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Atmospheric Measurement Techniques Discussions

Interactive comment on "Atmospheric mercury measurements onboard the CARIBIC passenger aircraft" *by* F. Slemr et al.

F. Slemr et al.

franz.slemr@mpic.de

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We thank Anthony Hynes for his thoughtful review and would like to respond as follows:

The authors state: P.4 line 17 "The arrangement similar to that described by Talbot et al. (2008) was optimized to transmit highly sticky HNO3 (Neumann et al., 1999) and can thus be presumed to pass sticky GOM as well."

Later: p.7 line 13.: "Talbot et al. (2008) tentatively ascribe their measurements made with a similar inlet system and the Tekran instrument to elemental mercury only. They believe that their inlet system which transmits very sticky HNO3 will also transmit GOM. But they are not sure about the response of Tekran instrument to GOM."

I would suggest it is unwise to presume anything about the behavior of RGM. In fact

Talbot et al. (2008) in "Implications " note: "At this time we are uncertain if our inlet arrangement quantitatively passes RGM [Talbot et al., 2007]." I don't find anything about the Tekran response. I don't believe that anyone in the mercury community suggests that if RGM gets to the Tekran gold trap it will not be captured, dissociate and be measured as Hg(0). The issue is transmission through the plumbing.

I would suggest that assessment of RGM transmission losses is the dominant issue in the mercury community and I disagree with the final statement in this paragraph. "Pyrolyzing of mercury compounds to GEM used by some researchers (e.g. Ambrose et al., 2013, 2015) is thus not necessary to measure GEM + GOM but helps to avoid GOM losses on the way from the pyrolyzer to the gold traps within the instrument."

I would suggest that that pyrolysis is essential to ensure quantitative measurement of total mercury. I think the consensus view is that PFA tubing will scavenge RGM. Unfortunately this is difficult to quantify and varies with sampling conditions and perhaps even with different samples of tubing.:

The comments of both reviewers point out that the transmission of GOM through PFA tubing is an unresolved issue and that it is unwise to make any assumptions about it. In the modified text we confine ourselves to the interpretation of our data. Text with assumptions about GOM transmission through the PFA tubing has been deleted as has been the whole paragraph starting with "Talbot et al. (2008).." about the Tekran response and pyrolysis.

This discussion about transmission continues in the later part of the paper with authors citing Temme et al (2003) (this citation is not actually listed in the references.) P. 15 line 5. "Our findings are consistent with Temme et al. (2003) who found that GOM is transmitted quantitatively by PFA tubing at low temperatures and humidities encountered in Antarctica, conditions similar to those encountered during the CARIBIC flights at cruise altitude." My reading of Temme et al. suggests that they made measurements with a Tekran 2537 sampling ambient air with no "pretreatment" and speciated Hg us-

ing a Tekran speciation system and got good mass balance. They inferred that the Tekran was measuring total mercury i.e. that oxidized mercury was efficiently transmitted through the sampling plumbing under their sampling conditions.

Landis and Stevens (2003) in a comment on Temme et al. noted that: “Our laboratory experiments indicate that RGM is not quantitatively transported through a heated Teflon sampling line. In fact, after running elevated HgCl2 concentrations through a Tekran 2537A at low humidity, we extracted the Teflon tubing from both the sampling line and the internal instrument components and found significant quantities of mercury. In addition, after exposure to elevated HgCl2 concentrations, the instrument (i) had elevated zero air concentrations; (ii) gave false positive responses to mercury free zero air injected with O3, elevated humidity, or elevated temperature; and (iii) had significantly elevated baseline standard deviations. The adsorption/desorption behavior of HgCl2 in the inlet line and internal analyzer components varied depending on the exact variables that scientists are using to elucidate atmospheric mercury chemistry (e.g., oxidation potential, meteorological conditions). We strongly recommend that researchers avoid allowing RGM species into the Tekran 2537A instrument by incorporating a Tekran model 1130 gas-phase speciation unit and/or a soda and lime trap into the inlet system.”

Unfortunately, “elevated concentrations” is not quantified in this comment. I can accept that fast flow through a large internal diameter tubing in the CARIBIC inlet has high RGM transmission but that still leaves the concern expressed by Landis and Stevens about the Tekran itself. The issue is not simply that the Tekran will scavenge RGM but that also that RGM deposited on the tubing can be reduced to elemental mercury at a later point in time. If the Tekran is sampling 0.3 ng m-3 of RGM during some sections of stratospheric flights, is deposition in the Tekran or the sample line that connects it to the manifold a problem?

I can only state that my view of this is biased by experience in my own laboratory where we find the both HgCl2 and HgBr2 are efficiently, but highly variably, scavenged by PFA

tubing.

The irreproducible and conflicting results on HgCl2 and HgBr2 transmission through the PFA tubing and in the Tekran instrument only underline the statement by P. Swartzendruber that this is an unresolved issue. It is clear that the ambient conditions play a role, among some other factors. Thus we do not find anything wrong in our statement that that our findings are consistent with those of Temme et al. (2003) and Lyman and Jaffe (2011). We do not generalize our findings in the revised manuscript and point this out. The reference list has been corrected.

The section of the manuscript on “Aerosol collection and mercury analysis by PIXE” is a little confusing to me. The statement (referring to Murphy et al. 2006) “Based on assumptions about the Hg ionization efficiency of their Particle Analysis by Laser Mass Spectrometry (PALMS) instrument, which was not calibrated, they estimate that PM constitutes 5 – 100% of all mercury in the LS.”

My reading of Murphy et al. is that they calculated a surface mixing ratio of 1.7pptm (parts per trillion by mass) based on a concentration of 2 ng m-3. Assuming this is conserved at the tropopause they calculate a total aerosol loading of 1200 pptm hence if all mercury was particulate bound it would constitute âĹij0.1% by mass, or they estimate 0.05% by mole. Mercury constituted âĹij0.2% of the ion current which is difficult to rationalize given its high ionization potential and leads to the conclusion that almost all mercury is oxidized and condensed onto particles, since elemental mercury would not condense at these temperatures. Since their estimate of 2 ng m-3 would now be accepted as too high it gets even more difficult to rationalize their results. Murphy et al. suggest that if the ionization of mercury was as efficient as sodium the fraction of mercury that is particulate bound could be between 5-30% but the ionization potential of sodium is half of that for mercury so in fact it needs to be much higher.

We are no experts on PALMS technique and our text is thus based on the personal correspondence with Daniel Murphy. They did not calibrate the PALMS sensitivity towards

mercury because of regulation on work with toxic substances.

The failure to observe PBM with the PIXE detector seems consistent with the suggestion of Murphy et al. and the author's explanation 2. i.e. that the oxidized mercury evaporates as the temperature increases. If this is the case shouldn't the CARIBIC sampling measure higher concentrations in the lower stratosphere. The authors report 0.3 ng m-3 for TGM in the lower stratosphere but shouldn't this be at least 0.7 ng m-3 (based on their statement that TGM is âĹij 1 ng m-3) even if all mercury is particulate bound, they capture 70% in their inlet and this 70% then evaporates?

The reviewer′s comment on the expected concentrations is based on the assumption of constant total mercury mixing ratio with increasing altitude above the tropopause. Our measurements and those of Lyman and Jaffe (2012) show that total mercury concentrations decrease with increasing altitude above the tropopause. The gradients observed by us are less steep than those predicted by Lyman and Jaffe (2012). We believe that the observed gradients result from a downward mercury transport using sulphur particles as a vehicle. Their downward flux is given by upward fluxes of COS and SO2.

Even given these discrepancies, if they are discrepancies, I find that one of the more fascinating observations is the variation in inferred RGM in flight #269 which points to significant inhomogeneity in the species responsible for Hg oxidation (Br atoms?). The original manuscript included a figure for this flight that I suggest should be reinserted. Later they state "In the troposphere at O3 < 100 ppb GEM and TGM concentration tend to be comparable whereas TGM concentrations tend to be larger than GEM at O3 > 200 ppb, i.e. in the stratosphere." However on #269 original figure the ozone mixing ratio seems to vary between 500-600 ppb and I cannot see a correlation between high and low RGM.

The overview of the flight #269 has been reinserted. As mentioned in its caption, uncorrected data are presented because many of the mercury loads were below 1

pg, outside of the range of the correction function. Because of the large uncertainty in TGM and even larger in GOM (difference between TGM and GEM) the data can be discussed only in qualitative terms. The scatter of both off-line processed TGM and GEM data in Fig.5 for the O3 range of 250 -350 ppb combined with substantially larger uncertainty of the unprocessed data would mask any GOM vs O3 function at O3 between 500 and 600 ppb.

A minor editorial point P.8 line 23 I would suggest stating "potential vorticity" rather than just PV and perhaps giving rough numbers i.e. PV less than 2 is characteristic of tropospheric air.

Done

Finally I would again congratulate the authors on their achievement with this project and ask if this corrected mercury data set and the ancillary observations are available for distribution?

CARIBIC mercury and the corresponding ancillary data are available on request from the CARIBIC coordinator Andreas Zahn (andreas.zahn@kit.edu). In fact, several researcher groups are already working with the data.

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