An update on the natural sources and sinks of atmospheric mercury

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Abstract

This paper summarizes recent advances in the understanding of the exchange of Hg between the atmosphere and natural terrestrial surfaces including substrates (soil, rocks, litter-covered surfaces and weathered lithological material) and foliage. Terrestrial landscapes may act as new sources of atmospheric Hg, and as repositories or temporary residences for anthropogenically and naturally derived atmospheric Hg. The role of terrestrial surfaces as sources and sinks of atmospheric Hg must be quantified in order to develop regional and global Hg mass balances, and to assess the efficacy of regulatory controls on anthropogenic point sources in reduction of human Hg exposure.

Continued field research has allowed for refinement of emission estimates for geothermal and volcanic, and Hg mineralized areas in the western USA to ∼1.2–3.0, and 10–20 Mg/a, respectively. The emission estimate for areas of Hg mineralization in the western USA includes only identified Hg deposits and occurrences, and since other areas of geologic Hg enrichment such as Au and Ag deposits are not considered, the range in values is most likely an underestimate. Laboratory and field measurements have improved understanding of air–surface Hg exchange associated with soils with low or natural background concentrations of Hg (<100 ppb), litter-covered forest floors, and foliar surfaces, all of which have large spatial coverage. Deposition of atmospheric Hg and re-emission are important processes occurring at these surfaces on diel and seasonal time scales. Foliage is a significant sink for atmospheric elemental Hg, however, the net flux associated with low Hg containing soils is uncertain. Mass balances developed for soil–air exchange using measured fluxes and estimated deposition indicate that over a year background soils may exhibit no net flux. This suggests that the residence time for elemental Hg in the air is on the order of hours to weeks. Short term exchange would result in a homogenous air Hg concentration due to constant mixing and in an apparent calculated residence time that is most likely too long (one year). Recycling of atmospheric Hg between natural background soils and foliar surfaces also provides a mechanism for long-term atmospheric contamination and continued deposition in pristine ecosystems well after anthropogenic sources are controlled.

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1. Introduction

Natural emissions of Hg to the atmosphere occur from areas with ongoing geologic activity (volcanic and geothermal) and from substrates with elevated

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Hg concentrations (>100 ppb) due to mineralization as a result of geologic processes that occurred in the past. Geologically-derived naturally Hg-enriched areas are in general concentrated in broad global belts that coincide with major plate tectonic boundaries (cf. Pennington, 1959; Johanson and Boyle, 1972). However, there are Hg-enriched areas outside these boundaries, i.e. areas of Fe mineralization in Michigan and Zn mineralization in Missouri and Canada (Rytuba, 2003, 2005) and Siberia (Obolenskiy, 1996). Some component of emission from these naturally enriched areas includes re-emission of Hg deposited from the atmosphere.

Other "natural" terrestrial sources of atmospheric Hg include emission from background or low-Hg containing soils/substrates (<100 ppb) and foliar surfaces, and biomass burning. Emission from these sources is hypothesized to be predominantly re-emission of Hg deposited from the air by wet and dry processes derived from both anthropogenic and natural sources. Important identified natural sinks for atmospheric Hg are soils, plant foliage, and regions where the atmospheric chemistry facilitates formation of reactive gaseous Hg (RGM) (i.e. polar regions, marine boundary layer).

Estimates of global natural source emissions range from 800 to 3000 Mg/a (Nriagu, 1989; Lindqvist et al., 1991; Mason and Sheu, 2002; Seigneur et al., 2001). Although estimates for individual anthropogenic point source emissions have an uncertainty of up to 50% (Pai et al., 1998; Pacyna et al., 2001), the range in published values for global anthropogenic releases (~2000–2400 Mg/a) is small compared to that reported for natural sources. Gustin and Lindberg (2005) indicated that the estimated Hg emissions to the atmosphere were significantly greater than known sinks, highlighting the uncertainties in the global Hg mass balance. This paper will summarize some recent advances in the authors' assessment of natural terrestrial sources and sinks for atmospheric Hg. Refinements in their understanding of air–substrate and air–foliar Hg exchange and the impacts of these advancements on assessment of the fate and transport of Hg in the environment will be discussed.

2. Natural geologic sources of atmospheric Hg

Estimation of Hg releases from volcanoes is difficult due to spatial and temporal variability in activity, and the overall lack of data (Gustin and Lindberg, 2005). Emission estimates are typically developed by applying the few available Hg/SO_2 mass ratios to measured SO_2 concentrations derived for volcanic systems. Mercury/SO_2 ratios span four orders of magnitude (cf. Pyle and Mather, 2003) and reflect the fact that Hg and SO_2 content of volcanic gases can vary as a function of the eruptive phase of the system and geologic setting (Pyle and Mather, 2003; Varekamp and Buseck, 1981, 1984, 1986). Estimates for total global volcanic emissions range from 1 to ~700 Mg/a (Nriagu, 1989; Fitzgerald and Lamborg, 2005; Varekamp and Buseck, 1986; Ferrara et al., 2000; Nriagu and Becker, 2003; Pyle and Mather, 2003). Using SO_2 emission data for Mt. St. Helens, the only recently active volcano in the United States, Engle and Gustin (2006) estimated that during non-eruptive years, as is currently the case, releases were negligible, and during eruptive years the amount released would be dependent upon the size of the eruption (~0.05–800 Mg/a).

Geothermally active areas exhibit spatial and temporal variability in terms of gas flux that is influenced by the age and type of geothermal system, system heat flow and geologic host rocks. Mercury releases are associated with three processes: (1) volatile loss driven by heat flow, (2) emission from fumaroles and hot springs as a gas phase, and (3) release from substrate enriched in Hg as a result of geothermal processes. Engle et al. (2006a) estimated that currently active geothermal and volcanic sources in the conterminous United States emitted 1.2–3.1 Mg/a. The only global estimate for geothermal emissions is that of Varekamp and Buseck (1984) of 60 Mg/a, developed based on the average Hg content in hot spring waters and global convective heat transport.

Factors thought to be important in controlling air–substrate exchange associated with naturally Hg-enriched (>100 ng Hg/g) substrates include 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 have been described as influencing the overall magnitude of emissions (Gustin, 2003; Rasmussen et al., 2005). Substrate Hg concentration is a parameter well correlated with Hg flux in Hg-enriched areas (Rasmussen et al., 1998; Feng et al., 2005; Gustin et al., 2003). Meteorological parameters, especially light (Gustin et al., 2002; Zhang et al., 2001), temperature (Lindberg et al., 1979; Gustin et al.,

1997), and precipitation (Lindberg et al., 1999; Nacht and Gustin, 2004; Song and van Heyst, 2005; Wang et al., 2005) have been clearly demonstrated to be important in influencing Hg flux. Recent work has shown that soil moisture plays an important role in controlling emissions from naturally Hg-enriched soils and low Hg containing soils (Gustin and Stamenkovic, 2005; Ericksen et al., 2005, 2006; Gustin et al., 2006; Song and van Heyst, 2005; Bahlmann et al., 2004). These four parameters in general enhance Hg emissions, and exhibit significant variability on diel and seasonal time scales. Since Hg flux is correlated with these parameters it is expected that Hg air–substrate exchange also exhibits significant variability across space and time. It is important to consider this variability when developing natural source emission estimates based on point source measurements and to collect empirical data that reflects this variability. Engle et al. (2005) demonstrated that atmospheric ozone will enhance Hg released from both Hg-enriched and natural background soils. This suggests that spatial variability in atmospheric chemistry can influence substrate Hg release, with those areas impacted by urban air pollutants potentially exhibiting exacerbated emissions.

3. Background soils

Soils with low or background Hg concentrations cover large spatial areas, therefore understanding their role as a net source or sink of atmospheric Hg as well as the parameters controlling the exchange is important. In most pristine ecosystems the soil Hg pool is the largest reservoir of Hg (Krabbenhoft et al., 2005). In areas without natural Hg-enrichment by geologic processes, Hg in the surface soils consists of a component derived from parent rock material plus that contributed by wet and dry deposition from the atmosphere. The average crustal abundance for Hg in rocks (60 ppb; Wedepohl, 1995) and the mean for igneous rocks (80 ppb; Turekian and Wedepohl, 1961) are indicative of indigenous Hg concentrations of soils. Mercury input from the atmosphere to these soils may be sequestered, mobilized to aquatic systems or re-emitted.

Mercury that is supplied to terrestrial surfaces in rain in the United States is measured at ∼90 sites across the United States as part of the National Mercury Deposition Network (MDN: nadp.sws.uiuc.edu/mdn). Wet deposition amounts vary across the United States from 2 to 20 $\mu g/m^2$ a.

Limited field experiments, using the addition of specific stable Hg isotopes as $HgCl_2$ to simulate precipitation inputs, suggest that only a small component of the Hg input to ecosystems by way of precipitation is released from soils immediately, and only about 10% is emitted over a year (Hintelmann et al., 2002; Amyot et al., 2004; Ericksen et al., 2005). Laboratory studies also support a low amount of immediate re-emission (Xin et al., 2007; Matilainen et al., 2001; Schluter, 2000).

All operationally defined forms of atmospheric Hg- elemental Hg (Hg°), reactive gaseous Hg (RGM) and particulate Hg (Hg$_p$) may be dry deposited. Dry deposition amounts are often estimated using models that apply measured air concentrations and estimated deposition velocities.

A standard deposition velocity for Hg° has not been established, and is confounded by the fact that the exchange of Hg° with most terrestrial surfaces is bi-directional. Empirical data indicate that the dry deposition of Hg° directly to soil and litter-covered surfaces is an important process (Lyman et al., 2007; Gustin et al., 2006; Ericksen et al., 2005; Kuiken et al., 2008a,b; Zhang et al., 2001; Nacht and Gustin, 2004; Engle et al., 2001). Field and laboratory data also indicate that Hg° flux associated with background soils can cycle between deposition and emission on diel and seasonal time scales depending on environmental conditions. For example, Gustin et al. (2006) showed for a site in Nevada, that net emission was characteristic of winter conditions when soil moisture was high, whereas net deposition was characteristic of summer months when the soils were dry. Dry deposition during warmer months has been shown to be an important flux in other studies (Gustin et al., 2006; Ericksen et al., 2005; Engle et al., 2001). Diel deposition and emission has also been reported with emission being important during light conditions and deposition occurring in the dark (Ericksen et al., 2005; Gustin et al., 2006; Zhang et al., 2001; Poissant et al., 2005; Stamenkovic et al., submitted for publication; Xin et al., 2007).

Dry deposition of RGM is typically modeled based on air concentrations and deposition velocities established for HNO_3 vapor. There have been several studies that have tried to measure dry deposition using the modified Bowen ratio (Lindberg and Stratton, 1998; Poissant et al., 2005). This is difficult due to current detection limits and analytical precision for instruments that quantify RGM. A more recent study focused on development of a surrogate

surface that would allow for estimation of dry deposition of reactive Hg (Lyman et al., 2007). Deposition of particulate Hg has been found to be important in both rural and urban areas (Lyman et al., 2007; Keeler et al., 1995).

Based on the limited data available, it is hypothesized that the re-emission of Hg that is wet and dry deposited may not occur immediately after deposition, but that this Hg may be contained in the surface soil pool where it may be sequestered and eventually re-emitted to the air (cf. Xin and Gustin, 2007). The relative importance of these processes are not understood; however, based on simple scaling exercises (see below) it is possible that re-emission occurs gradually over long periods of time depending on environmental conditions and soil properties. Meteorological parameters, described above, that control emissions from Hg-enriched soils also affect emission of Hg° from low Hg containing soils (Gustin et al., 2006; Zhang et al., 2001). Another factor that will influence the amount of Hg released is the available pool of Hg. The pool includes indigenous Hg within the soil column that may be transferred to the soil surface by diffusion and mass transport (Gustin and Stamenkovic, 2005; Zhang and Lindberg, 1999; Johnson et al., 2003) and all operationally defined forms derived from the atmosphere. Air Hg concentrations may also influence the direction of flux. For example, Xin and Gustin (2007) found in laboratory experiments that at air concentrations of $<5 \text{ ng/m}^3$, Hg deposition was the dominant flux in the dark and emissions were observed in the light; whereas at $>5 \text{ ng/m}^3$ deposition was the dominant flux in the light and dark. Additionally several studies have shown that the presence of clay, Fe oxide and Fe oxy-hydroxide minerals influence the adsorption of atmospheric Hg by background soils (cf. Fang, 1978; Landa, 1978; Xin and Gustin, 2007).

Published Hg fluxes described for low Hg containing soils range from −2 to 13 ng/m^2 h (Schroeder et al., 1998, 2005; Poissant and Casimir, 2005; Zhang et al., 2001; Nacht and Gustin, 2004; Ericksen et al., 2005, 2006). Much of these data were collected during the summer and in the daytime and therefore, do not provide an adequate data set for assessment of diel or seasonal flux (c.f. Gustin et al., 2006; Stamenkovic et al., submitted for publication). Recently developed empirical data indicate that in order to develop accurate Hg flux estimates, data should be collected over 24 h as a function of seasonal climatic conditions.

In many areas litter-covered soils dominate the surface. Kuiken et al. (2008a) have summarized the litter–air Hg exchange occurring from an eastern forest floor over a year. Mercury fluxes were low with the mean daytime flux being $0.4 \pm 0.5 \text{ ng/m}^2 \text{ h}$ and dominated by emission (81% of ~300 thirty-min flux measurements). Using data from a nearby MDN site, Kuiken et al. (2008a) found that calculated annual emissions from the forest floor could only account for 1/3 of the Hg input by way of wet deposition. They suggested that perhaps Hg deposited in rainfall is immediately re-emitted or becomes sequestered in the surface litter and soils. In another study, Kuiken et al. (2008b) measured air–surface exchange for six forested locations along the eastern seaboard, USA, during late spring to early summer. They found the fluxes were low $0.2 \pm 0.9 \text{ ng/m}^2 \text{ h}$ and that dry deposition of Hg° was measured 48% of the time ($n = 310$). Stamenkovic et al. submitted for publication found that fluxes measured from litter-covered soils of tall grass prairie monoliths housed in large mesocosms, were significantly lower than those associated with bare soil in the summer but similar in the winter.

As outlined above Hg released from background soils can be derived from the parent material or the atmosphere and a variety of factors, including light, soil moisture, soil and atmospheric chemistry (air Hg concentrations and presence of atmospheric oxidants) can influence deposition, emission and re-emission. Limited laboratory and field studies indicate that RGM input by way of precipitation will not be re-emitted immediately. This form could be gradually reduced to Hg° which would then be volatilized to the atmosphere (Xin et al., 2007). Since it appears that Hg° is cycled between the soil and air on diel and seasonal time steps, this confounds the ability to apply simple mass balance models to assess the global Hg cycle and to predict the effectiveness of regulatory controls.

4. The role of vegetation

The importance of foliar uptake of atmospheric Hg° has been demonstrated by numerous laboratory and field studies (c.f. Frescholtz et al., 2003; Ericksen et al., 2003; Millhollen et al., 2006a,b; Rasmussen et al., 1991). Research has shown that plant uptake is dependent upon plant species and age, as well as air Hg concentrations. It is now thought that foliar uptake and sequestration is an important net sink for atmospheric Hg° and emissions from

foliage do not reflect translocation of Hg from the soil through the plant but simply re-emission of Hg deposited from the atmosphere. Using a plant gas exchange chamber, Millhollen et al. (2006a) showed that although plants act as a net sink for atmospheric Hg, exchange at foliar surfaces is dynamic with emission, deposition and re-emission all occurring. Similarly, Graydon et al. (2006) suggested that some of the Hg (II) deposited to foliage in precipitation was rapidly reduced and re-emitted back to the atmosphere. Other studies have shown deposition rates measured with a dynamic chamber to be similar to foliar uptake rates developed based on the change in concentration over time supporting the hypothesis that Hg in foliage is derived from the atmosphere (Fay and Gustin, 2007; Stamenkovic et al., submitted for publication). There are limited data that suggest that Hg in the soil is transferred to plant tissue. For example, Bishop et al. (1998) estimated 3% of the methyl Hg and 11% of the total Hg in conifer needles could be derived from the soil. Frescholtz et al. (2003) found a statistically significant influence of soil Hg concentrations on foliar Hg concentrations at high (>20 μg/g) exposures.

In contrast, Lindberg et al. (1992), applied a modified bowen ratio method for measurement of Hg flux associated with a forest canopy and concluded that emission was the dominant flux based on a preponderance of gradient measurements (14 out of 23) indicating emission. It is possible that measured emission simply reflected re-emission of Hg deposited by dry and wet processes from the atmosphere and not translocation from the soil to the atmosphere. Deposition of Hg to foliar surfaces was found to be the dominant flux associated with tall grass prairie vegetation growing in large mesocosms (Stamenkovic et al., submitted for publication). This is in contrast to the conclusions developed by Obrist et al. (2005) who suggested the ecosystem was a source of atmospheric Hg. The latter estimate has now been shown to be an artifact of the experimental system (Stamenkovic and Gustin, 2007).

The vegetation sink for atmospheric Hg is important to consider in global Hg mass balance models. The transfer of atmospheric Hg to forested ecosystems by way of litterfall has been suggested to be the largest Hg flux to forest floors (Iverfeldt, 1991; Johnson and Lindberg, 1995; Munthe et al., 1995, 2004; St. Louis et al., 2001). Lindberg et al. (2004) estimated that the global flux of Hg in litterfall was ∼2400–6000 Mg/a. Given the size of this esti-

mate vegetation could be the missing sink in global mass balances.

The presence of a plant canopy may also impact the whole ecosystem flux by reducing emissions from underlying substrates. In controlled mesocosm studies, using Hg contaminated soils (12.3 μg Hg/g), it was clearly demonstrated that during leaf-out Hg flux declined as the soil was shaded by the developing leaf canopy (Gustin et al., 2004). Under the full canopy, Hg flux was reduced 1.2 to 1.5 times relative to that occurring from unshaded 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. Recent work by Kuiken et al. (2008a) showed that emissions from litter-covered forest floors were higher in the winter than in the summer and attributed this largely to lack of the leaf canopy in winter. Litter-covered surfaces have also been shown to suppress emissions from the underlying bare soils in summer (Stamenkovic et al., submitted for publication). These studies illustrate the need to include seasonality in estimates of the direction and magnitude of Hg flux from forested systems.

5. Other natural sources and sinks

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 is a source of atmospheric Hg. Measurement of Hg, CO and CO_2 concentrations in plumes of fires have been applied to estimate Hg released during biomass burning. Global emission estimates of Hg released are 200–1000 Mg/a (Brunke et al., 2001; Friedli et al., 2001). Friedli et al. (2003) estimated approximately 3.7 ± 1.9 Mg/a were released by fires in the United States. Biwas et al. (2007) suggested that soil burning released a significant amount of Hg during fires based on a study conducted in the Rocky Mountains. Engle et al. (2006b) found Hg in foliage, bark and litter to be the dominant pool of Hg released during three fires in Nevada/California, USA. Since soils contain more than 90% of the total ecosystem Hg reservoir (Krabbenhoft et al., 2005), the contribution of soils to emissions during fires still needs to be resolved.

Laboratory and modeling studies have shown that reactive halogens, can oxidize gaseous Hg° to reactive and shorter-lived airborne Hg (II) species (e.g. Ariya et al., 2002; Calvert and Lindberg, 2003; Lin and Pehkonen, 1999). This has been

observed after polar sunrise in the Arctic and in Antarctica where Hg° concentrations in the atmosphere decreased simultaneously with increases in air RGM and particulate Hg concentrations and snow Hg concentrations (Lindberg et al., 2002; Temme et al., 2003). Initially it was hypothesized that snow in polar regions was a significant Hg sink (e.g. Schroeder et al., 1998; Lindberg et al., 2002; Ebinghaus et al., 2002). However, recent work has shown that the size of this net sink is on the order of a few hundred Mg/a after accounting for re-emission (e.g. Lindberg et al., 2002; Schroeder et al., 2003; Skov et al., 2004). Other evidence suggests that in urban areas, similar halogen reactions mediated by oxidants such as the hydroxyl radical may occur along with direct interactions with atmospheric oxidants resulting in conversion of Hg° to RGM (c.f. Weiss-Penzias et al., 2003; Stamenkovic et al., 2007). It has also been suggested that oxidation and dry deposition of gaseous Hg over the oceans and seas in more temperate regions of the globe may contribute to a shorter residence time of Hg° than predicted (e.g. Mason and Sheu, 2002; Hedgecock and Pirrone, 2001, 2004).

6. Estimating the contribution of Hg to the atmosphere from natural sources

Scaling up emissions measured from areas naturally enriched in Hg to larger areas has been done using empirical data to develop algorithms between Hg flux and environmental or substrate parameters. Area average fluxes of 2–440 ng/m² h (2–110 kg/a) for regions of ∼1–900 km² have been reported (Gustin, 2003; Rasmussen et al., 1998; Coolbaugh et al., 2002; Zehner and Gustin, 2002; Ferrara et al., 1998). The size of the Hg-mineralized area included in the scaling exercise can influence the area average flux obtained as small areas of substrate with high levels of Hg enrichment will have greater amounts of Hg released than the surrounding terrain with low to background Hg concentrations. Rasmussen et al. (2005) offered some cautionary notes regarding estimating emissions from areas of natural enrichment. They noted that use of substrate Hg concentrations alone are not adequate for scaling up Hg emissions for: (1) the substrate Hg concentration versus flux relationship falls apart at low Hg concentrations, (2) there are other factors that impact emissions to a comparable degree that need to be considered, and (3) the databases needed to develop the flux estimates

are limited and will impact the accuracy of flux estimates.

In this section estimates of natural source emissions developed at regional scales are discussed and revised and the values obtained compared to estimates of wet and dry deposition. Empirical data used as the basis for these scaling exercises are limited in terms of spatial and temporal resolution. Spatial differences in deposition must also be considered. Lyman et al. (2007) found that wet and dry deposition data collected at two rural MDN sites in Nevada, similar in setting and ∼200 km apart, could differ by 2-fold on a seasonal and annual basis (Lyman et al., 2007).

Zehner and Gustin (2002) compiled flux data, substrate surface Hg concentrations and LANDSAT imagery to develop a Hg emission estimate of 5–10 Mg/a for the state of Nevada, USA with 2.2 Mg being derived from the naturally enriched areas. The range in values for the state reflects the fact that the emission estimate depended on the amount of Hg input by wet and dry processes that was assumed to be re-emitted. They applied a flux of 3.5 ± 1.2 ng/m² h to the land area considered to have background Hg concentrations. Here we revise the Zehner and Gustin (2002) estimate based on new flux data developed for natural background soils (Gustin et al., 2006; Ericksen et al., 2006), and using wet and dry deposition estimates developed for two MDN sites in Nevada. Applying an area flux of 0.5 ng/m² h for background soils, a statewide emission estimate of 1.2 Mg/y was obtained for the low Hg containing areas resulting in a Nevada flux of 3.4 Mg/y. Comparing these emissions with the annual estimate of Hg input via wet and dry deposition at two MDN sites developed by Lyman et al. (2007) for Nevada of 1.5 Mg/y (Table 1) shows that ½ of the emissions could be re-emission of Hg.

Another method for estimating Hg emissions from natural sources over a region was applied by Gustin et al. (2000) who used a database with locations of Hg deposits and occurrences and applied emission rates to these areas based primarily on the degree of mineralization and economic Hg production (Table 2). They obtained an emission estimate of 10 Mg/a for Hg mineralized areas along the western coast of North America (Nevada, California, Washington, Oregon, Idaho, Utah, Arizona, Alaska and Mexico). This estimate should be considered conservative for it did not account for emissions from areas of other types of mineralization

Table 1
Summary of estimates for emission and deposition provided in the text

Area considered	Emission estimate (Mg/a)	Deposition estimate (Mg/a)	References
United States			
Volcanoes	0		Engle and Gustin (2006)
Geothermal Areas	1.2–3		Engle et al. (2006a)
Fires	3.6 ± 1.9		Friedli et al. (2003)
Entire land area	44–150	120	Ericksen et al. (2006)
Nevada			
Hg-enriched areas	2.1–2.4		Gustin et al. (2000)/Zehner and Gustin (2002)
Background and enriched substrates	3.6–10	1.5–3.5	Zehner and Gustin (2002)/this paper/Lyman et al. (2007)
Western United States[a]			
Hg-enriched areas	10–20		Gustin et al. (2000)/this paper[a]
Background and enriched substrates	46–90	40	This paper[a]/Lyman et al. (2007)
United States Anthropogenic Point Source emissions			
	150		Seigneur et al. (2004)

[a] States include Arizona, California, Idaho, Nevada, Oregon, Utah and Washington.

Table 2
Models to estimate Hg emissions associated with areas of Hg mineralization in the Western United States

Area type	2000 Model		2007 Model 1		2007 Model 2		References
	Area	Flux	Area	Flux	Area	Flux	
>1000 Flasks	25	30	200	15	100	15	Engle et al. (2001)/Coolbaugh et al. (2002)/Gustin et al. (2002)
100–1000 Flasks	20	30	100	10	100	10	Engle and Gustin (2002)
<100 flasks	15	30	100	5	50	5	Engle and Gustin (2002)
Prospect or occurrence	100	10	100	5	50	5	Engle and Gustin (2002)/Coolbaugh et al. (2002)

Area types are designated based on their economic production of Hg in terms of flasks produced. One flask is 76 pounds or ~170 kg of Hg. An area designated as a prospect or occurrence is one where Hg was found but was not of high enough concentration to be extracted for a profit. The 2000 model is that described by Gustin et al. (2000) and the 2007 models were both developed using area and flux estimates developed based on field studies listed under references.

that have Hg associated such as Au and Ag deposits. Using this data set emissions for mineralized areas in Nevada were 2.1 Mg/a. This value is comparable to that developed for naturally enriched areas in Nevada by Zehner and Gustin (2002). In this paper the Gustin et al. (2000) estimate is refined using a similar approach but applying area flux estimates based on empirical data developed for Hg mineralized areas in the Western USA region (Table 1). A flux of 0.5 ng/m^2 h was applied to the background soils surrounding the areas of natural enrichment which comprised 96% of the total area. The estimated emission for areas of Hg mineralization alone was 11.4–19.3 Mg/a depending on the model used (Table 1) with an additional 35 Mg/a being emitted from the surrounding area of background soils. Note that the area of background soils is quite large and if flux for this land area is changed

only slightly to 1 ng/m^2 h the resulting flux is 70 Mg/a! Using the Lyman et al. (2007) deposition estimate for Nevada (which may not be applicable to other western states) the total deposition over the area of scaling is on the order of 40 Mg/a. Thus, deposition is roughly comparable to emission from background surfaces.

Ericksen et al. (2005) developed a crude estimate for Hg emissions from the conterminous United States using a mean empirically derived flux of 0.9 ± 0.7 ng/m^2 h for background substrates based on data collected during the summer from Midwestern and western United States locations. They assumed that the states of Washington, Oregon, California, Nevada and New Mexico were located within the global mercuriferous belt and applied the mean flux of 4.2 ng/m^2 h developed by Zehner and Gustin (2002) for Nevada. Because the number

for Nevada is most likely too high (as discussed above) and the background soil flux applied was based solely on summer data, there is significant uncertainty regarding the emission estimate of 95 Mg/a obtained (range 44–150 Mg/a). To place this emission estimate within the context of deposition, Ericksen et al. (2005) applied Hg wet deposition amounts from the MDN extrapolated across the United States (∼60 Mg/a). If the dry deposition flux is 50–100% of the calculated wet deposition inputs then emission and deposition estimates are comparable. The vegetation component was not considered in the scaling exercise of Ericksen et al. (2005). If included, since vegetation is an important sink for atmospheric Hg and forest and litter cover have been shown to reduce emissions from soils, forest and grassland cover will increase net deposition to an area. Since Hg assimilated by vegetation is a component of dry deposition this sink should be included in dry deposition estimates.

None of the emission estimates above take into account the spatial and temporal variability in flux that may occur due to environmental conditions. Spatially-explicit computer simulation modeling provides a mechanistic approach for scaling spatially and temporally limited field measurements to larger areas. Gbor et al. (2006) developed a Hg emission estimate for eastern North America using the CMAQ-Hg model. This study (1) assumed that transpiration from plants was important; (2) developed a soil Hg inventory that was gridded over their research domain; and (3) assumed that soil temperature was the major meteorological factor controlling emissions. All of these parameters have significant uncertainty, however the fact that they attempted to scale Hg fluxes using more than just area types and estimated fluxes is admirable. Gbor et al. (2006) obtained a simulated average flux for eastern North America of 1.8–3.7 ng/m^2 h, with the maximum occurring in the summer. Using a wet deposition input of 15 μg/m^2 a, the estimated hourly input would be 1.7 ng/m^2 which is at the low end of their range in emission rates.

Lastly, a crude way of calculating global natural source emissions is to apply one flux value to the global Hg belts. Lindqvist et al. (1991) applied a flux of 1 ng/m^2 h and obtained an annual flux of 500 Mg. If the flux obtained for Nevada in Zehner and Gustin (2002) is applied an annual flux of 1500 Mg is obtained. If the revised estimate for Nevada presented in this paper (1.5 ng/m^2 h) is used the annual flux is ∼750 Mg Hg/a.

7. Conclusions

The Hg research community is making steady progress towards understanding natural source Hg emissions. It appears that the amount emitted from volcanoes and geothermal areas from the conterminous United States is small (∼3 Mg/a) while releases from naturally Hg-enriched substrates is at the least 10–20 Mg/a. This range in values is based solely on areas of Hg mineralization in the western USA and should not be considered representative of the entire country. Additionally, the empirical databases used to develop this estimate are spatially and temporally limited.

In order to develop estimates of the regional and global significance of natural source emissions, Hg flux associated with natural background soils must be considered in addition to flux from enriched areas. Empirical data has shown that soils with low Hg concentrations can act as a sink or source for atmospheric Hg and due to their large spatial coverage small variations in fluxes applied in scaling can result in large flux differences. In addition, soil and foliar surface atmospheric Hg exchange are influenced by environmental conditions and this variation needs to be represented in scaling algorithms and emission estimates. All flux estimates must be placed within the context of wet and dry deposition when attempting to understand the significance of emissions. Data presented herein suggest that emissions from low Hg soils and litter reflects dominantly re-emission of Hg deposited from the atmosphere and emission and deposition over a year may balance each other. With climate change, the overall exchange of Hg between the air and the soils could result in more Hg in the air or more being sequestered in terrestrial ecosystems. It is also fairly clear that vegetation is an important net sink for atmospheric Hg. However foliar surfaces can also act as a dynamic surface of exchange for atmospheric Hg suggesting that measurements of foliar fluxes and over forest canopies will reflect the net flux and may not allow for adequate assessment of the input to forest floors. Foliar transfer of atmospheric Hg to substrates in litter fall estimated by Lindberg et al. (2004) indicates that vegetation is an important (and perhaps the missing) sink in the global Hg mass balance.

The simple exercises in scaling emissions from natural sources indicate that deposition inputs and re-emission of Hg derived from the atmosphere must be considered when making terrestrial source

estimates. If Hg is regularly recycled between substrates, foliage and the air, as recent data suggest, results of anthropogenic source controls may not be immediately realized except in those areas where local emissions dominate deposition. Regular exchange of Hg between the air and background substrates and foliage would also produce a homogenous air Hg concentration that would result in an apparent calculated long lifetime (year) for atmospheric Hg.

Acknowledgements

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