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Total depletion of Hg° in the upper troposphere–lower stratosphere

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[1] Our current understanding of atmospheric mercury lacks fundamental details. Gas phase elemental mercury (Hg°) was measured aboard the NASA DC-8 research aircraft during the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) conducted in spring 2006 over the North Pacific. Our data confirm efficient chemical cycling of Hg° in the tropopause region and show that it is strongly anti-correlated with O_3 there, yielding a tropospheric-stratospheric mixing curve of ~ -0.20 ppqv $\text{Hg}^\circ/\text{ppbv } \text{O}_3$. In addition, we found frequent total depletion of Hg° in upper tropospheric (8–12 km) air masses impacted by stratospheric influence. When O_3 mixing ratios were >300 ppbv, Hg° was rarely detected. It appears that in the tropopause and stratosphere Hg° is oxidized on the order of days followed by heterogeneous transformation to particulate mercury. These processes constitute an effective chemical sink for Hg° at the top of the troposphere, which may recycle mercury back to the gas phase as stratospheric aerosols are eventually dispersed into the troposphere. **Citation:** Talbot, R., H. Mao, E. Scheuer, J. Dibb, and M. Avery (2007), Total depletion of Hg° in the upper troposphere–lower stratosphere, *Geophys. Res. Lett.*, 34, L23804, doi:10.1029/2007GL031366.

1. Introduction

[2] Mercury is a serious environmental toxin that is distributed globally by large-scale atmospheric circulations. In the atmosphere mercury exists in diverse chemical forms that are comprised of gaseous elemental mercury (Hg°), reactive gaseous mercury (RGM = $\text{HgCl}_2 + \text{HgBr}_2 + \text{HgOBr} + \dots$), and particulate-phase mercury (Hg^{P}). Near the Earth's surface Hg° is observed ubiquitously with contemporary mixing ratios at the several hundred ppqv level, with RGM and Hg^{P} comprising only a few percent of the total mercury [Schroeder and Munthe, 1998].

[3] Many aspects of mercury chemical cycling in the atmosphere are essentially unknown, especially in the upper troposphere and lower stratosphere which until this work was devoid of comprehensive in situ gas-phase mercury measurements. Recent simulations with the GEOS-Chem global chemical transport model suggest that RGM should become an increasingly important form of mercury in the stratosphere [Selin *et al.*, 2007]. Nighttime downslope measurements on Mount Bachelor, Oregon indicate that the free troposphere has higher mixing ratios of RGM than observed in near surface air where it deposits rapidly

[Swartzendruber *et al.*, 2006]. However, in situ measurements of aerosols in the lower few kilometers of the stratosphere using laser mass spectrometry indicate significant enrichment of Hg^{P} compared to the troposphere [Murphy *et al.*, 1998, 2006].

[4] Together these results emphasize the point that sources and sinks of atmospheric mercury are poorly characterized and quantified. The majority of tropospheric Hg° measurements have been conducted at ground-level, and show mixing ratios varying over a range of 100–600 ppqv ($\sim 1\text{--}5 \text{ ng m}^{-3}$) [Valente *et al.*, 2007]. Information on the vertical distribution of Hg° is very limited, and has been obtained in situ from research aircraft primarily below 8 km [Ebinghaus and Slemr, 2000; Banic *et al.*, 2003; Friedli *et al.*, 2004; Radke *et al.*, 2007]. Samples for mercury analysis were collected at 6–12 km altitude over southern France and the North Sea during the late 1970's and yielded 250 ± 57 ppqv of Hg° [Slemr *et al.*, 1985]. In situ measurements were reported recently for one flight at ~ 10 km altitude from Frankfurt, Germany to São Paulo, Brazil [Ebinghaus *et al.*, 2007]. These studies produced differing results, ranging from tropospheric Hg° being well mixed to decreasing or increasing monotonically with altitude.

[5] Global chemical transport models can reproduce observed Hg° mixing ratios at the surface, especially over the continents [Lin *et al.*, 2006; Seigneur *et al.*, 2004, 2006; Selin *et al.*, 2007]. However, great uncertainty exists in these simulations due to incomplete understanding of mercury chemistry and the absence of simultaneous in situ measurements of Hg° , RGM, and Hg^{P} in the middle-to-upper troposphere. We conducted in situ measurements of Hg° from 0.15 to 12 km altitude over the central and north Pacific basins during the INTEX-B airborne campaign. These data provided a rare opportunity to explore the three dimensional distribution of Hg° in the troposphere, and validate our current understanding of mercury that is applied in regional to global models.

2. Measurements

[6] The INTEX-B flight series conducted in spring 2006 was composed of two NASA DC-8 aircraft deployments, with the first based out of Houston, Texas, and the second half split between Honolulu, Hawaii and Anchorage, Alaska. The DC-8 was housed at Moffett Field, California (NASA Ames Research Center) for a three week period between the two components. Flight durations were 8–10 hours, covered 0.15–12.5 km altitude, and incorporated constant altitude legs connected to spiral ascents and descents. The flight legs of interest here were flown at constant altitude above 10 km and latitudes covering 34° to 57°N .

[7] We flew a modified Tekran 2537A cold vapor atomic fluorescence spectrometer aboard the DC-8 to measure mixing ratios of Hg° with 150 s time response and limit

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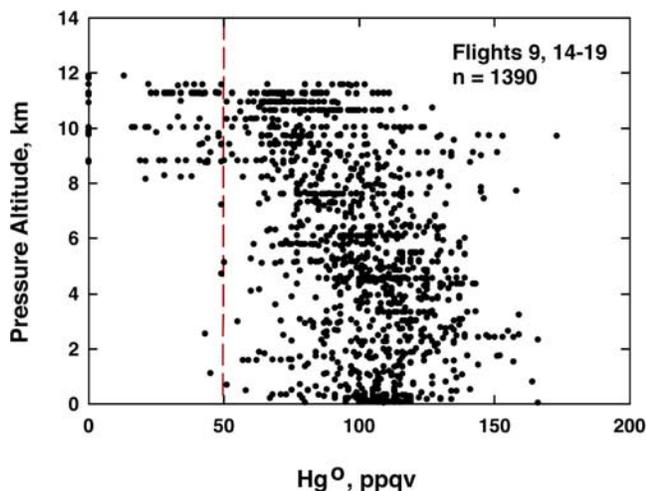


Figure 1. Vertical distribution of Hg⁰ over the North Pacific showing depletion (red line indicates ≤ 50 ppqv) above 8 km altitude.

of detection of ~ 10 ppqv [Talbot *et al.*, 2007]. The internal pressure of the instrument was maintained at a slight overpressure to sea level during the analysis stage using upstream control set to 1100 mbar. Standard addition calibrations were conducted on ambient air using an internal Hg⁰ permeation source. On non-flight days these calibrations were conducted on the ground and then on every science flight at altitudes ranging from 1–12 km. Together they yielded a reproducibility in the Hg⁰ permeation rate of 0.098 ± 0.009 ng min⁻¹ (9.2% for $n = 312$). Instrument calibration was verified using injections from the headspace of a thermoelectrically cooled Hg⁰ reservoir (Tekran model 2505). The inlet arrangement utilized our existing forward facing high ram flow manifold (1,500 standard liters per minute) for HNO₃ [Talbot *et al.*, 1999]. It is designed with a diffuser to boost the internal inlet pressure by up to 150 mbar over ambient to facilitate attaining high flow rates in the upper troposphere, especially when the DC-8 is cruising at Mach 0.88 [Talbot *et al.*, 2003]. For the Hg⁰ measurements the high flow air stream was sub-sampled through a heated (40°C) PFA Teflon line just a few cm after the flow entered the main 10 cm diameter manifold. The response factor, peak area counts pg⁻¹ Hg⁰, was found to be constant to $\pm 1\%$ for the entire data set. The average response factor for each channel (i.e., 7170 and 7325 counts pg⁻¹) was used in the preparation of the final data to provide an internally consistent data product.

[8] Ozone (O₃) was measured using the chemiluminescent reaction with pure nitric oxide yielding < 1 s response time, an accuracy of 5% (2 ppbv), and a precision of 2% (0.8 ppbv). The instrument was calibrated by reference to a U.S. National Institute of Standards and Technology standard ozone photometer [Gregory *et al.*, 1987]. The O₃ data were averaged to the 150 s Hg⁰ time base.

3. Evidence of Hg⁰ Depletion

[9] The vertical distribution of Hg⁰ during flights 9 and 14–19 is shown in Figure 1. Flights 9 and 14 were high altitude transit flights, while 15–19 were science missions

conducted out of Anchorage, Alaska. The pooled flight data from over the North Pacific depict a vertical profile centered around 100 ppqv with plumes of elevated Hg⁰ (> 150 ppqv) originating from the Asian continent [Talbot *et al.*, 2007]. Occasionally the aircraft encountered tropopause folding events where tropospheric air was influenced to varying degrees by stratospheric air. In these regions, dry stratospheric air rich in O₃ was transported down to tropospheric levels [Danielsen, 1968], and sampled by the DC-8. The vertical profile over the North Pacific showed depletion of Hg⁰ above 8 km altitude during folding events, with decreased mixing ratios of Hg⁰ occurring when O₃ exceeded 150 ppbv (Figure 2). Here, we define depleted Hg⁰ as mixing ratios < 50 ppqv, the minimum observed in the lower troposphere (Figure 1). These data show that Hg⁰ is strongly anti-correlated with O₃ in the tropopause region and rarely detected when O₃ > 300 ppbv (Figure 2). Our interpretation is that when O₃ exceeds 300 ppbv, tropospheric Hg⁰ has been in stratospheric air long enough to cause its total depletion.

[10] Total depletion of Hg⁰ was observed at latitudes of 34–57°N during flights 9, 14, 16, 17, 18, and 19. Two examples of this phenomenon are presented in Figure 3. Shown in the upper panel is data from flight 9, the transit from Houston to Moffett Field, with the last two constant altitude segments flown at 11.3 and 11.6 km. As the DC-8 ascended from 7.6 km stratospherically influenced air was encountered around 11 km with O₃ exceeding 200 ppbv. Immediately Hg⁰ decreased to zero ppqv, and then exhibited a “see-saw” pattern in its mixing ratio as O₃ fluctuated above and below 250 ppbv. Earlier in the flight O₃ > 100 ppbv was encountered at 9.5–9.8 km during the initial climb out, and a few hours later at 11.3 km. Both of these periods showed a striking anti-correlation between Hg⁰ and O₃. This is also visible in the lower panel depicting flight 14 as the DC-8 leveled off at 11.3 km (i.e., at $\sim 35,000$ s). In fact, every flight listed above showed this same “see-saw” pattern. This repeated behavior demonstrates that Hg⁰ is a very sensitive tracer of stratospheric air embedded in the troposphere.

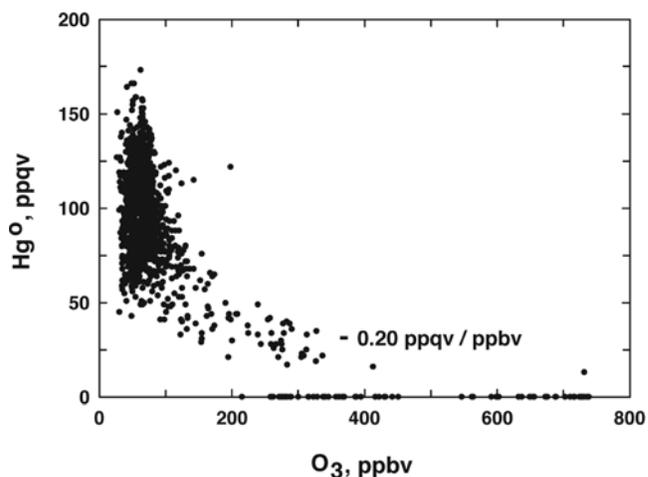


Figure 2. Mixing ratios of Hg⁰ as a function of O₃, showing removal of Hg⁰ as O₃ increases above ~ 150 ppbv. The slope was determined from a linear fit of the data for O₃ > 100 ppbv but not including Hg⁰ = 0 ppqv.

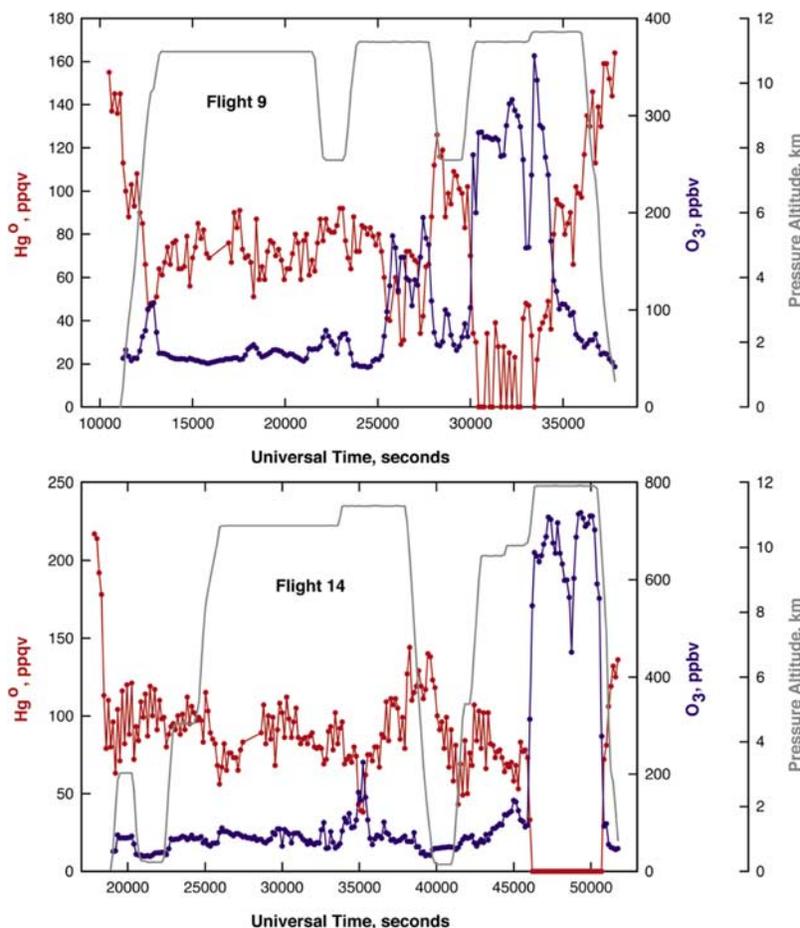


Figure 3. Time series of Hg⁰ and O₃ mixing ratios during flights 9 and 14.

[11] Flight 14 was the transit from Honolulu to Anchorage where the strongest stratospheric influence was observed during INTEX-B with O₃ mixing ratios approaching 1 ppmv. The differential absorption lidar (DIAL) system for O₃ onboard the DC-8 showed that the tropopause was around 8.5 km while in situ sampling was conducted at 11.9 km, well into the lower stratosphere [Talbot *et al.*, 2007]. Indeed, ⁷Be concentrations approached 15,000 fCi m⁻³ during this flight segment, a level indicative of stratospheric air. During this entire level flight leg the mixing ratio of Hg⁰ was essentially zero ppqv. We present this as robust evidence for total depletion of Hg⁰ in the stratosphere.

[12] We checked for an O₃ artifact in the Hg⁰ measurements during a test flight flown out of Grand Forks, North Dakota on February 23, 2006. During this flight the DC-8 flew in the stratosphere twice at 10.1 and 11.9 km. Standard additions were conducted at both altitudes with quantitative recovery and response factors within 0.5% of our average values reported here. Secondly, when the instrument was returned to our lab after the INTEX-B deployment standard additions into zero air were conducted with O₃ added at 300 and 500 ppbv. Again, no change in the instrument response was observed. These tests provide strong evidence that our measurements of essentially zero ppqv of Hg⁰ in stratospherically influenced air are highly reliable.

[13] A negative correlation between Hg⁰ and O₃ was also noted in stratospherically influenced air at 6–8 km altitude

during two flights along coastal California, Oregon, and Washington in spring 2002 during the Intercontinental Transport and Chemical Transformation Experiment-2002 [Radke *et al.*, 2007]. On two flights they observed significantly depleted Hg⁰ with coincident O₃ mixing ratios of up to 300 ppbv. Furthermore, they estimated that [Hg⁰] = 0 when O₃ = 333 ppbv, in harmony with our results. One notable difference was that total depletion of Hg⁰ was not observed; their lowest values were ~0.25 ng Hg⁰ m⁻³ (~30 ppqv).

[14] The large-scale spatial distribution of depleted Hg⁰ (<50 ppqv) in the upper troposphere (>8 km) is presented in Figure 4a together with O₃ > 150 ppbv in Figure 4b. The close correspondence between elevated O₃ and depleted Hg⁰ mixing ratios is clearly evident. In general, our high altitude sampling could only reach areas of tropopause folding or the lower stratosphere on the most northerly flight tracks. The proximity of these flights to the jet stream and associated tropopause folding was undoubtedly crucial for our sampling of stratospherically influenced Hg⁰ depleted air masses. The DIAL O₃ measurements over the Mexico City area revealed a tropopause height in the 12–13 km range, just above the altitude ceiling of the DC-8 [Talbot *et al.*, 2007]. Our measurements indicate that Hg⁰ depletion in the stratosphere is likely a global phenomenon.

[15] Previous in situ measurements of aerosols in the tropopause region indicate orders of magnitude enrichment

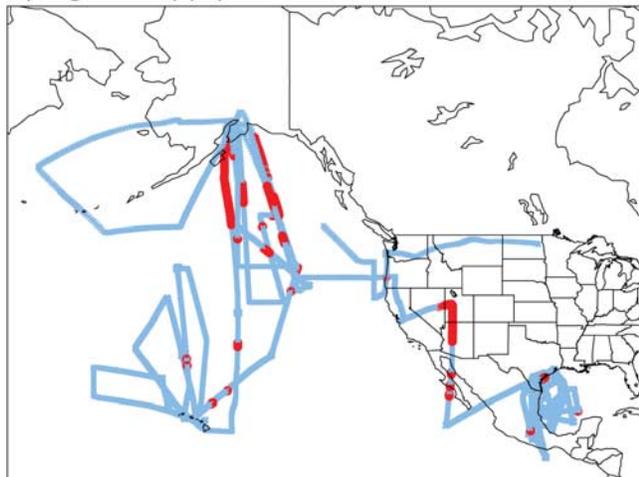
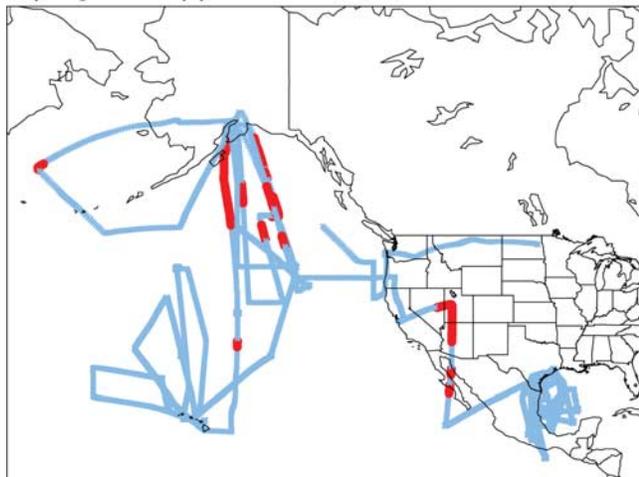
a) Hg⁰ <50 ppqvb) O₃ >150 ppbv

Figure 4. Spatial distribution of Hg⁰ depletion (<50 ppqv) during the INTEX-B flight series. Note that, as shown in Figure 3, Hg⁰ depletion occurs when O₃ exceeds 150 ppbv.

of Hg^P compared to the troposphere [Murphy *et al.*, 1998], and speculation of heterogeneous loss of Hg⁰ [Murphy *et al.*, 2006]. Our results combined with those of Murphy *et al.* [2006] suggest very active and rapid mercury chemistry occurs in the tropopause and lower stratosphere, which likely transforms Hg⁰ into a variety of reactive mercury species followed by quick uptake on aerosols. Although the loss mechanism is uncertain, it is likely due to oxidation by ppmv mixing ratios of stratospheric O₃ and halogen species such as atomic bromine (Br) [Holmes *et al.*, 2006] which is suspected to cause depletion of Hg⁰ in the springtime Arctic surface layer [Schroeder *et al.*, 1998]. Using 1 ppmv O₃ and 1 pptv Br in the lower stratosphere [Salawitch *et al.*, 2005], and temperature compensated reaction rate constants [Goodsite *et al.*, 2004; Pal and Ariya, 2004], a lifetime of 2 and 0.5 days for Hg⁰ (100 ppqv) was estimated for oxidation by O₃ and Br respectively. There are many other potential reactions, mainly with halogen compounds, which could be involved in the oxidation process and conversion to Hg^P. Until more complete reaction kinetic data is avail-

able for Hg⁰, it is difficult to pinpoint the key reactants involved in the depletion.

4. Implications

[16] The heterogeneous processes occurring in the tropopause region constitute an effective chemical sink for Hg⁰ at the top of the troposphere. At this time we are uncertain if our inlet arrangement quantitatively passes RGM [Talbot *et al.*, 2007]. Thus, future measurements are needed to determine if stratospheric depletion also includes RGM. In the tropopause/lower stratospheric regions we observed typically 100–150 pptv of aerosol sulfate, which should provide for ample uptake of mercury even though the surface area was too low to be quantified by the differential mobility analyzer and forward scattering spectrometer probe instrumentation aboard the DC-8. This oxidized mercury may return to the gas phase as the stratospheric aerosols are transported downward through the troposphere. The Murphy *et al.* [1998] data show that Hg^P is barely detectable in the troposphere and our data show no obvious indication of a middle-to-upper tropospheric Hg⁰ source from re-volatilization. These lines of evidence indicate that if Hg^P does return to the gas phase in the troposphere, it is a slow process that adds to the background Hg⁰ and varies in magnitude with the seasonal occurrence of tropopause-folding events. The rate limiting step appears to be transport of Hg^P into the troposphere. Clearly, simultaneous measurements of Hg⁰, RGM, and Hg^P are required to better understand the troposphere-stratosphere-troposphere cycling process of atmospheric mercury. Hg⁰ and RGM are removed from near surface air by dry deposition with potential re-emission to the gas phase; a process analogous to this may be operating in the upper troposphere. Dynamic cycling of mercury in the troposphere is a formidable new challenge for inclusion in global chemical transport models.

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