**Atmospheric
Chemistry
and Physics
Discussions**

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

E. Tas et al.

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General comments

We thank the reviewer for the high level of attention given to our paper and for the relevant and detailed comments. Several of the reviewer comments indicate that a number of key points presented in our paper were not entirely clear, and we will address these concerns in a revised manuscript as detailed below. The reviewer also suggests a series of other manuscript improvements and we below outline a point by point detailed description of the modifications that will be incorporated in the revised version to address these accordingly.

It would also be useful to present a short comparison of modeled and measured ozone

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mixing ratios as another evaluation of model performance. In our revised manuscript, we will provide measured and simulated ozone comparison for all days for which our analysis was performed.

Specific comments

Pg 24469 line 6: The Schroeder paper is outdated.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.

-We will provide a more updated reference for GEM lifetime in the revised manuscript.

Pg 24470 line 23: replace "particularly" with "including"

-We will do this correction.

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

-We will correct this.

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?

-This is indeed a critical point, which will be address more extensively in the revised manuscript. The present investigation is strongly focused on describing Br-Hg interaction during AMDEs, i.e., during the particular part of the day when we observe strong Hg depletions, ozone depletions, and high BrO levels. Our measurements indicate, however, that in addition to the RBS (reactive bromine species) chemistry, once RBS activity is over, both GEM and O3 are being advected from the area out of the domain in which RBS were active resulting in a very sharp increases in both ozone and GEM back to their background level. This rebounding of GEM and O3 levels can not be explained or modeled by chemistry alone and our box model hence needs to in-

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clude these fluxes as advection fluxes. Hence, by applying the model as described in Sects. 2.2 and 2.3 without additional fluxes, it was possible to obtain good agreements with measurements during AMDEs (please note new figures showing fits of measured and modeled GEM depletions in response to reviewer's comments below). However, agreements were somewhat lower during nighttime and in the mornings, and we therefore included small GEM fluxes to reach the pre-AMDE levels, which we attribute to transport and diffusion processes, and possibly GEM emissions from natural or anthropogenic sources. It should be noted, however, that the impact of these additional sources of Hg on Hg-Br interaction is insignificant during AMDEs. Fluxes were also added for ozone, during evening in order to recover ozone levels after AMDEs/ozone depletion events(ODEs) are over which was in agreement with similar work previously performed by Tas et al., 2006. We will clarify these points in a revised manuscript.

Pg 24474 line 8: Is the 1.5 x 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.

-This is an important point, and it is indeed difficult to estimate rate constants based on field observations. However, we will clarify the use of these rate constants in our revised manuscript as follows. First, the used 1.5 x 10-13 value is indeed higher than the upper limit (10-13) proposed by Raofie and Ariya (2003), but it is possible that the calculated rate by Raofie and Ariya, calculated for 298±1 k and 760±1 Torr, could be different under the Dead Sea conditions (although as far as we know, no specific dependency on temperature and pressure was reported for this reaction). Second, we emphasize that simulations were also presented for two additional lower reaction rates (10-15 and 5*10-14), as well as different reaction rates for Hg+Br (see combinations presented in Figs. 1,2, and supplementary Figs. 1 and 2, and discussed in detail in Sect. 3.1 and table 1). In the revised manuscript, we will present an additional figure (see Fig. 1 below) which directly compares the depletion rate (i.e., slope) of measured GEM obtained during AMDEs with the corresponding simulated GEM for all different

combinations of reaction rates. The figure indicates that the BASE simulation (i.e., L_Br_H_BrO) achieves best agreements on days with moderate BrO concentrations (i.e., JD=197,201 with BrO<∼45ppt), while the L_Br_M_BrO appears to achieve better results for days with high BrOX levels (for JD=188 with BrO>80ppt). This strongly supports that k(Hg+Br)=2.7e-13 is a good estimate, especially if we take into account that the [Br]/[BrO] ratio during AMDE on JD=188 was relatively high compared with the two other days. The new figure further suggests that k(Hg+BrO) is at least high as in L_Br_M_BrO (i.e., 5*10-14) and could be as high as in BASE (i.e., 1.5*10-13). It should be noted that ozone concentrations were slightly underestimated in our model (by ∼10-20%), and hence [Br]/[BrO] ratios in our model were probably lower than the actual [Br]/[BrO]. Based on Fig. 3, the [Br]/[BrO] in our model could be overestimated by up to a factor of ∼2 due to this reason. This is expected to result in an overestimation of the depletion rate of GEM by Br for both BASE and L_Br_M_BrO simulations as well as an underestimation of the depletion of GEM by BrO, unless if higher rate constant is used for k(GEM+BrO)(e.g., such in the BASE simulation). This is probably the reason for the underestimation of GEM depletion rates by L_Br_M_BrO during JD=197,201 and for the overestimation of GEM depletion rate of BASE during JD=188. The fact, however, that GEM depletion rate was overestimated by applying the BASE simulation for JD=188 (relatively high Br) and not for JD=197,201 (relatively high BrO) suggests that the rate of GEM depletion by Br could be overestimated by more than the applying a value of 1.5*10-13 for the rate constant of k(GEM+BrO). This is also being strongly supported by the fact that the contribution of BrO to GEM depletion is much stronger than this of Br under the studied conditions (Fig. 7), such that one would have expected more significant deviation from measured GEM associated with inaccuracy in the rate of GEM reaction with BrO. Therefore we may conclude that based on the used kinetics a value of 10-13 for the rate constant of k(GEM_Br) appears to be correct and a value of 5*10-14 appears to be a minimum for k(GEM+BrO), while 1.5*10-13 appears to be an upper limit and probably a better estimation for this reaction. Also, we will add a new table (see table 1 below) to show average correlation and error values for the different

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simulations compared with measurements during AMDE.

Julian day	L_Br_M_BrO	L_Br_H_BrO	L_Br_L_BrO	H_Br_L_BrO
	Corr/Err(%)	Corr/Err(%)	Corr/Err(%)	Corr/Err(%)
188	0.79/33.83	0.80/46.86	0.66/68.25	0.80/55.40
197	0.90/25.27	0.94/6.36	0.85/53.60	0.85/37.56
198*	0.66/70.62	0.68/50.43	0.62/106.32	0.63/90.67
201	0.75/27.33	0.76/8.52	0.75/68.73	0.76/34.30

Table 1. Correlation (R coefficient)and average error during AMDEs as an indicator for simulated GEM agreement with measured GEM during AMDEs. * Note that simulation for Julian day 198 (see also Fig. 1 in supplementary section) is used to demonstrate the occurrence of fluxes of background air masses into the measurement area. For this reason, simulated and measured data are not expected to show good agreements for this day.

Pg 24474 lines 20-21: It was already stated earlier that local temperatures were used in the model. Also, "averaged at 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.

-We will use alternative wording as indeed real-time temperature was used in the model. Any repetition will be excluded.

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

-We will include this reference.

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

-We will correct this.

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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 that BrO is the primary oxidant of GEM at the Dead Sea.

-We didn't mean using Tossel 2006 to justify our hypothesis that BrO is the primary oxidant of GEM at the Dead Sea, and will rephrase this to clarify. As discussed above, we will provide an additional figure showing what rate constant combinations best replicate AMDEs at the Dead Sea. Based on the chosen rate constants, we will then improve our discussion of results from figure 7 that shows that BrO at the Dead Sea explains most of the GEM depletions.

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.

-This is a good point, and a possible explanation may be as follows: Xie et al., (2008) used correlations between GEM (actually total gaseous mercury: TGM) and O3 as an indicator of GEM and O3 depletion rates by BrOX. Our Figures 4 and 6, however, indicate the correlation between O3 and GEM is highly dependent on absolute O3, GEM and BrOX levels. We hence don't determine GEM depletion rates based on correlations to O3 depletions, but instead use the ratio of [Br]/[BrO] (or the correlative O3 magnitude) as a qualitative indicator to study the relative influence of BrO and Br on GEM depletion rates. We will clarify this point in a revised manuscript.

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

-Sure, that is always possible, and we already state in the text that "the reason for this is unknown". However, given the relatively small dimensions of the area under investigation and taking into account changes in wind direction during the relevant time period, a likely the reason could in fact be advection of air masses with "background" (GEM, O3, BROX, etc..) levels. This was also found in previous studies at the Dead Sea (Tas

et al. 2006, 2008). Please also note that Fig. 1 in supplementary section is used to demonstrate the occurrence of such fluxes of background air masses into the measurement area. This figure shows that relatively moderate increase in BrO concentrations between ∼10:00-11:00am cause much sharper decrease in GEM compared with the insignificant change in GEM between ∼14:00-18:00 at time when BrO levels increased sharply. We strongly believe that this is the result of "fresh" air masses that were being advected into the measurement site.

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.

-(See also response above): We disagree that our agreements are poor, particularly during the specific period of AMDEs where we focused our box model simulations. We will present a new figure and table (see above) that show fits and statistics correlations (corr) and errors (err) between observed and modelled data during AMDEs for three of the four simulation days and various combinations of Br and BrO rate constants. Both the new figure and table indicate that best agreements were obtained between measurements and simulations under "BASE" simulations ("L_Br_H_BrO").

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

-We will address this.

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

-We will correct this.

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.

-We will clarify this in the revised manuscript.

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.

-The day here was mistakenly labeled 201 instead of 188, which we will correct. The reason that we only use Julian day 188 for Figure 4 and associated discussion points is that only for this day O3 concentrations dropped below $\sim$30ppb. However, the recovery patterns for BrO and O3 are different for different simulation days, and we will therefore better include all days to present the analysis results individually for each simulation day.

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

-The sentence will be reworded in the revised manuscript.

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.

-Yes, that could be an additional reason as reduction of deposited GEM is not taken into account by the model, and we will add this statement. It should be emphasized, however, that Fig. 6b shows that the lifetime of GEM against oxidation by BrOX suddenly dropped about an order of magnitude at GEM levels above $4–24\times10{-14}$ mol$\times$mol-1 (while no significant change in BrO occurred). This suggests that oxidation of GEM by BrOX became GEM-limited and very inefficient below GEM concentrations of $\_24\times10{-14}$. Therefore the sharp decease in GEM depletion efficiency below

a certain threshold probably doesn't result from additional source which is not included in the model. Further, our analysis is based on a highly detailed and most updated kinetic mechanism (Sect. 2.2) and while some recovery of GEM by reduction occur, the model indicates that the sharp decrease in GEM depletion efficiency below a certain threshold dominantly results from decrease in the efficiency of GEM oxidation by BrOX for low GEM levels (for cases of high BrOX). We will re-write this paragraph and discuss in more detail in our revised manuscript.

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?

-It is correct that in general BrOX concentrations are expected to be high when GEM are low, but this is not always the case over the Dead Sea. Since at the Dead Sea BrO can reach (frequently) very high concentrations, ozone and NO2 drop to very low concentrations such that BrO formation becomes ozone and NO2 limited, as is explained extensively in Tas et al.,(2006,2008), and is in agreement with Evans et al. (2003). Therefore BrO can drop to low levels when both ozone and GEM concentrations are low.

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.

-We will rephrase this and clearly mention that this analysis (Figure 7) is based on the rate constants used for BrO and Br that best reproduced observed AMDE patterns. It also should be taken into account that most of the analysis is focused directly on AMDEs periods and are less sensitive to processes which were not included in the model (such as additional ground sources, etc). We don't consider the rate constants as speculative as they are based on previously published rate constants (with the expection of slighely higher rate of BrO with GEM).

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?

-The latter, i.e., that the troposphere is always ozone-rich – we will clarify this.

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

-About a concentration at and below ~40-50ppt, which we will clarify.

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

-We will rephrase this: Figure 3 shows how with decreasing O3 levels (x axis of panel a) associated Br/BrO levels (x axis of panel d) increase. We will also refer to additional references to support this point (e.g., Wayne et al., 1995).

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

-We will delete this paragraph and remove the discussion points as we don't show SO2 measurements and this would exceed the scope of this paper.

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

-We will rephrase this: We now will mention that best agreements between observed and modeled AMDEs were achieved using rate constants between GEM and Br and BrO of 1.5x10-13 and 1.0 x 10-13, respectively. Then, we will clarify that based on these kinetics, BrO was found to be the dominant oxidant under Dead Sea conditions.

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.

-Again, we will add the stipulation "using the rate constants that best explained ob-

served AMDEs under Dead Sea conditions". Please also see our previous response relating to the new figure and table in this document. This, together with Fig. 7 are strongly support that BrO is the dominant oxidant under the Dead Sea conditions.

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?

-Yes, we mention this in Section 2.3. Please see justification for including these fluxes in our response to "Pg 24473 lines 20-25". GEM levels after the AMDEs would remain low as our model does not include source terms such as surface emissions or photoreduction of oxidized mercury, nor advection fluxes. Please note that no fluxes were added during the periods of AMDEs in any of our simulations

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?

-We now consistently describe it as "negative correlation between O3 and Br/BrO ratios (instead of positive correlations between O3 and BrO/Br ratios) in order to be consistent with Figure 3. We also reference two other paper that reported this relationship (Wayne et al., 1995 and Tas et al., 2006).

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

-We will change this.

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.

-We agree that the figure is too complicated and does not present a good comparison between model and observed data, and we hence delete this Figure. Instead, we added a new figure showing how modeled and measured data compared during the simulation days and during AMDEs.

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

-The purpose of this figure is to show the dependency of GEM depletion efficiency on BrO and GEM levels. The dependency was found to be very different between the two days due to inherently different BrO and GEM levels. It would be difficult (and confusing) to separate these data based on BrOX levels as we don't always observe negative correlations between BrO and GEM (as mentioned above).

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.

-We will address this point in the revised manuscript as responded above.

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).

-Reaction G15 should be marked as a multistage reaction according to Hall and Bloom (1993). The reference for this reaction will be corrected accordingly. Even though HgOBr appears as an optional product in Raofie and Ariya, 2004), there is a large degree of uncertainty regarding this product. In any case, the product appears to be formed predominantly in the condensed phase. Recent studies therefore included

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HgO as the only predominant product of this reaction (e.g., Shon et al., 2005; Xie et al., 2008). It should be further emphasized that our "L Br H BrO HgOp" simulation is identical to the "BASE" simulation, except that the reaction of BrO and Hg was assumed to yield only HgO(s), particulate HgO, which is completely removed from the system.(Sect. 2.3). This enabled as to demonstrate that even if all the produced HgO was treated as a termination product, which cannot contribute to recovery of GEM via heterogeneous recycling, no significant change in the depletion rate of GEM occurred compared with the BASE simulation for Julian days 188 and 201 (Figs 1 and 2). Therefore the fact that HgOBr was not included in the chemical mechanism appears to not being in conflict with the result that BrO is the predominant oxidant of GEM in the troposphere.

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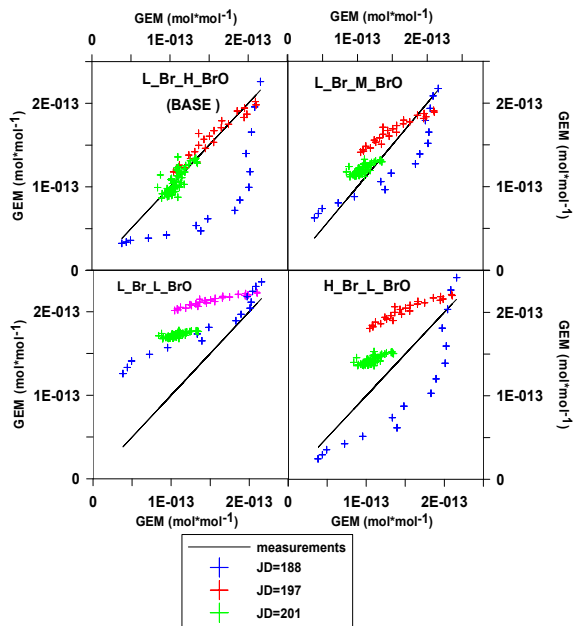Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24467, 2011.

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Fig. 1. Simulated vs. measured GEM depletion rates during AMDEs