Environ. Sci. Technol. **1998**, *32*, 49−57

Atmospheric Mercury Speciation: Concentrations and Behavior of Reactive Gaseous Mercury in Ambient Air

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Knowledge of atmospheric mercury speciation is critical to understanding its fate once released from point sources. The water-soluble compounds of Hg that exist in flue gases (termed reactive gaseous mercury, RGM) are subject to far greater local removal rates than is elemental Hg vapor, but few ambient air data exist. We developed a method using refluxing mist chambers to quantify the airborne concentrations of RGM in more than 250 ~1-h samples under ambient conditions and summarize here the results of several RGM sampling campaigns in Tennessee and Indiana from 1992 to 1995. Measured levels of RGM were generally on the order of 50−200 pg/m^3, representing about 3% of total gaseous mercury (TGM) and generally exceeding regional particulate Hg concentrations. RGM exhibits significant correlations ($p < 0.05$) with temperature, solar radiation, O_3, SO_2, and TGM, suggesting seasonal trends similar to those of other regional air pollutants. The concentrations of RGM show reproducible diel trends, peaking during midday and decreasing sharply at night. A sharp spike in RGM was measured during a local plume impaction event in Tennessee. Concentration gradients over vegetation suggested a strong ground-level sink for RGM, and RGM concentrations decreased sharply during rain events, as expected for a water-soluble gas. The levels of RGM measured here support the hypothesis that Hg dry and wet deposition may be strongly influenced by the behavior of RGM and that elevated ecosystem exposure may be possible near major point sources of RGM compounds.

Introduction

Mercury is a toxic environmental pollutant that is among the most highly bioconcentrated trace metals in the human food chain (*1*), and the U.S. EPA has targeted mercury in the Clean Air Act Amendments of 1990 for possible emission regulations. Mercury is present in coal and in municipal solid waste, and it is the one metal that is least effectively retained by emission controls. Once emitted, Hg may be deposited by wet and dry processes to environmental surfaces. In aquatic systems, mercury is methylated, incorporated into microorganisms, and bioaccumulated through the food chain where human exposure occurs.

Knowledge of the *speciation* of atmospheric Hg is crucial for predicting its deposition and understanding its biogeochemical cycling. Gaseous mercury speciation has been measured in flue gases, and a recent review of results from coal combustion systems suggests that flue gas Hg emissions are roughly equally divided between two oxidation states, elemental (Hg^0) and mercuric (Hg^{2+}) (*2*). In the atmosphere, Hg exists largely as gaseous Hg^0 plus trace amounts of Hg^{2+} compounds [sometimes designated as Hg(II)] (*3*). Atmospheric Hg^{2+} compounds may be associated with particles or occur as gases, most probably $HgCl_2$, $Hg(OH)_2$, or compounds of the other halides (hereafter referred to collectively as reactive gaseous mercury, RGM). These species are highly water-soluble (at least 10^5 times more so than Hg^0), and this water solubility strongly influences their removal processes and deposition rates from the atmosphere (*4*). Its solubility is also the basis for many proposed sampling schemes. The identification and quantification of the speciation and fluxes of atmospheric Hg will be crucial to predicting the effects of regulations on emissions from industrial sources.

Experts at two recent workshops agreed on the need for the development and testing of reliable measurement methods for Hg speciation in the atmosphere (*3, 5*). The reporting of water-soluble forms of gaseous Hg (e.g., $HgCl_2$) in combustion flue gases (*6*) and the suggestion that they can be formed from Hg^0 in the atmosphere (*7*) must be verified because RGM can be rapidly reduced back to Hg^0, at least in the aqueous phase (*8*). In this regard, the pertinent atmospheric transformations of Hg include the following:

(a) Oxidation of Hg^0 to Hg^{2+} by reaction with either ozone (O_3), hydroxyl radical (OH), or hydrogen peroxide (H_2O_2) in cloudwater.

(b) Reduction of Hg^{2+} to Hg^0 by reaction with SO_2(g) or SO_3^{2-}(aq).

(c) Direct oxidation of Hg^0 to Hg^{2+} by reaction with ozone (O_3) in the gas phase.

Several recent modeling studies over various spatial scales have confirmed that the speciation of airborne Hg is crucial to the modeling of its transport and removal processes (*5, 9, 10*). Although Hg^0 is the dominant form of atmospheric Hg, even trace amounts of RGM species may control the overall deposition of Hg. Theoretically, compounds like $HgCl_2$ or $HgBr_2$ would be efficiently absorbed by cloud droplets during formation of rain (*10*) and would dry deposit >100 times more readily than would Hg^0 (*4*). Hence even levels of RGM at a few percent of total gaseous Hg are important to Hg dry deposition. An improved understanding of the speciation of atmospheric Hg is clearly necessary for modeling the fate of atmospheric emissions of Hg.

Although the capability exists to determine the concentrations of Hg^0 and RGM in flue gas, without confirmation that RGM actually exists in ambient air at quantifiable levels, its use in transport and deposition models remains speculation. Despite this, very little published data exist. Brosset and Lord (*11*) reported limited measurements using gas bubblers and very long sampling times, but they concluded that Hg(II) was formed in the bubbler under these conditions and that better approaches were needed for measurements in ambient air. Solid-phase denuders, traps, or treated filters are one such approach, but most of these sorbents are limited to use with highly concentrated stack gases or long sampling periods until both the operational blanks and the effective detection limit can be reduced (*6*). Xiao et. al. (*12*) recently

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S0013-936X(97)00546-4 CCC: $14.00 © 1997 American Chemical Society
Published on Web 01/01/1998

reported successful laboratory tests of a low-flow KCl denuder for RGM in air. High-flow wet denuder systems provide another promising approach (e.g., ref 13) but have yet to be tested for RGM compounds.

Because of its reactivity, RGM is thought to exist in ambient air at very low concentrations. Lindqvist et al. (*3*) reported that RGM was not "present in any detectable amounts ... far from source areas". Since total Hg in air is present at sub-ppt_v levels, it is not surprising that early attempts to quantify ambient RGM have failed. What is needed is a method that combines a high flow rate with a consistently low blank to allow collection of short-term atmospheric samples. High frequency sampling is necessary to identify possible sources and to adequately understand the behavior of RGM in the atmosphere. The approach we chose for measuring RGM in ambient air was the high-flow refluxing mist chamber (MC), developed at the NASA Langley Research Center (*14*). The MC is a proven device for scrubbing soluble gases from air, but it had not previously been applied to any Hg species.

We have published results of limited tests of the applicability of the MC technology to ambient RGM sampling and a brief description of our initial data set of over 100 samples (*15*). In this and a related paper, we describe and summarize our recent results. The companion paper includes more extensive laboratory tests of the behavior of the MC in a controlled atmosphere and under variable field conditions and concludes that the method is an acceptably efficient approach for collecting RGM and is free from highly significant artifacts (*16*). This paper describes the results of six field sampling campaigns at two eastern U.S. sites over a 4-yr period in which over 260 samples of ambient RGM were collected. The MC approach is the first field method developed with the capability to quantify ambient levels of atmospheric RGM in short-term (~1-h) samples. Calibration standards for ambient RGM are not yet available, and any new method for RGM is subject to potential sampling artifacts. Therefore, it is necessary to demonstrate that any resulting field data behave as expected for a water-soluble reactive gas. We demonstrate here that the MC measures concentrations of RGM in ambient air that are predictable and reproducible under a number of conditions: over diel cycles, in a gradient over surfaces, during periods of rain, and during a ground level plume fumigation event.

Methods and Sites

The high-flow refluxing mist chamber (MC) has been widely used for various studies of trace gases in the atmosphere including formaldehyde (*17*), carboxylic acids (*18*), HNO_3 (*19*), SO_2 (*20*), HCl, and Cl_2 (*21*). An intercomparison of measurement systems for atmospheric carboxylic acid gases (*22*) found the MC to be superior. The MC operates by drawing the sampled air through water dispersed as a fine aerosol; this is as opposed to a traditional impinger in which air is bubbled through water. Details of our approach for measuring RGM in ambient air with the MC are published (*15*), and recent modifications are described in our companion paper (*16*). Briefly, air is aspirated through the MC for periods of 30−120 min at flows of ~15−20 L/min using a mass flow metered pump; water-soluble gases are absorbed by the nebulized mist. Droplets of ~3−10 μm containing the scrubbed RGM collect and coalesce on the surface of a hydrophobic membrane and then drain back into the chamber. The high-flow rate and the small solution volume (~10 mL of a dilute NaCl/HCl mixture in a total MC volume of ~75 mL) enable sampling times on the order of 1 h. Following each sample, the MC solution was stored in acid-washed and prefired vials until analysis (generally within 6 h). During ~85% of the sampling periods, total gaseous mercury (TGM, primarily Hg^0) was collected simultaneously on gold-coated sand absorbers. It should be noted that over the course of our tests and measurements with the MC, we made several improvements to the method involving MC solution chemistry, sample storage, use of front end filters (in 1-h samples no difference in RGM could be detected between filtered and unfiltered air), and flow rates (*15*). These changes increased the collection efficiency for RGM, suggesting that our earlier data may be biased low by up to 30−40% (*16*).

Mercury was determined by cold vapor atomic fluorescence using dual gold trap amalgamation (*23*) as modified by Lindberg et al. (*24*). The gold absorbers for TGM were analyzed directly. MC solutions were analyzed following reduction of water-soluble Hg^{2+} species to Hg^0 by stannous chloride ($SnCl_2$). In other speciation schemes this fraction is denoted as Hg(IIa), called "reactive", "acid-labile" Hg, or "ionic Hg", as distinguished analytically from both "strongly complexed" and "inert" Hg (*3, 25*). The analytical detection limit for MC solutions was *ca.* 5 pg of Hg (3× SD of bubbler blanks). For samples collected in the mist chamber, the detection limit was estimated to be *ca.* 10 pg of Hg (based on precision of the field blanks) corresponding to an atmospheric concentration of *ca.* 0.01 ng/m^3. The analytical precision for mist chamber samples based on lab splits was generally 5%. With one MC it was not possible to determine the precision of field samples; however, recent work with new replicate MCs suggests a precision of ~20−30% (*16*). We detected RGM at levels well above the system blank in nearly all of the samples collected over a 4-yr period; the typical RGM signal in a 1−2-h sample is on the order of 100 pg, compared to a system blank generally around 20 pg.

From August 1992 to October 1995, we sampled RGM during six field studies. About 30% of the data were collected at Walker Branch Watershed (WBW) in east-central Tennessee, during August−September 1992, June−August 1993, and June−August 1995. WBW is an upland forest at ~330 m elevation, located approximately 20 km from two large (~1 GW) coal-fired power plants that are often upwind of the site. Most of the samples were collected ~2 m above the ground in a forest clearing of 1.5 ha, but ~20% of the data were collected from elevated platforms: a 43-m meterological tower above the WBW forest and from the 15-m high roof of our nearby laboratory. Extensive atmospheric and meterological monitoring equipment at the forest clearing site, a NOAA CORE dry deposition facility (*26*), provided 15-min averages of O_3, SO_2, NO_2, temperature, solar radiation, humidity, wind direction, and wind speed. The remaining 70% of the data were collected on the Earlham College (EC) campus in Richmond, IN, during May−October 1993, April−August 1994, and April−October 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 are 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. Atmospheric chemistry and meterological data were not available at the Earlham site.

Results and Discussion

Factors Influencing RGM Concentrations. The MC data suggest that there is a small but measurable fraction of total gaseous mercury (TGM) that exists as RGM. Table 1 summarizes the complete data set collected at both sites from 1992 to 1995. The overall mean concentration of RGM is on the order of 0.1 ng/m^3, and RGM comprises about 3% of TGM, which ranged from ~2.2 ng/m^3 at WBW to ~4.1 ng/m^3 at the EC site. The limited data collected ~25−40 m above the ground near WBW consistently yielded the highest

TABLE 1. Statistical Summary of Concentrations of Reactive Gaseous Mercury (RGM) and Total Gaseous Mercury (TGM, Primarily Hg^0) in Ambient Air at Sites in Tennessee and Indiana over a 4-yr Period[a]

	RGM (ng/m^3)			TGM (ng/m^3)			RGM/TGM		
site and data[b]	mean	SD	*n*	mean	SD	*n*	mean	SD	*n*
all data	0.092	0.06	252	3.46	1.7	221	0.029	0.02	214
WBW ground	0.065	0.04	75	2.19	0.64	68	0.027	0.015	67
WBW elevated[c]	0.257	0.163	17	1.93	0.51	10	0.078	0.056	7
WBW 1992	0.050	0.030	11	1.99	0.43	11	0.023	0.014	10
WBW 1993	0.068	0.034	36	2.35	0.72	35	0.028	0.011	35
WBW 1995	0.066	0.04	28	2.05	0.55	22	0.027	0.019	22
WBW warm[d]	0.066	0.036	65	2.22	0.65	61	0.028	0.015	60
WBW cool	0.055	0.040	10	1.97	0.54	7	0.017	0.009	7
EC	0.104	0.057	177	4.02	1.78	153	0.030	0.022	146
EC ground	0.097	0.051	127	3.76	1.72	112	0.030	0.022	108
EC roof	0.121	0.069	50	4.73	1.77	41	0.031	0.021	38
EC 1993	0.156	0.084	15	3.88	1.96	17	0.051	0.039	15
EC 1994	0.097	0.057	105	4.32	1.94	97	0.025	0.017	92
EC 1995	0.103	0.040	57	3.34	0.92	39	0.032	0.017	39
EC warm[d]	0.108	0.060	148	4.05	1.88	128	0.031	0.023	122
EC cool	0.083	0.031	29	3.84	1.12	25	0.023	0.012	24

Meteorological and Atmospheric Parameters at WBW during RGM Sampling Campaigns

	O_3 (ppb)	SO_2 (ppb)	NO_2 (ppb)	temp (°C)	RH (%)	solar rad (W/m^2)	WS (m/s)	WD (deg)	SD WD (deg)
mean	57.4	29.2	3.4	29.8	51.4	610.4	1.1	182.3	54.3
SD	16.0	11.2	3.0	4.7	21.5	247.5	0.4	74.5	9.6

[a] Also shown is a statistical summary of the meteorological and atmospheric data from the WBW site. [b] Sites as follows: WBW, Walker Branch Watershed near Oak Ridge, TN; EC, Earlham College, Richmond, IN. [c] WBW elevated data collected from a 43-m meteorological tower ($n = 6$) and from the roof of a 15-m building ($n = 11$). The relatively high concentrations atop the tower may reflect removal of RGM near the ground due to deposition processes (as discussed below). The higher concentrations measured on our roof may reflect emissions of RGM from local sources such as fume hoods and vents located on buildings upwind. Because the RGM concentrations in the limited WBW elevated data set are significantly higher than those collected at ground level, the elevated data were not included in annual or seasonal means for WBW. [d] Warm period: May 1–October 14; cool period; October 15–April 30.

levels of RGM (mean ~0.25 ng/m^3 or 2–3 times the means for the WBW ground and EC sites) and the highest ratios of RGM/TGM (~0.08). The elevated concentrations of RGM sampled aloft near WBW appear to result from local sources (roof data) or to reflect gradients due to ground-level removal processes (tower data, discussed in detail below). For this reason the WBW tower data were not included with the WBW ground-level data in further analyses. At the EC site, there was no significant difference between the RGM concentrations or RGM/TGM ratios for data collected at the ground-level and roof sites, and they were combined for further analyses.

The frequency distribution of RGM illustrates a clear trend of generally lower concentrations at the WBW ground-level site as compared to the EC site (Figure 1a) by about 40% on average. However, the ratio of RGM/TGM shows a similar distribution at both sites (Figure 1b). The average RGM/TGM ratios for each sampling campaign ranged from 0.025 to 0.038 at EC and from 0.026 to 0.029 at WBW. Similar ratios were reported in limited sampling with a KCl denuder at a remote North Atlantic site (0.017–0.037, $n = 4$; *12*), suggesting that RGM may always comprise a small but measurable fraction of TGM. The levels of RGM reported here generally exceed concentrations of particulate Hg measured at WBW (0.01–0.03 ng/m^3; *27*) and at other non-urban sites in the eastern United States (*28*). Over the 4-yr period of sampling, the mean concentrations of RGM remained relatively steady at both sites, and there was a suggestion of somewhat lower RGM levels during cool months as compared to warm months at both sites (Table 1). This trend is commonly seen for other gaseous air pollutants and results from seasonal differences in air stagnation and atmospheric reaction rates influenced by temperature, radiation, and oxidant levels. The RGM/TGM ratio followed similar temporal trends: the average contribution of RGM to TGM increased from 1.7% during the cool months to ~2.9% during the warm months at WBW and from 2.7 to 3.1% at EC. TGM also exhibited moderately higher levels (~10%) during the warm months at both sites, as found in an earlier study (*4*).

For the entire data set, RGM and TGM concentrations are weakly correlated with each other ($r = 0.29$, $p < 0.01$; Figure 2), but the correlation is much improved for the WBW data set ($r = 0.43$, $n = 66$, $p < 0.01$). The reason for the much lower correlation at EC ($r = 0.14$, $n = 150$, $p < 0.10$) is not known but could result from a different mix of atmospheric Hg emission sources in this region. The correlation at WBW could result from common emission sources for both species (*2*) and/or oxidation of Hg° to RGM either in the atmosphere or within the MC itself. However, the gas phase oxidation of Hg° by O_3 is very slow (*7*), and we have shown that artifact formation of RGM from aqueous phase Hg^0 reactions with O_3 within the MC is also relatively small (*15*, *16*). At any rate, even at WBW, the variance in TGM accounts for <20% of the variance in RGM, suggesting the importance of other factors in controlling RGM concentrations. Ancillary chemical and meteorologic data were available for ~90% of the RGM measurements at WBW. RGM exhibited significant correlations with air temperature (Figure 3) and solar radiation ($r = 0.48$–0.50, $p < 0.01$) and with both SO_2 and O_3 ($r = 0.26$–0.31, $p < 0.05$; Table 2). The correlations with the meteorologic variables reflect the seasonality of RGM as well as its strong diel cycle (discussed below), while the correlations with SO_2 and O_3 may simply reflect trends with general air quality as influenced by air stagnation. In a multiple regression, these four variables explained 46% of the variance in RGM, with temperature and Hg° alone accounting for 40%. TGM showed a significant correlation only with temperature ($r \sim 0.3$, $p < 0.05$). More detailed near-source studies with continuous, high-frequency sampling would be necessary to identify the sources of all TGM species.

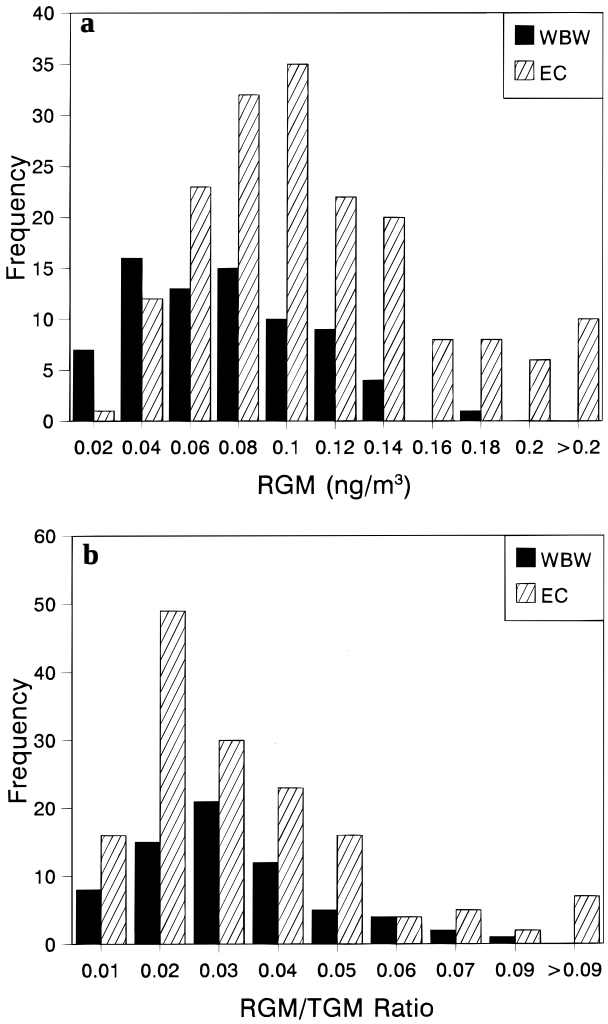

FIGURE 1. Frequency distributions for reactive gaseous mercury (RGM) concentrations (panel a) in ambient air at two sites in Tennessee (WBW, $n = 75$) and Indiana (EC, $n = 177$); data were collected over a 4-year period from 1992 to 1995. Panel b shows distributions for the ratio of RGM/TGM (TGM = total gaseous mercury).

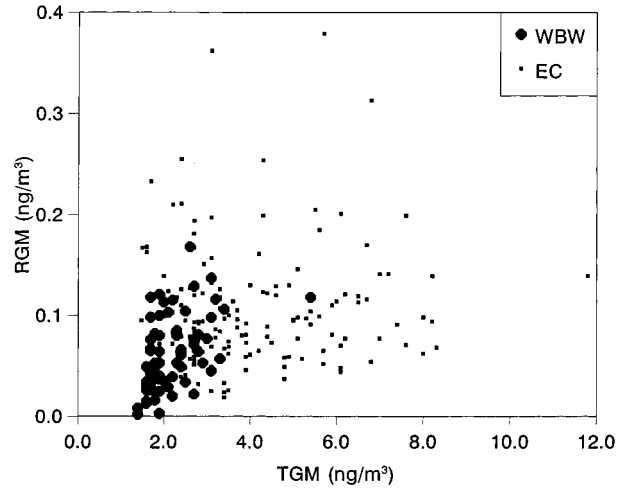

FIGURE 2. Relationship between ambient air concentrations of reactive gaseous mercury (RGM) and total gaseous mercury (TGM) for two sites in Tennessee (WBW, $r = 0.43$, $p < 0.01$) and Indiana (EC, $r = 0.14$, $p > 0.05$).

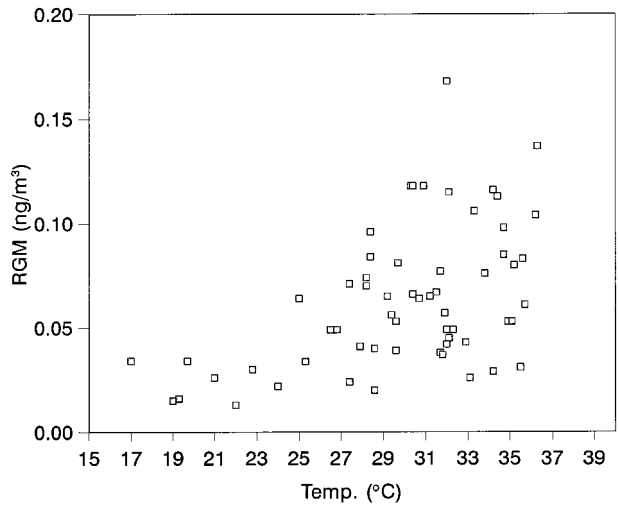

FIGURE 3. Relationship between ambient air concentrations of reactive gaseous mercury (RGM) and temperature at a site in Tennessee (WBW, $r = 0.50$, $p < 0.01$).

Diel Cycles in Gaseous Mercury Species. We measured the concentrations of RGM, TGM, and related meteorologic and air quality variables (where available) over 12−24-h periods during three sampling intensives in 1995: one each at two sites in Oak Ridge in July and one at EC in September. In each case, RGM showed consistent diel and diurnal cycles, reaching peak concentrations at midday and sharply decreasing at night (Figures 4 and 5). On July 18−July 19, RGM reached maximum values of ~0.05−0.06 ng/m^3 during each day, but decreased by more than a factor of 3 during the intervening night (Figure 4a). TGM displayed a different trend over this time, decreasing from >3 ng/m^3 the first afternoon to background values during the night and following day (Figure 4b), suggesting the possible influence of local source advection on July 18. RGM represented from <1 to ~3% of TGM during this period with the higher values occuring at midday. The behavior of SO_2 and O_3 did not correlate with that of RGM, although O_3 displayed a typical early morning minimum (Figure 4b). Over the following two days, both RGM and the RGM/TGM ratio displayed an even stronger diel cycle, with RGM increasing from ~0.03 ng/m^3 on the morning of July 20 to >0.12 ng/m^3 by late afternoon and then decreasing to values near the MC detection limit at night (<0.01 ng/m^3, Figure 5a). Although ancillary meteorologic data were not available, field notes indicated that this second sampling period was characterized by very hot weather and persistent southerly winds, which may have enhanced nighttime deposition. Two months later at the EC site, RGM was found to display a similar trend over a 12-h period, gradually increasing from ~930 to 1330 and then decreasing strongly near sunset (Figure 5b). In this case, there was little trend in the RGM/TGM ratio until sunset.

Some atmospheric trace gases are characterized by strong day/night differences in their concentrations, generally as a result of photochemistry and/or removal at the surface by nocturnal dry deposition. Perhaps the best example of this behavior for another rapidly depositing species is HNO_3, which exhibits day/night concentration ratios on the order of those seen for RGM (e.g., refs 29−31). Photochemical production rates for HNO_3 peak at midday, and the gas is depleted at night by removal to surfaces below the stable boundary layer. Both of these mechanisms may also influence the behavior of RGM. Atmospheric gas phase reactions between Hg^0 and photochemical oxidants to produce RGM are not well understood. Hall (*7*) studied the homogeneous oxidation of Hg^0 by O_3 and found the reaction to be significantly slower than previously reported; however, the reaction was seen to proceed about six times faster in sunlight than in dark. In addition, there are several other

TABLE 2. Summary of Linear Correlation Coefficients among Reactive Gaseous Mercury (RGM), Total Gaseous Mercury (TGM, Primarily Hg^0) and Selected Atmospheric and Meteorological Parameters

data set[a]	RGM vs TGM	O_3	SO_2	NO_2	T_a	RH	WS	Rg
WBW ground level data								
RGM vs ...		0.29*[b]	0.31*	0.05	0.50**	0.18	−0.18	0.48**
TGM vs ...		0.17	0.18	0.07	0.26*	0.20	0.06	0.15
RGM/TGM vs ...		0.24*	0.26*	0.05	0.46**	0.11	0.11	0.49**
all data	0.25**							
EC	0.05							
WBW tower	0.22							
WBW ground	0.48**							

[a] Degrees of freedom as follows: all data, 212; EC, 145; WBW tower, 8; WBW ground, 55−65. [b] *, $p < 0.05$; **, $p < 0.01$.

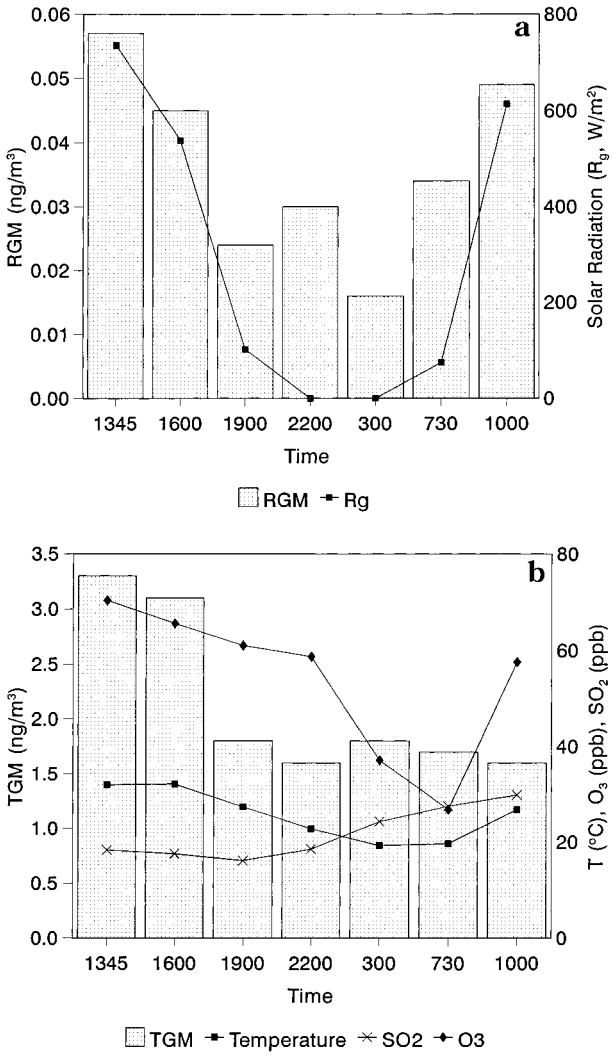

FIGURE 4. Diel cycles in reactive gaseous mercury (RGM, panel a) and total gaseous mercury concentrations (TGM, panel b) in ambient air in the city of Oak Ridge, TN, on July 18−July 19, 1995. Also shown are trends in related meteorological and air quality parameters (times shown are midpoints of ~3-h periods in EST).

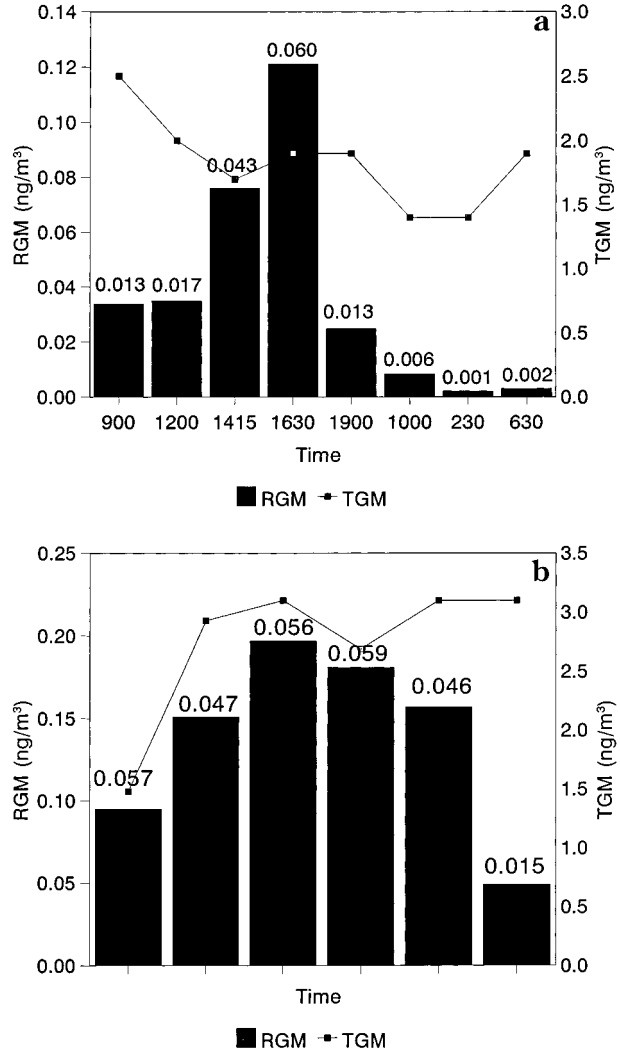

FIGURE 5. Diel cycles in reactive gaseous mercury (RGM) and total gaseous mercury concentrations (TGM) in ambient air at WBW (panel a), a rural site near Oak Ridge TN, on July 20−July 21, 1995, and at Richmond, IN (panel b), on September 30, 1995. Also shown are the trends in RGM/TGM ratios at each site (times shown are midpoints of ~3-h periods in EST). Values over bars represent RGM/TGM ratios. Times for panel b: 930, 1130, 1330, 1530, 1730, and 1930.

reactions pertinent to the issue of photochemical production of RGM that have not been investigated, including those with OH radical, H_2O_2, and Cl_2 (*5*). However, even if these reactions are not competetive with direct industrial releases of RGM to air, the nocturnal behavior of "sticky" (highly surface reactive) gases can result in strong diel cycles. For example, atmospheric emissions of RGM from many large-scale combustion sources probably occur near or above the nocturnal boundary layer, allowing for limited downward mixing at night. If RGM is a rapidly depositing species, as predicted by its solubility (*4*), then nocturnal dry deposition of RGM trapped below the boundary layer would explain the diel cycles reported here. In the following sections, we describe further observations of the behavior of RGM that support this hypothesis.

RGM in a Plume Fumigation Event. During the summer 1993 sampling campaign at WBW, we detected a sharp peak in RGM during one 8-h daytime period. We initially

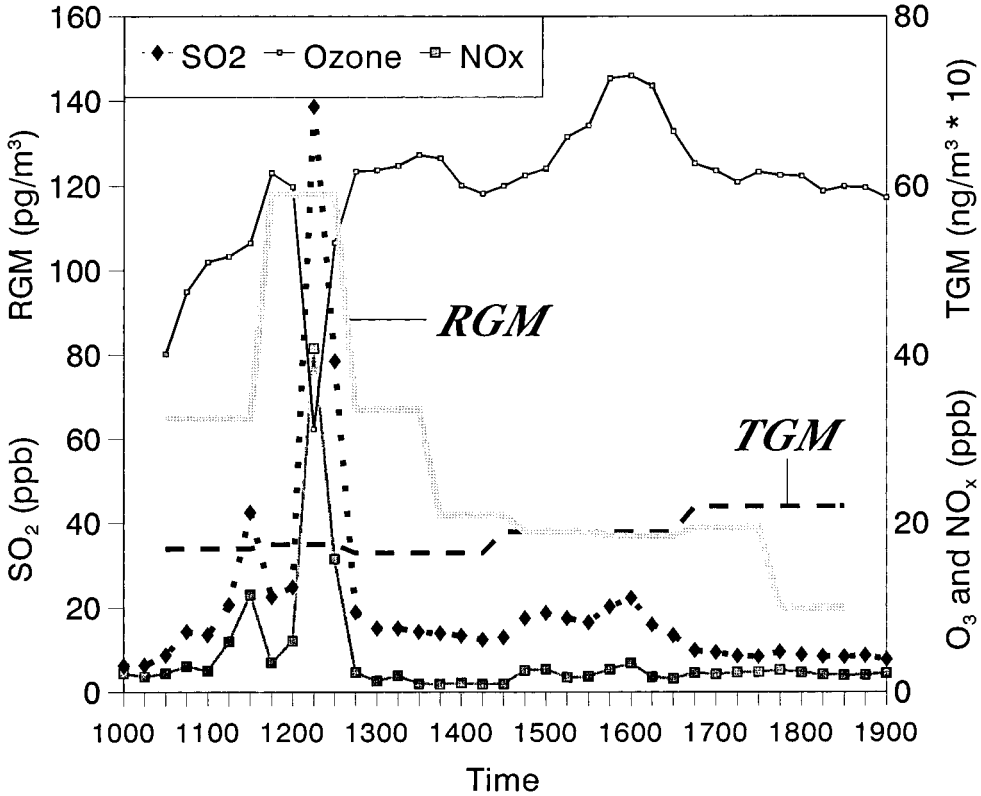

FIGURE 6. Trends in mercury speciation and concentrations of several atmospheric components during a mid-morning plume fumigation event sampled at Walker Branch Watershed on August 3, 1993 (times shown are EST).

published these data without comment (see Figure 2, data from August 3, in ref 15) but were struck by the trend in RGM concentration and RGM/TGM ratio. On later examination of the ancillary data from the NOAA sampling station at our sampling site, we realized that we had fortuitously sampled a mid-morning plume fumigation event (Figure 6). Such events are typically characterized by peaks in the combustion products SO_2 and NO_x and a consequent depletion of O_3 (e.g., ref 32), as clearly indicated by the data. These conditions result when a plume aloft is mixed to ground level upon breakup of the nocturnal bounday layer by radiation-induced turbulence and typically occur in late morning at this site during the summer (Meyers, personal communication). The primary event at 1200−1215 was preceded by a smaller fumigation, which began around 1100. We began sampling for RGM and TGM at 1030 and collected 1-h samples until 1730. The sample from 1130−1230 partially bracketed both fumigations and clearly included the major event. During this time, RGM doubled from the prior sample to ~0.12 ng/m^3 and then proceded to decrease throughout the day to more typical levels near 0.04 ng/m^3. The ratio of RGM/TGM mirrored the RGM signal, peaking at 0.064 in the plume and then dropping to more typical levels following the event (~0.02). The concentration of RGM in this near-plume sample remains one of the highest concentrations measured at ground level at WBW.

Wind direction measured at our nearby 42-m tower indicated that flow aloft was generally SW until the first fumigation and then gradually shifted to due W throughout the event, followed by a return to SW flow. There is a 1.2 GW Tennessee Valley Authority coal-fired electric utility station located 20 km to the WSW (~250°) of WBW, and this facility was the most probable plume source as wind direction remained between 250 and 270° between 0800 and the start of our sampling. Atmospheric turbulence as measured by sigma W increased and peaked during both fumigations, assisting in the breakup of the boundary layer, which allowed the downward mixing of the plume aloft. The electric utility releases combustion products from two unscrubbed 330-m stacks, and we estimate the upper level transport time from the plume source to WBW on this morning to be ~1 h. There is also a small steam boiler 2.5 km to the NNE of WBW that burns coal and another TVA power plant 13 km to the NE (0.9 GW), but it is unlikely that these sources contributed as wind direction remained SW around 0.5−1.5 m/s throughout the preceding night. We were initially surprised by the lack of a plume signal in TGM (primarily Hg^0) during this event. However, assuming a typical background TGM at WBW (2−3 ng/m^3; *27*) and assuming that RGM originates primarily from industrial sources (i.e., that no true "background" level exists), it is far more likely for a detectable plume signal for RGM to be seen at this distance than for TGM, especially for time-integrated samples. Assuming an emission signal of 80% Hg^0 and 20% RGM from a hypothetical power plant, the reactive plume model of Constantinou et al. (*33*) predicts a plume RGM/Hg^0 ratio at 20 km downwind under clear sky conditions very much in line with that measured during the fumigation event at WBW (~0.06, see Figure 6 in ref 33).

One further observation on the behavior of RGM is of interest. Despite the overall correlation between RGM and TGM at WBW ($r = 0.43$, $p < 0.01$), the high-frequency data from both diel and plume measurements indicate that these two species do not track each other in high frequency samples, but in fact may behave quite independently. This suggests that the correlation arises from more general trends in air pollutant concentrations over time, as influenced by climatology.

Gradients in RGM over the Surface. If the MC provides an accurate measure of RGM (a rapidly-depositing water-soluble form of gaseous Hg), one would expect MC data collected in a height profile over the ground to reflect a strong deposition gradient due to RGM removal near the surface. For example, gradients of HNO_3 (a well-known example of a soluble, surface-reactive gas) measured over the forest

TABLE 3. Gradients of Reactive Gaseous Mercury (RGM) Measured over Plant Canopies and Estimates of Dry Deposition Fluxes and Deposition Velocities (V_d) Computed Using Turbulent Mixing Coefficients (K_w) from Modified Bowen Ratio Approach (See Text)

date	location	time	height (m)	RGM (ng/m^3)	gradient (ng/m^3)	K_w (m/s)	flux (ng m^{-2} h^{-1})	V_d cm/s
7/27/93	grass	1008−1103	1	0.053				
		1112−1229	0.25	0.049	0.004	0.05	0.7	0.4
9/16/92	forest	1200−1300	40	0.350				
		1310−1400	20	0.310	0.040	0.4	58	5.2
8/2/95	forest	1119−1328	40	0.127				
		1119−1328	30	0.118	0.020	0.3	22	5.1
8/2/95	forest	1410−1514	40	0.147				
		1410−1514	30	0.098	0.029	0.2	21	5.9

canopy at WBW indicated 10−20% decreases in concentration just above and within the vegetation canopy as a result of removal of HNO_3 near the surface (*34, 35*). On four occasions, we measured concentration gradients of RGM over vegetation surfaces at WBW: three over the forest canopy and one over a grassy clearing. In each case, we found measurably lower concentrations immediately above the surface as compared to aloft (Table 3).

The uncertainties on these measurements are large, and it is not possible prove whether the concentration gradients are statistically significant. In our flux/gradient research on TGM, we normally collect six replicate samples at each height to quantify the very small gradients in Hg^0 over these surfaces (*15*), but this was not possible for RGM. The samples for the first two RGM gradients were collected sequentially with the same mist chamber over a ~2-h period, and temporal variability cannot be ruled out. The second two gradients were collected simultaneously with separate MCs, the precision for which is on the order of ±20−30% (*16*), comparable with the magnitude of the gradients seen here. Nevertheless, these observations are consistent with the behavior of a rapidly depositing atmospheric species (as opposed to showing random differences), and we can gauge the validity of the data by computing dry deposition velocities for each period (V_d = flux/concentration, expressed in cm/s). Table 3 includes RGM fluxes and values of V_d estimated from our gradients using the modified Bowen ratio approach we previously applied to Hg^0 (e.g., refs 36, 37, and 24). Our data yielded estimates of V_d of 0.4 cm/s over grass and 5−6 cm/s over the forest (Table 3). These values are in reasonable agreement with values reported for WBW and elsewhere for the dry deposition of HNO_3 to vegetation (*34, 38*). In comparison, our modeled V_d values for Hg^0 dry deposition to this forest are much smaller, on the order of 0.1 cm/s for midday summer conditions (*4*).

Implications for Mercury Deposition. The mist chamber (MC) is a viable method for quantifying reactive gaseous mercury (RGM) species in air, combining a high-flow rate with a low and controllable system blank to yield hourly concentrations well below 1 ppt (tens to hundreds of pg/m^3). We have developed, tested, and improved the method over a period of several years (*15, 16*) and propose that the method is now ready for wider scale applications. Despite the uncertainty of measuring and identifying a reactive species, which consitutes only a few percent of total gaseous Hg in air, the MC provides consistently believable results under a variety of conditions. In particular, we have demonstrated here that the RGM data collected by the MC are predictable and reproducible in their behavior over diel cycles, in gradients over surfaces, and during plume fumigation.

Numerous studies have suggested that RGM is an important species emitted from combustion sources and could dominate the flue gas composition from coal-fired boilers and from waste incinerators (e.g., refs 3 and 6).

TABLE 4. Estimates of Dry Deposition of Atmospheric Hg Species to Forest Canopy at Walker Branch Watershed in Tennessee Based on Measured Concentrations and Published Models (*4, 27*)[a]

species	concn (ng/m^3)	V_d (cm/s)	flux (ng m^{-2} h^{-1})
Hg-p	0.02	0.1	0.07
Hg^0	2.50	0.09	0−6.5[*]
RGM	0.07	2.0	5.7

[a] Deposition of RGM was modeled based on the HNO_3 vapor analog and a published inferential dry deposition model for Hg (*4*). Deposition of aerosol Hg (Hg-p) was estimated from the same model assuming a MMD for Hg-p of 2 μm. The values represent typical summer conditions. [b] Recent data suggest that Hg^0 exhibits a compensation point, possibly in the range of ~10−20 ng/m^3 (Hanson et al., 1995). Below this concentration, net dry deposition of Hg^0 may not occur, increasing the potential importance of RGM.

Attempts by others to sample RGM in combustion plumes and in air aloft have not been published (Prestbo, personal communication). To our knowledge, the data summarized here and in our previous paper (*15*) represent the only published values for RGM in ambient air in the vicinity of such sources. We sampled atmospheric Hg during a mid-morning plume fumigation event when RGM increased from ~0.06 to 0.12 and back to to 0.06 ng/m^3 in a 1-h spike. Plume presence was confirmed by coincident spikes in SO_2 and NO_x and a depletion of O_3 (Figure 6).

The behavior of RGM suggests it to be a highly surface-reactive species, and the trends reported here mirror those commonly reported for other sticky gases, such as HNO_3 (e.g., ref 31). Profiles of RGM concentrations over vegetation surfaces during the daytime support the hypothesis that RGM is rapidly dry deposited. The importance of quantifying RGM when evaluating Hg fluxes to the landscape has been cited by numerous authors (e.g., refs 3 and 5). Its reactivity should allow it to play a strong role in the removal of Hg from the troposphere by both precipitation scavenging (*39*) and dry deposition (*40*). We can roughly assess the potential role of RGM deposition at the Walker Branch site using the data presented here and elsewhere. Table 4 summarizes our calculations of the relative importance of Hg^0, RGM, and fine aerosol Hg to dry deposition at WBW on a typical summer day. It is clear that the gas phase species will dominate the dry deposition flux and that RGM is an important component. We have independently verified these modeled fluxes in the field (*41, 4*). Our WBW biogeochemical cycling data suggest average dry deposition fluxes on the order of ~0.5−3 ng m^{-2} h^{-1} from throughfall analyses and around 5−10 ng m^{-2} h^{-1} from litterfall fluxes (assuming that all of the Hg washed from trees in throughfall and the Hg accumulated in leaves during the growing season is derived from atmospheric sources; e.g., ref 42).

We can assess the potential role of RGM in wet deposition at WBW as well. The precipitation scavenging scheme in the

TABLE 5. Mean Concentrations of Reactive Gaseous Mercury (RGM) and Total Gaseous Mercury (TGM) in Ambient Air Sampled before, during, and after Summer Rain Events at Sites in Tennessee (WBW) and Indiana (EC)[a]

	RGM (ng/m^3)			TGM (ng/m^3)		
site	mean	SD	*n*	mean	SD	*n*
WBW-dry	0.097	0.031	6	2.89	0.42	6
WBW-rain[b]	0.048	0.006	3	2.57	0.29	3
% change[c]	−51			−11		
EC-dry	0.118	0.081	3	2.70	0.52	3
EC-rain[b]	0.062	0.035	3	2.75	1.06	3
% change[c]	−47			2		

[a] Rain/dry data sets were collected from 7/9/93 to 7/15/93 at WBW and from 4/21/95 to 5/24/95 at EC. [b] Samples designated "rain" were collected under a roof during rain periods (EC) or in the open immediately following a rain event (WBW). [c] Change in mean concentration before and after (or during) rain events.

model of Petersen et al. (*10, 39*) has been used to estimate wet deposition of Hg for summer conditions typical of the southeastern United States. Using a mean concentration of RGM of 0.05 ng/m^3, this model predicts total Hg concentrations in rain around 10 ng/L from direct scavenging of RGM alone (Petersen, personal communication). Including all airborne Hg species, the model predicts concentrations around 20 ng/L, indicating the potential importance of RGM. Typical concentrations of total Hg in summer rains at WBW are in the range 5−25 ng/L (*27*; Lindberg, unpublished). Another observation from our data set supports the potential role of wet deposition of RGM and provides further evidence of the water solubility of this species. During two month-long studies at each site, we sampled RGM before, during, and after during several rain events or rainy days. At the EC site, we sampled RGM below a roof during two days of rain and sampled non-rain periods prior to and following these days, while at WBW we sampled RGM within minutes to hours before and after two rain events. In each case, RGM decreased dramatically during or after periods of rain, by ∼50% on average (Table 5), while TGM did not vary significantly or consistently (on average <±10%).

It is apparent that RGM at the concentrations reported here can contribute significant Hg to the landscape by both wet and dry deposition and that ecosystem exposure could occur near major point sources of airborne RGM compounds. There is a clear need for further research on the quantification and behavior of RGM in ambient air as well as determination of the actual compounds that comprise this species.

Note Added in Proof. Recently published results from an Eulerian atmospheric transport model indicate that regional wet and dry deposition of Hg are dominated by a "divalent form of gaseous mercury" (*43*). This model also predicted ambient concentrations of RGM in Tennessee and Indiana that are remarkably similar to the frequency distributions presented in Figure 1 (*44*). Important progress on sorbents has recently been reported that may lead to an automated field method for RGM at ambient levels (*45*).

Acknowledgments

We thank the following colleagues for their help with this study: Jim Owens for field and laboratory support; John Munthe, Nicholas Bloom, and Eric Prestbo for helpful discussions; Bob Stevens and Meng-Dawn Cheng for comments on the manuscript; and the following Earlham College students, who collected much of the data reported here: Eric Dudas, Troy Gottfried, Matthew Koenig, Vuk Koprivica, Andrew Lover, and Olen Stephens. This research was sponsored by the Electric Power Research Institute under Contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., manager of Oak Ridge National Laboratory. One author (W.J.S.) also received financial support for sampling equipment from the Florida Department of Environmental Protection (T. Atkeson through a contract with G. Gill). This is Publication No. 4700, Environmental Sciences Division, ORNL.

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Received for review June 20, 1997. Revised manuscript received September 15, 1997. Accepted September 22, 1997.[⊗]

ES970546U

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1997.