Enhanced production of oxidised mercury over the tropical Pacific Ocean: A key missing oxidation pathway - by Wang et al.

Response to referee comments by Referee #2.

We thank this anonymous referee for the detailed comments on the mercury speciation measurement technique and QA/QC procedures. Below we provide a point-by-point reply to the comments. The points raised by the referee are written in bold characters whereas our response is shown in normal characters.

This manuscript reports on observations of halogens and mercury species in the tropical Pacific region and attempts to understand these relationships in light of refinements to the chemical oxidation mechanism for GEM. Unfortunately, like many previous Hg publications, we are stuck in a limbo where we don’t know how to measure the species correctly and, not surprisingly, we also don’t know how to model them! It seems that we either need more solid grounding in the measurements or the chemical mechanisms to move forward.

We fully agree with the referee that there are two major uncertainties in our current understanding of mercury chemistry in the atmosphere: 1) the definition and accurate measurement of oxidized mercury species, and 2) chemical mechanisms of oxidation of GEM. It is in the latter area where we believe our manuscript makes a major contribution.

While mercury is a global contaminant, so far the majority of the published studies are in the mid- and high-latitude regions. By applying a widely-used, commercially available mercury speciation technique (i.e., the Tekran 1130/1135/2537 system – hereafter the Tekran technique), our manuscript reports the first long-term, real-time series of mercury speciation in the marine boundary layer at a tropical Pacific location (the Galapagos). Our results reveal a much higher degree of GEM oxidation than can be modeled by known mercury oxidation pathways via reactive bromine species, ozone or OH radicals. We show that atomic iodine could play the role of the missing oxidant, explaining not only the RGM levels observed, but also the daily variability. However, more recent theoretical calculations indicate that the thermal dissociation rate of HgBr is much faster, by an order of magnitude, than previously reported, which implies that only trace gases at relatively high mixing ratios forming stable complexes with HgBr (such as HO$_2$ and NO$_2$) could compete to generate levels of RGM similar to those observed in our study.

We have highlighted this in the revised manuscript: “our results indicate that the oxidation mechanisms included in mercury transport and chemistry models are missing a major process and therefore do not provide an adequate description of atmosphere-ocean exchanges of mercury in the tropical oceans. To solve this problem, new laboratory and field studies on the kinetics and
mechanism of mercury oxidation are needed.” We believe this recognition alone represents an important step forward.

The authors mention, but mostly brush aside, the challenges in measuring RGM and the recent reports on substantial problems with the existing methods. In addition, the authors fail to discuss in any detail the detection limit for RGM, which is fundamental to their analysis. Instead, they quote the detection limit from the manufacturer (Tekran). Given that nearly all instrument manufacturers inflate their specifications, and the apparent problems with the method that have not been acknowledged by the manufacturer, it seems the authors need to present something more convincing to show that they have actually detected RGM. This is especially true since their mean concentrations are just barely above the stated DL.

Details about the DL for RGM can be found below in addressing the referee’s specific comment. However, it is important to recognize that almost all the published air mercury speciation data so far were based on the Tekran- or equivalent techniques. It is also the standard technique used by Environment Canada, by the Atmospheric Mercury Network (AMNet) of USA, and by the Global Mercury Observation System (GMOS) of the European Union. It is premature to discard all these literature data (including the long-term time series from Alert and many other locations around the globe) and the scientific knowledge we gained from them.

It is important to note that all the recent comparative studies (Gustin et al., 2013; Huang et al., 2013; Ambrose et al., 2013; note all were published after the completion of our field work) showed that the RGM data measured by the Tekran method always equal to or less than gaseous oxidized mercury (GOM) measured by newer trapping techniques. Therefore, at the very least we can consider RGM values measured by Tekran as the lower limit. This implies that the actual GOM in our study site could be much higher that the RGM and Hg₀ values we measured, which will only strengthen our conclusions.

We stated this very clearly in the original manuscript and has clarified it further in the revised ms.

For this reason, it is also important that, as we did in the original ms, one retains the terminology RGM for any Tekran-based measurement to make it comparable with the vast amount of literature data generated by the same technique.

Potentially, the most useful part of this analysis could be the October event, IF the authors have more information to understand the cause. Here (we think) the RGM measurements are above DL. Even there, 10-15 pg/m3 is not very high above the DL. That said, what QC measures were employed to ensure there were no leaks, contamination, etc that could have caused the high RGM for those days? The Steffen reference, cited in the methods section is
relatively old and there are better citations if you are trying to say you used standard Canadian or AMNET procedures.

See our detailed response below. Our QA/QC procedure indeed followed the standard Environment Canada (developed primarily by Ms. Alexandra Steffen with whom one of our co-authors, Debbie Armstrong, was trained and worked in the field) procedures which are comparable with the AMNET procedures. We have updated the reference by citing Steffen et al. (2012) in the revised manuscript.

Overall, I would say, the following issues must get resolved before this ms could or should be published:

1) Discuss implications of errors in RGM on your measurements.

With strict QA/QC procedures followed (see below), errors associated with the RGM measurement could include the following:

- Errors when the RGM levels were near or below DL: This error was eliminated in data processing as only RGM values that were above 3 times of the DL (see below) were used in the manuscript.

- Errors associated with “unnatural” events in the surroundings: This could be due to exhaust from traffic (people, automobiles, ships, etc.) and tend to overestimate RGM. This error was eliminated by removing any data points associated with logged traffic data and ancillary data (e.g., NOx) measured at the same time. Note also our study sites were located in very remote areas.

- Memory effects of the denuder: This could occur if RGM from the previous cycle did not desorb completely, which would underestimate the RGM for the previous interval and overestimate it for the present interval. This error was eliminated by carefully screening the data points during a denude desorb cycle which involving heating the denuder to 500 °C) and measuring the Hg released in three consecutive 5-min cycles. Only those data that included a peak value in the first cycle decreasing to zero in the third cycle were used in the manuscript. The denuder desorb cycle was preceded by a Hg₈ desorb in which the final measurement was zero.

- Errors related to the nature of the denuder: This could occur if the denuder did not retain all the GOM species during the measurement. As mentioned earlier, this is the most probable error associated with this study, and would tend to underestimate GOM. As we were following the standard operating protocols with the Tekran system, no action was taken to correct for this error. As a result, our RGM measurement can only be considered as the lower limit of GOM in air. This would actually make our conclusion even stronger.
2) **Describe how DL was obtained or show tests that prove 4 pg/m³ is above your DL.**

Since there are currently no available certified reference material for RGM, we could only estimate the DL for RGM based on the DL for GEM which was better than 0.1 ng/m³ for a 5-L sample volume (Tekran, 2011), a value generated by various approaches and has been widely adopted for the Tekran-based technique used by Environment Canada, AMNET and GMOS. Since the flow rate was 10 L/min for 120 minutes in each RGM cycle, the DL for RGM was then calculated to be

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0.1 \text{ ng/m}^3 \times (5 \text{ L}/1200 \text{ L}) = 0.00042 \text{ ng/m}^3 \text{ or } 0.42 \text{ pg/m}^3 \text{ for RGM}
\]

The same applies to the DL for Hgₚ.

Therefore, the 4 pg/m³ RGM is at least 10 times the DL. We have included this information in the revised ms.

3) **Describe QC to convince reader that the October events were in fact real.**

Our QC followed strictly the standard QC produces developed by Environment Canada and AMNET (Steffen et al., 2012). Specifically, GEM was measured continuously at 5 minute intervals while Hgₚ and RGM every two hours in order to have enough material concentrated for a reliable measurement above the DL. The calibration was done by a two-point internal calibration involving a zero (produced by Hg-removed air) and a spike (produced by an internal reference mercury source) on a regular basis (every 25 hours in our method), and by monthly by using an external calibration mercury source (Tekran 2505) to calibrate the internal reference source. For external calibration, six injections of a known external source were spiked into the system and the results were always within 5% of set values.

Daily checks included monitoring the baseline voltage for stability, agreement between the dual cartridges to be within 10% of each other, the monitoring of zero air checks during the desorb cycle for the collection of RGM such as the initial desorb flag 1 to be zero and final flags of Hgₚ desorb and RGM desorb to also be zero, internal calibration completed every 25 hours and comparable to the one before.

Maintenance included the weekly replacement of filters and sample inlet frit as well as the soda lime trap. The denuder was changed on a biweekly basis along with the PHg filter and glass wool. After all changes of filters or glassware, a leak test was performed to ensure the system there was no leakage in the system. The system was then fully desorbed until zero levels were reached before ambient sampling and measurement again.

When screening for the data, any data points associated with traffic influence (as documented by the log book and/or indicated by NOx values) were removed. Bias between cartridges A and B
was checked to be less than 10%, and no correlation was found between GEM values and the baseline voltage.

4) Provide some useful analysis of the October event to help identify the cause for high RGM on these days.

We think the referee was referring to a three-day, unusually high RGM event from Oct. 23-25. As mentioned in the original manuscript, not only did the RGM show the highest values in the entire campaign, it also peaked during night-time, which cannot be explained by in situ photochemical oxidation of GEM. Since the influence of the free troposphere was negligible (as per Section 3.5 of the original manuscript), the most plausible explanation we could think of would be that it was due to a localized condition under which the RGM taken up by sea-salt aerosols did not immediately deposit into the ocean and was subsequently re-emitted from the aerosols to the MBL. Unfortunately, we do not have any direct evidence to support that. Indeed, as pointed out in the manuscript, night-time rising of RGM has been sporadically reported in the literature with the reason poorly understood. We will highlight this additional knowledge gap in the revised manuscript.

Lacking any of the above, it is not clear to me what new results this paper brings to the topic.

A few other specific comments: Abstract, line 5: I think the statement staring with “Measurements of oxidized mercury in the polar: : :” is way over-stated. This is probably true in the Arctic. In lower latitudes there are perhaps two or three papers that suggest this.

Agreed. Some of the mid-latitude data were modeling results. Therefore, in the revised manuscript we have change that sentence to “Measurements and modeling studies of oxidized mercury in the polar to sub-tropical…”.

Line 10-11: “Considerable concentrations: : :” 4 pg/m3 is not what I would call “considerable”.

By “considerable” we meant they were higher than we would have expected based on the known oxidation pathways. We have replaced “considerable concentrations” with “higher than expected levels” in the revised manuscript.

References:


