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Seasonal Variations in the Inputs and Fate of Mercury in a Northern Hardwood Forest

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Abstract

The Adirondack region of New York is sensitive to atmospheric mercury deposition. In this study, the fate of mercury inputs to the Huntington Wildlife Forest (HWF) of the Adirondack region was examined by conducting a mercury mass budget over the annual cycle. Mercury cycling processes analyzed included wet mercury deposition, dry mercury deposition, foliar mercury accumulation, throughfall mercury, litterfall mercury, soil mercury evasion, and soil solution mercury fluxes. The mercury transport processes were quantified by integrating data collected from different sources in recent years (2004-2011) over a monthly time step. Dry mercury deposition (16.3 μg m^{-2} yr^{-1}) was more important than wet mercury deposition (6.3 μg m^{-2} yr^{-1}) at the HWF. Most of the atmospheric mercury deposition (> 60%) was retained in the forest soils where litterfall (17.2 μg m^{-2} yr^{-1}) was the major input pathway. Soil evasion (6.5 μg m^{-2} yr^{-1}) was the most important mercury export mechanism, exceeding mercury fluxes in lateral and vertical drainage from soil (2.8 μg m^{-2} yr^{-1}). This analysis showed marked seasonal variation in the transport of mercury that was strongly mediated by the forest ecosystem. The upland hardwood forest ecosystem was a net sink for atmospheric mercury deposition. Controls on mercury anthropogenic emissions would likely decrease mercury accumulation in the forest soils and lengthen the residence time of soil mercury at the HWF.

SEASONAL VARIATIONS IN THE INPUTS AND FATE OF MERCURY IN A NORTHERN HARDWOOD FOREST

by

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1. Introduction

Mercury is a toxic pollutant that is a substantial ecological and public health concern. The exposure of humans and wildlife to mercury mainly occurs through the consumption of contaminated aquatic organisms. Studies suggest that elevated exposure to mercury leads to significant damage to the central nervous system, kidneys and other human organs (Clarkson et al., 2006). It has been estimated that more than 410,000 new born children each year in the United States are exposed in wombs to methylmercury that will impair neurological development (Mahaffey, 2005).

Mercury emissions to the environment include both natural and anthropogenic sources. Important anthropogenic sources include electric utilities, incinerators, industrial manufacturing, wastewater treatment plants, and improper disposal of consumer products (Driscoll et al., 2007). Atmospheric mercury emissions are considered to be the largest source of mercury to the environment both in the United States and globally. Mercury inputs to remote ecosystems are predominantly contributed by atmospheric deposition (UNEP, 2007; Obrist et al., 2011). Most atmospheric mercury (>95%) exists in the form of elemental mercury (Hg^0) which has a long residence time (0.5-2 years), making mercury readily transported throughout the atmosphere and a global pollutant (Schroeder and Munthe, 1998).

Watersheds receive inputs of mercury from atmospheric deposition that may eventually be transported to aquatic ecosystems and be converted to methylmercury. Methylmercury is the form of mercury that bioaccumulates in the aquatic food chain and thus threatens the health of humans and wildlife. As a result, it is important to understand the ultimate fate of atmospheric mercury deposition to terrestrial ecosystems.

Studies indicate that multiple processes of forest ecosystems affect mercury transport. For example, the forest canopy enhances atmospheric mercury deposition through the exchange of mercury between the atmosphere and foliage (Driscoll, et.al, 2007). Litterfall is considered a significant input of mercury deposition to the forest floor (Sheehan et al., 2006, Demers et al. 2007). Mercury evasion from the forest floor is a substantial loss process of mercury inputs which is influenced by solar radiation, temperature, soil moisture and other factors (e.g. Lindberg et al., 1995; Zhang et al., 2001; Fitzgerald and Lamborg, 2003; Mason et al., 2005). Despite this understanding, there have been few comprehensive studies of mercury cycling processes for atmosphere-plant-soil systems (Choi and Holsen, 2009; Ericksen et.al, 2003).

The Adirondacks of New York is an important region to investigate atmospheric mercury deposition and its fate in forest, wetland and aquatic ecosystems. The Adirondack is considered a "biological mercury hotpot" due to its high sensitivity to moderate inputs of atmospheric mercury deposition (Evers et al., 2007). The objective of this study was to examine the fate of mercury in a northern forest ecosystem and evaluate the role of the forest ecosystem in mediating mercury transport.

This study was conducted at the Huntington Wildlife Forest (HWF), a deciduous forest ecosystem located at the Adirondacks. Using data obtained from different sources, I quantified the mercury cycling processes across air-plant-soil interface at the HWF. Important mercury cycling processes in this analysis included atmospheric mercury deposition (precipitation, dry deposition), mercury accumulation in foliage, throughfall mercury deposition, litterfall mercury deposition, mercury transport via soil water, and soil mercury evasion. A mass budget on mercury in the forest canopy, the forest floor and the entire forest ecosystem was conducted over

a 12-month cycle. I discuss the significance of these processes and the fate of mercury inputs in the context of other studies in the literature.

2 Literature Review

2.1 Mercury emissions

Currently the global mercury emission rate is nearly 7527 Mg per year, with natural sources (direct natural emissions and secondary emissions) accounting for 5207 Mg per year and direct anthropogenic sources 2320 Mg per year (Pirrone et al., 2010). The vast majority of anthropogenic mercury emissions originate from numerous industrial point sources (e.g. fossil-fuel fired power plants, artisanal small scale gold mining, and non-ferrous metals manufacturing). Mercury is emitted from point sources to the atmosphere typically in three forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM) also known as reactive gaseous mercury (RGM), and particulate-bound mercury (PBM) (Driscoll et al., 2007b; Choi et al., 2008a). The amount and speciation of mercury emissions vary widely with emission sources and region (Driscoll et al., 2007b; Pirrone et al., 2010). Globally, GEM predominates the atmospheric mercury (~ 95%) with a long residence time of ~ 0.5-2 years, while GOM and PBM make up to much smaller contribution (~5%) with shorter residence times of ~ 0.5-3 days (Slemr et al, 1985; Driscoll et al., 2007b; Choi et al., 2008a).

Actions have been taken to control mercury emissions among developed countries since the 1980s, in order to decrease the adverse impact of mercury. However, estimates suggest that total global anthropogenic emissions have increased by 17% since 1990 (Pirrone et al., 2010). It is anticipated that global mercury emissions will continue to rise in the following decades due to the increasing energy need in developing countries (Streets et al., 2009; Pacyna et al., 2010;

Slemr et al., 2011). Surprisingly, the worldwide background atmospheric concentration of GEM has declined by ~ 20-38% since 1996 (Slemr et al., 2011). This pattern is in contrast with the increasing global mercury emissions, indicating biogeochemical cycle of mercury including oceans and soil reservoirs is an important controller of net mercury deposition (Slemr et al., 2011).

2.2 Atmospheric deposition

As the primary source of mercury to the forest ecosystem, atmospheric deposition includes two forms: wet deposition and dry deposition. Wet deposition refers to Hg removal by rain and snow; dry deposition refers to Hg removal in the absence of precipitation, which includes the gaseous and particulate deposition of GOM and PBM, cloud and fog deposition, and leaf uptake of GEM in forest ecosystems (Driscoll et al., 2007b). Regional-scale studies indicate that wet mercury deposition and dry mercury deposition are similar in magnitude. Moreover, in contrast to wet mercury deposition, dry mercury deposition exhibits substantial spatial and temporal variability (Keeler and Dvonch, 2005; Miller et al., 2005; Engle et al., 2010; Zhang et al., 2012).

In the United States and Canada, wet mercury deposition estimates have been largely made from measurements at sites in the Mercury Deposition Network (MDN). The MDN currently includes 28 active sites in the northeastern US. Driscoll et al. (2007) reported the average annual mercury wet deposition ranged from 3.8 to 12.6 ug m^{-2} yr^{-1} for seven MDN sites in northeastern US region that were in operation at that time. Choi et al. (2008b) estimated the annual mercury flux in wet deposition at the Huntington Wildlife Forest was ~ 4 - 8 ug m^{-2} yr^{-1}, similar to the estimation from the MDN. A field study by Rea et al. (2002) suggests ~ 9 ug m^{-2} yr^{-1} for annual mercury flux in wet deposition in northern forest watersheds.

Unlike wet deposition which can be estimated through the measurement of precipitation samples, direct measurements of dry deposition are difficult to conduct. A substantial experimental obstacle to measurements is that synthetic surfaces typically used to capture dry mercury have very different characteristics than natural surfaces (St. Louis et al., 2001; Lyman et al., 2007; Graydon et al., 2008; Zhang et al., 2012). Therefore inferential methods which involve monitoring concentrations of different Hg species in the atmosphere and transport models to determine values of deposition velocities are commonly used to quantify dry deposition (Zhang et al., 2012). There are much larger uncertainties in estimating dry deposition than wet deposition (Mason and Sheu, 2002; Lindberg et al., 2007; Zhang et al., 2009). Model assessment by field measurements and model intercomparisons suggests that transport models (e.g. CMAQ2002, CMAQ2005, GRAHM2005) tend to overestimate the concentrations of GOM and PBM. The Community Multi-scale Air Quality model (CMAQ2005) underpredicted the night-time GEM deposition velocities in Great Lakes region (Zhang et al., 2012). Zhang et al. (2009) indicate that the deposition velocity of GEM has a typical range of 0.1-0.4 cm s^{-1} for vegetated surfaces. These values are much lower than GOM deposition velocities with the range of 0.02-2 cm s^{-1}. The range of PBM deposition velocity is 0.02-2 cm s^{-1}, suggested from limited data. Despite the lower deposition velocity of GEM compared with the deposition velocity of GOM and PBM, field measurements and model simulations indicate that GEM could be a large component of dry deposition, as important as GOM and PBM (Lindberg et al., 2007; Gustin et al., 2008; Zhang et al., 2012).

Field studies of northern hardwood watersheds have suggested GEM dry deposition flux was ~6-16 μg m^{-2} over growing season and ~11 μg m^{-2} yr^{-1} annually (Rea et al., 2002). An estimation of mercury dry deposition by Miller et al. (2005) using inferential methods indicated that annual

GEM deposition was 7.2 μg m^{-2} yr^{-1} while annual GOM and PBM deposition was 10.5 μg m^{-2} yr^{-1} in New Brunswick, Canada, where forest coverage was 93%. A long-term study by Graydon et al. (2008) suggests that the annual dry deposition of total mercury under forest canopies of NW Ontario had a range of 10.5-20.1 μg m^{-2} yr^{-1} using a direct calculation method (dry deposition = throughfall + litterfall – open deposition).

Paleolimnological studies indicate deceases in mercury deposition of approximately 25% for the northeastern US region over the past two decades, in accordance with decreases in US emissions (Kamman and Engstrom, 2002; Driscoll et al., 2007b; Drevnick et al., 2011). Kamman and Engstrom (2002) suggest annual sediment mercury deposition rates of ~15 μg m^{-2} yr^{-1} in Spring Lake and ~40-50 μg m^{-2} yr^{-1} in Villingford Pond, Vermont (Kamman and Engstrom, 2002). Field studies show the annual atmospheric deposition rate for the northern United States was ~15 μg m^{-2} yr^{-1} (Fitzgerald et al., 1986; Brigham et al., 1991). Miller et al. (2005) demonstrated a similar total atmospheric mercury deposition range of 10.5 to 21.9 μg m^{-2} yr^{-1} across northeastern America using inferential estimates. VanArsdale et al. (2005) showed wet mercury deposition was generally higher during summer months. Moreover, recent decreases in mercury emissions were not reflected in wet mercury concentration or deposition in the MDN data from 1996 to 2002 in northeastern North America. Risch et al. (2012) found no inter-annual change in wet mercury deposition in the Great Lakes region and its subregions from 2002 to 2008 (mean wet deposition for this period: 8.6 μg m^{-2} yr^{-1}), using data from 5 monitoring networks in the USA and Canada.

2.3 Foliar mercury accumulation

Mercury concentrations in foliage of many different hardwood tree species have been shown to increase over the growing season (e.g. Rea et al., 2002; Millhollen et al., 2006; Bushey et al.,

2008). In a field study Rea et al. (2002) observed up to 10 fold increases in foliar mercury concentrations from ~3 to ~37 ng g^{-1} during the growing season with no significant species differences at mixed hardwood forests of the northern US. Field and laboratory studies have demonstrated atmospheric deposition is the predominant source to mercury in leaf tissue with minimal mercury uptake from soil via soil transpiration (Rea et al., 2002; Eriksen et al., 2003; Millhollen et al., 2006; Bushey et al., 2008; Bishop et al., 1998).

Field measurements of Bishop et al. (1998) suggest limited contribution (~11%) of soil transpiration to the mercury accumulation in foliage and some degree of mercury exclusion (by ~75%) during the water uptake by roots. Rea et al. (2002) suggest mercury uptake via soil transpiration accounted for 0.5-1.6 µg m^{-2} yr^{-1} or 3-14% of the litterfall mercury for northern hardwood forested watersheds.

Foliar accumulation of mercury from the atmosphere occurs by two pathways: total leaf interior stomatal uptake of GEM and retention on the leaf surfaces by atmospheric Hg deposition (primarily GOM) (Ericksen et al., 2003; Miller et al., 2005; Graydon et al., 2006; Stamenkovic et al., 2009; Rutter et al., 2011). Factors controlling mercury uptake which affect foliar resistance include environmental conditions (e.g., temperature, CO_2 concentration, solar radiation), enzyme activity, leaf wetness, photoreduction on the surface of leaves (which controls the GEM emission from foliage), precipitation and atmospheric mercury concentrations (Du et al., 1983; St Louis et al., 2001; Rea et al., 2002; Graydon et al., 2006; Bash et al., 2009; Warren 2008; Stamenkovic et al., 2009; Rutter et al., 2011). The understanding of leaf uptake of atmospheric mercury remains limited due to large uncertainties in estimating mercury dry deposition velocities and foliar resistances (Graydon et al., 2008; Stamenkovic et al., 2009; Rutter et al., 2011). Inferential estimates of Rutter et al. (2011) using resistance-temperature-irradiance relationship indicate the

leaf uptake of GEM for one-sided leaf area (OSLA) over the growing season was in the range 2.3-3.7 μg m^{-2} yr^{-1} while foliar accumulation by GOM dry deposition was in the range of 0.1-6 μg m^{-2} yr^{-1} OSLA.

2.4 Throughfall and litterfall

Throughfall and litterfall are often considered to be external pathways of the mercury deposition captured by forest canopy, rather than recycled mercury inputs of the forest ecosystems (Zillioux et al., 1993; Rea et al., 1996; St Louis et al., 2001; Ericksen et al., 2003; Millhollen et al., 2006; Graydon et al., 2008; Bushey et al., 2008).

Mercury concentrations in throughfall during the leaf-on period are typically higher than in precipitation (from 1.5 up to 4 times) due to wash-off and leaching (less important) of the previous mercury deposited on leaf surface (Iverfeldt et al., 1991; Munthe et al., 1995; Schwesig and Matzner, 2000; St Louis et al., 2001; Graydon et al., 2008).

Mercury in litterfall has been observed to be an important pathway of mercury deposition to the forest floor, ranging from ~50% to 70% of the total inputs at many remote sites of North America (St. Louis et al., 2001; Rea et al. 2002; Miller et al., 2005; Demers et al., 2007; Graydon et al., 2008). Reported findings for the differences of mercury concentrations in foliage and litter among plant species are mixed, indicating further study of the inter-species variations in mercury uptake is needed (Lindberg, 1996; Rasmussen, 1995; St Louis et al., 2001; Rea et al., 2002; Grigal, 2003; Sheehan et al., 2006; Teixeira et al., 2012). A field study at the forests of Maine suggests annual mercury flux in litterfall was approximately 10 μg m^{-2} yr^{-1} without significant differences among plant species, while the mercury concentrations in litter were varied among vegetation classes (Sheenhan et al., 2006). Long-term studies at the remote Experimental Lake Area (ELA) in Canada have shown no significant differences among four different forest types in

both annual litterfall mass (~280 g/m^2, most of which occurred before the end of October) and annual mercury flux in litterfall (~9-11 $\mu g/m^2$) (Graydon et al, 2008). Juillerat et al. (2012) showed that annual litterfall in forest ecosystems of Vermont had a range of 12.6 to 28.5 ug m^{-2} yr^{-1}without relation to forest type. Conversely, Risch et al. (2012) reported annual litterfall mercury deposition differed among forest types with the range of 3.5-23.4 ug m^{-2} yr^{-1} in a field study across the eastern USA.

2.5 Soil mercury evasion

It has been observed that atmosphere-soil exchange of mercury is bi-directional. In addition to sequestering the deposited mercury by adsorption to soil organic matter (SOM) (St. Louis et al., 2001; Hintelmann et al., 2002; Grigal 2003; Obrist et al., 2011), soil has been shown to emit significant amount of GEM back to the atmosphere (Lindberg et al., 1995; Gustin et al., 2000; Zhang et al., 2001; Fitzgerald and Lamborg, 2003; Mason et al., 2005). Mercury evasion from the soil surface is driven by complex physical, chemical and biological interactions, and has been correlated with multiple factors, such as air chemistry, precipitation, light, temperature, soil moisture, soil organic matter content, substrate mercury concentration and speciation, and microbiological activity (Zhang and Lindberg, 1999; Schlüter 2000; Gustin 2003; Engle et al. 2004; Gustin and Stamenkovic, 2005; Eriksen et al., 2006). There is considerable uncertainty in the estimates of soil mercury evasion (Denkenberger et al., 2012), including forest soils. This uncertainty is due to incomplete understanding of mechanisms controlling evasion, technical difficulties in measurements and limited field investigations (Moore and Carpi, 2005; Zhang et al., 2002; Choi et al., 2009; Denkenberger et al., 2012). Field studies have shown soil mercury evason rate ranged from 0 to ~ 4 ng m^{-2} h^{-1} across mixed forest sites in California (Ericksen et al., 2006). Model estimates (HgSIM) of Bash et al. (2004) suggest the average forest floor evason

rate of GEM was 1.5 ng m^{-2} h^{-1} at noon in the northeastern US. The average mercury evasion from forest soils in the Great Lakes Basin was 7.0 µg m^{-2} yr^{-1} based on the field measurements (Denkenberger et al., 2012).

2.6 Mercury in soil water transport

Soil drainage has been suggested to be an insignificant export pathway of mercury from the watersheds by several studies (e.g. Driscoll et al., 1998; Schwesig and Matzner, 2001; Sunderland and Mason, 2007). While small in magnitude, this process is key to the transport of ionic Hg to zones of methylmercury production which drives trophic transfer and exposure. Upper horizons of the forest floor (Oa or Oe horizons) usually have the highest soil mercury concentrations according to many investigations of different regions (Orbrist et al., 2011; Demers and Driscoll, 2007; Schwesig and Matzner, 2000). The pattern of soil profile mercury is thought to reflect the legacy of mercury deposition (Orbrist et al., 2011; Juillerat et al., 2012). Mercury concentration in water have been observed to be strongly correlated with dissolve organic carbon (DOC) concentrations because of the binding of mercury with dissolved organic matter (Driscoll et al., 1995; Scherbatskoy et al., 1998; Brigham et al., 2009). Several field studies suggest that catchment runoff has a minor contribution to the transport of total mercury deposition from soil to water. Brigham et al. (2009) estimated that fluvial mercury load was in the range of 0.87 - 4.36 µg m^{-2} yr^{-1} at the sites in Florida, Oregon, and Wisconsin. The annual areal mercury watershed flux of THg was estimated to be 2.2 µg m^{-2} yr^{-1} for a wetland in the Adirondack region of New York, considerably smaller than atmospheric deposition (Driscoll et al., 1998). Schwesig and Matzner (2001) suggest that only a small part (29%) of THg input to the forest floor was lost by runoff in a forested watershed in Central Europe; while upper soil layer (O and A horizons) retained mercury with poor efficiency and most (~60%) of the THg input

into the forest floor was transported into mineral soil through water movement. Field studies in forest ecosystems in Sweden indicate only ~4% of the THg input to the forest was contributed by catchment runoff (Munthe and Hultberg, 2004).

2.7 Anthropogenic impacts on mercury in terrestrial systems

Many studies indicate that anthropogenic emissions have lead to increases in both mercury deposition and storage in terrestrial ecosystems. It is suggested that mercury deposition to terrestrial ecosystems has been currently elevated by three times compared to pre-anthropogenic conditions (around 1850) according to the sediment archives (Lorey and Driscoll, 1999; Swain et al., 1992). In contrast, global surface soil mercury pool has increased by 10% - 15% since industrialization based on model simulations (Mason and Sheu, 2002; Selin et al., 2008). Smith-Downey et al. (2010) have developed a global model considering terrestrial mercury cycling in the framework of soil carbon cycling, in which atmospheric deposition, leaf uptake, littefall, surface photoreduction, revolatilization and soil respiration were considered as the associated cycling processes. The global terrestrial mercury model suggests that global mercury storage in organic soil has increased by ~20% since preindustrial time. Moreover, controlling anthropogenic emissions will likely lead to immediate and large decreases in soil mercury emissions (Smith-Downey et al., 2010).

3. Methods

3.1 Site description

The Huntington Wildlife Forest (HWF) is a 6000 ha experimental northern hardwood forest located in the Town of Newcomb, western Essex County and in the Town of Long Lake, eastern

Hamilton County, New York State, USA (43.97°N, -74.22°W). The forest lies near the geographic center of the Adirondack Park and has a mountainous topography, with elevations ranging from 457m to 823m (Huntington Forest research website: http://www.esf.edu/hss/huntington_forest_research_overview.htm). The climate is cool, moist, and continental, with an annual average temperature of 4.4 ℃ and annual average precipitation of 1010 mm for the period 1951-1980 (Shepard et al., 1989). The property contains five lakes: Catlin (area=217 ha; max. depth=17 m), Rich (160 ha; 18 m), Wolf (58 ha; 14 m), Arbutus (49 ha; 8 m) and Deer (38 ha; 3 m). Arbutus Lake and its associated watershed have been extensively studied (NYSERDA, 2009).

Vegetation at the HWF is 72% northern hardwoods, 18% mixed hardwood-conifers and 10% conifer. Northern hardwood species are dominated by American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and yellow birch (*Betula alleghaniensis*), with some red maple (*A. rubrum*). The upland watershed soils are coarse-loamy, mixed frigid typic Haplorthods with a depth generally less than 1m and underlain by a thin boulder glacial till derived from local bedrock (Johnson and Lindberg, 1992).

3.2 Approach

The following conceptual model (Figure 3.1) briefly demonstrates the approach used in performing mercury mass balance for my study. For the forest canopy mass balance, the inputs are atmospheric mercury deposition (wet and dry deposition) and mercury in soil transpiration, and the outputs are throughfall and litterfall mercury. For the forest floor mass balance, the inputs are throughfall and litterfall mercury, and the outputs are soil mercury evasion, and mercury loss in soil water transport (soil transpiration, soil surface runoff and soil surface vertical flow out of the lowest soil layer). For the mass balance of mercury for the entire forest

ecosystem, atmospheric deposition (precipitation and dry deposition) were considered as the inputs; and surface runoff, vertical flow out of the deepest soil layer and soil evasion were considered as the outputs.

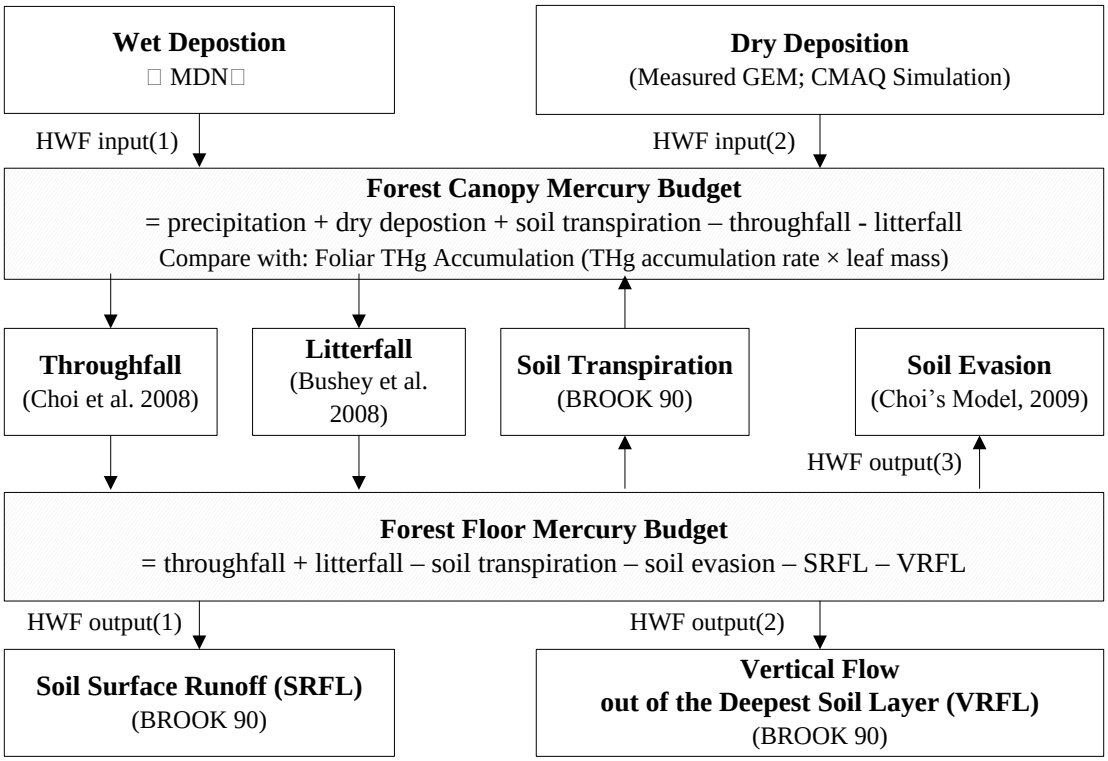

Figure 3.1 Conceptual model of the approach and the data sources used for the canopy, forest floor and overall ecosystem mercury mass balance.

3.3 Data Sources

In this study, I conducted a mercury mass budget on the canopy, forest floor and entire forest ecosystem for the HWF for a 12-month annual cycle, by conducting analysis of datasets compiled from different sources over the period 2004 - 2011, e.g. Syracuse University (SU), Clarkson University, and SUNY College of Environmental Science and Forest (SUNY-ESF). The source, time interval and measurement period of most source datasets used in the mass

balance calculation are summarized in Table 3.1. A monthly time-step was chosen for the mass balance calculation largely due to limitation in the frequency of throughfall, leaf tissue and soil solution mercury measurements. The multi-year datasets were averaged on a monthly basis to support the selected time step. The collection period for the mass balance analysis represents the period 2004 - 2011.

Table 3.1 Summary of the sources, time intervals and measurement periods of the important datasets used in the mass budget.

Datasets	**Source**	**Time-interval**	**Measurement period**
Hg fluxes in precipitation	MDN (NY20) http://nadp.sws.uiuc.edu/mdn/	~1 week	2004.1 – 2011.4
Hg concentrations in the atmosphere	Clarkson University	3 hours	2009.1-2011.12
Hg fluxes in throughfall	Clarkson University	~1 month	2004.1 – 2006.12
Hg concentrations in leaf tissues and litters	Bushey et al. (2008)	~1 month	2004. 5 - 2004.10, 2005. 5 - 2004.10 (fresh leaf); 2004. 5 - 2004. 10, 2005. 10 - 2005.12 (litter)
Hg concentrations in soil water	Syracuse University	~1 month	2004.7 - 2006.6
Hydrological data (stream flow)	SUNY-ESF: Arbutus Lake inlet data http://www.esf.edu/hss/em/huntington/archive.html	1 day	2004.1 -2006.6
Meteorological data (temperature, wind speed, solar radiation, humidity, etc.)	The Clean Air Status and Trends Network (CASTNET) (HWF 187) http://java.epa.gov/castnet/clearsession.do	1 hour	2004.1 - 2006.12, 2009.1 – 2011.12

3.3.1 Mercury in precipitation

Wet deposition (precipitation) data were obtained from the Mercury Deposition Network (MDN) of National Atmospheric Deposition Program (NADP), which provides a long term record of total Hg concentration and deposition in precipitation. Mercury deposition has been monitored at the HWF as part of the Mercury Deposition Network since December 10, 1999. The MDN monitoring site NY20 (43.97°N, -74.22°W) of HWF is at an elevation of 500m. Weekly precipitation samples were collected and analyzed for total Hg concentration and deposition.

3.3.2 Dry deposition of mercury species

Concentrations of gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM) in the atmosphere were measured at approximately 3-hourly intervals from 2009 to 2011, at a large open clearing site at the HWF, where the MDN (NY20) and CASTNET (HWF 187) measurements are made. Mercury concentrations were analyzed using a Tekran model 2537A, 1130 and 1135 (Choi et al., 2008a). Yu et al. (in review) has estimated the deposition velocities of GEM, GOM, and PBM at an interval of 1h for the year 2009 using the transport model CMAQ2005. Total mercury flux by dry deposition was therefore calculated by multiplying the modeled deposition velocity by corresponding measured mercury concentrations of individual Hg species (GOM, PBM, and GEM).

3.3.3 Mercury in throughfall

Choi et al. (2008b) collected and analyzed deciduous throughfall samples at the HWF from December 2004 to December 2006. The throughfall sample collector was placed southeast of Arbutus Lake (43.98°N, -74.23°W), 1 km from the forest edge, at an elevation of 530m. Weekly samples were collected using a modified MIC-B automatic precipitation collector. Total mercury in the samples was quantified using a dual amalgamation technique followed by a cold-vapor atomic fluorescence spectrometer (CVAFS) with Tekran 2600.

3.3.4 Mercury in leaf tissues

Plant tissue samples of three dominant tree species (yellow birch, sugar maple, American beech) were collected at upland plots at the HWF, about 200 m southeast of the Arbutus Lake complex, at an elevation of 530m. Fresh leaf samples were collected approximately monthly over the growing season (May to October) from July 2004 to October 2005. Litter samples were collected monthly during the growing season of 2004 and October to December of 2005. Total mercury concentrations (THg) in all fresh leaf tissue and litter samples were analyzed using a DMA-80 Direct Mercury Analyzer (Bushey et al., 2008).

3.3.5 Mercury in soil water

Two soil pits were excavated at the HWF on June 2004 and replicate zero tension lysimeters were installed to sample soil water. One pair was placed beneath the Oa, Bh, and Bs_2 horizons for Plot 1 and the Oa and Bh horizons for Plot 2. Soil water was collected approximately monthly using clean techniques (EPA 1996) from July 2004 to June 2006. Total mercury

concentrations in soil water were analyzed using oxidation, purge and trap, and CVAFS (Method 1631, revision E – EPA 2002) (Driscoll, unpublished data).

3.3.6 Hydrological data of Huntington Wildlife Forest

Stream flow at the Arbutus Lake inlet was used to represent the hydrology condition at the HWF in this study. Stream flow datasets of the Arbutus Lake inlet monitored in 1-day interval of year 2004-2006 were downloaded from SUNY-ESF website (http://www.esf.edu/hss/em/huntington/archive.html). The stage height at Arbutus Lake inlet was measured with a pressure transducer and downloaded by the AEC (Adirondack Ecological Center) from 1999 to 2007. Stream flow at Arbutus Lake inlet was normalized by watershed area for convenience of computation.

3.3.7 Meteorological data at Huntington Wildlife Forest

Meteorological data for the HWF for the periods 2004 - 2006 and 2009 - 2011 were downloaded from The Clean Air Status and Trends Network (CASTNET) of USEPA (http://www.epa.gov/castnet/javaweb/site_pages/HWF187.html). The EPA CASTNET site (HWF 187) at the HWF is located at 43.9731°N, -74.2232°W, at an elevation of 502 m. Hourly meteorological data including wind speed, temperature, precipitation, solar radiation, and relative humidity were measured and recorded on the site.

3.4 Computation methods

3.4.1 Wet deposition

Total Hg (THg) flux in precipitation for each month from January 2004 to December 2011 was calculated by summing up weekly values during corresponding period (for time period when data were unavailable, linear interpolation was used to estimate the value). Average Hg flux in precipitation for each month was determined by calculating the mean value of the three years. Average cumulative Hg flux was calculated by cumulating average monthly Hg fluxes.

3.4.2 Dry deposition

Estimates of mercury dry deposition are highly uncertain due to the complexity of the existing atmospheric mercury forms and the technical difficulties in measurements. Dry mercury deposition fluxes were estimated using the following methods.

Inferential method

A transport model CMAQ was used to estimate the deposition velocities of mercury species in the atmosphere for the year 2009 at the HWF coupled with the measured mercury concentrations to estimate dry mercury deposition. The atmospheric Hg concentrations of GEM, GOM and PBM were measured every 3 hours, and deposition velocities were estimated by CMAQ at an interval of 1 hour. Daily atmospheric Hg concentration and deposition velocity were determined as the mean value for the corresponding period. Daily Hg flux of GEM, GOM and PBM through dry deposition for the year 2009 was calculated by multiplying daily atmospheric Hg concentration for each Hg species (GEM, GOM or PBM) with its daily deposition velocity. Total Hg flux through dry deposition was calculated as the sum of GEM, GOM and PBM. As CMAQ only simulates estimates of one-directional mercury deposition, these values result in

redundancies in estimates of dry mercury deposition at the HWF, due to the mercury emissions (photoreduction and revolatilization) from the leaf surfaces during the leaf-on period.

Foliar GEM uptake estimate by growing season GEM depletion

The monitored GEM time series from 2009 to 2011 (Figure 3.2) at the HWF reveals that the concentrations of GEM exhibited an apparent depletion during growing season (May to October) while concentrations were relatively constant during non-growing season (November to April). In this study, I considered the summer depletion of GEM was due to GEM exchange between air and the plant tissues via stomata, as many studies suggest that leaf uptake of GEM is an important pathway of mercury atmospheric deposition to forest canopy (e.g. Rutter et al., 2011; Ericksen et al., 2003). The dry deposition of GOM and PBM were not considered in this estimation because that measured concentrations of GOM and PBM are much smaller than GEM concentrations (by a factor of ~11 - 4500) and that CMAQ simulations of this study suggest that these species contribute a small portion to the total dry mercury deposition.

The stomatal uptake of GEM during growing season was calculated as the average of 2009 and 2011 data (the computation method is discussed below). The monitored GEM data of 2010 were excluded in the calculation because the GEM time-series for this year shows a poor depletion pattern during growing season (Figure 3.2). The unusual GEM pattern for 2010 appears to be due to meteorological events transporting elevated GEM from the Midwest and equipment maintenance issues (T. Holsen, personal communication)

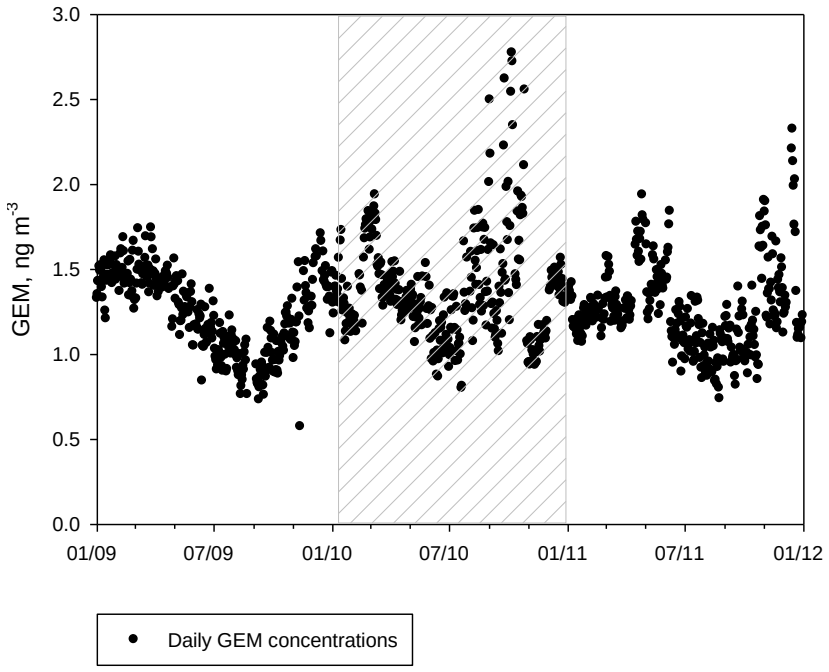

Figure 3.2 The concentrations of daily GEM at 5m-height of Huntington Wildlife Forest, 2009-2011. The cross-hatched period (2010) was not used because of an inconsistent pattern of depletion, due to equipment maintain issues and meteorological events resulting in transport of elevated GEM.

In this study, leaf uptake of GEM during the growing season (May to October) was estimated using the following conceptual model.

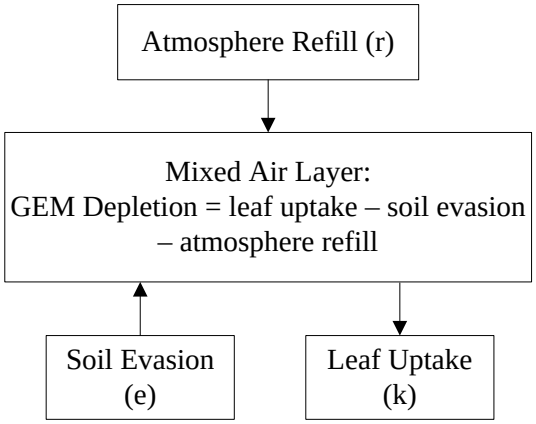

Figure 3.3 The conceptual model of the GEM depletion during the growing season.

The resulting GEM concentration in the atmosphere is thought to be controlled by the combination effect of leaf uptake, atmosphere refill (the complex air movement process that leads to mercury input to the mixed air layer, e.g. diffusion movements, winds, etc.) and soil gaseous mercury emissions. Assuming atmosphere refill rate "r" is constant during GEM depletion period, "r" was estimated by performing linear regression on GEM concentrations over early December, when the GEM was still depleted while leaf uptake and soil evasion were both considered to be zero. The emission rate of GEM from soil ("e") was estimated using an empirical model developed by Choi et al. (2008). Previous studies suggest the height of mixed atmospheric boundary layer is about 500m at the HWF (Han, 2003; Choi et al., 2008). The height of the mixed layer used in this study was 526 m, mean value based on the measurement of atmospheric boundary layer height at the HWF by Clarkson University during the period of December 2007 to November 2009.

This inferential method is oversimplified, but it suggests an approach to estimate net dry GEM deposition between the canopy and the atmosphere without the need to evaluate leaf mercury emission during leaf-on period.

Foliar GEM uptake estimate by foliar Hg accumulation subtracting soil transpiration

Foliar GEM uptake was calculated using foliar mercury accumulation subtracting mercury uptake via soil transpiration (discussed in section 3.4.7), considering foliar mercury uptake consisted of stomatal uptake of GEM and mercury uptake via soil transpiration at the HWF. Foliar mercury accumulation at the HWF was estimated using the following method.

The THg accumulation rate (ng g^{-1} day^{-1}) of each tree species sampled (yellow birch, sugar maple, and American beech) during growing season was estimated by performing linear regression of THg concentrations in fresh leaf tissue for the year 2005 (Bushey et al., 2008). The

regression for 2004 was not used due to limited data. Total mercury accumulation flux in fresh leaf tissue (ug m^{-2}) during growing season for each tree species was calculated by multiplying foliar THg accumulation rate with leaf mass per ground area and the time duration of growing period (May 1st to October 1st).

There have been few comprehensive studies on the biomass of plant species at the HWF. Smith and Martin (2001) have estimated the values of leaf mass per unit of leaf area (LMA) for different tree species including YB, SM and AB on Bartlett Forest in New Hampshire, which are, however, apparently lower than the biomass levels measured at the HWF according to the limited investigations (Table 3.2). Therefore, areal litter mass values of the three tree species (YB, SM, AB) measured by Bushey et al. (2008) instead of leaf mass values were used to calculate the foliar mercury accumulation in this study. Foliar mercury accumulation of the overall forest was calculated as the sum of YB, SM and AB accumulation (mercury accumulation mass per ground area) over growing season, considering their predominant contribution to the forest canopy coverage.

Dry deposition of GOM+PBM estimate by net throughfall

Net throughfall mercury (throughfall mercury – precipitation mercury) is considered to be mostly the wash-off of mercury (GOM and PBM) deposited previously on the leaf surface (Iverfeldt et al., 1991; Munthe et al., 1995; Schwesig and Matzner, 2000; St Louis et al., 2001; Graydon et al., 2008). Therefore, dry deposition of GOM+PBM at the HWF was estimated by subtracting precipitation mercury from throughfall mercury.

Table 3.2 Summary of leaf mass data per ground area of yellow birch (YB), sugar maple (SM), American beech (AB) and overall forest at the HWF by different investigators, unit: g m^{-2}.

Investigator/Source	YB	SM	AB	Overall Forest	Basis
Smith and Martin[1] (2001), IFS (1992)	35.5	131.8	86.7	248.0	canopy biomass
Blair (unpublished data)	NA	NA	NA	341.4	
IFS (1992)	NA	NA	NA	354.4	
Bushey et al. (2008)	3.8	209	145.5	358.3	litter biomass
IFS (1992)	NA	NA	NA	313.1	
Blair (unpublished data)	NA	NA	NA	348.0	

3.4.3 Throughfall

Monthly THg concentrations and fluxes in throughfall at the HWF from December 2004 to November 2006 were obtained from Clarkson University (Choi et al., 2008). Average monthly Hg fluxes in throughfall were determined by averaging the throughfall mercury data of 2004 to 2006. Average cumulative Hg fluxes were calculated by cumulating average monthly Hg fluxes.

3.4.5 Litterfall

As the values of litter mass collectedly monthly over growing season of 2004 indicated that litterfall was dominated by the autumn period, the litter traps were collected only twice during 2005, October 22 and December 1. The collected litter samples indicated that majority of litterfall occurred in October (Bushey et al., 2008). In this study, to simplify the computation of

[1] Smith and Martin (2001) measured LMA values for yellow birch, sugar maple and American beech at the Bartlett Forest in New Hampshire, which were 66.3, 62.6 and 61.1 g/m^2 respectively. LMA data were converted to leaf mass per ground area as shown in Table 3.2, by multiplying with canopy coverage percentage of each tree species and leaf area index (LAI) determined by IFS (Integrated Forest Study) on the Adirondack (Jonhson and Lindberg, 1992).

mercury budget in the forest ecosystem, all the litterfall was considered to occur only during October.

3.4.6 Hg in soil evasion

The flux of GEM emitted from the forest floor from 2004 through 2006 was estimated using an empirical model developed by Choi et al. (2009) at a 1h resolution:

$$F_{leaf-off} = a[R_s] + bEXP(c[T_A])$$

$$F_{leaf-on} = a' + \frac{b'EXP(c'[T_A] - 1)}{c'}$$

Where $F_{leaf\text{-}off}$ is Hg emission rate during leaf-off period (April and November) (ng Hg m^{-2} h^{-1}); $F_{leaf\text{-}on}$ is Hg emission rate during leaf-on period (May to October) (ng Hg m^{-2} h^{-1}); R_s is solar radiation reaching the forest floor (W m^{-2}); T_A is ambient air temperature (^{0}C); coeffients (a=0.0068, b=0.075, c=0.169; a'=0.108, b'=0.0718, c'=0.0814) were developed from meteorological data of the EPA's CASTNET HWF site (HWF187).

The GEM emissions from soil are assumed to be zero during winter (December to March) due to snow cover. The GEM flux from the soil was considered to be zero during precipitation events. Mercury evaporation is suppressed and net mercury flux was nearly zero or slightly negative during precipitation events (Choi et al., 2009).

3.4.7 Hg transport in soil water

The following conceptual model (Figure 3.3) demonstrates the computation approach used to calculate mercury transport in soil water. Net mercury change in soil water was considered as the result of THg flux in soil surface infiltration flow subtracting THg flux in vertical matrix flow out of the soil bottom layer and soil transpiration. Mercury loss from the forest floor through soil

water transport was calculated as the total of THg fluxes in soil surface runoff, soil transpiration and vertical matrix flow out of the lowest layer of soil.

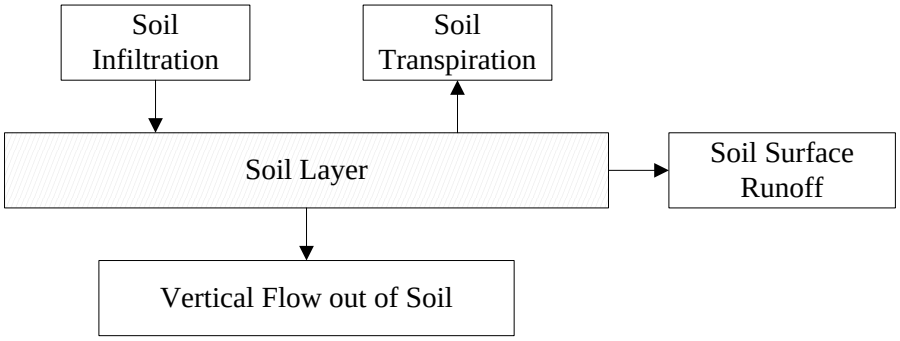

Figure 3.4 The conceptual framework of mercury in soil water used in this study.

To estimate temporal and spatial variations of Hg in soil water, soil water movement at the HWF from January 2004 to June 2006 was simulated using a hydrological model BROOK90 version 4.5. BROOK90 is a bucket hydrological model that simulates vertical soil water movement and evapotranspiration for land surfaces using a process-oriented approach with physically-meaningful parameters (http://home.roadrunner.com/~stfederer/brook/brook90.htm; Federer, 2002; Federer et al., 2003). Simulations made by BROOK90 separate soil transpiration and soil evaporation. The model estimates water movement between soil layers by integration using Darcy's Law and variable time-steps (Figure 3.5).

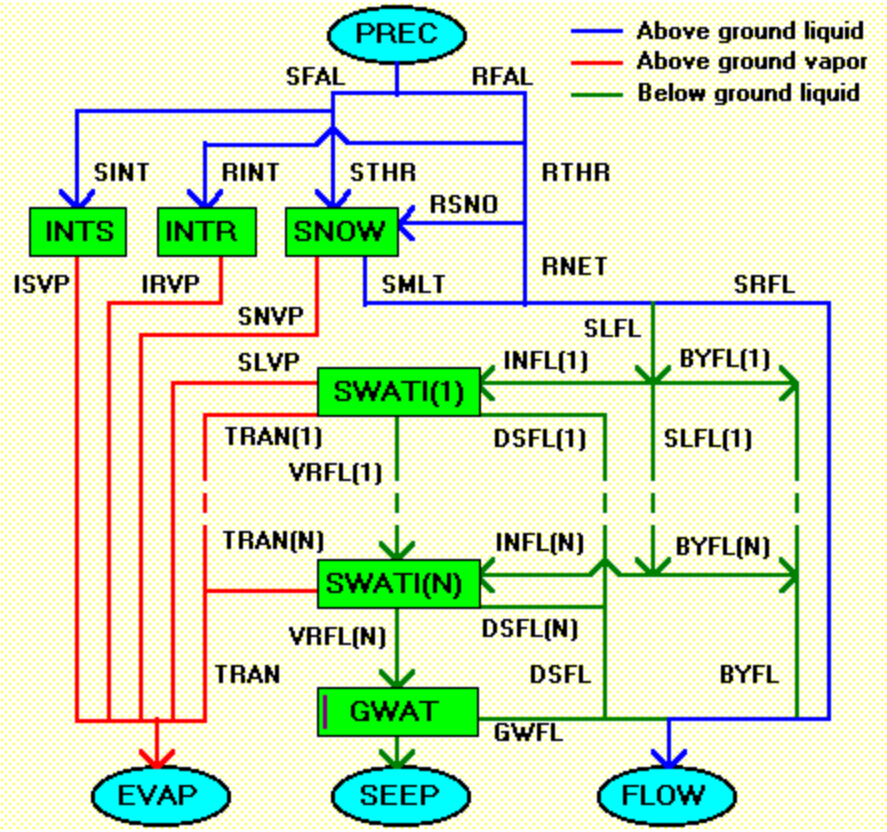

Figure 3.5 The flow chart of the BROOK 90 simulation
(http://home.roadrunner.com/~stfederer/brook/brook90.htm)

Input data files of BROOK 90 include precipitation, maximum and minimum temperature, daily solar radiation, vapor pressure, and wind speed in daily interval from January 2004 to June 2006, which were obtained from USEPA CASTNET. Physical parameters for the HWF for location, infiltration, drainage, canopy and soil previously determined by Mitchell et al. (2001) were used in the simulation. The eight soil layers were used in the simulation.

Table 3.3 Soil parameters used in BROOK90 simulation for the HWF.

LAYER	THICK	STONEF	PSIF	THETAF	THSAT	BEXP	KF	WETINF	Horizon
1	80	0	-12	0.32	0.9	6	2	0.92	O
2	35	0.05	-12	0.23	0.61	3.5	2	0.92	A
3	45	0.18	-12	0.44	0.71	7	2	0.92	E
4	42	0.15	-10	0.25	0.68	5	2	0.92	Bh
5	77	0.18	-10	0.25	0.64	5	2	0.92	Bhs
6	113	0.28	-10	0.25	0.61	5	2	0.92	Bs1
7	125	0.28	-10	0.2	0.47	5	2	0.92	Bs2
8	139	0.32	-10	0.2	0.47	5	2	0.92	Bs3

THICK: vertical thickness of each soil layer, mm.

STONEF: the stone volume fraction in each soil layer.

PSIF: water potential at field capacity for each layer, kPa.

THETAF: water content (volume fraction) at field capacity for each soil layer.

THSAT: matrix porosity of each layer.

BEXP: the negative slope of the log psi, ranges from 3 for very coarse soil to 12 for very fine soil

KF: hydraulic conductivity at field capacity for each layer, mm/d

WETINF: wetness at the inflection point in the Clapp-Hornberger (1978) equation.

BROOK90 estimates surface runoff as the rate of overland flow from a constant impervious area fraction and a variable saturated source area fraction determined by soil wetness and parameters (http://home.roadrunner.com/~stfederer/brook/brook90.htm). The model calculates the infiltration rate into soil surface as the liquid reaches soil surface minus soil overland flow. Vertical flow out of the deepest soil layer is calculated using a gravity gradient. Soil transpiration of each layer is distributed as the lesser of Shuttleworth-Wallace potential transpiration and the maximum supply rate of water by the roots which is determined by root parameters, the canopy parameter and the soil water potential in each layer.

Outputs of the model (daily surface runoff, infiltration rate into soil surface, vertical matrix flow out of the deepest soil layer, soil transpiration flow and soil water content in each soil horizon) were multiplied by monthly Hg concentrations in soil water of each soil horizon to evaluate mercury transport in soil water. The loss of THg flux of the forest soils via water transport (surface water runoff mercury + mercury in vertical out flow + mercury in soil transpiration) and net THg flux accumulated in the soil via water transport (infiltration mercury – surface water runoff mercury – mercury in vertical out flow – mercury in soil transpiration) were analyzed for the HWF. The THg concentrations for soil horizons (E, Bhs) without lysimeters were estimated by interpolation of THg concentrations at measured soil horizons (Oa, Bh, and Bs2).

4. Results

4.1 Wet deposition

During 2004 to 2011, the THg concentration in precipitation at the HWF ranged from 0.24 to 53.97 ng L^{-1}. Monthly mean THg flux and cumulative flux in precipitation averaged from 2004-2011 is shown in Figure 4.1. The cumulative mean THg flux in precipitation during growing season (May to October) is 4.05 ug m^{-2} yr^{-1}, and 2.28 ug m^{-2} yr^{-1} during non-growing season (November to April), contributing to an annual cumulative THg flux of 6.33 ug m^{-2} yr^{-1}. The THg fluxes in precipitation at the HWF during 2004 to 2011 did not show significant inter-annual difference (standard error for annual THg fluxes: ± 0.55 ug m^{-2} yr^{-1}).

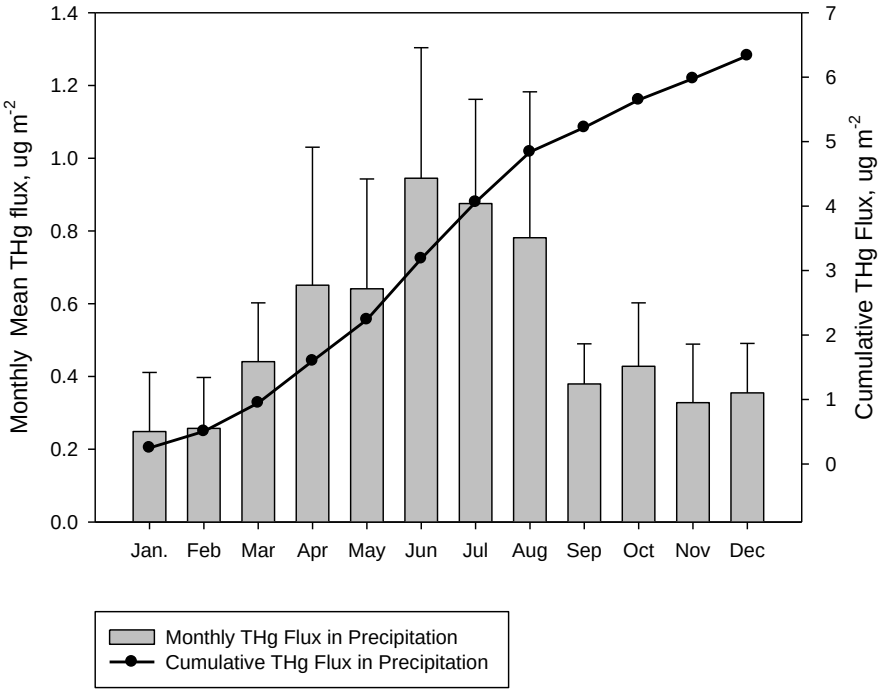

Figure 4.1 Monthly THg fluxes and cumulative fluxes in precipitation at the HWF (mean values for the period 2004-2011; error bars represent for the standard errors of the monthly THg fluxes for the study period).

4.2 Dry deposition

4.2.1 Inferential method

The ranges of measured concentrations of GEM, GOM and PBM at the HWF for the study period were 0.38 - 3.38 ng m^{-3} (mean 1.32), 0 - 43.53 ng m^{-3} (mean 1.27), and 0 - 102.40 ng m^{-3} (mean 4.32), respectively. The ranges of deposition velocities of GEM, GOM, and PBM at the HWF simulated by CMAQ for the year 2009 were 0 - 0.21 cm s^{-1}, 0 - 4.16 cm s^{-1}, and 0.05 - 0.13 cm s^{-1}, respectively. THg flux in dry deposition estimated by measured concentrations and CMAQ deposition velocities was 17.24 μg m^{-2} yr^{-1} for the year 2009, vast majority of which is contributed by GEM deposition (17.05 μg m^{-2} yr^{-1}). The annual cumulative GOM and PBM flux

in dry deposition is 0.14 μg m^{-2} yr^{-1} and 0.05 μg m^{-2} yr^{-1}, respectively. The flux of mercury in dry deposition is highest during spring (April and May) and summer (June to August) (Figure 4.2).

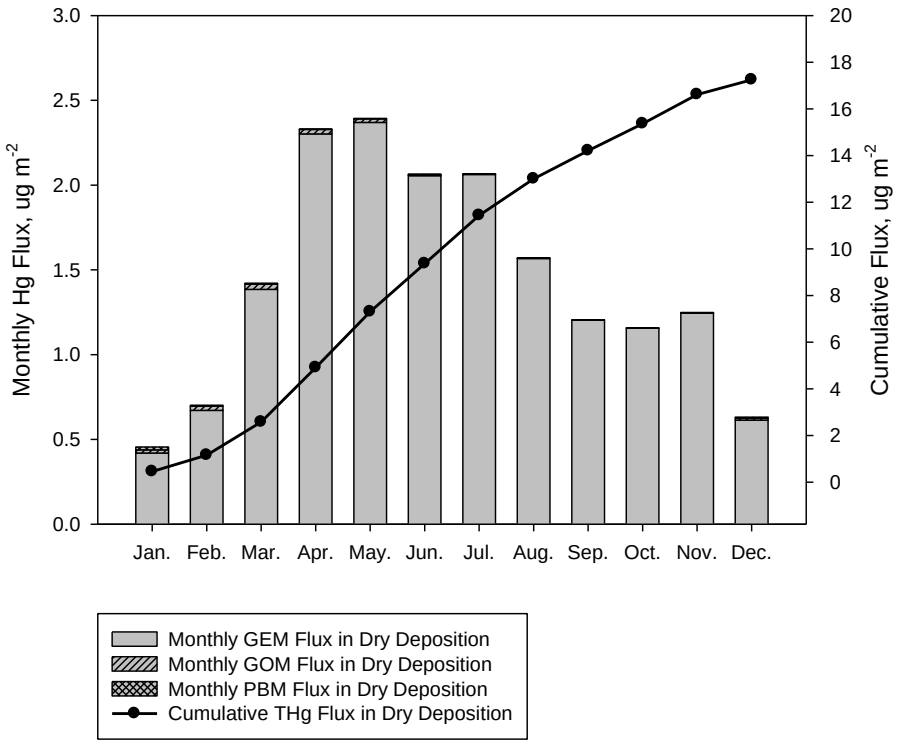

Figure 4.2 The monthly and cumulative fluxes in dry deposition of Hg species at the HWF (estimated by measured concentrations and deposition velocities simulated by CMAQ).

4.2.2 Stomatal uptake of GEM

The estimate of dry mercury deposition according to the depletion of measured GEM concentrations indicates that cumulative leaf uptake of GEM was 7.56 μg m^{-2} yr^{-1} during growing season, and the largest monthly leaf uptake occurred in July (Figure 4.3).

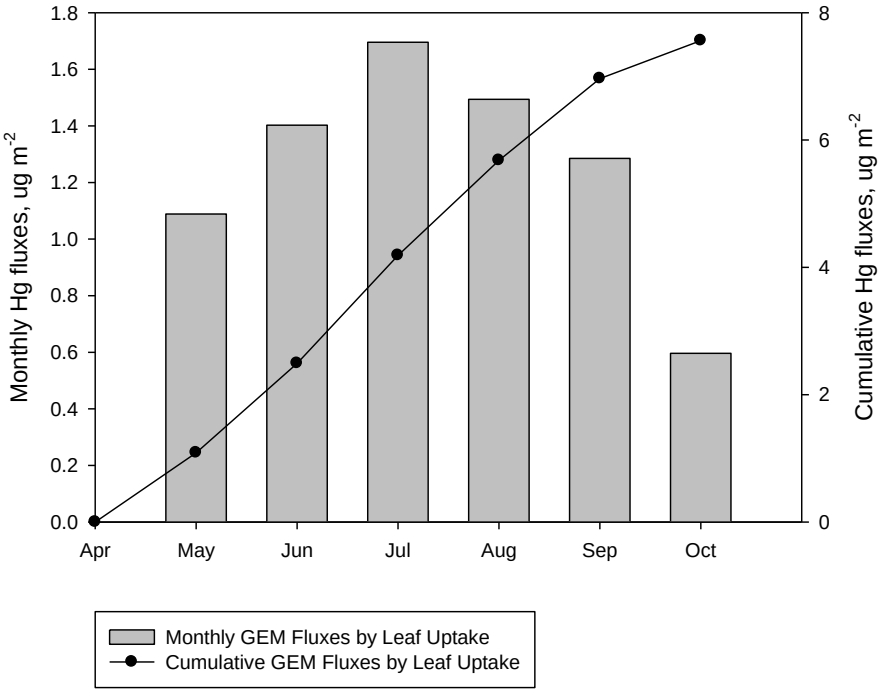

Figure 4.3 The monthly and cumulative Hg fluxes in leaf uptake at the HWF (estimated by measured GEM depletion).

4.3 Throughfall and net throughfall

Average cumulative THg flux in throughfall at the HWF during the growing season and non-growing season through 2004-2006 is 4.91 ug m^{-2} and 2.05 ug m^{-2}, respectively, contributing to a total annual THg flux in throughfall of 6.96 ug m^{-2} yr^{-1} (Figure 4.4). Throughfall during winter period (December to March) was not considered in this calculation due to the absence of canopy cover.

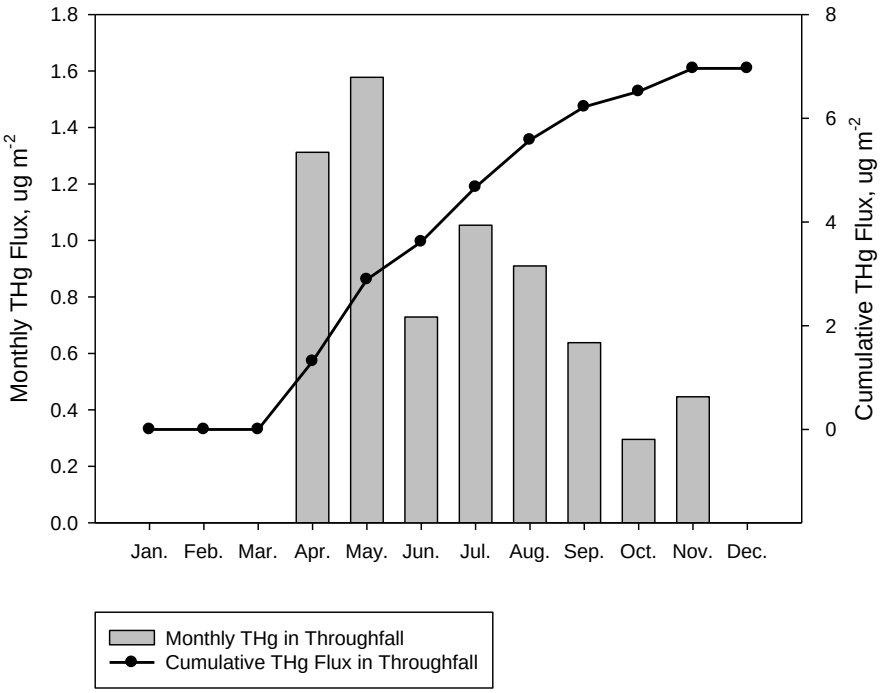

Figure 4.4 The monthly and cumulative THg fluxes in throughfall at the HWF.

Net throughfall mercury (throughfall mercury – precipitation mercury) over an annual period at the HWF is shown in Figure 4.5 as the monthly mean for 2004-2006. For individual months with calculated net throughfall mercury that was negative, the net throughfall mercury was assumed to be 0. The negative result of the net throughfall mercury calculation is thought to be due to uncertainties in the measurements of throughfall mercury and precipitation mercury.

THg fluxes in throughfall were assumed to be equal to the THg fluxes in precipitation during winter period. Net throughfall mercury during the growing season and the non-growing season at the HWF was 1.30 ug m^{-2} and 0.76 ug m^{-2}, respectively, contributing to a total annual THg flux in net throughfall of 2.06 ug m^{-2} yr^{-1}.

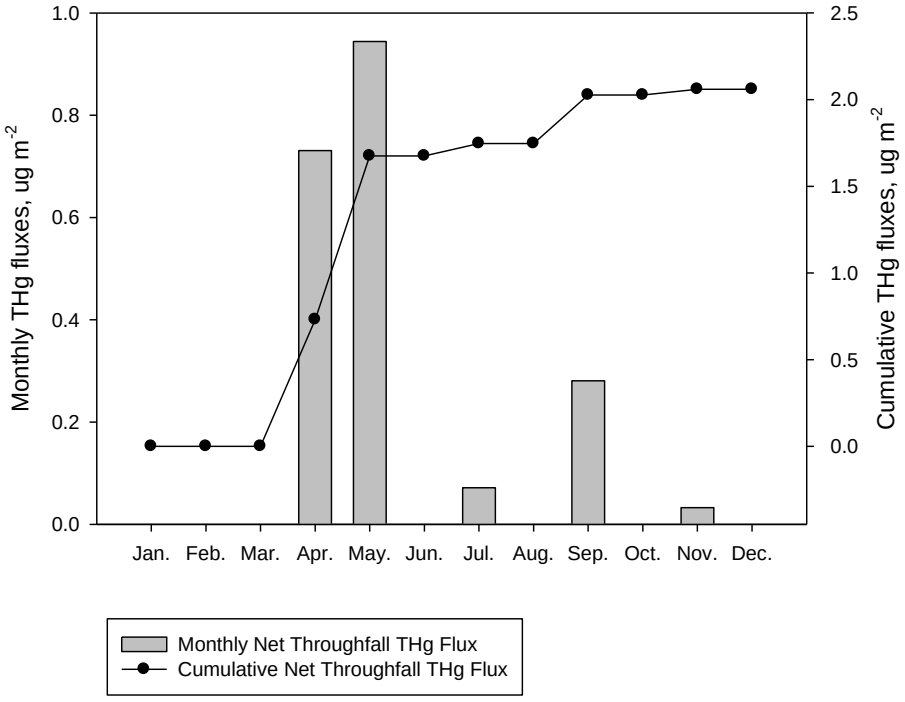

Figure 4.5 The monthly and cumulative net throughfall THg fluxes at the HWF (mean values for the period 2004-2006).

4.4 Foliar mercury accumulation and litterfall

The foliar mercury accumulation through growing season for yellow birch, sugar maple and American beech is 0.12, 7.28 and 9.30 μg m^{-2} yr^{-1}, respectively, contributing to a total foliar mercury accumulation of 16.7 ug m^{-2} yr^{-1} at the HWF. Mean THg fluxes in litterfall estimated as the average of year 2004 and 2005 were 0.16, 7.97, and 9.06 ug m^{-2} yr^{-1} for yellow birch, sugar maple and American beech respectively (based on the estimation of Bushey el al. 2008), composing a total litterfall THg flux of 17.2 ug m^{-2} yr^{-1} at the HWF. The estimated total mercury contents in foliage and litter at the HWF are shown in Table 4.1. The estimates of foliar mercury accumulation and litterfall mercury deposition at the HWF were comparable, while both were considerably higher than the estimate of stomatal uptake of GEM by measurements of GEM depletion during the growing season (7.6 ug m^{-2} yr^{-1}, discussed in section 3.4.2 and 4.2.2).

Table 4.1 Foliar THg accumulation rates, fluxes and litter THg fluxes over growing season at the HWF.

	YB	**SM**	**AB**	**Overall Forest**
Foliar THg accumulation rate (ng g^{-1} day^{-1})	0.21	0.23	0.35/ 0.47 (over/ under story)	NA
Foliar THg accumulation flux (μg m^{-2} yr^{-1})	0.12	7.28	9.30	16.7
Litter THg flux (μg m^{-2} yr^{-1})	0.16	7.97	9.06	17.2
Growing season GEM depletion (μg m^{-2} yr^{-1})	NA	NA	NA	7.6

4.5 Soil mercury evasion

Using the empirical model with meteorological data derived from US EPA CASTNET (HWF 187), GEM emissions from the forest floor were estimated at a 1 h resolution from January 2004 to December 2006. The estimated cumulative Hg fluxes in soil evasion for 2004, 2005 and 2006 are similar: 6.16, 6.91, 6.28 ug m^{-2} yr^{-1}, respectively, contributing to a mean cumulative Hg flux of 6.45 ug m^{-2} yr^{-1}. Mean monthly Hg fluxes in soil evasion were estimated by averaging the three year's data, reflecting the major contribution of Hg emission from the soil during April to September (Figure 4.6).

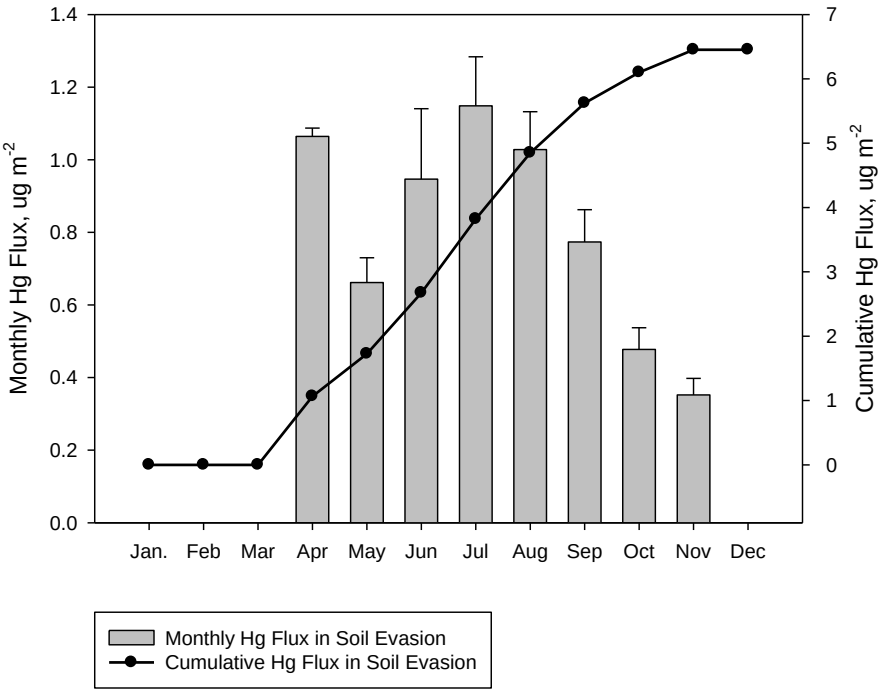

Figure 4.6 Estimated monthly Hg fluxes and cumulative Hg fluxes in soil evasion at the HWF.

4.6 Mercury in soil water

Soil water movement from January 2004 through June 2006 was simulated using BROOK 90 for Huntington Wildlife Forest. The comparison between the simulated stream flow (BROOK 90) and the measured stream flow on the HWF reveals that BROOK 90 simulates hydrology at the HWF considerably well (Figure 4.7).

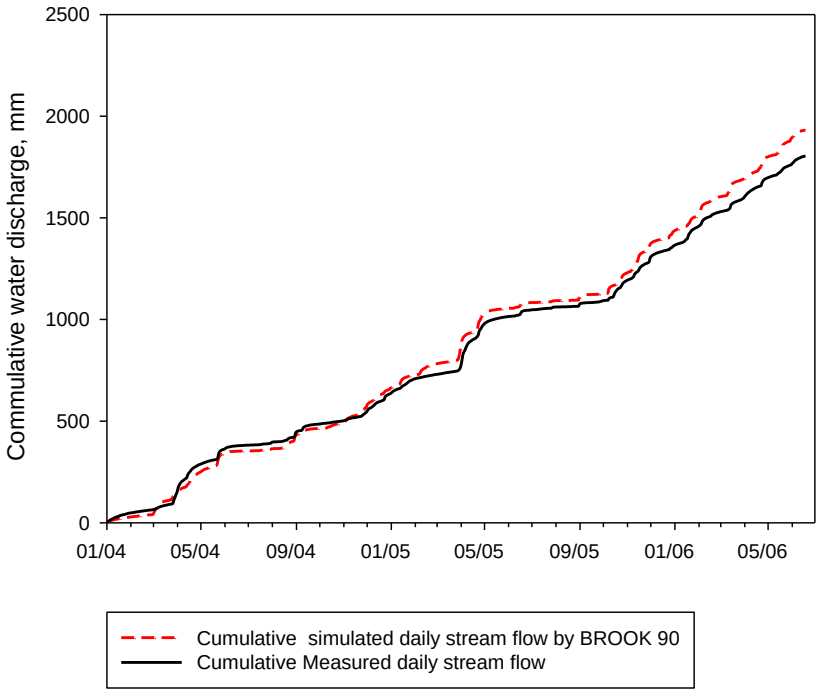

Figure 4.7 The comparison between BROOK 90-simulated steam flow and measured stream flow at the HWF over the study period.

The simulation of BROOK 90 on soil water transport reveals that there is no significant difference between the growing season and the non-growing season in soil surface infiltration at the HWF for the study period (growing season 510 mm, non-growing season 447 mm; Figure 4.8). In contrast, soil leaching flow (vertical flow out of the deepest soil layer) and soil transpiration had significant seasonal variations at the HWF. Soil leaching flow over the growing season (143 mm) was considerably lower than the non-growing season (412 mm) while soil transpiration (water uptake by the roots) was considered to occur only during the growing season (336 mm; May to October).

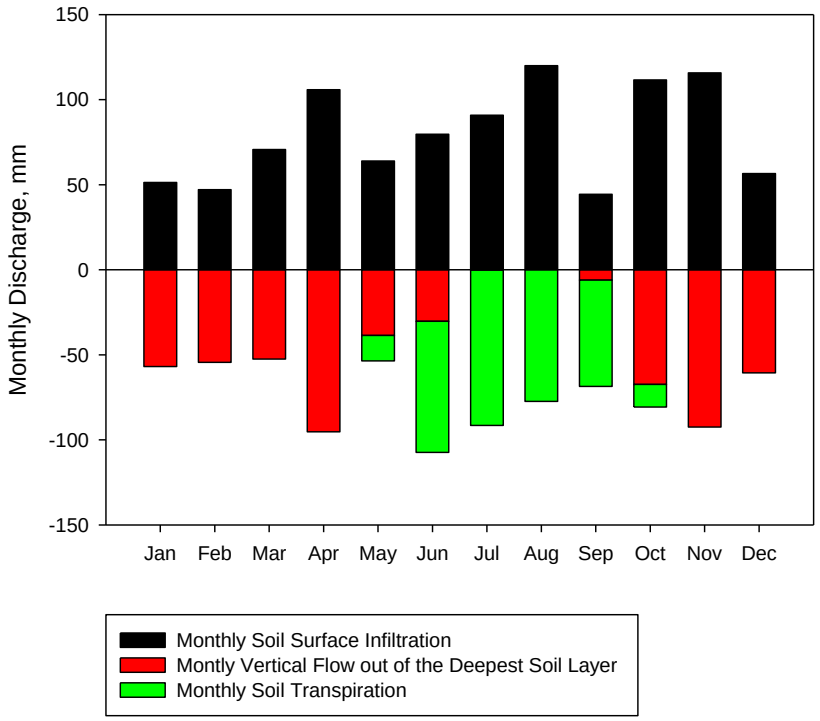

Figure 4.8 Monthly in and out flows (mm) for the HWF soils over 12-month period (mean values of the monthly flows simulated by BROOK90 for the period 2004-2006; positive values represent for input flows, and negative values represent for output flows for the soil).

The estimated storage of mercury in soil solutions to a soil depth of 656 mm at the HWF is 0.50 µg m^{-2}. The mercury content in each soil horizon solutions (average values of the measurement period; Figure 4.9) indicates a decreasing pattern of solution THg pool with soil depth (ranging from 0.24 ug m^{-2} in O horizon to 0.03 ug m^{-2} in Bh3 horizon) and shows low THg concentrations in E and Bh horizon solutions. Both findings are in accordance with soil water mercury patterns reported in the literature (Hempel et al., 1995; Åkerblom et al., 2008).

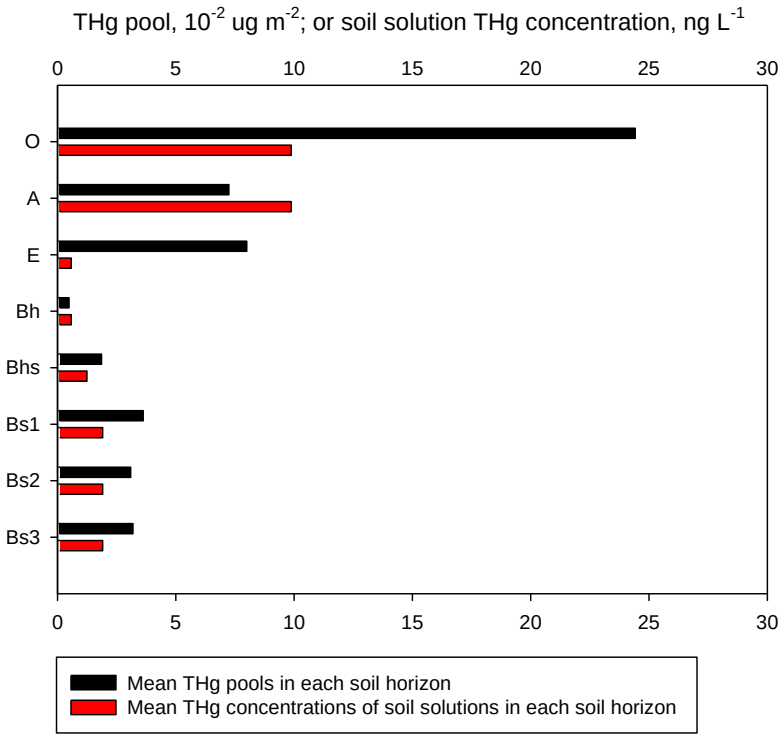

Figure 4.9 Horizontal patterns of mercury concentrations and pools in soil solutions at the HWF for 2004-2006.

The estimated THg fluxes in soil surface runoff, soil surface infiltration flow, soil transpiration and vertical flow out of the soil bottom layer are 1.67, 7.72, 2.00 and 1.11 μg m^{-2} yr^{-1}, respectively. Cumulative THg flux in soil surface infiltration during growing season (5.52 μg m^{-2}) is higher than non growing season (2.20 μg m^{-2}) while cumulative THg flux in vertical flow out of lowest soil layer during the non-growing season (0.86 μg m^{-2}) is higher than during growing season (0.25 μg m^{-2}). There was no significant difference between the cumulative THg fluxes in surface runoff during growing season (0.83 μg m^{-2}) and non-growing season (0.84 μg m^{-2}). The annual mercury loss of the forest floor through soil water transport is 4.78 ug m^{-2} yr^{-1} (the sum of mercury in surface runoff, soil transpiration, and soil vertical out flow). Mass budget on mercury in soil solutions suggests that mercury was retained in soil via water transportat with a net annual THg accumulation flux of 4.61 μg m^{-2} yr^{-1} (net mercury accumulation via water transport =

infiltration mercury – mercury in vertical out flow – mercury in soil transpiration; infiltration mercury was calculated as the product of simulated infiltration flow and measured throughfall mercury concentration; Figure 4.10). Net mercury accumulation in the forest soils via soil water transport over the growing season (3.27 µg m^{-2} yr^{-1}) was considerably higher than the non-growing seaon (1.34 µg m^{-2} yr^{-1}) at the HWF.

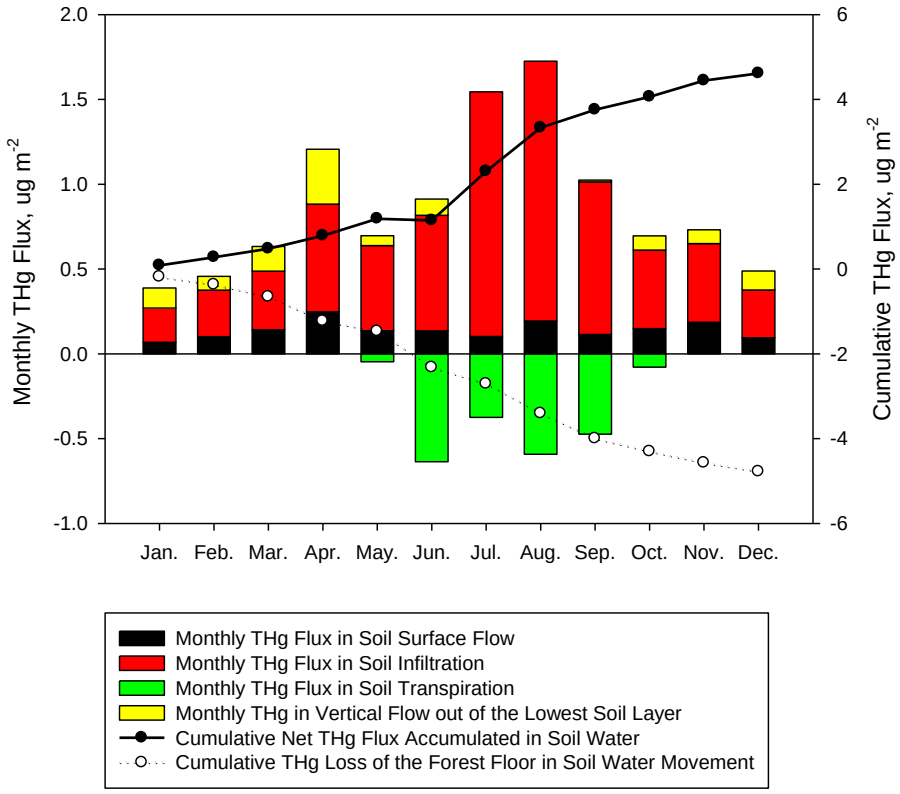

Figure 4.10 Monthly THg fluxes in vertical out flow, surface flow, soil transpiration, and soil surface infiltration; Cumulative net THg fluxes accumulated in soil water and cumulative THg loss of the forest floor through water transport; all the values are monthly mean values for the period 2004-2006.

5 Discussion

5.1 Comparison of foliage mercury uptake estimates at the HWF

Foliage mercury uptake during the growing season was estimated using the following three methods: direct estimate on mercury accumulation in fresh leaf tissue (accumulation rate of foliar Hg concentration × leaf mass per ground area); litterfall mercury deposition (litter Hg concentration × litter mass per ground area); and growing season GEM depletion plus mercury uptake via soil transpiration. The results of the three methods should, in theory, be consistent with one another.

In this study, measurement of foliar mercury accumulation over the growing season at the HWF was 16.7 μg m^{-2} yr^{-1}. Litterfall mercury deposition at the HWF was 17.2 μg m^{-2} yr^{-1}, similar to the estimate result of foliar mercury accumulation. The value of growing season GEM depletion plus soil transpiration at the HWF was 9.6 μg m^{-2} yr^{-1} (growing season GEM depletion 7.6 μg m^{-2} yr^{-1}, soil transpiration 2.0 μg m^{-2} yr^{-1}), considerably lower than the estimate results of foliar mercury accumulation and litterfall mercury deposition.

The consistency between the direct estimate on foliar mercury accumulation and the estimate of litterfall mercury deposition at the HWF can be partially attributed to the use of same biomass data (litter mass data analyzed by Bushey et al., 2008) for the two methods. However, canopy and litterfall biomass estimates for the hardwood forest at the HWF are comparable (Table 3.2). The discrepancy between the results of the direct estimate via foliage field measurements (foliar mercury accumulation and litterfall mercury deposition) and GEM depletion plus soil transpiration at the HWF could be due to multiple reasons as all the three estimate methods have substantial uncertainties. Uncertainties of the estimation from foliage measurements (foliar mercury accumulation or litterfall mercury deposition) are mostly likely due to uncertainty in the

quantity of leaf biomass for the major tree species at the HWF. The assumption of a constant (linear) foliar mercury accumulation rate could also affect the estimate of foliar mercury accumulation. In a field study, Rea et al. (2002) revealed smaller accumulation rates at the beginning and the end of the growing season, than in the middle of the growing season. Uncertainties of estimation of foliage mercury uptake at the HWF using the inferential method (growing season GEM depletion + soil transpiration) could be attributed to two major factors: an oversimplification of the inferential method in estimating GEM leaf uptake as it considers no changes in the atmosphere refill rate, leaf mercury uptake rate, and atmosphere boundary layer height over the estimation period (which is an unlikely scenario; several studies suggest that leaf mercury uptake rate varied during the growing season; many studies indicate that there is significant difference in atmosphere boundary layer height between day-time and night-time); and an overestimate of foliage mercury uptake via soil transpiration due to the exclusion of Hg in water uptake by roots (Bishop et al., 1998). Note that the flux of mercury associated with transpiration was estimated assuming complete uptake of soil solution mercury by roots, which is an unlikely occurrence. In addition, the assumption that GEM depletion is associated with foliage uptake might not be accurate, as the GEM depletion pattern could be largely affected by the complex atmospheric refill process rather than the process of foliar mercury uptake.

It is difficult to determine which estimate of the three methods used for foliage mercury uptake at the HWF is closer to the true value. All are within the reported range of foliage mercury accumulation (from 3 to 28 μg m^{-2} yr^{-1}) in the literature for North America (Rea et al., 2002; Graydon et al., 2006; Risch et al., 2012), and all could have substantial uncertainties (discussed above). Therefore the foliar mercury accumulation at the HWF probably falls between these estimates (9.6 - 17.2 μg m^{-2} yr^{-1}), and the exact value cannot be verified. I personally think the

estimate of litterfall mercury deposition at the HWF (~17 μg m^{-2} yr^{-1}) could best represent the foliage mercury uptake. Because both litter mercury concentrations and litter mass used in the litterfall mercury estimation were obtained through direct measurement at the HWF, whereas the other two estimations used several assumptions (discussed above), potentially leading to increased uncertainties.

5.2 Comparison of dry mercury deposition estimates at the HWF

Table 5.1 Comparison of the results of different estimate methods on dry mercury deposition at the HWF; unit, ug m^{-2}.

	Growing Season		Non-growing Season	
Litterfall – Soil transpiration	GEM	15.2		NA
Foliar accumulation – Soil transpiration	GEM	14.7		NA
GEM depletion	GEM	7.6		NA
Inferential method (measured atmospheric mercury concentrations × CAMQ deposition velocities)	GEM	10.4	GEM	6.6
	GOM +PBM	~ 0	GOM+PBM	~ 0.2
Throughfall - Precipitation	GOM+PBM	1.3	GOM+PBM	0.8

5.2.1 Dry deposition of GEM at the HWF

Dry deposition of GEM at the HWF over growing season could be estimated using the following three methods: 1) the inferential method (measured concentration × modeled deposition velocity); 2) the stomatal GEM uptake estimated by measurements of GEM depletion; and 3) foliar mercury uptake lessing mercury uptake flux in soil transpiration from foliage mercury uptake flux (Table 5.1).

Multiple studies have suggested bidirectional mercury exchange between foliage and the atmosphere where following uptake mercury could be reemitted to the atmosphere via

photoreduction or revolatilization on leaf surfaces (Graydon et al., 2006; Zhang et al., 2009). The calculation of dry deposition by the inferential method (measured air concentrations and CAMQ estimated deposition velocities) is one-directional without the consideration of mercury reemission.

The stomatal uptake of GEM at the HWF was 15.2 μg m^{-2} yr^{-1}, estimated by subtracting mercury uptake flux in soil transpiration (2.0 μg m^{-2} yr^{-1}) from litterfall mercury deposition (17.2 μg m^{-2} yr^{-1}). Given the discussion in section 5.1 that mercury flux in soil transpiration at the HWF is likely an overestimation, the stomatal uptake of GEM was probably higher than 15.2 μg m^{-2} yr^{-1} but no more than 17.2 μg m^{-2} yr^{-1}.

The stomatal uptake of GEM estimated by the growing season GEM depletion at the HWF was 7.6 μg m^{-2} yr^{-1}, considerably lower than the estimate above (litterfall mercury deposition – mercury flux in soil transpiration). The estimate of stomatal mercury uptake by GEM depletion could have substantial uncertainties (discussed in section 5.1). The discrepancy indicates that the stomatal uptake of GEM using measured GEM concentrations at the HWF was likely underestimated to some extent.

One-directional dry deposition of GEM over growing season estimated by the inferential method (measured concentration × CMAQ simulated deposition velocity) was 10.4 μg m^{-2} yr^{-1} at the HWF. In a model assessment for the Great Lakes region, Zhang et al. (2012) suggested that the transport model CMAQ likely underestimates the night-time deposition velocities of GEM. It would seem that calculations of dry deposition for GEM as well as GOM+PBM using the inferential method are underestimates of the true value. This pattern is suggested because net estimates by foliar litter fluxes (for GEM) and net throughfall (for GOM+PBM) are greater than the one directional fluxes obtained from the inferential method (Table 5.1).

5.2.2 Dry deposition of GOM+PBM at the HWF

Dry deposition of GOM+PBM at the HWF was estimated using two methods: the inferential method (measured concentration × modeled deposition velocity); and net throughfall method (subtracting measured mercury flux in precipitation from measured mercury flux in throughfall; Table 5.1).

There could be substantial uncertainties in estimating GOM+PBM dry deposition by the inferential method (measured concentration × modeled velocity) in this study. Zhang et al. (2012) suggested that modeled dry deposition of GOM+PBM with CMAQ for the Great Lakes region revealed similar deposition velocities to values obtained from experimental measurements. The uncertainty of measurements of atmospheric mercury concentration could be considerable due to multiple factors such as the consistency of measurement methods, sampling frequency, meteorological factors, and the distance from the emission sources (Driscoll et al., 2007a; Landis et al., 2002; Lyman et al., 2007). In this study, a single senser was placed at the canopy of the HWF for the measurement of atmospheric mercury concentrations. The measured concentrations of GEM at the HWF used in this study were greater than the analytical detection limit (0.1 ng m^{-3}, provided by Huang et al., 2010) while the measured concentrations of GOM and PBM were intermittently (46% and 7% of the study period, respectively) below the detection limits (0.46 and 0.10 pg m^{-3}, respectively), indicating the likely underestimation of GOM and PBM concentrations. The resulting one-directional dry deposition of GOM+PBM estimated by the inferential method was 0.2 μg m^{-2} yr^{-1}, considerably lower than the estimate of net throughfall mercury (2.1 μg m^{-2} yr^{-1}). It indicates that the dry deposition of GOM+PBM at the HWF calculated by the inferential method was probably underestimated (also discussed in section 5.2.1).

5.3 Mercury mass balance at the HWF

5.3.1 Mercury mass balance for the forest canopy

A mercury mass balance of the forest canopy was only conducted for the growing season due to the absence of deciduous foliage during non-growing season (Figure 5.1). Foliar uptake of GEM during growing season (estimated by foliar mercury accumulation subtracting mercury uptake via soil transpiration) was used as the net dry deposition of GEM in the mass budget at the HWF. The net throughfall mercury was used as the net dry deposition of GOM+PBM at the HWF.

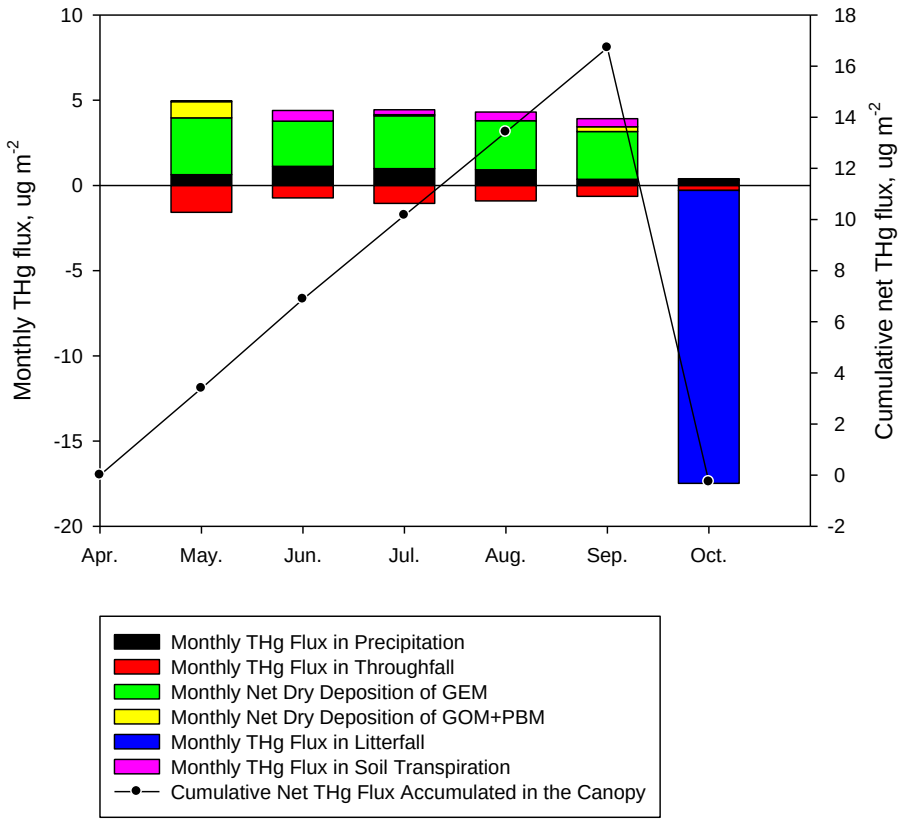

Figure 5.1 The mass balance for mercury in the forest canopy: the monthly Hg fluxes (positive flux represents input, negative flux represents output) in precipitation, throughfall, net dry deposition of GEM, net dry deposition of GOM+PBM, litterfall, and soil transpiration; and cumulative net THg fluxes accumulated in the forest canopy.

During growing season, the total input of mercury to the canopy at the HWF was 22.1 μg m^{-2} yr^{-1} on an annual basis. Foliar uptake of GEM was the largest single source of mercury to the canopy (67% of the total input), while the other sources had smaller contributions (precipitation 18%, net dry GOM+PBM deposition 6%, soil transpiration 9%). The total output of mercury from the canopy during growing season was 22.4 μg m^{-2} yr^{-1}. Litterfall was the predominant mercury output pathway for the canopy (77%), while throughfall was a less important pathway (23%). Net mercury flux in the forest canopy at the HWF increased through the growing season until litterfall occurred (Figure 5.1), indicating that the canopy was a temporary sink for mercury during leaf-on period. Ideally, the net mercury flux in the canopy through the growing season should be zero, because the canopy coverage will be lost through litterfall at the end of the growing season. The estimated total mercury input (22.1 μg m^{-2} yr^{-1}) and output (22.4 μg m^{-2} yr^{-1}) over growing season were consistent for the canopy at the HWF.

5.3.2 Mercury mass balance for the forest floor

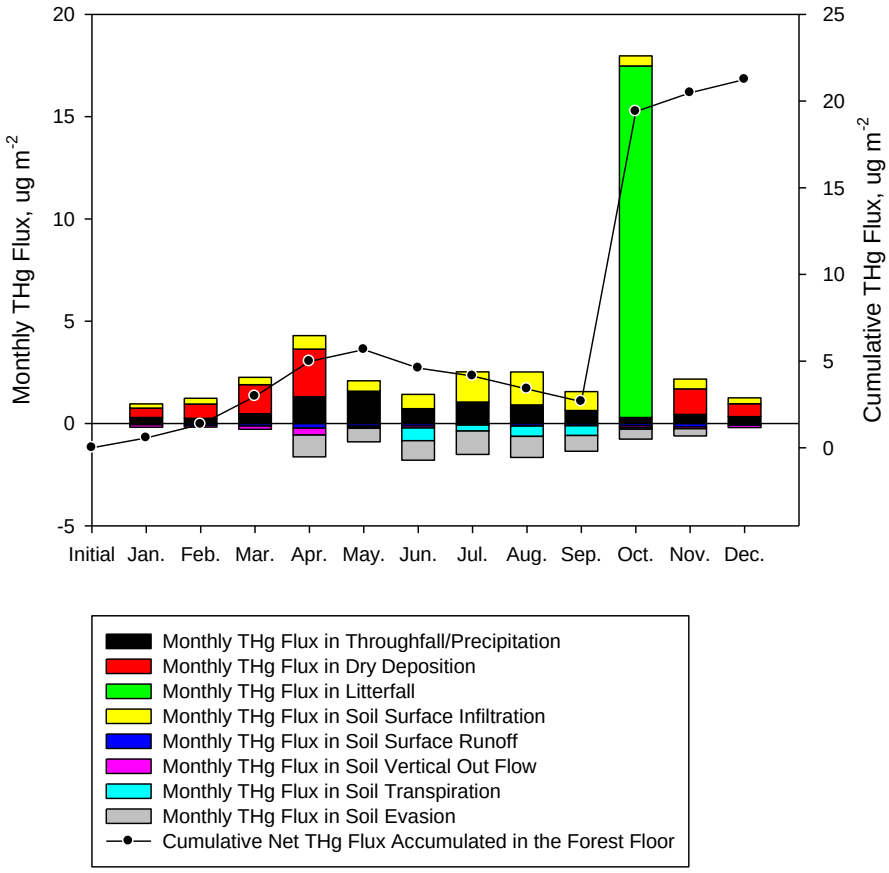

Figure 5.2 The mass balance of mercury for the forest floor: the monthly THg fluxes in dry deposition during the non-growing season, throughfall/precipitation, and litterfall during the growing season, soil surface infiltration, soil surface runoff, vertical matrix flow out of the lowest soil layer, soil transpiration, and soil evasion; cumulative net THg fluxes accumulated in the forest floor.

Mass balance for mercury on the forest floor at the HWF is shown in Figure 5.2. Both wet and dry atmospheric mercury were considered to deposit directly to the forest floor during winter (December to March) due to the absence of canopy cover during the period. Dry mercury deposition estimated by the inferential method (measured concentrations × modeled deposition velocities) was used as an input for the mass budget during the non-growing season.

The mass balance suggests that the total mercury input to the forest floor at the HWF was 32.2 μg m^{-2} yr^{-1} on an annual basis. Litterfall (17.2 μg m^{-2} yr^{-1}) was the most important mercury source to the forest floor, contributing to 53% of the mercury inputs. The other mercury sources were less important (throughfall/precipitation 26%, dry deposition during the non-growing season 21%). The total mercury output of the forest floor at the HWF was 11.2 μg m^{-2} yr^{-1}. Soil evasion (6.5 μg m^{-2} yr^{-1}) was the most important mercury export mechanism, contributing to 57% of the mercury outputs; while the other sources had smaller contributions (soil transpiration 18%, soil surface runoff 15%, soil vertical out flow 10%).

The pattern of cumulative net mercury flux varied over the 12-month period was shown in Figure 5.2. Net mercury flux to the forest floor at the HWF increased through the non-growing season (November to April). The increasing net mercury flux was mostly attributed to the low mercury flux from soil evasion and soil transpiration during the non-growing season. During the growing season, net mercury flux in the forest floor decreased until litterfall occurred. The decreasing net mercury flux through leaf-on period was predominantly caused by the high soil mercury evasion at the HWF.

Net mercury accumulation in the forest floor on an annual basis was 21.0 μg m^{-2} yr^{-1} at the HWF. Vast majority of the net mercury accumulation (82%) was attributed to litterfall mercury deposition; the other net accumulation (18%) was contributed by mercury retention via soil water transport.

5.3.3 Mercury mass balance for the overall forest ecosystem

The mercury mass balance for the overall forest ecosystem suggests the total atmospheric mercury deposition at the HWF was 29.2 μg m^{-2} yr^{-1}. The estimated dry mercury deposition (78%) was significantly higher than wet mercury deposition (22%). The total mercury output

from the forest ecosystem at the HWF was 9.2 μg m^{-2} yr^{-1}. Soil evasion (70%) was the most important mercury export mechanism for the forest ecosystem, while the other export pathways had smaller contribution (soil surface runoff 18%, vertical flow out of the lowest soil layer, 12%). Mercury was found to be retained in the HWF forest ecosystem with a net THg flux of 20.0 μg m^{-2} yr^{-1}, accounting for 68% of the atmospheric deposition, suggesting the forest ecosystem is a net sink for atmospheric mercury.

The total input of mercury over the growing season (20.1 μg m^{-2}) was higher than the non-growing season (9.1 μg m^{-2}), because both wet deposition and dry deposition were higher during growing season. The total output of mercury over the growing season (6.1 μg m^{-2}) was higher than the non-growing season (3.1 μg m^{-2}) as well, mostly caused by the considerably higher soil mercury evasion over the growing season. The Hg losses by drainage water were greater during the non-growing season (1.7 μg m^{-2}) than the growing season (1.1 μg m^{-2}), which has important implications for the transport of Hg to downstream zones of methylation. The net mercury flux accumulated in the forest ecosystem over the growing season (14.0 μg m^{-2}) was higher than the non-growing season (6.0 μg m^{-2}).

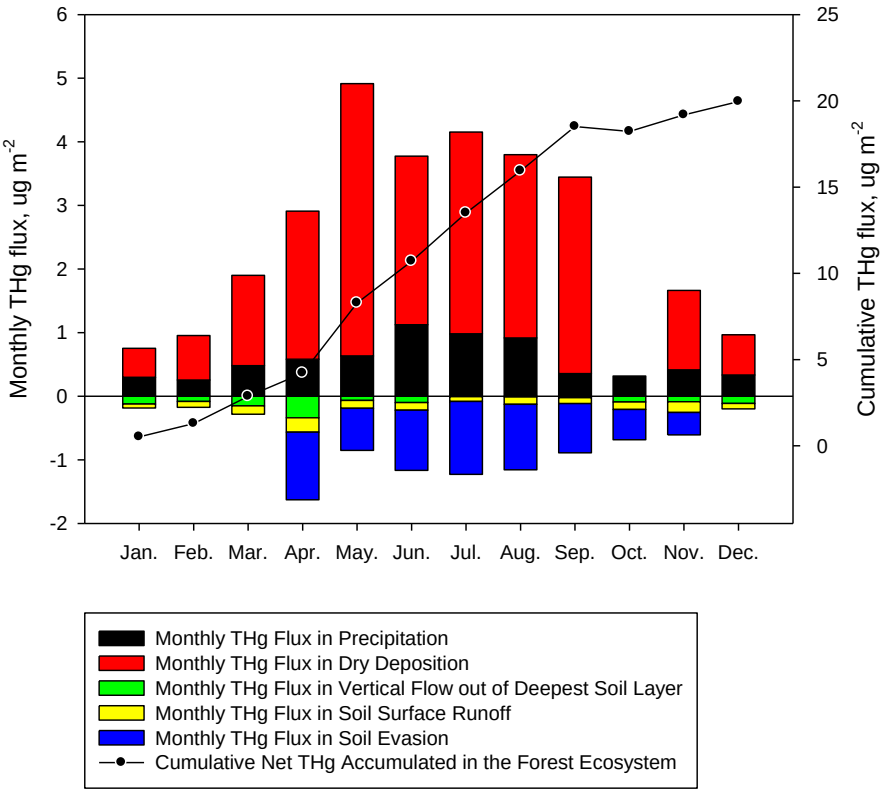

Figure 5.3 The mass balance for mercury in the overall forest ecosystem: the monthly THg fluxes in precipitation, dry deposition, soil evasion, soil surface runoff, and vertical matrix flow out of the lowest soil layer; cumulative net THg fluxes accumulated in the forest ecosystem.

5.3.4 Data limitations to mercury mass budgets at the HWF

Although comprehensive analysis of mercury cycling was made for the HWF in this study, there could be some uncertainties in the mercury mass budgets due to the data limitations.

Seven-year data (2004-2011) for wet mercury deposition at the HWF were analyzed in this study; however, time periods of the other original data were variable and were all shorter than the seven-year period of the wet deposition data (Table 3.2), restricting the analysis on the interannual variations of mercury cycling at the HWF. The mercury mass balance at the HWF (discussed in the above sections) indicates that litterfall mercury deposition and soil mercury evasion were relatively important mercury cycling processes. However, only 2-year litterfall data

for the HWF (2004 and 2005) were available in this study; soil mercury evasion at the HWF was only estimated for the period 2004-2006 and the empirical model used for estimating soil evasion neglected winter soil evasion due to snow cover (few winter measurements have been made for soil mercury evasion at the HWF), which is likely to cause underestimations. Therefore, long-term studies on litterfall mercury deposition, soil mercury evasion (especially for winter period study), and mercury transport in soil water (to make comparison with wet mercury deposition) are needed in future to complement the analysis on mercury cycling at the HWF.

Nevertheless, in this study, the mercury mass balance (discussed in the above sections) would be considered to depict the actual mercury cycling conditions at the HWF for the study period appropriately. Because wet mercury deposition at the HWF showed no remarkable interannual variations (6.3 ± 0.5 μg m^{-2} yr^{-1}) for the period 2004-2011 (Figure 4.1), indicating that mercury cycling was not likely to have significant interannual differences for the study period.

5.4 Comparison of mercury cycling at the HWF with other studies

Many studies have investigated the individual mercury cycling processes in terrestrial ecosystems. However, comprehensive investigations of mercury exchange of air-plant-soil systems are limited. Smith-Downey et al. (2010) developed a global terrestrial mercury model (GTMM) to quantify the mercury cycling processes between atmosphere and soil on global scale. They examined the impacts of anthropogenic emissions on soil mercury dynamics in the framework of soil carbon cycling. A comparison between the mercury cycling processes at the HWF and other studies (including GTMM estimation, as well as several other studies of individual mercury cycling processes) is shown in Table 5.2.

Table 5.2 Comparison of the mercury cycling processes at the HWF and other studies.

	Wet Deposition	Dry Deposition		Foliage Uptake	Surface Emission		Water Runoff
This Study HWF, NY, USA	**6.3**	**THg**	**22.9**	**17.2**	**Soil**	**6.5**	**2.8**
		GEM	20.6		soil respiration	0.9	
		GOM+PBM	2.3		soil revolatilization + photoreduction	5.6	
Terrestrial system[2], Global scale (a)	**5.3**	**THg**	**16.6**	**8.3**	**Soil + Leaf**	**19.6**	**2.6**
		GEM	9.3		soil respiration	5.0	
		GOM	7.3		revolatilization	7.2	
					photoreduction	7.4	
Mixed-hardwood forest, VM, USA (b)	**9.0**	THg	**18.4**	**15.8**			
		GEM	15.8				
		GOM+PBM	2.6				
Deciduous forest, ON, Canada (c)	**3.1**	**THg**	**10.7**	**9.3**			
		GEM	9.3				
		GOM+PBM	1.4				
Deciduous forests, Eastern USA (d)	**4.4-19.4** (median 9.6)			**3.5-24.3** (median 12.3)			
Several land cover types, Great Lakes Basin (e)					**7.0-21.0** (median 10.2)		
Hardwood forest, Sweden (f)	**11.2**	**THg**	**28.8**	**23**			**2.2**
		GEM	23				
		GOM+PBM	4.8				
Coniferous forest, Germany (g)	**Total deposition (wet + dry)**		**55.2**	**15.1**			**15.9**

(unit, μg m^{-2} yr^{-1}; bold means total mercury flux values for the systems; references for the other studies listed here are a: Smith-Downey et al. 2010, b: Rea et al. 2002, c: Graydon et al. 2008, d: Risch et al. 2012, e: Denkenberger et al. 2012, f: Munthe and Hulberg 2004, and g: Schwesig and Matzner 2001, respectively.)

[2] The terrestrial mercury cycling processes were originally estimated by GTMM in the unit of Mg yr^{-1} on global basis. Areal numbers in the unit of μg $m^{-2}yr^{-1}$ for the processes as listed in Table 5.2 were obtained based on the reported global land area (UNEP, 2005) and forest area (FAO, 2000). GTMM didn't estimate mercury in watershed runoff, the value of watershed runoff mercury for the global terrestrial system listed here was from the estimate of Sunderland and Mason (2007).

5.4.1 Atmospheric mercury deposition

Total atmospheric mercury deposition (29.2 μg m^{-2} yr^{-1}) at the HWF was slightly higher than the global scale value (21.9 μg m^{-2} yr^{-1}), while within the reported range (~10-50 μg m^{-2} yr^{-1}) for other sites in the eastern US (Risch et al., 2012; Miller et al., 2005; Kamman and Engstrom, 2002; Brigham et al., 1991; Fitzgerald et al., 1986). In contrast, the atmospheric mercury deposition at the HWF was considerably lower than the reported values for Europe (Table 5.2; Munthe and Hulberg 2004, Schwesig and Matzner 2001).

Wet mercury deposition (6.3 μg m^{-2} yr^{-1}) at the HWF was slightly higher than the global average (5.3 μg m^{-2} yr^{-1}), while it was in the reported range (3.8-12.6 μg m^{-2} yr^{-1}) for the northeastern US (Driscoll et al., 2007). Dry mercury deposition at the HWF (Table 5.2) was obtained from foliar mercury accumulation subtracting soil mercury transpiration for the growing season and the inferential approach (measured concentrations × CMAQ simulated deposition velocities) for the non-growing season. Dry mercury deposition at the HWF (22.9 μg m^{-2} yr^{-1}) was higher than reported values (~7-18 μg m^{-2} yr^{-1}) for northeastern North America (Rea et al., 2002; Miller et al., 2005; Graydon et al., 2008), as well as the global estimate (16.6 μg m^{-2} yr^{-1}; Smith-Downey et al., 2010). Dry mercury deposition was more important than wet mercury deposition at the HWF, in agreement with multiple observations of forested watersheds for North America (Graydon et al., 2008; Risch et al., 2012).

5.4.2 Foliar mercury accumulation

As discussed in section 5.1, three methods (direct estimate of foliar mercury accumulation, litterfall mercury deposition, and inferential method: stomatal uptake of GEM + mercury uptake via soil transpiration) were used to estimate the foliar mercury accumulation at the HWF. All the three estimates (16.7, 17.2, and 9.6 μg m^{-2} yr^{-1}, respectively) are within the reported range for

North America region (Rea et al. 2002, Graydon et al. 2008, Risch et al. 2012), but higher than the foliar mercury accumulation in global scale (8.3 μg m^{-2} yr^{-1}, Smith-Downey et al., 2010). Mercury flux in soil transpiration (< 2.0 μg m^{-2} yr^{-1}) was a minor contribution to foliar mercury accumulation at the HWF. Litterfall mercury (17.2 μg m^{-2} yr^{-1}) is considered to be the most appropriate estimation for foliage mercury uptake, mercury uptake via soil transpiration accounted for no more than 12% of foliar mercury accumulation at the HWF, consistent with the contribution (3-14%) of soil transpiration reported in other studies (Bishop et al., 1998; Rea et al., 2002).

5.4.3 Soil mercury accumulation and losses

The estimated net mercury accumulation at the HWF (20.0 μg m^{-2} yr^{-1}) was substantially higher than the estimated terrestrial mercury accumulation on the global scale produced by GTMM (2.4 μg m^{-2} yr^{-1}). In addition to higher atmospheric mercury deposition at the HWF (29.2 μg m^{-2} yr^{-1}) than the global terrestrial system (21.9 μg m^{-2} yr^{-1}), surface mercury emissions (soil evasion from the forest floor at the HWF: 6.5 μg m^{-2} yr^{-1}; mercury emissions from soil and leaf surfaces for the global terrestrial system: 19.6 μg m^{-2} yr^{-1}; Table 5.2) could also be an important factor explaining the difference between soil mercury accumulation at the HWF and the global scale.

The modeled gaseous mercury emissions from the forest floor at the HWF are likely to depict the actual soil evasion during the leaf-on period but may underestimate the soil emissions during leaf-off period by <20% (< 0.2 μg m^{-2} yr^{-1}), as suggested by the comparison between the modeled and measured soil mercury emission fluxes (Choi et al., 2009). The process of mercury reemission (revolatilization and photoreduction) from leaf surfaces was not included in this analysis of the HWF mercury mass balance, as foliar uptake of GEM used in the mass balance depicts net mercury exchange between the leaf surface and the atmosphere. Graydon et al. (2012)

reported 45% of wet deposited mercury was reemitted from the canopy to the atmosphere by examining the fate of spike mercury at the Experimental Lake Area in Canada. Therefore, the difference (by ~13 μg m^{-2} yr^{-1}) in soil emissions estimated for HWF and global terrestrial system could be attributed to the unaccounted mercury reemission from the leaf surfaces at the HWF in some degree. In addition, variations of soil mercury evasion in different land cover types could also explain the substantial difference of soil mercury evasion at the HWF and the global terrestrial system. Several studies have suggested that land cover type could affect soil mercury evasion (Denkenberger et al., 2012; Miller et al., 2005). Soil mercury evasion rates are relatively low in forest lands compared to agricultural lands and grass lands. This difference is likely due to lower rate of photoreduction associated with the attenuation of solar radiation by the forest canopy and slower rates of soil organic carbon turnover.

Using the average organic carbon turnover flux (240 g C m^{-2} yr^{-1}) for hardwood forest floors (Currie and Aber, 1997), mean Hg/C ratio (2.35×10^{-8} g / g) for the HWF soils (Driscoll, unpublished data), and the fraction of mercury released as GEM during decomposition (0.16, suggested by Smith-Downey, et al., 2010), soil mercury respiration flux was estimated to be 0.9 μg m^{-2} yr^{-1}, substantially lower than the average estimate for global terrestrial system (Table 5.2 ; 5.0 μg m^{-2} yr^{-1}). In this case, mercury revolatilization and photoreduction from soil surface would be estimated to be 5.6 μg m^{-2} yr^{-1} at the HWF, contributing to vast majority of the soil mercury emission under the forest canopy (86%), indicating biotic process was a less important factor for soil mercury evasion on the HWF, consistent with the results of experimental studies for the HWF soils (Choi and Holsen, 2009a).

Mercury output via watershed runoff (2.8 μg m^{-2} yr^{-1}, soil surface runoff + vertical flow out of the lowest soil layer) at the HWF was a less important export mechanism compared with soil

mercury evasion, consistent with the estimated mercury flux values reported in several studies for US region as well as global terrestrial system (Brigham et al., 2009; Driscoll et al., 1998; Sunderland and Mason, 2007). Mercury flux in watershed runoff at the HWF accounted for 34% of the throughfall mercury, similar with the importance of watershed runoff reported by a study in Germany (39% of throughfall mercury, Schwesig and Matzner 2001), while higher than the importance reported by a study in Sweden (14% of throughfall mercury, Munthe and Hulberg 2004). Overall drainage outputs were 10% of total mercury inputs at the HWF, similar to the importance of drainage mercury loss for the global terrestrial system (Table 5.2; 12% of the total mercury inputs, estimated from Sunderland and Mason, 2007, and Smith-Downey et al. 2010)

5. Role of HWF in mediating mercury transport

5.5.1 Effect of the foliage on mercury transport

The mercury mass balance at the HWF suggests that the canopy was a temporary net sink for the atmospheric mercury during the leaf-on period until litterfall occurred (net accumulation flux 17.2 μg m^{-2} yr^{-1}, upper-end estimate). Dry mercury deposition was more important than wet mercury deposition at the HWF, mostly because the forest foliage elevated dry deposition of GEM via stomatal uptake, as suggested by other studies (Driscoll et al., 2007). Given that atmospheric mercury deposition dominated foliage mercury accumulation as discussed above, it indicates that litterfall is an important pathway of atmospheric mercury deposition to the forest floor. This finding has been noted in multiple studies (Demers et al., 2007; Juillerat et al., 2012; Risch et al., 2012).

5.5.2 Effect of the forest soils on mercury transport

The mercury mass balance at the HWF suggests that the forest soil was an ultimate net sink for mercury inputs (net accumulation flux 21.0 μg m^{-2} yr^{-1}). Besides receiving litterfall mercury deposition, the forest soil was also found to retain mercury via water transport (net accumulation flux 4.6 μg m^{-2} yr^{-1}; Figure 4.10).

Mercury in throughfall was predominantly contributed by atmospheric mercury (precipitation mercury and wash off of dry atmospheric mercury deposition on leaf surface). As considerable amount of throughfall mercury was retained when throughfall solution was transported through the forest soils at the HWF, it indicates that the forest soil was a substantial mercury solution filter between atmosphere and hydrosphere. This observation has been reported by several studies at different sites in Scandinavia, Europe and North America (Munthe and Hultberg, 2004; Schwesig and Matzner, 2001; Lindberg, 1996).

Mercury in and out fluxes to the forest soils via water transport include soil infiltration, soil leaching, and soil transpiration in this analysis. During the growing season, mercury input to the forest soils via soil water transport (mercury in soil infiltration) had no significant seasonal difference, while mercury out flux in soil leaching over the growing season (0.25 μg m^{-2}) was considerably smaller than the non-growing season (0.86 μg m^{-2}) due to the lower soil leaching flow over the growing season (Figure 4.8, Figure 4.10). The lower soil leaching flow over the growing season was mostly likely due to soil transpiration during that period (Figure 4.8). This indicates that soil transpiration was likely a controlling factor of mercury transport in the forest soils during the growing season.

5.6 Potential response of the HWF to mercury emissions control

The mercury mass balance shows that the HWF is a net sink for atmospheric mercury deposition with the accumulation rate of 12.8 μg m^{-2} yr^{-1} (conservative estimate). Given the total soil mercury pool (72 mg m^{-2}; Driscoll, unpublished data), Oa horizon mercury pool (12 mg m^{-2}; Driscoll, unpublished data) at the HWF, the residence times of total soil mercury and Oa horizon mercury with respect to present atmospheric deposition (29.2 μg m^{-2} yr^{-1}) are ~ 2500 years and ~ 400 years, respectively.

Smith-Downey et al. (2010) suggests that compared to preindustrial condition, the residence time of global soil mercury has decreased by nearly half due to the increases in atmospheric emissions and deposition associated with human activities. To examine the potential response of the HWF to mercury emissions control, a simplified scenario was assumed that all the anthropogenic emissions are eliminated and atmospheric mercury deposition returns to preindustrial condition. Mercury mass balance for the HWF was conducted for this scenario, using the preindustrial wet mercury deposition for the Adirondack region (3 μg m^{-2} yr^{-1}) estimated by Lorey and Driscoll (1999) and the assumption that all mercury in and out fluxes at the HWF would downscale by the same magnitude. The mass budget suggest that, under the scenario of eliminating anthropogenic deposition, net mercury accumulation rate (~20 μg m^{-2} yr^{-1}) at the HWF would be decreased by 52%; meanwhile, the residence time of total soil mercury and of Oa horizon mercury would be increased to ~ 5250 years and ~ 860 years, respectively.

Although this analysis may be oversimplified considering the complex soil mercury dynamics associated with soil carbon cycling as well as the transformations among different mercury forms, it suggests a first order approximation of the response of the forest ecosystem to controls in mercury emissions.

6 Conclusion

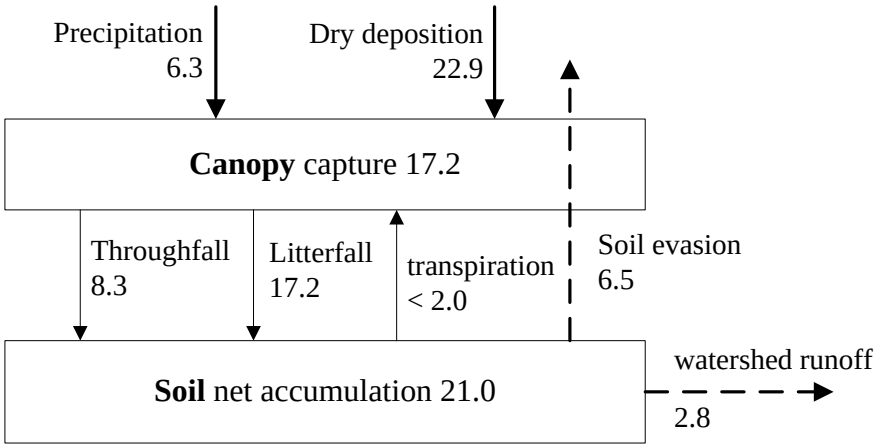

Figure 6.1 Schema of the HWF mercury mass balance. Numbers in the boxes represent net accumulation fluxes of THg; the other numbers are THg fluxes of the mercury cycling processes; unit, μg m^{-2} yr^{-1}.

In this study, the fate of mercury at the HWF and the function of forest ecosystem in the transport of mercury were examined by quantifying mercury cycling processes and conducting mercury mass balance for the site using a suite of measurements.

The mass balance (Figure 6.1) suggests the forest ecosystem at the HWF was a substantial net sink for atmospheric mercury as well as an important mercury filter between atmosphere and hydrosphere. The dry mercury deposition, foliar mercury accumulation and soil mercury accumulation shown in Figure 6.1 were likely upper-end values for the HWF. Most (68%) of the atmospheric mercury deposition was retained in the ecosystem; the losses of mercury from the system predominantly occurred via soil mercury evasion (22%) while only a small fraction (10%) was exported via watershed runoff.

The forest canopy was a temporary sink for mercury over the growing season, by accumulating mercury (dominated by atmospheric dry mercury) in leaf tissues. The foliar accumulated mercury was sequentially deposited to the forest floor via litterfall. Litterfall was the single

largest source (53%) of mercury entering the forest floor and predominant contribution (82%) of mercury retention in the forest soils.

Forest soils were found to be the ultimate net sink for atmospheric mercury at the HWF.

Decreases in anthropogenic mercury emissions would decrease the accumulation of mercury in soils and as well as lengthen the residence time of mercury in soils at the HWF.

Suggestions for future research

1. Uncertainties in the estimates of foliar mercury accumulation call for the need of comprehensive investigation of canopy biomass for individual tree species at the HWF.

2. Monitoring points need to be increased for the atmospheric mercury measurements with in order to reduce uncertainties in mercury concentration measurements and the uncertainties in the estimation of mercury exchange between the atmosphere and leaf surfaces.

3. Soil mercury evasion was likely to be underestimated in this study as winter evasion was ignored considering snow cover; meanwhile as another emission source, evasion from leaf surface was not included in this study. Further investigations on mercury emissions from leaf surfaces and winter-season measurements are needed to strengthen the understanding in mercury emissions at the HWF.

4. Long-term measurements of atmospheric mercury, foliar mercury, and mercury in soil solutions would be valuable to evaluate inter-annual and/or inter-seasonal variations in mercury cycling processes.

Appendix I – Figures

Appendix II – Tables

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Seasonal Variations in the Inputs and Fate of Mercury in a Northern Hardwood Forest
Advisor: Charles T. Dirscoll

- Examine the fate of mercury in a forest ecosystem and evaluate the role of forest ecosystem in mediating mercury transport, by quantifying the mercury cycling processes through integrating data of long-term field study and model simulations

Independent Study 2012.2-2012.5
Concentration-Discharge Relationship in Urban Area
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- Checked the concentration-discharge relationships across several urban sites of Syracuse and Baltimore area
- Discussed the possible factors influencing hydrology behaviors in watersheds

Bachelor Thesis 2009.2-2010.6
Impact of Nitrobenzene on Sediment Oxygen Consumption
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- Measured dissolved oxygen in sediment utilizing combined-microelectrode
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Undergrad Student Research Training 2008.9-2009.4
Policy Analysis on Recycling Economy in China
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Extracurricular Design 2007.12-2008.5
Freezing Desalination Model for Industrial Wastewater Treatment

- Devised an energy-saving wastewater treatment model using the climate characteristics in Northwestern China
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PUBLICATIONS & PRESENTATIONS

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Zhou XH., **Wang XY.**, Shi HC. 2012. Inhibitory Effect of Nitrobenzene on Oxygen Demand in Lake Sediments, Journal of Environmental Sciences, Vol 24. No 5: 934-939.

WORKING EXPERIENCE

Syracuse University, Department Civil and Environmental Engineering 2012.1- 2012.5
Teaching Assistant
- Taught lab sections of the undergrad class "Water Resources Engineering"
- Tutored students by holding office hours and graded homework and quizzes

AguaClara-Cornell Program, Ithaca, NY 2011.6- 2011.8
Research Intern
- Improved previous design of stock tank mixing applied in AguaClara Honduras drinking water treatment plants
- Provided rough guideline for stock tank mixing operators

The Corporate Office of EHS, Siemens Ltd., China (SLC) 2010.3- 2010.6
Admin Intern
- Fulfilled daily administration work and office supplies
- Translated EHS (Environmental Protection, Health Management and Safety) related regulations published by the Chinese government and European Union
- Successfully supported the manager to arrange 2010 Siemens EHS Northeast Asia Council Meeting

EXTRACURRICULAR ACTIVITIES

NYPIRG (the New York Public Interest Research Group) 2011.9-2011.12
Syracuse University Chapter Intern
- Helped promoting voter registration (by hundreds) on campus
- Advocated the students to focus on environment issues by organizing events

Student Association for Science and Technology, Tsinghua University 2009.3-2009.7
Chair of the Information Department
- Managed relevant information issues utilizing campus media such as website, TV, and newspapers, etc.
- Selected as "the Best Department of SAST, Tsinghua Univ. of Year 2009"

2009 Tsinghua Univ. Environmental Friendly Sci & Tech Competition 2008.9-2009.6
Publicity Chair
- Organized the competition successfully, which attracted nearly 200 students to attend from not only Tsinghua Univesity but also other universities

2008 Beijing Olympic and Paralympics Games 2008.8-2008.9
Leader Volunteer
- Provided spectator service in National Aquatic Center, Beijing, China
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LANGUAGE AND COMPUTER SKILLS

Languages: Chinese, English
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