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^0) 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^0 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: 7.0–21.0 μg/m²-yr), with higher rates associated with urban (12.6 μg/m²-yr) and agricultural (21.0 μg/m²-yr) lands. Uncertainty in these estimates could be partially remedied through a unified methodological approach to estimating Hg^0 fluxes.

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1. 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^0) is oxidized through different mechanisms to mercuric ion (Hg^{2+}), and Hg^{2+} is in turn reduced through various pathways to Hg^0. 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^0 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^0. Evasion of Hg^0 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^0, resulting in volatilization of Hg^0. Loss of Hg^0 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^0 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^0 (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, 1995), and reduction of Hg^{2+} involving oxygen radicals such as $O_2^{\bullet-}$, HO•, and

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H_2O_2 (Dommergue et al., 2003; Schroeder et al., 1992). Photode-composition of MeHg directly to Hg^0 has also been suggested (Tossell, 1998; Bloom et al., 2001). Because photo-reduction of Hg^{2+} is an important driving mechanism, studies are characterized by marked diel changes in evasion rates.

Published measurements of Hg^0 volatilization rates include both aquatic and land surfaces. The rates of Hg^0 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^0 has an atmospheric residence time of around 1 year (Fitzgerald and Mason, 1997; Smith-Downey et al., 2010). As a result, Hg^0 may be transported globally prior to being deposited back to the Earth's surface following volatilization. Deposition occurs following oxidation of Hg^0 to Hg^{2+}, and subsequent complexation of Hg^{2+} with airborne particulates or dissolution in water. In forest systems Hg^0 can enter the stomata of leaves which can be deposited to the forest floor during litterfall (Driscoll et al., 2007b). Hg^{2+} returns to the Earth's surface as wet (i.e., rain), dry (i.e., particulate, gaseous), or litterfall deposition. Recent estimates have suggested that Hg^0 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^0 from Lake Ontario was estimated by Lai et al. (2007) to be approximately 5.8 μg/m^2-yr. Likewise, in a Hg mass balance for Arbutus Lake in the Adirondack Mountains, New York, Selvendiran et al. (2009) esti-mated fluvial Hg loss to be 1.2 μg/m^2-yr and Hg^0 volatilization to be 7.8 μg/m^2-yr.

Given the importance of Hg^0 evasion to the overall mass balance of watersheds, we review the literature on surface-air fluxes of Hg^0 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^0 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.

2. Literature review of mercury evasion estimates

Our review of Hg^0 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^0 evasion were selected for each land cover, and used to calculate total Hg^0 evasion for the GLB. For the purpose of this analysis, Hg^0 fluxes discussed and selected for scaling purposes are net gaseous exchange values (i.e., flux values presented account for both gaseous Hg^0 deposition and emission).

Surface Hg^0 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^0 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^0 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^0 evasion than solar radiation during the dry period. While some studies have suggested that prolonged soil moisture might inhibit Hg^0 evasion (Schroeder

et al., 2005; Selvendiran et al., 2008), others have noted elevated Hg^0 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^0 evasion between some pavement sites in Tor-onto, and suggested this difference was a result of different pave-ment compositions.

Some studies have measured Hg^0 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 radia-tion 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^0 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 incorpo-rated daily and seasonal variability in developing annual flux esti-mates, as well as studies from within/near the GLB.

Surface Hg^0 fluxes can be measured/modeled using several approaches. For soils, dynamic flux chambers (DFC) and micro-meteorological methods (MM) are the most common techniques and for aquatic ecosystems, DFCs and purge/trap methods are routinely applied. Additionally, both Hg^0 detectors and mathe-matical models used to estimate Hg^0 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^0 flux, some component of the variability in Hg^0 fluxes among landscapes reported is a function of differences in flux measure-ment 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^0 evasion during periods of snow cover is minimal. While this may be true for the soil itself, studies have reported substantial rates of Hg^0 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 esti-mated Hg^0 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^0 emission from the snow cover period in the GLB.

2.1. 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