

Development and First Results of an Aircraft-Based, High Time Resolution Technique for Gaseous Elemental and Reactive (Oxidized) Gaseous Mercury

P. C. SWARTZENDRUBER,^{*,†,‡,§}
D. A. JAFFE,^{†,‡} AND B. FINLEY[‡]

Department of Atmospheric Sciences, University of Washington, Seattle, Washington 98164, and Interdisciplinary Arts and Sciences, University of Washington, Bothell, Washington 98011

Received May 8, 2009. Revised manuscript received August 4, 2009. Accepted August 4, 2009.

We developed a high time resolution (2.5 min) aircraft instrument for gaseous elemental mercury (GEM) and reactive gaseous mercury (RGM). The system measures RGM with complementary denuder and difference techniques, which can be compared to check for consistency. In laboratory tests, the agreement of the two techniques was 15% ($\pm 13\%$). In five test flights, RGM was generally below the detection limit of the difference technique (0.08–0.16 ng/m³) except for values of 200–500 pg/m³ in airmasses between 600–700 mb (Flight 1) and 850–550 mb (Flight 4), which is consistent with previous observations of RGM at Mt. Bachelor. There was a linear correlation between the denuder and difference techniques in each flight (range of slopes, 0.27–1.24) and across all flights (slope = 0.37, $p < 1e-6$). The correlation is evidence that the difference technique is able to measure RGM in real time, although RGM appears to not be fully captured or recovered by the denuder. The only factor common to all RGM enhancements was the low aerosol scattering coefficient (< 2 M/m). Particulate mercury was below the detection limit (27 pg/m³) for all samples. The mean GEM and total mercury (THg) profiles are in the middle of the range of other published profiles. The THg profile showed no gradient to 5.5 km ($p = 0.12$, $r^2 = 0.009$).

Introduction

Our understanding of the tropospheric redox chemistry of mercury remains limited (1, 2). It has generally been assumed that oxidized mercury is present in the free troposphere at only negligible mixing ratios distant from anthropogenic sources. Several recent studies have challenged this assumption (3, 4). An accurate understanding of the distribution and redox chemistry of mercury species in the free troposphere is important because of their different deposition rates and behaviors. Gaseous elemental mercury (GEM) is believed to have a relatively long lifetime in the free troposphere (~1

yr) (5), while gaseous oxidized mercury (generally referred to as reactive gaseous mercury or RGM) is rapidly lost to particles, surfaces, and sequestered by clouds and rain drops (5). Mercury can also be bound to particles (PHg), but the lifetime of PHg is limited by the lifetime of the carrier particle, which is typically less than 10 days. There is very little information on the distribution of RGM in the free troposphere (3). Landis et al. (6) report some of the first observations of RGM in the free troposphere at Mauna Loa, HI, and in an aircraft study in Florida. Swartzendruber et al. (3) report on continuous observations of mercury speciation at Mt. Bachelor Observatory (2.7 km asl) in Oregon. In free tropospheric air, they observed periodic enhancements of RGM up to about 40% of the total airborne mercury. The enhancements could not be linked to anthropogenic sources and appeared to be generally correlated to an upper tropospheric influence. Modeled ozone and OH oxidation mechanisms were unable to reproduce the magnitude of the enhancements, which implied that other oxidants, particularly halogen radicals, may be involved (3). Similar observations have since been reported by Fain et al. (7) at a high elevation site in Colorado and by Sheu et al. (8) at a mountain site in Taiwan, and elevated RGM at surface sites has been linked to free tropospheric RGM in Nevada (9). The sources and mechanisms responsible for this RGM remain poorly understood.

Aircraft studies of the vertical distribution of mercury have generally shown little to no gradient in the lower and middle free troposphere (10–14). A contrasting observation of a gradient throughout the troposphere was reported by Radke et al. (15), and there is evidence of GEM depletion near the tropopause and in the stratosphere reported by Swartzendruber et al. (10), Talbot et al. (11), and Slemr et al. (16). In light of the uncertainties on the speciation of mercury in the free troposphere, we developed a high time resolution aircraft speciation system to address the following questions: (1) Can existing Hg measurement methods be adapted to measure mercury speciation in real time in an aircraft? (2) What is the distribution of total airborne Hg (THg), gaseous elemental Hg (GEM), and reactive gaseous mercury (RGM) in the free troposphere?

Methods. Five test flights were conducted in July and August, 2008. The aircraft was a Beechcraft Duchess 76, which has been used in previous studies in the Pacific Northwest (17, 18, 10). Ancillary measurements included ozone, aerosol scattering coefficient, H₂O, and CO₂. See Supporting Information for further details on the flights and other measurements.

Hg Instrumentation. Aircraft Specific Issues for the Tekran 2537. The Tekran 2537B was used to quantify GEM, THg, and RGM in real time, and RGM and PHg collected on denuders and particulate filters. The Tekran 2537 uses two Au cartridges and alternates between preconcentrating Hg on the cartridges and thermally desorbing the Hg, which is detected by cold vapor atomic fluorescence spectroscopy (CVAFS). The functioning of the Tekran 2537 has been previously described (19). For this research, the collection cycle was 2.5 min, with a detection limit of about 0.10 ng/m³, using values from the serial output (Flights 1 and 2), or 0.05 ng/m³ when the peaks are quantified offline (Flights 3–5). The detection limit for an individual instrument is inferred from the detection limit of the difference technique (discussed below) and the propagation of uncertainty for the difference of two measurements, $\sigma[A - B] = (\sigma[A]^2 + \sigma[B]^2)^{1/2}$. The two detection limits are due to an improved fluorescence peak integration technique that was developed after Flight 2 and is described in detail by Swartzendruber et al. (20).

* Corresponding author email: philswartz@rsmas.miami.edu.

[†] Department of Atmospheric Sciences.

[‡] Interdisciplinary Arts and Sciences.

[§] Current address: University of Miami/Rosenstiel School of Marine and Atmospheric Science (RSMAS), 4600 Rickenbacker Causeway, Miami, FL 33149.

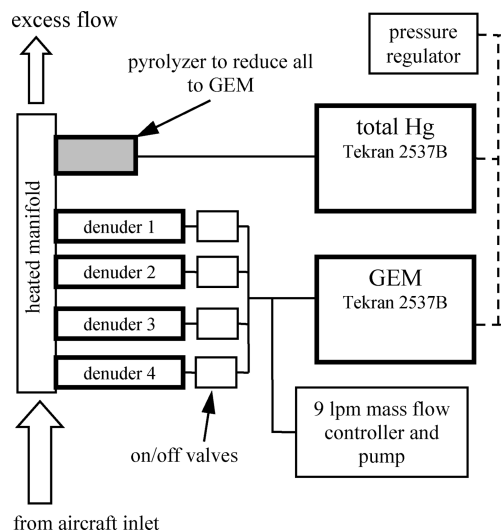


FIGURE 1. Schematic of aircraft speciation system with complementary RGM techniques. Auxiliary flow controller and pump pulled additional air through the denuder to bring the total flow to about 10 slpm. An additional pump was connected to the end of the intake manifold (excess flow) and pulled about 10 slpm to increase the flushing rate of the manifold. In laboratory tests, the test atmosphere entered the manifold in the same location as during sampling (from aircraft inlet).

The sample flow rate of the Tekran 2537s was set to 1.0 standard liters per minute (slpm). At higher altitudes (and lower pressures) the flow rate could not be maintained because of restrictions within the instrument, primarily the Au cartridge. At maximum altitude, the flow dropped to a minimum of about 0.75 slpm. All mercury concentrations are reported per standard cubic meter, which is a mass/standard volume (i.e., at 1013 mb, 273 K) mixing ratio. The CVAFS method has an inherent pressure sensitivity (10, 16) which was mitigated by controlling the pressure of the fluorescence cell with an MKS-640 (MKS Instruments) pressure controller. The cell exhaust line was leak tested in the laboratory before the study.

Calibration and quality assurance procedures included verifying the rate of the permeation tube between flights, multiple permeation spans before each flight, and a single in-flight span calibration near maximum altitude. The permeation rates of the internal permeation tubes as certified by the manufacturer were verified by comparison with injections from a temperature controlled primary standard (21) and were found to agree to 3.2% ($\pm 1.7\%$) before and after the campaign. Repeated permeation calibrations before each flight had a precision of better than 2%. Calibration from the permeation tube, in-flight, could not be conducted as normal because the delivery of Hg can be significantly biased because of changes in ambient pressure and pressure differences between the permeation chamber and ambient air. We accomplished an in-flight span calibration using the following technique: Immediately before taxiing for takeoff, the permeation tubes were sampled exactly as is done for normal calibrations, but the instruments were stopped and set to idle before they could analyze the cartridges. Once the airplane took off and reached maximum altitude, the instruments were started and the spans were analyzed. The agreement of these in situ spans ($n = 20$) with the spans performed immediately before takeoff ($n = 20$) was better than 1% ($\pm 2.7\%$). On the basis of a one sample t -test of agreement (i.e., true ratio of spans, in situ/ground = 1), the difference is not significant ($p = 0.15$).

RGM by Complementary Denuder and Difference Systems. A schematic is shown in Figure 1. In this approach, two 2537s are synchronized and sampled from a common

manifold. The first system samples through a pyrolyzer maintained at 500 °C, which reduces oxidized species (RGM and presumably most PHg) to GEM, and so is measuring total airborne mercury (THg). The second system collects through speciation trains, which each have a KCl denuder to collect RGM and a quartz-fiber filter to collect PHg (identical to the method of Landis et al. (22)). The total denuder flow was 10–11.5 volumetric liters per minute, which corresponds to lower mass flow rates (10–6.5 slpm) at higher altitudes and lower ambient pressures. The denuders were not temperature controlled, so they remained at the temperature of the aircraft cabin (15–25 °C). The 2537 in this second system unambiguously measures GEM. RGM + PHg in 2.5 min resolution is then determined by the difference (i.e., THg – GEM). Because our observations at MBO (3) found negligible PHg in RGM enhancements and Murphy et al. (23) report no unambiguous detection of PHg in a range of free tropospheric air masses, for this study we regard PHg as negligible and designate the difference (THg – GEM) as being RGM.

Four denuder trains are connected in parallel to a manifold (URG Corp) and are selected by activating on/off valves that are downstream of the speciation trains. After each flight, the denuders and particulate filters are taken to the laboratory for analysis. The RGM on each denuder was manually quantified as described by Landis et al. (22). Two denuder field blanks were collected for each of Flights 2–5. The mean ($1 - \sigma$) of the blanks was 0.22 (0.23) pg. At a typical sample volume, the $3 - \sigma$ detection limit of the denuders was about 3 pg/m³.

The mercury obtained from the denuders can then be compared to the Hg mass that would be *expected* on the basis of the RGM by difference technique. While the terms *expected* and *recovery* are generally applied in reference to well-known values such as calibration standards, here they are not used in this sense. *Expected* refers to the Hg mass that would be collected on a denuder on the basis of the RGM by difference concentration and the denuder sample volume. *Recovery* indicates the Hg mass obtained from the denuder as a fraction of the *expected* mass in only a relative sense and is not meant to imply that RGM by difference values are necessarily more accurate.

Detection Limit. The detection limit of the difference technique was determined by the precision of the difference between the THg and GEM systems while sampling RGM-free air for at least an hour. This test was performed on all four denuders before all flights and after two flights. Using the 2537 serial output (Flights 1 and 2) the detection limit ($3 - \sigma$) of the difference technique is about 0.16 ng/m³. When integrating the peaks offline (Flights 3–5), it is about 0.08 ng/m³ for a 2.5 min collection period.

Results and Discussion

Laboratory Tests of Speciation System Performance. The difference-denuder collection principle was tested in the laboratory before the campaign. The system was run identically as in flight. Outdoor air was spiked with an RGM proxy (HgCl₂) at 0.5–2 ng/m³. Delivery of HgCl₂ was accomplished with a diffusion capillary in a small vial containing solid HgCl₂. In our system, GEM was observed to increase along with HgCl₂. The final test is shown in Figure 2. Here, the denuder–difference agreement was 15% (relative percent difference) ($\pm 13\%$) with the Hg mass on the denuder (recovery) averaging 90% ($\pm 16\%$) of the mass expected from the RGM by difference measurement. See Supporting Information for further details.

Flight Performance. Figure 3 shows a scatter plot of the denuder versus expected mass for all flights, $n = 18$. (Two denuder values were lost on Flight 3 because of a leak.) A regression line between the denuder Hg mass and the

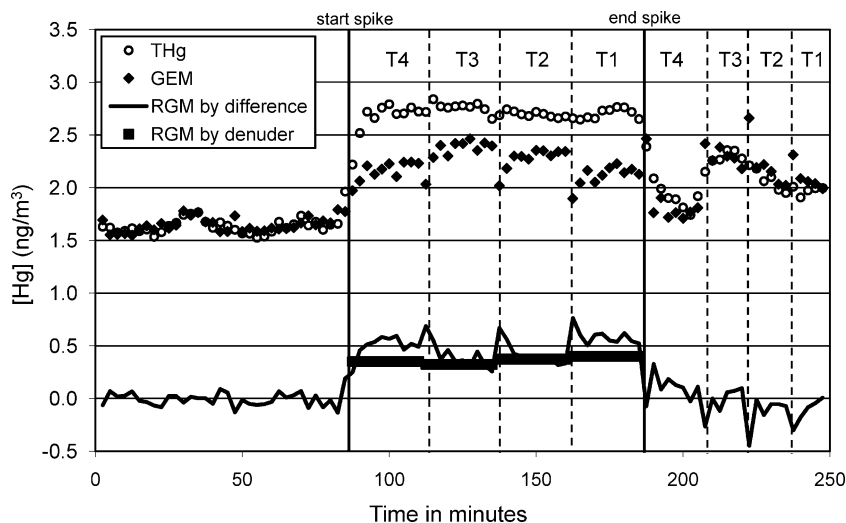


FIGURE 2. Time series of the June 17, 2008, laboratory test of speciation by denuder–difference. Two 2537s sampled simultaneously with the first measuring GEM and the second measuring THg. A spike of an RGM proxy (HgCl_2) is added at $t = 80$ min and removed at $t = 180$ min. The concentration of RGM based on the denuder measurements is indicated by the solid horizontal lines. In this test, RGM is collected on all four denuders. T1, T2, etc., indicate the denuder sample train ID. The denuder–difference recoveries for T4–T1 were 103, 79, 105, and 75%, respectively, with a mean of 90% ($\pm 16\%$).

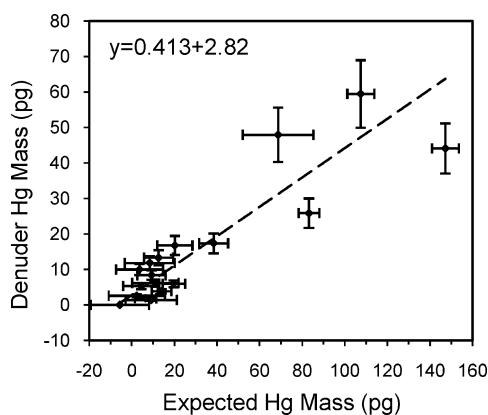


FIGURE 3. Scatter plot of the mercury mass collected on each denuder versus the mass of mercury expected to be on the denuder on the basis of the RGM by difference concentration and sample volume for all flights. The fit line was determined by reduced major axis regression (RMA). An ordinary least-squares (OLS) regression line (not shown) has a slope of 0.37 with $R^2 = 0.79$ ($p < 1 \times 10^{-6}$).

expected Hg mass was determined by reduced major axis (RMA) regression because the independent uncertainties of the two variables are similar in magnitude and heteroscedastic (not constant throughout the range). Ninety-five percent confidence intervals were estimated with a 5999 member bootstrap technique following Wilcox (24). The slope (and 95% confidence interval) is 0.41 (0.28–0.63), and the offset is 2.8 pg (–0.45 to 5.6). Ordinary least-squares (OLS) regression yields a slope of 0.37 with $R^2 = 0.79$ ($p < 1 \times 10^{-6}$). Table 1 summarizes the speciation performance measures in each flight.

The denuder-expected mass comparison of all flights shows a linear correlation. A linear correlation is also present in each flight, even when the Hg mass collected per denuder ranged from as low as 2–15 pg. This corresponds to [RGM] of 10–40 pg/m^3 for denuder collection times of less than 1 h. The linearity argues that, throughout the range of conditions encountered in our flights, the RGM measured by difference is not an artifact of the GEM and THg systems but is a quantitative response to a real ambient Hg species.

The discrepancy between the denuder mass and the expected mass during sampling was not seen during the

TABLE 1. Summary of Speciation Performance Measures Using All Data

flight	denuder-expected		max RGM ^a		bias in ng/m^3	
	slope	R^2	pg/m^3	(pg)	pre	post
1	0.69	0.97	360	48	0 ^b	–
2	1.24	0.59	145	12	0.091	–
3	N/A ^c	N/A ^c	165	13	0.050	0.13
4	0.27	0.57	500	44	0.061	–
5	0.50	0.97	157	17	0.046	0.062
comp.	0.41	0.79	N/A	N/A	0.057	–

^a Maximum RGM concentration for a 2.5 min cycle (bias corrected) in each flight and maximum pg of Hg on a denuder in each flight. ^b Bias was checked before the first flight and was found to be highly variable, although during the flight no bias was apparent. ^c Correlation is not applicable on this flight because RGM by difference values were not available for two of the denuder segments because of a leak.

laboratory testing. Several plausible explanations of the discrepancy are (1) inconsistent contamination or a positive artifact in the THg instrument, (2) inconsistent low response in the GEM instrument, (3) an inaccurate correction of the bias between the THg and GEM systems, or (4) less than 100% recovery of the RGM that reaches the denuder. Explanation 1 is highly improbable based on the insignificant vertical trend in THg (Results and Discussion–Vertical Profiles). Explanation 2 also seems unlikely based on the consistent agreement between the GEM and THg measurements before and after each flight. Explanation 3 is also highly improbable because an inaccurate bias correction would produce an offset in the correlation, i.e., because the denuder sample volumes are similar, a bias of 0.075 ng/m^3 would manifest in a 15 pg offset in the correlation; the actual offset is 2.8 pg, which is only marginally different from zero ($p = 0.049$, one tailed). Explanation 4 is the most likely, but there is no clear indication as to where or when this loss is occurring.

The most plausible hypotheses are that (A) Hg is coming off the denuder (and is lost) after sampling stops but before it is connected to the analytical train in the laboratory, (B) a fraction of oxidized Hg is passing through the denuder and is being lost downstream, or (C) during desorption, Hg is being lost in the analytical train or the Au cartridges are

TABLE 2. Summary of Flights in the Speciation System Test Campaign

flight	date	location	synopsis
1	July 20	N-S in Puget Sound	high RGM 600–700 mb, no UTLS signature
2	August 1	SW to Astoria, OR	UTLS signature above 700 mb, little RGM
3	August 4	W, Strait of Juan de Fuca	UTLS signature above 700 mb, little RGM
4	August 23	SW to Astoria, OR	high RGM above 850 mb
5	August 29	W, Strait of Juan de Fuca	very low H ₂ O above 700 mb, little RGM

being temporarily passivated. Note that hypothesis B would include particulate bound mercury passing through the denuder as expected but subsequently evading from the filter media and not reaching the 2537 while in flight or being lost when the filter is being prepared for analysis. This issue requires further investigation and suggests that development of an in situ RGM calibration technique is needed.

Synopsis of Observations. Five flights were conducted in July and August, 2008. Table 2 lists the flight dates, location, and summarizes the results of each flight. The average profiles of ozone, aerosol scattering coefficient, water vapor, and CO₂ from all five flights, binned by pressure with the observed standard deviation, are shown in Figure S1 of the Supporting Information. Particulate Hg samples were collected on Flights 2–4. All samples were below the estimated detection limit of 27 pg/m³ (per sample), and the average of all samples was not different from zero ($p = 0.86$).

RGM Distribution. RGM was detected on all denuders on all flights but was below the detection limit for a 2.5 min difference measurement (0.16 or 0.08 ng/m³, Section 2.3) for most of Flights 2, 3, and 5. Figure S2 of the Supporting Information shows the vertical profiles of GEM, THg, and RGM by difference from each flight along with the average. Table 1 summarizes the speciation performance measures from all flights.

Figure 4 shows the profiles of ozone, RGM, and THg, and GEM from Flight 4, which had the largest concentrations of RGM (by difference) of all five flights. The high RGM was observed exclusively above the boundary layer (<850 mb) and occurred in two distinctly different airmasses. Above

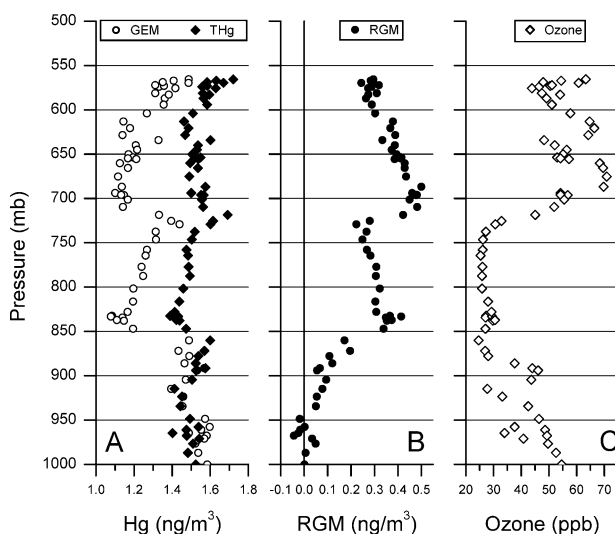


FIGURE 4. Vertical profiles from Flight 4: (A) THg and GEM, (B) RGM by difference, and (C) ozone averaged to the Hg data time periods. The boundary layer extended to about 850 mb. There were distinct airmasses in the free troposphere above and below 730 mb.

TABLE 3. Summary of Pearson's Correlations (r) for Free Tropospheric Data by Flight^a

flight	RGM versus		O ₃ versus		
	O ₃	H ₂ O	GEM	THg	H ₂ O
1	-0.45	0.25	0.54	0.32	-0.82
2	-0.04	0.04	-0.65	-0.71	<0.01
3	0.46	-0.56	-0.54	-0.31	-0.67
4a ^b	0.44	-0.78	-0.45	-0.33	-0.70
4b ^c	-0.16	-0.17	0.39	0.52	-0.77
5	0.39	0.17	-0.52	-0.23	0.19

^a Flight 4 appeared to have two different airmasses above the boundary layer so was split for these statistics. ^b Flight is above 720 mb. ^c Flight is above 890–720 mb.

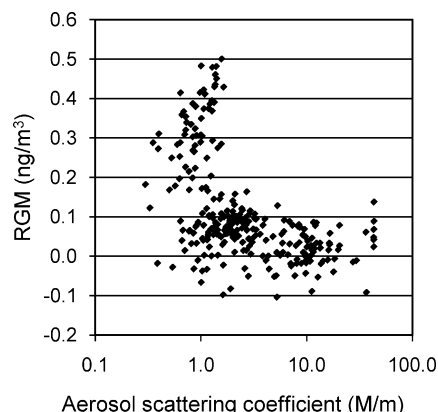


FIGURE 5. RGM versus aerosol scattering coefficient for all flights. Detection limit of RGM is 0.08 or 0.16 ng/m³. Large RGM enhancements were observed only with aerosol scattering coefficients below 2 M/m.

720 mb (Flight 4a), ozone was moderately high (56 (± 7.7) ppb) and H₂O was low (1.8 g/kg), while between 720 and 850 mb (Flight 4b), ozone was much lower (30 (± 5.5) ppb) and H₂O was higher (7.2 g/kg). The correlations of ozone with THg, GEM, and RGM are opposite in these two airmasses.

The key correlations of free tropospheric data are summarized in Table 3. For most flights, the relationships were dramatically different in the boundary layer compared to those in the free troposphere. So, data from the boundary layer have been excluded from these statistics. There was evidence for a source of RGM from the upper troposphere and lower stratosphere (UTLS) in Flights 3 and 4a and a roughly similar pattern in Flights 2 and 5. In these segments, ozone was negatively correlated with GEM and THg. The relationships between H₂O and ozone and RGM are, however, not consistent through these flights. In Flights 1 and 4b, there was also evidence for the inverse relationship between ozone and RGM, GEM, and THg. RGM was present in Flights 1 and 4b with mean ozone mixing ratios of 45 and 30 ppb, respectively. In both of these flights, ozone is positively correlated with GEM and THg and negatively correlated with RGM, although ozone and H₂O were negatively correlated.

The only factor common to elevated RGM is low aerosol scattering coefficient values, as can be seen in Figure 5. RGM values above the detection limit (for a 2.5 min cycle) are only present when the scattering coefficient is less than about 2 M m⁻¹. A similar relationship was not found between RGM and RH, water vapor, or ozone. At this point, we are aware of two possible interpretations. The first and simplest interpretation is that GEM oxidation (RGM production) chemistry is predominantly occurring at higher altitudes, where there are generally fewer particles. A second interpretation is that particles entrained into high RGM air provide

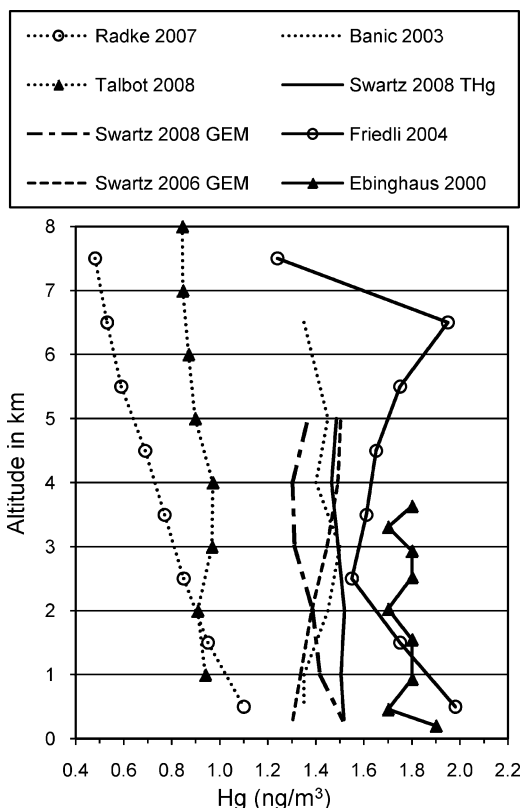


FIGURE 6. Comparison of all known published studies with vertical profiles. See Supporting Information for a description of the data origins. The total uncertainty for these data is likely to be at least 10–20%, although for most studies it was not reported. The four middle profiles do not have point markers in order to minimize visual clutter. The legend (top to bottom, left column then right column) approximately follows the respective profiles from left to right.

a reactive surface that allows for RGM to be destroyed. In either case, these data suggest that low aerosol scattering (little surface area) is necessary for RGM to increase above the level of 10s of pg/m³, which would be consistent with Swartzendruber et al. (3).

Vertical Profiles. The mean vertical profiles of THg and GEM and RGM by denuder and difference are shown in the Supporting Information. It is shown that there is no mean vertical trend in THg. A correlation of all THg data with altitude is statistically insignificant ($p = 0.12$, $r^2 = 0.009$), and the vertical gradient (and 95% confidence limit) was $-0.52\%/km$ ($\pm 0.65\%$). For RGM, the gradient (and 95% confidence limit) was $+11$ (± 10) pg/m³/km ($p = 0.05$). For GEM, the gradient (and 95% confidence limit) was -1.8% ($\pm 0.8\%$)/km ($p < 1e-5$). On the basis of a Kruskal–Wallis test of population difference above and below 730 mb, only THg showed no difference ($p = 0.27$).

Comparison with Other Vertical Profiles. Mean vertical profiles from this campaign and all other published comparable studies (to the best of the author’s knowledge) are shown in Figure 6. Most of these studies did not attempt to explicitly include or exclude RGM but assumed there was either negligible RGM or that their system was also sensitive to RGM, and thus their data represent THg. The exceptions are the present study and Swartzendruber et al. (10), who excluded RGM by scrubbing with a KCl trap. The data obtained in the present study fall in the middle of the published range and agree closely with Banic et al. (12) and Swartzendruber et al. (3). All mean profiles show little vertical trend to 7 km or their maximum altitude, with the exception of the Radke profile and the highest km of the Friedli profile.

It is difficult to reconcile the vertical gradient reported by Radke et al. (15) with the nearly constant profiles shown in the other studies and the long atmospheric lifetime (>6 months) of GEM (or THg) (5).

In this work we have developed the first real-time instrument for airborne observations of GEM and RGM. The instrument incorporates two techniques for the measurement of RGM, a relatively fast difference technique, and a slower denuder technique. Our laboratory tests and flight data demonstrate that the difference and denuder techniques show good correlation. There is, however, a significant discrepancy in the magnitude of RGM reported when measuring ambient air. We are currently working to understand the cause of this discrepancy.

Acknowledgments

This research was funded by the NASA Tropospheric Chemistry Program. Thanks to Northway Aviation and their pilots. The authors acknowledge helpful discussions with Eric Prestbo and the comments of anonymous reviewers.

Supporting Information Available

Additional technical details on the aircraft, mercury measurements, and analysis of system performance; also figures of vertical profiles and a scatter plot of denuder versus expected mass from flight. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Calvert, J. G.; Lindberg, S. E. Mechanisms of mercury removal by O₃ and OH in the atmosphere. *Atmos. Environ.* **2005**, *39*, 3355–3367.
- Lin, C. J.; Pongprueksa, P.; Lindberg, S. E.; Pehkonen, S. O.; Byun, D.; Jang, C. Scientific uncertainties in atmospheric mercury models I: Model science evaluation. *Atmos. Environ.* **2006**, *40*, 2911–2928.
- Swartzendruber, P. C.; Jaffe, D. A.; Prestbo, E. M.; Weiss-Penzias, P.; Selin, N. E.; Park, R.; Jacob, D. J.; Strode, S.; Jaegle, L. Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory. *J. Geophys. Res.* **2006**, *111*, D24301, doi: 10.1029/2006JD007415.
- Sillman, S.; Marsik, F. J.; Al-Wali, K. I.; Keeler, G. J.; Landis, M. S. Reactive mercury in the troposphere: Model formation and results for Florida, the northeastern United States, and the Atlantic Ocean. *J. Geophys. Res.* **2007**, *112*, D23305, doi: 10.1029/2006JD008227.
- Selin, N.; Jacob, D. J.; Yantosca, R.; Strode, S.; Jaegle, L.; Sunderland, E. Global 3-D land–ocean–atmosphere model for mercury: Present day versus preindustrial cycles and anthropogenic enrichment factors for deposition. *Global Biogeochem. Cycles* **2008**, *22*, GB2011.
- Landis, M. S.; Lynam, M.; Stevens, R. K. The Monitoring and Modeling of Mercury Species in Support of Local, Regional, and Global Modeling. In *Dynamics of Mercury Pollution on Regional and Global Scales*, Pirrone, N. Mahaffy, K. R., Eds.; Kluwer Academic Publishers: New York, 2005; pp 123–151.
- Fain, X.; Obrist, D.; Hallar, G.; McCubbin, I.; Rahn, T. Speciated mercury measured at a high elevation research station, Colorado: In situ conversion and long range transport. *EOS Trans. AGU*, **2008**, 89(53), Fall Meeting Supplement, Abstract A53D-0323A.
- Sheu, G.; Lee, C.; Lin, N.; Wang, J.; Ouyang, C. Factors Controlling the Distribution of Atmospheric Mercury in the East Asian Free Troposphere. *EOS Trans. AGU*, **2008**, 89(53), Fall Meeting Supplement, Abstract A53D-031.
- Weiss-Penzias, P. S.; Gustin, M. S.; Lyman, S. N. Observations of speciated atmospheric mercury at three sites in Nevada, USA: evidence for a free tropospheric source of reactive gaseous mercury. *EOS Trans. AGU*, **2008**, 89(53), Fall Meeting Supplement, Abstract A53D-0307.
- Swartzendruber, P. C.; Chand, D.; Jaffe, D. A.; Smith, J.; Reidmiller, D.; Gratz, L.; Keeler, J.; Strode, S.; Jaegle, L.; Talbot, R. Vertical distribution of mercury, CO, ozone, and aerosol scattering coefficient in the Pacific Northwest during the spring 2006 INTEX-B campaign. *J. Geophys. Res.* **2008**, *113*, D10305, doi: 10.1029/2007JD009579.

- (11) Talbot, R.; Mao, H.; Scheuer, E.; Dibb, J.; Avery, M.; Browell, E.; Sachse, G.; Vay, S.; Blake, D.; Huey, G.; Fuelberg, H. Factors influencing the large-scale distribution of Hg⁰ in the Mexico City area and over the North Pacific. *Atmos. Chem. Phys.* **2008**, *8* (7), 2103–2114.
- (12) Banic, C. M.; Beauchamp, S. T.; Tordon, R. J.; Schroeder, W. H.; Steffen, A.; Anlauf, K. A.; Wong, H. K. T. Vertical distribution of gaseous elemental mercury in Canada. *J. Geophys. Res.* **2003**, *108* (D9), 4264, doi: 10.1029/2002JD002116.
- (13) Friedli, H. R.; Radke, L. F.; Prescott, R.; Li, P.; Woo, J.-H.; Carmichael, G. R. Mercury in the atmosphere around Japan, Korea, and China as observed during the 2001 ACE-Asia field campaign: Measurements, distributions, sources, and implications. *J. Geophys. Res.* **2004**, *109*, D19S25, doi: 10.1029/2003JD004244.
- (14) Ebinghaus, R.; Slemr, F. Aircraft measurements of atmospheric mercury over southern and eastern Germany. *Atmos. Environ.* **2000**, *34*, 895–903.
- (15) Radke, L. F.; Friedli, H. R.; Heikes, B. G. Atmospheric mercury over the NE Pacific during spring 2002: Gradients, residence time, upper troposphere lower stratosphere loss, and long-range transport. *J. Geophys. Res.* **2007**, *112*, D19305, doi: 10.1029/2005JD005828.
- (16) Slemr, F.; Ebinghaus, R.; Brenninkmeijer, C. A. M.; Hermann, M.; Kock, H. H.; Martinsson, B. G.; Schuck, T.; Sprung, D.; van Velthoven, P.; Zahn, A.; Ziereis, H. Gaseous mercury distribution in the upper troposphere and lower stratosphere observed onboard the CARIBIC passenger aircraft. *Atmos. Chem. Phys.* **2009**, *9*, 1957–1969.
- (17) Price, H. U.; Jaffe, D. A.; Doskey, P. V.; McKendry, I.; Anderson T. L. Vertical profiles of O₃, aerosols, CO and NMHCs in the Northeast Pacific During the Trace-P and ACE-Asia experiments. *J. Geophys. Res.* **2003**, *108*, D20, 8799, doi: 10.1029/2002JD002930.
- (18) Bertschi, I. B.; Jaffe, D. A.; Jaegle, L.; Price, H. U.; Dennison, J. B. PHOBEA/ITCT 2002 airborne observations of trans-Pacific transport of ozone, CO, VOCs, and aerosols to the northeast Pacific: Impacts of Asian anthropogenic and Siberian Boreal fire emissions. *J. Geophys. Res.* **2004**, *109*, D23S12, doi: 10.1029/2003JD00432.
- (19) Schroeder, W. H.; Keeler, G.; Kock, H.; Roussel, P.; Schneeberger, D.; Schaedlich, F. International field intercomparison of atmospheric mercury measurement methods. *Water, Air, Soil Pollut.* **1995**, *80*, 611–620.
- (20) Swartzendruber, P. C.; Jaffe, D. A.; Finley, B. Improved fluorescence peak integration in the Tekran 2537 with sub-optimal Hg mass loadings. *Atmos. Environ.* **2009**, *43*, 3648–3651, doi: 10.1016/j.atmosenv.2009.02.063.
- (21) Comparison of Gaseous Mercury Vapor Calibrations with NIST Traceable Liquid Standards. Technical memorandum. Tekran Instruments Corporation: Ontario, Canada, 2006; fshaedlich@tekran.com.
- (22) Landis, M. S.; Stevens, R. K.; Schaedlich, F.; Prestbo, E. M. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive mercury in the ambient air. *Environ. Sci. Technol.* **2002**, *36*, 3000–3009.
- (23) Murphy, D. M.; Hudson, P. K.; Thomson, D. S.; Sheridan, P. J.; Wilson, J. C. Observations of mercury containing aerosols. *Environ. Sci. Technol.* **2006**, *40*, 3163–3167, doi: 10.1021/es052385x.
- (24) Wilcox, R. R. *Introduction to Robust Estimation and Hypothesis Testing*, 2nd ed.; Elsevier Academic Press: Burlington, MA, 2005.

ES901390T