1.4 Use of Enriched Stable Mercury Isotopes as Environmental Tracers

Mercury has seven natural stable isotopes: $^{196}\text{Hg}$, $^{198}\text{Hg}$, $^{199}\text{Hg}$, $^{200}\text{Hg}$, $^{201}\text{Hg}$, $^{202}\text{Hg}$ and $^{204}\text{Hg}$, of which $^{202}\text{Hg}$ is most abundant (29.7%) (Bergquist and Blum 2009). As these stable isotopes are commercially available in enriched form, they as well as the radioisotope $^{203}\text{Hg}$ have become increasingly utilized in mercury biogeochemical research as tracers. Enriched stable Hg isotopes have been applied at a variety of scales; from soil cores (Schlüter 1996), to upland plots (Hintelmann et al. 2002; Munthe et al. 2001), to entire wetlands, lakes and uplands (Branfireun et al. 2005; Harris et al. 2007; C.P.J. Mitchell pers. comm.). Applied isotope tracers can provide valuable insight into Hg transport processes as well as biogeochemical transformations such as Hg methylation due to the ability to distinguish between ambient and added Hg with inductively coupled plasma – mass spectrometry (ICP-MS) analytical techniques.

Recent studies under the Mercury Experiment to Assess Atmospheric Loadings in Canada and the United States (METAALICUS) project have made use of enriched stable Hg isotopes to ultimately investigate the impact of atmospheric mercury deposition on fish Hg uptake (Harris et al. 2007). By applying different labeled isotopes to each of the sub-units (lake, wetland and upland) within a watershed, this project has facilitated the determination of the relative contributions of each of these compartments to bioaccumulation of Hg in aquatic food chains and the timing by which the ecosystem responds to enhanced Hg deposition (Harris et al. 2007). In addition, the transport and transformations of Hg occurring within each of the watershed compartments were able to be tracked, as well as the assessment of the behavior of newly-
deposited Hg in relation to that of old, legacy Hg. For instance, at the plot scale Hintelmann et al. (2002) determined that newly-deposited Hg was more reactive in terms of volatilization and Hg methylation than legacy Hg in upland soils. The mobility of the new Hg was also deemed to be limited with less than 1% of the isotope observed in runoff. In the boreal wetland, Branfireun et al. (2005) observed that newly-added Hg was readily methylated as well as significantly transported to downstream aquatic ecosystems via shallow groundwater flowpaths. Collectively, these studies illustrate the value of using applied enriched stable isotopes at the landscape scale to elucidate detailed process information pertaining to Hg cycling.

Mercury isotopes have also been applied at smaller scales such as soil columns as a means of investigating vertical translocation of Hg in soil. Such studies often involve the addition of large doses of labeled Hg, most commonly radioactive $^{203}$Hg, to the surface of intact soil cores followed by flushing simulating rainfall (Schlüter 1996; Schlüter et al. 1995; Semu et al. 1985). Investigations of this nature have concluded that the majority of added Hg was immobilized in the surface soil layers with only a small fraction of the isotope being observed in runoff (Semu et al. 1985; Schlüter 1996); similar to the field results of Hintelmann et al (2002). Conducting research at the soil core scale affords the opportunity to control and manipulate certain variables, such as hydrologic factors, and assess the subsequent response of Hg transport dynamics. Significant heterogeneity and variability at the landscape scale can often confound the results of studies attempting to investigate the relative contributions of hydrological processes to biogeochemical dynamics. However, few recent studies utilizing applied stable Hg isotopes at smaller scales under controlled conditions have been performed. Therefore, in addition to a field study investigating the impact of snowpack depth and the subsequent volume of spring runoff on Hg transport, I also conducted a laboratory soil core microcosm experiment using an applied Hg tracer to elucidate the relative influences of precipitation and soil moisture in controlling Hg mobility.

Experiments using intact, undisturbed soil cores for hydrological applications such as leaching studies often encounter introduced bias due to the material used to encase the soil and maintain its structure. Studies often use polyvinyl chloride (PVC) pipe, paraffin wax, (i.e. McIntosh et al. 1999) or resin (i.e. Vanderborght et al. 2002) to encase soil cores. However, the use of PVC can result in wall effects or smearing in leaching experiments, while wax and resin can intrude into the soil pores thereby clogging pore spaces and potentially inhibiting flow paths. Consequently,
I conducted a small pilot study, the full details of which are discussed in Appendix 2, to test the use of polyurethane spray foam insulation, similar to the method of Bagarello and Sgroi (2008), as a soil-encasing material for both hydrological and Hg biogeochemical applications.

1.5 Objectives and Research Questions

The overall objective of this research was to directly couple an in-depth understanding of hillslope hydrological processes in a watershed to the mobilization of mercury stored in upland soils. Firstly, this research used hydrological and mercury biogeochemical monitoring over two contrasting spring snowmelt seasons as a means of quantifying the effect of smaller and later snowpack development, and the subsequent diminished volume of spring runoff on the mobility and transport of mercury. Second, an enriched stable mercury isotope was applied to intact soil columns subjected to similar soil moisture and precipitation levels observed during the two spring melts in order to determine the relative controls of these hydrologic factors on mercury mobility in soil. The research set forth to address the following questions:

1.) How will a diminished snowpack and a subsequent reduction in snowmelt runoff affect the mobility and transport of mercury in a forested hillslope?

2.) What effect does the antecedent soil moisture condition have on the vertical transport of mercury through the soil profile?

3.) How is the transport of mercury through the soil affected by the magnitude of snowmelt input?

4.) Does the magnitude of snowmelt input have the same effect on mercury transport at different levels of antecedent soil moisture?

Chapter 2 addresses Question #1, while Questions #2-4 will be addressed in Chapter 3.
1.6 Thesis Structure and Publication Information

1.6.1 Chapter 1

Chapter 1 provides an overview of literature pertinent to the research, identifying current knowledge gaps which my research endeavoured to address. The objectives and associated research questions are also outlined in this Chapter.

1.6.2 Chapter 2

Chapter 2 involved an intensive field study spanning two spring snowmelt periods investigating the impact of diminished snowpack accumulation, as is forecasted with climate change, on mercury transport in forested hillslope environments. This Chapter has been accepted for publication, and is currently available online in the Journal of Environmental Monitoring (doi:10.1039/C2EM30267E), with Carl P.J. Mitchell as a co-author. Reference made to the research presented in this Chapter is cited as (Haynes and Mitchell 2012) in subsequent Chapters.

1.6.3 Chapter 3

Chapter 3 details a laboratory experiment using an enriched stable mercury isotope applied to intact soil cores under varying controlled hydrologic conditions in order to assess the relative controls of precipitation and soil moisture on Hg mobility and transport. This Chapter is currently being prepared for submission to the Journal of Hydrology. The co-author on this paper will be Carl P.J. Mitchell.

1.6.4 Chapter 4

Chapter 4 synthesizes the results and conclusions of the field study in Chapter 2 with those of the controlled laboratory experiment in Chapter 3. Potential future research ideas are also discussed.
1.6.5 Appendices

Appendix 1 comprises two supplementary figures associated with Chapter 2. Appendix 2 describes the pilot study conducted in order to test the viability of using polyurethane spray foam insulation as a soil-encasing material for both hydrological leaching studies as well as for mercury biogeochemical applications. This method was applied to the experiments conducted in Chapter 3.

1.7 References


Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. *Ecosystems*, **6**, 301-312.


Chapter 2
Inter-annual Variability in Hillslope Runoff and Mercury Flux during Spring Snowmelt

2

2.1 Introduction

Mercury (Hg) is a potent neurotoxin with severe toxicological and teratological effects on both vulnerable human and wildlife populations (Mergler et al. 2007; Scheuhammer et al. 2007). Mercury sorbs to mineral and organic surfaces in soil; thus terrestrial environments store large amounts of Hg (Grigal 2003; Gabriel and Williamson 2004). Watersheds can also be important sources of Hg to surface waters through slow leaching from soils (Grigal 2003; Branfireun et al. 1996). From forested catchments the release of Hg from the organic-rich forest floor is likely a very important, early stage of Hg mobilization (Schwesig and Matzner 2001). Since the transport of Hg from forested upland systems may seriously affect Hg bioaccumulation in aquatic organisms downstream, understanding the spatial and temporal variability in upland Hg mobilization is essential.

The mobility and export of Hg from watersheds is directly linked with hydrological processes. Recent research has demonstrated that both high-flow storm events (Bushey et al. 2008; Dittman et al. 2010; Scherbatskoy et al. 1998) and spring snowmelt (Mitchell et al. 2008a; Demers et al. 2010; Bishop et al. 1995; Babiarz et al. 1998) are significant periods of Hg export from watersheds. Bishop et al. (1995) found that 34% of the total annual Hg flux from a catchment in northern Sweden occurred during the three-week spring melt period. Similarly, a study conducted at the Marcell Experimental Forest in northern Minnesota concluded that 26-39% of the annual total Hg (THg) flux and 22-23% of the annual methylmercury (MeHg, the organic, bioaccumulative form of Hg) flux occurred during the 12-day spring snowmelt period (Mitchell et al. 2008a). Such episodic pulses of Hg are also observed in surface waters downstream from watersheds (Scherbatskoy et al. 1998). Given the significant amount of atmospherically-deposited Hg stored in upland soils (Grigal 2002), any slight adjustment in the mobility of this
Hg pool has the potential to trigger deleterious consequences for Hg bioaccumulation in the downstream aquatic food chain.

Related studies have also examined the role of snowmelt events on the flushing of dissolved organic carbon (DOC) (Dittman et al. 2010; Ågren et al. 2008), as well as nutrients such as nitrate, ammonium and sulphate and trace metals such as cadmium and aluminum (Stottlemyer et al. Toczydlowski 1991; Petrone et al. 2007) from upland soil profiles to surface waters. The flux of some constituents, such as DOC in snowmelt runoff, may influence the mobility and transport of Hg. The tendency of Hg to form complexes with organic matter (Driscoll et al. 1995) suggests that Hg may be preferentially exported with DOC, particularly when flowpaths are directed through shallow, organic-rich soil layers during episodic high-flow events (Dittman et al. 2010). Similarly, the export of dissolved solutes such as sulphate and DOC in meltwaters from upland soils may affect Hg methylation in low-lying wetlands and subsequent MeHg export (Mitchell et al. 2009).

Inter-annual variability in the timing of the winter snowpack and the subsequent volume of spring runoff may impact the mobility of Hg species and solutes associated with Hg methylation. Generally, recent research has investigated only a single spring snowmelt event (Mitchell et al. 2008a; Bishop et al. 1995), which does not facilitate an investigation of the effects of inter-annual variation in hydrology on Hg transport. However, Schelker et al. (2011) recently investigated mercury and DOC mobility over two spring melts, although their intention was to assess the associated hydrological controls during all high-flow events and not specifically as an inter-annual comparison of snowmelt periods. Inter-annual studies may have notable applications when considering the potential effects of global climate change on snow accumulation and predicting the subsequent implications for Hg mobility. For example, snow accumulation is forecasted to decrease with climate change in north-central Minnesota (Mohseni and Stefan 2001), the region in which this study was conducted. With shallower and/or later snowpack development the volume of spring runoff may diminish or flow paths and soil water dynamics may change due to effects on soil freezing (Iwata et al. 2010; Hardy et al. 2001). Increased soil freezing, attributed to a lack of insulating snow cover, may have notable implications in soil biogeochemical processes (Hardy et al. 2001) as well as the chemistry of streamflow and snow meltwater (Fitzhugh et al. 2003). Iwata et al. (2010) found that reduced snow accumulation greatly enhanced the depth of soil freezing, hindering the infiltration of
spring snowmelt and enhancing nearer surface runoff generation. Using both hydrometric and stable isotope methods, Laudon et al. (2004) emphasized that the depth of soil frost impacts hydrologic flow paths particularly during the early spring melt period; exerting less of an influence as the spring progresses. Under a warmer climate, diminished snowpack depth and duration may promote nutrient losses such as nitrate, potassium and calcium from upland soils due to more frequent, harsh and extensive soil freezing episodes (Fitzhugh et al. 2003).

The potential impact of inter-annual variability on snowpack accumulation and the volume of spring runoff, specifically in relation to the influence on Hg and solute mobility and transport in forested watersheds, have not been studied. The overall objective of this research was to assess the potential impacts of inter-annual climate variability on Hg mobility in forested upland watersheds, in addition to spatial variability in hillslope hydrology and Hg fluxes. We compared hydrological flows and Hg and solute mobility between the spring of 2010, when winter snowpack accumulation had been severely diminished and an abnormally early melt occurred (earliest lake ice-out date on record), to the spring of 2011, when significantly greater winter snow accumulation was recorded. We also compared the spatial dynamics of hillslope hydrology and Hg transport through replication of measurements on three adjacent, identically instrumented hillslope plots.

2.2 Methods

2.2.1 Study Site

This study was conducted in an upland-peatland watershed (S7) within the Marcell Experimental Forest (MEF) in north-central Minnesota (47° 31’ 21” N, 93° 28’ 7” W). Similar to much of the western Great Lakes region, the glaciated landscape encompasses numerous headwater catchments comprised of rolling upland topography that surrounds low-lying wetlands or small lakes. The climate at the MEF is characterized as sub-humid continental, with an average daily temperature of 4.2°C (average temperatures of 13.9°C during the months of April to September and -5.6°C for the months of October to March) (MEF Hydrology and Climate Database 2007). Typical annual precipitation for the MEF is approximately 780 mm (MEF Hydrology and Climate Database 2007). The upland overstory vegetation in the S7 watershed is predominately comprised of sugar maple (Acer saccharum), quaking aspen (Populus tremuloides) and balsam poplar (Populus balsamifera).
The hillslope is north-facing, has a mean slope of 10°, and drains into a low-lying peatland. The upland mineral soils were formed as a result of Wisconsinan glacial drift. The soil profile above the clay-rich B-horizon consists of a shallow O-horizon (generally <2 cm) below which there is a well-defined sandy loam A-horizon (mean depth to base of A-horizon 50 ± 27 cm). The B-horizon has low permeability and acts as a confining layer, directing subsurface runoff as shallow interflow (Figure 2-1a) during high-flow events (Timmons et al. 1977), with minimal seepage losses to deep groundwater. As the S7 watershed is in a headwater area and elevated well above the regional groundwater system, the only hydrological input to the study hillslope is via net precipitation.

Figure 2-1  a.) Side-view of S7 hillslope illustrating position of confining B soil horizon, converting snowmelt inputs to runoff as shallow interflow.  b.) Contour map confining soil layer (50 cm contours) in the S7 watershed, with the locations of the runoff collectors and wells in each of the S7A, S7B and S7C hillslope plots.
2.2.2 Hydrological Measurements and Sampling

Along the 4.1 ha upland, three instrumented, hillslope sub-catchment plots – S7A, S7B and S7C were instrumented adjacent to one another (Figure 2-1b). A trench was dug to the confining layer near the toe of each hillslope plot and runoff was directed through drainage piping to a large recording tipping bucket flow meter. Runoff contributing areas to each trench were calculated using ArcGIS 9 after measuring depth from surface to B-horizon at more than one hundred points along the hillslope, georeferencing these points using a sub-meter GPS unit, and then overlaying the depth measurements with a LiDAR-derived digital elevation model to arrive at a B-horizon (confining layer) surface map (Figure 2-1b). The runoff contributing areas of plots S7A, S7B, and S7C were 437, 339, and 439 m², respectively. The mean depth to the base of the A-horizon was 45 ± 21 cm in S7A, 46 ± 24 cm in S7B and 58 ± 35 cm in S7C. Subsurface runoff samples were collected, in accordance with ultraclean trace metal sampling techniques (Shanley et al. 2008), from the outflow of the tipping bucket runoff collectors in each plot at least daily during both the 2010 (March 18 – April 8) and 2011 (April 8-16) spring melt periods.

Snow water equivalent (SWE) in the S7 watershed in 2011 was determined from snow course measurements made prior to the onset of spring melt. For the 2010 winter, SWE was estimated from snow course measurements conducted in deciduous-upland environments throughout the MEF. Soil frost depths for both 2010 and 2011 were obtained by hammering a steel point into the soil over the course of both winter seasons. Available soil water measurements were made by neutron probe in the north-facing hillslope plot in the adjacent S6 watershed in November prior to snowfall. Prior to the 2011 spring melt, ten snowpack profile samples were collected in each of the three plots using hydrochloric acid (HCl)-rinsed polycarbonate corers. The snow samples were melted in darkness at room temperature in acid-rinsed (10% HCl) sealed, plastic bags, transferred to polyethylene terephthalate glycol (PETG) bottles, and acidified with 0.5% trace-metal grade HCl. Total Hg concentrations of blanks (n = 3) of the HCl-rinsed plastic bags were below the detection limit. Although both filtered and unfiltered snow THg samples were collected, unfiltered THg concentrations were used because they represent the total Hg input. Snowmelt lysimeters (Teflon-lined; 1.40 m²) were installed in each hillslope plot prior to the winter of 2010-2011 only. Due to mid-melt leakage at two of the lysimeters, reliable snowmelt data was collected only from the S7C plot and is assumed to be representative for the hillslope. The lysimeter drained through an electronically logged tipping bucket rain gauge in order to
determine melt intensity. Daily snowmelt Hg release was measured by intermittent, ultraclean grab sampling. Average lysimeter blank THg concentrations were 1.15 ± 1.11 ng L⁻¹. In 2011, samples of melting snow were collected from the snowmelt lysimeter daily from April 1-11, with twice daily sampling April 2-5 and April 10. Mass balance revealed a 99% agreement between the unfiltered THg load determined from the snow cores and the total load determined from the snow lysimeter. As snow samples could not be collected prior to the spring 2010 melt period the snow THg concentration was estimated as a precipitation-weighted mean concentration from NADP/MDN data (National Atmospheric Deposition Program Mercury Deposition Network 2011).

Perched water table elevations were monitored in an array of eight georeferenced and surveyed wells across the hillslope (see Figure 2-1b). Each well was equipped with a Hobo® water level logger that recorded water table elevations at 15-minute intervals. Water table elevations were corrected for changes in atmospheric pressure using a logging barometer located in the middle of the plots. Water samples were drawn from newly flushed wells on 2 occasions in spring 2010 and 4 occasions in spring 2011, approximately weekly, starting before the onset of melt. Samples were drawn using a peristaltic pump and acid-washed Teflon tubing.

Runoff samples for THg analysis were collected in PETG bottles, preserved with 0.5% trace-metal grade HCl and stored in darkness at 4°C until analysis. During the 2011 melt both filtered and unfiltered samples were collected whereas only unfiltered samples were collected during the 2010 melt period. Samples were filtered using ashed 0.7 µm glass fibre filters. The same trend in filtered and unfiltered THg concentrations was observed throughout the sampling periods despite a difference in absolute concentrations. Therefore, unfiltered THg concentrations are used in this study to determine overall runoff THg fluxes and yields. Runoff samples for DOC analysis were collected in high-density polyethylene (HDPE) bottles and were also stored in darkness at 4°C until analysis (up to one month). Ultra-clean trace metal techniques were strictly adhered to for both field sample collection (Shanley et al. 2008) and laboratory analysis.

During the 2011 melt period we conducted hillslope-scale, stable isotope hydrograph separations of runoff (event water vs. pre-event water) to further understand the timing and likely pathways of melt water through the hillslope. The pre-event and event proportions of hillslope runoff were calculated by:
\[ Q_{\text{pre--event}} = Q_{\text{runoff}} \left( \frac{C_{\text{runoff}} - C_{\text{event}}}{C_{\text{pre--event}} - C_{\text{event}}} \right) \] and
\[ Q_{\text{event}} = Q_{\text{runoff}} - Q_{\text{pre--event}} \] (2.1)

where \( Q = \) runoff in mm, of which total runoff \( (Q_{\text{runoff}}) \) is partitioned into runoff due to snowmelt \( (Q_{\text{event}}) \) and runoff contributed by soil water \( (Q_{\text{pre--event}}) \), and \( C =^{18}O \) concentration (expressed as \( \delta \) values in ‰ variation from Vienna Standard Mean Ocean Water) in runoff \( (C_{\text{runoff}}) \), pre-event \( (C_{\text{pre--event}}) \) or event \( (C_{\text{event}}) \) water. The event water signal was determined through the analysis of snowmelt lysimeter output and was weighted over time using the intra-event weighting procedure of McDonnell et al. (1990). The pre-event water signal was assessed through soil pore water equilibration (Wassenaar et al. 2008), the results of which were not statistically different from well water samples retrieved prior to the onset of melt. Briefly, for pore water equilibration, we retrieved three soil cores from each of the runoff plots (ridge, midslope and toeslope) prior to the onset of melt using steel core tubes driven into the soil by hammering. Cores were immediately returned to the laboratory at MEF where they were sectioned by depth and in relation to saturation. Approximately 20 g of soil from each section were equilibrated with dry air in sealed zipper lock plastic bags for approximately one hour. Six replicate 20 ml withdrawals of saturated water vapour from each bag were retrieved by gas tight syringe and analyzed sequentially with equilibrations of known standards using a Los Gatos Research Liquid Water Isotope Analyzer. The depth profile soils collected for the pore water equilibration isotope analysis were subsequently frozen for later THg analysis. Runoff samples for isotope analysis were collected at least daily from each of the subsurface runoff collectors. Liquid water stable isotope samples were collected in 20 ml glass vials with cone-lined caps that excluded any headspace.

2.2.3 Interpolation of Missing 2010 Runoff Data

Due to logistical reasons and episodes of equipment freezing, runoff from March 11-17, 2010 could not be reliably measured. In order to estimate runoff fluxes from the hillslope a regression model was created based on the runoff data from a north-facing hillslope of the similar, nearby (<0.5 km) S2 watershed. The S2 watershed in the MEF has very similar soils, topography and vegetation to that of the S7 watershed. As a result, daily subsurface runoff data from the S2-
south (north-facing) hillslope was regressed against known runoff data (March 31-April 8) from each of the S7A, S7B and S7C runoff collectors in order to create an empirical relationship. The missing runoff data from March 11-17 for each plot was then estimated based on these linear relationships, with a mean standard error of 0.13 mm d⁻¹.

In addition, THg fluxes were also estimated for this period. Total Hg concentrations for the period of missing data (March 11-17) were conservatively estimated as the flow-weighted mean concentrations (FWMC) of the known THg concentrations throughout the remainder of the melt period. Total Hg fluxes from each plot for this period were estimated using the FWMC and the average daily discharge from March 11-17 as modelled based on S2 discharge. Any other missing THg concentrations were linearly interpolated (March 19-21 for S7A, March 20 for S7B and S7C, March 25-27 and 31 for all three plots) between actual measurements. As these periods of missing THg data range from one to three days, the assumption of linear interpolation is considered to be a conservative estimate of daily THg concentrations.

2.2.4 Analytical Methods

THg concentrations were determined using a Tekran model 2600 total mercury analyzer by cold vapour atomic fluorescence spectroscopy (CVAFS) following US EPA Method 1631 (2002). Recovery of a 5 ng L⁻¹ (mass = 0.25 ng) total mercury spike was 99 ± 12% (n = 37), replication of duplicates was 1.8 ± 1.7% (n = 37), and the detection limit, calculated as three standard deviations of matrix water blanks, was 0.20 ng L⁻¹ (n = 81). DOC was analyzed using a Shimadzu TOC-VCSH Total Organic Carbon analyzer with an in-line total nitrogen unit (TNM-1) and a high sensitivity combustion catalyst (720°C). Soil samples were lyophilized, nitric acid-digested using a microwave digestor, and diluted prior to THg analysis as for waters. Soil organic matter content was determined by loss on ignition (LOI, 550°C for 4 hours).

2.2.5 Statistical Analyses

Inter-annual comparisons of mean THg and DOC yields and fluxes, as well as runoff ratios (source/sink functions) were achieved using paired t-tests, with hillslope sub-catchment plots used as replicates in each year. The THg and DOC runoff ratios (source/sink functions) were calculated as follows:
effectively determining the snowpack contribution of THg and DOC to runoff. Data were tested for normality (Shapiro-Wilk W test) and heteroscedasticity and were log-transformed when parametric assumptions were not met. All statistical tests were performed using SAS Version 9.2. Statistical significance of comparisons was set at $\alpha < 0.1$ due to the low number of replicates (i.e. 3), inherent in such a field study where field replication is limited. Similar studies are often conducted at the scale of a single watershed, or at best involve the paired watershed approach (i.e. Martin et al. 2000), wherein it is not possible to conduct similar statistical comparisons.

2.3 Results

2.3.1 Inter-annual Comparison of Climate and Hydrology

Overall, hydrological conditions were very different between the 2010 and 2011 snowmelt periods. The 2010 snowmelt period had less snow (48 mm SWE), drier antecedent moisture conditions (65 mm soil water in upper 45 cm soil), more soil frost (279 mm mean thickness), and an earlier onset of melt (March 11, 2010). Approximately twice as much snow (98 mm SWE), 30% wetter conditions (84 mm soil water), and practically no soil frost (patchy with maximum depth of 50 mm) were observed prior to the 2011 snowmelt, which began on April 1, 2011 (Table 2-1). The 2010 spring melt yielded a total of 22 ± 5 mm of runoff, while approximately 2.8 times more runoff was observed for the 2011 spring melt (61 ± 17 mm).

**Table 2-1** Inter-annual comparison of mean maximum snow water equivalent (SWE) prior to melt, mean soil frost thickness, average THg concentrations of snow and runoff, timing (duration) of melt period and available soil water in fall prior to snowfall.

<table>
<thead>
<tr>
<th>Year</th>
<th>Max. Snowpack SWE (mm)</th>
<th>Frost Thickness (mm)</th>
<th>Avg. [THg]$_{snow}$ (ng L$^{-1}$)</th>
<th>Avg. [THg]$_{runoff}$ (ng L$^{-1}$)</th>
<th>First-Last Day of Runoff (Duration)</th>
<th>Available Soil Water (mm) in Surface 45 cm **</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>48</td>
<td>279</td>
<td>5.05*</td>
<td>23.09</td>
<td>Mar 11 – Apr 8 (29 days)</td>
<td>65</td>
</tr>
<tr>
<td>2011</td>
<td>98</td>
<td>0-50</td>
<td>6.12</td>
<td>24.03</td>
<td>Apr 8 – Apr 16 (9 days)</td>
<td>84</td>
</tr>
</tbody>
</table>

* Calculated as precipitation-weighted average from NADP/MDN data
** Measured in S6 (adjacent to S7) north-facing plot in Nov. prior to snowfall
Significant differences in the melt patterns between the two snowmelt periods were observed. The hydrograph for 2010 showed two distinct peaks in runoff; the first of which can be attributed to snowmelt with the second peak the result of melting soil frost (Figure 2-2). Evidence of the melting of soil frost was also observed in the sudden and considerable increase in the perched water table positions in the lower-slope wells around March 27, which peaked on April 2, 2010 in S7A and S7B (simultaneously with runoff), while water tables in S7C remained elevated throughout the month of April (Figure 2-3). The snowmelt runoff response accounted for approximately 72% of the total spring runoff with the remaining 28% due to the melting of soil frost. In comparison, the hydrograph for the 2011 spring melt had only a single peak of flow associated with snowmelt runoff, with no distinct frost melt (Figure 2-2).

**Figure 2-2** Daily runoff and THg yield in replicate S7 plots A, B and C for both the spring melt of 2010 and 2011 (note differences in scale). Runoff data for Mar11-Mar17, 2010 based on empirical model (see methods text). * = last day of snow present on the ground. Dashed line in 2010 S7C due to poor agreement with empirical model.
Figure 2-3 Hillslope runoff, water table position with respect to surface, snowmelt rates (2011 only) and event water contributions (2011 only) in S7A, S7B and S7C during the 2010 and 2011 melt periods.

2.3.2 Spatial Variability in Hillslope Hydrology

Temporal differences in the subsurface hydrological flow paths between the two snowmelt periods were evidenced by the perched water table levels over the course of the melt period (Figure 2-3). In spring 2011 the hillslope water table was closer to the surface (average maximum WT -0.118 m with respect to surface in the lower slope wells) than during the 2010 melt (average maximum WT -0.420 m with respect to surface in the lower slope wells), peaking at or just prior to peak runoff.

As well, considerable spatial variability in flow paths existed among the three hillslope plots, particularly throughout the 2011 melt period. The perched water table at the toe slope of S7A rapidly peaked on April 2, 2011 and remained within 10 cm of the surface until April 14, 2011 (Figure 2-3). In contrast, the water table of S7B gradually increased from the onset of snowmelt and peaked at the same time as runoff; receding following peak runoff. Beginning much deeper
(> 1 m) than the perched water tables of S7A and S7B (~ 0.4 m and 0.7 m, respectively) the S7C water table increased gradually throughout the melt period peaking within 10 cm of the surface simultaneously with peak runoff on April 10, 2011. These differences manifested as major differences in the isotopic runoff separation patterns as well. In S7A the proportion of event water contributing to runoff, as determined by stable water isotope analysis, peaked at the beginning of the runoff period (with event water accounting for 56% of runoff) and decreased steadily over time (Figure 2-3). In contrast, the contribution of event water in both S7B and S7C peaked slightly after peak runoff, at 76% and 64% respectively.

2.3.3 THg and DOC Fluxes

The 2011 snowmelt period resulted in an approximately 2.8 times greater THg yield (1479 ng m\(^{-2}\)) than the 2010 snowmelt (524 ng m\(^{-2}\)) (Figure 2-4). Similarly, the 2011 spring melt yielded approximately 2.7 times more DOC per square metre (1292 mg m\(^{-2}\)) than the 2010 melt period (483 mg m\(^{-2}\)). For the spring 2010 melt period, melting of soil frost accounted for approximately 30% of the total THg flux. These proportions in inter-annual flux differences were nearly identical to the differences in inter-annual runoff.

![Figure 2-4](image)

**Figure 2-4** Inter-annual comparison of runoff, THg and DOC yields, and THg and DOC runoff ratios (source/sink functions). Error bars represent standard error.

The overall snowpack THg (or DOC) load for each plot was divided by the THg (or DOC) load observed in spring runoff to constrain the proportion of snow THg and DOC that appeared in runoff (source/sink function). No significant difference in the THg (\(p = 0.65\)) and DOC (\(p = \)
0.48) source/sink functions were observed between the two years (Figure 2-4). The concentrations of THg in snow were very similar between the two years studied (Table 2-1). As well, the THg concentrations in runoff were also comparable between the 2010 and 2011 spring melt periods (Table 2-1). An inter-annual comparison of DOC concentrations in both snow and runoff exhibited a similar trend to that of THg.

There was a significant, but relatively weak relationship between filtered runoff THg concentrations and DOC concentrations in both 2010 \((R^2 = 0.44)\) and 2011 \((R^2 = 0.55)\) (Appendix Figure A-2-1). The slopes of the DOC-THg relationships were similar between years, but the intercepts differed indicating that slightly higher concentrations of DOC but lower concentrations of THg were observed in 2010 than in 2011.

Both the THg and DOC runoff concentrations exhibited similar temporal variability throughout the 2010 and 2011 melt periods. During the 2010 melt period both THg and DOC concentrations peaked at or just prior to peak runoff in all three hillslope plots (Figure 2-5). In contrast, spatial variability in runoff THg concentrations throughout the 2011 melt period was evident among the three plots. The runoff THg concentrations in plots S7B and S7C decreased steadily throughout the 2011 melt period following an early maximum before which the THg and DOC concentrations were inversely proportional to runoff in S7B and S7C (Figure 2-5). Runoff THg concentrations in S7A peaked much later than was observed in the other plots; early on the hydrograph recession limb on April 12, 2011 (Figure 2-5).
2.3.4 Total Hg and Organic Matter in Soil

The THg concentrations of the upland soils ranged from 4.69 – 44.4 ng g\(^{-1}\) dry weight (wt), with organic matter content ranging from 0.85 - 10.6\%. The surface soils (0 – 7.5 cm) had the highest THg concentration (17.81 ± 5.13 ng g\(^{-1}\) dry wt.) and organic matter content (3.70 ± 0.78\%); decreasing with subsequent depths (Appendix Figure A-2-2). However, THg concentrations in the surface silt of the confining layer increased slightly to 12.59 ± 4.59 ng g\(^{-1}\) dry wt, compared to the lower depths of the transmissive sand layer above.

2.4 Discussion

2.4.1 Climate and Hydrological Impacts on Mercury Flux

With enhanced snow accumulation and subsequently greater magnitude of snowmelt runoff upland THg yield was proportionally increased. Total Hg, DOC, and water yields all increased by the same proportion following the winter with greater snow accumulation, suggesting strongly that inter-annual differences in upland THg and DOC export are predominately flow-driven in this landscape. The tendency of Hg fluxes to increase with flow has previously been
observed during high-flow events such as spring snowmelt and high-intensity rain events, particularly at the watershed scale (Scherbatskoy et al. 1998; Bishop et al. 1995; Lee et al. 2000). This increase in Hg export with flow has been attributed to greater flushing of particulate- and organic matter-bound Hg during high-flow events (Scherbatskoy et al. 1998; Babiarz et al. 1998; Schuster et al. 2008). In this study, a significant, but relatively weak correlation was observed between the filtered runoff THg and DOC concentrations during both years’ spring melt. By taking into account the inter-annual differences in runoff when considering the observed differences in THg, effectively normalizing the inter-annual variation for flow, essentially no difference in THg export existed between the two years; despite very large differences in hydrology. As THg export appears to be controlled by flow, increases in winter snow accumulation in certain regions due to climate change would significantly enhance the flux of Hg being delivered to ecologically-sensitive downstream ecosystems. Conversely, as global climate change is forecasted to diminish snow accumulation in northern Minnesota (Mohseni and Stefan 2001), as well as other regions in North America (Moore and McKendry 1996), overall spring THg export to downstream water bodies would be expected to proportionally diminish with flow.

The timing at which this reduced THg flux is released from forested upland systems may be critical when considering the potential effects of global warming on Hg methylation and bioaccumulation. Soil frost may play an important role in transporting a significant portion of the spring Hg flux following winters with minimal snow accumulation. In this study the considerable THg flux as a result of frost melt occurred nearly three weeks after the onset of snowmelt and more than two weeks after the disappearance of the snowpack. By significantly delaying a large portion of upland THg export later into the spring, thick frost development due to a lack of insulating snow cover (Hardy et al. 2001) may have deleterious effects to downstream aquatic organisms. Even though the 2010 spring melt period finished (by Julian date) before the onset of the 2011 spring melt (Table 2-1), the spring season commenced earlier in 2010, with spring-like temperatures earlier than typically observed. In conjunction with rising Hg methylation rates that might be expected with warmer temperatures (Gilmour et al. 1992) during the spring season, the augmented contribution of THg as well as solutes such as DOC later into the presumably warmer spring season may act to enhance Hg methylation in downstream wetlands (Mitchell et al. 2009). This enhanced methylation has the potential to increase the bioavailability of Hg for biotic uptake. Although the overall THg load was less
following the winter with minimal snow accumulation, by starting earlier in the spring season, the period during which the conditions may be conducive to MeHg production is prolonged. This trend in the timing of runoff and THg export may become more prominent as global warming is predicted to result in reduced precipitation and therefore diminished winter snowpacks (Mohseni and Stefan 2001; Moore and McKendry 1996); thereby potentially promoting deeper soil frost development, despite the observed and projected increases in atmospheric temperatures in the northern Minnesota and western Great Lakes area (Sinha et al. 2010; Isard et al. 2007). We acknowledge that different climate change scenarios could potentially occur, such as warmer winters with minimal snow accumulation that do not promote deep frost development, or early spring melts interrupted by hard freezes. However, very little research has been conducted on such scenarios. Variability is inherent in climatic processes, which highlights the need for further study.

The differential THg-DOC relationship between 2010 and 2011 (Appendix Figure A-2-1) suggests that there were significant differences in hydrological flow paths between years. The slopes for the relationships between runoff THg and DOC were the same for both spring melt periods; however the relative concentrations differed as evidenced by the difference in intercept (Appendix Figure A-2-1). Surface soils have the highest THg concentrations and organic matter content, thus greater flow through the surface organic horizons may result in not only greater DOC concentrations but also DOC of different quality (Dittman et al. 2010; Demers et al. 2010) than that found in the underlying mineral soil; which may contribute to the observed differences in THg fluxes. Unfortunately, we did not measure DOC quality, but the greater amount of mercury per mass of DOC suggests that differences in DOC structure may affect the amount of mercury complexed for transport or the partitioning of soil-bound mercury into the mobile, DOC-bound phase.

2.4.2 Spatial Differences in Mercury Flux and Upland Flow Paths

The level of replication in this study facilitated the assessment of fine-scale variability of hydrological and biogeochemical processes along an upland, forested hillslope. Watershed-scale studies, which are more common (Mitchell et al. 2008a; Shanley et al. 2002), do not generally provide such spatially replicated process information reporting rather on overall watershed hydrologic export and contaminant loads. Since we had fully continuous data through the 2011
snowmelt period, we have investigated spatial variability during this year only. Considerable spatial variability in water table response to snowmelt inputs, event water contributions, and runoff THg concentrations during the spring melt period existed between the three adjacent hillslope plots. For example, one of the study plots (S7A) had a much larger and more rapid, sustained water table response to snowmelt than our other two plots (Figure 2-3). The S7A plot has the shallowest soil depths to the low permeability confining layer which governs runoff generation from the upland. As a result of the shallower upper soils in S7A, snowmeltwater infiltrating into the S7A soils may have more rapidly fulfilled soil moisture deficits in the upper soil layers and resulted in earlier peak runoff generation, predominantly comprised of event water. Subsequent snowmelt inputs resulted in greater subsurface flow through the more transmissive upper soil layers, consistent with the theory of transmissivity feedback (Bishop et al. 2011; Kendall et al. 1999). The transmissivity feedback mechanism has commonly been observed in glacial till environments, similar to our study site (Kendall et al. 1999; Buttle 1994; Redding and Devito 2010). Support for the transmissivity feedback hypothesis in S7A was also provided by the isotopic composition and biogeochemical variability in subsurface runoff over the course of the melt period. The increasing contribution of pre-event water throughout the duration of the melt further supports this mechanism as pre-event water is known to be mobilized upon input of event water (Kendall et al. 1999) and is flushed rapidly from the system via shallow flowpaths (Lundin 1995). With the progression of snowmelt, the input of event water stimulated an early rise in the perched water table in S7A facilitating mixing with stored pre-event water and resulting in a greater proportion of pre-event water to be contributed to runoff via more transmissive surface pathways. In concert with the increase in pre-event water contributions in S7A, runoff THg concentrations peaked as shallow flowpaths flushed Hg from surface soils, which had the highest THg concentrations. Kendall et al. (1999) observed a similar increase in DOC concentrations as groundwater levels rose through the more transmissive soil layers. The subsequent decrease in runoff THg concentration may be the result of flow receding into deeper soil layers with lower Hg concentrations or may suggest a limit on the amount of Hg available to be flushed from upland soils. In contrast to the runoff THg dynamics observed in S7A, the dilution of runoff by event water accounts for the decreasing THg concentrations in both S7B and S7C. The greater depths to the confining till layer in S7B and S7C may account for the lack of a clearer transmissivity feedback response in these hillslope plots, as event water dominates runoff generation and no dramatic, sustained rise in water table was observed.
Subtle differences in slope morphology among study plots may also contribute to the observed hydrological responses to snowmelt. Recent research has highlighted the significance of watershed topography and hydrologic connectivity between landscape elements in controlling source areas during events, subsurface pathways and runoff generation (Kendall et al. 1999; Detty and McGuire 2010). At the scale of the hillslope, subsurface topography can influence both the spatial and temporal heterogeneity observed in water table and runoff responses (Detty and McGuire 2010; Freer et al. 2002). In addition to having the shallowest surface soil depth to the confining layer, S7A also has a gradual levelling of its slope before reaching the toeslope. In contrast, S7B and S7C are more uniformly sloped from the ridge to the base of the toeslope. It is likely that the morphological depression in the S7A hillslope plot resulted in an area of convergent flow, similar to the geomorphic hollow studied by Kendall et al. (1999). The marked and sustained response of the perched S7A water table to snowmelt inputs may be accounted for by the zone of convergent subsurface flowpaths, allowing for greater hydrologic connectivity with upslope regions and maintaining more saturated conditions after peak runoff at the toeslope. The rise and recession of the S7B and S7C perched water tables in concert with runoff suggests that these planar hillslopes experienced a more transient period of hydrologic connectivity along the hillslope gradient than did S7A. Spatial and temporal variations in hillslope hydrologic connectivity have also previously been shown to be instrumental in controlling the release of nutrients from upland systems (Stieglitz et al. 2003). The sustained connectivity along the hillslope in S7A may give rise to the temporal pattern in runoff THg concentrations which, in association with the transmissivity feedback mechanism, peaked just following peak runoff. However in S7B and S7C runoff THg concentrations steadily decreased throughout the melt period in accordance with dilution by event water inputs, following a transient period in hydrologic connectivity.

2.4.3 Implications

Spring snowmelt accounts for a considerable proportion of the annual flux of THg, MeHg (Mitchell et al. 2008a; Bishop et al. 1995; Babiarz et al. 1998) and other dissolved solutes including ions and DOC (Demers et al. 2010; Stottlemyer and Toczydlowski 1991). Large pulses of the solutes (i.e. Hg, DOC) known to be instrumental in Hg methylation in low-lying wetland environments (Mitchell et al. 2009; Branfireun and Roulet 2002) are delivered during spring snowmelt. This provision of large fluxes of THg as well as labile carbon and other ions
may in fact stimulate “hot moments” (McClain et al. 2003; Mitchell et al. 2008b) in wetland MeHg production. Our study suggests that diminished snowpacks, as may increasingly be observed due to global change (Mohseni and Stefan 2001; Moore and McKendry 1996), will result in significant soil frost development. The subsequent melt of this soil frost layer constitutes a large and delayed upland THg input. It is possible that uplands prone to concrete frost such as glacial till soils with minimal organic horizons or agricultural soils with subsurface fragipan layers will be significantly impacted by climate change-induced soil frost development. Delayed flux of Hg to downstream wetlands and water bodies as a result of soil frost melt may notably affect Hg methylation, Hg bioavailability and subsequent biotic uptake. Because spring snowmelt represents the onset of sensitive developmental stages for aquatic organisms (Bishop et al. 1995), alterations in processes governing the timing and magnitude of contaminant fluxes such as Hg may negatively impact biota due to the potential for enhanced Hg bioavailability.

With respect to the timing of Hg flux to low-lying wetland systems, spatial variability in hillslope flowpaths should be considered. As flowpaths were altered as a function of the magnitude of snowmelt inputs and as a result of the subsequent variability in event vs. pre-event water contributions due to slope morphology, the runoff THg concentrations were either diluted by incoming event waters or enhanced as flowpaths shifted and pre-event water dominated. With less snow accumulation in this region as predicted due to climate change (Mohseni and Stefan 2001), the timing and magnitude of hillslope THg export will likely be a function of hydrologic inputs, but may also be sensitive to changes in hydrologic flowpaths.

The level of spatial variability in hillslope hydrological and biogeochemical processes observed in this study highlights the value of performing research of this nature at a smaller, compartmentalized scale. Given the important contribution of Hg from hillslopes to receiving wetlands during high-flow events, research into the controls on Hg transport and mobility at the hillslope-scale is essential. As the heterogeneity of the landscape often stimulates spatial variation in hydrological and biogeochemical processes, as was observed in this study, elucidating the extent of spatial and temporal variability, and its associated controls, may be significant when investigating the potential impacts on Hg methylation in downstream wetlands.
2.5 References


Chapter 3  
Effect of Precipitation Inputs and Antecedent Soil Moisture on Mercury Mobility in Soil – Laboratory Experiments with an Enriched Isotope Tracer

3

3.1 Introduction

The predominant input of mercury (Hg), a global pollutant, to terrestrial systems is via atmospheric deposition (Fitzgerald et al. 1998; Driscoll et al. 2007). Terrestrial environments act not only as sinks for large amounts of atmospherically-deposited Hg (Grigal 2003; Gabriel and Williamson 2004), but can also be important sources of Hg and its toxic, organic form methylmercury (MeHg) to receiving wetlands and downstream aquatic environments via runoff (Branfireun et al. 1996; Harris et al. 2007). Mercury fluxes from upland systems have been observed to be enhanced as a result of high-flow events such as spring snowmelt at both the hillslope and watershed scales (Haynes and Mitchell 2012; Mitchell et al. 2008a; Demers et al. 2010; Bishop et al. 1995). Given the role of upland systems in conveying atmospherically-deposited Hg to downstream water bodies, and the toxicological threats of Hg to human and wildlife populations (Mergler et al. 2007; Scheuhammer et al. 2007), research investigating the controls on Hg mobility in terrestrial environments is warranted.

It is difficult to discern the relative control of antecedent soil moisture on Hg transport in field studies due to confounding factors such as precipitation inputs and subsequent runoff production, as well as groundwater contributions. At the hillslope scale, Haynes and Mitchell (2012) observed that Hg yield was flow-driven, increasing proportionally with snowmelt runoff with no conclusive influence of antecedent soil moisture in controlling the magnitude of runoff Hg fluxes. Previous research, specifically in wetland environments (i.e. Gustin et al. 2006; Babiarz et al. 1998) has suggested that high-flow event runoff enhanced Hg mobility, particularly following a period of low soil moisture. These contrary results between studies suggest that both the amount of runoff and the antecedent moisture condition of the soil may be potentially instrumental in controlling Hg transport fluxes. However, the relative controls of hydrological
factors such as antecedent soil moisture and the magnitude of precipitation inputs on Hg mobility are not well understood.

Due to the myriad of variables influencing natural environmental systems it is often difficult to accurately identify the hydrologic controls on contaminant mobility, and the extent to which these factors act on various processes. Several studies have therefore performed microcosm-scale laboratory studies in which considerable variability can be controlled for, and hydrological variables can be altered in a controlled manner. Experiments of this nature have commonly been used to investigate the role of different hydrologic factors such as rainfall intensity or soil moisture on nutrient and pesticide leaching and transport in soil (i.e. Sigua et al. 1993; Vendelboe et al. 2011; Phillips 2001; Phillips and Burton 2005). In a recent study Reinmann et al. (2012) simulated soil frost development and spring snowmelt conditions using intact soil columns to determine the potential effects of frost on carbon and nitrogen losses from forested upland soils. Undisturbed soil columns have also been used to study the leaching of heavy metals such as lead, copper and cadmium under different rainfall intensities (Kim et al. 2008). Studies conducted at the scale of a soil column can provide valuable insight into the factors controlling leaching and transport of nutrients and contaminants in soil by facilitating the manipulation of key hydrologic variables in a controlled manner. However, few recent studies have employed the use of intact soil columns to investigate the impact of hydrological factors on Hg mobility, despite numerous advances in Hg analytical techniques including the increasing use of stable isotopes as environmental tracers (Björn et al. 2007).

Isotope tracers have been used more recently to study reaction rates and fluxes of Hg in terrestrial and aquatic environments at a variety of scales from soil columns to watersheds (i.e. Schlüter et al. 1995; Hintelmann et al. 2002; Harris et al. 2007). Given that Hg in the environment is transported in a highly non-conservative manner, the use of stable isotopes as tracers is an invaluable tool; yielding information not only as to the transport of Hg but also speciation under various conditions. The METAALICUS (Mercury Experiment to Assess Atmospheric Loading In Canada and the United States) study applied a stable Hg isotope at the landscape scale in order to investigate the potential impacts of altering atmospheric deposition of Hg and the subsequent downstream effects on bioaccumulation in fish (Harris et al. 2007). A recent study under the METAALICUS project added an enriched stable Hg isotope to a forested subcatchment as a means of assessing the reactivity and mobility dynamics of newly-deposited
Hg as opposed to the large legacy soil pools of Hg at the plot scale (Hintelmann et al. 2002). This field study found that less than 1% of the added Hg appeared in runoff, suggesting that the majority of newly-deposited Hg is incorporated into the bound Hg pool in soil and vegetation. Minimal research has been conducted using Hg isotopes in small-scale laboratory experiments to investigate Hg mobility throughout the soil profile. Semu et al. (1985) used the radioisotope $^{203}\text{Hg}$ in soil column experiments to investigate the potential for groundwater contamination by Hg leaching through the soil, observing that minimal vertical translocation of Hg occurred, with the majority of added Hg being immobilized in the surface soil horizons. Schlüter (1996) similarly used $^{203}\text{Hg}$ to assess the translocation of Hg through soil using small-scale column experiments in order to address the fate of Hg in soils under different rainfall intensities and volumes; concluding that predominantly all of the added $^{203}\text{Hg}$ is sorbed in the upper organic soil horizons and the translocation of Hg is facilitated by complexation with dissolved organic matter. Conducting experiments at this scale can provide detailed process information as a means of deciphering the relative importance of potential factors controlling contaminant mobility and transport at greater scales, such as the hillslope or watershed scale. Previous studies using intact soil cores encased the cores in materials such as polyvinyl chloride (PVC) piping or paraffin wax which may have introduced wall effects or the blocking of soil pores, thereby potentially influencing the reliability of their hydrological conditions and results. In this study, I employed the use of expandable spray foam as a soil-encasing material (similar to the work of Bagarello and Sgroi 2008) to prevent wall effects while manipulating two hydrologic variables (soil moisture and precipitation) in combination. This method had not previously been performed to investigate the hydrologic controls on Hg mobility. I also used smaller amounts of stable Hg isotope per core than previously used by similar studies (i.e. Semu et al. (1985) = 800 μg; Schlüter (1996) = 120 – 1000 μg), which may have yielded more realistic results.

The overall purpose of this study was to determine the relative influences of antecedent soil moisture conditions and the amount of precipitation input on the mobility and transport of Hg throughout the soil profile. This was achieved through the application of an enriched stable Hg isotope to intact, foam-encased soil cores which had been altered for soil moisture (high = field capacity and low = 0.15 volumetric moisture content (VMC) treatment levels), followed by variable treatments of precipitation input (high = 100 mm and low = 50 mm levels) in a full factorial design. The experiment was conducted to simulate real soil moisture and precipitation
input conditions observed in association with the 2010 and 2011 spring snowmelt periods, as outlined in previous research (see Chapter 2: Haynes and Mitchell 2012). A pilot study, the full details of which can be found in Appendix 2, was also conducted in order to ensure the feasibility of using polyurethane foam as a soil-encasing material, similar to the methods of Bagarello and Sgroi (2008), for the purpose of performing Hg leaching experiments while minimizing wall effects.

3.2 Methods

3.2.1 Field Sampling

Thirty intact soil cores were collected with a 15 cm deep soil corer with 10 cm internal diameter in the forested upland of the S7 watershed in the Marcell Experimental Forest (MEF) in north-central Minnesota. These soil cores were collected from outside of the three delineated hillslope plots previously described in Chapter 2 – Haynes and Mitchell (2012), within a 5 m² area in order to minimize variability among cores. Each core was extruded in the field onto a flat wooden board. A 20 cm length of lined cardboard mold was placed around each soil core, following which the cavity between the soil and tube was filled with expandable polyurethane spray foam insulation, similar to the methods of Bagarello and Sgroi (2008). A second board was then placed on top of each filled mold to contain the expansion of the foam. The foam was allowed to cure overnight. Once fully cured, each foam-encased core was removed from the wood and the exposed base of each core was covered with spray foam insulation. The foam-encased soil cores were stored at room temperature after removing the outer cardboard mold until performing the microcosm experiments. The purpose of this elaborate core encasing methodology was to hypothetically remove much of the wall effect, smear and other issues affecting water movement that normally occur in intact core studies conducted in rigid tubes. A separate study was conducted in order to test the feasibility of using foam-encased soil cores for the study of hydrological and biogeochemical processes. This study is detailed in Appendix 2.

3.2.2 Experimental Design

The soil core microcosm experiments were conducted in a full factorial design in which the two controlled variables (antecedent soil moisture and amount of hydrologic input) incorporated both a low and high treatment level with three replicate cores per treatment combination (see Table 3-
1). For precipitation input, the low and high levels were 50 mm and 100 mm, respectively. These values were selected in order to mimic natural snowpack snow water equivalent (SWE) levels observed in the S7 upland of a previous study (Haynes and Mitchell 2012) prior to spring snowmelt in 2009-2010, a year with severely diminished snow accumulation, and 2010-2011 with significantly greater snowpack depth. The low antecedent soil moisture treatment level was designed to simulate the 65 mm of available soil water in the surface 45 cm of soil recorded in fall 2009 prior to the 2010 winter. The high antecedent soil moisture treatment level was represented by field capacity, as a means of presenting a distinct contrast to that of the low moisture treatment. For each antecedent moisture treatment level, a control experiment in which no further input was added to each core following isotope addition was performed to determine the level to which the isotope was transported as a baseline prior to meltwater addition. These experiments were conducted at room temperature, as experimental temperature does not influence tracer mobility and sorption.

Table 3-1 Full factorial design with snowmelt input and antecedent soil moisture as the experimental variables; each with a low and high treatment level.

<table>
<thead>
<tr>
<th>ANTECEDENT SOIL MOISTURE</th>
<th>SNOWMELT INPUT</th>
<th>SNOWMELT INPUT</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>LOW</td>
<td>HIGH</td>
</tr>
<tr>
<td>LOW</td>
<td>L/L</td>
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<td>HIGH</td>
<td>H/L</td>
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For the treatment combinations with low antecedent soil moisture levels, water was slowly added to the top of relatively dry cores. Cores subjected to the high antecedent moisture level were placed in a basin of water overnight to saturate the soil from the base of each core and to evenly distribute the moisture throughout the core. These cores were then briefly drained by gravity the following day, effectively reaching field capacity. Once the moisture manipulations were complete, 90 µg of enriched stable $^{199}$Hg isotope (approximately three times ambient soil Hg load in core volume equivalent) was applied evenly to the top of each core in a 10 mL solution of $^{199}$HgCl (91.09% $^{199}$Hg) via an hydrochloric acid (HCl)-washed Teflon sieve (mean blank $^{199}$Hg concentration between uses = 0.6 ± 0.5 ng L$^{-1}$) (see Figure 3-1a). A 5 mL water rinse of the Teflon sieve followed the isotope addition to ensure complete delivery of the isotope application. Immediately following the tracer addition, each core was secured to a ring stand balanced on top
of a wire mesh above an HCl-washed glass funnel (see Figure 3-1b). Once secured, a rainfall simulator delivered the prescribed level of precipitation input via a metered peristaltic pump. The two levels of snowmelt input (low = 50 mm, high = 100 mm) were comprised of tap water (to minimize ionic imbalances) acidified with trace metal grade nitric acid to simulate the pH of natural snowmelt water (pH~5-6). Outflow from each core was collected in 50 mL intervals in polyethylene terephthalate glycol (PETG) bottles. A sub-sample for dissolved organic carbon (DOC) analysis was transferred into a 20 ml high density polyethylene (HDPE) scintillation vial and refrigerated until analysis. Outflow samples for $^{199}$Hg analysis were preserved with 0.5% trace metal grade HCl, stored in darkness and refrigerated until analysis, which was within approximately one month. Once outflow from the core had ceased, each core was cut vertically into two equal parts and the soil from each half was sampled in five 3 cm depth intervals (0-3, 3-6, 6-9, 9-12, 12-15 cm). Soil samples were immediately frozen and then lyophilized prior to analysis.

a.)
Figure 3-1 Depiction of procedure for experiments: a.) Following alteration of soil moisture, $^{199}$Hg isotope (as $^{199}$HgCl) applied to soil surface with Teflon sieve. b.) Immediately after isotope addition, foam-encased core secured to ring stand above acid-washed glass funnel. Precipitation input delivered to soil surface via peristaltic pump and rainfall simulator.

3.2.3 Hydrologic Viability of Polyurethane Foam as Soil-Encasing Material

For full details, please refer to Appendix 2. Briefly, additional soil cores ($n = 6$) were collected and encased in polyurethane foam as described above from a forested area on the University of Toronto Scarborough campus (with sandy soils similar to those of the study area) in order to test the reliability of the foam as a soil-encasing material for hydrologic purposes. Salt breakthrough flow experiments were conducted on each core in which a high concentration (50 mmol L$^{-1}$) sodium chloride (NaCl) solution was applied to the top of each core followed by a tap water flush delivered via a rainfall simulator. The outflow from each core was collected at regular
intervals and conductivity was measured. A sub-set of these cores was also used to determine if applied Hg is sorbed to the encasing foam by applying non-labeled Hg to the surface of the soil cores. The added Hg was subsequently flushed through the soil with water delivered via the rainfall simulator. Outflow samples were collected in a similar manner to that of the salt breakthrough experiments. Foam samples were collected in intervals of 0-2, 2-4 and 4-6 cm from the top of the foam to the soil surface after outflow had ceased. Each soil core was also sectioned as described above for the factorial experiment.

3.2.4 Analytical Methods

Total Hg (\(^{199}\)Hg and ambient \(^{202}\)Hg) samples were oxidized by the addition of concentrated bromine monochloride (BrCl) and concentrations were determined following stannous chloride reduction using a Tekran model 2600 total mercury analyzer hyphenated to an Agilent 7700 Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). Recovery of an ambient total mercury spike was 99 ± 8% (n = 20), replication of duplicates was 6.4 ± 5.5% (n = 20), and the detection limit, calculated as three standard deviations of matrix water blanks, was 0.05 ng L\(^{-1}\) (n = 72). Replication of \(^{199}\)Hg duplicates was 18.3 ± 21.8% (n = 20) and the \(^{199}\)Hg detection limit, also three standard deviations of matrix water blanks, was 0.06 ng L\(^{-1}\) (n = 44). Dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC-VCSH Total Organic Carbon analyzer with an in-line total nitrogen unit (TNM-1) and a high sensitivity combustion catalyst (720°C). Absorbance of the outflow samples was measured at both 254 and 365 nm using matched quartz cuvettes on a Spectronic Genesys 5 UV-VIS Spectrophotometer. I used these two absorbance values to calculate the ratio A254/A365, which has previously been used to assess the quality of organic matter as this ratio is negatively related to the increasing molecular weight of dissolved organic substances (Berggren et al. 2007). Specific UV absorbance (SUVA) at 254 nm was also calculated to describe the quality of organic matter in outflow samples by dividing the absorbance at 254 nm by the DOC concentration while taking into account the cuvette path length. The freeze-dried soil samples were nitric acid-digested using a microwave digestor and diluted prior to THg analysis as for waters. Recovery of standard reference material of known ambient Hg concentration, digested and analyzed with the soil samples, was 97 ± 4% (n = 10). Loss on ignition (LOI, 550°C for 4 hours) was also performed on the soil samples to determine organic matter content.
3.2.5 Statistical Analyses

A two-way (factorial) analysis of variance (ANOVA) was performed to determine any significant differences between hydrologic treatment combinations on both $^{199}$Hg and $^{202}$Hg outflow loads as well as the proportion of $^{199}$Hg in relation to $^{202}$Hg. A one-way ANOVA (with post-hoc analysis using the Tukey adjustment) was conducted on the total $^{199}$Hg and $^{202}$Hg outflow loads to assess significant differences between treatment combinations. Correlation matrices were created in order to assess any significant relationships between the measured outflow variables, as well as between soil $^{199}$Hg concentrations and organic matter. The data for replicate Core #1 for the LH treatment and Core #2 for the LL treatment, as well as Core #3 for the HL treatment were omitted from these correlations due to the presence of outliers. Both of the removed LH and LL cores had exceedingly high organic matter content in the surface layers due to the presence of decomposing woody debris, while the HL core did not drain sufficiently possibly due to compaction. A one-way ANOVA with post-hoc Tukey test was also performed in order to determine any significant differences in soil $^{199}$Hg concentrations among treatments (including controls) for each of the five depths. Data were tested for normality (Shapiro-Wilk $W$ test) and heteroscedasticity and were successfully log-transformed ($^{199}$Hg outflow load, $^{202}$Hg outflow load, $^{199}$Hg/$^{202}$Hg outflow load ratios, $^{199}$Hg outflow concentrations, soil $^{199}$Hg concentrations and organic matter) or inverse-transformed (outflow concentrations of $^{202}$Hg, DOC and SUVA measurements) when parametric assumptions were not met. All statistical tests were performed using SAS Version 9.2. Statistical significance of comparisons was set at $\alpha < 0.05$.

3.3 Results

3.3.1 Viability of Polyurethane Foam as Soil-Encasing Material

For full details, please refer to Appendix 2. Briefly, the results of the salt breakthrough experiments illustrated a distinct rising limb, peak and recession limb in conductivity (Appendix Figure A-2-1). The smooth progression of conductivity in this curve supports the viability of using polyurethane foam as soil-encasing material for hydrological applications, with no evidence of hydrologic wall effects, which is similar to the work previously described by Bagarello and Sgroi (2008). The slight initial decrease in conductivity for Core #1 (Appendix
Figure A-2-1a) is due to the initial flushing of solutes from the soil that resulted from the wetting up of the soil core prior to the addition and intrusion of the salt solution.

The foam encasing methodology is suitable for soil leaching experiments using an added Hg tracer. Less than 0.5% of the added Hg was sorbed to the surrounding foam above the soil surface, which was in direct contact with the ponded Hg solution. By depth, the foam directly above (0-2 cm) the soil surface had the highest Hg concentrations decreasing in the foam depths 2-4 and 4-6 cm above the soil surface (Appendix Figure A-2-2). This suggests that Hg sorption by the foam is directly related to the time of exposure of the Hg solution to the encasing material. This contact between the foam and the applied Hg tracer was avoided for the main experiment through the use of the Teflon sieve isotope delivery vessel.

3.3.2 $^{199}$Hg and $^{202}$Hg Outflow Loads by Treatment Combinations

Overall, less than 0.5% (range of 0.03 – 0.38%) of the added 90 µg of the $^{199}$Hg tracer was present in the total outflow collected across all treatments combinations. The highest total $^{199}$Hg outflow load occurred in the low soil moisture – high precipitation input (LH) experiments with an average total load of 341 ng (Figure 3-2). The LH outflow $^{199}$Hg load was significantly higher than that of any of the other treatment combinations. The second highest $^{199}$Hg outflow load was observed in the low moisture – low input (LL) experiments. There was not a statistically significant difference between the tracer outflow loads resulting from the two high soil moisture treatments (HH and HL). Both of these treatments were significantly less in outflow $^{199}$Hg than those resulting from the low moisture treatments ($p < 0.0001$); regardless of the level of precipitation input (Figure 3-2). Similarly, the outflow $^{199}$Hg loads resulting from the high input treatments exceeded the low input treatments at both levels of soil moisture ($p = 0.001$). The total $^{202}$Hg loads followed the same general pattern by treatment as the $^{199}$Hg loads (Figure 3-2). However, no significant differences in outflow $^{202}$Hg were present among any of the treatment combinations ($p = 0.07$).
Figure 3-2 $^{199}$Hg and $^{202}$Hg outflow loads (ng) for all hydrologic treatment combinations. Error bars represent standard deviation and lower-case letters represent significant differences for $^{199}$Hg, while upper-case letters represent significant differences for $^{202}$Hg.

The factorial ANOVA results suggest that both antecedent soil moisture ($p < 0.0001$) and the volume of precipitation input ($p = 0.001$) were significant controls on $^{199}$Hg transport and mobility through soil. The lack of interaction ($p = 0.16$) between these hydrologic variables suggests that these controls on $^{199}$Hg mobility acted independent of one another in an additive manner. Neither antecedent soil moisture ($p = 0.06$) nor the volume of precipitation input ($p = 0.18$) exerted a strong influence on the mobility of ambient $^{202}$Hg mobility.

The time course plots in Figure 3-3 present the data for a single core in each of the experimental combinations. An average could not be adequately depicted due to slight differences in the timing of the outflow for each core, thereby staggering the data. As a result, one replicate from each experiment was selected to be representative as the overall pattern in outflow was similar between replicates despite differences in the timing. The time course plots of the $^{199}$Hg and $^{202}$Hg concentrations for each of the treatment combinations (Figure 3-3) illustrated a slight delay in the $^{199}$Hg peak for the high soil moisture treatments, with $^{199}$Hg concentrations peaking with the second to fourth sample with a mean maximum concentration of $106 \pm 27$ ng L$^{-1}$. However, for the low moisture treatments, $^{199}$Hg were highest in the first outflow sample (mean maximum
199Hg concentration = 939 ± 664 ng L⁻¹) decreasing with subsequent samples regardless of the input treatment. Tracer isotope concentrations in outflow were notably higher for the low moisture treatments.

The first 50 mL sample was collected after 10 ± 3 minutes on average from the high antecedent moisture experiments and after approximately 17 ± 13 minutes for the low moisture experiments. The runoff rate, or rate of outflow, was relatively consistent throughout the course of the experiments with high soil moisture. For the low moisture soils, the runoff rate was typically highest for the first sample with a slight recession in rate for the second sample, which was generally maintained over the course of the experiment (Figure 3-3). Overall, of the 393 mL of added precipitation for the low input treatments, on average 380 mL for the LL experiments and 404 mL for HL was recovered in outflow. For the high input treatments, approximately 745 mL for the LH treatment and 787 mL for HH of the 785 mL added as precipitation were collected. The low input experiments were completed over approximately 1.5 hours per core, while the high input experiments took approximately 3 hours to complete.

![Figure 3-3](image)

**Figure 3-3** Time course plots of ¹⁹⁹Hg and ²⁰²Hg concentrations as well as runoff rates for each of the four treatment combinations. One replicate, representative core was selected from each treatment.
3.3.3 Proportion of Old vs. New Hg in Outflow

Average ratios of $^{199}$Hg to $^{202}$Hg outflow loads for each of the treatment combinations were calculated to assess the proportion of ‘new’ ($^{199}$Hg) vs. ‘old’ ($^{202}$Hg) in outflow. All ratios were greater than one with the mean $^{199}$Hg/$^{202}$Hg ratios for both the HH and HL treatments approximately 4 ± 1 and 4 ± 0.2, respectively, while the ratio for LL was approximately 9 ± 4 and the LH treatment had the highest ratio at nearly 16 ± 6. The $^{199}$Hg/$^{202}$Hg ratio for the low moisture – high input (LH) treatment was significantly greater than both of the high moisture treatments (HL and HH), however not statistically different from the LL ratio.

Factorial analysis of the $^{199}$Hg/$^{202}$Hg ratio across treatment combinations revealed soil moisture to be a significant control on ‘new’ Hg mobility ($p = 0.002$). The volume of precipitation input exerted no significant influence ($p = 0.26$) on the proportion of ‘new’ Hg present in the outflow runoff.

3.3.4 New and Old Hg Proportions by Hydrologic Factor

Under high soil moisture conditions the amount of both new and old Hg flushed from the soil was nearly doubled (~1.7 – 1.8X), however not significantly for new Hg ($p = 0.06$) when the amount of input was doubled (Figure 3-4a). With low moisture conditions nearly three times (~2.7X, $p < 0.01$) as much new Hg was mobilized in runoff with two times as much precipitation input, whereas the amount of liberated old Hg remained nearly unchanged (~1.3X increase, $p = 0.35$).

With the high level of precipitation input, significantly more new Hg (~6X, $p < 0.01$) and approximately 1.5 times as much old Hg ($p = 0.02$) were flushed from the low moisture soil as compared to the soil with high antecedent moisture (Figure 3-4b). Low soil moisture soil cores subjected to low levels of precipitation input mobilized significantly more (~4X, $p < 0.001$) new Hg and approximately twice as much old Hg ($p = 0.25$) as compared to those under high antecedent moisture conditions.
Figure 3-4 Average $^{199}$Hg outflow loads grouped according to a.) antecedent soil moisture for both input levels and b.) precipitation input for both moisture levels.

3.3.5 Relationships between Outflow Solutes – $^{199}$Hg, $^{202}$Hg, DOC

A significant correlation ($p < 0.0001$) existed between the $^{199}$Hg and $^{202}$Hg outflow concentrations with all samples included from all replicates within all experimental combinations (Figure 3-5i). However, only the low soil moisture treatments, LL and LH, displayed significant correlations ($p < 0.01$ and 0.0001, respectively) between the $^{199}$Hg and $^{202}$Hg outflow concentrations (Figure 3-5ii). Neither of the high moisture treatments exhibited significant relationships between these two variables.

A similar trend was observed for the relationship between $^{199}$Hg and DOC concentrations in outflow. A significant correlation ($p < 0.0001$) existed between these variables when considering all outflow samples across all treatments (Figure 3-5iii), as well as for each of the low moisture treatments individually ($p < 0.01$ for both LH and LL) (Figure 3-5iv). No significant relationship existed however between $^{199}$Hg and DOC for either of the high soil moisture treatments. For all treatments (overall (Figure 3-5v) and individually (Figure 3-5vi)) a significant correlation was observed between the outflow concentrations of ambient $^{202}$Hg and DOC.
Figure 3-5 Scatterplots of correlations between outflow variables: i) $^{199}$Hg concentrations vs. $^{202}$Hg concentrations including all treatments, ii) $^{199}$ vs. $^{202}$ with treatments designated, iii) $^{199}$Hg concentrations vs. DOC concentrations including all treatments, iv) $^{199}$ vs. DOC with treatments designated, v) $^{202}$Hg concentrations vs. DOC concentrations including all treatments, and vi) $^{202}$ vs. DOC with treatments designated. *denote significant correlations.

Significant positive relationships ($p < 0.0001$) between the ratio of A254/A365 and both the outflow $^{202}$Hg concentrations and $^{199}$Hg concentrations were observed when considering all treatment combinations. However, only the high moisture – high input (HH) treatment exhibited a significant correlation individually. A significant correlation between $^{199}$Hg and A254/A365 was also observed for the high moisture – low input treatment, but not for $^{202}$Hg and A254/A365.

3.3.6 Soil Depth Profiles

The majority of the added $^{199}$Hg was sorbed in the surface 0-3 cm sections of soil across all experimental combinations. A similar trend in $^{199}$Hg concentrations was observed across all treatments (Figure 3-6). There were no significant differences in $^{199}$Hg concentrations when comparing the same soil depths (0-3, 3-6, 6-9, 9-12 and 12-15 cm) across all treatments including controls. The soil $^{199}$Hg concentrations were significantly correlated ($p < 0.0001$) with the percentage of organic matter in the soil, as determined by loss on ignition.
Figure 3-6 Soil depth profiles of $^{199}\text{Hg}$ concentrations (ng g$^{-1}$) for all treatment combinations including moisture controls: i) Low Moisture Control, ii) High Moisture Control, iii) Low Moisture Low Input, iv) High Moisture Low Input, v) Low Moisture High Input, and vi) High Moisture High Input.

3.4 Discussion

3.4.1 Hydrological Controls on Soil Mercury Mobility

The results of this study suggest that both antecedent soil moisture and the volume of precipitation input were instrumental in controlling new, contemporary Hg mobility in soil. As there was no observed interaction between these factors, it can be concluded that these hydrologic variables act independently of one another, in an additive manner. However, old, legacy Hg was not significantly influenced by either soil moisture or precipitation input. The mobility of contemporary Hg through soil and its presence in runoff was greatly enhanced by the volume of precipitation input applied to the soil due to greater flushing. Field studies investigating hydrologic transport of Hg at the watershed and hillslope scales have similarly observed increased Hg fluxes as a result of high-flow rain events and spring snowmelt (i.e.

Haynes and Mitchell (2012) observed that runoff Hg fluxes appeared to be flow-driven, as both runoff and Hg flux increased by the same factor when compared between two spring melts of very different snowpack SWE (2010 SWE = 48 mm, 2011 SWE = 98 mm). This field research suggested that Hg transport is predominantly flow-controlled, with no evident influence of soil moisture on runoff Hg fluxes. However, the present study exhibited a significant soil moisture effect, with new $^{199}$Hg mobility being greatly enhanced from low moisture soils; regardless of the amount of precipitation. The observed lack of influence of antecedent moisture and volume of precipitation input on ambient $^{202}$Hg mobility in this study may account for the results of Haynes and Mitchell (2012), given the relatively minimal wet Hg deposition via melting snow (mean snowpack THg load in 2011 = 6 µg m$^{-3}$) as compared to the large soil legacy Hg pool, and the potential dominance of legacy Hg in the observed snowmelt runoff. The lack of congruence between the present study and the field study of Haynes and Mitchell (2012) with regard to the influence of antecedent soil moisture may also be due to the disparate nature of the moisture levels selected for the laboratory study. The moisture treatments chosen for the current study were intended to present a distinct comparison in soil moisture, not observed in the field study, in order to identify the potential of antecedent soil moisture in controlling Hg mobility.

The observed increase in $^{199}$Hg mobility from low moisture soils may be due to the formation of preferential flowpaths throughout the soil profile, as suggested by the early timing of the $^{199}$Hg peak. Such preferential transport pathways formed due to the maximal hydrologic connectivity between pore spaces throughout the entire soil column may provide less opportunity for deposited Hg to be sorbed to the organic and mineral surfaces in the soil. Instead, more contemporary Hg was rapidly flushed from the drier soil via preferential flowpaths, potentially due to cracking in the dry soil. A similar flushing of contaminants from dry soils was observed by Kazemi et al. (2008), with the transport of the herbicides atrazine and alachlor enhanced due to preferential flow when applied on initially dry claypan soils. Conversely, under high soil moisture conditions, I observed less new, contemporary Hg in runoff as compared to the low soil moisture treatments. Upon wetting the soil cores to the point of field capacity, multiple pathways in the soil are created through which the added Hg can be flushed. These abundant, non-direct potential flowpaths in high moisture soils may provide greater opportunity for the added Hg to
encounter and to be sorbed to the organic and mineral soil surfaces, thereby decreasing the amount and delaying the peak of $^{199}\text{Hg}$ observed in runoff.

The observed timing of contemporary and legacy Hg release may also be the result of piston flow. As precipitation was applied to the high moisture soils (at field capacity), the water collected in the early outflow samples may have been already present in the soil, which upon outflow resulted in the transport of legacy Hg. This is supported as outflow $^{202}\text{Hg}$ concentrations were highest initially and subsequently decreased upon further input (Figure 3-3). As the wetting front progressed through the high moisture cores, new $^{199}\text{Hg}$ became increasingly exported in outflow and the time to peak $^{199}\text{Hg}$ concentrations was delayed. A similar piston flow effect was not observed for the low moisture soils as only minimal moisture was present in the soil prior to subsequent precipitation inputs. Together, antecedent soil moisture and precipitation, whether it is rain or snowmelt, may be instrumental in controlling the provision of newly-deposited Hg to downstream wetlands which are known to be sites of Hg methylation (Mitchell et al. 2008b).

Recent research under the METAALICUS project suggested that newly-deposited Hg was more readily volatilized and methylated than old, legacy Hg as well as initially more mobile following deposition (Hintelmann et al. 2002). In the present study, the proportion of $^{199}\text{Hg}$ as compared to ambient $^{202}\text{Hg}$ present in outflow runoff was significantly affected by soil moisture, with more new $^{199}\text{Hg}$ being flushed from low moisture soils. However, the volume of precipitation input had no significant effect on the proportion of new vs. old Hg in runoff. As new Hg is more readily mobilized from upland soils under dry conditions, MeHg production in receiving wetlands may be impacted by larger influxes of new, reactive Hg from adjoining uplands. The provision of large amounts of reactive Hg during high-flow events, in association with DOC and other ions known to be instrumental in MeHg production (Mitchell et al. 2009; Branfireun and Roulet 2002), may stimulate the production of “hot spots” of methylation in low-lying wetlands (McClain et al. 2003); particularly at the upland-peatland interface (Mitchell et al. 2009). This could have deleterious consequences in the magnitude of Hg and MeHg fluxes from watersheds and the subsequent bioavailability of Hg for uptake by aquatic organisms.
3.4.2 Dissolved Organic Carbon and Mercury Transport

Numerous field studies have observed Hg transport associated with that of DOC (i.e. Bishop et al. 1995; Dittman et al. 2010; Schuster et al. 2008). The tendency of Hg to complex with organic matter (Driscoll et al. 1995; Schuster 1991) may act in facilitating the preferential mobilization of Hg during high-flow events. The outflow concentrations of old $^{202}$Hg were significantly correlated to those of DOC for all four experimental combinations; both individually and collectively. Old, legacy Hg, which had been in the soil for a longer duration than newly-deposited Hg, may have equilibrated with the soil organic matter over this period. Through the formation of complexes with DOC, the mobility of legacy Hg may be mediated; regardless of the hydrologic conditions of the soil. The formation of DOC-Hg complexes may account for the similarity in the $^{202}$Hg-DOC relationships, as well as the overall legacy Hg outflow loads across the four experimental combinations.

Complexation with DOC in soil may also be important when considering the mobility of newly-deposited, contemporary Hg. Hintelmann et al. (2002) proposed that the initial mobile fraction of newly-deposited Hg, flushed from the system during rain events, was bound to DOC. Similar laboratory studies have also found that the mobility of added Hg is facilitated by the complexation of Hg with dissolved organic matter (Schlüter 1996). In the present study, I observed the outflow concentrations of new $^{199}$Hg to be significantly correlated to those of DOC and $^{202}$Hg, particularly under low moisture conditions (Figure 3-5). These observations suggest that contemporary Hg is being mobilized from drier soils in a similar manner to that of legacy Hg; in that new Hg may be mobilized as a result of complex formation with DOC. The relationship between contemporary Hg and DOC in outflow runoff may also account for the greater proportion of $^{199}$Hg being mobilized under low moisture conditions as more new Hg may be partitioned into the mobile, DOC-bound phase. However, there was no significant relationship between $^{199}$Hg and either of $^{202}$Hg or DOC for the soils under high moisture conditions. Both high soil moisture experiments (HL and HH) exhibited significant positive correlations between the $^{199}$Hg concentrations and the absorbance ratios (A254/A365); from which it can be inferred that the contemporary Hg was potentially associated with DOC of lower molecular weight. It can therefore be proposed that the new Hg being flushed from wet soils may be in a different form than that from dry soils. The contemporary Hg mobilized from low
moisture soil may be found in the colloidal phase bound to DOC, while that from high moisture soils may instead be in the true dissolved fraction.

3.4.3 Distribution of $^{199}$Hg in Soil Column

Overall, across all treatments less than 0.5% of the added Hg tracer was observed in runoff with the majority being retained in the surface 3 cm section of soil. This result is similar to that of the field study by Hintelmann et al. (2002), in which less than 1% of the added tracer appeared in runoff over the course of one season. A significant portion of the newly-deposited Hg was rapidly immobilized by equilibrating with the native pool in both soil and vegetation (Hintelmann et al. 2002). Similarly, in the present study, the vast majority of the $^{199}$Hg tracer was immobilized in the surface, organic horizons of the soil regardless of both the soil moisture and precipitation conditions. The $^{199}$Hg concentrations decreased rapidly with subsequent depths within the soil with only negligible $^{199}$Hg reaching the lower 9 cm of soil across all treatments. The pattern of $^{199}$Hg distribution throughout the soil profiles may be attributed to sorption to soil organic matter, as these variables were significantly correlated. Similar soil column studies using an applied Hg tracer concluded that the majority of the added Hg was sorbed near the soil surface with no considerable vertical translocation through the soil (Schlüter 1996; Semu et al. 1985). It has been proposed that a large proportion of newly-deposited Hg is not immediately mobile, rather being initially bound to soil and vegetation (Hintelmann et al. 2002). However, upon repeated flushing with multiple precipitation events following deposition, it is possible that the mobility of this new Hg pool may be altered as the hydrologic conditions of the soil change. A similar field investigation by Munthe et al. (2001) using an applied $^{199}$Hg tracer at the plot scale observed the isotope ratio of 202/199 stabilized after a period of approximately three months. During an initial rainstorm following the application of the tracer, Hintelmann et al. (2002) observed a significant decrease in runoff tracer concentrations, which was not observed for native Hg, and was sustained throughout the rest of the season. Future research could focus on the potential effects of repeated precipitation events of varying magnitudes over soils of different antecedent moisture in a controlled manner in order to assess the mobility of an applied Hg tracer to such changes in soil hydrologic conditions.
3.4.4 Summary and Implications

Both the antecedent moisture condition of the soil and the volume of precipitation input are important controls on new Hg mobility in upland systems, with soil moisture exerting considerable influence on the proportion of new, contemporary Hg mobilized. Mercury mobility is enhanced as a result of high-flow events and from soils of low moisture. Preferential transport flowpaths may be critical in facilitating Hg fluxes when soils are dry, in addition to complex formation with solutes such as DOC. Despite significant differences in Hg mobility according to hydrologic treatments, the majority of added Hg was sorbed to the mineral and organic particles in the surface 3 cm of soil with less than 0.5% of $^{199}\text{Hg}$ appearing in runoff.

The dependence of Hg transport on hydrologic factors may be important when considering the potential impacts of climate change on hydrological processes. Further research on Hg mobility and transport in upland systems is warranted given the potential manifestations of alterations in upland Hg export on downstream processes such as Hg methylation in wetlands (Mitchell et al. 2009) and subsequent biotic uptake of MeHg; particularly during times of greatest Hg export such as spring snowmelt (Mitchell et al. 2008a; Bishop et al. 1995; Lee et al. 2000).

Performing studies of this nature at the scale of a soil column is an invaluable tool given the level of control and manipulation of key hydrological variables afforded by such a technique. Studies involving the use of undisturbed, intact soil cores also provide a more realistic and natural medium for investigation as opposed to an artificial or repacked soil. Given the level of heterogeneity at the landscape scale, investigations such as this study at smaller scales facilitate the determination of the relative controls of hydrological processes on contaminant transport in the environment.

3.5 References


Chapter 4
Synthesis and Potential Future Research

4

4.1 Synthesis

Inter-annual variability in hydrology including winter snowpack depth, volume of runoff and antecedent soil moisture during the spring snowmelt period significantly influenced the magnitude and timing of hillslope Hg fluxes, as evidenced by the results of these two complementary studies. The microcosm laboratory study illustrated the important contributions of antecedent soil moisture and the volume of precipitation input in controlling the vertical transport of newly-deposited Hg throughout the soil profile. As only approximately 0.5% of contemporary Hg was observed in runoff following vertical transport, it can be suggested that only a small fraction of newly-deposited Hg will be transported to the confining silt layer in the glacial till soil which is instrumental in subsurface runoff generation in the watershed studied in this research (Figure 2-1a). The primary finding of the field-based inter-annual snowmelt comparison was that overall hillslope Hg fluxes were flow-driven, increasing proportionally with runoff and with no apparent influence of antecedent soil moisture on Hg transport. It may be that hillslope Hg fluxes were dominated by legacy Hg being flushed from the soil, given the observed lack of soil moisture influence on old Hg mobility and the minimal vertical translocation of new Hg through the horizons of the soil columns regardless of the hydrologic treatments. Similar relationships between DOC and Hg runoff concentrations in the field study, and DOC and legacy Hg concentrations across all of the microcosm experiments may support the predominance of legacy Hg in hillslope runoff. It may also be suggested that Hg mobility may in part be facilitated by complexation with organic matter and subsequent flushing in a mobile, DOC-bound phase. Further spatial variability in Hg dynamics across the hillslope as well as temporal variability throughout the melt periods may be accounted for by variations in water table positions, flowpaths and transmissivity feedback responses due to hillslope morphology.

As global climate change is likely to diminish precipitation, particularly snow accumulation, in the Midwestern states including the study area of north-central Minnesota (Mohseni and Stefan...
2001), soil moisture may be similarly impacted. With global warming a greater proportion of new, contemporary Hg may be flushed from upland environments via preferential flowpaths during high-flow events such as spring snowmelt as soils become increasingly dry. It has been suggested that new Hg is more reactive in the environment than legacy Hg in terms of methylation (Hintelmann et al. 2002). Greater fluxes of new Hg to downstream, receiving wetlands and water bodies may result in enhanced MeHg production and greater Hg availability for biotic uptake. This research also observed the melting of soil frost to be important in transporting approximately 30% of the overall hillslope Hg load later into the spring season following the winter with less snow accumulation. When considering that lower antecedent soil moisture may coincide with low snow years as was observed in this research, the melting of soil frost may in fact contribute a large flux of new, reactive Hg to receiving wetlands later into the spring. Warmer spring temperatures, known to increase methylation rates (Gilmour et al. 1992) in association with a large influx of reactive Hg may enhance MeHg production in low-lying wetland environments. Therefore, this may ultimately have deleterious effects on aquatic organisms through enhanced bioavailability of Hg.

4.2 Potential Future Research

Although this research has contributed to knowledge gaps pertaining to the hydrologic controls on Hg mobility and transport in upland environments during spring snowmelt, much remains to be understood with regard to the potential impacts of global climate change on such hydrological and Hg biogeochemical processes. As no two spring snowmelt periods are often the same, this line of research would benefit from similar hydrological and Hg biogeochemical monitoring over multiple spring melts; most likely with differing antecedent soil moisture, snowpack depth and timing, and runoff conditions. Further elucidation of the mobility of new Hg in the landscape could be achieved with the application of an enriched stable Hg isotope at either the plot- or hillslope-scale. This would allow the applied tracer to be distinguished analytically from ambient Hg, and therefore the behavior of newly-deposited Hg in the environment could be better understood.

The microcosm experiments presented here highlight the value of performing studies at smaller scales in order to be able to manipulate key variables to assess their relative influence on
contaminant transport. Expandable polyurethane spray foam insulation was found to be an effective soil-encasing material for the purpose of conducting both flow-through and contaminant leaching studies. As some field studies using an applied Hg tracer at the ecosystem scale suggest that Hg mobility in soil decreases over time (Hintelmann et al. 2002; Munthe et al. 2001), a soil column experiment could be performed similar to the factorial experiment conducted in this research. However, repeated precipitation events could be applied to the soil and a sequential destructive sampling method would allow for the determination of tracer transport in the soil. Such studies would aid in modeling the potential impacts of global climate change on Hg transport in forested upland environments during spring snowmelt. Given the important linkages between mercury in runoff and downstream bioaccumulation, accounting for the hydrological controls on Hg mobility provides insight into potential hydroclimatic-biogeochemical feedbacks that could affect the timing and magnitude of Hg inputs into aquatic systems.

4.3 References


Figure A-1-1 Relationship between filtered THg and DOC runoff concentrations during 2010 and 2011 melt periods.
Figure A-1-2 Depth profile of soil THg concentrations and organic matter content (represented as % loss on ignition (LOI)). THg concentrations and %LOI at each depth (excluding surface silt) represent an average of nine soil cores collected in each of the S7A, S7B and S7C plots from the hillslope ridge, midslope and toeslope regions (surface silt is average of three cores, one core collected the midslope region of each plot).
Appendix 2: Using Expandable Polyurethane Foam as an Encasing Material for Intact Soil Cores: Hydrological and Biogeochemical Applications

A2.1 Introduction

Studies investigating hydrological and biogeochemical processes in the environment are often conducted at large field scales such as the hillslope (i.e. Haynes and Mitchell 2012) or watershed scale (i.e. Mitchell et al. 2008; Shanley et al. 2002). However, in order to determine the controlling factors governing a certain process, physical variables must be controlled for; which can only be achieved at a laboratory micro- or mesocosm scale. Small-scale laboratory studies have been performed to investigate the controls on soil hydrologic flowpaths (McIntosh et al. 1999) as well as nutrient and contaminant transport through soils (Kim et al. 2008; Schlüter et al. 1995; Sigua et al. 1993; Reinmann et al. 2012); often employing the use of both hydrologic and chemical tracers. Studies of this nature typically use large intact soil cores extracted from the field and encased in a variety of materials including PVC pipe (Reinmann et al. 2012), epoxy cement (Sigua et al. 1993) and paraffin wax (McIntosh et al. 1999). However, when performing hydrological experiments the encasing material can interfere with hydrological results via the production of zones of preferential flow at the interface between the encasing material and soil known as wall effects. Encasing materials such as resin (Vanderborght et al. 2002) and paraffin wax can also intrude into the larger pores along the side walls of the soil cores altering hydrologic flowpaths within the cores. The purpose of this study was to investigate the feasibility of using expandable polyurethane spray foam insulation as an encasing material for intact soil cores, similar to the work of Bagarello and Sgroi (2008), for both hydrological applications (with salt breakthrough experiments) and mercury (Hg) biogeochemical tracer applications (with applied mercury).

A2.2 Methods

A2.2.1 Field Sampling

Six intact soil cores were collected using a 10 cm diameter, 15 cm deep steel soil corer from a mixed conifer/hardwood forest on the University of Toronto Scarborough campus. The soils in
the area are predominately classified as luvisols and are similar to the sandy soils found in the Marcell Experimental Forest (MEF). Each core was extruded in the field onto a flat wooden board following which a 14 cm diameter lined cardboard mold was placed around the soil core. The cavity between the soil and the mold was filled with expandable polyurethane spray foam insulation (MONO® brand). A second board was placed on top of the mold to contain the foam expansion and ensure that the entire cavity was filled by encouraging downward expansion. Once cured the foam-encased soil core was removed from the wood and the mold was removed from the cured foam. Additional foam was applied to cover the base of each core. The foam-encased soil cores were stored at room temperature until use.

A2.2.2 Salt Breakthrough Experiments

Two of the soil cores collected were used to conduct salt breakthrough experiments. As the soils were initially dry, each core was pre-moistened with deionized water via a rainfall simulator prior to salt addition. Once each core was wetted and outflow (effluent flow) was observed, a 100 mL 50 mmol L⁻¹ sodium chloride (NaCl) solution (of known conductivity) was ponded on the soil surface. The depth of the pond was monitored to assess the infiltration rate. Once the salt solution was fully infiltrated, more deionized water was applied to the soil surface via the rainfall simulator. Outflow was collected in 30 mL intervals and the conductivity of each outflow sample was measured.

A2.2.3 Mercury Addition Experiments

Two soil cores were wetted with approximately 400 mL of tap water (to minimize ionic imbalances) via a rainfall simulator until outflow was observed and collected in volumes of 50 mL. Approximately 400 mL of a 200 ppb total mercury (THg) solution, acidified with nitric acid to simulate slightly acidic rainwater (pH ≈ 5.5 – 6.0), was ponded on the top of each soil core. The falling head of the ponded solution was monitored at regular intervals to determine the rate of infiltration. Outflow samples were collected in 50 mL intervals in polyethylene terephthalate glycol (PETG) bottles, acidified with 0.5% trace metal grade hydrochloric acid and stored in darkness at 4°C until analysis. Once outflow had stopped, each core was cut vertically in two equal halves and sectioned into five 3 cm depths on both halves (for in-core replication). These soil samples were subsequently frozen until analysis. Foam samples were also collected in three 2 cm depths (0-2, 2-4, and 4-6 cm) from the area above each soil core, which was in contact with
the ponded THg solution. A third soil core was similarly sectioned for both soil and foam samples without any Hg addition in order to determine ambient Hg concentrations in both the soil and foam.

A2.2.4 Analytical Methods

Outflow water samples were analyzed by cold vapour atomic fluorescence spectroscopy (CVAFS) following USEPA Method 1631 (2002) using a Tekran Model 2600 automated total mercury analyzer, following dilution with deionized water. Replication of duplicate samples was 1.6 ± 1.6% (n = 2), recovery of a total mercury spike was 96 ± 6% (n = 5) and the detection limit, calculated as three standard deviations of matrix water blanks, was 0.34 ng L⁻¹ (n = 10). Soil samples were lyophilized and nitric acid-digested using a microwave digestor, following which they were diluted and analyzed as for water samples. Foam samples were similarly nitric acid-digested and also analyzed for THg as above. Additional cores of known volume were sectioned by depth and oven-dried at 105°C to determine soil bulk density.

A2.3 Results

A2.3.1 Conductivity Breakthrough Curves (BTCs)

Breakthrough curves of the relative outflow conductivities, normalized for the initial conductivity of the input solution (C₀), were plotted for each core (Figure A-2-1). The BTCs were consistent with the addition of a salt pulse through each soil column resulting in peak conductivity (approximately 30-50% of the input solution’s conductivity), following which the subsequent flushing with additional water input accounts for the recession in conductivity. The small initial decrease in relative conductivity for the first core (Figure A-2-1a) may be the result of an initial flush of ions present in the soil prior to the intrusion of the salt pulse. The shape of the BTCs provides support for the lack of preferential flow at the soil-foam boundary, as evidenced by the smooth progression of outflow conductivity. The lack of wall effects introduced by the polyurethane foam suggests that this material is suitable for encasing intact, undisturbed soil cores for the purpose of conducting hydrologic and solute transport laboratory-scale studies.
A2.3.2 Validation for Mercury Biogeochemical Tracer Applications

Total Hg analysis of the foam in contact with the ponded Hg solution on top of the soil core revealed that less than 0.5% of the added 79-80 µg THg was sorbed by the surrounding foam in both cores (Table A-2-1).

Table A-2-1 Percentages of added Hg in both outflow and foam for replicate Cores #1 and #2, as well as mean Hg load in outflow runoff prior to Hg addition.

<table>
<thead>
<tr>
<th></th>
<th>% Added Hg in Outflow</th>
<th>% Added Hg in Foam</th>
<th>Avg Hg load (ng) per interval in outflow prior to Hg addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core #1</td>
<td>0.42</td>
<td>0.48</td>
<td>2.02</td>
</tr>
<tr>
<td>Core #2</td>
<td>0.55</td>
<td>0.31</td>
<td>2.43</td>
</tr>
</tbody>
</table>

The surface 4-6 cm section of foam had the lowest THg concentration, while the 2 cm foam section above the soil surface had the highest THg concentration (Figure A-2-2). It can therefore be concluded that increased exposure of the foam to the Hg solution resulted in greater Hg sorption.
Figure A-2-2 Concentrations of added Hg (ng g\(^{-1}\)) in 2 cm sections of foam above the soil surface. Error bars represent standard deviations.

The outflow samples (six to seven following Hg addition) together accounted for 0.42-0.55% of the added THg, thereby suggesting that the majority of the added THg was sorbed by the soil. The time course plots of the outflow THg loads for both cores (Figure A-2-3) exhibited a similar pattern to those of the salt breakthrough curves, with effluent Hg loads gradually increasing over time until peak loads of 98.8-112.7 ng were reached after which recession of the Hg load began. The average initial THg load present in the outflow (per 50 mL interval) prior to its addition was 2.0 and 2.4 ng, respectively for the two cores (Table A-2-1).

Figure A-2-3 Time course plots of THg in 50 mL outflow intervals for both replicate Hg addition cores.
The minimal sorption (<0.5%) of added Hg by the encasing foam validates the use of polyurethane foam for studies investigating mercury transport through soils by means of an applied Hg tracer. Application of the Hg tracer to the top of the soil core via an acid-washed Teflon delivery system would ensure complete addition of a known Hg load as well as minimizing contact of the Hg solution with the surrounding foam.

A2.4 Summary

Polyurethane spray foam insulation is a preferred material for use in encasing intact soil cores for the purpose of investigating both hydrological and mercury biogeochemical transport processes in small-scale laboratory experiments. No zones of preferential flow were observed between the soil-foam boundary indicating the absence of wall effects introduced as a result of the encasing foam. Unlike other encasing materials such as paraffin wax and resin, expandable polyurethane foam does not intrude into the soil pores along the side wall of the core, thereby preventing the alteration of flow paths within the core. For studies employing the use of a stable mercury isotope, minimal adsorption of mercury by the surrounding foam was observed, increasing only as the duration of exposure of the Hg solution to the foam increased.

The use of microcosm-scale soil studies to investigate hydrological controls on mercury transport and mobility would benefit from the use of polyurethane foam as an encasing material. Such studies would allow for the controlling of certain hydrologic variables such as antecedent soil moisture in order to be able to constrain the controls governing biogeochemical processes such as mercury transport.

A2.5 References


