

## Application of a laboratory gas exchange chamber for assessment of in situ mercury emissions

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**Abstract.** The potential for the use of a laboratory gas exchange system to estimate of mercury emissions from naturally and anthropogenically mercury-enriched areas was assessed by comparison of mercury fluxes measured from the same substrate in situ and in the laboratory. In general, mercury emissions measured with the laboratory chamber for daytime conditions were of the same magnitude as mean mercury emissions measured in situ with field chambers. Mercury emissions measured with both the field chamber and laboratory chamber were lower than those measured with micrometeorological methods. Within the controlled experimental regime of the laboratory chamber, data were developed that demonstrated that substrate mercury concentrations and light are important parameters in controlling mercury emissions. However, with light and other parameters interacting with the soil, the correlation between mercury fluxes and substrate mercury concentrations declined. Mercury emissions from a variety of substrates in the dark were ~25% of those emissions measured in the light at the same soil surface temperature.

### 1. Introduction

Although the ultimate goal of quantifying mercury (Hg) fluxes from naturally and anthropogenically enriched terrains is to provide reliable, spatially representative data, achieving this goal is not always easy. This often requires numerous in situ monitoring campaigns in rugged, remote terrains, which in practice are difficult, expensive, and labor-intensive. This paper explores the viability of using a cost-effective laboratory-based approach to augment field studies, by comparing Hg emissions data obtained in the field with data obtained using a controlled gas-exchange laboratory system.

Three methods are commonly applied toward the measurement of trace gas fluxes: micrometeorological methods, field flux chambers, and laboratory chambers. The first two are in situ methods that provide a measurement of flux from areas of ~10–200 m<sup>2</sup> and ~0.1 to 0.3 m<sup>2</sup>, respectively. Laboratory chambers provide a measurement of flux from an area comparable to that obtained with field chambers to much smaller (~0.00001 m<sup>2</sup>), and from a volume of substrate which is significantly less than that from which trace gas emissions are measured in the field. Micrometeorological methods measure gas emissions from an unconstrained surface where a multitude of environmental and substrate factors may influence emissions. Field chambers measure gas emissions from a constrained surface that is shielded from some environmental parameters such as wind, turbulence, precipitation, and some light wavelengths. The laboratory chamber provides an exper-

imental regime in which environmental parameters may be precisely controlled to reflect a range of environmental conditions.

Mercury emissions measured in situ typically exhibit a diel pattern of low emissions at night and higher emissions during the day [Carpi and Lindberg, 1998; Casimir *et al.*, 1998]. Many environmental parameters also exhibit diel patterns making it very difficult to establish which variable is the dominant factor influencing soil-to-air Hg flux. The controlled nature of the laboratory chamber experimental regime allows for investigation of the magnitude of influence of environmental and substrate parameters on trace gas fluxes and their antagonistic and synergistic effects [cf. Gustin *et al.*, 1997]. The influence of substrate Hg concentration, temperature, and light on Hg emissions have all been investigated using a laboratory chamber [cf. Gustin *et al.*, 1998, 1996; Lindberg *et al.*, 1979; Carpi and Lindberg, 1997]. In this paper, the importance of substrate Hg concentrations in controlling Hg emissions is investigated, as is the effect of light on the enhancement of Hg emissions from a variety of substrates.

### 2. Methods

#### 2.1. Samples Utilized for Study

Samples utilized in the laboratory study were collected from field chamber sampling locations at most in situ sampling locations, which included four natural mercuriferous areas and one anthropogenically Hg-contaminated site (Figure 1 and Table 1). Two naturally enriched areas, the Steamboat Springs and Ivanhoe Mining District, were located in the United States. The Steamboat Springs geothermal (SBG) area contains substrate enriched in HgS and Hg<sup>0</sup> as a result of ongoing geothermal activity [Gustin, 1998]. Samples for laboratory Hg flux measurements were collected as part of the Nevada Study and Tests of the Release of Mercury From Soils (STORMS) project from the Oak Ridge National Laboratory (ORNL) and the Environment Canada (EC) field chamber sampling locations [cf. Gustin *et al.*, this issue]. Surface samples collected

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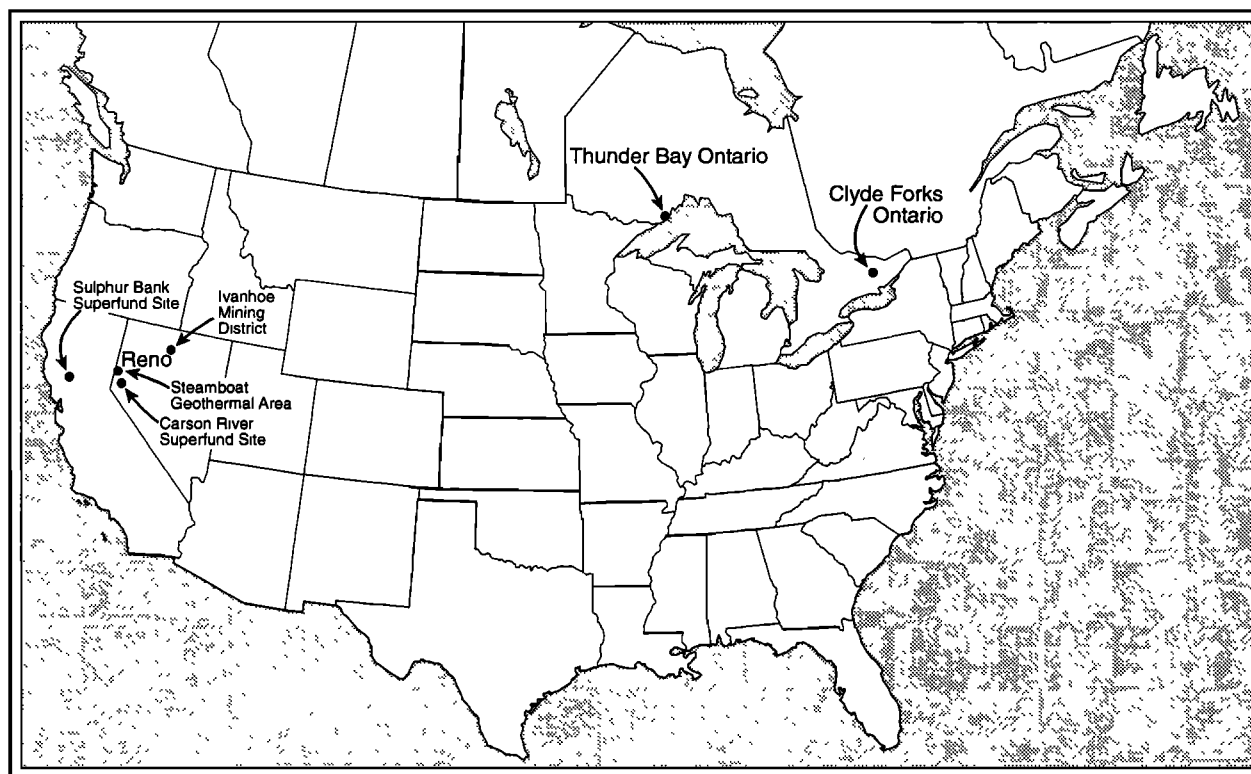


Figure 1. Location map for field samples used in this study.

from these two locations consisted of poorly sorted alluvium and well-sorted silt-sized ephemeral stream sediments, respectively. Mercury concentrations at these sites were found to be inhomogeneous with depth [cf. Gustin, 1998]. Field chamber and micrometeorological methodologies used for the measurement of Hg fluxes from this area are discussed by Gustin *et al.* [this issue] and Poissant *et al.* [this issue]. Mercury emissions were measured from cinnabar ore at the Ivanhoe Mercury Mining District (IMD) using a field chamber developed at Oak Ridge National Laboratory [cf. Kim and Lindberg, 1995; Gustin *et al.*, this issue]. This mining district, which is an ~15 m.y. old geologic analogue of the Steamboat Springs area, contains Hg as cinnabar and metacinnabar in silicified tuffs and opalite [Bartlett *et al.*, 1991].

The other two naturally enriched sampling locations, Clyde Forks and Thunder Bay, were located in Canada (Figure 1). The Clyde Forks, Ontario (CF), samples were collected from a natural forest soil overlying a mineralized fault zone in the Precambrian shield. Tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) and cinnabar ( $\text{HgS}$ ) were identified as the primary Hg-bearing minerals in the fault zone [Nikols, 1972]. The Clyde Fork samples were taken from three sampling locations representing high (CF 1 with  $\sim 1000 \mu\text{g g}^{-1}$ ), intermediate (CF 2 with  $\sim 350 \mu\text{g g}^{-1}$ ), and low concentrations of Hg in substrate (CF 4 with  $\sim 1 \mu\text{g g}^{-1}$ ). The Clyde Fork samples used in the laboratory chamber included the following: the  $<2$  mm fraction of the organic soil horizon (O), the topmost soil horizon upon which the field chamber was placed; the  $<2$  mm fraction of the mineral horizon immediately beneath the organic horizon (A); and the clay-sized fraction ( $<0.002$  mm) of the mineral horizon (C). The Thunder Bay sample (BS) consisted of weathered carbonaceous black shale fragments from the Proterozoic Rove Formation in the Precambrian Shield of Canada. This marine

shale unit is spatially significant and has been identified as the source of a regional-scale Hg anomaly in lake sediments [Rasmussen *et al.*, 1998]. Field chamber and micrometeorological methods used to determine in situ Hg emissions from the Canadian localities are described by G. Edwards *et al.* (unpublished manuscript, 1999).

The anthropogenically Hg-contaminated site from which samples were obtained for this study was the Carson River Superfund Site, Nevada (CR). The area, designated a superfund site in 1990, has elevated Hg concentrations in all environmental media [Gustin *et al.*, 1994]. Mercury was imported into this area for amalgamation of gold and silver from the Virginia City Comstock Ores in ~1860–1890 [Hogan and Smucker, 1994]. The predominant Hg species reported for Carson River tailings are  $\text{Hg}^0$  and  $\text{HgS}$  [Hogan and Smucker, 1994; Lechler *et al.*, 1995]. Micrometeorological measurement of Hg fluxes from this area are described by Gustin *et al.* [1996].

## 2.2. Laboratory Chamber for the Measurement of Hg Flux

Flux of Hg vapor from substrate was measured using a single-pass gas-exchange system [cf. Gustin *et al.*, 1997]. The sample chamber consisted of a Pyrex cuvette (12.3 L) containing a Teflon-coated fan. Mercury flux was calculated as follows:

$$F = (C_o - C_i)/AQ,$$

where  $F$  was flux ( $\text{ng Hg m}^{-2} \text{ h}$ ),  $C_o$  and  $C_i$  were concentrations of  $\text{Hg}^0$  ( $\text{ng m}^{-3}$ ) at the outlet and inlet, respectively,  $A$  was the surface area of the substrate exposed in the chamber ( $\text{m}^2$ ), and  $Q$  was the flow of air through the chamber ( $\text{m}^3 \text{ h}^{-1}$ ). The concentration of  $\text{Hg}^0$  at the inlet,  $C_i$ , represented the system blank ( $0.15 \pm 0.17 \text{ ng m}^{-3}$ ,  $n = 9$ ), determined by measuring the air Hg concentrations at the chamber outlet with no sample

**Table 1.** Mercury Concentrations and Fluxes Measured From Naturally and Anthropogenically Enriched Substrate

Substrate Samples	Mean Soil Hg Concentration, $\mu\text{g Hg g}^{-1}$	Micrometeorologically Derived Daytime Fluxes, $\text{ng m}^{-2} \text{h}^{-1}$	Field Chamber Derived Daytime Fluxes, $\text{ng m}^{-2} \text{h}^{-1}$	Laboratory Derived Fluxes With Light and $30 \pm 2^\circ\text{C}$ , $\text{ng m}^{-2} \text{h}^{-1}$	Laboratory Derived Fluxes for Dark Conditions $30 \pm 2^\circ\text{C}$ , $\text{ng m}^{-2} \text{h}^{-1}$
Steamboat Springs geothermal area, Nevada, United States					
SBG-EC	4.6	$595 \pm 1253$	$364 \pm 146$	91	35
SBG-ORNL	3.6	$213 \pm 224$	$120 \pm 57$	119	108
Ivanhoe Mining District Nevada, United States					
IMD	7,000		59,000		60,000
Clyde Forks Mineralized Fault Zone, Ontario, Canada					
CF1-O-organic horizon	860		$1,823 \pm 438$ (14) $789 \pm 92$ (8)	1,400	653
CF1-A-mineral horizon	1,570			13,340	7,950
CF2-O-organic horizon	350	$3110 \pm 529$	$1,466 \pm 122$ (3) $1,144 \pm 113$ (13) $675 \pm 46$ (12)	1,668	884
CF2-A-mineral horizon	240			1,758	990
CF2-clay-sized fraction	350			9,267	2,370
CF4-O-organic horizon	2.1	$75 \pm 28$	$-6.8 \pm 7.7$ (9) $4.7 \pm 2.4$ (6) $23 \pm 8.1$ (8) $29 \pm 3.8$ (3)	51	
CF4-A-mineral horizon	1.10			114	30
CF4-clay-sized fraction	0.85			48	33
Proterozoic Rove Formation, Thunder Bay, Ontario, Canada					
BS-Black Slate	1.3	$35.7 \pm 5.2$	$40 \pm 6$	48	7
Carson River Superfund Site, Nevada, United States					
CR	200	20,000*		17,023	1,167

Concentrations are in units of  $\mu\text{g Hg/g}$ , and fluxes are in units of  $\text{ng m}^{-2} \text{h}^{-1}$ . Mercury fluxes measured with the laboratory chamber have a standard deviation of  $<10\%$  of the flux measured. Field chamber fluxes for the Clyde Forks site are given as daily means and standard deviations with the number of samples taken during each day noted in parenthesis.

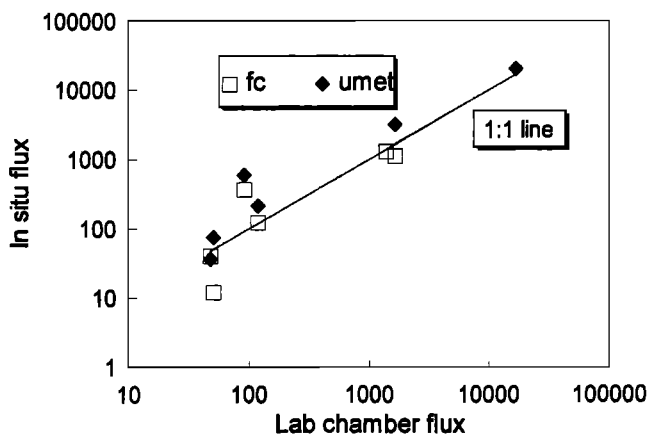
\*Gustin *et al.* [1996].

in the chamber. Chamber blanks were routinely monitored between samples. Upon removal of samples from the sample chamber, outlet concentrations declined to system blank concentrations indicating that there was essentially no loss of Hg to the chamber wall. Triplicate atmospheric Hg samples were collected on the chamber outlet using gold-coated quartz sand traps and analyzed using dual amalgamation and cold vapor atomic fluorescence spectrometry [Bloom and Fitzgerald, 1988; Gustin *et al.*, 1997]. Precision for triplicate outlet trap concentrations averaged  $4 \pm 3\%$ . The temperature of the substrate surface was measured with an infrared sensor (Everest Interscience, Inc.). Temperatures of air and substrate material in the chamber were measured with T-type exposed-junction thermocouples (OMEGA Engineering, Inc.). Flow of clean dry air (Aadco Pure Air Generator) through the chamber was maintained at a constant rate of  $0.27 \text{ m}^3/\text{h}$  resulting in a chamber turnover rate of 2.7 min. A xenon arc lamp was used to generate light of  $\sim 40 \mu\text{mol m}^{-2} \text{s}^{-1}$  measured with a Licor® net radiometer. This light intensity, which is well below the maximum light energy of the sun ( $2000 \mu\text{mol m}^{-2} \text{s}^{-1}$ ), was used to avoid excess heating of the soil samples in the gas exchange chamber. The light wavelength band and energy was 400–600 nm and  $0.75$  to  $1 \mu\text{W}/\text{cm}^2 \text{nm}$ , respectively, measured with an Ocean Optics® Fiber Optic Spectrometer. For comparison of Hg emissions from substrate under light and dark conditions, the same sample was used for both exposures, and the temperature of the soil surface was maintained at  $30 \pm$

$2^\circ\text{C}$ . Reported fluxes obtained with the laboratory chamber in this paper represent the mean of two Hg flux measurements (each of which was calculated using triplicate outlet air concentrations) measured from the same substrate sample.

Gustin *et al.* [1997] demonstrated, through application of a laboratory chamber for the measurement of Hg fluxes from mill tailings, that emissions declined as a function of sample residence time in the chamber. On the basis of comparison with in situ Hg flux measurements they concluded that emissions, measured from substrate, immediately after initial placement of the sample in the chamber, were the most representative of those occurring in the field. A general decline in Hg emissions with sample chamber residence time was also found to occur with substrate used in this study. Because of this decline, the timing of the Hg flux measurement with respect to placement of the samples in the chamber was critical in order to obtain results that are comparable with each other and with in situ flux measurements. Mercury fluxes presented herein represent those obtained within 48 hours of sample placement in the laboratory chamber.

Treatment of substrate samples prior to placement in the chamber was also found to be very important. Three different methods were used for collection and storage of samples from the Steamboat Springs geothermal area. Two 2 cm deep  $\times$  3  $\text{cm}^2$  “undisturbed” surface samples were collected onto watch glasses from the Nevada STORMS field chamber sampling sites. One of the undisturbed samples was wrapped in alumi-



**Figure 2.** Comparison of in situ derived mercury emissions ( $\text{ng m}^{-2} \text{h}^{-1}$ ) with emissions measured using the laboratory chamber.

num foil and frozen for later Hg flux measurements, and the other was stored at room temperature and Hg emissions were measured within 2 weeks of collection. The third sample type consisted of bulk soil samples, taken to 5 cm depth, which were stored in a freezer until the substrate was poured into a petri dish and emissions were measured. The frozen undisturbed samples consistently produced a 4 to 6 times lower Hg emission rate than that of the bulk sample and the not frozen undisturbed sample. This suggests that the freezing and thawing of the undisturbed sample removed Hg that was readily available at the surface and therefore resulted in a lower emission from the substrate surface. Thus sample handling and storage may affect measured Hg emissions. The not frozen undisturbed samples were used to determine Hg emissions for the Steamboat site for this study. Mercury emissions for the other areas were measured from bulk samples contained within a petri dish.

### 3. Results and Discussion

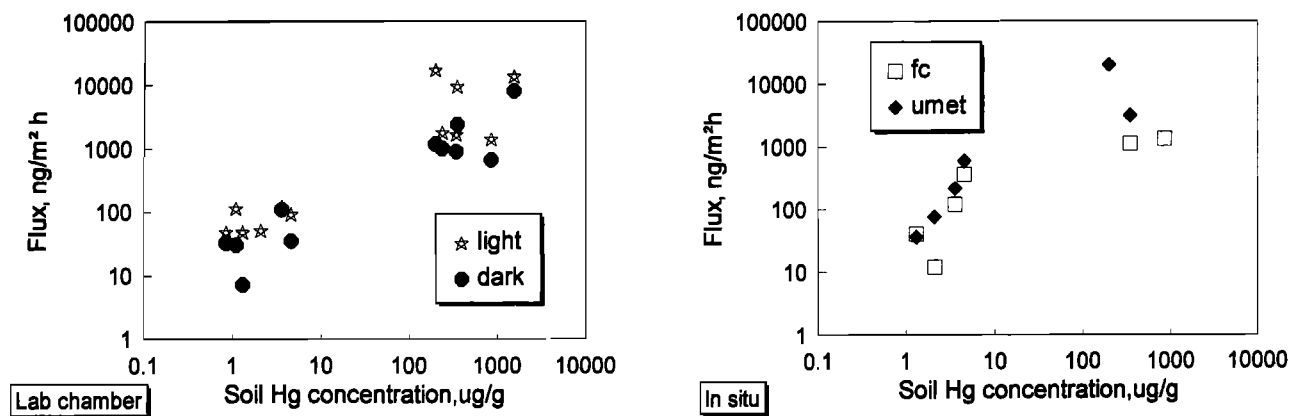
Table 1 compares the measured mean daytime in situ Hg emissions with those measured in the laboratory at a soil surface temperature of  $30 \pm 2^\circ\text{C}$ . This temperature was chosen for it represented an upper limit on soil temperatures that

occurred when the in situ data were obtained. For statistical comparisons the mean of the mean daytime emissions presented in Table 1 were utilized. In comparison of laboratory and in situ Hg emissions from Clyde Forks, Hg fluxes for the organic horizon were utilized for this was the immediate surface contributing to emissions. There was good agreement between the field and laboratory chamber derived Hg emissions ( $r^2 = 0.88$ ,  $p < 0.05$ ) and between micrometeorologically derived and laboratory chamber derived emissions ( $r^2 = 0.995$ ,  $p < 0.05$ ) (Figure 2). In general, laboratory-derived Hg emissions were higher than field chamber emissions and lower than micrometeorological emissions (Figure 2). Micrometeorologically derived Hg fluxes were  $\sim 3$  times higher than field chamber derived emissions. The latter finding is similar to the results obtained during the Nevada STORMS Hg flux comparison and discussed by *Gustin et al.* [this issue].

Mercury emissions as a function of substrate Hg concentration were best correlated with data obtained using the laboratory chamber in the dark ( $r^2 = 0.75$ ,  $p < 0.05$ ) and for the field chamber ( $r^2 = 0.79$ ,  $p < 0.05$ ) (Figure 3). A low coefficient was obtained for Hg emissions as a function of substrate Hg concentrations for light exposures ( $r^2 = 0.28$ ,  $p = 0.08$ ). No correlation was obtained for the micrometeorologically derived Hg fluxes and soil Hg concentrations. This data indicate that Hg concentration in substrate is an important parameter controlling Hg emissions, but not necessarily the predominant factor controlling in situ emissions. As other environmental parameters, such as light, interact with the substrate, Hg emissions are affected.

Mercury emissions were measured with the laboratory chamber from samples from Clyde Forks representing the  $< 2$  mm component of the organic horizon and the mineral horizon, and the clay-sized ( $< 0.002$  mm) fraction of the mineral horizon. Mercury fluxes measured from the organic horizon were most similar to those obtained in situ and less than emissions from the mineral fractions. The lower Hg emissions from the organic layer of CF 2 and CF 4 samples, despite a higher total Hg concentration relative to the mineral fraction, may be a result of organic binding of Hg.

The effect of light on Hg flux was determined by measurement of emissions from the same substrate samples in the dark and with incident light while maintaining constant soil surface temperature. Figure 3 illustrates that for all samples there was



**Figure 3.** Graphs illustrating the relationship between soil mercury concentration and laboratory chamber and in situ derived mercury emissions.

a light-enhanced emission of Hg. In general, Hg emissions from substrate in the dark were ~25% of those measured in the light. Light-enhanced Hg emissions have been recently documented in situ using field chambers and micrometeorological methods at the Steamboat Springs geothermal area [Gustin, 1998], Carson River Site (M. S. Gustin et al., manuscript in preparation, 1999) and during more recent field studies at the New Idria mining district, California (A. Vette et al., manuscript in preparation, 1999). At Steamboat Springs, during the Nevada STORMS intercomparison [Gustin et al., this issue], a field chamber shading experiment was conducted to investigate the influence of light on Hg emissions. A reduction in Hg emissions was observed with the shading of several field chambers while the surface temperature within the chambers remained the same [Gustin, 1998]. If temperature were the only factor controlling Hg emissions, one would expect emissions to remain roughly constant with shading of the chamber rather than the observed reduction in Hg flux. At the Carson River and New Idria locations, in the early morning, light-enhanced Hg emissions were observed with little to no concurrent increase in soil surface temperature. The light-enhanced Hg emissions measured in this study may not necessarily reflect the effect of light that occurs in situ for laboratory light exposures were at significantly less light intensity than that measured in the field. In addition, in situ other environmental factors, that is, soil temperature, air temperature, make it difficult to sort out the magnitude of the influence of light on emissions.

Little experimental work has been done on photo-induced reactions or photo-enhanced emissions of Hg from dry substrate [cf. Gustin et al., 1998]. Most studies have focused attention on photo-induced reactions occurring in solution [cf. Allard and Arsenic, 1991; Schroeder et al., 1991; Amyot et al., 1994; Lin and Pehkonen, 1997] and direct photolysis of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  in solution [Iverfeldt, 1984; Munthe and McElroy, 1992]. Gustin et al. [1998] demonstrated that light-enhanced Hg emissions occurred primarily with Hg sulfide containing substrate. They postulated that two mechanisms could be responsible for the light enhancement of Hg flux, either physical desorption of  $\text{Hg}^0$  or photoreduction of Hg iron or sulfur complexes. Cinnabar ( $\text{HgS}$ ), the predominant Hg mineral found in naturally enriched substrate, is constantly breaking down and emitting  $\text{Hg}^0$  to the air [cf. Kothny, 1971; Gustin et al., 1997]. In addition, if  $\text{Hg}(\text{SH})_2(\text{g})$  were forming as a weathering product of cinnabar, it could migrate through soil pores toward the soil-air interface. In the case of physical desorption,  $\text{Hg}^0$  would migrate upward toward the air-substrate interface where it becomes adsorbed to electrostatically charged mineral grains as well as to organic material. The energy from the incident radiation on the substrate surface could cause the  $\text{Hg}^0$  to vaporize and move away from the surface just like the evaporation of water. An alternative mechanism Gustin et al. [1998] suggested would be oxidation of  $\text{Hg}^0$  that has moved toward the surface and binding of the resulting  $\text{Hg}^{2+}$  with sulfur and iron complexes at the surface. Sulfur and iron complexes have been demonstrated to participate in photoreduction of  $\text{Hg}^{2+}$  [cf. Stromberg et al., 1991; Lin and Pehkonen, 1997]. Alternatively, if  $\text{Hg}(\text{SH})_2(\text{g})$  were produced, it could be decomposed at the air:soil interface upon interaction with sunlight resulting in the production of  $\text{Hg}^0$  [Stromberg et al., 1991].

Another explanation Gustin et al. [1998] proposed was weathering of Hg minerals at the air-substrate surface resulting in the production of photo-reactive species. Mercury sulfide

has long been known to degrade from red to black in sunlight [Kothny, 1971]. The transformation of cinnabar to the mineral schuetteite  $\text{HgSO}_4 \cdot 2\text{HgO}$  was reported to occur as a thin film associated with cinnabar ore and Hg amended tailings in situ [Bailey et al., 1959]. Bailey et al. [1959] suggested that this mineral formed as a thin film on cinnabar ore when  $\text{HgS}$  and  $\text{H}_2\text{O}$  react in the presence of sunlight. A similar reaction may result in production of photo-reducible forms of Hg in sulfide-enriched soils. With this hypothesis, Hg available for the light enhancement mechanism is only found in the immediate surface of the soil. This imposes a constraint of a limited pool of Hg available for the light enhancement mechanism to operate upon. If the Hg pool were available only at the immediate substrate surface, light-enhanced Hg emissions would decline and disappear as a function of time. Because of this limitation, a mechanism involving  $\text{Hg}^0$  and/or  $\text{Hg}(\text{SH})_2(\text{g})$  that seems most plausible for both of these species is gaseous species that could constantly be produced by weathering and/or biological degradation of  $\text{HgS}$  within the substrate column. Continued migration of these gases toward the soil-air interface would provide a long-lived pool of Hg allowing the light enhancement mechanism to operate indefinitely.

#### 4. Conclusions

Mercury emissions obtained from naturally and anthropogenically enriched substrate using a controlled laboratory gas exchange system compare well with emissions obtained using in situ methods. This indicates that a laboratory-based Hg flux measurement approach is a viable, cost-effective method of augmenting field studies. Sample handling and chamber experimental designs can influence measured Hg emissions, and it is important to regulate chamber conditions so that they mimic environmental conditions in the field as closely as possible. This method requires measurement of Hg emissions from multiple representative samples in order to obtain an average flux for an area.

Data developed indicate that total Hg concentration plays an important but not dominant role in controlling Hg emissions from substrate. In situ other environmental and substrate parameters exert their influence on controlling Hg emissions. Mercury emissions from natural and anthropogenically enriched samples in the dark were in general 25% of emissions occurring in the light. It is hypothesized that the light enhancement mechanism is either a physical desorption of  $\text{Hg}^0$  from the soil surface, or photo-reduction of  $\text{Hg}^{2+}$  (that originated as  $\text{Hg}^0$  in the substrate column) or  $\text{Hg}(\text{SH})_2(\text{g})$ . Elemental Hg or  $\text{Hg}(\text{SH})_2(\text{g})$  could be produced indefinitely within the substrate as a function of weathering of  $\text{HgS}$ . This enhancement of Hg emissions with incident radiation has significant implications for Hg cycling. If Hg is released from soil and other surfaces with incident radiation daily, it is possible that Hg cycling on a local scale may be much more important than currently recognized and the atmospheric residence time of Hg may need to be reassessed.

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