

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

**Response to referee comments by T. S. Dibble**

We thank Dr. Dibble for his helpful comments on the modelling part of the manuscript. 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.

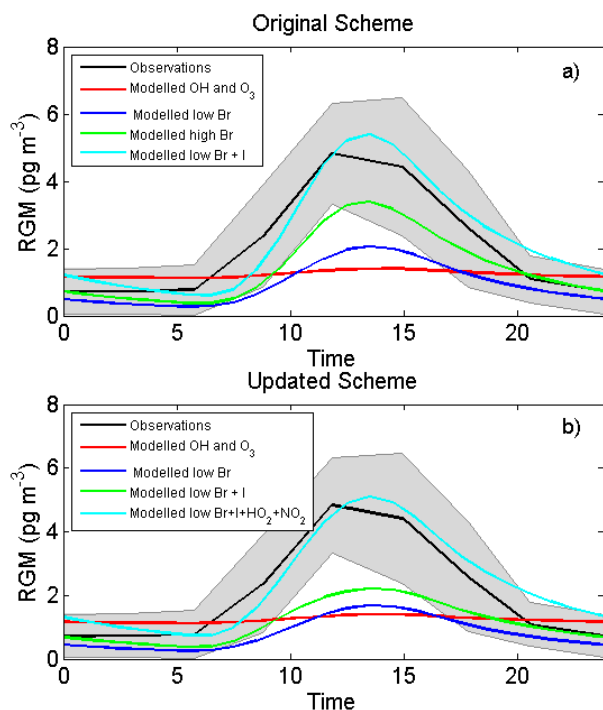
**This manuscript presents experimental measurements of GEM, RGM, Hg<sub>p</sub> and key meteorological parameters, analyzes correlations among these variables, and presents modeling of RGM diurnal profiles. The topic is clearly appropriate for this journal. The authors clearly and carefully describe experimental measurements of mercury in the tropical MBL and correlations (or lack thereof) between mercury and Chl a and temperature, and correlations among concentrations of various forms of mercury. By contrast, the modelling effort is not described or analyzed as well. Critically, the apparent change in RGM lifetime from ~3 hours to > 8 hours between panels (a) and (b) of Figure 6 is most likely explained by an error in the modelling. This error undermines much of the results and analysis of the modelling. Therefore, it is my judgment that this manuscript be revised and resubmitted for review. Once this error is fixed and the modelling results more carefully analyzed, I expect the manuscript to be acceptable for publication.**

Detailed responses, including a response to the comment about the lifetime of RGM, are given below.

**1) Lifetime of RGM loss in Figure 6a and 6b. The measured lifetime of RGM and the modelled lifetime of RGM in panel (a) is roughly ~3 hours. This is consistent with other results, such as Holmes et al (2009) cited in the manuscript. Loss of RGM in the model is due to deposition, uptake on sea salt aerosol, and boundary layer ventilation. The fact that the RGM lifetime in panel (b) is more like 12 hours for all chemical mechanisms suggest that the loss mechanisms were not properly included in the modelling. Alternative explanations are possible, but in any case, the origin of this difference should be clearly explained. In any case, the revised manuscript should report the relative importance of different RGM loss mechanisms in the model.**

Dr. Dibble raised a good point regarding the lack of explanation for the difference in the night time RGM between Figure 6a and 6b. The lifetime of RGM is not about three hours in 6a, but closer to about 5 hours (similar to Holmes et al., 2009 for the Pacific subtropics scenario). We had tuned the losses to try and get the closest match with the night time observations, as mentioned in the manuscript. The lifetime was increased in Figure 6b to 9 hours to get a match with the peak values, which the referee has pointed out as an error. The reason for doing this was to match the peak value during the daytime assuming a background NO<sub>2</sub> mixing ratio of 15 pptv

(consistent with other open ocean sites such as Cape Verde in the Atlantic). However, considering the  $\text{NO}_2$  was mostly under the detection limit of the instrument ( $\sim 50$  pptv) during daytime, it is possible that it was higher than the prescribed 15 pptv. We have now used the same lifetime of RGM for both the panels as suggested by the referee to enable a direct comparison. In doing so, to match the peak value of RGM, the  $\text{NO}_2$  mixing ratio prescribed in the model is 40 pptv instead of 15 pptv. This is still possible because it would be under the detection limit of our instrument at the Galapagos. The new Figure 6 (below), showing the results of the modified model runs is now included in the revised manuscript. The results do not change the conclusions of the manuscript, although now the diurnal profile and peak concentrations are reproduced by both chemistry schemes. This discussion has now been added to the revised manuscript.



2) The manuscript states that “Entrainment of  $\text{Hg}(\text{II})$  from the free troposphere is calculated according to Holmes et al. (2009).” However, the method of Holmes et al (as described in the second paragraph of their model description) parameterizes free-tropospheric [RGM] to allow models to match the daily average [RGM] in the MBL. In the present study, daily average [RGM] clearly varies with different chemical models, so the method of the present manuscript appears to be different than described. Clarification of the method of computing entrainment is clearly needed. In addition, the used of a parameterized entrainment (which accounted for 25-40% of the RGM source in Holmes et al) can hide significant errors in the modelling. I suggest the authors specifically report the level of entrainment in their model, so that readers can evaluate the robustness of the model results.

The entrainment from the free troposphere is, as mentioned, calculated using the scheme in Holmes et al. (2009): The entrainment flux at the top of the boundary layer is the product of an assumed entrainment velocity  $v_e = 0.5 \text{ cm s}^{-1}$  (Faloona et al., 2005) and the concentration difference between the MBL and the free troposphere  $F_e = v_e(c_{FT} - c)$ . The free tropospheric concentration is assumed to be  $20 \text{ pg m}^{-3}$ . The referee is right in saying that the entrainment is a function of the concentration in the MBL; however the change in entrainment is not dependent on the chemical scheme used, but only the MBL concentration and hence should not add to the errors considering we now reproduce the diurnal profiles with both the schemes. These details are now included in the revised manuscript.

**3) In reporting the model parameters, the authors do not provide sufficient information for others to reproduce their modelling results. They authors need to report diurnal concentration profiles of key species (input to or output of the model), along with time-dependent photolysis rate constants, and parameters relevant to loss of RGM. This can be placed in Supplementary Material in order to avoid page charges.**

See our detailed response below. We have incorporated some key sentences in the revised manuscript and hope they suffice. We are willing to include a Supplementary Material section should the editor so desire.

*4) In section 3.6 the authors report, without providing supporting data, that there is no correlation between  $[NO_2]$  and 24 hr average  $[RGM]$ . This is stated more forcefully in the abstract, and the conclusion about the lack of correlation is extended to  $[HO_2]$  and  $[RGM]$ . Note that, with the rate constants for  $HgBr + NO_2$  and  $HgBr + HO_2$  being similar, a correlation analysis should consider a weighted average of  $[NO_2]$  and  $[HO_2]$ . More importantly, a correlation analysis is not necessarily sufficient. If the fate of  $HgBr$  were to be 99% reaction with  $NO_2$  and 1% dissociation, then a 90% reduction in  $[NO_2]$  would lead to the fate of  $HgBr$  being 90% reaction with  $[NO_2]$ . The corresponding 10% decrease in the fraction of  $HgBr$  oxidation to  $Hg(II)$  would be lost in the noise of the data. In the present study, I suspect that  $[NO_2]$  and  $[HO_2]$  are so low that most  $HgBr$  dissociates, in which case the correlation analysis would provide insight. The validity of a correlation analysis should be specifically addressed. To this end, it would be helpful for the authors to report on the fraction of  $HgBr$  that dissociates instead of forming  $Hg(II)$  in their model of this site.*

In the warm season (February-May) relatively high  $NO_2$  levels were observed at night and twilight (~500 pptv), which fell below the detection limit (~50 pptv) at daytime. This behaviour was driven by enhanced local emissions during the tourist season combined with calm wind conditions occurring during the night (wind speed was zero at night). At daytime the wind from the south was reactivated and the stagnant polluted air was flushed away by the incoming clean background air from the open ocean. In order to distinguish between these two states, correlation coefficients of 24-hour averages and 12-hour (daytime) averages between  $NO_2$  and RGM were calculated. Lack of correlation is indicated by the low correlation coefficients obtained:  $R=0.105$

( $p=0.6$ ) and  $R=0.279$  ( $p=0.18$ ) respectively. We did not make measurements of HO<sub>2</sub>, although the modelled HO<sub>2</sub> did not show any direct correlation for the 24 hour averages.

Considering the complexity of the chemistry involved and the many existing uncertainties in thermodynamic constants, the referee is right in suggesting that this lack of correlation may not be indicative of NO<sub>2</sub> not playing a role in mercury oxidation. One of the main reasons, which has not been mentioned by the referee, is the effect of NO<sub>2</sub> on bromine chemistry. In the presence of larger levels of NO<sub>2</sub>, the reservoir bromine species that forms is BrNO<sub>3</sub>, which will limit the reactive bromine available for the formation of HgBr.

Hence, this section has been reworded in the manuscript and we no longer suggest that we should expect a correlation between NO<sub>2</sub> and RGM, and have highlighted the possible interactions which could limit the observation of such positive correlations. It should, however, be noted that the only direct positive correlation we observed for RGM was with iodine species.

***5) Page 21549. It is great that the authors estimated rate constants for HgBr with several radicals (copying the method of Goodsite, et al, 2004), and this probably deserves to be highlighted more than has been done here. The manuscript should, however, should point out that these rate constants are rather approximate. For example, mercury models almost all use the rate constant of Goodsite et al. (2004) for  $\text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2$ , but a more rigorous analysis by Balabanov, Shepler, and Peterson (J. Phys. Chem. A 2005, 109, 8765-8773) gives a rate constant about 6-8 times lower.***

***Note that the same paper by Balabanov, Shepler, and Peterson reports a gas phase rate constant for  $\text{Hg} + \text{Br}_2 \rightarrow \text{HgBr}_2$  of about 10-31 cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>. This low rate constant is entirely reasonable for the reaction of a closed shell molecule with an atom possessing a closed subshell (electron configuration [Xe]5d106s2). Therefore, this gas phase reaction should not be included in modeling mercury.***

We use in our master equation calculations (MEC) ab initio vibrational frequencies and energies calculated at the same level of theory used by the referee in his recent ab initio study in ACP (Dibble et al., 2012), which is higher than the one used by Goodsite et al. (2004). We agree with the referee that MEC rate coefficients are approximate, but we would like to point out that our estimate for  $\text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2$  is only a factor of  $\sim 2$  larger than the value calculated by Balabanov et al. (2005). Note that the quasiclassical trajectory (QCT) calculations performed by Balabanov et al. (2005) do not include interaction with a collision partner, which would increase the number of reactive trajectories trapped inside the well of the HgBr<sub>2</sub> adduct by relaxation of highly excited ro-vibrational states. Therefore, their QCT rate constant is a lower limit, which is consistent with our factor of 2 larger MEC estimate. On the other hand, the rate coefficients calculated by variational transition state theory by Balabanov et al. (2005) ( $\sim 10^{-10}$  molecule cm<sup>-3</sup> s<sup>-1</sup>) are high pressure limits and are also very consistent with our calculation.

In any case, given the fast dissociation of HgBr, this reaction would not have an impact on mercury oxidation.

Regarding  $\text{Hg} + \text{Br}_2 \rightarrow \text{HgBr}_2$ , we have considered in the model the experimental upper limit rate constant determined by Ariya et al. (2002). This is in any case a slow reaction and in addition the concentration of  $\text{Br}_2$  in the open ocean MBL is low, and therefore does not play any significant role in the chemistry of mercury and can be ignored.

**6) Table 1 has a reaction forming HgCl (a Hg(I) compound), but no reactions of the HgCl radical! Also, the use of (+Y) in the reactions of Hg + Cl is not explained.**

HgCl reacts with atmospheric Cl and Br, which are represented at Y in the reaction table at the rate mentioned. This is however a small channel considering the low concentration of atomic Cl in the atmosphere.

**7) The heading to section 3.3 indicates Hg(0) oxidation by iodine, but the section actually describes oxidation of Hg(I) (in the form of HgBr) to Hg(II).**

This has been changed in the revised manuscript.

**8) Page 21566 line 25. The “correlation” between RH and RGM (or Hgp) is actually an anticorrelation”**

This has been corrected in the revised manuscript.

## References:

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- Dibble, T. S., Zelig, M. J., and Mao, H.: Thermodynamics of reactions of ClHg and BrHg radicals with atmospherically abundant free radicals, *Atmos. Chem. Phys.*, 12, 10271-10279, 2012.
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- Goodsite, M. E., Plane, J. M. C., and Skov, H.: A theoretical study of the oxidation of Hg<sup>0</sup> to HgBr<sub>2</sub> in the troposphere, *Environ. Sci. Technol.*, 38, 1772-1776, 2004.

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