Chapter-11

TERRESTRIAL MERCURY FLUXES: IS THE NET EXCHANGE UP, DOWN, OR NEITHER?

Mae S. Gustin[1] and Steven E. Lindberg[2]

[1] *Department of Natural Resources and Environmental Science University of Nevada-Reno, NV*
[2] *Environmental Science Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA*

INTRODUCTION

Natural terrestrial sources of atmospheric mercury (Hg) include geologically enriched substrate, volcanoes, geothermal areas, forest fires, vegetation, and "background soils" (soils that have low concentrations of Hg ($<0.1\mu g$ Hg/g) and have not been enriched by geologic processes). Emissions from the latter three are probably dominated by re-emission of previously deposited atmospheric Hg derived from anthropogenic and natural sources. Natural terrestrial sinks include soils, plant foliage, and regions where the atmospheric chemistry facilitates formation of reactive gaseous Hg (RGM) (i.e. Polar Regions).

Modeled estimates of natural source emissions in the literature range from 800 to 3000 Mg/y (Nriagu, 1989; Lindqvist et al., 1991; Mason et al., 1994; Mason and Sheu, 2002; Lamborg et al., 2002; Seigneur et al., 2001; Bergan et al., 1999) (Table 1). Most of these were derived by difference, using measured air Hg concentrations, wet deposition rates, and anthropogenic emissions estimates in mass balance models, and are based on precious few (if any) actual flux measurements from substrate. Mercury is also known to be dry deposited although this is often not considered. Lindberg et al. (1998) used measured terrestrial flux data to develop an estimate of emissions from forests and background soils ranging from 1400

to 3400 Mg/y. However, their estimate did not include Hg fluxes from naturally geologically enriched substrates, volcanoes, geothermal systems and fires; which, as new data described below demonstrates, will add significantly to the emissions.

Point source anthropogenic emission estimates remain highly uncertain (up to 50%) (Pai et al., 1998; Pacyna et al., 2001); yet, the range applied in global mass balance models is more limited than that for natural sources (~2000 to 2400 Mg/y) (Bergan et al., 1999; Mason and Sheu, 2002; Lamborg et al., 2002; Seigneur et al., 2004) (Table 1). Dastoor and Larocque (2004) concluded that known anthropogenic emissions can account for only ~1/3 of the measured concentration of gaseous elemental Hg (Hg^0) at ground level, and suggested that natural sources and re-emission account for 2/3 of the total estimated 6400 Mg emitted each year. Pirrone et al. (2001) suggested that natural and anthropogenic emissions in Europe were approximately equal.

Table 1. Summary of recent Global flux estimates for the sources and sinks of atmospheric mercury.

Source	Range in emissions Mg/y	References
Anthropogenic	2000 to 2400	Bergan et al., 1999; Mason and Sheu, 2002; Lamborg et al., 2002; Seigneur et al., 2004
Natural terrestrial	800 to 3000	Nriagu, 1989; Lindqvist et al., 1991; Masonet al., 1994; Mason and Sheu, 2002; Lamborg et al., 2002; Seigneur et al., 2001; Bergan et al., 1999
Re-emission	?	
Total emissions	6000 to 6600	Bergan et al., 1999; Mason and Sheu, 2002; Lamborg et al., 2002; Seigneur et al., 2004
Sink	Deposition, Mg/y	
Oceans	500, 1230	Lamborg et al., 2002; Mason and Sheu; 2002
Wet and dry deposition	3000	Mason and Sheu, 2002

Global estimates for wet deposition to the continents are 2000 Mg/yr with dry deposition estimates at 1000 Mg/yr (Mason and Sheu, 2002) (Table 1). This is not enough to balance the estimated 6000 to 6600 Mg/y (Bergan et al., 1999; Mason and Sheu, 2002; Lamborg et al., 2002; Seigneur et al., 2004) emitted.

The arctic sink (see below) appears to account for only a few hundred Mg/y (Schroeder et al., 2003). Recent models indicate that the ocean could

be a sink; however, as Mason and Sheu (2002) point out, there is limited and variable data for assessing the role of the ocean in the Hg biogeochemical cycle. Mason et al. (1994) first suggested that the net ocean flux was zero; however, Mason and Sheu (2002) revised this estimate, based on new data on concentrations of RGM in the marine boundary layer, and concluded that the ocean is a net sink (~500 Mg/y). Lamborg et al. (2002) assumed significantly lower ocean evasion rates than Mason and Sheu (2002) (820 Mg/y versus 2665 Mg/y, respectively), and suggested the ocean is a net sink (1230 Mg/y). These differences in numbers illustrate that the quantitative role of the ocean remains uncertain.

Based on current data and the uncertainty associated with flux estimates, we appear to have too many sources and not enough sinks for atmospheric Hg. If air concentrations are not increasing, then we must be missing or underestimating some important sinks, or perhaps Hg is constantly recycled between terrestrial ecosystems and the atmosphere. The latter process would give Hg the overall appearance of exhibiting a long residence time when it actually is rather short for any particular atom. In this paper we will summarize our current understanding of natural terrestrial sources and sinks for atmospheric Hg. Advances in our ability to measure atmospheric Hg concentrations and speciation have allowed us to improve the estimates of emissions from geologically enriched substrates, assess the potential significance of atmospheric Hg exchange with background soils, and allowed us to generate data that will help us understand the significance of vegetation in Hg cycling.

ASSESSMENT OF THE SIGNIFICANCE OF GEOLOGIC SOURCES

Natural geologic sources of Hg include volcanic emissions, enhanced Hg flux from zones of high crustal heat flow, areas of fossil and current geothermal activity, and volatilization from substrate naturally enriched in Hg (which may include areas of precious and base metal mineralization) (Table 2). These natural sources tend to be concentrated within, but are not limited to, three broad global belts that include plate tectonic boundaries (cf. Pennington, 1959; Jonhanssan and Boyle, 1972).

Volcanic emissions. Volcanic emission estimates are typically based on a few measured Hg/SO_2 mass ratios, which are then scaled up using SO_2

concentrations derived for volcanic systems. Hg/SO2 ratios span four orders of magnitude (Pyle and Mather, 2003).

The wide range in the data is due to the fact that Hg content of volcanic gases can vary as a function of the eruptive phase of the system and geologic setting (Pyle and Mather, 2003; Varenkamp and Buseck, 1981; 1984; 1986).

Table 2. Summary of estimated fluxes of Hg for terrestrial sources and sinks.

Source	Range in emissions, Mg/y	References
Volcanoes	94-700	Nriagu and Becker, 2003; Mather and Pyle, 2003
Geothermal	60	Varenkamp and Busek, 1984
Naturally enriched substrate	>1500	This paper
Background soils (re-emission and natural)	?	
Vegetated ecosystems	Forests-850 to 2000 Grasslands- 800 to 2300	Lindberg et al., 1998 Obrist et al., 2004
Forest fires	200 to 1000	Brunke et al., 2001; Friedli et al., 2001
Sink		
Litterfall sink	2400 to 6000	Lindberg et al., 2004
Arctic sink	100-300	Lindberg et al., 2002b; Schroeder et al., 2003; Skov et al., 2004
Background soils	?	

Estimates for volcanic emissions range from 1 to ~700 Mg/yr (Nriagu, 1989; Fitzgerald and Lamborg, 2003; Varenkamp and Buseck, 1986; Ferrara et al., 2000; Nriagu and Becker, 2003; Pyle and Mather, 2003). Pyle and Mather (2003) suggested that lower estimates were not accurate due to inappropriate extrapolation of data collected from low temperature degassing systems to active volcanoes. They suggested that 700 Mg/y was a more reasonable estimate of emissions with continuous degassing accounting for 10% of the flux, 75% being accounted for by small sporadic eruptions, and rare large events accounting for 15%. In contrast, Nriagu and Becker (2003) suggested that 94 Mg/y were emitted. As demonstrated by recent discussion (cf. Nriagu and Becker, 2004; Mather and Pyle, 2004) these estimates are highly uncertain.

Emissions from geothermal areas

In geothermal areas, Hg releases to the atmosphere will occur via three processes: evaporation from substrate enriched in Hg, volatile loss driven by high heat flow, and emission as a gaseous phase from fumaroles and hot springs. Emissions from geothermal systems are highly variable because factors such as the age and type of geothermal system as well as the host rock type will influence the amount of Hg released. For example, at the Steamboat Springs geothermal area, Nevada, USA, average Hg emissions from substrate (over the 8 km^2) were quite high (180 ng/m^{2}h) although soil Hg concentrations for the dominant substrate type were fairly low (1.9 ± 2.0 µg Hg/g) (Coolbaugh et al., 2002). The elevated soil flux was hypothesized to be due to the high heat flow in the area. Limited data for fumarole gases in this area indicated that concentrations ranged from 3040 to 100,000 ng/m^3 and were responsible for a small component of the total emissions (0.3 kg/y out of ~12 kg/y). Engle et al. (2004) found substrate Hg fluxes at Lassen National Park, California, USA, to be elevated (mean area flux from background soils was ~10 ng/m^{2}h) and suggested that subsurface heat flux was driving Hg through the soils. Based on measurement of fumarole gas concentrations, they estimated geothermal gas emissions of 2 to 9 kg Hg/yr, which are slightly less than estimated substrate emissions of 10 to 20 kg/y from 637 km^2. In contrast, recent work at Yellowstone National Park, WY, USA, indicated that in the caldera (2284 km^2), soil fluxes were only high in association with areas altered by acidic hydrothermal fluids (Engle et al., 2004). Fluxes measured from substrate with background Hg concentrations were extremely low, with no evidence of heat driving additional Hg from the substrate. The Yellowstone hydrothermal system is associated with a mantle hot spot and heat has been moving through substrate in the area for hundreds of thousands of years. It is possible here that much of the Hg may have been released in previous eruptions and during earlier heating events, or that there is not much Hg associated with the host rocks (Engle et al., 2004).

Varenkamp and Busek (1984) estimated that geothermal sources contributed roughly 60 Mg/y to the atmosphere based on the average Hg content in hot springs and global convective heat transport. Their estimate did not include volatilization from naturally enriched soils or fumaroles, which could be a more significant source than hot springs. Because of the variability from system to system, their estimate is highly uncertain. Scaling up geothermal emissions to obtain a global estimate is difficult without additional flux data from a variety of representative systems.

Emissions from naturally Hg-enriched soils

In order to scale up emissions from substrate geologically enriched in Hg, the factors controlling emissions must be understood. Process level information is now being developed with this objective. Gustin (2003) summarized the current understanding of the controlling mechanisms, and separated them into two groups: those that control the magnitude of the flux, and those that control seasonal and diel variations in flux. Substrate Hg concentration, rock type, the presence and type of hydrothermal alteration, and the presence of heat sources and geologic structures will influence the overall magnitude of emissions. Meteorological parameters, especially increases in light (Gustin et al., 2002), temperature (Lindberg et al., 1979; Gustin et al., 1997), and precipitation (Lindberg et al., 1999), as well as soil moisture (Gustin et al., 2004), will enhance Hg emissions and dictate diel trends. The potential for constituents of ambient air, to enhance Hg release from soils by a simple exchange process was suggested by Zhang and Lindberg (1999). Recent research by Engle et al. (2004) has demonstrated that atmospheric ozone will enhance Hg release from enriched soils.

Scaling up emissions for areas naturally enriched in Hg is usually done by making in situ flux measurements from representative substrate in an area and then developing algorithms between Hg flux and environmental parameters that allow for extrapolation of Hg fluxes to larger areas. Reported area average Hg fluxes, determined for naturally Hg-enriched terrains ranging in size from ~1 to 900 km^2, are 2 to 440 ng/m^2 hr (2 to 110 kg/yr) (Gustin, 2003). The magnitude of these flux estimates depends on the proportion of the surface area with high Hg-enrichment relative to that of the entire area studied. Mercury flux from substrate has been found to the strongly correlated with substrate Hg concentrations (Rasmussen et al., 1998; Coolbaugh et al., 2002; Zehner and Gustin, 2002). Typically, areas with high Hg concentrations in substrate are surrounded by areas with lower levels of enrichment that grade into regions with substrate of background concentrations. When emissions are scaled up for areas including predominantly the mineralized zone with high Hg concentrations, area average fluxes are quite high (i.e. Knoxville District, CA, USA, 114 ng/m^2 h, 37 km^2 (Gustin et al., 2003); Almaden, Spain, ~200 to 1500 ng/m^{2}h, ~1 km^2 (Ferrara et al., 1998)). If the area of scaling includes zones of concentrated Hg mineralization, the surrounding area with low levels of Hg enrichment and some background soils, the area average flux becomes less due to the lower fluxes from the background terrain (i.e. Medicine Lake, CA, USA, 2 ng/m^2 h, 242 m^2 (Coolbaugh et al., 2002); Flowery Peak, NV, USA, 18.5 ng/m^2 h, 251 m^2 (Engle and Gustin, 2002)). In areas typical of the Hg global

belts there are zones of concentrated Hg enrichment surrounded by vast areas of substrate with low and background Hg concentrations. When scaling most of the emissions occurs from the terrain covered by the latter two substrates because they cover a larger surface area (Gustin, 2003).

In order to understand the significance of natural source emissions we need to develop defensible approaches to scale the spatially limited measured fluxes to larger areas. This is difficult, and only one rigorous attempt has been reported in the literature. Zehner and Gustin (2002) estimated area average Hg emissions for the state of Nevada, USA, which is located within one of the global mercuriferous belts. Their GIS approach entailed the use of a detailed geologic map of the state, the average Hg concentration for specific rock types published in the literature, a database of ~71,000 Hg concentrations in substrate, an algorithm developed from field data (n=303) relating Hg flux to soil Hg concentration (r^2=0.71 for a log-log plot, p<0.005), and delineation of areas of hydrothermal alteration using LANDSAT imagery. Based on their compiled data, the mean area average flux for the state ranged from ~3 to 4 ng/m^{2}h depending on assumptions made regarding the proportion of wet and dry deposition, and re-emission amounts (30-50%). They estimated an overall net emission of 10 Mg/y which is ~1/4 of that thought to be contributed to the atmosphere by coal-fired utility plants in the United States (EPA, 1997). If one scales up their minimum estimate for Nevada to the land area of the global mecuriferous belts given in Lindqvist et al. (1991), a global geologic substrate emission estimate of ~1500 Mg/y is obtained. This should be considered a minimum estimate, however, because not all Hg enriched areas are located within these global belts. Early global models applied a value of ~1 ng/m^{2}h to these broad belts which resulted in a global estimate of 500 Mg Hg/y (cf. Lindqvist et al., 1991). Based on measured fluxes reported by Zhang et al. (2001) and Nacht and Gustin (2004) for background substrates, the flux of 1 ng/m^{2}h is more representative of emissions from terrestrial landscapes with background Hg concentrations.

THE ROLE OF BACKGROUND SOILS

In areas without natural Hg-enrichment by geologic processes after rock formation, Hg in the surface soils consists of a fraction that exists in the parent rock material (USGS, 1970), plus that deposited from the atmosphere over time. For example, Obrist et al. (2004) reported that in tall grass prairie soils the top 1 cm had Hg concentrations of 20 $\pm$ 1.4 ng Hg/g while

concentrations at 170 cm were 3.7 ± 0.2 ng Hg/g. The concentration at depth represents the natural geologic signature of the substrate, and the surface concentration, the natural signature plus enrichment from atmospheric deposition directly to the soil and to the overlying vegetation. Atmospheric deposition can include dry deposition of Hg^0 and RGM and wet deposition of what is thought to be predominantly RGM (Schroeder and Munthe, 1998). In the past the contribution from wet deposition was considered the major input. It has been suggested that dry deposition of gaseous elemental Hg^0 to soils could be important (cf. Engle et al., 2001; Kim et al., 1995) and with the developed capability to measure RGM (cf. Landis et al., 2002), which has a high deposition velocity (Lindberg and Stratton, 1998), we are beginning to realize that the oxidation of Hg^0 to RGM, and its subsequent dry deposition could be an important process.

Only recently has work been systematically done to investigate the potential for background soils to be a source or sink of Hg^0. Laboratory studies, using cleaned air (stripped constituents other than nitrogen and oxygen), have revealed a very low range in Hg^0 compensation point air concentrations for soil types with different characteristics (0.1 to 2.4 ng/m^3) (Xin et al., in prep). At air concentrations above the compensation point Hg^0 is deposited to substrate, while below that concentration Hg^0 is emitted. However, when similar experiments are done using ambient air, the data are noisy, resulting in poor regression coefficients for air Hg concentration versus flux, and a higher range for the compensation point (3 to 9 ng/m^3). These observations suggest that in cleaned air, soil physicochemical properties are influencing the compensation point, while in ambient air the compensation point is also influenced by atmospheric chemistry. Engle et al. (2004) have demonstrated in the laboratory that Hg^0 is liberated from soils when they interact with air containing ozone. In addition to heterogeneous reactions between soils and the atmosphere, precipitation, light and increased temperature promote the release of Hg from background soils, as they do for Hg enriched substrates (Gustin et al., 2002; Zhang et al., 2001; Gustin et al., 2004). Once deposited, atmospheric Hg can also become sequestered in surface soils, and its residence time will vary and cannot be generalized. It can be re-emitted by processes described above, removed from the soil surface by processes such as transport via erosion or burial, or it can become strongly adsorbed to soil mineral or organic constituents. The potential for sequestration in the soil and re-emission is being investigated as part of the METALLICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the United States) project (cf. Hintleman et al. 2002). This project, now in its 5th year, uses stable Hg isotope spikes to different ecosystem compartments to see how Hg moves through the system. Lindberg

et al. (2003) estimated that short-term re-emission, immediately following deposition, removed ~10 to 40% of the Hg added as $HgCl_2$, with the percentage dependant upon the surface (the highest re-emission rates occurred for deposition to water surfaces).

Thus, these new data indicate that background soils can accumulate Hg^0 by direct dry deposition, and a variety of physicochemical parameters, including light, moisture, and atmospheric chemistry can facilitate re-emission. Data from the METALLICUS project suggests that RGM deposited in precipitation, as Hg (II), may be rapidly re-emitted once deposited. This process of cycling of Hg between background substrate and the atmosphere would significantly affect the ability of simple mass balance models to successfully model the global Hg cycle.

THE ROLE OF VEGETATION

Vegetation has been demonstrated to function as a sink and source for atmospheric Hg. Foliar uptake of Hg^0 has been suggested to be an important pathway for atmospheric Hg to enter terrestrial ecosystems, and may represent a significant unrecognized sink within the biogeochemical cycle (Lindberg et al., 1992; Ericksen et al., 2003; Lindberg, 1996). Frescholtz et al. (2003), using multiple plant growth chambers and different air and soil Hg exposure concentrations, demonstrated that Hg^0 was accumulated by aspen foliage as a function of air concentration and time. They showed that air concentrations were the dominant factor controlling foliage concentrations and that soil Hg concentration exerted a minor influence. Mosbaek et al. (1988) also demonstrated that the atmosphere was the primary source of Hg in three crop species.

Atmospheric Hg accumulated in foliage could then be transferred to terrestrial and aquatic ecosystems by way of litterfall. Mass balance data collected in forested ecosystems suggests that litterfall is the largest single flux of Hg and methyl Hg to forested systems (Iverfeldt, 1991; Johnson and Lindberg, 1995; Munthe et al., 1995; St Louis et al., 2001). Some authors (e.g. Driscoll et al., 1994; Johnson and Lindberg, 1995; Rea et al., 2002; Ericksen et al., 2003) have suggested that dry deposition to the forested landscape can be estimated from simple measures of throughfall (includes dry deposited $RGM+Hg_p$) plus litterfall. A very crude estimate of the global flux of Hg in litterfall was made by Lindberg et al. (2004) assuming a range of Hg concentrations in background foliage of ~20-50 ng/g (e.g. Friedli et al., 2001; Lindberg, 1996; Rea et al., 2002; Frescholtz et al., 2003) and

global litterfall rates (e.g. Matthews, 1997). This Hg dry deposition flux, if real, could represent an additional Hg sink on the order of ~2400 to 6000 T/y. Some of this additional sink is temporary, of course, with the ultimate net sink depending on the rate of Hg sequestration in soils. However, since Hg sequestered in soils resides initially in the organic horizon, it too is subject to some degree of re-emission, either slowly by evasion, or quickly by fire or other types of disturbance.

Laboratory studies have demonstrated, depending on air and soil Hg concentrations, plants can emit Hg to the atmosphere. To predict whether Hg will be deposited or emitted from foliar surfaces, compensation point concentrations need to be identified for various plant species under different conditions. At concentrations above the compensation point atmospheric Hg^0 will be deposited to the leaf surface and below this concentration Hg^0 will be emitted. Ericksen and Gustin (2003) demonstrated a compensation point of 3 to 4 ng/m^3 in the light and 2 to 3 ng/m^3 in the dark for aspen saplings using a single plant gas exchange chamber. A higher range was determined for red maple, white oak and Norway spruce (10 to 25 ng/m^3) by Hanson et al. (1995). Work is ongoing to determine the compensation point for a variety of other plant species.

Deposition and emission fluxes of Hg to terrestrial and aquatic vegetated systems have been measured in field studies (Lindberg et al., 1998; 2002a; Lee et al., 2002). Lindberg et al. (1998) determined that the net flux was emission for a mature deciduous forest and a pine plantation (mean 20-30 ng/m^2 hr) growing in soils with low Hg concentrations (~50 – 500 ng/g). Lindberg et al. (1998), 2002a suggested that emissions from forests alone could range from 850 to 2000 Mg/y (Table 2). Obrist et al. (2004) measured Hg fluxes over a year in large mesocosms containing intact monoliths of tall grass prairie (soil Hg = 4 to 20 ng/g), and determined that the annual net exchange was 61 ± 25 ug/m^2 with some deposition occurring only in the winter months. They scaled up measured Hg^0 fluxes to the area of the world's grasslands (~3.75 x 10^7 km^2 (DeFries and Townshend, 1994)), and found that Hg emissions to the atmosphere could be ~ 800 to 2300 tons year[1]. It is unclear however, for these two estimates how much Hg was moved from the soil through the plant to the atmosphere for fluxes associated with foliar surfaces were not directly measured. Mercury being moved from the soil to the atmosphere by plants can be new Hg derived from the soil pool and re-emission of previously deposited atmospheric Hg.

The presence of a foliar canopy can reduce substrate emissions. In controlled mesocosm studies, using Hg contaminated soils (12.3 μg Hg/g), during leaf-out, it was clearly demonstrated that Hg flux declined as the soil was shaded by the developing leaf canopy (Gustin et al., in review). Under

the full canopy, Hg flux was reduced 1.2 to 1.5 times relative to that occurring from bare soil. Zhang et al. (2001) compared Hg emissions occurring from soils in shaded versus open field sites and found that fluxes were reduced in the shaded site. Gustin et al. (in review) determined that reduction of light on the soil due to the plant canopy was the primary factor causing the reduced flux.

Thus, plants can assimilate atmospheric Hg^0 in their tissue, they can move gaseous Hg^0 from soil pools to the atmosphere (thereby enhancing the net emission over that of bare soils), and they can reduce Hg^0 emissions from soils by way of shading the soil surface. The relative significance of these processes is highly uncertain, and cannot readily be considered in global models.

Because the volatility of Hg is well known and its accumulation in foliage has been demonstrated, it should come as no surprise that biomass burning has recently been suggested to be a significant source of atmospheric Hg. New aircraft measurements of Hg, CO and CO_2 in plumes have been applied for making estimates of Hg released during biomass burning. Mercury emissions of 200 to 1000 Mg/y, were estimated by Brunke et al. (2001) and Friedli et al (2001). Biwas et al. (2003) suggested that soil burning released a more significant amount than biomass, and estimated that 100 Mg/y was removed by this process.

THE POLES AND OTHER NEW SINKS

New laboratory and modelling studies of the role of reactive halogens, especially bromine (e.g. Ariya et al., 2002; Calvert and Lindberg, 2003) clearly indicate their ability to oxidize Hg^0 from the global pool to more reactive and shorter-lived airborne Hg (II) species. This process has been observed during the polar winter and spring after polar sunrise where Hg^0 becomes depleted in the atmosphere, and simultaneously, RGM and particulate Hg concentrations increase with subsequent increases in Hg concentrations in snow (Lindberg et al., 2002b). Initially the atmospheric Hg depletion events measured in the Arctic were postulated to be an important Hg sink (e.g. Schroeder et al., 1998; Lindberg et al., 2002b; Ebinghaus et al., 2002). However, estimates of the size of this net sink (perhaps a few hundred T/y after accounting for re-emissions (e.g. Lindberg et al., 2002b; Schroeder et. al., 2003; Skov et al., 2004) suggest that this may not be a large enough sink to offset the various new sources recently quantified. New data suggests that Polar warming could alter this cycle dramatically (e.g. Schroeder et. al.,

2003), increasing the area over which depletion event occur (Lindberg et al., 2002b). Other evidence suggests that similar halogen reactions, mediated by oxidants such as hydroxyl radical (e.g. Weiss-Penzias et. al., 2003), and oxidation and dry deposition of gaseous Hg (II) over the oceans in more temperate regions of the globe (e.g. Mason and Sheu, 2002) may contribute to a shorter residence time of Hg than predicted. The magnitude of the latter potentially important sink throughout the marine boundary layer as suggested by Mason and Sheu (2002) remains to be quantified.

Finally, the recent reporting of a highly enriched layer of aerosol Hg at the tropopause (associated with elevated halogens, e.g. Murphy and Thompson 2000), makes one question whether stratosphere/troposphere cycling should be included in the global cycle.

CONCLUSIONS

Current emissions estimates for Hg inputs to the atmosphere are on the order of 6000 to 6600 Mg/y, with natural source estimates ranging from 800 to 3400 Mg/y, and anthropogenic sources estimates ranging from 2000 to 2400 Mg/y (Table 1). Re-emission of previously deposited Hg derived from natural and anthropogenic sources is an unquantified source that would add to the atmospheric pool. As discussed above, there is significant uncertainty associated with these estimates. If air concentrations are not increasing, dry and wet Hg deposition estimates (~3000 Mg/y) do not balance the estimated inputs. The role of the ocean as a source or sink is uncertain and based on limited and variable data. Litterfall could be an important unaccounted for sink (though temporary); however, plants may also move Hg from the soil to the atmosphere, and the relative significance of these two processes is not known. In addition, the significance of the role of background soils as a sink, source or temporary resting place for Hg is not known. Based on recent work it appears that Hg can be fairly rapidly cycled between terrestrial surfaces and the atmosphere. This would cause us to have to rethink the year long residence time that is usually attributed to Hg and revolutionize our thinking with the respect to the whole Hg biogeochemical cycle. Investigations of soil compensation points suggest that the balance between deposition and emission can occur at low air concentrations. This work along with the ongoing work to characterize the significance of re-emission is critical for understanding whether simple mass balance models are adequate for characterizing global Hg fluxes.

Because of the large range of uncertainties in estimates of the significance of natural sources or sinks (Table 2), and our incomplete understanding of processes controlling Hg cycling, the question of whether the true net flux of Hg is directed towards or away from the Earth's surface may not yet be answered. Recent research is pointing towards a more rapid recycling between terrestrial surfaces and the atmosphere than has previously been realized, leading us to speculate that the atmospheric residence time is much shorter than models predict. If this is true, global reductions of Hg emissions to the atmosphere should have significant impacts on Hg cycling. However, reductions of industrial emissions will be offset by the degree to which previous deposition is being re-emitted. New isotope manipulation data suggest that deposited Hg is rapidly re-emitted at rates, which decrease over time (Lindberg et al. 2003). New point source controls will initially be most effective in reducing the deposition of the most reactive forms of Hg emitted, and it may require years after major controls to see significant reductions of the overall global pool of Hg^0 because of recycling.

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