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Mercury Cycling in Peatland Watersheds

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CONTENTS

Introduction

Mercury (Hg) is of great environmental concern due to its transformation into the toxic methylmercury (MeHg) form that bioaccumulates within the food chain and causes health concerns for both humans and wildlife (U.S. Environmental Protection Agency 2002). Mercury can affect neurological development in fetuses and young children. In adults, exposure to Hg can lead to the deterioration of the nervous system, decreased sensory abilities, and a lack of muscle control (Ratcliffe et al. 1996). Methylmercury in fish poses a severe health risk for fish-eating animals such as otter, mink, bald eagle, kingfisher, osprey, and the common loon (Walcek et al. 2003), and even for fish themselves (Sandheinrich and Miller 2006).

Studies in Minnesota, Wisconsin, and Sweden indicate that 18%–25% of the atmospheric Hg deposited on terrestrial basins ultimately reaches associated lakes; most of the deposited Hg is initially retained by the terrestrial landscape (Swain et al. 1992; Lee et al. 2000). In most terrestrial landscapes in northern latitudes, peatlands play a key role in determining the fate of Hg (St. Louis et al. 1994; Driscoll et al. 1995; Kolka et al. 1999a). Peatlands are sources of dissolved and particulate organic carbon (OC) that have sulfur (S) groups that bind Hg (Skyllberg et al. 2000), leading to transport Hg to surface waters (Mierle and Ingram 1991; Kolka et al. 1999a, 2001). Peatlands are also areas of high-MeHg production and contribute to MeHg loading of downstream aquatic ecosystems (Branfireun and Roulet 2002; Branfireun et al. 2005). These studies demonstrate the importance of determining the loadings of Hg from terrestrial components of watersheds to aquatic systems. Additional research is needed to better understand the fate and transport of Hg in terrestrial environments (Wiener et al. 2006).

In the mid-1990s, studies at the USDA Forest Service's Marcell Experimental Forest (MEF) began to measure the transport of Hg through the terrestrial environment (Kolka et al. 1999a,b, 2001). These studies assessed the mechanisms responsible for the deposition of Hg (including that in litterfall) and the uptake of Hg by trees (Fleck et al. 1999). Because of the organic soil peatlands present in the watershed and the documented role of OC as a carrier of hydrologically transported Hg (Aastrup et al. 1991; Johansson and Iverfeldt 1994; Driscoll et al. 1995; Ravichandran 2004), total Hg (THg) relationships with dissolved organic carbon (DOC) and particulate organic carbon (POC) (OC $> 0.45\,\mu m$) were assessed. More recently, scientists have investigated in-lake cycling of Hg, the impact of sulfate deposition on the production of MeHg, the influence of the snowmelt period on annual Hg transport, and the presence of MeHg "hotspots" in peatland landscapes. In this chapter, we review the progression of Hg research conducted on the MEF and its significance with respect to the larger scientific questions related to environmental Hg.

Total Mercury Mass Balance in Upland–Peatland Watersheds

The first major effort to study Hg at the MEF was aimed at understanding both the inputs and outputs of THg and the influence of DOC and POC on Hg transport at the watershed scale. See Chapter 2 for description of study watersheds. A conceptual model was developed of the major hydrologic pathways that transport Hg (or other constituents) through the terrestrial system (Figure 11.1). Studies of each component in the mass balance made it possible to determine the ecosystem level THg inputs and outputs and the sinks and sources within upland–peatland watersheds at the MEF (Grigal et al. 2000; Kolka et al. 2001).

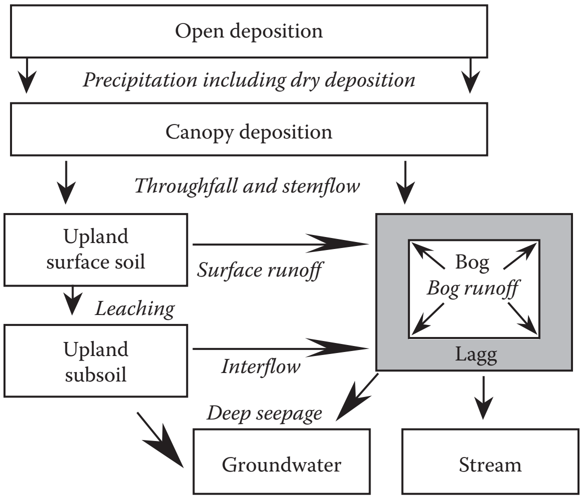

FIGURE 11.1
Conceptual hydrological model used to assess the transport of Hg through upland/peatland forested watersheds. (Modified from Kolka, R.K. et al., *Soil Sci. Soc. Am. J.*, 65, 897, 2001.)

Mercury in Atmospheric Deposition

The majority of atmospheric THg deposition in a typical-forested watershed occurs on terrestrial landscapes due to (1) the greater proportion of land relative to surface water and (2) the higher rate of dry deposition associated with tree canopies (Kolka et al. 1999b). As a result, a study was initiated to measure the atmospheric deposition of THg and DOC in throughfall and stemflow in both the upland and peatland portions of the S2 watershed (Kolka et al. 1999b). Throughfall collectors were installed across a range of canopy densities and canopy types, while stemflow collectors were installed across a range of tree species and diameters. Although a minor hydrologic flux (~2%), THg in stemflow accounted for 8% of the open wet-only deposition for THg (Kolka et al. 1999b). Deposition of THg in throughfall is a function of both canopy cover and canopy type (Figure 11.2), providing strong evidence that dry deposition is an important contributor to the total Hg load to terrestrial environments. Deposition of DOC in throughfall is related only to canopy cover, indicating that DOC fluxes appear to be a function of the leaching of the vegetative material and that dry deposition apparently exerts little influence on DOC concentrations (Figure 11.3). Because of greater apparent leaf and branch surface area (Oliver and Larson 1996), conifer canopies collect greater dry deposition of Hg than deciduous canopies, leading to greater Hg accumulation and deposition to the forest floor (Figure 11.2). Significantly, more THg (2×) and DOC (7×) deposition occurs under a forest canopy than

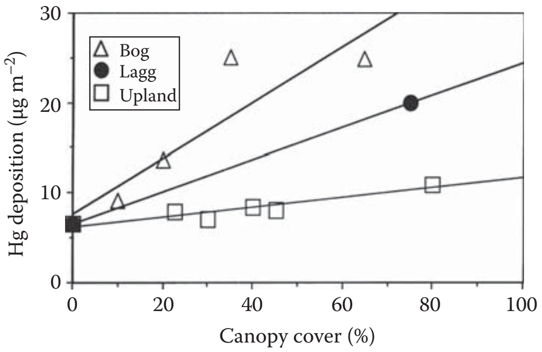

FIGURE 11.2
Relationship between canopy cover and annual Hg deposition for groups of collectors based on canopy type and density in the watershed (slope = 0.31 for bog, $r^2 = 0.82$; slope = 0.06 for upland, $r^2 = 0.87$; slope = 0.18 for lagg). The bog canopy consists of conifers (mainly black spruce), the lagg canopy is a combination of conifer and deciduous species, and the upland canopy is primarily deciduous (mainly aspen and paper birch). (From Kolka, R.K. et al., *Water Air Soil Pollut.*, 113(1), 273, 1999b.)

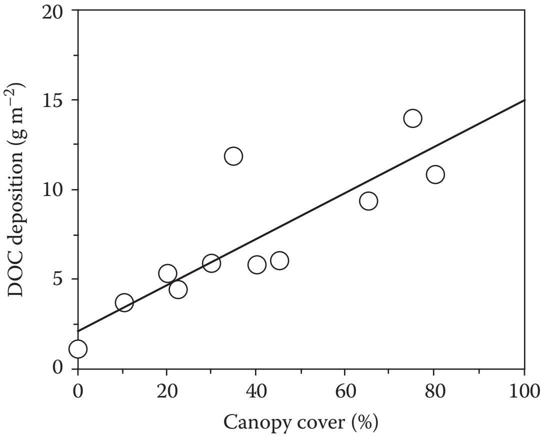

FIGURE 11.3
Relationship between canopy cover and annual DOC deposition in throughfall for all collectors, DOC = 2.3 + 0.13 (Canopy%), $R^2 = 0.72$. (From Kolka, R.K. et al., *Water Air Soil Pollut.*, 113(1), 273, 1999b.)

in a nearby opening (Figure 11.4). Throughfall deposition of THg at MEF (130 mg ha^{-1} year^{-1}) is similar to that measured at Walker Branch, TN (140 mg ha^{-1} year^{-1}; Lindberg 1996), which is considerably higher than that measured at the relatively remote Experimental Lakes Area (ELA) in Ontario, Canada (80 mg ha^{-1} year^{-1}; St. Louis et al. 2001), but less than that from areas in northern Sweden (150 mg ha^{-1} year^{-1}) and considerably less than the more polluted southern Sweden (240 mg ha^{-1} year^{-1}; Lee et al. 2000). From this work, it is

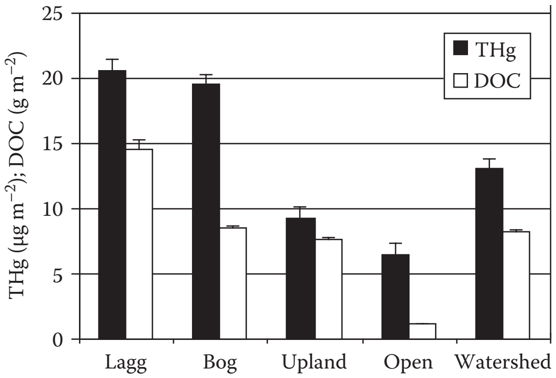

FIGURE 11.4
Annual throughfall + stemflow deposition of THg and DOC at the MEF. (Modified from Kolka, R.K. et al., *Water Air Soil Pollut.*, 113(1), 273, 1999b.)

clear that any attempt to quantify Hg inputs to forested systems must consider both wet and dry deposition as well as the influence of forest types on deposition (Kolka et al. 1999b).

Mercury in Litterfall and Tree Uptake

Inputs of THg from litterfall are of similar magnitude to inputs from atmospheric deposition (Grigal et al. 2000). In a study on the MEF, litterfall was collected in the fall of 1995 (August 8–November 15) within the two main forest types (upland aspen/birch, and peatland black spruce) in the S2 watershed. Although leaf litterfall in the upland (38.3 ng g^{-1} ± 1 standard error of 1.4 ng g^{-1}) had significantly higher Hg concentrations than the leaf (needle) litterfall in the peatland (29.7 ng g^{-1} ± 2.4), differences in the mass of deposition and the Hg concentrations of nonleaf material in litterfall led to similar areal deposition of THg among uplands (12.5 μg m^{-2} ± 0.85) and peatlands (11.7 μg m^{-2} ± 1.36; Grigal et al. 2000). Litterfall THg deposition at MEF (123 mg ha^{-1} $year^{-1}$) is similar to that at ELA in Ontario (120 mg ha^{-1} $year^{-1}$; St. Louis et al. 2001), but much less than that from areas in northern Sweden (180 mg ha^{-1} $year^{-1}$) and southern Sweden (230 mg ha^{-1} $year^{-1}$; Lee et al. 2000) and Walker Branch in Tennessee (300 ha^{-1} $year^{-1}$; Lindberg 1996).

An assessment of tree uptake of Hg found no relationships between Hg in soil or forest floor and that in woody tissue or foliar concentrations (Fleck et al. 1999). The lack of relationships between the plant tissues and the soil indicated that Hg, in plant tissue, is derived directly from the atmosphere and not the soil.

Hydrologic Pathways of Mercury

To better understand the importance of various hydrological pathways by which both THg and OC (including DOC and POC) are transported, measurements were made in each component of the hydrologic cycle in a typical upland/bog watershed (i.e., the S2 watershed) and modeled with the Peatland Hydrologic Impact Model (Guertin et al. 1987; Kolka et al. 2001; Chapter 15; Figure 11.1). In addition to measuring concentrations of THg and OC, water flow from one hydrologic component to the next was estimated. Because water flows were dominated by the peatland (bog in this case), most of the THg and DOC fluxes originated from the bog (Figure 11.5). Fluxes from the upland are important in the spring during snowmelt and in the fall following the cessation of evapotranspiration. Upland and bog waters both flow to the lagg (Figure 11.1), which ultimately coalesces into the stream that exits the watershed (Chapter 7). THg fluxes to the lagg are approximately twice those that exit the S2 watershed, while DOC fluxes are comparable to those of the stream (Figure 11.6). These results suggest that the bulk of the THg losses from the lagg can be attributed to

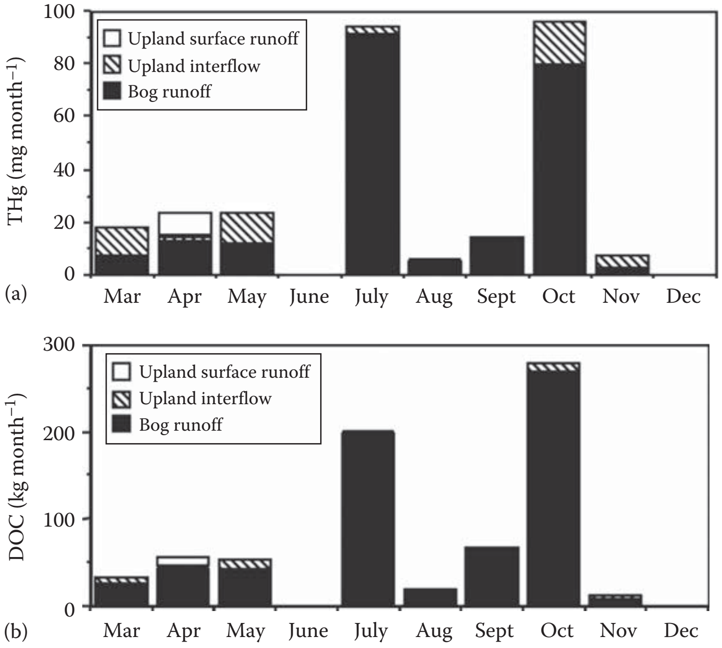

FIGURE 11.5
Hydrologic fluxes of (a) THg and (b) DOC from upland (surface runoff and interflow) and bog components of the S2 watershed at the MEF in 1995. Annual precipitation in 1995 was 890 mm and the long-term mean was 775 mm. (Modified from Kolka, R.K. et al., *Soil Sci. Soc. Am. J.*, 65, 897, 2001.)

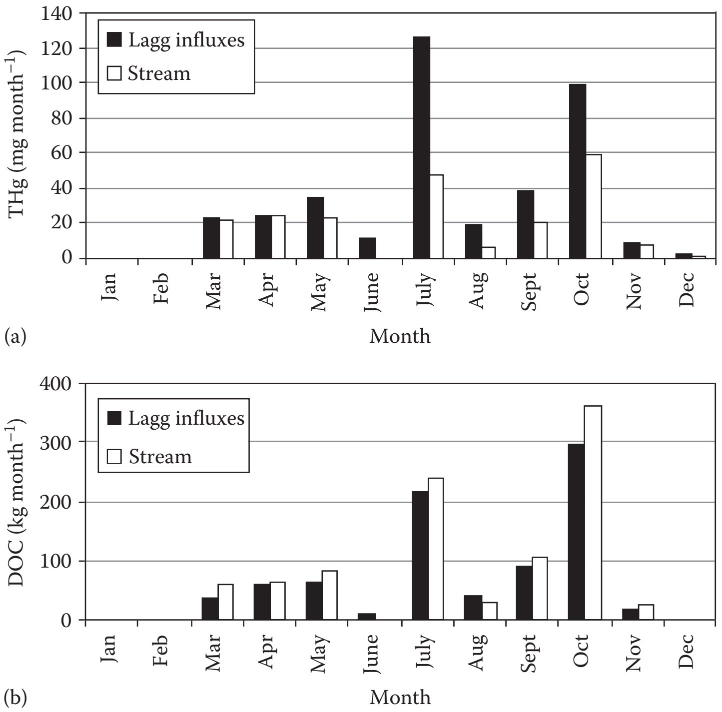

FIGURE 11.6
Hydrologic fluxes of (a) THg and (b) DOC to the lagg compared to the fluxes in the stream exiting the S2 watershed in 1995. (Modified from Kolka, R.K. et al., *Soil Sci. Soc. Am. J.*, 65, 897, 2001.)

either accumulation in lagg soils or volatilization between our sampling points and the stream outlet. The soils in the lagg are organic and likely have a high ability to complex THg. If we assume that soil accumulation was the only loss of Hg, the lagg soil would accumulate about 35 μg THg m^{-2} year^{-1}, within the range of that reported for bog soils (Benoit et al. 1994). If volatilization is considered, the only Hg loss, the mean rate from the lagg is 6.8 ng m^{-2} h^{-1}, which is near the upper end of the range reported by Kim et al. (1995) but lower than the geometric mean of 11 ng m^{-2} h^{-1} reported in a review of studies by Grigal (2002). Both processes (soil accumulation and volatilization) likely contribute to THg losses in the lagg.

Stream Fluxes of Mercury

To better understand watershed fluxes of THg and OC, outlet waters were sampled from other experimental watersheds at the MEF to compare with results from the S2 watershed. Streams exiting the other MEF watersheds

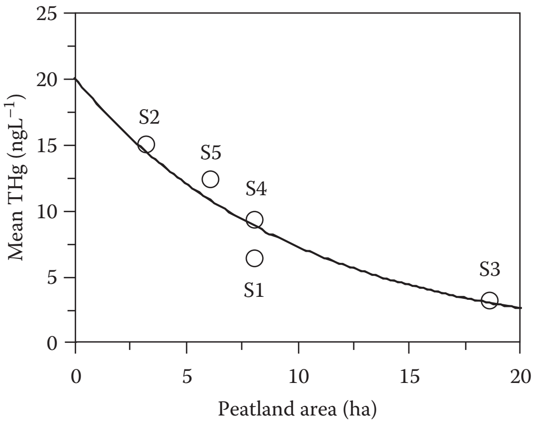

FIGURE 11.7
Relationship between mean flow-weighted THg concentration and peatland area for watersheds at the MEF, $HgT = 20.0 \times 10^{(-0.044 \times \text{peatland area})}$, $r^2 = 0.94$, $p = 0.01$. (Modified from Kolka, R.K. et al., *J. Environ. Qual.*, 28(3), 766, 1999a.)

originate from a range of peatland types including oligotrophic bogs similar to S2 to a mesotrophic fen (S3). Watershed flow-weighted concentrations of Hg are related to the area of peatland (Figure 11.7), demonstrating that larger peatlands had lower THg concentrations. As peatland size increased, there was an increase in overall flow from the watershed and a greater connection with regional groundwater sources that are lower in THg concentration than runoff from perched water tables such as found in the S2 bog. Regression models relating THg flux to landscape variables for five watersheds indicated that upland and peatland areas combined explained approximately 89% of the variation in THg stream flux from MEF watersheds (Kolka et al. 1999a). Through further regression analysis, it was estimated that 67%–98% of stream THg is derived from peatlands while 2%–33% is derived from upland sources. Similar regressions indicated that 92%–99% of DOC and 49%–96% of POC originate from the peatland component of the watersheds (Kolka et al. 1999a). Streamflow yields of THg range from 0.70 to 2.82 μg m^{-2} $year^{-1}$ at MEF, which brackets the mean yield of 1.7 μg m^{-2} $year^{-1}$ reported by Grigal (2002) and is similar to comparable wetland ecosystems at ELA in Ontario (range for export from wetland watersheds = 0.7–2.1 μg m^{-2} $year^{-1}$; St. Louis et al. 1996), Finland (1.0–1.8 μg m^{-2} $year^{-1}$; Porvari and Verta 2003), and Sweden (1.0–3.4 μg m^{-2} $year^{-1}$; Lee et al. 2000).

An important feature of watershed export at MEF is that short-term events can play a large role in annual fluxes. Earlier studies on the hydrologic fluxes of THg (Kolka et al. 1999a) did not isolate the importance of event-based stream fluxes; however, more recent studies indicate that 26%–39% of the annual THg flux (depending on the watershed) and 22%–23% of the annual MeHg flux occur during the short snowmelt period (~12 days; Mitchell et al. 2008a; Table 11.1). Both upland and peatland fluxes were important during snowmelt periods, whereas peatland fluxes of both THg and MeHg dominated watershed fluxes later in the growing season. Studies in northern

TABLE 11.1

Upland, Peatland, and Total Watershed Fluxes of THg and MeHg during the Studied Snowmelt Period Compared to Total Watershed Annual Fluxes

	S2 Watershed		S6 Watershed	
	THg Flux (mg)	MeHg Flux (mg)	THg Flux (mg)	MeHg Flux (mg)
Snowmelt upland runoff flux	24	0.14	8.5	0.054
Snowmelt peatland runoff flux	35	0.52	13	1.0
Total snowmelt watershed flux	59	0.66	21	1.1
2005 annual	230	3.0	54	4.7

Source: Mitchell, C.P.J. et al., Biogeochemistry, 90, 225, 2008a.

Sweden in comparable wetland watersheds also showed that snowmelt is an important time for Hg transport, accounting for 34% of THg and 12% of annual MeHg fluxes (Bishop et al. 1995). From the event-based data, it is apparent that the temporal distribution and frequency of sampling can substantially increase our understanding of the sources of Hg from terrestrial to aquatic ecosystems.

Total Mercury Relationships with Organic Carbon

For waters sampled at MEF in the 1990s, we analyzed unfiltered samples, primarily because clean filtering techniques were still untested. Although many studies have identified a strong relationship between Hg species and DOC concentrations (e.g., Driscoll et al. 1995), it was found that POC (>0.45 µm) explained more of the variation in unfiltered THg at the MEF (Kolka et al. 1999a, 2001). Relationships between THg and POC among terrestrial waters in S2 included an r^2 of 0.52 for upland surface runoff, r^2 of 0.65 for upland interflow (subsurface runoff), r^2 of 0.84 for bog runoff, and r^2 of 0.49–0.76 for streamflow (Kolka et al. 1999a). Few relationships are evident between THg and DOC as correlation coefficients did not exceed 0.40. If our THg samples had been filtered, correlations with DOC may have been higher. When all stream data were merged, POC was clearly an important carrier of THg (Figure 11.8). Other studies have found a close relationship between particulate THg and POC (e.g., Shanley et al. 2002) and showed that POC is an important carrier of Hg during high-flow events and in larger, more disturbed watersheds (Grigal 2002). A new technique using specific ultraviolet absorbance at 254 nm to determine the amount and type of DOC is successfully predicting THg in streams (Dittman et al. 2009).

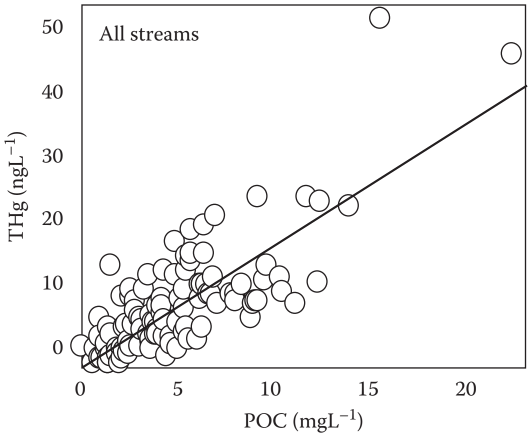

FIGURE 11.8
Relationship between THg and POC concentrations for watersheds (S1–S5) at the MEF, THg = 0.99 + 1.86 (POC), $r^2 = 0.60$, $p = 0.0001$. (Modified from Kolka, R.K. et al., *J. Environ. Qual.*, 28(3), 766, 1999a.)

Total Mercury Mass Balance

Mass balance studies at the MEF indicate that the terrestrial portion of a watershed is a sink for THg (Grigal et al. 2000; Kolka et al. 2001). The mass balance for the S2 watershed in 1995 showed that the forest canopy captured significant amounts of atmospheric THg as measured in throughfall and stemflow, while the watershed soils are a major sink. The overall THg accumulation is about 4.3 μg THg m^{-2} $year^{-1}$, if volatilization back to the atmosphere is not considered (Kolka et al. 2001). When litterfall inputs are included, the S2 watershed becomes a larger sink for THg, approximately 22.5 μg m^{-2} $year^{-1}$ (Table 11.2; Grigal et al. 2000). St. Louis et al. (1996) found that similar watersheds in Ontario are sinks for THg and range from 1.9 to 3.4 μg THg m^{-2} $year^{-1}$(excluding litterfall inputs), similar in magnitude to the S2 watershed, excluding litterfall. Research in Acadia National Park in Maine indicated that watersheds are a sink for about 9.0 μg THg m^{-2} $year^{-1}$ not including litterfall inputs (Nelson et al. 2007). Presumably, the Acadia watersheds represent a larger sink for THg than those in central North America, because atmospheric Hg inputs are higher on the East Coast. Similarly, a

TABLE 11.2

Total Hg Mass Balance for the S2 Watershed at the MEF

Component	Entire Watershed (μg m^{-2} $Year^{-1}$)
Throughfall and stemflow inputs	13.0 (0.35)
Litter input	12.3 (0.73)
Hydrologic output	2.81 (0.28)
Input–output	22.5 (0.8)

Note: Standard errors in parentheses; Grigal et al. (2000).

watershed in the Adirondack Mountains is a sink of THg of 12.9 μg THg m^{-2} $year^{-1}$, when litterfall is not included (Selvendiran et al. 2009). When litterfall is included as an additional input to the mass balance, watershed sinks range as high as 44 μg THg m^{-2} $year^{-1}$ in Sweden (Lee et al. 2000) and as low as 6.9 μg THg m^{-2} $year^{-1}$ in Norway (Larssen et al. 2008). Although the work at the MEF and from other regions indicates that watershed soils are important long-term storage compartments for Hg (Grigal 2003), the mass of Hg transported from these small watersheds remains an important contributor to downstream ecosystems.

Lake Cycling of Mercury

Beginning in 2000, a series of studies were conducted investigating Hg dynamics of a small seepage lake with no defined inlets or outlets (Spring Lake) on the MEF. These studies found that sediment accumulation rates were 21.4 μg THg m^{-2} $year^{-1}$ and 0.20 μg MeHg m^{-2} $year^{-1}$, respectively, from 1990 to 2000 (Hines et al. 2004). The rate of lake sediment THg accumulation is nearly identical to the calculated watershed sink rate of 22 μg m^{-2} $year^{-1}$ at the MEF (Grigal et al. 2000), indicating that watershed soils and lake sediment accumulate THg at similar rates in these ecosystems. Accumulation rates of both THg and MeHg are higher at the sediment surface than at depth (Figure 11.9), approximately 4 and 10 times preindustrial rates for THg and MeHg, respectively (Hines et al. 2004). Patterns of accumulation rates are

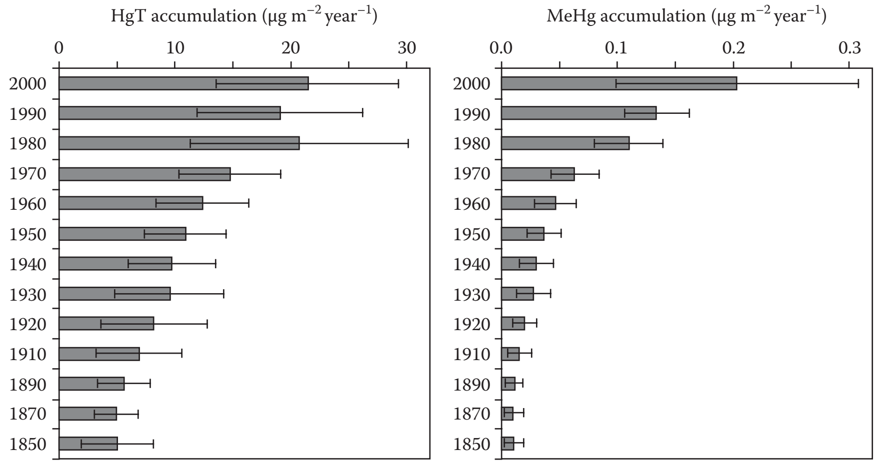

FIGURE 11.9
THg (HgT) and MeHg accumulation rates since preindustrial times in Spring Lake on the MEF. (From Hines, N.A. et al., *Environ. Sci. Technol.*, 38(24), 6610, 2004. With permission.)

similar for lakes in northeastern Minnesota (Engstrom et al. 2007). However, it is important to note that the apparent increase in MeHg accumulation near the surface may be a consequence of the demethylation of MeHg following deposition and burial. Sediment pore water concentrations (5 and 15 cm depth) of MeHg were low in the spring and peaked in late summer and roughly correlated with peaks in sulfate reduction (Hines et al. 2004). Because of temporal gradients in pore water concentrations, there was an apparent diffusive flux of MeHg from sediment to lake water. However, there was also advective transport of MeHg to deeper sediment within the sediment column that occurred in late summer and early fall leading the lake sediment to be an overall sink of MeHg (Hines et al. 2004).

Additional research on Spring Lake assessed the role of photochemistry on Hg dynamics. Evasional losses of Hg^0 during midsummer were 5–6 pmol m^{-2} h^{-1} as a result of photoreduction, which tended to be twice the rate of photooxidation (Hines and Brezonik 2004a,b) and similar to rates observed at the ELA in Ontario (Sellers et al. 2001). For Spring Lake, wet deposition was the largest THg input, while outputs from the lake were dominated by burial in the sediment (67% of outputs) and evasion of Hg^0 from the lake surface (26% of outputs; Hines and Brezonik 2007). For MeHg, wet deposition only accounted for 9% of inputs while runoff and sediment pore water contributions only accounted for an additional 7% of inputs, indicating that the bulk of the MeHg production was occurring in the water column of the lake (Hines and Brezonik 2007). Photolysis of MeHg was the dominant sink (output), removing approximately three times the entire lake mass of MeHg annually. During open water season, residence times of THg and MeHg in the lake were 61 and 48 days, respectively, while the residence time of Hg^0 in the photic zone was on the order of hours (Hines and Brezonik 2007). Finally, sampling of seston, zooplankton, and fish indicated that seston accounted for the highest mass of Hg in lake biota, much higher (10–100×) than the higher trophic levels. The bioconcentration factor of Hg (dry mass concentration in biota: concentration in water) for northern pike, the top fish predator, was 1.2×10^7 (Hines and Brezonik 2007), which is in the range for northern pike in lakes on nearby Isle Royale National Park in Lake Superior (range, 7.4×10^6–2.3×10^7) (Gorski et al. 2003).

Factors Affecting Methylmercury Production

Following the characterization of the pools and fluxes of THg in upland–peatland watersheds at the MEF, much of the research has focused on the factors that lead to methylation of Hg. Previous laboratory experiments (Gilmour et al. 1992) and small-scale field mesocosm research (Branfireun et al. 1999, 2001) established a link between sulfate inputs and Hg methylation in S-limited sediments. In 2001, an ecosystem-scale manipulative experiment began in the S6 wetland to determine the effects of sulfate deposition on both peatland and watershed-level MeHg production. The wetland was divided into an upgradient control and a downgradient experimental treatment. Samples were collected along transects that extended north to south across the treated and untreated halves of the peatland. From 2001 to 2006, four times the annual ambient sulfate deposition was applied via a sprinkler system to the experimental treatment. Shallow sampling wells were located throughout the lagg and bog zones of S6 both in the treated and untreated halves of the peatland. Sampling occurred 1 day prior to each addition and periodically following the addition (e.g., 1, 3, 7, and 14 days after sulfate application). In 2006, the experimental treatment was further divided, and sulfate addition was halted to the upgradient one-third of the treatment to simulate a recovery phase after excess sulfate deposition. Sulfate applications ceased after 2008.

Relationships developed via the paired watershed approach between MeHg fluxes from the S6 treatment watershed and the S7 reference watershed allowed comparisons at the watershed scale. The first year of enhanced sulfate deposition resulted in a 2.4-time increase in MeHg flux from the watershed (Figure 11.10; Jeremiason et al. 2006). Following the spring sulfate addition, peat pore water concentrations of MeHg in the experimental treatment peaked at three times those in the control half of the S6 peatland (Jeremiason et al. 2006) and remained elevated relative to the control

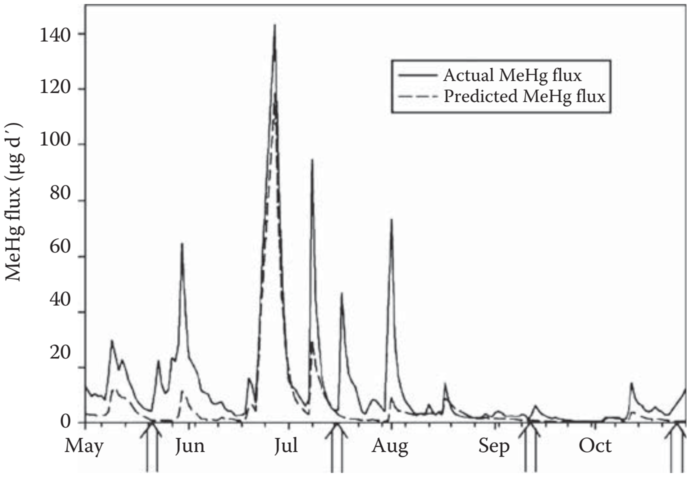

FIGURE 11.10
Actual and predicted fluxes of MeHg from the S6 watershed for 2002. The predicted flux is that which would have occurred in the absence of sulfate addition and is based on a correlation of 2001 MeHg fluxes from S6 with those from a nearby reference wetland (S7). Arrows indicate dates of experimental sulfate applications. The pretreatment r^2 was 0.77. (From Jeremiason, J.D. et al., *Environ. Sci. Technol.*, 40(12), 3800, 2006. With permission)

throughout the remainder of the year. It is clear from the data that increased sulfate deposition led to increased in situ methylation and increased MeHg flux from the watershed. Other researchers have demonstrated that sulfate-reducing bacteria (SRB) can methylate Hg and that the methylation process is stimulated in the presence of sulfate (Gilmour et al. 1998; Benoit et al. 1999). The current working hypothesis for the S6 sulfate-addition study is that SRB populations in this S-limited system increase MeHg production when they are stimulated by a dose of sulfate; they continue to methylate Hg at an elevated rate so long as sulfate is available. The focus of the sulfate addition work changed in 2005 with an assessment of chronic effects of sulfate addition, wetland recovery processes, and the overarching influence of climatic and hydrologic processes on Hg and S cycling (Coleman-Wasik 2008). Preliminary results indicate that a wetland affected by elevated sulfate deposition may take years to return to baseline conditions and that climatic and hydrologic variability affects the recovery process.

Following the early results from the sulfate addition experiment, investigations into the controls on MeHg production continued. More recent mesocosm studies have assessed the influence of both labile carbon (C) and sulfate additions on MeHg production. Mesocosms were installed in the Bog Lake peatland site, and a factorial experiment assessed the influence of three levels of sulfate and two levels of five C sources including glucose, acetate, lactate, deciduous litter leachate, and conifer litter leachate on MeHg production (Mitchell et al. 2008b). There was little response to the labile C additions, indicating that C was not limiting methylating bacterial metabolism in the peatland. Responses to 4 and 10 times annual sulfate deposition were strong but not different among the two levels, indicating that sulfate was limiting, but also that the fourfold treatment was adequate to alleviate the microbial limitation. However, when labile C and sulfate were combined, there was generally an increase in MeHg compared to the response of sulfate alone, indicating a potential for colimitation of organic C and sulfate (Figure 11.11). The C additions with the 10-fold sulfate addition did not increase MeHg production above those with fourfold sulfate plus C additions, indicating that sulfate limitations were alleviated, even with additional labile C, at fourfold annual deposition (Mitchell et al. 2008b).

Additional studies have assessed important methylation locations or hotspots in these upland–peatland landscapes. To identify location of hotspots, porewater was collected from the S2 and S6 watersheds at the MEF as well as two watersheds at the ELA in Ontario in landscape positions just upslope from the upland peatland margin and then into the lagg and bog zones of the peatland (Mitchell et al. 2008c, 2009). Methylation hotspots were based on the distribution of MeHg:THg with a location designated as a methylation hotspot when 22% of the THg was present as MeHg (i.e., the 90th percentile of all measurements). Results indicated that the lagg zone (Figure 11.1), both spatially and temporally, was the location that typically met the hotspot criterion (Figure 11.12; Mitchell et al. 2008c). It appears that methylation is

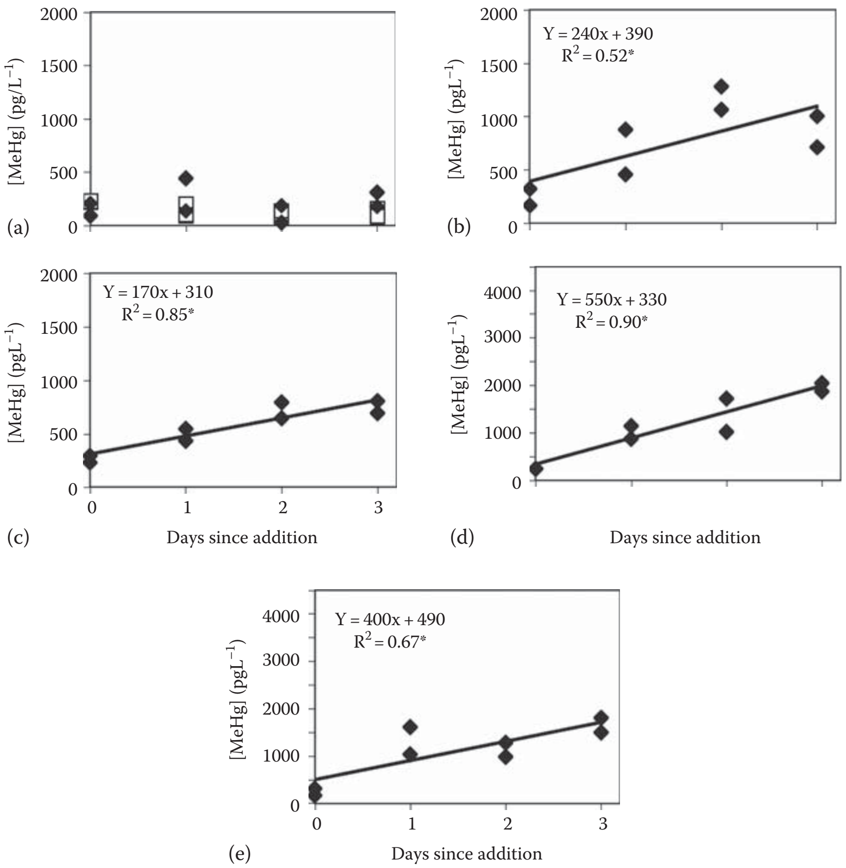

FIGURE 11.11

Response of MeHg to C and sulfate additions (From Mitchell, C.P.J. et al., *Appl. Geochem.*, 23(3), 503, 2008b). No response was seen when adding C as glucose (a). Responses were similar when adding 4× (b) and 10× (c) annual sulfate deposition, and methylation was higher when combining C as glucose plus 4× (d) and 10× (e) sulfate additions. There were no differences between the 4× and 10× sulfate plus C additions.

enhanced in the lagg zone when upland-derived soil water, which is relatively rich in sulfate, nutrients, and labile DOC mix with bog water, which is relatively low in nutrients and has DOC that is more recalcitrant to microbial degradation. Upland waters may be too well oxygenated for sulfate reduction to occur, while bog waters lack the labile DOC and sulfate needed for methylation. When the waters mix in the lagg zone, conditions are ideal for methylation because sufficient sulfate and labile DOC present under saturated conditions allows sulfate reduction to occur.

Further investigation of the landscape influences on methylation indicates that upland topographic configuration plays an important role in the location of MeHg hotspots within the lagg. Upland positions that focus subsurface

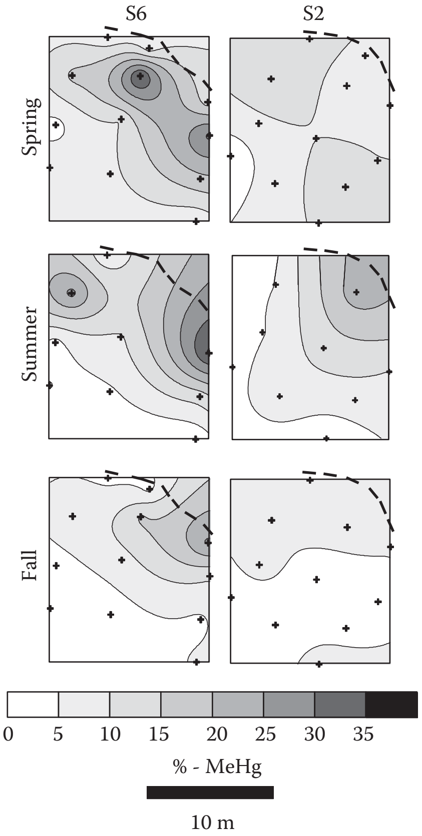

FIGURE 11.12
Contour plots of %MeHg in high-resolution sampling grids illustrate seasonal variability in spatial pattern of %MeHg in pore water at the upland–peatland interfaces in the S6 and S2 watersheds. The dashed line in the upper right corner of each plot represents the upland–peatland interface, corresponding to a change in topography and a change from organic to mineral soils. Upland hillslope runoff is from the upper right toward the lower left of each plot. Each + symbol represents a pore water sampling point (From Mitchell, C.P.J. et al., *Environ. Sci. Technol.*, 42(4), 1010, 2008c).

flow to the lagg (concave configuration) generally exhibit higher MeHg, sulfate, and DOC concentrations than upland landscape positions that lead to more diffuse flow to the lagg (Figure 11.13). Focused flow from the uplands transported greater quantities of labile DOC and sulfate to the lagg zone, likely promoting MeHg production. Lagg areas that received lower, diffuse, upland flow receive primarily low-sulfate, recalcitrant-DOC waters from the bog, resulting in significantly less methylation.

Conclusion

The extensive hydrologic and biogeochemical monitoring across varied upland–peatland ecosystems has created unique opportunities to address important Hg research questions at the MEF. Research in the northern ecosystem at the MEF has shown that forest canopies enhance Hg deposition

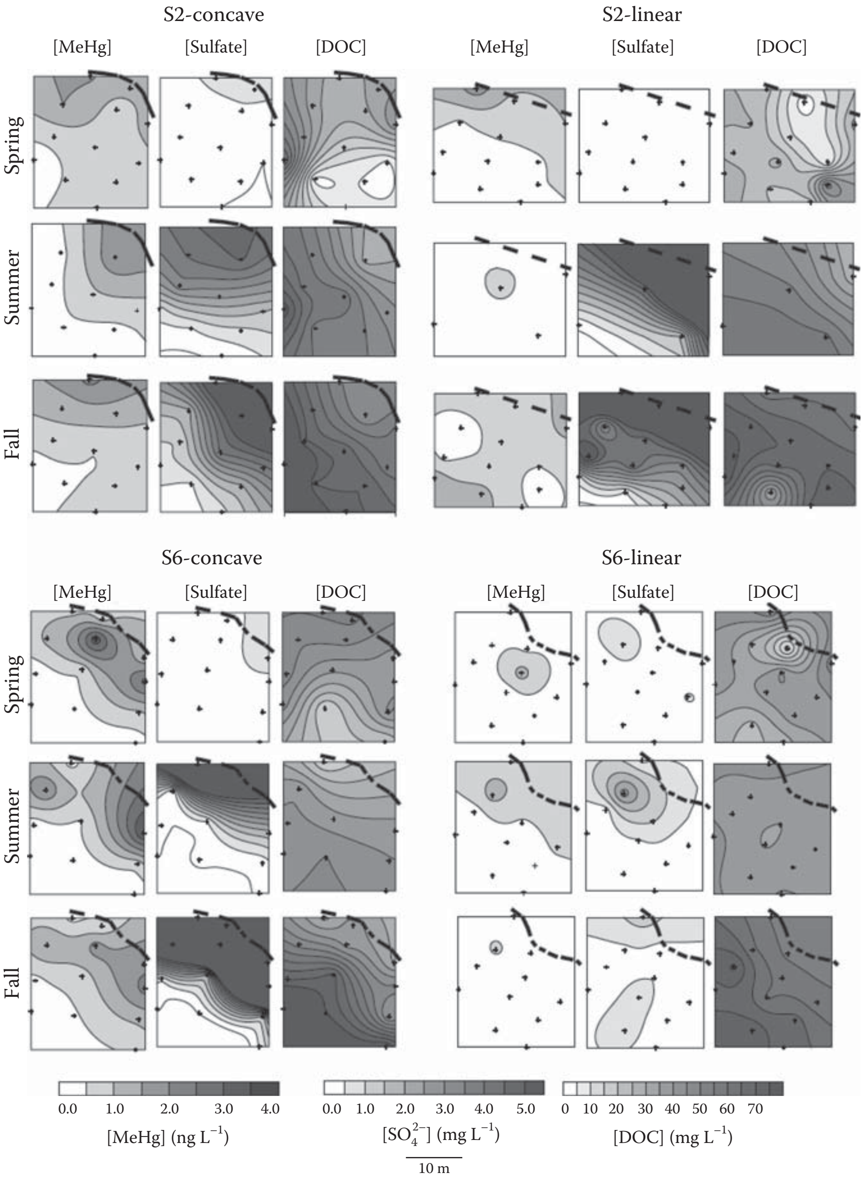

FIGURE 11.13
Spatial patterns of pore water MeHg, sulfate, and DOC concentration at the upland–peatland interface adjacent to concave or linear upland hillsopes in the S2 and S6 watersheds. The dashed line in each represents the upland interface. Fluxes from the upland are across the interface from the upper right of each plot toward the lower left (From Mitchell, C.P.J. et al., *Water Resour. Res.*, 45:W02406, 2009).

and has documented the important hydrologic pathways through which Hg is transported to surface waters. Because of enhanced atmospheric deposition, storage in peat soils, and efficient methylation, the ecosystem represented by the MEF is sensitive and vulnerable to global atmospheric Hg contamination. Watershed mass balances of Hg at the MEF are revealing the perturbations that mobilize and methylate Hg that already is present in the environment. Such knowledge can help direct human activities to minimize the negative impact of Hg pollution, even as governments work to reduce the amount of Hg released into the atmosphere.

After Hg reaches aquatic systems, additional processes such as photoreduction and demethylation can occur and affect whether lakes are a source or a sink of atmospheric Hg. Studies at the MEF indicate that both THg and MeHg accumulate significantly in lake sediment, although most of the MeHg is eventually demethylated. In Spring Lake, most of the MeHg in the lake is not transported from connected terrestrial systems or from atmospheric deposition but is formed by the methylation of inorganic Hg in the water column or surface sediment. Photoreduction is by far the largest sink (loss) of MeHg from the lake system, with uptake by biota a minor sink. Although uptake by biota is minor in the overall mass balance, it is a critical link between abiotic Hg sources and bioaccumulation in the food web.

Identifying the processes that lead to the methylation of Hg is critical to efforts aimed at mitigating the effects of global Hg contamination. Recent work indicates that both increased sulfate and labile C lead to higher methylation rates. Within watersheds, MeHg production is highest at the upland–peatland interface or lagg, which is considered a hotspot for MeHg production because of available Hg, labile C, and sulfate, and the anaerobic conditions present there. Understanding both the controls on MeHg production and locations in the landscape where methylation occurs can foster management approaches and land-use decisions that will lessen the contribution of MeHg to aquatic systems where it can accumulate in the biota.

On the basis of well-cited past studies and novel current Hg studies, the MEF is poised to address research aimed at new questions related to Hg. Future research in MEF will investigate the chemical and hydrologic controls on Hg methylation, particularly those relating to organic matter composition controls on Hg dynamics. The use of Hg isotopes has considerable promise to elucidate processes that lead to methylation. A new study will use Hg isotopes to determine the effects of forest harvesting on Hg transport and MeHg production in upland soils. Preliminary investigations have measured Hg in terrestrial invertebrates. Future research could build on this work to assess the trophic cycling of Hg and OC in ecosystem food chains. Climate change has considerable potential to exacerbate Hg contamination in northern ecosystems through enhanced bacterial growth and metabolism, sulfate cycling, or the release of stored Hg from peat. We anticipate a number of opportunities related to the impact of climate change on Hg cycling. Past and current research clearly demonstrates that the MEF is an ideal field laboratory to investigate these important questions about Hg in the environment.

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