Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2015-376-AC2, 2016

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

Received and published: 6 April 2016

We thank Phil Swartzendruber for his thoughtful review and would like to respond as follows:

The only major comment I have is that the article follows the current convention in mercury research, which I think is incorrect, in describing the non-GEM mercury as "species" and the process as "speciation." Ultimately, we may end up learning that all the GOM in the atmosphere is a single species, so when we are operationally separating the fractions, we are fortuitously also doing "speciation", but we are not there yet. Please see the IUPAC definitions of "fractionation" vs "chemical species". fractionation: http://goldbook.iupac.org/FT06825.html chemical species: http://goldbook.iupac.org/CT01038.html Until we have truly speciated GOM, I think it is

inappropriate to presume that one system – which is really just a fractionation system – represents other systems in other environments or that they are even observing the same chemical compound(s).

We agree that the current convention of mercury community on using the term "speciation" is incorrect because the "speciation" methods now in use are not designed to detect and quantify the individual chemical compounds, i.e. species. We agree also that "fractionation" is the better term to describe the techniques used by us and are using this term in the revised text.

Page 4, middle paragraph: PFA tubing is presumed to quantitatively pass sticky GOM as well. This is a common assumption, but there are observations to the contrary and I don't think it well understood why this is the case. I think the author should note that this is not well understood and others have observed this. Some factors that may be affecting this are absolute or relative humidity, temperature, the sampling history/previously deposited gases on the surface, the flow regime laminar/turbulent, and where the subsampling inlet is located within the bulk inlet. E.g. in the development of the sampling system for the Mt Bachelor observations (Swartzendruber et al., 2006, and others), I found only about 80% transmission of HgCl2 through a Teflon coated, heated inlet, about 1 m in length and with a 3" diameter and Reynolds number < 1800 (so laminar flow should develop and not all molecules will interact with the wall before reaching the 1130/5 inlet). Note, this is not described in Swartzendruber 2006 article, but is in the dissertation: The distribution and speciation of mercury in the free troposphere of the Pacific Northwest, by Swartzendruber, Philip C., Ph.D., UNIVERSITY OF WASHINGTON, 2009, 182 pages; 3356667.

We agree that GOM transmission by PFA tubing is an unresolved issue (see also the comments by A. Hynes) and that there is not much which can be assumed for. In the revised text we deleted any reference to related assumptions. The thesis of Swartzendruber has been inserted into the reference list.

Page 5, line 7-9: “Mercury is detected. . . which only responds to gaseous elemental mercury. . .” In the context of the previous sentence (after describing desorption), I think this is a bit misleading or inaccurate. The detection is due to resonance fluorescence of GEM in an inert (non-quenching) carrier gas. CVAFS refers to the combined process of preconcentration/amalgamation, desorption, and resonance fluorescence detection. I suggest changing this sentence to “Mercury is detected by resonance fluorescence, which when used in a CVAFS system, only responds to gaseous elemental mercury (GEM)."

We disagree with the reviewer on this point for two reasons: First we use the term “CVAFS” only for a detector, as opposite to graphite cell high temperature AAS and AFS analysers for other elements. Our notion of CVAFS thus does not include the preconcentration. Secondly, the modification of the sentence proposed by the reviewer would imply that RGM species captured by gold surfaces are thermodesorbed as such and not detected by the AFS detector. This is in disagreement with statement by the second reviewer that “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, dissociated and measured as Hg(0).” The opinion of A. Hynes is also our opinion.

Page 5, line 16-19: “Lyman and Jaffe (2012). . .” See also my comment about GOM and speciation/fractionation. Reporting the Lyman and Jaffe claim is appropriate, and I think it fine to conduct your study under this assumption. But this claim deserves significantly more critical discussion. It is an unsupportable over-generalization that one group’s observation represents a complete and universal conclusion about GOM. They tested their surrogates and sampled on their flights, but this doesn’t come close to a complete sampling of all environments and potential Hg2+ compounds. Until we have much narrow range on the true speciation of GOM, we shouldn’t extrapolate these claims as much better than “assumptions”, which may not be correct. I suggest adding the following at the beginning of Line 18 “We make a similar assumption for the removal of GOM in our system and therefore presume that the CARIBIC mercury analyzer. . .”

The wording has been revised as suggested.

Page 7, line 21: “If all GOM compounds behave as HgCl2. . .” Yes, this is a very important assumption that we can’t yet generalize, also for the next claim. . . Line 24: “Pyrolyzing of mercury compounds to GEM . . . is thus not necessary. . .” There are two assumptions/implications here, the previous that desorption of GOM follows HgCl2, and two that GOM losses in the line aren’t a significant concern. Considering the ongoing challenge of quantifying mercury and mercury fractions (not species), much less the fact that we still don’t have actual speciation information, I don’t agree with these assumptions. Ultimately they may prove correct, but until we have better information, these aren’t good assumptions, in my opinion.

The text has been revised to take into account the comments of both reviewers on this point.

Page 8, line 11: “We have developed a procedure. . .” I think it’s great to see others trying different techniques on the off-line peak integration – in fact I think it’s critical. But, as a part of this effort, it is crucial to present some comparison data of your technique with one of the others previously described or, to provide some other metric to help assess the quality, accuracy, and objectivity of the technique. This may be as simple as trying a subset of peaks with an automated or different algorithm and reporting the correlation/bias. Please add some supporting evidence or comment for your particular algorithm/procedure.

We provide a comparison of the Tekran default integration with our off-line data processing and use it for correction of the old data. It would surely be worth to compare our off-line procedure with those of other groups but such intercomparison goes beyond the scope of this paper. We are prepared to take part in an intercomparison of different off-line procedures and would be pleased to provide data sets for it.

Line 17: “The uncertainty of the off-line. . .” Please describe how you determined this uncertainty, or clarify what is meant. Is this precision of the integration procedure, or

of your CVAFS instrument, or of the CARIBIC mercury system? I doubt it is the later, please clarify. Page 9, line 3: ". . . precision of the off-line processed data is thus âĹij 5%..." and the rest of the paragraph. See previous comment.

Under "precision" we mean the reproducibility of the off-line processing of a raw dump data of a given measurement. In the revised text we calculate an expanded precision including the precision of the calibration of $\sim$3% (as a square root of sum of square precisions).The contribution of calibration precision is negligible at integration precision of > 10%. Because of the issues related to GOM transmission we avoid the term "accuracy" throughout the text.

Page 12, line18: "Consequently, 70% of particulate mercury represents. . ." Is this based on the particle mass for the fraction < 0.5μm mentioned in the previous line? I would like to see the fraction of the surface area that the <0.5μm particles contain so I can have an idea how crude of an estimate the 70% value is. Do you have sufficient information to estimate the surface area distribution?

This estimate is based on the particle mass fraction for particles with diameter < 0.5 μm in UT and LS. We observe a strong gradient in aerosol surface area above the tropopause with surface area increasing with the altitude above the tropopause. This makes an estimate of a representative fraction of PM observed in LS difficult. We can only say that the deeper in the stratosphere the larger fraction of PM will be measured. More detailed estimates will be presented in a paper analysing the CARIBIC data in detail. This paper is in preparation.

Page 13, line 23: ". . . demonstrate qualitatively that GOM is transmitted through . . ." This wording implies or could imply that all GOM is transmitted, when the data aren't strong enough to support this strong of a conclusion. To be more clear, I recommend revising the statement to something like ". . . demonstrate qualitatively that at least some GOM is transmitted through . . ." Page 14, line 9: similar to above, should be " . . . at least some GOM in transmitted. . ."

The text has been revised as suggested.

Page 14, line 12: "TGM concentration remained with 0.3 ng/m3 nearly constant while . . ." I don't understand this. Should this be something like: "The TGM concentration remained about 0.3 ng/m3 and was nearly constant. . ."?

Following the recommendation by A. Hynes we added the flight overview of the flight #269. This should improve the understanding of the text.

Page 15, line 1: see previous comments. Until we know what GOM is, and have a much broader range of experience critically testing the transmission, I think this is too strong of a statement. I recommend revising to ". . . at least some GOM is transmitted. . ." Line 3-15: Understood, this appropriately points out that the transmission, at least for those species, in those environments, may be quantitative. Page 16, line 11-12: See previous comments. I strongly encourage some caveats here. Specifically, after ". . . measured quantitatively." I recommend something like ". . . in our system, but it is unknown if this can be generalized to other environments or all GOM compounds."

In the revised text we now point out that the GOM transmission through PFA tubing is an unresolved issue and that our results cannot be generalized.

Page 3, line 13: should read "Since May 2005, mercury *has been* measured. . ." Page 3, line 21: should read ". . .Lufthansa Airbus A340-600 *has been* flown . . ."

Done.

Page 12, line 13: This line is hard to read: "Based on the above discussion, our measurements will in addition to all gaseous mercury also likely encompass mercury evaporated from the particles which pass through the CARIBIC trace gas inlet." I suggest: "Based on the above discussion, our measurements likely include mercury volatilized from the particles that pass through the CARIBIC trace gas inlet, in addition to all gaseous mercury compounds."

Done.

Page 15, line 23, “With this data availability it belongs to the most reliable instruments in the container.” This is non-standard English, I suggest something like “With this data availability, it is one of the most reliable instruments in the container.”

Done

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-376, 2016.