2012

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## Recommended Citation
Denkenberger, J. S., Driscoll, C. T., Branfireun, B. A., Eckley, C. S., Cohen, M., & Selvendiran, P. (2012). A synthesis of rates and controls on elemental mercury evasion in the Great Lakes Basin. Environmental Pollution, 161, 291-298. doi: 10.1016/j.envpol.2011.06.007

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# A Synthesis of Rates and Controls on Elemental Mercury Evasion in the Great Lakes Basin

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## Abstract

Rates of surface-air elemental mercury ($Hg^o$) fluxes in the literature were synthesized for the Great Lakes Basin (GLB). For the majority of surfaces, fluxes were net positive (evasion). Digital land-cover data were combined with representative evasion rates and used to estimate annual $Hg^o$ evasion for the GLB (7.7 Mg/yr). This value is less than our estimate of total Hg deposition to the area (15.9 Mg/yr), suggesting the GLB is a net sink for atmospheric Hg. The greatest contributors to annual evasion for the basin are agricultural (~55%) and forest (~25%) land cover types, and the open water of the Great Lakes (~15%). Areal evasion rates were similar across most land cover types (range: 7.0 to 21.0 μg/m$^2$-yr), with higher rates associated with urban (12.6 μg/m$^2$-yr) and agricultural (21.0 μg/m$^2$-yr) lands. Uncertainty in these estimates could be partially remedied through a unified methodological approach to estimating $Hg^o$ fluxes.

**Keywords: evasion, Great Lakes, land cover, mercury, volatilization**

**Capsule:** A synthesis of Hg evasion was conducted and this information was used to develop an estimate of Hg evasion for the Great Lakes Basin.

## Introduction

The global mercury (Hg) pool includes inputs from both natural processes and anthropogenic activities. Industrial emissions, mainly from coal combustion, waste incineration, and industrial processes are the primary sources of Hg to the atmosphere (Driscoll et al. 2007a). Important natural Hg sources include volcanic activity, soil mineral weathering and forest fires (Rasmussen

1994). The global biogeochemical cycle of Hg is characterized by numerous oxidation/reduction reactions, where elemental Hg ($Hg^o$) is oxidized through different mechanisms to mercuric ion ($Hg^{2+}$), and $Hg^{2+}$ is in turn reduced through various pathways to $Hg^o$. In aquatic and terrestrial ecosystems, the majority of Hg is $Hg^{2+}$ (typically bound to particulate matter or other complexing ligands) with lesser amounts occurring as $Hg^o$ and methyl mercury (MeHg). There is a critical interplay of processes for $Hg^{2+}$, where $Hg^{2+}$ can be either methylated to MeHg or reduced to $Hg^o$. Evasion of $Hg^o$ from lands and waters is a significant input to the atmosphere, and at the same time is an output of Hg from the terrestrial environment.

Terrestrial and aquatic processes can result in the chemical reduction of oxidized Hg species to $Hg^o$, resulting in volatilization of $Hg^o$. Loss of $Hg^o$ to the atmosphere can occur from water, vegetation, and soil surfaces (Amyot et al. 1994; Ericksen and Gustin 2004; Ericksen et al. 2006). For soils, Hg volatilization has been shown to vary spatially, as a function of surface characteristics such as Hg concentration, moisture content, and grain size distribution; and temporally as a function of changing meteorological conditions such as solar radiation, temperature, and soil moisture (Selvendiran et al. 2009; Choi and Holsen 2009a; Ericksen et al. 2006; Eckley et al. 2011). In lakes, photo-reduction of $Hg^{2+}$ appears to be the primary process driving the production of dissolved gaseous mercury (DGM) and its subsequent loss to the atmosphere (e.g., O'Driscoll et al. 2003a; Amyot et al. 1994; Lindberg et al. 2000). Several proposed mechanisms include direct photolysis of $Hg^{2+}$ to $Hg^o$ (Amyot et al. 1994; Munthe and McElroy 1992) including photosensitizing of $Fe^{3+}$ complexes (Ababneh et al. 2006; Zhang and Lindberg 2001), sulfite complexes (Munthe et al. 1991; Van Loon et al. 2000), DOC and humic substances (Nriagu 1994; Xiao et al. 1991; Xiao et al. 1995), and reduction of $Hg^{2+}$ involving oxygen radicals such as $O_2^{\bullet -}$, $HO^{\bullet}$, and $H_2O_2$ (Dommergue et al. 2003; Schroeder et al. 1992). Photodecomposition of MeHg directly to $Hg^o$ has also been suggested (Tossell 1998; Bloom et al. 2001). Because photo-reduction of Hg is an important driving mechanism, studies are characterized by marked diel changes in evasion rates.

Published measurements of $Hg^o$ volatilization rates include both aquatic and land surfaces. The rates of Hg volatilization reported in the literature range from < 5 ng/m$^2$-hr from pristine lakes and forest soils to >10 000 ng/m$^2$-hr from contaminated soils (Amyot et al. 2004; Gustin et al. 2003). Gaseous $Hg^o$ has an atmospheric residence time of around 1 year (Fitzgerald and Mason 1997; Smith-Downey et al. 2010). As a result, $Hg^o$ may be transported globally prior to being deposited back to the Earth's surface following volatilization. Deposition occurs following oxidation of $Hg^o$ to $Hg^{2+}$, and subsequent complexation of $Hg^{2+}$ with airborne particulates or dissolution in water. In forest systems $Hg^o$ can enter the stomata of leaves which can be deposited to the forest floor during litter fall (Driscoll et al. 2007b). $Hg^{2+}$ returns to the Earth's surface as wet (i.e., rain), dry (i.e., particulate, gaseous), or litter fall deposition. Recent estimates have suggested that $Hg^o$ evasion may account for a substantial fraction of Hg loss from ecosystems. For example, Quémerais et al. (1999) estimated that the fluvial loss of total Hg from Lake Ontario to its only outlet, the St. Lawrence River, is approximately 5.9 µg/m$^2$-yr. The volatilization rate of $Hg^o$ from Lake Ontario was estimated by Lai et al. (2007) to be approximately 5.8 µg/m$^2$-yr. Likewise, a Hg mass balance for Arbutus Lake in the Adirondack Mountains, New York, Selvendiran et al. (2009) estimated fluvial Hg loss to be 1.2 µg/m$^2$-yr and $Hg^o$ volatilization to be 7.8 µg/m$^2$-yr.

Given the importance of $Hg^o$ evasion to the overall mass balance of watersheds, we review the literature on surface-air fluxes of $Hg^o$ in terrestrial and freshwater aquatic environments and provide a synthesis of these studies. The focus of our analysis is the Great Lakes Basin (GLB). Here we estimate the overall $Hg^o$ losses from the GLB and compare this flux with estimates of Hg emissions and inputs from wet, dry and litterfall Hg deposition through a synthesis of the best available information in the published literature.

## Literature Review of Mercury Evasion Estimates

Our review of $Hg^o$ evasion studies is organized by land cover type: forest, agriculture, grassland, urban, wetlands, inland lakes, and the open waters of the Great Lakes. Based on this review, rates of $Hg^o$ evasion were selected for each land cover, and used to calculate total Hg evasion for the GLB. For the purpose of this analysis, Hg fluxes discussed and selected for scaling purposes are net gaseous exchange values (i.e., flux values presented account for both gaseous Hg deposition and emission).

Surface $Hg^o$ fluxes are influenced by diel and seasonal variability under environmental conditions. Variables that have been found to be important in influencing fluxes include solar radiation, temperature, precipitation and atmospheric turbulence and chemistry (summarized in Gustin et al. 2008; Stamenkovic et al. 2008). There is considerable variation in estimates of $Hg^o$ evasion for various land cover types. This large overall variability occurs due to large temporal variability over the time of day and season, relatively large spatial variability, and substantial differences in the nature and intensity of measurements among studies. For example, Poissant et al. (2004) observed a greater than 50% increase in $Hg^o$ volatilization from the same wetland site under dry conditions compared to when it was flooded. Moreover, soil temperature became a more important controller of $Hg^o$ evasion than solar radiation during the dry period. While some studies have suggested that prolonged soil moisture might inhibit $Hg^o$ evasion (Schroeder et al. 2005; Selvendiran et al. 2008), others have noted elevated $Hg^o$ evasion rates immediately following precipitation events (Eckley et al. 2011; Engle et al. 2001; Lindberg et al. 1999). Marked spatial variability has also been documented in the literature. Eckley and Branfireun (2008) noted an approximate four-fold difference in $Hg^o$ evasion between some pavement sites in Toronto, and suggested this difference was a result of different pavement compositions.

Some studies have measured $Hg^o$ flux during different seasons to establish an annual ecosystem flux which accounts for temporal variability, whereas other studies conduct measurements over a range of days (or hours) during a single season. Several studies have identified that flux increases with temperature and solar radiation and as a result, fluxes are higher during the daytime than at night and generally higher in the summer than in winter (Choi and Holsen, 2009a; Gabriel et al. 2006; Eckley et al. 2011); however some studies have also identified that lower solar radiation under deciduous canopies and lower soil moisture content results in lower summertime fluxes (Hartman et al. 2009; Kuiken et al. 2008). Because several studies have shown diel $Hg^o$ fluxes to generally follow a curve similar to solar elevation, measurements conducted only during daylight hours will greatly overestimate mean daily emissions (Engle et al. 2001; Gabriel et al. 2006; Gustin et al. 2003). Therefore, for land cover types where multiple studies had been conducted, we prioritized selecting data that incorporated daily and seasonal variability in developing annual flux estimates, as well as studies from within/near the GLB.

Surface $Hg^o$ fluxes can be measured/modeled using several approaches. For soils, dynamic flux chambers (DFC) and micrometeorological methods (MM) are the most common techniques and for aquatic ecosystems, DFCs and purge/trap methods are routinely applied. Additionally, both $Hg^o$ detectors and mathematical models used to estimate $Hg^o$ evasion vary. Studies that compare different techniques used to measure flux suggest that the methodological approach and operating parameters influence the magnitude of the calculated flux (Gustin et al. 1999; Eckley et al. 2010; Rolfhus and Fitzgerald, 2001). Therefore, because there is no standard protocol for conducting measurements of gaseous $Hg^o$ flux, some component of the variability in $Hg^o$ fluxes among landscapes reported is a function of differences in flux measurement techniques. To minimize this artifact, flux datasets that used similar methodological approaches were selected as part of this review. For soil surfaces, fluxes measured using DFCs were available for all surface types and were prioritized for scaling. For aquatic surfaces, where DFC measurements were available they were selected; however for some surfaces purge/trap data was only available and was applied for scaling.

Note that in many of the studies reviewed it was assumed that soil $Hg^o$ evasion during periods of snow cover is minimal. While this may be true for the soil itself, studies have reported substantial rates of $Hg^o$ evasion from snowpack (e.g., Ferrari et al. 2005, Lalonde et al. 2002). A considerable portion of the GLB is snow-covered during the winter season. We found few studies estimated $Hg^o$ evasion from snowpack in the GLB (Schroeder et al. 2005), and many of the emission studies reviewed had no or limited measurements during winter. Additional studies are necessary to quantify $Hg^o$ emission from the snow cover period in the GLB.

### *Forests*

DFC fluxes from a deciduous forest in the Adirondack region of New York were selected for scaling forest lands that incorporated diel measurements conducted during each season (Choi and Holsen, 2009a Table 1). The seasonal flux data were then scaled annually to account for seasonal changes in canopy coverage in the summer and snow coverage in the winter—expressed as an annual hourly average this flux was 0.8 $ng/m^2$-hr. Other studies of Hg flux from North American forests using DFCs include Carpi and Lindberg (1998) and Zhang et al. (2001) both of which measured spring/summer daytime-only fluxes from the soil beneath a deciduous forest in Tennessee (flux range: 2 to 7 $ng/m^2$-hr) and Michigan (average flux: 1.4 ±1.4 $ng/m^2$-hr) and Schroder et al. (2005) which measured summertime fluxes from forest soil in Nova Scotia (flux average: 1.1 $ng/m^2$-hr). While the Choi and Holsen (2009a) flux value appears lower than measurements from other studies, this is because their value incorporates diel and seasonal variability, whereas the other measurements do not. During warm, sunny conditions, Choi and Holsen (2009a) measured $Hg^o$ fluxes that were in excess of 10 $ng/m^2$-hr, which is of similar magnitude as measured during peak emissions in the other studies.

### *Agricultural Lands*

Agricultural lands include areas used for crop production. Grasslands, including areas used for livestock pasture, are discussed in the *Grasslands* section. Using the DFC method, Carpi and Lindberg (1998) measured $Hg^o$ fluxes from a simulated plowed agricultural field in Tennessee (vegetation was manually removed from the surface before measurements were conducted) and found fluxes ranging from -0.66 to 44.8 ng/m$^2$-hr. This large range incorporates values at different sample locations (two different fields) and levels of daytime solar radiation. The fluxes from the Nelson field site in Carpi and Lindberg (1998) are considered more representative of the GLB because the Hg concentration of the soil (61±19 ng/g) was similar to values measured from crop and pastureland within the GLB (see Table 1). Because these measurements were conducted during the spring/summer daytime conditions, they needed to be adjusted to account for diel and seasonal flux variability. Flux measurements obtained during only specific periods of the day can be extrapolated to diel averaged fluxes assuming a Gaussian distribution (Nacht and Gustin, 2004; Engle et al. 2001). Using the daytime sunny conditions average flux of 12.5 ng/m$^2$-hr to represent noontime emissions and the average from measurements obtained in the shade to represent nighttime fluxes (-0.66 ng/m$^2$-hr) to fit a Gaussian distribution resulted in an estimated diel flux of 3.4 ng/m$^2$-hr. Furthermore, since this flux was measured during the spring/summer, it is not representative of fall and winter emissions. If we assume a similar decrease in fluxes during the fall as was observed from the seasonal measurements from a GLB forest (Choi and Holsen, 2009a), then the diel autumn Hg$^o$ fluxes are estimated to be 2.7 ng/m$^2$-hr. During the winter, Schroeder et al. (2005) measured low fluxes (0.09 ± 0.03 ng/m$^2$-hr) from an agricultural area in Southern Ontario covered in snow. Averaging these fluxes by their respective seasonal time periods would result in an estimated annual average flux from GLB cropland of 2.4 ng/m$^2$-hr. Several studies have shown that Hg$^o$ fluxes increase following surface disturbance, however these elevated emissions are temporary and fluxes return to pre-disturbance levels within a week after soil disturbance (Gustin et al. 2003; Eckley et al. 2011). While the results of Carpi and Lindberg (1998) indicate that $Hg^o$ fluxes from agricultural lands can be elevated during periods of active plowing/harvesting, it is not clear from their study how long the emissions remained elevated. In the annual average flux applied for scaling, the fluxes from the disturbed surfaces from Carpi and Lindberg (1998) were applied over a 6 month period, which may be an overestimation of the emissions during this period depending on how often the fields are disturbed from farming activities and how long the emissions remained elevated following surface disturbances. Other MM measurements of $Hg^o$ fluxes on agricultural lands found values ranging from an average autumn diel flux of 0.1 ± 0.2 $ng/m^2$-hr at an Ontario cropland field (Cobett and Van Heyst, 2007) to an average spring diel flux of 9.67 $ng/m^2$-hr at a Minnesota cropland field (Cobos et al. 2002). The large range in reported $Hg^o$ fluxes for croplands does not appear to be related to differences in soil Hg concentrations, which were highest in the Cobett and Van Heyst (2007) study where the fluxes were the lowest; instead variations in $Hg^o$ fluxes may reflect varying levels of surface disturbance associated with agricultural activity.

Our analysis (see below) suggests that agricultural lands account for more than 50% of total Hg evasion from the GLB. It is not clear from these studies when and for how long $Hg^o$ evasion rates are elevated from agricultural lands. Elevated $Hg^o$ evasion rates also may reflect high rates of carbon mineralization and $Hg^{2+}$ cycling associated with land disturbance or materials added to agricultural lands. Based on our literature review and the elevated rates associated with this review, there is a clear need for more rigorous evasion studies on agricultural lands, quantifying rates and climatic and landscape level drivers that control evasion rates.

### *Grasslands*

For grasslands/pastures, Schroeder et al. (2005) used both the DFC and MM techniques to measure average diel summertime $Hg^o$ fluxes in Ontario (3.0 and 1.1 $ng/m^2$-hr respectively) and Quebec (MM only: 2.9 $ng/m^2/h$) and Zhang et al. (2001) used a DFC to measure mid-day summer fluxes from the Upper Peninsula in Michigan (7.6 ± 1.7 $ng/m^2$-hr). While the values from Zhang et al. (2001) appear much larger than those from Schroeder et al. (2005) values, this difference is likely due to the fact that the later considered diel conditions. Assuming the Gaussian flux distribution the diel flux from the Zhang et al. (2001) was estimated to be 2.6 $ng/m^2$-hr, which is similar to values of Schroeder et al. (2005), suggesting that these measurements are representative of grassland emissions. Ericksen et al. (2006) measured diel fluxes with a DFC from grasslands in Wisconsin and found that some fluxes were similar in magnitude to those of Schroeder et al. (2005) and Zhang et al. (2001) (maximum flux: 3.5 $ng/m^2$-hr), but overall they report a much lower mean flux of 0.3 ± 0.07 $ng/m^2$-hr (the season these measurements were conducted is not reported). Their lower flux may be a function of their grassland site being under forest cover and not exposed to direct sunlight, which is not typical conditions for grasslands. As such, an average of the Schroeder et al. (2005) and Zhang et al. (2001) values were used for scaling in our GLB analysis (i.e., 2.8 $ng/m^2$-hr). Because this value represents summer conditions, it was adjusted to be seasonally represented as was described for the agricultural lands resulting in an annual estimated average flux of 2.0 $ng/m^2$-hr. This value is slightly lower, but of similar magnitude as the fluxes reported for agricultural cropland. We would anticipate similar rates of $Hg^o$ evasion for agricultural lands and grasslands of the GLB, as both land covers are exposed to full solar radiation (i.e. limited canopy cover, which can decrease emissions). The slightly lower fluxes from the grasslands may reflect the lower level of disturbance these surfaces encounter relative to croplands.

*Urban Lands*

Urban areas largely consist of impervious surfaces, such as pavement, and pervious soils. Eckley and Branfireun (2008) used DFCs to measure fluxes from both types of surfaces from several locations from a major urban center within the GLB (Toronto, Ontario). The median fluxes they reported were based on summertime daytime measurements (1.0 and 6.2 ng/m$^2$-hr for pavement and soil, respectively). Using the Gaussian distribution to estimate diel Hg$^o$ fluxes, we estimate values of 0.3 and 2.0 ng/m$^2$-hr for pavement and soil respectively. These values are very similar to a more intensive diel and seasonal sampling campaign conducted from urban soils and pavement from outside of the GLB (Tuscaloosa, Alabama—Gabriel et al. 2006). Gabriel et al. (2006) found a median annual flux of -0.01 ng/m$^2$-hr for pavement, and 2.64 ng/m$^2$-hr for urban soils. The similarity in flux magnitudes may be due to similar soil Hg concentrations between the two sites (Table 1). The measurements of Eckley and Branfireun (2008) included good spatial coverage. In contrast, Gabriel et al. (2006) characterized temporal variability (which was based on a single location). However, because the magnitude of measurements from these two studies is similar, we averaged them to obtain values for urban lands of the GLB that are both spatially and temporally representative (pavement: 0.15 and soil: 2.3 ng/m$^2$-hr). We assumed that urban lands of the GLB are 40% impervious surfaces and 60% pervious land (Akbari et al. 2003). The relatively few urban evasion studies in the GLB, as well as the spatial heterogeneity noted in Eckley and Branfireun (2008) (i.e., median values at six sample sites in one city ranging from below detection limit to 5.2 ng/m$^2$-hr), suggests that additional research is needed to better characterize Hg emissions from urban environments.

### *Wetlands*

Of the three surface-air Hg-flux studies for wetlands reviewed, two used DFCs (Poissant et al. 2004; Selvendiran et al. 2008) while the other applied MM gradients (Lindberg and Meyers 2001). Poissant et al. (2004) compared Hg$^o$ evasion from a wetland in Quebec during a flooded period with values during a dry period. Diurnal measurements were made during both periods; the median values were calculated from both daytime and nighttime measurements. They found a median Hg$^o$ flux of 0.83 ng/m$^2$-hr during the dry period (August to September, 1999), and a median Hg$^o$ flux of 0.5 ng/m$^2$-hr during the flooded period (May 2000). Selvendiran et al. (2008) found a similar pattern from a riparian zone in the Adirondack region of New York. During flooded conditions, net volatilization was -1.3, -3.9, and -3.6 ng/m$^2$-hr for spring, summer and fall, indicating deposition; during drier conditions, net volatilization was observed (3.8 ng/m$^2$-hr). They also evaluated a beaver meadow, estimating an annual Hg$^o$ evasion flux of 0.52 ng/m$^2$-hr. This estimate included both seasonal and diurnal measurements from a wetland in close proximity to the GLB, and as a result may be more representative of the annual evasion rate for wetlands in the GLB. Note, however, the differences observed between flooded and dry conditions at different wetlands. Seasonal changes, as well as periods of drought or elevated precipitation, could have considerable effects on Hg$^o$ evasion rates from wetlands.

### *Lakes (Inland)*

In addition to the MM gradient and DFC methods typically used for $Hg^o$ evasion work on soils, estimates of evasion from aquatic environments include the use of a purge and trap system (O'Driscoll et al. 2003a). While DFC and MM methods measure net $Hg^o$ exchange, the purge and trap methods measure dissolved gaseous Hg (DGM), and use models to determine air-water $Hg^o$ exchange. Selvendiran et al. (2009) applied the purge and trap system to estimate $Hg^o$ evasion from Arbutus Lake in the Adirondacks, New York. They developed an annual estimate of $Hg^o$ evasion from the lake surface, 0.89 $ng/m^2$-hr. During the study, mean daytime evasion was 1.6 $ng/m^2$-hr and mean nighttime evasion was estimated at 0.7 $ng/m^2$-hr. The value proposed as an annual estimate accounts for diurnal as well as seasonal variation. Vandal et al. (1991) developed an annual estimate of $Hg^o$ evasion (0.17 $ng/m^2$-hr) for seepage lakes in Wisconsin. All other studies provided estimates specific to the study period, or did not define a study period: O'Driscoll et al. (2003b) noted a daytime range of 2.1 to 3.8 $ng/m^2$-hr during the summer for two lakes in Nova Scotia; Xiao et al. (1991) developed a mean daily estimate of 7.9 $ng/m^2$-hr during the warmer season for four lakes in Sweden; Wollenberg and Peters (2009) noted a range of 0.14 to 20.95 $ng/m^2$-hr from a dimictic lake in eastern Pennsylvania during fall turnover. Of these, the Selvendiran et al. (2009) estimate, which accounts for both diurnal and seasonal variations, was used to represent $Hg^o$ evasion from inland lakes in the GLB. Of the literature reviewed, $Hg^o$ evasion estimates for inland lakes exhibit the greatest variability in methodological approach. It is therefore difficult to reconcile values across a region and objectively compare Hg evasion values among different lakes.

### *Great Lakes*

Estimates of gaseous $Hg^o$ evasion from the surfaces of the Great Lakes have largely been developed using data collected from grab samples that were promptly analyzed for DGM. Four recent studies were reviewed, and the only one not employing grab samples simply estimated gaseous Hg evasion by difference to close a $Hg^o$ budget (i.e., Rolfhus et al. 2003). That study estimated an annual $Hg^o$ volatilization rate of 1.0 ng/$m^2$-hr from Lake Superior. The remaining studies reviewed focused on Lake Superior, Lake Ontario and Lake Michigan.

Jeremiason et al. (2009) estimated evasional $Hg^o$ fluxes for Lake Superior and Lake Michigan, with annual values of 0.22 and 0.75 ng/$m^2$-hr, respectively. Vette et al. (2002) also studied Lake Michigan, and found a similar estimate of 0.89 ng/$m^2$-hr. Due to the more recent observations that are based on DGM measurements, the estimates of Jeremiason et al. (2009) were used to represent $Hg^o$ evasional flux from both Lake Superior and Lake Michigan in our analysis. As part of an atmospheric deposition study for Lake Ontario, Lai et al. (2007) estimated an annual $Hg^o$ evasion rate of 0.66 ng/$m^2$-hr. This was the only report in the literature for Lake Ontario, and was therefore used to represent that lake's annual $Hg^o$ emission rate. No studies were found for either Lake Huron or Lake Erie. However, since Lake Huron and Lake Michigan are geologically considered the same body of water (Great Lakes Environmental Research Laboratory 2006), the Lake Michigan $Hg^o$ evasion rate was used to represent Lake Huron as well. Due to the proximity of Lake Ontario and Lake Erie, the $Hg^o$ evasion rate for Lake Ontario was used for Lake Erie. More studies on Hg evasion from the Great Lakes would be beneficial, particularly with respect to Lakes Erie and Huron, and also to estimate localized influences of large river discharges and urban centers.

## Relative importance of Hg evasion for the Great Lakes Basin

To attempt to place estimates of rates of $Hg^o$ evasion in the context of the Hg dynamics across the GLB, we utilized a geographic information system (GIS) approach. We used values of $Hg^o$ evasion rates for land cover type based on our review of the literature (discussed above). We applied these rates to the distribution of land cover for the GLB from US Geological Survey (USGS) Global Land Cover Characterization (http://edc2.usgs.gov/glcc/glcc.php) (Table 2). Due to the limited number of evasion studies that have been conducted for certain land cover types, we lumped land cover classes to describe forests, agricultural lands, grasslands, urban lands, inland waters including lakes, reservoirs, rivers and wetlands; and the individual Great Lakes. Rates of $Hg^o$ evasion for the GLB are compared with: values of Hg emissions for the US and Canada for 2005 (www.epa.gov/ttn/chief/net/2005inventory.html#inventorydata); wet Hg deposition for 2002-2008 obtained from the Mercury Deposition Network (http://nadp.sws.uiuc.edu/mdn/; Risch et al. this volume a); estimates of Hg dry deposition calculated from the Community Multi-scale Air Quality (CMAQ) model (http://www.epa.gov/asmdnerl/EcoExposure/depositionMapping.html) for 2001; and forest litterfall Hg deposition in the GLB.

Litterfall Hg deposition was estimated by litter studies conducted by forest type (Risch et al. this issue b; Demers et al. 2007) and GIS forest cover. For the U.S., forest cover type data were available by tree species association classes from the USGS (http://rnp782.er.usgs.gov/atlas2/mld/foresti.html, e.g., maple-birch-beech, spruce-fir, oak-hickory). We multiplied litter fall Hg deposition rates for forest species classes by the land area of these classes for the U.S. area of the GLB. Unfortunately a comparable GIS of tree species association classes are not available for Canada. As a result, we used the forest cover classes in the USGS Global Land Cover Characterization for Canada (discussed above for land cover classes), which include hardwood, conifer and mixed forest cover classes. We used the mean litterfall Hg deposition reported in Risch et al. (this issue b) for conifer and mixed forest classes. We assumed in the GLB in Canada the hardwood forest class is largely comprised of maple-birch-beech forest class and used the data for that forest association class in Risch et al. (this issue b). We summed the values of litterfall Hg deposition for forest species association classes in the U.S. and the three forest cover classes in Canada. Note that forest lands represent 36% of the Great Lakes watershed area (Table 2). We prorated the total litterfall Hg deposition estimated for forest lands to the entire GLB. We estimate total Hg deposition as the sum of wet Hg deposition, dry Hg deposition and litterfall Hg deposition (Driscoll et al. 2007b).

Our analysis suggests an overall $Hg^o$ evasion for the GLB of about 7.7 Mg/yr, corresponding to an areal rate of 10.2 $\mu g/m^2$-yr (Tables 2 and 3). Total $Hg^o$ evasion is distributed among the various land cover types (Table 2; Figure 1). As the areal evasion rates reported in the literature for urban lands, agricultural lands and grasslands are greater than the other land cover types and the region as a whole, these land cover types had a disproportionate contribution to the total emissions. Evasion from agricultural lands, grasslands and urban lands is estimated to have contributed 55%, 0.4% and 1.5% to the total, respectively. Forest land contributed a relative large fraction of total $Hg^o$ evasion (25.1%) due to its large area of the GLB. Inland waters and the Great Lakes also contributed to the total $Hg^o$ evasion of the GLB (2.4 and 15.4%, respectively). It appears that areal evasion rates from inland waters (7.8 $\mu g/m^2$-yr) are somewhat greater than the Great Lakes (4.9 μg/m$^2$-yr). The lower value for the Great Lakes is in part due to lower areal rates for Lake Superior (1.9 μg/m$^2$-yr).

Total direct anthropogenic Hg emissions for 2005 for the GLB were 10 200 kg/yr, which corresponds to an areal flux of 13.4 μg/m$^2$-yr across the entire GLB (Table 3). Of these emissions about 60% are as Hg$^o$ and 40% occurred as oxidized Hg. The Hg emissions in the GLB represent 8.8% of the total anthropogenic Hg emissions for the U.S. and Canada (115 300 kg/yr). The Great Lakes are 32% of the area of the GLB. As a result of this relatively large fraction of open water area, the total and areal fluxes of anthropogenic Hg emissions give the appearance of being relatively low. Note however, there are numerous Hg emission sources in close proximity to the GLB. As we consider 50, 100 and 200 km buffers adjacent to the GLB, there is an exponential increase in total Hg emissions to a value of 30 200 kg /yr for the GLB plus a 200 km buffer or 26.2% of the Canadian and U.S. total Hg emissions (Table 3). Increasing the buffer area from 50 to 100 and to 200 km around the GLB direct, increases the areal fluxes of total anthropogenic Hg emissions over these areas from 14.2 to 15.2 to 17.1 μg/m$^2$-yr, respectively (Table 3), demonstrating the importance of emission sources adjacent to the Great Lakes watershed. Note that these proximate emission sources are highly relevant to Hg dynamics for the GLB because they are within the spatial scale for deposition of oxidized species of Hg emissions (reactive gaseous Hg and particulate Hg; Driscoll et al. 2007a). Within the GLB plus the 200 km buffer region, emissions of oxidized Hg are 12 900 kg/yr, or 43% of total Hg emissions. This pattern suggests that regional and local scale Hg emissions are undoubtedly important to the ecosystem effects of Hg deposition for the GLB (Drevnick et al. this issue). For the GLB, direct anthropogenic Hg emissions are somewhat greater but comparable in magnitude to our estimate of Hg re-emissions indicating that re-emission (i.e., evasion) is an important pathway of Hg to the atmosphere.

We find that rates of $Hg^o$ evasion are less than total atmospheric Hg deposition, within the uncertainty of this analysis. From the MDN, we estimate 6100 kg wet Hg deposition for the GLB, or an areal rate of 8.1 $\mu g/m^2$-yr. This input is somewhat less than our estimate for $Hg^o$ evasive losses. Estimated dry Hg deposition from EPA CMAQ simulations for 2001 is 7450 kg/yr or 9.8 $\mu g/m^2$-yr, somewhat greater than the estimate of wet Hg deposition for the GLB. Our estimate of litter fall Hg deposition for forest lands of the Great Lakes watershed is 2370 kg/yr, for an areal rate of 8.3 $\mu g/m^2$-yr. As forest cover is 36%, this flux is prorated as 3.1 $\mu g/m^2$-yr over the entire GLB. The sum of our estimates of these three deposition fluxes is 15 950 kg/yr or 21.0 $\mu g/m^2$-yr, more than double our estimate of evasion Hg losses. Quémerais et al. (1999) observed fluvial Hg losses for Lake Ontario of 112 kg/yr, suggesting a total fluvial Hg loss of approximately 0.15 $\mu g/m^2$-yr from the entire GLB. This analysis suggests that the GLB is currently a net sink for atmospheric inputs of Hg.

## Conclusions

In summary, we have synthesized rates of $Hg^o$ evasion from a comprehensive literature review to develop an estimate of annual $Hg^o$ evasion from the GLB. Our literature review identifies the need for standardized analytical and reporting methods for Hg evasion measurements. In addition, specific land cover areas would benefit from increased research efforts, particularly agricultural lands, where few studies have been conducted, and Lakes Erie and Huron, which appear to be unstudied relative to $Hg^o$ evasion. Some difficulty arises in synthesizing $Hg^o$

evasion rates from the literature due to seasonal and diel changes in evasion rates, coupled with methodological variations between studies. There is a need for additional measurements of $Hg^o$ evasion in the winter and from snowpack. Within the GLB, areal evasion rates for urban, agricultural, and grasslands are greater than other landcover types, and the estimate for evasion in the region as a whole. Agricultural, forest, and the Great Lakes together contribute approximately 95% of the region's total Hg evasion, due in large part to the high areal coverage of the Great Lakes and forest, and both coverage and evasion rates of agricultural land. In conjunction with mass balance elements of the GLB, our analysis indicates that the GLB is a net sink for atmospheric inputs of Hg.

## Acknowledgements

We thank Marty Risch, David Gay, Tom Holsen and Kim Driscoll for their help with this analysis. We also appreciate the assistance of the reviewers, who provided constructive and helpful critiques, and whose comments have benefited the paper. Support for this study was provided by New York Energy Research and Development Authority and the U.S. Environmental Protection Agency.

## Tables

Table 1. Summary of terrestrial Hg fluxes measured in or near the Great Lakes Basin. Note: some studies only measured Hg fluxes during the daytime—to estimate diel fluxes from daytime measurements, a Gaussian distribution was assumed following the methods of Engle et al. (2001) and Nacht and Gustin (2004). All estimated diel fluxes are presented in italics in the Table and the measured hourly fluxes given in parenthesis (ng/$m^2$-hr). For land covers where multiple DFC measurements exist, a potential range of values is given in parenthesis that reflects diel and seasonally adjusted flux estimates.

| **Land cover** | **Site Description** | **Season** | **Method** | **Daily flux (ng/$m^2$-d)** | **(Hourly flux) (ng/$m^2$-hr)** | **Flux used for scaling (ng/$m^2$-d)** | **Conc. (ng/g)** | **Reference** |
|---|---|---|---|---|---|---|---|---|
| Forest | Deciduous forest--Adirondacks, NY, USA | Spring | DFC | 15 | (0.64$^{a}$) | 19<br>(Potential range: | 81.9±24.7 | Choi and Holsen, 2009a, b |
| | | Summer | | 32 | (1.34$^{a}$) | | | |
| | | Fall | | 19 | (0.77$^{a}$) | | | |
| | | Winter | | 22 | (0.09$^{a}$) | | | |
| | | Annual Ave | | 19 | (0.80$^{b}$) | | | |
| | Deciduous forest--Oak Ridge, TN, USA | Spring/ Summer | DFC | *10 to 33** | (2.0 to 7.0$^{c}$) | | 469 ± 75 | Carpi and Lindberg, 1998 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Forest-- Nova Scotia, Canada | Summer | DFC | *8.5*<br>(1.1[c]) | 6.2 to 33) | 150 - 330 | Schroeder et al. 2005 |
| | Deciduous forest—Upper Peninsula Michigan, USA | Summer | DFC | *22*<br>(1.4 ± 1.4[c]) | | 69 - 98 | Zhang et al. 2001 |
| | Deciduous forest—Standing Stone State Forest, TN, USA | Spring | DFC | 0 (0.0±0.3[c]) | | | Kuiken et al. 2008 |
| | | Summer | | 3.1 (0.4±0.3[c]) | | | |
| | | Fall | | 7.0 (0.9±0.6[c]) | | | |
| | | Winter | | 4.7 (0.6 ±0.5[c]) | | | |
| | | Annual Ave | | *6.2*<br>(0.4 ± 0.5) | | | |
| Agriculture | Disturbed soil—Tennessee, USA | Spring/<br>Summer | DFC | *82 to 230*<br>(12 ± 5.4 to 45 ± 5.2[c]) | 58<br>(Potential range: 82 to 230) | 61± 19 to 111±14 | Carpi and Lindberg, 1998 |
| | Cropland- Maryhill, Ontario, Canada | Fall | MM | 2.4 (0.1 ± 0.2[d]) | | 400[e] | Cobbett and Van Heyst, 2007 |
| | Cropland- Minnesota, USA | Spring | MM | 230 (9.67[d]) | | 24.8 ± 4.2 | Cobos et al. 2002 |
| | Snow covered rural soil—Elora, Ontario, Canada | Winter | DFC | *1.0* (0.09±0.03[c]) | | NA | Schroeder et al. 2005 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Grassland | Pasture, Ontario and Quebec, Canada | Summer | DFC | 43* (3.0[d]) | 40<br>(Potential range: 36 to 43) | 6 | Schroeder et al. 2005 |
| | | | MM | 26 (1.1[d]) | | 47 | |
| | | | MM | 70 (2.9[d]) | | 100 | |
| | Pasture—Upper Peninsula Michigan, USA | Summer | DFC | *36** (7.6 ±1.7[c]) | | 16 | Zhang et al. 2001 |
| | Wisconsin | Not specified | DFC | 7.2 (0.3± 0.07[d]) | | <10 to 28 | Ericksen et al. 2006 |
| Urban | Pavement—Toronto, Ontario, Canada | Summer | DFC | *4.3** (1.0[f]) | Pavement: 3.6<br>(Potential range: -0.24 to 4.3) | 16 | Eckley and Branfireun, 2008 |
| | Soil—Toronto, Ontario, Canada | Summer | DFC | *29** (6.2[f]) | | 61 | |
| | Pavement—Tuscaloosa, Alabama, USA | Spring | DFC | 139 (5.8[a]) | Soil: 55.2<br>(Potential Range: 29 to 62) | Not measured | Gabriel et al. 2006 |
| | | Summer | | 264 (11[a]) | | | |
| | | Fall | | 26 (1.1[a]) | | | |
| | | Winter | | 34 (1.4[a]) | | | |
| | | Annual Ave | | 62 (2.6) | | | |
| | Soil—Tuscaloosa, Alabama, USA | Spring | DFC | -0.48 (-0.02[a]) | | 25 to 47 | |
| | | Summer | | 0.48 (0.02[a]) | | | |
| | | Fall | | -3.6 (-0.15[a]) | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Winter | | 2.2 (0.09[a]) | | | |
| | | Annual Ave | | -.24 (-0.01) | | | |

[a] Median value from diel measurements

[b] Annual estimate adjusted (+20%) to account for limited UVB permeability of polycarbonate chamber

[c] Hourly average measurements during daytime/sunlight conditions.

[d] Diel average

[e] Concentration after biosolids application

[f] Median value from daytime measurements conducted at several locations

*Adjusting this value to account for seasonal variability based on the findings of Choi and Holsen (2009a)

Table 2. Area of land cover types, areal Hg evasion rate for land cover type, and total and percentage of Hg evasion by land cover type for the Great Lakes Basin.

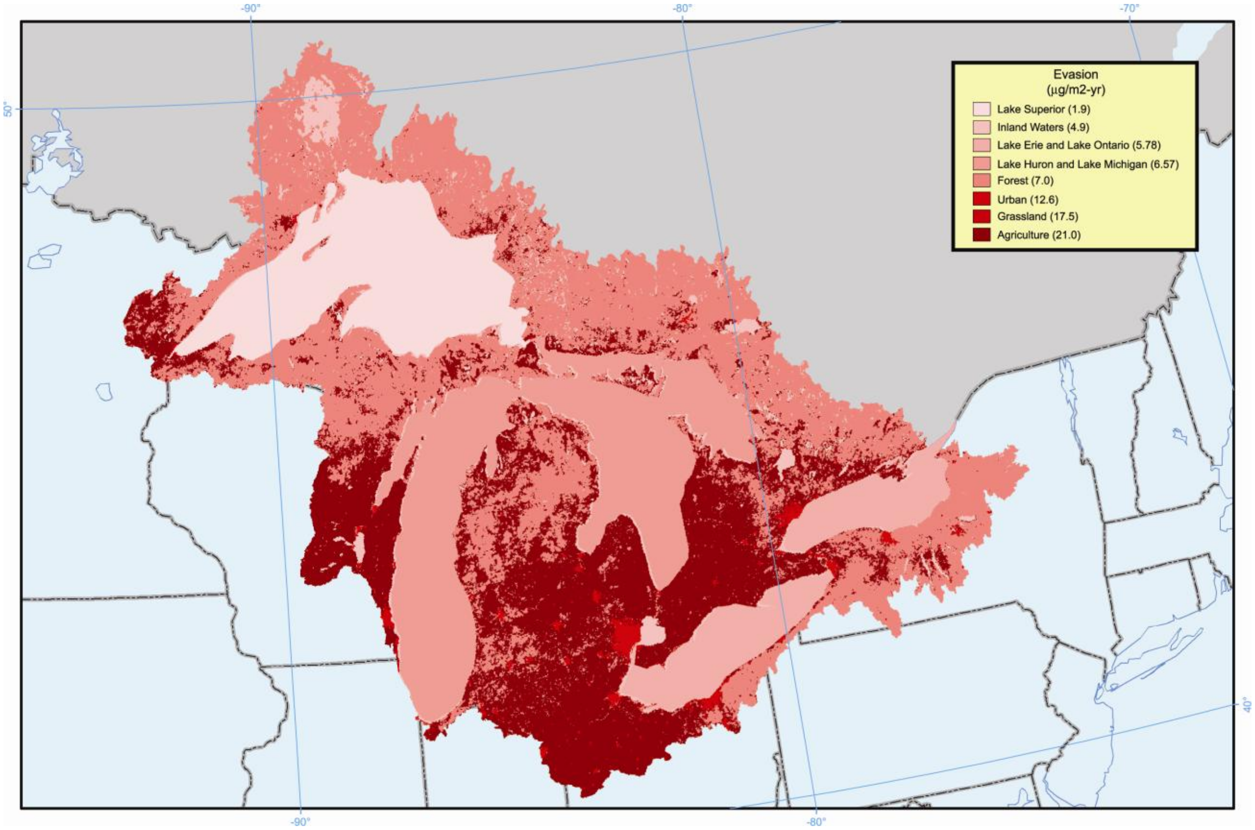
| **Land cover** | **Area** | | **Hg evasion rate** | | **Total Hg evasion (kg/yr)** | **Percentage of total Hg evasion** |
|---|---|---|---|---|---|---|
| | **($km^2$)** | **(% of total)** | **(µg/$m^2$-yr)** | **(ng/$m^2$-hr)** | | |
| Urban | 9420 | 1 | 12.6 | 1.4 | 120 | 1.5 |
| Agricultural | 202 600 | 27 | 21 | 2.4 | 4260 | 55.0 |
| Grassland | 198 | 0.03 | 17.5 | 2.0 | 35 | 0.4 |
| Forest | 277 700 | 37 | 7.0 | 0.8 | 1900 | 25.1 |
| Inland waters | 24 200 | 3 | 7.8 | 0.9 | 190 | 2.4 |
| Great Lakes | 244 160 | 32 | 4.9 | 0.6 | 1190 | 15.4 |
| Total | 760 000 | 100 | 10.2 | 1.2 | 7700 | 100 |

Table 3. Comparison of rates of Hg evasion estimated for the Great Lakes Basin with direct total Hg emissions (including $Hg^o$ and oxidized (ox) Hg), wet, dry and litter Hg deposition. Note that total Hg deposition is the sum of wet, dry and litter deposition. Because many emission sources are proximate to the Great Lakes Basin also included are direct total Hg emissions for the GLB plus for the lands within 50, 100 and 200 km buffer areas. Note that areal fluxes are prorated across the entire GLB (plus any buffer area), including the Great Lakes.

| **Flux** | **Total Hg flux (kg/yr)** | **Areal Hg flux (µg/$m^2$-yr)** |
|---|---|---|
| Evasion | 7700 | 10.2 |
| Direct anthropogenic emissions | 10 185 (ox 4100, $Hg^o$ 6100) | 13.4 |
| Direct emissions with 50 km buffer | 14 608 (ox 5200, $Hg^o$ 9500) | 14.2 |
| Direct emissions with 100 km buffer | 19 200 (ox 7500, $Hg^o$ 11 700) | 15.2 |
| Direct emissions with 200 km buffer | 30 200 (ox 12 900, $Hg^o$ 17 300) | 17.1 |
| Wet deposition | 6100 | 8.1 |
| Dry deposition | 7400 | 9.8 |
| Litter deposition | 2400 | 3.1 |
| Total deposition | 15 900 | 21.0 |

## Figure

Figure 1. Map of the Great Lakes Basin showing rates of elemental mercury evasion.



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