Vertical Distribution of Gaseous Elemental Mercury Over the Pacific Northwest in the Spring of 2006

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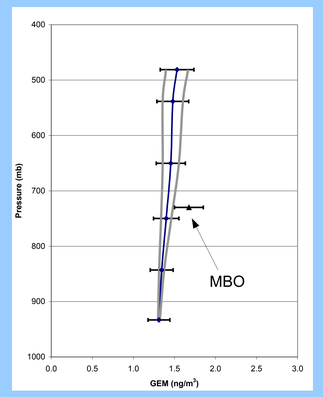
ABSTRACT In the spring of 2006, we measured the vertical distribution (up to 6km) of Gaseous Elemental Mercury (GEM), CO, ozone, and aerosol scatter over the Pacific Northwest. Flights dates were selected when the modeled CO values suggested long-range transport of Asian emissions to the Northwest. We observed a nearly constant vertical profile of GEM (~1.4 ng/m3) above the boundary layer along with several well correlated enhancements of GEM and CO above the mean profile. A composite of the enhancement values of the three largest events had a GEM-CO correlation slope of (0.0063 ng/m^3/ppbv CO) which agreed with previous observations of the Asian industrial plume. Kinematic back trajectories support eastern Asia as the source region for the observed GEM-CO enhancement. Local anthropogenic emissions were observed to have a statistically insignificant GEM-CO correlation. Several episodes of GEM depletion at higher altitudes were observed which had a similar signature to reactive gaseous mercury (RGM) enhancement events observed at Mt. Bachelor. This implies we observed > 100 pg/m^3 RGM. The concentrations of GEM were generally lower below 700 mb than above. This suggests a rapid loss of GEM either in-situ with anthropogenic pollution, or prior to mixing.

Mean Vertical Profile

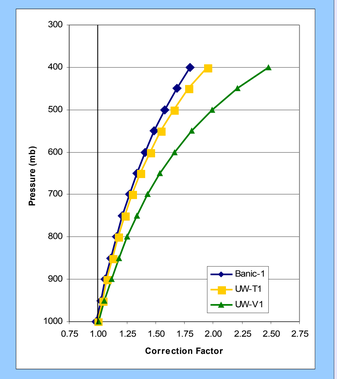
The mean vertical profile of GEM for the spring of 2006 is shown to the right. The gray lines indicate the 95% confidence interval about the mean due to the pressure correction factor. The error bars indicate the total uncertainty. Also plotted is the mean and total uncertainty of the Mt. Bachelor observations of GEM from Apr-May 2006.

Below about 700mb the mean mercury concentrations appear to be lower with many trajectories suggesting recent anthropogenic and/ or marine influence. Analysis of the behavior in the lower free-troposphere is still ongoing.



Pressure Correction Method (Right)

GEM was quantified with a Tekran 2537A at ambient pressure. The sensitivity of the 2537A is dependent on the ambient (vent) pressure because of the fluorescence cell residence time and fluorescence broadening and quenching. A sensitivity correction factor was determined in the laboratory by controlling the cell vent pressure and performing permeation source calibrations. A non-linear correction factor was obtained that was in good agreement with that reported by Banic et al. (2003). The correction factor used is shown at right (UW-T1) with a Banic et al. (2003) factor, and a factor based solely on fluorescence cell residence time (UW-V1). The difference between these curves is evidence of an increase in sensitivity at lower pressure due to reduced pressure broadening and/or quenching.



Background

The control of the oxidation of mercury above the boundary layer remains one of the most salient areas of uncertainty in its global cycle. Also, long-range transport (LRT) is the most important input source for most remote regions and makes a significant contribution to local deposition in most other regions. Therefore, understanding the free-tropospheric chemistry is crucial for understanding and predicting local deposition.

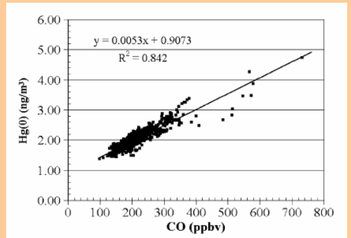
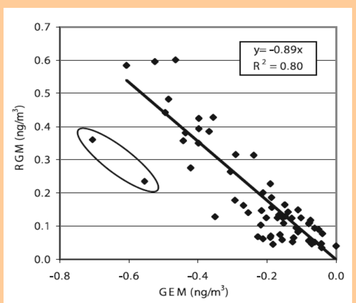


Fig. 2. Scatterplot of Hg^0 vs. CO for all Okinawa data.



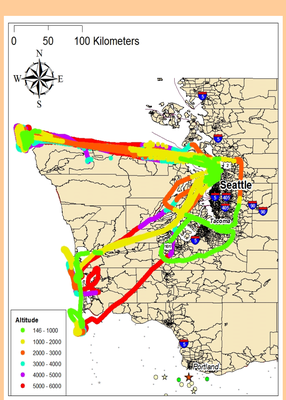
This airplane work continues our mercury work which has had several important findings: Jaffe et al. (2005) describe observations of Asian outflow to Okinawa, JP and LRT to Mt. Bachelor (MBO) and showed the GEM-CO ratio (**Above**) was a good marker of the Asian industrial plume. These findings were later confirmed by Weiss-Penzias et al. (2006).

Swartzendruber et al. (2006) describe observations of mercury speciation in the free-troposphere at MBO and report strong interconversion of species (**Left**) that could not be explained by currently modeled chemistry.

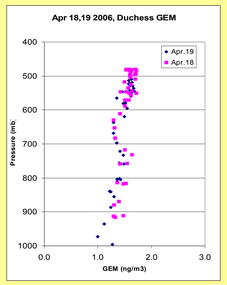
Experimental

We used a Beechcraft Duchess (ceiling 20k ft) to conduct 8 flights in Western Washington between Apr 12 and May 9. We measured:

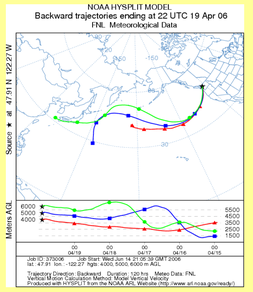
- ozone (Dasibi 3-B)
- aerosol scatter (3-λ)
- gaseous elemental mercury (Tekran 2537A)
- CO
- temperature, RH, GPS



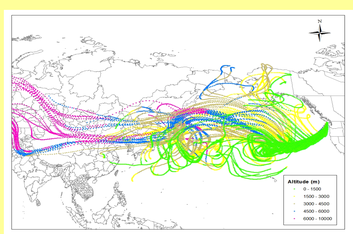
Asian Long-Range Transport (ALRT)

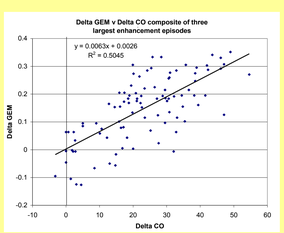


Enhancement events on April 18,19. (**Left**) The GEM profile was observed on consecutive days and demonstrated excellent precision in capturing a well correlated GEM-CO enhancement (above 600 mb). A set of back trajectories from Apr 19 is shown **right**.



3-D kinematic back trajectories were calculated using NOAA's HYSPLIT model. Trajectories support industrial east Asia as a major source region for the higher altitude air masses
Below Left shows back trajectories started along the entire profile for the Apr 12 flight.
Below Right shows a composite of the ΔGEM vs. ΔCO values for the three largest events (Apr 12, 18, May8).





Conclusions

- Asian Long-Range Transport (ALRT) was clearly identified with GEM-CO ratio (0.0063 ng/m3/ppbv CO) in good agreement with previous studies
- Local anthropogenic signature was distinctly different than ALRT with an insignificant GEM enhancement and insignificant GEM-CO correlation
- GEM depletion at altitude shows similar signature to MBO-RGM rich air which suggests we encountered several small episodes of RGM > 100 pg/m3.

References

Jaffe, D. et al. (2005), *Atmos. Environ.*, 39, 3029 – 3038, doi:10.1016/j.atmosenv.2005.01.30.

Swartzendruber, P. C., et al. (2006), *J. Geophys. Res.*, 111 , D24301, doi:10.1029/2006JD007415.

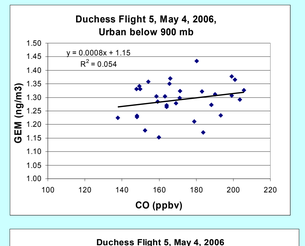
Peter Weiss; Daniel A Jaffe; Phil C Swartzendruber; William Hafner; Duli Chand; Eric Prestbo, Quantifying Asian and biomass burning sources of mercury using the Hg/CO ratio in pollution plumes observed at the Mount Bachelor Observatory, *Atmos. Environ.* In-Press, 2007.

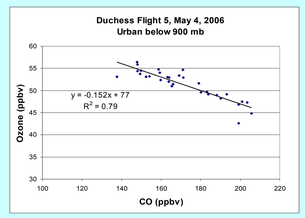
Banic, C. M., *J. Geophys. Res.*, 108(D9), 4264, doi:10.1029/2002JD002116, 2003.

Local Flight Contrast to LRT

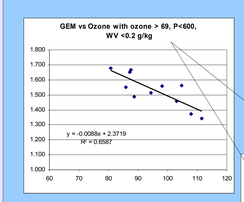
A local flight in the boundary layer around the Seattle Tacoma area showed no significant GEM enhancement and a statistically insignificant GEM-CO correlation. The industrial urban signature can be seen in the strong correlation of CO and scatter with water vapor along with an inverse correlation with ozone suggesting Nox titration of ozone. Note that even if the GEM-CO correlation was significant, it would still be an order of magnitude smaller than the Asian GEM-CO ratio.

	GEM	*CO*	*Ozone*	*TSG*
CO	0.23	1		
Ozone	-0.25	**-0.89**	1	
TSG	0.09	**0.76**	**-0.64**	1
H20	-0.02	**0.71**	**-0.72**	**0.73**

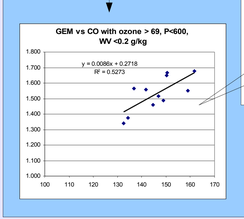




GEM Depletion with Upper Tropospheric/Stratospheric RGM signature?



Duchess Data



Several flights encountered short episodes of GEM depletion which had a chemical signature that was very similar to that observed at MBO in the summer of 2005 (Swartzendruber et al.(2006)). This suggests we sampled RGM > 100 pg/m3 in the free-troposphere.

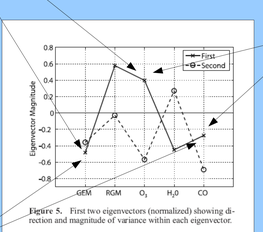
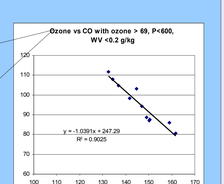


Figure 5. First two eigenvectors (normalized) showing direction and magnitude of variance within each eigenvector.



Duchess Data

The correlations of the aircraft data mirror the 'factor loadings' from the first principal component in the MBO-RGM rich air. GEM and ozone, CO and ozone are negatively correlated, while GEM and CO are positively correlated.