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# Mercury distribution in the upper troposphere and lowermost stratosphere according to measurements by the IAGOS-CARIBIC observatory: 2014–2016

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**Supporting information**

The reviewers of this paper have raised concerns about the use of the quartz wool GOM traps and the resulting biases in the GEM data presented. The discussion on the use of scrubbers and denuders has been going now for more than a decade, so far without any firm conclusion on a reliable and accurate method of separating GEM, GOM, and PBM (Jaffe et al., 2014; Gustin et al., 2014; Hynes et al., 2017). From several methods on offer before 2014 when we started our measurements, we selected the method using quartz wool scrubbers to capture GOM and leaving GEM for detection (Lyman and Jaffe, 2012). Measurements by this technique, called DOHGS (Detector for Oxidized Hg Species), have been reported by Lyman and Jaffe (2012), Ambrose et al. (2013; 2015), Gratz et al. (2015) and Shah et al. (2016). The technique has taken part in a Reno Atmospheric Mercury Intercomparison eXperiment (RAMIX) with other techniques to measure total mercury, GOM, GEM, and PBM (Gustin et al., 2013; Ambrose et al., 2013; Hynes et al., 2017). The major reason for selecting this method was its proclaimed ozone insensitivity (Ambrose et al., 2013) which is important for measurements in the stratosphere.

Our quartz wool scrubbers were constructed according to the information and advice from Daniel Jaffe. They were operated as described in the above references with two differences: a) no zero air tests of quartz wool traps GOM bleeding were made during the flight because there was no place for additional zero air supply in the CARIBIC instrument and b) the quartz wool trap was switched on during the whole outbound flight and shunted out during the return flight. Apart from blank tests after trap pre-blanking (at 500°C for >2 h) no other laboratory test were made. In assessment of quality of our GEM data we thus rely on the published information on interferences such as by humidity and ozone which we summarize below:

Interference by humidity: Quartz wool traps can release GOM when subjected to high humidity. The interference is documented by RAMIX by spiking the air stream with 7.2 – 9.9 g $kg^{-1}$ water vapor (WV), together with WV in the air stream the total WV concentration was ~13 – 16 g $kg^{-1}$ (Ambrose et al., 2013, supporting information (SI)). In this document the authors claim that the GOM release from the quartz wool traps occurs only at WV concentrations > 10 g $kg^{-1}$. To avoid contamination in the vicinity of airports the sampling pumps of the CARIBIC instruments are switched on at a pressure below 500 hPa. By this precaution we also avoid most encounters with air with high humidity. The highest WV concentration encountered during the tropospheric sections of the CARIBIC flights presented here was 4.3 g $kg^{-1}$ (average 0.12 ± 0.28 g $kg^{-1}$), below the limit mentioned above. The highest WV concentration encountered in the stratosphere was 0.25 g $kg^{-1}$ (average 0.015 ± 0.017 g $kg^{-1}$). With the information provided by Ambrose et al. (2013) we conclude that, at CARIBIC conditions, air humidity might cause a slight positive bias in some tropospheric GEM measurements but none in the stratosphere.

Ozone: Lyman and Jaffe (2012, SI) report a loss of 6 – 20% of loaded $HgCl_2$ or $HgBr_2$ from quartz wool traps when exposed to 30 ppb of $O_3$ for 30 min, measurements at other $O_3$ mixing ratios are not mentioned. Ambrose et al. (2013) report experiments during RAMIX with $O_3$ spikes of ~110 ppb added to 25 – 63 ppb of ambient $O_3$ and quartz wool traps loaded with ambient GOM or spiked additionally with $HgBr_2$. Table S2 of their supporting information shows a 100 ± 20% (n=6) the recovery of loaded $HgBr_2$ with $O_3$ spikes. As $HgBr_2$ may not represent the ambient GOM compounds, the $O_3$ influence on the ambient GOM was also investigated. Mean (±95% confidence interval) ambient GOM concentration with $O_3$ spike was with 7 ± 11 pg $m^{-3}$ (n=47) lower than 24 ± 18 pg $m^{-3}$ (n=18) without $O_3$ spike. The difference between the two averages is statistically not significant but their large confidence intervals make the test quite uncertain. In summary, the $O_3$ spike tests with loaded $HgBr_2$ and with ambient GOM do not show any significant interference with $O_3$ but their large uncertainty cannot rule out its existence, especially when the $O_3$ levels exceed the tested range of up to ~170 ppb. The highest $O_3$ mixing ratio measured in the troposphere during the CARIBIC flights presented here was 177 ppb (average 61 ± 20 ppb) and thus we do not expect substantial bias in the tropospheric GEM measurements. The highest $O_3$ mixing ratio in the stratosphere, however, was with 1042 ppb (average 250 ± 146 ppb) substantially larger than ~170 ppb mentioned above. Although insignificant, the test with loaded ambient GOM indicates lower GOM concentrations with $O_3$ spike than without, i.e. release of captured GOM from the quartz wool traps when exposed to $O_3$ >170 ppb levels. We thus cannot rule out positive bias on GEM measurements in the stratosphere.

Difference in CARIBIC and DOHGS operations: As mentioned above, the quartz wool trap was switched on during the whole CARIBIC forward flight and shunted off during the return flight. Because of high CARIBIC cruising altitudes and limited pumping speed, the effective sampling flow rate was almost always smaller than 0.25 l(STP) $min^{-1}$, i.e. ~1 l(volume) $min^{-1}$ at the cruising altitude, which should lead to smaller breakthrough than ~2.3 % and ~4.8 % reported by Lyman and Jaffe (2012, SI) for flow rates of 1.3 and 3.0 l $min^{-1}$, respectively. Two forward intercontinental CARIBIC flights lasted less than 30 h of total flight time, corresponding to 450 l(STP) or 1800 l(volume) of sampled air. This is within the sample size range (flow rate up to 3 l $min^{-1}$ and sampling duration of up to 16 h, i.e. 2880 l(volume)) for which the breakthrough of quartz wool traps was tested by Lyman and Jaffe (2012). We have not made any zero air tests of quartz wool traps GOM bleeding during the flight for technical and certification reasons. We thus cannot rule out occasional GOM bleeding from the traps which would cause a positive bias on the GEM results.

Intercomparison with other instruments: An in-flight intercomparison of the CARIBIC instrument (without the quartz wool trap) with the DOHGS was planned for the NOMADSS campaign in 2013 but because of bad weather it could not be done. The DOHGS method took part in the RAMIX intercomparison in 2012 with the Tekran speciation systems, nylon and cation exchange filters, and two-photon laser-induced fluorescence (2P-LIF) instrument, operated with and without a pyrolyzer of mercury compounds. The results of this intercomparison were discussed in detail by Gustin et al. (2013), Ambrose et al. (2013) and Hynes et al. (2017), each with different interpretations. Gustin et al. (2013) and Ambrose et al. (2013) find some agreement between GOM measurements using DOHGS, nylon, and cation exchange filters with substantially higher values than those from the Tekran speciation system. On the contrary, Hynes et al. (2017) finds agreement between GOM measurements by 2P-LIF and Tekran speciation system but a disagreement with the DOHGS yielding a substantially higher GOM concentrations. The measurements by Hynes et al. (2017) have a special weight because they use pyrolyzer to determine total mercury as DOHGS does, but based on the physics of 2P-LIF technique they can detect GEM directly without any filter. In summary, the RAMIX results are, to our opinion, inconclusive. To the best of our knowledge, no other intercomparison involving the DOHGS technique with quartz wool traps has been made so far.

Summary: The CARIBIC GEM measurements using quartz wool may be biased, both by the method itself and by the way we operated the traps. Most of the DOHGS biases discussed above are related to the release of GOM from the quartz wool traps which would cause a positive bias in GEM measurements. However, RAMIX results as interpreted by Hynes et al. (2017) suggest also the possibility of GOM overestimation by DOHGS, i.e. a negative bias in GEM measurements. Consequently, we discuss the GEM measurements only in qualitative terms.

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