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Assessing the Contribution of Natural Sources to Regional Atmospheric Mercury Budgets

Mae Sexauer Gustin* and Steven E. Lindberg#
* Department of Environmental and Resource Sciences, University of Nevada, Reno 89557
# Environmental Sciences Division, Oak Ridge National Laboratories,
P.O. 2008, Oak Ridge, TN 38731

Abstract

Contributions to the global atmospheric mercury budget originate from natural and anthropogenic sources. Constraining inputs from anthropogenic point sources has been the emphasis of past research leaving the contribution from diffuse natural and anthropogenic mercury enriched landscapes poorly constrained and underestimated. From September 1 to 4, 1997 mercury researchers convened in Reno, NV, USA to intercompare methods used to determine *in situ* mercury flux from a naturally enriched landscape. Data collected indicate that naturally mercury-enriched areas constitute a significant atmospheric Hg source term. Mercury fluxes of 30 to 2000 ng/m^2 h were measured at the Steamboat Springs Geothermal Area (0.8 to 10 μg Hg/g soil). These values are one to three orders of magnitude greater than that applied for natural sources in global mercury budgets (1.5 ng/m^2 h). Air concentrations measured in the area (2 to 450 ng/m^3) indicate that natural sources can increase ambient levels above background concentrations (1-3 ng/m^3). Assessment of these and other data indicate that natural sources constitute a significant source of atmospheric mercury that is available to the global mercury budget, and that the strength of the source is influenced significantly by environmental factors. Determining the contribution of mercury to the atmosphere from diffuse terrestrial sources is necessary to develop local and regional baselines for environmental regulations and risk assessments, and valid emission inventories. A scaling up mercury fluxes measured for diffuse terrestrial surfaces suggests that the natural atmospheric mercury source term in the United States is comparable to the anthropogenic source term.

Introduction

As a function of high vapor pressure elemental mercury (Hg°) is readily transported from the geosphere and hydrosphere to the atmosphere. Atmospheric mercury (>95% Hg°) is considered a global pollutant due to a ~ 1 year residence time and is derived from anthropogenic and natural sources. Because of the long residence time and ease in cycling between environmental compartments, the potential for the transport and deposition of atmospheric mercury (Hg), to pristine ecosystems is high.

The area chosen for the intercomparison was located 15 km south of Reno, Nevada (Figure 1). The area was on properties managed by the Bureau of Land Management and SBGeo, Inc. a geothermal energy production company. Mercury enrichment at the site is associated with an active geothermal system currently utilized for energy production by two geothermal power plants producing ~ 50MW. Small scale mining operations in the early 1900's removed ~ 100 flasks of Hg (1 flask ≈ 34 kg) from altered granodiorite, basaltic andesite and siliceous sinter in the area[19]. Mercury occurs as cinnabar (HgS) in opalite of siliceous sinter deposits and as fracture fillings in bedrock[20]. Brannock et al.[21] reported that Hg^{o} was deposited on brass armor housing thermometers used to measure fumarole temperatures.

The intercomparison site was a 500 x 500 m^2 slightly hummocky surface covered with high desert vegetation such as sagebrush and rabbit brush. Roughness elements consisted of sparse (10%) vegetation of 0.5 m with a few < 5 m coniferous trees. Sampling sites were located within a 150 m x 75 m area (Figure 1). Soil Hg concentrations at the site ranged from 0.08 to ~10 μg Hg/g with concentrations decreasing from west to east across the site. Typical background concentrations for Hg in soil are ~ < 0.3 μg Hg/g [9].

Table 1
List of Participants and Hg flux Measurement Methodologies Applied during the NvMEP

Organization and participants	Method	Method summary
Oak Ridge National Laboratory (ORNL), USA S. Lindberg, J. Owens	CMBR	*Design*: Teflon rectangular box (60 x 20 x 20 cm^3) *Total flow*: 5 lpm *Hg measured**: Gold coated quartz sand traps or 1 Tekran and TADS *Footprint*: 0.12 m^2
GKSS Research Centre Geesthacht, Germany R. Ebinghaus, H. Kock	CMBR	*Design*: Teflon ORNL *Total flow*: 1.5 lpm *Hg measured*: 2 Tekrans *Footprint*: 0.12 m^2
Chalmers University, Sweden Z. Xiao, J. Sommar	CMBR	*Design*: Teflon ORNL *Total Flow*: 1 to 1.8 lpm *Hg measured*: GARDIS-1A *Footprint*: 0.12 m^2
Frontier Geosciences, USA R. Turner, D. Walschlager, J. London	CMBR	*Design*: Plexiglass "pastry cover"*Total flow*: 20 lpm *Hg measured*: 1 Tekran and TADS *Footprint*: 0.26 m^2

University of Nevada, USA M. Sexauer Gustin **United States Geological Survey, USA** M. Majeski	MM	*Aerodynamic vertical profile and Integrated Horizontal Flux methods* *Footprint*: 200 m^2 *Hg measured*: 1 Tekran and TADS at two heights and gold coated quartz sand traps at two heights *Parameters monitored*: Air temperature and wind velocity at 6 heights, soil temperature, wind direction, incident radiation, relative humidity

MM=micrometeorological technique; CMBR= field flux chamber; TADS= Tekran automated dual sampling system

**Hg measured* category indicates method used for quantifying atmospheric Hg concentrations.

Sampling methods

Three methods are commonly used to assess the flux of a trace gas from environmental media: field flux chambers, laboratory flux chambers and micrometeorological techniques. Seven field flux chambers and four micrometeorological methods were used to measure Hg flux during the Desert SToRMs intercomparison (Table 1). Variation among the field chambers and micrometeorolgical methods existed at three levels: 1. basic experimental design; 2. similar experimental design but variation in applications; and 3. method of collection and analysis of total gaseous Hg (TGM).

Of the seven field chambers utilized, three were of the same dimensions and design of the chamber developed and utilized by S. Lindberg of Oak Ridge National Laboratories (ORNL) (cf. refs. 22-23). These chambers were constructed of Teflon Durafilm and supported by a metal frame. Air was pulled through the chamber using a pump and inlet and outlet air streams were sampled for Hg using either gold coated quartz sand traps, or automated the real time Hg analyzers, Tekran 2537A[24-26] or GARDIS-1A[27]. The chamber had a 2.5 cm thick continuous rubatex foam gasket placed between an aluminum base and a Teflon skirt that made the ground to chamber seal when 40-50 kg of lead bricks were placed on the aluminum base. The method for determining TGM was different for each group using the ORNL chamber as was the total flow through each chamber (cf. Table 1. GKSS, Chalmers, ORNL methods). Major differences in the design of the other four field chambers from the ORNL chamber included dimensions, materials of construction, flow rates, and the presence or absence of fans and heating elements (Table 1).

Notable differences include:

- The GSA and U. of Guelph chamber was constructed of Teflon-lined plexiglass and had two fans mounted on the top of the chamber to ensure that the chamber functioned as a continuously stirred tank reactor;
- The U. of Michigan chamber was constructed of the same material as the ORNL

four heights, two with a Tekran 2357 and TADS, and two with collection of Hg using gold coated quartz sand traps.

Three methods were utilized for collection and measurement of TGM: gold coated quartz sand traps analyzed in the laboratory using cold vapor atomic fluorescence spectrophotometry (CVAFS)[32,33]; Tekran 2537 automated Hg analyzers alone or with Tekran model 1110 Synchronized Two Port sampler (TADS) with data collection on five minute intervals[24-26], or the GARDIS-1A, a semicontinous cold vapor atomic absorption spectrophotometer [27].

Table 2
Summary of Preliminary Hg Fluxes Estimates for Specific Soil Conditions from Desert SToRMS

Conditions	Dry soil mid-day	Dry soil midnight	Wet soil mid-day
Method	**Flux range, ng/m^{2}h**		
Field chamber	$^+14$ to $^+176$	$^-50$ to $^+70$	$^+100$ to $^+500$
Micrometeorological	$^+170$ to $^+900$	$^-200$ to $^+200$	$^+1000$ to $^+2000$

Discussion

Air TGM concentrations measured at the site ranged from 2 to 80 ng/m^3 at the upper sampling heights of micrometeorological methods and 4 to ~450 ng/m^3 for the inlets to the field flux chamber and at the lower sampling heights of micrometeorological methods. These concentrations are significantly higher than the 1 to 3 ng/m^3 concentration range considered as representative of ambient background levels. Preliminary data indicated that Hg fluxes from this site measured using both micrometeorological and chamber techniques ranged from 14 to 900 ng/m^{2}hr in day light under the condition of dry soil and at night the Hg fluxes declined with the area still constituting a source term (Table 2). Each method applied during Desert SToRMS had a different footprint or area contributing to the Hg flux measurement. Because of this individual fluxes may not be directly comparable, but the ranges presented herein are representative of the site. High Hg fluxes were measured as a response to two unexpected rainfall events and additional soil wetting experiments. The order of magnitude increase in Hg flux associated with the rainfall event, that began around 1230, declined gradually with time (Figure 2). Additional factors demonstrated to enhance Hg flux during the intercomparison were light and temperature. Chamber Hg fluxes appeared to correlate somewhat with the soil Hg concentrations at each site. Understanding the effect of environmental factors on flux is important for determining if flux measurements are representative of ambient climatic conditions at Hg-enriched sites.

These data demonstrate that an area of natural enrichment can constitute a significant and

Steamboat Springs #1/ Low levels of Hg enrichment	0.6 to 10	100	2.5	11 kg	Desert SToRMS
Steamboat Springs #2 / High levels of Hg enrichment	10 to 30	300	1	13	UNR/ORNL
Hg contaminated mill tailings/ Anthropogenic	60 to 1000	5000 3000	5	108	Gustin et al., 1995; 1997 UNR/ORNL
1000 MW Coal fired power plant				310	ref. 36

*Flux calculation based on a 12 hour day.

For each of the types of Hg enrichment an average Hg flux is given based on field flux measurements. These mercury fluxes were then applied to the area assumed to represent that type of enrichment in the 1000 km^2 area. The additive Hg contribution (272 Mg/y) to the atmosphere from the diffuse areas of natural and anthropogenic enrichment in this 1000 km^2 area is roughly equivalent to that of a 1000 MW coal fired power plant (310 Mg/y).

If the Hg flux values measured in the slightly enriched Lousetown drainage basin are used to project Hg contribution from naturally enriched areas of Nevada and California, values of 4.3 Mg/y and 3.1 Mg/y are obtained, respectively. These values are based on the assumption that 1/10th of Nevada and 1/5th of California contain low levels 0.1 to 2 μg/g Hg in substrate. This is a conservative estimate for it does not include Hg flux from areas of higher substrate Hg concentrations found in both states which can have a one-to-three orders of magnitude higher Hg flux and the calculations were done for a 12 hour day assuming that no Hg flux occurs at night.

The western United States lies within a mercuriferous belt that extends from Alaska to the tip of South America[7] so a doubling of the atmospheric Hg contribution estimated for California and Nevada seems a reasonable estimate of total contribution from the Western United States (~15 Mg/y). Estimated anthropogenic Hg emissions for the United States are 150 Mg/y[1]. Natural terrestrial source terms for atmospheric Hg include biogenic emissions, forests soils, agricultural soils and naturally enriched areas. Biogenic emissions have been estimated to contribute ~ 40 Mg/y[37], forest soils ~15 Mg/y[23] and sludge amended agricultural soils ~80 Mg/y [6]. Additional natural sources that were not included in this estimate include surface waters, geothermal areas

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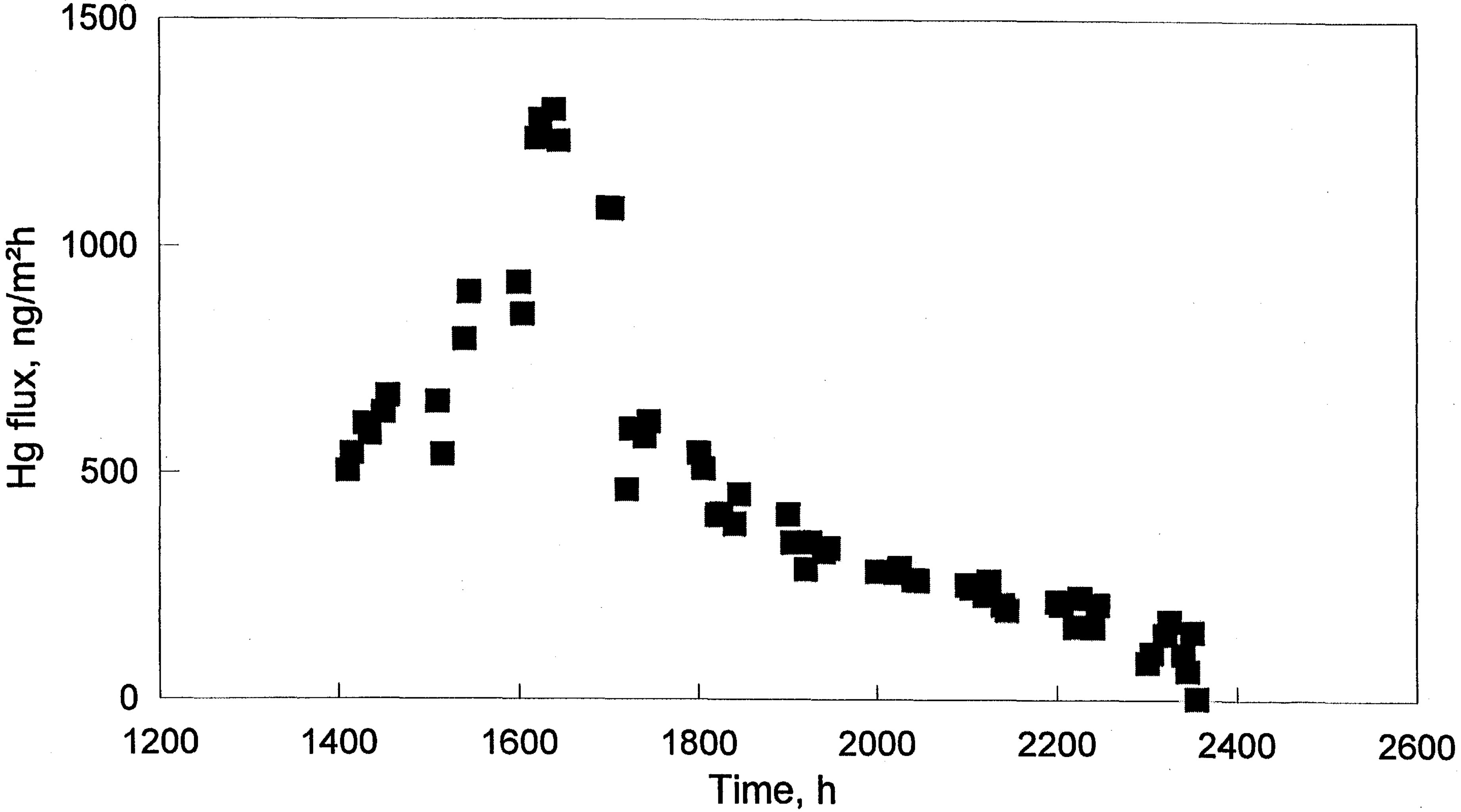
Figure 2. Change in mercury flux in response to rainfall event



Data obtained with ORNL field flux chamber