

## ***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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Many thanks once again to referee 1 for the time and effort and for the level of attention invested in the review of our manuscript. It seems that some important issues are still not entirely clear. Before we answer each of the comments individually, we thought it best to explain those aspects of the model that were not presented adequately in the original manuscript and in our previous responses. We will clarify these issues in the revised version of the manuscript.

- The model is unconstrained: Both referees repeatedly mention that the model is constrained in a variety of ways. We must first clarify that the model was not constrained at all, including reaction rates and concentrations of species, and that the inclusion of

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fluxes was not done as a constraint on the system. Reaction H2 was the only degree of freedom allowed in the model, and was determined as explained below.

- The scope of the research: Second, we must clarify that the purpose of the present paper was not to provide a complete and detailed description of the Reactive Bromine Species (RBS) chemistry at the Dead Sea area. Instead, our main objective was to establish for the first time a basic description of the RBS chemistry at the Dead Sea, and to identify those parameters that are the most important in determining the overall structure of RBS chemistry at this location. In order to accomplish this, we created a model that could simulate correctly the basic photochemistry at the Dead Sea and also describe the RBS chemistry that occurs there. Since this system had not been successfully modeled in the past, we chose a model that could reproduce the gas phase chemistry as accurately as possible in a detailed and straightforward way. This model can then incorporate the important heterogeneous processes as a parameterization. The consideration of all possible heterogeneous reactions is therefore beyond the scope of this paper, and should be the focus of future research.

- Introduction of NO<sub>x</sub> and hydrocarbon fluxes: In order to provide a baseline for the concentrations of NO<sub>x</sub> and hydrocarbons (HC) at the Dead Sea, we had to describe the conditions that were prevalent on days when Reactive Halogen Species (RHS) were not active. We are interested in the fluxes that enter the area, rather than the concentrations of these species which are affected by the RHS. The fluxes of NO<sub>x</sub> and HC into the region were thus determined based on measurements taken on days with no evidence of significant activity of RHS at the evaporation ponds. This was done by performing dozens of preliminary simulations which did not include the RBS mechanism. These first stage results provided a reasonable agreement with estimates of hydrocarbon levels, and between the measured and simulated time series of ground level NO<sub>x</sub> and ozone for these days. The next stage was to run the model with the addition of the RBS mechanism using the same fluxes determined in the baseline scenario which did not include RBS activity. We assume that the external fluxes entering the evaporation

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ponds in the absence of RHS activity also represent the external fluxes on days with the RHS activity, since the RHS have no influence outside of the area in which they are present. In this way the model could incorporate the external contribution of NO<sub>x</sub> and HC into the RBS chemical system.

-Choice of heterogeneous processes: The basic gas phase model was not able to reproduce the results obtained from our measurements campaign at the Dead Sea evaporation ponds. Based on previous studies, two important heterogeneous mechanisms were identified and included in the model through a parameterization of their first order rate constant. These processes are the 'Bromine Explosion' and the heterogeneous decomposition of BrONO<sub>2</sub>. Previous research indicated that at the Dead Sea, the 'Bromine Explosion' is the most probable mechanism for the release of Br into the gas phase. The levels of NO<sub>2</sub> at the Dead Sea are high (several ppb) compared to the other sites where BrO was identified. Therefore, the formation and subsequent heterogeneous decomposition of BrONO<sub>2</sub> was suggested as an important process for recycling RBS at the Dead Sea (Tas et al., 2005).

-Characterization of "Bromine Explosion" (reaction H2) in the model: The rate constant of H2 was obtained as the only degree of freedom in the model, whereas all other reactions used in the model were calculated explicitly, and other parameters were provided as inputs. Initially, a reasonable rate for H2, based on the literature, was input into the model. During this first stage, the same value was used for all of the update times every 15 minutes during the entire day. This initial stage gave a good match between model results and measurements. A range of values for H2 was tested, and the final value which gave the best agreement between simulations and measurements was still in good agreement with the literature.

Only if the reaction rates were changed by about an order of magnitude, was there a major change in the behavior of the RBS chemical system in the model. This sensitivity analysis showed that the model was much less sensitive to changes in reaction H2 than to the rates of some other reactions, e.g. reaction H1.

The next stage of the analysis examined in greater detail the dependence of the ‘Bromine Explosion’ (H<sub>2</sub>) on aerosol concentrations. Equation 4 was used to calculate the aerosol concentrations from on-site field measurements of the wind speed at 10 m for each 15 minute update interval, and the rate of H<sub>2</sub> was modified accordingly, based on the relationship shown in Equation 3. The average rate constant of reaction H<sub>2</sub> was then compared to best value obtained in the initial stage, and then each value was normalized accordingly. Thus, the daily average value of the rate constant of reaction H<sub>2</sub> remained the same. A range of conditions was explored, and the results were shown to be insensitive to the wind speed and direction parameterizations.

-Introduction of ozone fluxes: Our simulations clearly indicated that the inclusion of the two heterogeneous reactions was necessary in order to account for the efficient production of BrO at the evaporation ponds, but it was insufficient in order to explain several observations in the BrO and ozone diurnal time series and the relationships between them (see sections 3.1, P. 4939, 4940 and section 3.4, P. 4946, lines 3-8, P. 4946, lines 22-29, P. 4947, lines 1-3). In particular, the repeated swift rise of ozone from near-zero levels could not be explained either by the photochemical gas phase reactions or the two heterogeneous processes. Based on the measurements and a comparison with model simulations it was obvious that ozone fluxes were being advected into the evaporation ponds during RBS activity, and that they must be added into the model (see sections 3.1.1 and 3.4). Since the model used in this work is one dimensional, it cannot account for external advection of chemical species, and it was, therefore, necessary to add horizontal O<sub>3</sub> fluxes during the simulations. The inclusion of these fluxes was performed based on direct measurements of ozone and thus it did not introduce a real constraint on the model. As explained in the paper and in our previous response, the BrO/ozone chemistry changes dramatically at a threshold level of ozone near about 1 to 2 ppb. The O<sub>3</sub> fluxes were added into the model in a time resolution of 15 minutes, and adjusted so that the simulated ozone trends near this threshold level were similar to the measured ozone trends.

In light of the preceding explanations, we provide the following responses to each of the referee's comments:

Methodical problems:

Comment 1. The model used in our study was sufficient for the purpose of the present paper, which was not to provide a full description of the RBS chemistry at the Dead Sea area. Our main objective was to establish for the first time a basic description of the RBS chemistry at the Dead Sea. Thus, our challenge was to identify the most influential factors on RBS activity, rather than ensuring that we included all possible interactions. The two heterogeneous processes that we included in the model were chosen because there were many indications that they were the most relevant (see our previous reply to the same comment of referee #1). Since the model was successful in describing the RBS activity with only these two processes included, we concluded that these two reactions are indeed important in the RBS chemistry at the Dead Sea, and should provide the basis for all further studies. We believe that we have achieved our objective of providing a basic description of the RBS chemistry, and have identified two important reactions that are sufficient (together with ozone fluxes) in order to provide this basic description. It will certainly be appropriate to explore the contributions of other reactions in future work, based on the mechanisms presented in this paper.

Regarding the issue of model constraining: The model that was used was definitely not constrained by the addition of fluxes, as explained above. The fluxes were a necessary addition to the model in order to provide the baseline concentrations of NO<sub>x</sub> and hydrocarbons. It was impossible to fix these concentrations on the days when RBS were active, since these concentrations are not the direct result of the fluxes that enter the area of RBS activity. They are instead changed by RBS activity, and must be entered into the model as an external source provided by fluxes. Thus, in order to provide a baseline for the concentrations of NO<sub>x</sub> and hydrocarbons, we had to describe the conditions that were prevalent on days when no RBS activity was present. Therefore, in the model, the fluxes were first established as a base case by running the model

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without the bromine chemistry, based on these days on which no RBS activity was observed. At the next stage the same fluxes were entered unchanged into the model which now included the RBS mechanism.

In addition to the fluxes of NOX and hydrocarbons, ozone fluxes were also included as explained in detail in sections 3.1.1 and 3.4, and in the reply to the first comments of referee #1 (methodical problems, comment no. 4). These fluxes were based on direct measurements of ozone concentrations at the site of the evaporation ponds at the Dead Sea. These fluxes should be included in every model aimed at describing the RBS activity at the Dead Sea, due to the entrainment of ozone fluxes into the area of the evaporation ponds (see sections 3.1.1 and 3.4). Finally, a negligible flux of Br<sub>2</sub> (10 molecules\*cm.<sup>-2</sup> s<sup>-1</sup>) was added for the initiation of the bromine species activity. This was done in order to provide the initial source of Br<sub>2</sub> for the RBS chemistry, which in reality comes from the salt pans, and/or the Dead Sea waters and/or from local sea salt aerosols.

In response to this comment we will emphasize in the text that the main objective of this study was to establish for the first time a basic description of the RBS activity at the Dead Sea, using this model. Furthermore, the technical, physical, and chemical aspects of the fluxes will be given in more detail in the revised version.

Comment 2. In order to clarify this point as much as possible, we will describe the overall process of obtaining the rate of the 'Bromine Explosion' mechanism (H2) from the model. The rate of H2 was obtained as the only degree of freedom in the model, whereas all other reactions used in the model were calculated explicitly. Initially, a reasonable rate for H2 was input into the model, based on the literature. During this first stage, the same value was used for all of the update times every 15 minutes during the entire day. This initial stage gave a good match between model results and measurements. A range of values for H2 was tested, and the final value which gave the best agreement between simulations and measurements was still in good agreement with the literature.

Only if the reaction rates were changed by more than a factor of 7, was there a major change in the behavior of the RBS chemical system in the model. This sensitivity analysis showed that the model was much less sensitive to changes in reaction H2 than to the rates of some other reactions, e.g. reaction H1 (see also Fig. 3).

Our assumption was that the ‘Bromine Explosion’ mechanism takes place mainly in sea salt aerosols (see section 2.1, P. 4935, lines 15–23). In order to investigate this issue on one hand and to take into account the influence of wind speed on the rate of reaction H2 on the other hand, the influence of the wind speed on the aerosols concentrations was taken into account. Thus, the next stage for obtaining the rate of H2 was to take the rate obtained in the previous stage and modify it every 15 minutes based on the changes in the concentrations of the aerosols. Equation 3 shows that there is a linear 1:1 relationship between the rate of H2 and the surface area of the aerosols. Therefore, the rate of H2 will increase directly with an increase in aerosol concentrations.

Equation 4 was used to calculate the aerosol concentrations from on-site field measurements of the wind speed at 10 m for each 15 minute update interval, and the rate of H2 was modified accordingly, based on the relationship shown in Equation 3. The average of the rates of H2, modified for changes in aerosol concentrations, was compared to the original value obtained in the first stage. Finally, each value of the modified rate of H2 was then normalized to the average rate of H2 obtained in stage 1, to keep the average rate of H2 consistent with the best fit for the model.

An important point that needs to be clarified is that the rate of H2 is not calculated, but is instead obtained as a degree of freedom in the model, by varying this rate, as was previously explained, in order to obtain the best match between simulations and measurements. All other reactions and parameters in the model were either calculated explicitly or entered into the model as inputs. Additional information is given in the reply to the first comments of referee 1, methodical problems, comment no. 2. This issue will be edited for clarity in the revised version.

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Comment 3. We would like to clarify again that none of the concentrations and reactions in the model were constrained, and we agree with the referees that such an approach should not be preferred. We will certainly ensure that this point is completely clear in the revised version of the manuscript.

There seems to be some confusion about the terms “fluxes” and “concentrations” and the process of adding the fluxes of NO<sub>x</sub> and hydrocarbons to the model. As explained above in detail in the introduction to this reply, none of the concentrations were fixed in the model. The concentrations of NO<sub>x</sub> and hydrocarbons could not be fixed in the model because they are affected by the reactions with the RBS. On the other hand, there must be a source of these compounds that is external to the model, because they are transported into the region and not created there. The introduction of these fluxes was thus based on measurements taken at the evaporation ponds on the days during which no RHS activity was observed, and simulations that did not include the RBS mechanisms. This was done in order to base the model on the amounts of these chemicals that enter the area, and not on those affected by the RHS. In summary of the process, the fluxes were first established as a base case without the RHS activity, and were then entered unchanged into the model, which now included the RBS mechanism. To the best of our judgment, this procedure is the best proxy for the physical mechanisms that occur in reality.

The focus in the present research was only on the ground level height, so all of the measurements were taken at ground level and were not vertically resolved. The results of the model were evaluated and presented for ground level only. The calculations of the model were resolved by height up to above the height of the inversion layer, and the fluxes were entered up to the height of the inversion layer. The magnitude of the fluxes at each height was estimated from the initial simulations in the absence of RBS chemistry. As described above, these fluxes were then used as input to the model in the next stage that included the RBS activity.

The exact vertical structure of the fluxes is not central to the issues explored in this

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manuscript, because they had only a marginal effect on the results of the model or the interactions among its constituent parts. The sensitivity of the results to meteorology was evaluated by changing parameters, including the height of the boundary layer and of the inversion layer, vertical temperature profile (stability conditions), and effects of wind direction and speed. No significant effect was observed on the results of the simulation. Furthermore, the phenomena caused by the RBS chemistry was much stronger and faster, and varied greatly compared to the effects of external effects such as the fluxes of NO<sub>x</sub> and hydrocarbons.

Comment 4. In our first reply to referee 1, we stated that we completely agree that in general, the magnitude of ozone concentrations, at all levels, does affect the amounts of BrO. Our main objective in this paper was to describe and explain the recurring major trends in the BrO time series, specifically the frequent and severe transitions between increases and decreases in BrO which form a jagged pattern (see Fig. 4). We showed that these transitions are controlled by ozone concentrations crossing a threshold value of  $\sim 1$  to 2 ppb (see our previous reply to referee #1, methodical problems, comment no. 4). In other words,  $d[\text{BrO}]/dt$  is positive for  $[\text{O}_3] > \sim 2$  ppb, and also,  $d[\text{BrO}]/dt$  is negative for  $[\text{O}_3] < \sim 1$  ppb.

We also agree that it is important to show that even though the high levels of ozone (greater than  $\sim 5$  ppb) are not described accurately in our model, our results and conclusions are robust and insensitive to this approximation. Referee 1 would like us to show that our conclusions would not be affected by changes in the concentrations of ozone ( $d[\text{O}_3]/dt$ ) above the threshold level of  $\sim 1$  to 2 ppb. In other words, that the effects on  $d[\text{BrO}]/dt$  caused by  $d[\text{O}_3]/dt$  near the threshold level are much more significant than for  $d[\text{O}_3]/dt$  at higher ozone levels.

In order to perform such a sensitivity analysis, one should compare  $d[\text{BrO}]/dt$  at different levels of ozone, and the concurrent  $d[\text{O}_3]/dt$ . Our results provide such a comparison, and clearly show that for concentrations of ozone of  $\sim 1$  to 2 ppb, even a small  $d[\text{O}_3]/dt$  has a tremendous impact on  $d[\text{BrO}]/dt$  (Fig. 7). For example, a drop

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in ozone from above the threshold level to below this threshold causes a change in  $d[\text{BrO}]/dt$  from positive to negative. Conversely, a rise in ozone to above the threshold changes  $d[\text{BrO}]/dt$  from negative to positive. In contrast, any of the changes in ozone at higher levels do not lead to such extreme changes in  $d[\text{BrO}]/dt$ , indicating that our conclusions are not sensitive to the actual ozone concentrations at high levels. These observations are confirmed by the model results for the two other simulations describing RBS activity in two other days, and which were not presented in the paper due to space limitations.

In addition to the data presented in the paper, earlier stages of the modeling process tested the effects of much higher concentrations of ozone. At these ozone levels, even a large  $d[\text{O}_3]/dt$  did not lead to a jagged shape of the BrO concentrations, and the BrO time series were inconsistent with BrO measurements.

We contend that, taken together, all of these observations demonstrate that our description of BrO concentrations, and our explanation of their jagged shape, are robust and insensitive to the inaccuracies in the magnitude of ozone concentrations at high levels (above  $\sim 5$  ppb). We will expand our description in the revised version and we will state that these effects were also observed on the two other days for which simulations were performed.

The use of the inert species X in the model provides, for each individual reaction, a direct measure of its rate and products at any given grid point and any given time. Once this inert species is formed in the model, its concentration cannot be affected by other reactions, but is affected by the physical processes incorporated into the model, e.g. dispersion, advection, and deposition. In practice, this approach is used in order to compare the time series of the reaction rate, represented by the magnitude  $D[X]/Dt$ , with the modeled concentrations of a product which was formed by this reaction. This comparison provides information on the direct contribution of the reaction to form its products, because once this inert species is formed in the model, its concentrations can only be changed due to physical processes incorporated into the model. Thus, the

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chemical effects can be isolated from the physical effects because species X is subject to the same physical effects as the product of the reaction.

For example, reaction G1 is defined in the model as  $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 + \text{X}$ .  $D[\text{X}]/Dt$  represents the de facto rate of creation of the products of reaction G1, modified by the physical effects of deposition and dispersion. If we want to evaluate the contribution of this reaction to the concentration of BrO, we compare the time series of the magnitude  $D[\text{X}]/Dt$  with the time series of BrO. A value of 0 cm/s will be defined for the deposition velocity of X, since this is the deposition value that was defined for BrO. An important advantage of this method is that the same atmospheric dynamic processes that influence BrO concentrations have the same influence on  $D[\text{X}]/Dt$ .

‘Another advantage that was given in the paper and the reply to referee 1 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  $D[\text{X}]/Dt$  provides more accurate description of the contribution of a specific reaction to yield its products.

The explanation given in the text for the advantages of the usage of the inert species X and the technical method by which it was done will be edited for clarity in the revised version .

Comment 5. We agree that this information is important and we will include details regarding the vertical model resolution in the revised manuscript. We will also state clearly that the results are only shown for ground level where the measurements were taken.

Further major points:

1. We agree that Cycles 1 and 2 should be included in the introductory section. However, Cycle 3 belongs in the results and discussion section, because it presents for the first time a coherent cyclical unit of RBS chemistry, and, furthermore, it is shown to be a central component of this chemistry in a physical location.

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To the best of our knowledge, this combination of reactions was not yet presented as an integrated process. It emphasizes the combined effect of H1 and H2 on the production of Br, the sensitivity of this combined process to anthropogenic NO<sub>2</sub>, and enables us to establish a variety of chemical parameters: the rate limiting step, the net of the reaction cycle, and those parameters to which these processes are sensitive. Beyond the theoretical contribution to the understanding of RBS chemistry, our paper demonstrates the validity of this cycle in a physical location - the Dead Sea - that happens to provide the conditions that enhance the importance of this cycle, in particular the levels of NO<sub>2</sub> which are high relative than at other RBS activity locations. One of the purposes of this paper is to present this chemical cycle so that it may be considered for studies of other areas with RBS activity, especially in mid-latitudes.

2. We agree that the explanations regarding the threshold level should be improved. This threshold level of about 1 to 2 ppb was determined based on both model kinetic calculations and model simulations (see our previous reply to this comment of referee #1). Information on how this threshold value was determined will be included in the new manuscript version. Relevant comments and responses presented here will provide the basis for this explanation.

3. The respective parts will be reworded.

4. The morning peak in BrO will be discussed although this peak (see Figs. 3 c and d) is not a special interest at the Dead Sea, because in this area the BrO profile contains several other peaks during RBS activity time. This is due the cyclic periodic process described in section 3.4 which leads alternately to the efficient production of BrO and then to its fast destruction. We will include a short discussion regarding this point in the revised version. It should also be remarked that the peak which is strongly evident in figure 3a and 3b does not appear in the measurements, and only appeared for incomplete stages of the model simulations.

The explanation for the strong structure in BrO concentrations, as shown in Fig. 3

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c,d, is a central goal of this paper: this is what we refer to as the “jagged shape” and the extreme changes in BrO concentrations. This subject is discussed in sections 3.1.1 and 3.4 In the revised version the discussion may also be based on Fig. 3. The unrealistically high Br<sub>2</sub> fluxes were needed in those modeling scenarios that did not include both heterogeneous mechanisms H1 and H2. Adding unrealistic values of Br<sub>2</sub> fluxes is an indication that the model is not complete and must be improved. Once both heterogeneous reactions and the ozone fluxes are added, only an initiation of the Br chemistry is needed, demonstrating that this scenario of the model is capable of describing the RBS chemistry. This issue will be discussed in greater clarity.

6. The sharp increase in BrOX and BrO concentrations between 7:30am and 08:15am is higher than one should expect by looking only on figure 8. This is mainly due to two reasons:

a. Between 07:15 and 8:15 am the concentrations of HOBr are still high, in the level of about 125 to 300 ppt. Shortly after, the concentrations of HOBr deplete very sharply, reaching levels of about 10 ppt (see Fig. 6). Based on these high levels and the photochemical decomposition rate of HOBr, in the order of  $\sim 1 \cdot 10^{-3}$ , the photolysis of HOBr may account for about 450 to 1080 ppt of Br atoms which can then potentially react with O<sub>3</sub> to yield BrO.

b. While looking at Figure 8 it should be taken into account that the contribution of reaction H2 to the production of Br is nearly exponential rather than linear. Each Br atom in the reactant HOBr molecule leads to the release of two Br atoms in the form of Br<sub>2</sub>. Thus, the rate of production of Br by reaction H2 is higher than the reaction rate of H2 that appear in figure 8.

It should be emphasized again that there is no other source of bromine in the model. The role of the photolysis of HOBr via Cycle 3a will be discussed in more detail in the revised version.

Minor points:

3./4. We agree that model results should be distinguished from ideas inferred from the results. We will clearly distinguish them in the revised version.

References:

Tas, E., Peleg, M., Matveev, V., Zingler, J., and Luria, M.: Frequency and extent of bromine oxide formation over the Dead Sea, *J. Geophys. Res.*, Vol. 110, No. D11, D11304 10.1029/2004JD005665,2005.

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