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Atmospheric
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Discussions

Interactive comment on “Modelling chemistry over the Dead Sea: bromine and ozone chemistry” *by* L. Smoydzin and R. von Glasow

L. Smoydzin and R. von Glasow

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Reply to comment (1) by E. Tas

The Reply to the second comment by E. Tas is also included in this document.
Thank you very much for your comment.
We followed the suggestion of Referee 1 for the revised version of the manuscript and list the major differences between our model study and the study by Tas et al. (2006) in a tabular form.

(1a)

The authors claim incorrectly that Tas et al. (2006) stated that the only source for the high bromine levels is the Bromine Explosion reaction taking place within sea salt aerosols.

This is defiantly wrong, and must be corrected in the text. It was explicitly stated by Tas et al. 2006 that: In the present simulation study, it was assumed that Br2 was released solely from the sea salt aerosols.
This is not necessarily true, since it is also possible that part of the Br2 is released directly from the water or salt surfaces (Sect. 3.1.2), or from sulfate aerosols (Von Glasow et al., 2002; Fan and Jacob, 1992).

>> Tas et al., 2006 assumed for their model setup that Br2 was released solely from the sea salt aerosols. And further it is written in Tas et al., 2006 (p.5593): *"As supported by the model results, the release from sea salt aerosols is assumed to be the major contributor because there were limited solid salt depositions in the investigation region."*
As this is one of the main differences in the approach by Tas et al. (2006) and our model approach, we must clearly point out this aspect. We do not claim that Tas et al., 2006 missed the **discussion** of a different bromine source but we point out that they only **included** this one Br_2 source in their model setups. We only want to compare the different results of different studies and not the discussion of the results. As the results by Tas et al., 2006 must be based on their model simulations (assuming that Br_2 was released solely from the sea salt aerosols) we think our statement is correct.

(1b)
Therefore we kindly ask the authors to exclude or change their statement that (P. 4527, lines 18-21: A recent model study by Tas et al. (2006) claims that the only source for the high bromine levels is the bromine explosion reaction taking place within sea salt aerosols which are emitted from the Dead Sea water and the related release of bromine species out of these aerosol particles.

>> We rephrased the section to point out more clearly that our statement refers to the model approach by Tas et al.(2006):

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"A recent model study by Tas et al. (2006) tries to explain the high bromine levels observed at the Dead Sea by using a model setup including only the source for gas phase bromine by the release of bromine species from sea salt aerosols which are emitted from the Dead Sea water. They suggest that sea salt aerosols are the predominant source of bromine for the atmosphere above the Dead Sea.**"**

(2)

The authors claim that Tas et al. (2006) chose the rate of this reaction in a way that it will fit better to the measurements. It was demonstrated by Tas et al. (2006) that the model results were not sensitive to changes in time of the rate of Br2 production by this reaction. Furthermore, it was shown that the exclusion of this reaction did not influence the diurnal profiles of BrO, in terms of correlation with the measured BrO. Only the levels of BrO were changed but not the diurnal profile shape.
This reaction was included in our model simulation only in order to supply the realistic amount of Br2, which, in fact, could be contributed also by additional sources, as explicitly stated by Tas et al. (2006), and also in order to investigate what is the release rate of bromine into the gas phase that can account for the RBS activity at the Dead Sea.
Therefore we kindly ask the authors to exclude or change their statement that (P.4550, lines 14-17) : In general, it has to be questioned that, choosing this reaction rate as the only degree of freedom in a numerical model, as done by Tas et al. (2006), and varying this rate until model simulations agree best with measurements is an appropriate approach to explain observations.

>> Our statement regarding the difference in reaction rates in Tas et al., 2006 and our approach refers to the following statement in your article (Tas et al. 2006, p.5593, left column):
"The rate of Reaction (H2, HOBr $+ H^{+} + Br^{-}$ $Br_{2} + H_{2}O$*) was obtained as the only*

degree of freedom in the structure of the model. A range of values for Reaction (H2) was tested, and the best agreement between simulations and measurements was obtained for a daily average value of $\sim 1.35\text{x}10^{-6}$ *ppb/s."*

We think that simulating a realistic source strength of Br_2 is crucial in order to achieve a detailed understanding of the process underlying the release of bromine and that this is a key issue of investigating bromine chemistry in the Dead Sea area.

As you have written yourself in the comment, changing the reaction rate for reaction (H2) leads to different BrO levels in the work by Tas et al., 2006. The investigation of how these high BrO levels can be build up is one of the key questions addressed by Tas et al, 2006 as well as in our paper. Thus changing the reaction rate **has** indeed a significant impact on your results.

A primary focus of our work (and as far as we understood as well of the work by Tas et al., 2006) is to simulate the high BrO levels, not the exact diurnal evolution of a specific day.

From the description in Tas et al., 2006, we understand, that they must prescribe the source of Br_2 in their model as they do not explicitly calculate aqueous phase chemistry. However, we point out that when we calculate aqueous phase chemistry explicitly (and include an additional source for Br_2 by direct degassing out of the Dead Sea water), we come to the conclusion that with the assumptions made by Tas et al., 2006, they overestimate the release of Br_2 by sea salt aerosols. We understand that by your approach you want to test how large the flux of Br_2 from sea salt aerosols must be in order to simulate high BrO levels. However, under the ambient conditions (low relative humidity, high temperature) it is not possible to release this amount of Br_2 from sea salt aerosols. We can establish this statement, as we can calculate chemistry explicitly in the aqueous phase and thus the release of Br_2 into the gas phase.

Thus we compare the (parameterised) source for gas phase Br_2 as used by Tas et al., 2006 and our (explicitly calculated) source for gas phase Br_2 and come to the conclusion that it is very likely that Tas et al., 2006 overestimate the importance of this source under the prevailing conditions at the Dead Sea.

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In none of the cases we simulated, the release of Br_2 out of sea salt aerosols was sufficient to obtain BrO mixing ratios in the order of about 60-100 pmol/mol. This was still true if the relative humidity was increased to a certain extent and the temperature decreased (still in a realistic range for Dead Sea conditions) or the wind speed increased compared to the values we report in our article.
Even in cases, where we increased the wind speed which lead to an increase in the number of sea salt aerosols in the boundary layer, the total amount of aerosol phase Br^- available in the boundary layer is simply not sufficient to release enough Br_2 (or in addition BrCl) to the gas phase in order to produce BrO mixing ratios in the order of about 50 pmol/mol. Calculating scenario NOEX with a wind speed exceeding 15 m/s constantly, BrO mixing ratios at 2 m altitude increased up to a maximum value of 5 pmol/mol after 6 hours of simulation time. Furthermore, in southerly air masses, the fetch over the salt pans where salt aerosols can be released from is rather small, implying that overall not enough bromine can be released.
Please, refer further to point (4) in the reply to Referee 2.
We have extended and improved the discussion of this issue in the revised manuscript.

(3)
The authors claim that Tas et al. (2006) chose an unrealistic value for the Bromine Explosion mechanism. This is not correct, because this value was not chosen, but was found to be most appropriate according the measurements and model simulations, in order to account for the realistic release rate of bromine to the gas phase. As mentioned above, the release mechanism, anyhow, can be different.
Therefore we kindly ask the authors to exclude or change their statement that (P. 4550 , lines 11-12: Tas et al. (2006) chose an unrealistically high reaction rate of 1.35Ã 10 â6 nmol/s. It should be also remarked that the average value used in the model is in a good agreement with other published values (e.g., Michalowski et al., 2000).

$>>$ Again, our statement regarding the difference in reaction rates in the work by Tas et al. 2006 and our approach refers to the following statement in the article by Tas et al. 2006, p.5593, left column:

"The rate of Reaction (H2, HOBr + H^+ + Br^- Br_2 + H_2O*) was obtained as the only degree of freedom in the structure of the model. A range of values for Reaction (H2) was tested, and the best agreement between simulations and measurements was obtained for a daily average value of* $\sim$ *1.35x*10^{-6} *ppb/s."*

We do not question that this rate which has been chosen agrees with other published values and is required to reproduce observed gas phase BrO mixing ratios. An offer source strength of this order of magnitude can be calculated by back-of-the-envelope calculations. Our approach was to try and find out what the most realistic process leading to a flux of this order of magnitude would be. This cannot be done by changing the rate coefficient of a key reaction sequence so that the BrO levels resulting from this flux agree with measurements.

The literature values (Michalowski et al., 2000) that you refer to in your comment as well as in Tas et al. (2006) are for polar conditions where the bromine release mechanism is distinctly different from the Dead Sea.

(4)

The authors claim that (P. 4551, lines 4-7): Tas et al. (2006) chose the strength of fluxes into the model domain such, that their simulations agree best with measurements.

This is defiantly not precise. All fluxes in the model, except for O3, were set based on measurements concluded at the measurement site, on days for which there were no signs for RBS activity and definitely not in order to achieve agreement between measurements and simulations (Tas et al., 2006). The input of O3 fluxes was based on O3 measurements at the measurement site. The contribution of Tas et al. (2006) was in pointing out for the first time that these O3 fluxes are crucial in order to achieve agreement with measured BrO profile. However, the input timing of O3 fluxes was determined only based on the measured O3 at the measurement site, rather than on

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the measured or simulated BrO.
Therefore we kindly ask the authors to exclude or change their statement that: Tas et al. (2006) chose the strength of fluxes into the model domain such, that their simulations agree best with measurements. (P. 4551, lines 6-12) -

$>>$ Please, see also the reply to point(6).
We want to point out that as soon as you prescribe fluxes into the model domain of a 1-dimensional model, you constrain the model. Under certain circumstances this might be a necessary approach, however, this has to be considered in the discussion of the results. No matter whether the prescribed fluxes are based on measurements, they clearly influence the model results. When you adjust the O_3 concentrations in the model (every timestep (?)) to the observed O_3 concentrations one would expect a good agreement between observations and simulations but this is because the model is constrained and not because the underlying processes are correctly represented in the model.

(5)
It should be further noted that the advection of air mass was controlled by wind speed, however the O3 flux was controlled by the spatial gradient of reactive bromine and O3 itself, at the measurement site, while the wind direction was quite stable for the specific date of simulation.
It is very wrong to assume that O3 will be transported over the evaporation ponds without being depleted by the reactive bromine over the ponds, and will be dominated by advection.

$>>$ The statement above was given in a similar formulation by Tas et al., 2006 in order to explain the unregular O_3 and BrO profiles as observed on several days. However, we disagree with this explanation as far as we understood it correctly.
Maybe we misunderstood your comment however, we think you contradict yourself by

writing that *"..the advection of air mass was controlled by wind speed, however the O3 flux was controlled by the spatial gradient of reactive bromine and O3 itself..."*.

We don't fully understand what you regard as the difference between *advection* of O_3 and the *flux* of O_3.

We assume that you use the term *advection* when referring to an inflow due to meteorological conditions (pressure gradient, wind, larger scale flow patterns....) and that you use the term *flux* when you refer to transport on a molecular level (molecular diffusion). In the boundary layer molecular diffusion is under almost all conditions negligible; change of the concentration of a gas due to transport is due to advection which is controlled by the windspeed and the tracer concentrations upwind and due to turbulent transport, which under conditions with appreciable windspeed is largely leading to changes in the vertical profile of a tracer.

We further refer to the following sentences in Tas et al. (2006), p. 5600:

"...This strengthens the motive force of transition to the first stage, and ozone can now be transported into the area resulting in higher ozone concentrations. ....

The depletion of Br concentrations resulted in an increase of advected O_3 *due to a lower rate of reaction with Br. ....*

In this periodic process the decrease in O_3 *concentrations beneath the threshold value of 1-2 ppbv, acts as a motive force for fresh* O_3 *fluxes to move into the evaporation ponds......"*

We understand these statements such that you assume that spatial concentration gradients lead to the flux of molecules of a certain species, in this case of O_3, independent of the windspeed and direction. However, we do not believe that this can explain the inflow of several ppb of O_3 into the air masses at the measurement site. At first, Tas et al., 2006 assume a flux of O_3 into their model domain - and thus their O3 concentrations *are* influenced by advection. Furthermore, (as you say yourself) it is very likely that O_3 is depleted to a similar extent all over the evaporation ponds. Thus to balance a spatial gradient in O_3 concentrations in an area of several (dozens of) square kilometres, new (O_3) molecules have to be transported over a distance of several kilometres. This is not possible purely by molecular diffusion on the relevant timescales.

(6)

The authors claim that the model used by Tas et al. (2006) is constrained for a large extent. This is not correct. The model simulations were highly supported by intensive measurement campaign performed at the evaporation ponds. This makes the simulations more realistic and reliable, however the simulations were defiantly not constrained for a large extent.

Therefore we kindly ask the authors to exclude or change their statement that (P. 4527, lines 22-24): However, as Tas et al. (2006) have chosen a set up constraining their model to a large extent and as several of their assumptions are strongly simplified the conclusions drawn from this study have to be thoroughly reconsidered.

$>>$ Maybe we use a different definition of what it means to *constrain* a model. We use the term, when certain parameters or concentrations are prescribed and therefore not explicitly and consistently calculated in the model. As far as we understand the work by Tas et al. (2006) they constrain the source flux of inorganic bromine and the flux and/or concentration of O_3. In our simulations, the model was constrained by prescribing a constant decrease in H^+ concentrations in the Dead Sea water in order to yield a gradient in the pH in the Dead Sea water between the southern evaporation ponds and the northern part of the Dead Sea. Apart from this ’manual interference’ in the model, all chemical reactions (gas, liquid phase, heterogeneous) were calculated explicitly, based on measured reaction rates and dependant on chemical concentrations, temperature etc.... As Tas et al. (2006) did not calculate chemistry explicitly in the aqueous phase they had to constrain their model to a larger extent than we did, as they had to prescribe (or parameterise) certain reactions, such as the source for Br_2. It is a further constraint to the model if one inserts advection fluxes, no matter whether they are based on measurements, simply because they are

not calculated by the model itself. As you have written yourself, both these boundary conditions strongly influence the results of your simulations.
The fact, that the model results reproduce measurements closely is no indication that the model is unconstrained. In many cases a good agreement is often due to strong constraints and if we understood the work of Tas et al., 2006 correctly also in their study.

Reply to comment (2) by E. Tas

(7)

A basic assumption applied in the present study is that the aerosol chemistry is always active if the ambient relative humidity is above the relative humidity of deliquescence (RHD) of sea salt (75%) or sulfate (70%) aerosols, but is not active (except for the lower most level) under the crystallization point of the aerosols, which assumed by the authors to be 40% for sulfate and 42% for sea salt aerosols. This assumption has an extremely high impact on the results and conclusion presented in the paper and therefore should be treated carefully.

$>>$ The deliquescence and crystallization humidity is not based on assumptions but on laboratory measurements (E.g. summarised in table 17.4 P.575 in Jacobson (Fundamentals of atmospheric modeling) and references therein, e.g. Robinson and Stokes,1955, Tang,1997). We have added these references to the text. The hysteresis effect (the effect that aerosol particles stay in a metastable stadium when the humidity drops below the deliquescence humidity but stays above the crystallisation humidity) is well documented in the literature.

(8)

It is not clear to me to what extent and in what way aerosol calculations are performed for RH values range between the deliquescence point and the crystallization point. This information is missing in the text.

>> It is explained in detail in Section 4.1, p.4531.

(9)
It should be taken into account that RHD of sea salt aerosols can be estimated by about 32% (e.g., Metzger et al., 2007), which is significantly lower than the value assumed by the authors.

>> The RHD of '32%' in Metzger et (2007) only refers to mixed sea salt aerosols that contain magnesium chloride.
We state in the discussion in Section 8 (P.4550) that it is possible that chemical reactions might still take place on aerosol particles that dried below the crystallization point. Thus we calculated a sensitivity study allowing reactions also on/in 'dry' aerosols. However, our conclusion are unchanged: Even though we consider an enhanced halogen recycling by allowing reactions on/in 'dry' aerosol particles we need an additional bromine source other than aerosols. Neither can we observe a significantly faster O_3 destruction as described in the manuscript.
The overall limiting factor for a fast halogen recycling on aerosols is the low liquid water content of the aerosol particles which slow down especially phase transfer reactions which are crucial for the halogen recycling process.

(10)
The authors may also take into account that the results published by Levin et al. (2005), indicate a layering of haze at heights of about100m and 250m above the Dead Sea surface, during daytime. The results further show that large particles (even >2um) were found in the lower haze layer.

>> We are aware that the aerosol load in the Dead Sea Basin can be very

high. This is the reason why we also did some sensitivity tests with different aerosol background concentrations. However, even if a large number of aerosols is available at the Dead Sea as a reaction surface for the recycling of halogens, there needs to be a source for bromine compounds different than aerosols.
Please, see also our reply to point (11).

(11)
Recycling of RBS via heterogeneous processes on sulfate aerosols is expected to play significant role in RBS activity at the Dead Sea area. For instance, studies have shown that the dependence of the rate of heterogeneous decomposition of BrONO2 on sulfate aerosols 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, and is very efficient under dry conditions (Hanson and Ravishankara, 1995), such as exist at the Dead Sea. Taking into account the high levels of sulfate aerosols over the Dead Sea (Tas et al., 2006; Andreae et al., 2002; Wanger et al., 2000; Formenti et al., 2001), it should be important to include this heterogeneous reaction, as well as other reactions involving sulfate aerosols active in the model, in order to avoid significant deviations from RBS activity that occur in reality at the area.
Moreover, the efficient heterogeneous decomposition of BrONO2 at the Dead Sea is also supported by measurements performed at the Dead Sea, which show a sharp depletion in NO2 concentrations together with significant increase in NOz concentrations (Tas et al., 2005; Tas et al., 2006), which expected to account for the formation of HNO3 due to the heterogeneous decomposition of BrONO2 (Fig. 9 in Tas et al.(2006)).

$>>$ Please refer also to our reply to comment (1) by Referee(1).
The heterogeneous reaction of $\mathrm{BrONO_2}$ on sulphate and salt aerosol is explicitly calculated in our model as well as aqueous phase chemistry in sulphate aerosol particles. We don't claim that this reaction is negligible but we come to the conclusion

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that under the prevailing conditions at the Dead Sea these reactions are not efficient enough to lead to the enhanced BrO levels as observed (see p. 4545/4546).
We did a large number of sensitivity tests regarding ambient conditions (temperature, humidity), aerosol background concentrations, initial concentrations of O_3 and NO_x, inclusion of reactions on dry aerosols: All these parameter influence the model results however, if we do not take into account the direct degassing of bromine species out of the Dead Sea water (or more generally: an additional bromine source other than salt aerosol particles) it is not possible to simulate BrO levels on the order of 60-100 pmol/mol. The key point, as explained above, is that the amount of bromide that is emitted into the atmosphere as salt aerosol is not sufficient to lead to BrO concentrations of 50-100 pmol/mol.

We improved the discussion of this issue in the revised version of the manuscript.

(12)
Variable diurnal profile of NO2:
(P 4548, lines 19-22) The authors suggest that in addition to the variable wind direction over the southern part of the Dead Sea, the potentially very variable bromine source strength due to variable bromine release strength of each single pond might explain the irregular pattern of BrO mixing ratios as detected at the evaporation ponds.
This hypothesis, suggested by the authors, was thoroughly investigated by our research group based on measurements performed at the evaporation ponds. Defiantly, the jugged shape of the BrO profile was found to be insensitive to wind direction. An alternative explanation for the sharp decreases and increases in the diurnal profile (i.e., jugged shape) of BrO at the evaporation ponds is related to the periodic increases and decreases of O3 below and about the threshold level of about 1-2 ppb (Tas et al., 2006).

$>>$ Please see our reply to point (5)

(13)

NO2 levels and agreement with measurements:

According the measurements performed at the Dead Sea NO2 concentrations shouldnt be high during the whole day (e.g., 0.8 nmol/mol, during STAT simulation), especially over the southern part of the Dead Sea (Tas et al., 2005; Tas et al., 2006). This is mainly the result of the heterogeneous decomposition of BrONO2 on sulfate aerosols (Fig. 9 in Tas et al. (2006)).

>> The cited value of 0,8 nmol/mol is given as an average value for the first day of simulation time in scenario STAT (indicated by: '≈'). Thus minimum NO_2 values are lower during daytime when photochemistry is active. Regarding the reported NO_2 concentrations by Tas et al., 2006, our simulated NO_2 mixing ratios are in good agreement regarding the observed order of magnitude. However, it is possible to mention the maximum and minimum NO2 mixing rations at 2m altitude in the manuscript.
We want to point out again, that it was not our objective to reproduce specific days of measurements but rather the general features of the underlying chemistry and meteorology based on the actual processes. Our overall scientific objective is to better understand the chemical mechanism being responsible for the observations made at the Dead Sea rather than performing simulations representing a specific measurement day.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4525, 2009.