

EMISSION OF MERCURY TO THE ATMOSPHERE FROM NATURAL SOURCES IN NEVADA AND CALIFORNIA

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ABSTRACT

There is currently controversy regarding the relative contribution of mercury from naturally enriched areas versus anthropogenic point sources to the atmospheric mercury budget. Natural mercury enriched areas are found in three broad belts associated with recent volcanism, high crustal heat flow and plate tectonic boundaries. In order to resolve this controversy, emissions of mercury from natural sources need to be measured and scaled up to provide area emission estimates. In this study mercury emissions measured *in situ* were scaled up to provide an area estimate of mercury emissions from five naturally enriched areas. Area emissions ranged from 2.6 to 300 ng of mercury/m²h. These mercury emissions are greater than the value applied to naturally enriched areas in global models of ~1.5 ng/m²h and suggest that natural sources may be more important sources of atmospheric mercury than previously realized.

INTRODUCTION

Natural mercury (Hg) enrichment is distributed globally in three broad belts associated with high crustal heat flow, geothermal activity, plate tectonic boundaries and recent volcanism. Lindqvist et al. (1991) suggested that Hg emissions from global mercuriferous belts were on the order of 1.5 ng/m² h. Using this value global Hg models have been developed which suggest that emission of Hg to the atmosphere from anthropogenic sources is greater than emissions from natural sources (cf. Mason et al., 1994; Lindqvist et al., 1991). When these models were developed there was no physical data characterizing Hg emissions from natural geologically- enriched mercuriferous areas. Recent work has demonstrated that Hg emissions from substrate enriched in Hg through geologic processes range from 10 to 1000's of ng/m² h (cf. Rasmussen et al., 1998, Gustin et al., 1999; Gustin et al., 1999a, Gustin et al., in press).

Quantifying the magnitude of Hg emissions from natural sources is important for understanding the biogeochemical cycle of Hg and for assessment of the relative importance of anthropogenic versus natural source emissions. To quantify natural source emissions Hg flux data derived *in situ* must be scaled up to the landscape level. Naturally enriched areas are large in scale and spatially heterogeneous. However, spatial heterogeneity and Hg concentration in substrate (an important parameter controlling emissions) may be correlated with geologic features such as rock types, rock alteration, faults and areas of high heat flow. Information on the distribution of relevant geologic features may be incorporated into a Geologic Information System framework. This information along with data on *in situ* environmental parameters which influence Hg emissions may be used to develop an emission estimate for an area. This type of data analysis is needed to adequately assess the contribution of Hg from natural sources to the atmospheric Hg budget. This paper summarizes some of the work that has been done to scale up Hg emissions from naturally Hg enriched areas. Naturally enriched areas can be subdivided into two types: areas where Hg enrichment was high enough that the area was mined or prospected for Hg, and areas where there are low levels of Hg enrichment (0.1 to ~20 µg/g). The latter concentrations are found in areas of high heat flow, recent volcanic activity and in association with base and precious metal mineralization. Emissions from both of these types of areas has been scaled up in this study. We hypothesize that areas with low levels of enrichment will contribute more Hg to the atmosphere for they are much larger in areal extent than those locations with high concentrations of Hg.

STUDY AREAS

Mercury emissions were measured *in situ* from soils in five areas including two Hg mining districts, one area with Hg enrichment associated with precious metal mineralization, one area that is geothermally active and one area associated with recent volcanism. The New Idria Mining District, located in Central California, includes the New

Idria Mine, the second largest producer of Hg in the United States (Eckel and Myers, 1946). Mercury concentration in substrate at flux measurement sites not associated with mining ranged from 0.3 to ~170 $\mu\text{g/g}$, whereas in areas where mining occurred and mine wastes were present concentrations ranged from ~9 to 870 $\mu\text{g/g}$. The Ivanhoe Mining District, located in central northern Nevada was a small Hg mining district that produced ~2180 flasks (1 flask=34.5 kg). Soil Hg concentrations at locations where Hg fluxes were measured distal from mining area ranged from 0.05 to ~20 $\mu\text{g/g}$; concentrations in the areas where Hg was mined were 30 to 7000 $\mu\text{g/g}$. The Steamboat Springs Geothermal area, located ~ 10 km south of Reno, NV, is currently being exploited for geothermal energy and ~ 100 flasks of Hg were removed from one location. Mercury concentrations in substrate not associated with the area of mining ranged from <0.5 to 30 $\mu\text{g/g}$. The Flowery Peak area is ~30 km southeast of Reno and represents an area with low levels of natural enrichment associated with a mineralized area. This area includes the northern extend of the Comstock fault zone from which gold and silver were mined in the late 1800's. A small Hg mine, that produced ~260 flasks of Hg, is located in the study area. Mercury concentrations in substrate from which Hg flux was measured ranged from ~0.05 to 1.0 $\mu\text{g/g}$. The Medicine Lake study area is centered on a broad caldera developed on the summit of a shield volcano east of Mount Shasta in northern California. Recent volcanic activity (~1300 yrs ago) is present in the area and a geothermal field underlies the eastern part of the caldera. Mercury concentrations in soils from this area ranged from 0.01 to 30 $\mu\text{g/g}$.

METHODS APPLIED

Mercury emissions were measured using a field flux chamber and micrometeorological methods (cf. Gustin et al., 1999), and the automated Tekran[®] 2357A Mercury Analyzer. Simultaneously with Hg flux measurements, micrometeorological data, including air and soil temperature, light, barometric pressure, relative humidity were recorded. Soil samples were collected for total Hg analysis at each site. For scaling up emissions to the landscape level the Geographic Information System (GIS) program ArcView was utilized.

SCALING

Mercury fluxes in the New Idria Mining District were measured from mine and retort sites, representative areas of rock hydrothermal alteration and rock units representative of the district. Scaling was accomplished by multiplying the average flux for each of the above by their respective area. Topographic maps and the geologic map of Eckel and Meyers (1946) within the GIS were used to calculate area.

For the Ivanhoe district, a stepwise regression analysis was done to determine those factors most important in controlling emissions. Based on this analysis rock type, soil Hg concentration and proximity to faults were determined to be the primary factors controlling Hg flux. A mean Hg flux was calculated for each geologic unit and applied to that unit in the scaling exercise. The diel Hg flux pattern observed at several naturally enriched areas followed a Gaussian distribution. This allowed for calculation of an average daily flux for each sampling location using flux data obtained at different times of the day.

The Steamboat Springs Geothermal area was divided into 4 geologic units based on bedrock geology; heat flux (determined with Thermal Infrared Multispectral Scanner Images); the presence of siliceous sinter or microcrystalline quartz deposited in association with hot springs (from White et al., 1964); and rock alteration (determined using Airborne Visible/ Infrared Imaging Spectrometry). Mercury emissions measured from the 4 units *in situ* were applied to these units and used to scale up emissions for this area.

For the Flowery Peak area a nearest neighbor inverse distance weighting method was applied to interpolate fluxes between sampling sites. There was little variation in mercury concentrations throughout the study site, so this method allowed us to integrate emissions across an area that was fairly homogenous in terms of Hg concentrations.

Mercury flux has been demonstrated for some locations to have a strong correlation with soil Hg concentration (cf. Gustin et al., in press; Rasmussen et al., 1998). This relationship was used to scale up emissions for the Medicine Lake area since a contour map of Hg concentrations in substrate was available (Van Kooten, 1987). Soil concentration contours were digitized into ArcView and the appropriate Hg flux (determined using *in situ* measurements) for each range of soil concentrations was determined and multiplied by the area covered.

RESULTS and CONCLUSIONS

The range in Hg fluxes measured at the five sites is shown in Figure 1. The Steamboat Springs, New Idria and Medicine Lake fluxes represent 24 hour averages for the different types of substrate. The Ivanhoe and Flowery Peak fluxes are those measured at sites representing the different levels of Hg enrichment at different times of the day. At all areas of natural Hg enrichment fluxes ranged from background values (1-5 ng/m²h) to values in the 100's to 1000's ng/m² h. Fluxes measured at background sites were similar to the value suggested by Lindqvist et al. (1991) for naturally Hg enriched areas. The enriched sites exhibited emissions up to four orders of magnitude greater than the projected value. This flux data alone is not sufficient to demonstrate the overall impact of natural emissions on the atmospheric Hg budget: the fluxes must be scaled up to represent areas. Table 1 summarizes the results of scaling up of Hg emissions for each of the five areas. The area averaged emissions for the five areas studied were ~3 times to 2 orders of magnitude greater than the flux used to represent natural source emissions. Many areas in the western United States contain elevated Hg concentrations similar to those modeled here. The results of these scaling exercises indicate that natural Hg emissions may be more important than previously recognized. Based on the five areas studied, large areas with low levels of natural enrichment, as found at the Steamboat Springs and the Flowery Peak areas, are more significant sources than small areas of high levels of enrichment found in mining districts.

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Table 1 . Summary of scaling calculations

| Location | Area (km ²) | Annual Flux (kg/y) | Area averaged flux (ng/m ² h) |
|-------------------------------|-------------------------|--------------------|--|
| New Idria Mining District, CA | 387 | 11 | 3.2 |
| Ivanhoe Mining District, NV | 586 | 90 | 17.5 |
| Steamboat Springs Area, NV | 8 | 21 | 300 |
| Flowery Peak Area, NV | 250 | 61 | 28 |
| Medicine Lake, CA | 244 | 5 | 2.6 |

Figure 1. Summary of mercury emissions measured at naturally enriched areas. Bkg represents fluxes measured from areas with $\leq 0.1 \mu\text{g Hg/g}$; low indicates areas with 0.1 to $5 \mu\text{g Hg/g}$; high areas with $> 5 \mu\text{g/g}$; and Hg mine emissions from an area where mercury was mined. The Steamboat, New Idria and Medicine Lake fluxes represent 24 hour averages.

