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**CONCENTRATIONS OF A WATER SOLUBLE,
GAS-PHASE MERCURY SPECIES IN AMBIENT AIR:
RESULTS FROM MEASUREMENTS AND MODELING**

S. E. Lindberg
Environmental Sciences Division, Oak Ridge National Laboratory¹,
PO Box 2008, Oak Ridge, TN 37831
W. J. Stratton
Department of Chemistry, Earlham College, Richmond, IN
P. Pai
Atmospheric and Environmental Research, San Ramon, CA
M.A. Allan
Electric Power Research Institute, Palo Alto, CA

Abstract

There are few reliable data on the speciation of Hg in ambient air, although this information is critical to understanding the fate of Hg once released from point sources. The water soluble species of Hg that are thought to exist in flue gases would be subject to far greater local removal rates than is elemental Hg vapor, but methods are lacking to quantify this species. We developed a method using refluxing mist chambers to measure the airborne concentrations of reactive gaseous mercury (RGM) in short-term samples under ambient conditions. The method exhibits an effective detection limit of 0.02 ng/m³ and a precision for ambient concentration levels of ± 20 – 30%. Using a model that simulates atmospheric transport and fate of anthropogenic mercury emissions over the contiguous United States, we generated 24-hr RGM concentrations to compare to the measurement data. The average RGM concentrations measured with our mist chambers at sites in Tennessee (TN) and Indiana (IN) were 0.065 ng/m³ and 0.100 ng/m³, respectively. These averages represent about 3% of total gaseous mercury (TGM), and RGM generally exceeds regional particulate Hg. The 24-hr model-simulated RGM concentration averages in the modeling grid cells representing TN and IN are 0.051 ng/m³ and 0.098 ng/m³ respectively, in good agreement with the data. The measured concentrations at the two sites exhibit weak positive correlations with temperature, solar radiation, O₃, SO₂, and TGM. These concentrations are high enough to suggest that RGM can play an important role in both wet and dry deposition on a regional scale.

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Measurement Methods

The high-flow refluxing mist chamber (Figure 1) consists of a glass base and a Teflon top. Ambient air at 15-20 SLPM is pulled in through the bottom and mixes with a fine mist of a suitable scrubbing solution to remove water-soluble gases^{8,12}. A hydrophobic membrane at the outlet retains the micron-sized liquid droplets so that the liquid refluxes continuously. In this fashion, a small volume of solution (*ca.* 0.02 L) can scrub *ca.* 1000 L of air in a one-hour sampling period. For efficient retention of RGM (i.e. Hg(II) species), the essential characteristic of the scrubbing solution is a relatively high concentration of Cl⁻ ion, (either as HCl or an NaCl/HCl mixture) to facilitate formation of the HgCl⁻ ion which has a high water solubility. Studies reported here used either 0.05 M HCl or 0.25 M NaCl/0.05 M HCl. Samples were collected in glass or plastic vials for transport to a laboratory, where they were analyzed (usually within 6 hours) for reactive Hg by stannous chloride reduction and cold vapor atomic fluorescence with dual gold trap amalgamation¹³. We have recently developed an approach for rapid in-field analysis of MC samples using a Tekran Hg analyzer. With this method we can quantify RGM in ambient air within a few minutes. The method detection limit (3x std. dev. of mist chamber blanks) is estimated to be 20 pg which corresponds to 0.02 ng/m³ for 1-hour samples; lower for longer sampling times. Figure 2 shows a representative set of data for side-by-side measurement of RGM using two matched mist chambers. There is a significant amount of scatter at the low levels of RGM found in ambient air and this pair of mist chambers showed a modest bias on the order of 20%.

Two possible sources of artifact RGM have been investigated in our lab: (a) formation of RGM within the mist chamber by reaction of Hg(0) with ozone or other photochemically-induced oxidants and (b) co-sampling of particulate Hg. Challenge tests with elevated Hg(0) and ozone indicate negligible (<5%) artifact formation under normal ambient conditions for short (*ca.* 1 hour) samples. Likewise, co-sampling of particulate Hg was found to be negligible at our rural sites.

Measurement Sites

From 1992 - 1995 we sampled RGM and TGM at two field sites: ~30% of the data were collected at Walker Branch Watershed (WBW) in east-central Tennessee, during the summers of 1992, 1993, and 1995. WBW is an upland forest at ~330 m elevation, located approximately 20 km from two large (~1 GW) coal-fired power plants which are often upwind of the site (SW and NE). Most samples were collected ~2m above the ground in a forest clearing of 1.5 ha. Related atmospheric chemistry and meteorological data were collected by NOAA¹⁴. About 70% of our data were collected on the Earlham College (EC) campus in Richmond, Indiana during spring and summer 1993, 1994, and 1995. Richmond is a small city at the Ohio/Indiana border, ~60 - 120 km from the nearest large cities and numerous major coal-fired power plants located along the Ohio River Valley to the south and west (generally upwind) of the site. Most sampling was done over open grass and paved surfaces, approximately 1.5 m above the ground, but ~25% of the samples were collected on the roof of a 12-m tall building. A 0.06 GW coal-fired power plant is located ~3 km generally downwind of the site.

monitors indicated a sharp spike in SO_2 following late-morning breakup of the local inversion layer. The WBW site is often impacted by plume fumigation events from one of three local power plants (two coal plants of 0.9 and 1.2 GW, located ~15-20 km NE and SW, respectively, and a small, variable-fuel steam boiler to the N, not operating in summer and therefore not relevant to this study), and such spikes in SO_2 are common¹⁵. Upon later analysis, our data revealed a similar spike in RGM which coincided with the behavior of SO_2 (Figure 5). During this period, the RGM/TGM ratio increased three-fold, then dropped to more typical levels as both SO_2 and RGM decreased. Winds measured aloft on our nearby 44-m tower indicated that transport during this period was from the SW, site of the 1.2 GW power plant. These observations are not direct evidence of a source/receptor relationship, but the data clearly point to the need for source-related studies of RGM in both plume and ambient air, such as those published for TGM¹⁶.

Regional Modeling of the Behavior of RGM in Ambient Air

Approach

The long-range transport and fate of atmospheric mercury was simulated using the Trace Elements Analysis Model (TEAM), the details of which are described elsewhere¹⁷. Here we briefly describe the model features that are relevant to the simulation results described in the next section.

The regional transport, chemistry, and deposition of a three-species mercury system (gaseous elemental mercury, gaseous divalent mercury or RGM, and particulate mercury) was modeled using an Eulerian, i.e., fixed, three-dimensional grid system with regular spacing in the horizontal and non-uniform spacing in the vertical. The horizontal spacing is 100 km on a map that projects locations on the spherical earth onto a horizontal plane; the method used to perform this transformation is referred to as polar stereographic projection. The horizontal grid system has 63 by 47 grid cells and is shown in Figure 6.

The three-dimensional grid system of TEAM uses 6 levels in the vertical, with spacing that varies from 60 m close to the surface to 1500 m at the highest level. In each three-dimensional grid box the partial differential equation (pde) describing the mass conservation equation for the three mercury species is solved. The pde represents mass balance of each mercury species in the grid box and accounts for the following processes: emissions of the species in the box, inflow and outflow of mass into the box through transport of winds, the formation and destruction of species in the box through chemical transformation, and removal of mass by wet and dry deposition. Before the pde's can be solved they are transformed into a set of coupled algebraic equations in which the unknowns are the concentrations of the three mercury species in each grid box of 100 km x 100 km in the horizontal. The removal of mass by wet and dry deposition is also kept track of by TEAM for each of the grid boxes in the lowest, i.e., surface, model layer. Thus the output from the model consists of estimates of concentrations (in mass/volume), wet deposition flux (in mass/area), and dry deposition flux (in mass/area) for the following three mercury species: gaseous elemental mercury, i.e., Hg^0 , reactive gaseous mercury, i.e., $\text{Hg}(\text{II})$ or RGM, and particulate mercury, i.e., $\text{Hg}(\text{p})$. The model estimates are saved as model output for

Results from Model Simulations

In a previous study the base case simulation results of TEAM were compared against concentrations and deposition measurements published for several locations in the states of MI, MN, WI, TN, FL, NY, and VT¹⁷. These comparisons showed that the model captured the range of observed values for both concentrations and deposition of total Hg in most states. Moreover, the model estimates also reproduced the observed spatial gradients in mercury wet deposition amounts and ambient concentrations. For each of the 7 states, the range of model estimates in the surface layer grid cells comprising a state was compared to the range of surface measurements in one or several locations in that state. The rationale for comparing the ranges in model estimates and measurements rather than comparing point measurements in a given year with grid-cell average estimates in a different year has been discussed elsewhere¹⁷. We will use the same evaluation technique in this study and compare the RGM and TGM measurements at Walker Branch Watershed (WBW) and Earlham College (EC) against 24-hour average concentrations estimated by the model in the grid cells comprising the states of TN and IN, respectively. There are approximately 20 grid cells comprising each of the two states as shown in Figure 6.

A frequency distribution of the 24-hour average concentrations of RGM and RGM/TGM ratio in the grid cells of TN and IN for each day of the year 1990 is shown in Figure 7a. Also shown is the corresponding distribution of all the grid cells of the modeling "domain" (the domain includes all 2961 cells shown in Fig. 6). Overall the 24-hr concentration of RGM in the domain averaged to 0.025 ng/m^3 , while the 24-hr concentrations in TN and IN averaged to 0.05 ng/m^3 and 0.098 ng/m^3 . These are comparable to the average of 0.065 ng/m^3 measured at WBW in TN and of 0.10 ng/m^3 measured at EC in IN (Table 1). However, it should be noted that over 90% of the data summarized in Table 1 represent daytime measurements, and not 24-hr means. As shown in Figure 7(a), most 24-hr RGM concentrations in the TN grid cells ranged from 0.04 to 0.1 ng/m^3 while a significant fraction of the IN grid cells experienced RGM concentrations over 0.1 ng/m^3 . The frequency distribution of modeled RGM concentrations in TN and IN compares quite well with the frequency distribution of measured RGM concentrations at Walker Branch Watershed, TN and Earlham College, IN (Fig. 8).

The 24-hr TGM concentrations averaged 1.6 ng/m^3 , 1.7 ng/m^3 and 1.8 ng/m^3 for the grid cells in the domain, TN, and IN, respectively. Most RGM concentrations in the domain represent only 1-2 % of the TGM concentrations which are dominated by a model input background concentration of 1.6 ng/m^3 . However, the RGM concentrations in TN represent 2-5 % of TGM which is consistent with the measurements at WBW. A comparison of frequency distributions of modeled RGM/TGM ratio shown in Figure 7b against measurements indicates that the model estimated ratio in TN and IN compares well with the measurements in these states (e.g., see Fig. 16 in Ref. 10). An examination of Figure 7b shows that model estimates of RGM represent a range of 5-9 % of TGM in a significant number grid cells in IN whereas measurements at EC indicate a generally lower fraction of data in that range (Table 1). The reason for this is not clear at this time but it is interesting to note in Table 1 that the measurements at Earlham College show a much stronger seasonal trend in mercury concentrations as compared to the measurements at WBW. If these seasonal trends in concentrations are related to emissions and/or chemistry, we

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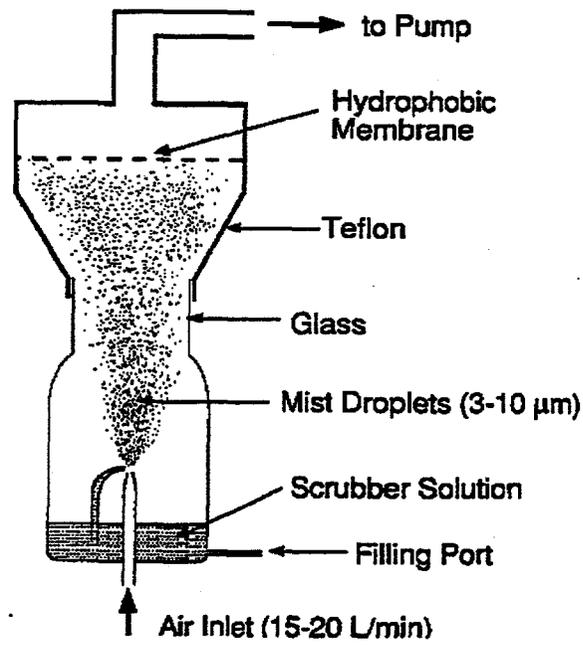


Figure 1

Schematic of the refluxing mist chamber used to collect RGM

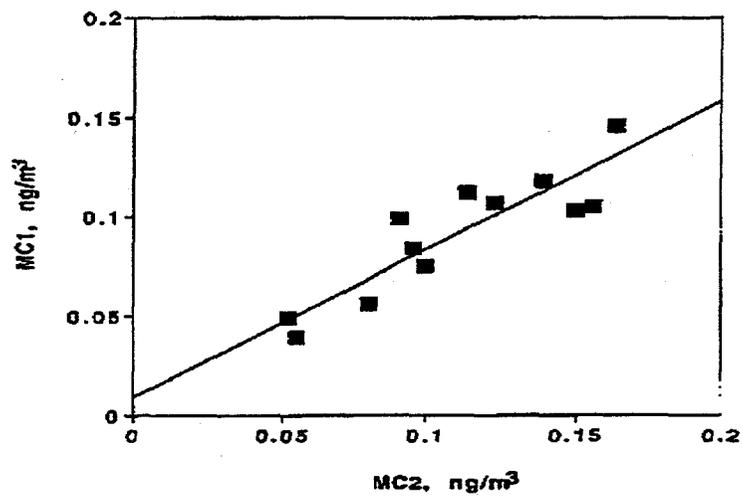


Figure 2

Comparison of results for RGM measurements in adjacent mist chambers

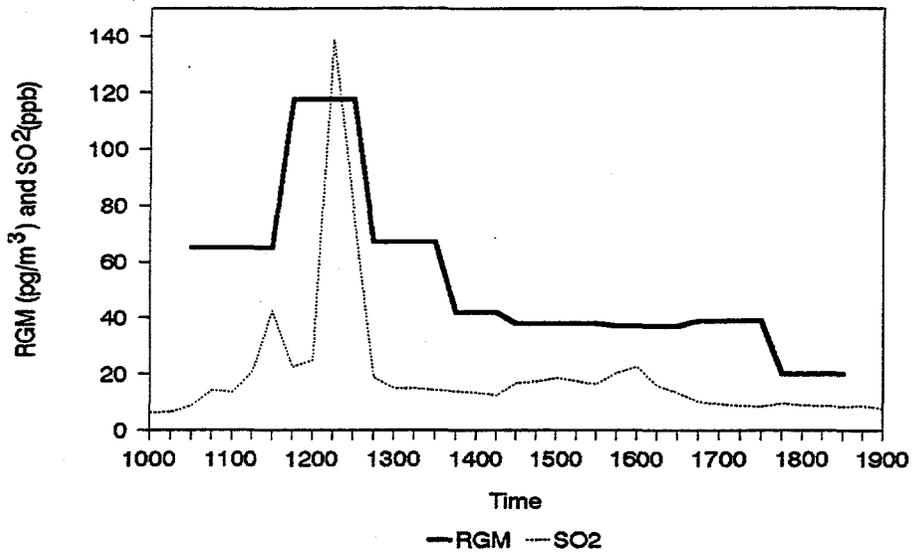
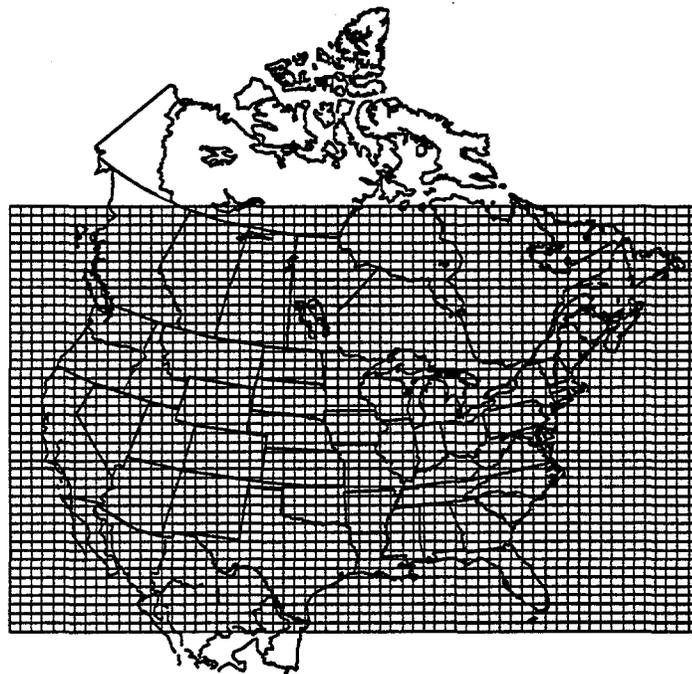


Figure 5
 Temporal trends in SO₂ and RGM measured at WBW on August 3, 1993
 (times are EST)



Domain and grid system for regional modeling of trace metals

Figure 6
 The modeling domain

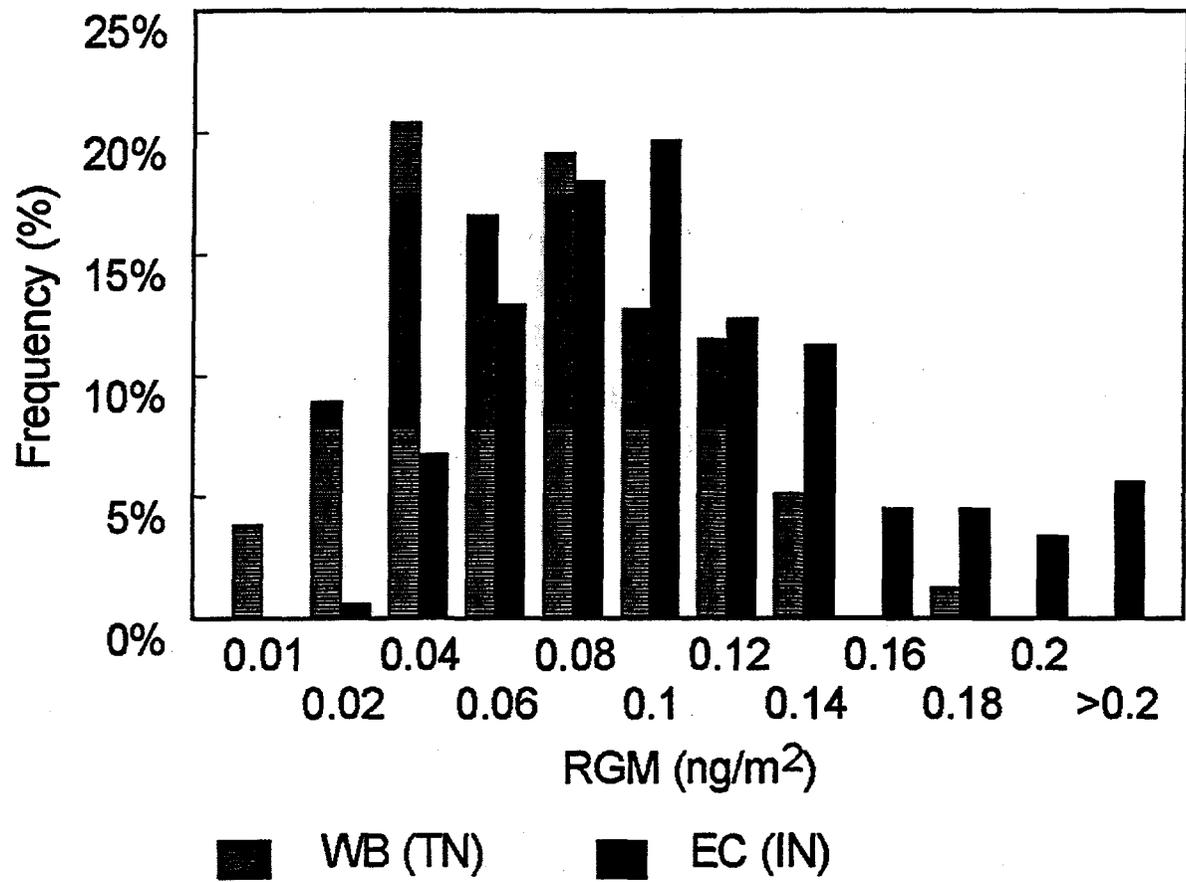


Figure 8