

## ***Interactive comment on “Measurement-based modeling of bromine-induced oxidation of mercury above the Dead Sea” by E. Tas et al.***

**Anonymous Referee #1**

Received and published: 13 September 2011

This is an interesting analysis that explores the potential chemical mechanisms behind mercury oxidation associated with reactive bromine compounds in the mid-latitudes. It is an important contribution to the field of atmospheric mercury chemistry. I do, however, suggest that the authors make a number of significant changes to the manuscript before publication.

In general, the paper relies too heavily on the assumptions included in the model and doesn't spend enough time using measurements and results from other studies to justify and evaluate the assumptions made. The authors need to examine their model results more critically, and they need to spend more time dealing with the limitations of the hypotheses they present. It would also be useful to present a short comparison of modeled and measured ozone mixing ratios as another evaluation of model

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performance.

Specific comments are as follows:

Pg 24469 line 6: The Schroeder paper is outdated. More current work gives a global lifetime for mercury of a few months to one year.

Pg 24470 line 23: replace “particularly” with “including”

Pg 24472 lines 2-3: The name and manufacturer of the DOAS system was already given on the previous page.

Pg 24473 lines 20-25: Please provide a more complete justification for adding fluxes of GEM and ozone in the model after AMDEs and in the morning. Why did you need to do this? Is it because the model doesn't adequately simulate reduction of oxidized Hg compounds or because it misses some other critical atmospheric process?

Pg 24474 line 8: Is the  $1.5 \times 10^{-13}$  value higher than the upper limit of kinetics studies? Are you proposing that kinetics studies are wrong? Please justify the decision to use this value.

Pg 24474 lines 20-21: It was already stated earlier that local temperatures were used in the model. Also, “averaged at  $\sim 310$  K” is confusing. To me it seems to imply that you used a constant average temperature in the model, rather than the real-time local temperature. Some alternative wording here might help.

Pg 24475 lines 6-7: Consider including Holmes et al., 2006 with the Lin et al. Reference.

Pg 24475 line 19: Consider replacing “liquid phase” with “aqueous phase”.

Pg 24476 lines 11-13: It's not clear how the Tossell 2006 paper justifies your hypothesis that BrO is the primary oxidant of GEM at the Dead Sea. Please explain this further, and please justify more completely your contention that BrO is an important oxidant for GEM.

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Pg 24476 lines 17-19: Your study contradicts this conclusion of Xie et al. 2008. Why don't the two studies agree? Please expound on this.

Pg 24476 lines 24-28: Or this could be happening because your model is missing an important physical or chemical process (or processes).

Pg 24476 line 28 to pg 24477 line 1: To me none of your simulations look like they reproduce the observations very well, and that's even after you add an arbitrary GEM flux to try to force them to agree. It seems like the agreement isn't good enough to independently support your contention that GEM oxidation rates by BrO are higher than has been previously reported. Please justify this further, and please show a statistical analysis of the agreement between measurements and your different simulations. It is important to show statistically 1) the overall level of agreement between the measurements and the model, and 2) the relative agreement of the different simulations.

Pg 24477 line 26 to 24478 line 7: This paragraph is confusing and needs to be reworked.

Pg 24478 line 17: change "was [greatly]" to "was greatly"

Pg 24478 lines 19-22: This sentence could be made more clear. It would be good to state more clearly that high ozone periods tend to have low BrO and vice versa. Figure 4 is very interesting, but it could be explained better also.

Pg 24478 line 24: Why did you only use Julian day 201 for this analysis? If there is a good reason for using only that day, please state it. If there isn't a good reason, please use all days in the analysis. Please follow this rule throughout the manuscript.

Pg 24478 line 26 to 24479 line 2: These sentences are difficult to follow.

Pg 24479 lines 11 to 12: Or oxidized Hg could be reduced quickly back to GEM, either in the gas phase or after deposition, and it could be that the model isn't capturing this process well.

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Pg 24479 lines 13 to 15: But BrOx is always high when GEM is low, so how could reduced GEM depletion efficiency be due to a decrease in BrOx levels?

Pg 24480 lines 2 to 4: This sentence assumes that your "Base Case" scenario is reality. The rate constants used in that scenario were fitted to your data, and are speculative. Please reword this and other sections to more fully capture the high degree of uncertainty in your analysis.

Pg 24480 line 5: Please be clear about what constitutes the "O3-rich troposphere". Does this mean the troposphere whenever there is a lot of ozone? Or does it mean the troposphere is always ozone-rich?

Pg 24481 line 3: What are "relatively moderate BrO levels"? It would be better to make this statement more quantitative.

Pg 24481 line 20: It's not clear how Figure 3 shows this.

Pg 24483 first paragraph: But do these model results match observations or not?

Pg 24483 lines 13-14: This is too strongly worded. The model results represent one possible explanation for the observed measurements.

Pg 24483 lines 17-18: Either BrO is the dominant oxidant or the model is missing some physical or chemical process that leads to the same result. The model could be giving the right answer for the wrong reason.

Figure 1: Why does GEM bounce back up suddenly after depletions in this figure? Is this because of the added GEM flux? What would this figure look like without the added GEM flux?

Figure 3: Please provide a reference for the "known positive correlation" between ozone and [Br]/[BrO]. If there is a positive correlation between these, why does [Br]/[BrO] drop as ozone increases on the y axes in Figure 3?

Figure 4: first sentence of caption, change to "The simulated relative influence of O3

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and BrO...”.

Figure 5: It would be good to use the same units for a given species throughout the entire text and figures. It is hard to differentiate between crosses and horizontal lines with all the individual points in the way. It might be good to only show outlier individual points. It would make the figure clearer. This figure would also be improved if the model lines were for the same sets of data as the measured datapoints. Since all the measurements are included but only two selected model days are shown as a line, it is difficult for a viewer to draw a definite conclusion from this figure about how well the model reproduces results.

Figure 6: would this figure be clearer if you differentiated A and B by the BrOx mixing ratios, not by day?

Figure 7: It might be beneficial to more clearly and quantitatively explain why days 188 and 201 are significant – in detail in the text, and briefly in the figure caption.

Supplementary Table 1: reaction G15 is not balanced. Also, production of HgOCl from Hg and ClO is given as reaction G18, but production of HgOBr is not shown, even though some evidence exists that it may be produced from Hg + BrO (Raofie and Ariya 2004).

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