

## ***Interactive comment on “Measurement-based modeling of bromine chemistry in the boundary layer: 1. Bromine chemistry at the Dead Sea” by E. Tas et al.***

**E. Tas et al.**

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We thank the reviewer for the level of attention given to our paper and for the relevant and detailed comments. Many of the reviewer comments indicate that a number of points presented in our paper were not entirely clear. Our responses to the reviewer's comments clarify these issues point by point, and most of these explanations will be incorporated into the revision of the paper. In general we believe that our paper presents new information and a better understanding of the topic but it needs editing for clarity.

We would sincerely appreciate further comments from the reviewer on any issue that still remain unclear.

Methodical problems:

1. The main purpose of this study was to establish for the first time a basic description of the RBS activity at the Dead Sea. We found the one-dimensional gas-phase model (one-dimensional Chemical Transport Model, UAHCTM\_1D) (Pour Biazar, 1995) to be appropriate for this purpose.

Previous research (Stutz et al., 1999; Matveev et al. 2001, Tas et al., 2003 and Tas et al., 2005) has shown that these two processes were expected to have a very significant influence on Reactive Bromine Species (RBS) chemistry. These studies suggested that the ‘Bromine Explosion’ mechanism is the most probable process of Br release into the gas phase. The heterogeneous decomposition of BrONO<sub>2</sub> was suggested as an important process basing on the relatively high NO<sub>2</sub> concentrations at the area of the Dead Sea. The model simulations indeed showed the necessity of the addition of two heterogeneous processes (H1 and H2) to the gas phase mechanism in order to account for the observed measurements. One of the major contributions of this paper is to demonstrate that the addition of only these two heterogeneous reactions - the heterogeneous decomposition of BrONO<sub>2</sub> (H1) and the ‘Bromine Explosion’ mechanism (H2) are not only necessary but also sufficient to reconstruct the BrO time-series measured at the Dead Sea (see section 3.1.2, Figs. 3 and 4). Other heterogeneous reactions may take place at the Dead Sea, however our simulations showed that their role in the RBS chemistry at this area expected to be less significant.

In addition to the fact that the inclusion of these two reactions was crucial for obtaining reasonable validation of the model (see section 3.1.2, figures 3 and 4) there are other important indications that the heterogeneous decomposition of BrONO<sub>2</sub> (reaction H1) plays a central role in the RBS chemistry at the Dead Sea:

a. Due to the relatively high levels of NO<sub>2</sub> at the Dead Sea the heterogeneous decomposition of BrONO<sub>2</sub> is essential to explain the low levels of BrONO<sub>2</sub> measured (Peleg et al unpublished data, Dead Sea ,2006) at the Dead Sea. If the heterogeneous decomposition of BrONO<sub>2</sub> was not included in the model, the simulated levels of BrONO<sub>2</sub> were unrealistically high.

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b. The present research has shown that the conversion of NO<sub>2</sub> to NO<sub>z</sub> (on the order of ~2ppbv) detected during the measurements (see section 3.6, P. 4949, lines 14-28 and P.4950, lines 1-8) can be explained by the formation of the stable product, HNO<sub>3</sub>, detected as part of NO<sub>z</sub>. As far as we know there are no other reactions that can account for such dramatic depletion of NO<sub>2</sub> with a simultaneous increase in NO<sub>z</sub> concentrations.

2 Reactions H1 and H2 were included in the model by first order parameterization according to the well known expression, presented by equation 3 (i.e.,  $R = (Y < c > A) / 4$ ) (e.g., Atkinson et al., 1997, P. 963).

Regarding reaction H1:

The inclusion of reaction H1 as a simplified parameterization is justified since its rate is relatively insensitive to external physical and chemical conditions, as stated in the paper: ‘Studies have shown that the dependence of the rate of reaction H1 on atmospheric conditions is essentially very weak (Hanson et al., 1996). The uptake coefficient for this reaction is only slightly dependent on particle size, composition of sulfuric acid, and temperature (Hanson et al., 1996; Hanson and Ravishankara, 1995)’. (P. 4935, lines 5-8). In addition to that, ‘The first order rate constant for reaction H1 was based on direct measurements (Matveev et al., 2001) of sulfate aerosol concentrations’ (P. 4935, lines 10-12).

With respect to the reviewer comments regarding the total sulfate aerosols calculations we provide the following additional data: The total surface area of the sulfate aerosols was estimated based on measured concentrations of sulfate aerosols (Matveev et al., 2001), the average value for the sulfate aerosols density and the average radius of the sulfate aerosol. The total surface area values used are in the range of 50-65 ug/cm<sup>3</sup>.

Any other missing data regarding the heterogeneous parameterization can be provided if necessary.

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In order to clarify the comment regarding the method by which parameterizations were taken into account the following explanations are provided and may be included in the paper:

Regarding reaction H2:

The rate constant for reaction H2 was determined based on comparison of model simulations and measurements. The rate of reaction H2 is a degree of freedom in the structure of the model. Basically, the average rate was modified (by multiplying the rate at each update time by the same factor) until an agreement obtained between the simulated and measured BrO time series. 'The average rate obtained for reaction H2 was  $\sim 1.35 \cdot 10^{-6}$  ppb/s', in good agreement with reported values' (P. 4936, lines 14-15). Further, model simulations have shown that the results are relatively insensitive to the timing of changes of the rate of reaction H2.

Model simulations showed that reaction H2 is necessary to provide the exponential growth in bromine concentrations required in order to match the simulations to the measurements. However, even if reaction H2 is not included in the model, the model is successful in describing the changes of BrO with time as long as Br2 flux was appropriately included\* (Fig. 3c). The importance of reaction H2 is to provide sufficient levels of Br2, but the timing of this addition does not affect the model results significantly (see Figs. 3c and 3d). Therefore, it is not necessary to describe the changes of reaction H2 with time beyond the simple parameterization used here.

We agree with the reviewer that more detailed information about the wind speed and wind direction parameterizations should be provided as shown below:

As stated above, the results were relatively insensitive to diurnal changes in the rate of reaction H2. Two parameterizations were included in the rate of reaction H2 in order to test the influence of wind speed and wind direction on the results as explained below. However, the results were insensitive to both these parameterizations. Thus, although these parameterizations were included in the 'FULL' simulation, they did not lead to any

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significant change in the results. Therefore, in our opinion it may be more correct not to include a detailed information about these parameterizations and to include only the statement that the model results were insensitive to these parameterizations. However, the procedure used in order to include these parameterizations is described as follows:

It should be emphasized that the average 24h value of reaction H2 rate was not changed due to the wind speed and wind direction parameterizations.

Wind speed parameterization: The rate of reaction H2 was modified every 15 minutes (the update time interval of the model) to reflect the influence of wind speed using equation 4 (P. 4936, lines 16-18 and P. 4937, line 1), making sure that the average 24h value of reaction H2 matched the value obtained from the model, as a degree of freedom (as was explained above). Different parameters for equation 4 were taken from Gong et al, 1983.

Wind direction parameterization: The Wind direction parameterization was obtained by the same procedure as described for the wind speed parameterization, employing the expression  $\langle \text{BrO} \rangle \cdot n(i)/n(i)$  (P. 4936, line 7) instead of equation 4 in order to account for the influence of the wind direction on the rate of reaction H2. A positive correlation relation between the magnitude of this expression and the rate of reaction H2 was assumed. For 'FULL' (see Table.4). simulation a linear relation between this expression and the rate of reaction H2 was assumed. The rate of reaction H2 was insensitive to this linear relation as well as for other relations that were checked.

\* In Fig. 3c it should be mentioned that the Br2 was normalized to the actinic flux as it is explained in Table. 4.

3. With respect to the comment regarding the fluxes added to the model, the following is provided to explain this question:

Since the model used in this work is only one-dimensional, it cannot account for external advection of chemical pollutant, and it was, therefore, necessary to add horizontal

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fluxes. The fluxes of NOX were determined based only on the measurements campaign that was performed at the (Dead Sea) evaporation ponds. Thus, they reflect real time conditions. The fluxes of hydrocarbons were determined based on another campaign that was performed at Ein Bokek site located about 25 km north of the evaporation ponds (P. 4938, lines 27-29).

The fluxes of NOX and hydrocarbons were determined based on days with no significant Reactive Halogen Species (RHS) activity. Dozens of iterations (base-case simulations) were performed for these days, in which the fluxes were modified until the model diurnal time-series matched those measured. These simulations were performed without including the bromine mechanisms. The resulting fluxes were then provided as input to simulations including the bromine mechanism.

The justifications and the method used for the inclusion of ozone fluxes in the model appear in the answer to the following comment and in sections 3.1.1 and 3.4 of the paper

None of the data used in order to determined the hydrocarbons or NOX fluxes were taken from measurements performed at Metzoke Dragot. The only data from Metzoke Dragot presented in this paper was used for the comparison of NOZ to NO2 at this site.

As can be understood from the above description, the NOX and hydrocarbons fluxes where changed from one update time to the another within the same day, but the same fluxes were used for each of the simulations.

4. One of the most important conclusions of our study is that ozone fluxes must be added into the area of the evaporation ponds in order to enable the model to reconstruct the diurnal profiles of ozone and BrO that are unique to the Dead Sea, and the relation between them. We agree with the reviewer that the magnitude of ozone concentrations is important for BrO mixing ratios. It appears that our choice of the phrase 'relatively insensitive' was misleading, and did not explain our ideas correctly. Our intent was that BrO is much more sensitive to changes in O3 concentrations at very low levels of

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ozone in the following way: When O<sub>3</sub> drops below a threshold level of ~ 1 to 2 ppb, the Br chemistry is driven to termination, and the most significant effects on levels of BrO occur when O<sub>3</sub> concentrations cross this threshold. Therefore, the times at which O<sub>3</sub> crosses this threshold have the greatest influence on BrO levels. For this reason we focused our attention on these times. The changes in O<sub>3</sub> concentrations at the Dead Sea are so extreme compared to other regions of RHS activity, and occur faster so that they couldnt be captured by the model due to adjustment limitations. Since the threshold level is the most important range of ozone concentrations, and because the model has a difficulty in capturing the extremes of the ozone time series, we chose to focus on the timing at which O<sub>3</sub> concentrations crossed the threshold level of ~1 to 2 ppb. This approach led to a good agreement between simulations and measurements (Fig. 4, section 3.1.2).

The difference in ozone concentrations from the measurements and the simulations are most likely an overestimation, considering that the O<sub>3</sub> measurements were conducted at the edge of the evaporation ponds, while the simulated BrO was affected by the ozone concentrations over the evaporation ponds (P. 4940 22-27).

The airmass that moves along the DOAS light path and over the ozone monitor is the same (P.4938, lines 8-15). Since ozone does not regenerate in some minutes, it is highly probable that fresh air masses, containing higher levels of ozone, mix with the air masses advected over the evaporation ponds in the areas outside of the evaporation ponds. Thus, the ozone measured by the monitor (at the edge of the ponds) will show higher concentrations than expected from the model.

With respect to the reviewer comment regarding the inclusion of the inert species 'X':

' Ëthe contribution of each reaction to the formation of its products was investigated by including an inert species as an additional product in the reaction. For example, reaction (G1) appeared in the model as  $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 + \text{X}$ , where X is an inert gas product specific to reaction (G1)' (P. 4937, lines 11-14)' There are two reasons for

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the use of an inert species (X) in the simulations: a.' The obtained magnitude,  $D[X]/Dt$ , is the actual contribution of the reaction to the formation of its products, including the influence of atmospheric dynamic and deposition velocity of the products. Thus, this magnitude includes additional information than that obtained by direct calculation of the reaction rate' (P.4937, lines 17-20).

With respect to the reviewer comment regarding the ability of species X to be transported or deposited:

The species X is transported and deposited since it was defined in such a way in the model.

b. ' ĘAnother advantage is that it was calculated with the same time resolution as the model time step' (P. 4937, lines 20-21). Thus, in term of a time resolution, the magnitude  $D[X]/Dt$  provides more accurate description of the contribution of a specific reaction to yield its products.

5. The present study focused only on simulations at ground level . The description of the vertical profiles was beyond the scope of the present study.

The one-dimensional model was used for two reasons: 1. to provide a better modeling of the ground level meteorological parameters. 2. to provide a basis for further studies including vertical profiles.

If required, details regarding the vertical parameters used in the model can be provided.

Further major points:

1. Both of the heterogeneous processes H1 and H2 have been mentioned in other papers. However, the present study presents the significant influence of these two reactions as they appear together as in Cycle 3b. To the best of our knowledge, this is the first time that this cycle is presented.

Under most of the existing atmospheric chemistry conditions we predict that Cycle

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3b will be significantly enhanced under higher NOX levels (see section 3.6, P.4950, lines 9-29 and P.4951, lines 1-24). Thus, Cycle 3b is predicted to be much more important in other mid-latitude areas than in to polar regions. Because of the enhanced potential for BrOX production, together with its sensitivity to NOX levels, this cycle represents an important link in the interaction between photochemical air pollution and RBS chemistry.

2. We agree that it is not surprising that ‘Ėat the Dead Sea, O3 can occasionally function as a limiting factor in the formation and recycling of BrOXĖ (P.4944, lines 23-24). It is the implications derived from this effect that are very important. This point should be included in the text in a clearer way, as follows.

Since at the Dead Sea ozone drops frequently below the termination threshold value (~ 1 to 2 ppb), extreme transitions between Br termination to the absence of termination occur. This lead to the repeated penetration of ozone fluxes into the center of the evaporation ponds, alternating with enhanced destruction of O3 to near zero levels. This cyclical process leads to the unique profiles of O3 and BrO. Based on this cyclic process our presentation of the mechanism of the RBS chemistry explains the negative correlation between BrO concentrations and O3 concentrations for higher O3 concentrations, as well as the apparently unexpected positive correlation between BrO concentrations and O3 concentrations obtained for low O3 concentrations (see section 3.1.1:P. 4939, lines 18-26 and P. 4940, lines 1-10 and section 3.4: P. 4946 lines 24-29 and P. 4947, lines1-3).

The termination threshold level ~1 to 2 ppb was determined based on the model simulations and kinetic calculations. At these low concentrations the termination reactions of Br become faster than the reaction of Br with ozone, and dominate the fate of Br. Below this threshold value RBS chemistry tends to terminate.

This tendency toward termination below this threshold value was described by the model simulations (see Fig. 7, section 3.4). The threshold value was calculated from

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measured concentrations and relevant reaction rates. Additional explanations regarding the method used to determine this value, can be included in detail in the paper if necessary.

3. The changes in Br concentrations with time serve as a chemical regulator for the entrainment of ozone fluxes. It does not mean that these changes in time of Br concentrations influence the entrainment of air masses, however they influence the levels of ozone in these advected air masses. This issue is explained in detail in section 3.4.

4. The reason for the morning peaks in figures 3a and 3b, was not explained in the text, since at the present it is still speculative. It may possibly be due to the fast photochemical decomposition of BrONO<sub>2</sub> at early morning in those simulations (NOHET, NOH1) that do not include the heterogeneous decomposition of BrONO<sub>2</sub> (reaction H1). This issue can be further investigated and be included if required. The strong structure of BrO in figures 3c and 3d is the result of the sensitivity of BrOX (BrO+Br) levels to the ozone concentrations as they cross the threshold value of ~1 to 2 ppb. In simulations that include the decomposition of BrONO<sub>2</sub>, more efficient production/recycling of Br occurs resulting in greater rate of ozone depletions. Thus, in these simulations the ozone frequently crosses the threshold value of ~1-2 ppb, resulting in the strong BrO structure.

Indeed, the difference between figure 3c and 3d looks nearly negligible, however, the comment included in the caption of figure 3 should be taken into account: 'In plots a, b and c, the Br<sub>2</sub> flux was multiplied by ~109 (see caption of Fig. 3).' Thus, although these diurnal profiles are the same, it should be understood that the profile obtained by simulation 'NOH2' was obtained by multiplying the Br<sub>2</sub> fluxes by an unrealistic factor of about 109, while in the 'FULL' simulation only a negligible Br<sub>2</sub> flux of maximum 10 molecules/(cm<sup>2</sup>\*s) was used. This information should be made more clear in the caption of Figure 3.

5. The 'Sum Br' does not have an initial value of about 400 ppt. The time series

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in figure 6 represents diurnal profiles of different bromine species that were obtained for 'FULL' simulation. These profiles represent the concentrations that were obtained in equilibrium, after repeatedly running the model, for 24 hours time periods with the same data. Thus, the initial concentrations obtained in these profiles, represent the concentrations that were obtained during the night, as a result of the RBS activity during the daytime (of Julian day 221). We agree that this point should be explained better in the text.

6. It should be noted that the contribution of reaction H2 to the production of Br is exponential rather than linear. 'The reason for the importance of cycle 3b is that it leads to a nearly exponential growth of Br production via reaction H2...' (Page 4949, lines 5-6). There is no other source of bromine in the model. This could be explained more clearly in the paper.

7. It was thought that separating section 3 into subsections might be more helpful for the reader. However this issue can be reconsidered and this section will be edited for clarity. Unnecessary repetitions will be deleted as suggested. Regarding the content of the second half of section 3.6: we believe it is important to summarize the significance of the heterogeneous processes with respect to other mid-latitude areas, at this point. We are open to changes in the structure of section 3 under the recommendations of the editors/reviewers.

Minor points comments:

3. 'The simulated results were relatively insensitive to the parameterization of wind speed  $\tilde{E}$ ' (P.4941, line 13), Indicating that the sea salt aerosol concentrations are independent of wind speed. The reason for this may be: '...that the sea salt aerosols are not the only source of airborne Br, and that Br may be released directly from the seawater or from salt pans by reaction (H2)' (P. 4941, lines 14-16). In addition to that, it should be remarked again that the model simulations showed that the BrO profile is insensitive to changes in the rate of reaction H2 (see answer to comment 2 in the methodical prob-

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lems section). To the best of our understanding the 'Bromine Explosion' mechanism is taking place at the Dead Sea (see answer to comment 1 in the methodical problems section). However, the physical form in which this takes place is still speculative.

4. 'This may imply that the sea salt aerosols are not the only source of airborne Br' (P. 4941, lines 14-15). In the model it was assumed that the 'Bromine Explosion' mechanism (reaction H2) is taking place. Reaction H2 is centrally important, but it is not clear exactly how it occurs and on which surfaces. In the model it was assumed that reaction H2 took place in sea salt aerosols, but H2 could release Br into the gas phase by other physical process. For example, if Br were released from sea water or salt surfaces with similar release rates, the same results would be observed. This should be the subject of future research.

5 OBrO was included in section 3.3, figure 6 in order to show its negligible contribution.

6 We accept the suggestion of replacing the expression 'profiles' with the expression 'time-series'.

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