

# Laboratory Study for Gaseous Mercury Uptake by Atmospheric Water

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## Abstract

Mercury is a notorious pollutant causing severe nerve diseases. This metal has a semi-volatile nature under the STP condition, therefore, it is emitted to atmosphere as gaseous elemental mercury (GEM) from variety of sources, such as the ocean surface, volcanoes, and fossil fuel combustion. Because of the long atmospheric life time, mercury is transported for long distance and spreads globally, consequently ubiquitous in the natural environment. The current global model for mercury cycle assumes that oxidation is a predominant pathway for the removal of GEM from the atmosphere. To the best of our knowledge, however, none of heterogeneous uptake of GEM by atmospheric water, such as cloud, fog, and rain droplets, has been evaluated to date. For more accurate understanding of the mercury cycle, the evaluation of this process is necessary. We conducted laboratory experiments to evaluate GEM uptake by artificial atmospheric water. The experiments were carried out using a 3 L glass cell. 500 mL of acidified water was transferred into the cell, and approximately 50 to 10 ng m<sup>-3</sup> of GEM gas mixture was continuously flowed into and out of the open space above the solution in the cell. After a definite time the solution was quantitatively analyzed for mercury to investigate the uptake. At this presentation preliminary results of the uptake experiments will be presented.

### Background and Objective

The Minamata convention on mercury (Hg) was enforced at United Nation in 2017 to reduce the mercury concentration in the natural environment. For its effective implementation, more accurate understanding of the mercury cycle is important. Here we report the preliminary results of laboratory experiments for the uptake of gaseous elemental mercury (GEM) by acidified water, representing atmospheric fog, cloud, and rain, the information of which is very limited.

### Method

In a 2.5 L vessel under 25 ° C and the atmospheric pressure, 500 mL of water acidified with HCl, HNO<sub>3</sub>, or H<sub>2</sub>SO<sub>4</sub> (Nakarai Tesque, Japan) was exposed to the continuously flown GEM standard gas in *ca.* 60 ng m<sup>-3</sup> generated by a permeator (Dynacalibrator-345, VICI, Fig. 1). After the exposure for a specific duration, the gas flow was ceased and the solution was quickly stirred and siphoned out into a clean container. 450 mL of the exposed sample was mixed with 50 mL of 36% HCl to stabilize Hg ions. Hg ions in the sample was reduced to GEM by 3% SnCl<sub>2</sub> in 10% HCl, and GEM was captured by the gold-amalgam method and then analyzed by a flash vaporizer coupled with cold-vapor atomic absorption spectrometry.

### Results and Discussion

During the experiment a small amount of Hg was detected from the water exposed to the GEM gas for more than a day (0.01 ng or less in 500 mL water). Results exhibited that the uptake of GEM by the acidified solution was very weak (Table 1) even to the water with high acidity (pH = 3.2), which may be found in fog water in the polluted area. The masses found in water were not comparable to the estimated solubility of GEM, 0.09 ng per 500 mL of water according to the Henry's law with the dimensionless constant of 0.32 at 298K,<sup>1</sup> but the masses found in the acidified solutions by either HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> were compatible with this value. Using the data of temperature and GEM concentration measurements, the reactive uptake coefficients ( $\gamma_{\text{rxn}}$ , defined by the eq. below), were determined. The estimated  $\gamma_{\text{rxn}}$  were between 7 and 22 × 10<sup>-6</sup>, very small as compared to the  $\gamma_{\text{rxn}}$  of ozone, glyoxal, N<sub>2</sub>O<sub>5</sub> by the PM surface.<sup>2-4</sup> Given the size and number concentration of fog droplets as 10 μm and 10<sup>2</sup> cm<sup>-3</sup>, respectively,<sup>4,5</sup> the lifetime of GEM was calculated as 5 days. Comparing to a year of the atmospheric GEM life time, which is predominantly due to the oxidation by OH radicals, the heterogeneous uptake of GEM by atmospheric water can be an important process. Further careful evaluation, such as on the discrepancy between the result of this experiment and the solubility to water estimated by the literature values, is needed.

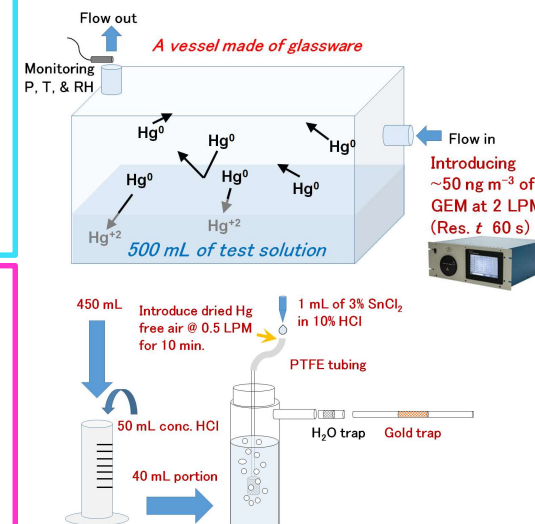


Fig. 1. Scheme of Uptake Experiment.

Table 1. Summary of Uptake Experiment.

	pH	Exposure time (h)	GEM conc. (ng m <sup>-3</sup> )	Total Hg in the solution (ng)	$\gamma_{\text{rxn}}$
Sample 1	3.21 (HNO <sub>3</sub> )	2.4	55 ng / m <sup>3</sup>	0.071	6.7 × 10 <sup>-6</sup>
Sample 2	3.24 (H <sub>2</sub> SO <sub>4</sub> )	6	60 ng / m <sup>3</sup>	0.094	22.2 × 10 <sup>-6</sup>

$$\gamma_{\text{rxn}} = \frac{\text{Number of Hg ions found in the solution}}{\text{Number of GEM atoms collided to the surface}}$$

**References:** <sup>1</sup>Andersson et al. (Chemosphere, 2008); <sup>2</sup>Liggio et al. (JGR Atmos, 2005); <sup>3</sup>Smith et al. (JPC-A, 2002); <sup>4</sup>Brown et al. (JGR Atmos., 2009); <sup>5</sup>Podzimek, J. (Stud. Geophysica et Geod., 1997); <sup>6</sup>Eliezer et al. (AE, 1993).