Chemosphere 131 (2015) 209–216

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Gas-exchange chamber analysis of elemental mercury deposition/emission to alluvium, ore, and mine tailings

Matthieu B. Miller, Mae Sexauer Gustin *

Department of Natural Resources and Environmental Science, University of Nevada-Reno, Reno, NV 89557, United States

HIGHLIGHTS

- Atmospheric deposition and emission of Hg was investigated in a laboratory setting.
- Deposition/emission of elemental Hg to and from 3 materials was investigated.
- The impact of water addition, light, and ozone showed synergistic effects.
- Mean elemental Hg deposition velocities (0.13–0.46 cm s^{-1}) varied with material.
- Flux was also influenced by material grain size, chemistry, and primary mineralogy.

ARTICLE INFO

Article history:
Received 21 November 2014
Received in revised form 19 February 2015
Accepted 4 March 2015
Available online 14 April 2015

Handling Editor: X. Cao

Keywords:
Soil moisture
Gold mining
Tailings
Oxide ore
Ozone
Light

ABSTRACT

Deposition of mercury (Hg) from the atmosphere is an important source of this contaminant to terrestrial ecosystems. Once deposited, all forms of Hg can be retained or emitted back to the atmosphere. Distinguishing between volatilization of geogenic or indigenous Hg and that deposited from the atmosphere is difficult. Field flux measurements in the general area of two industrial scale gold mining operations, showed local deposition of Hg emitted from point and nonpoint sources, and subsequent re-emission. The work presented in this paper investigated deposition/emission of elemental Hg to and from alluvium and two mine materials before, during, and after exposure to high air concentrations, for both wet and dry conditions, using a laboratory gas exchange chamber and a Hg permeation source. In general, results showed a range in mean elemental Hg deposition velocities ranging from 0.13 to 0.46 cm s^{-1} that varied with material. A significant influence of atmospheric ozone (O_3) on flux was observed that depended on the material and whether wet or dry. A synergistic relationship existed between O_3 and light promoting Hg flux, and flux was also influenced by material grain size, chemistry, and primary mineralogy.

1. Introduction

Mercury (Hg) released from natural substrates is a significant source of atmospheric Hg (Gustin et al., 2000; Gustin, 2003; Pirrone et al., 2009). It is thought that the primary form of Hg in the atmosphere is gaseous elemental (Hg^0) with the remainder being operationally defined reactive gaseous Hg (Hg (II) compounds), or particulate bound (Hg_P) (Schroeder and Munthe, 1998). All forms of Hg can be deposited to surfaces by both wet and dry processes (Lindberg and Stratton, 1998; Lindberg et al., 2007). Measured dry deposition velocities over terrestrial surfaces for reactive gaseous Hg (0.5–6.0 cm s^{-1}) are much higher than that suggested for the relatively inert and insoluble Hg^0 (0.01–0.19 cm s^{-1}; see review of Hg deposition in Zhang et al., 2009). Limited work with Hg(II) isotopes applied to water and soils in Canadian Boreal ecosystems and the desert of Nevada have shown a small percentage is re-emitted over time (Hintelmann et al., 2002; Amyot et al., 2004; Ericksen et al., 2005), and one limited study in the laboratory, using low Hg containing soils, showed Hg^0 was continually adsorbed over time (Xin et al., 2007).

Hg released from anthropogenic point sources can be Hg^0, Hg(II), or $Hg_{P,}$ whereas geogenic natural sources are thought to emit primarily Hg^0 (Seigneur et al., 2004; Pirrone et al., 2009). However, this has not been investigated, and thus, is currently a hypothesis. Recent work (Eckley et al., 2011a; Miller et al., 2011) showed the potential for deposition and subsequent emission of Hg derived from point and nonpoint emission sources at two industrial gold mines. These and other studies demonstrate that Hg^0 is cycled between the air and soils (cf. review by Gustin,

---

* Corresponding author. Tel.: +1 775 784 4203.
E-mail address: mgustin@cabnr.unr.edu (M.S. Gustin).

http://dx.doi.org/10.1016/j.chemosphere.2015.03.014
0045-6535/

2011). Although this bidirectional exchange of Hg^0 has been incidentally observed, the process has not been investigated in detail on short time steps (20 min).

This work was done to further investigate the potential for deposition and emission of Hg^0 to occur in the vicinity of industrial gold mines, and better understand the mechanisms controlling deposition and emission of Hg^0. In the field, Hg deposition velocities of up to 0.7 cm s^{-1} were observed, although it is not certain if this was Hg^0 or Hg(II) + Hg^0 (Miller et al., 2011). Field measurements were made with uncovered Teflon sampling lines and a Teflon® particulate filter and soda lime trap at the inlet to the Tekran® 2537. Such a configuration is assumed to remove Hg(II) from the sample stream, but the observed deposition velocities are higher than the range reported by Zhang et al. (2009) for Hg^0, and given this, deposited Hg could be in the form of Hg(II) compounds.

In this study we investigated the deposition of Hg^0 using a controlled laboratory gas exchange system in which air Hg concentrations were controlled to be similar to those observed in the field. The potential for Hg deposition and re-emission associated with geogenic Hg enriched material (oxide ore); unenriched substrate (alluvium), and anthropogenically produced waste material from gold ore processing (mine tailings), collected from an area of active gold mining, was investigated. Experiments were configured to address the question of whether deposited elemental Hg^0 would be readily re-emitted once deposited, as suggested by Gustin et al. (2008), or retained by the substrate. After Hg^0 deposition was observed the potential for subsequent emission was investigated by manipulating environmental parameters known to stimulate Hg release, including light, soil moisture, and air chemistry under controlled conditions. Deposition velocities were calculated and retention time for deposited Hg^0 was estimated.

2. Methods

2.1. Gas-exchange system and sample measurement

Elemental Hg^0 deposition and emission in ambient air were investigated using a single pass laboratory gas exchange chamber linked to a Tekran® 2537A Mercury Analyzer (Tekran®, Toronto, Canada) and Hg^0 permeation source (Fig. 1; Ericksen et al., 2005; Xin et al., 2007; Xin and Gustin, 2007; Stamenkovic and Gustin, 2009). The chamber was constructed of a Pyrex® dome (volume 12.3 L) placed on a Teflon base supported by galvanized steel frame. The contact between the dome and base was sealed with a polystyrene foam ring. A stainless steel fan mixed chamber air and flow was regulated at 4.9 L min^{-1} (vacuum pump, Model R-G557X, Gast®; mass flow controller, Model FC-280, Tylan®). Air entered and exited through ports located in the chamber base. Given the placement of the Petri® dish in the center of the chamber each sample was exposed to similar air flow. Chamber inlet and outlet air were alternately sampled at 1.5 L min^{-1} through PFA Teflon® tubing using a Tekran Automated Dual Switching (TADS) unit. Sample air passed through a PTFE filter (0.22 μm Cole-Parmer®) and soda lime trap (ACS 4-8 mesh, Alfa Aesar®) prior to the Hg analyzer to remove particulate matter and acid aerosols.

Hg flux was calculated using the equation:

$$F = Q^*(C_o - C_i)/A, \tag{1}$$

where F is the total flux (ng m^{-2} h^{-1}), Q is the sampling flow rate (m^3 h^{-1}), A is the area of the soil sample (m^2), C_o is the mean Hg concentration (ng m^{-3}) of two consecutive outlet samples, and C_i is the mean Hg concentration (ng m^{-3}) of the inlet samples before and after C_o. The value $C_o - C_i$ is referred to as ΔC. A positive ΔC indicates emission, and a negative ΔC indicates deposition. The average chamber blank, measured for approximately 12 h with air flowing through the chamber between samples, was 0.18 ± 0.20 ng m^{-3} for alluvium measurements, 0.62 ± 0.28 ng m^{-3} for oxide ore, and 0.98 ± 1.05 ng m^{-3} for tailings. The increase in blank concentrations after Hg^0 exchange was measured from a material was caused by contamination of the chamber by Hg emitted from the material. The chamber was cleaned between each flux measurement by rinsing with clean water and drying with Chem Wipes®. These blank values represent less than 10% of the average dry ΔC for each respective sample type.

Three separate aliquots of each sample type were exposed to the same sequence of conditions. All materials were collected from the area of the Twin Creeks mine (N41.2 W117.1, elevation 1425–1730 m), and included valley alluvium, oxidized low grade ore, and tailings. Sample material was stored in 5 gallon plastic buckets after collection in the field (coarse oxide ore that is blast fragmented and heaped on leach pads was sieved to ⩽2 mm). Approximately 60 g of material was placed into clean acid-washed glass petri dishes at least 6 d prior to placement in the chamber, allowing any effects of physical disturbance to dissipate. Each sample was in the chamber for approximately 144 h. Flux was first measured for 24 h from dry material in ambient air. The sample was then wetted to approximately 25% soil moisture by mass and allowed to dry for 24 h (≈1% decrease in soil moisture per hour). This was followed by exposure of the material to elevated air Hg^0 concentrations (100–300 ng m^{-3} similar to events observed at the mines) in clean air for 24 h. After the period of elevated air Hg^0 exposure, the chamber air source was returned to ambient air for 24 h, and watered one final time. Measurement for each sample took 5 d.

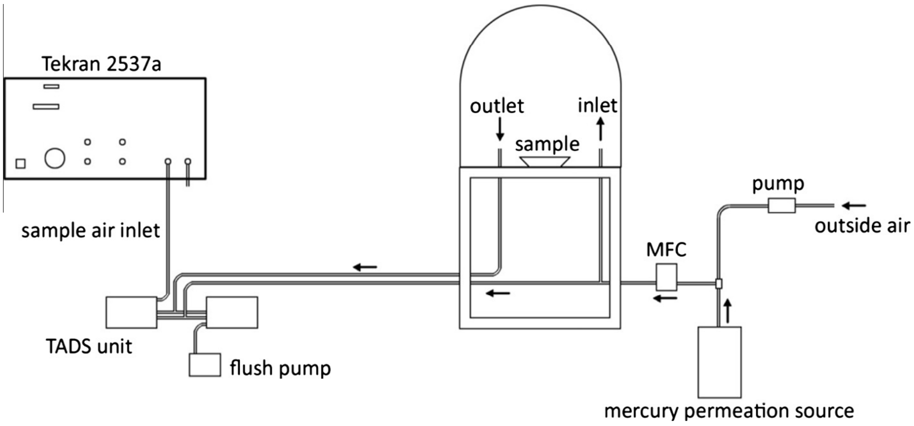

Fig. 1. Diagram of single pass gas exchange chamber system used for Hg deposition/emission experiments.