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Atmospheric Chemistry and Physics Discussions

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

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Reply to Referee 2

Thank you very much for your helpful comments and interesting suggestions in order to improve our manuscript.

From an overall point of view, after an appropriate introduction the two following sections seem to be somewhat imprecise (see below). During the model part of the paper, the outline is clearer. In the discussion section, the tone of the authors facing the work of E. Tas has been mentioned already in other comments and should be revised.

(1)

Generally spoken, it is surprising that iodine species are missing in the model. Iodide concentration is increased in the Dead Sea brine and Iodine Oxide has been measured repeatedly and up to significant mixing rations of 10 ppt [Zingler and Platt, 2005]. Iodine chemistry should be implemented in order to draw a complete image of halogen chemistry, or it should be discussed why iodine chemistry does not influence bromine and ozone chemistry, which would be in contradiction to the sensitivity runs in [von Glasow, 2009 et al, 2002], where the inclusion of iodine chemistry resulted in quicker Br activation and greater ozone loss.

We also performed a series of sensitivity studies including iodine chemistry. We decided to not include the results from these simulations in the manuscript as it had lengthened it by at least 3-6 pages, such that we considered such a manuscript as too long and too extensive for publication. A separate publication on these studies is in preparation.
Overall, the main conclusions that we draw in this manuscript did not change when including iodine chemistry.
The key results of our simulations including iodine were that even though O_3 destruction rates were faster with iodine chemistry, the very fast O_3 depletion events as they were observed at the Dead Sea can only be simulated with the model if an inversion is assumed or the rate of air-sea exchange of halogen species is enhanced. Furthermore, A source for halogens in addition to aerosols is required in order to simulate BrO or IO mixing rations in the order of magnitude as was observed for these species.

(2)
Further on I wonder if orography is taken into account in MISTRA. The model contains meteorology and uses meteorological parameters (relative humidity) as decision maker for the activation of aerosol-chemistry (P4531). The strong orographic structure of the Dead Sea area significantly influences meteorology and therefore also microphysics

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and chemical composition of the atmosphere.

The special orography of the Dead Sea basin is definitely relevant for a number of features observed during the field campaigns when halogen oxides and O3 have been measured. The deep Dead Sea basin leads especially to a strong channelling of the flow. As MISTRA is a 1-dimensional model, the orography of the Dead Sea valley can however not be taken into account. To consider orographic effects, a 3-dimensional model would be required. Using MISTRA in the Lagrangian mode, i.e. moving column mode we implicitly make use of this strong channelling of the flow.
However, we regard a 1-dimensional modelling study as a good tool to improve our understanding of the key chemical and meteorological processes that are responsible for the observed high BrO mixing ratios.

(3)
A remark should be made if UTC or Local Time is used for time reference. This is related to photochemistry which is somewhat missing in section 6. However, it is mentioned on P4544 last paragraph, but with a relation to ozone which is not observed by measurements. The authors find that ozone mixing ratios start to decrease immediately after sunrise. Measurements show that ozone mixing ratios generally do not decrease before 6:00 UT which is about 3 hours after sunrise (in summer). During the same measurements, BrO also appeared only with a 3 hours delay after sunrise. This unexpected reality is not reflected in the model runs of this publication. The authors aim to find an explanation for measurements taken along the Dead Sea (P4528 L1). Thus, real conditions should be carefully addressed for model input.

The time refers to local time, which we have now added more explicitly in the manuscript .

We agree that we cannot reproduce exactly all measured features with our model

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simulations. However the main scientific objective of our study was to try to reproduce the general features observed at the Dead Sea (formation of high BrO mixing ratios and Ozone depletion events), based on as few assumptions as possible. As we mention several times, our model simulations are very sensitive to ambient meteorological conditions. As these conditions, especially vertical profiles of temperature and humidity, are not known for each single measurement day, we don't want to try to reproduce measured conditions on any specific days.
As mentioned in the introduction, scenario STAT was not designed to represent accurately the conditions and daily variations at one particular point at the Dead Sea but it was meant to better understand the general chemical mechanisms taking place at the Dead Sea and their sensitivity to changing background conditions.
We will try to point this out more clearly in the revised version of the manuscript.

For reasons of simplicity, the following comments are given in listed style.
(4)
On P4528 L18 the authors write without giving any citation: "The wind speed over the Dead Sea is very low." This statement is generally not true. Wind speed at the Dead Sea is rather variable, up to stormy.

We agree that the windspeed at the Dead Sea is not always as low as assumed for our model simulations.
However, the only published data regarding the wind speed during a measurement campaign at the Dead Sea is given by Hebestreit et al., 1999. They detected up to 80 pmol/mol BrO while the wind speed was about 5 m/s. Furthermore, Matveev et al. (2001) report windspeeds of 3 m/s or even lower which were prevailing during their measurement campaign at the Dead Sea. We have chosen the lower limit of observed windspeeds at the Dead Sea for our model simulations as also under these conditions high BrO mixing ratios can build up. Thus, a stronger sea salt aerosol

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formation (equivalent to a stronger bromine source) due to higher windspeeds or stormy conditions at the Dead Sea cannot be the explanation for the observations along the Dead Sea.
Furthermore, the windspeed data published by Bitan (1977) indicate as well that at least during the morning hours the wind speed above the evaporation ponds is rather low while it increases in the afternoon hours. However, the highest BrO mixing ratios were detected in the late morning hours or at around noon.
We rephrased the above mentioned statement in the revised manuscript and we describe why we have chosen a low windspeed in our model simulations.

(5)
On P4528 L19f it is stated (again without any citation) that "... the relative humidity along the Dead Sea valley is very low". This is not in agreement with measurements which show a rather strong diurnal variation of relative humidity.
P4528 L24f: "... the ambient relative humidity can be as low as 40% at an altitude of only 10 m above the water surface." Where did the authors get this information from?

The assumptions used for our model simulations regarding the low relative humidity are based on Alpert et al. (1997) as well as on the personal communication with J. Zinger and M.Piot (both formerly Univ. Heidelberg, Germany).
We will carefully check the manuscript and give the citation where it is needed.
We want to point out again that it was not our objective to perform model simulations for one particular day but to represent average conditions in order to explain the observed features at the Dead Sea (please see also our reply to point (3)). Furthermore, we could show, that even though the relative humidity was increased up to 65% near the water surface as was done in scenario LOWBL, aerosol chemistry alone could still not explain the observed high BrO mixing ratios.

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(6)

P4529f L23ff: I agree with the authors that the topography at the Dead Sea strongly influences the wind regime, and that the local flow pattern is insufficiently understood. However, the remarks on prevailing wind directions are in contradiction to literature and observation. The authors write that "the main wind direction is roughly South to North", and later on that due to a lake breeze the wind at the northern shore is almost always southerly. In reality, a very complex wind system of overlaying valley winds, cross valley winds, lake breezes and synoptic influences needs to be addressed, which causes a large variability of the wind direction. [Sirkes et al, 1997] show a comparison of several stations along the Dead Sea including one at the very northern end (Bet HaArava).

It is indeed true that the local flow pattern at the Dead Sea is very complex (please see also our reply to point (2)).
We will point out more clearly in the revised manuscript, that the lagrangian model setup is idealised.
As we cannot represent the complex flow pattern with a 1-dimensional model we have chosen a lagrangian setup in order to avoid advection fluxes into the model domain and in order to investigate the impact of the gradient in the pH in the Dead Sea water on bromine chemistry.
Regarding the wind direction data given by Matveev et al. (2001) the wind direction is on numerous days southerly while high BrO mixing ratios were observed. Even if we assume, that air masses that crossed the evaporation ponds from the South towards the North do not reach the northern End of the lake but are redirected (e.g. due to the lake breeze) after reaching the centre of the lake (thus stopping our simulations after about 3 hours or continuing them without further increasing the pH of the water), our main conclusions still hold (we need a bromine source in addition to aerosols and an ODE is likely only to occur under certain meteorological conditions).
We also performed tests assuming that the model column crosses the Dead Sea from the North to the South (from areas with lower pH into areas with higher pH) and still

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come to the same conclusions.

(7)
P4530 L7 and P4550 L6: the fact that "pers. comm. M. Piot" is cited appears a bit strange. By chance it is known to the referee that M. Piot was only accompanying during measurements at the Dead Sea. Maybe it would be good practice to cite the person responsible for measurements referred to.

We agree and have changed the text to: (pers. comm. Jutta Zingler, Matthias Piot).

(8)
P4530 L19: The authors have choosen an aerosol size distribution for rural areas. It might have been more appropriate to put in an aerosol size distribution for arid areas or the choice for rural should be justified.

The aerosol size distribution is only called 'rural' based on the terminology used by Jaenicke (1988).
No measurements regarding the aerosol size distribution along the Dead Sea valley are available for the periods of the field campaigns. Thus we have chosen an aerosol size distribution that represents average conditions in areas that are neither maritime areas (very clean air with a comparatively low particle load) nor areas which are strongly anthropogenically influenced (highly polluted areas with a very high particle load). Even though the Dead Sea is surrounded by a desert, sulfate concentrations in the area are not negligible (but are neither very high, e.g. Tas et al., 2006, Stutz et al., 1999) as well as the load of sulfate aerosol particles which is represented in the chosen aerosol size distribution.

(9)

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P4534 L21ff: It might be interesting to add not only O3 and NO2 advective fluxes, but also SO2. In the lower boundary layer, SO2 is generally not observed in significant amounts. But it could be of importance in higher levels of the boundary layer.

In principle we agree that SO2 should not be neglected, but the only impact advection of SO_2 would have had on the chemistry in our model simulations, is on the aerosol pH, which however, was well below the threshold for bromine recycling so that the effect would have been very limited.
In addition, these model simulations were only meant as sensitivity studies to show what the - rather unrealistic - scenario of stagnant airmasses would have yielded in terms of bromine levels and to show that even under these conditions sea salt aerosols as the only bromine source are insufficient to explain the BrO observations.

(10)
P4547 L13: It might enrich the paper if the results of the modified EXLIM scenario (exchange of Br2 and BrCl allowed) would be shown. The absolute maximum values of BrO tend to be overestimated compared to measurements. Therefore, further modification of the model (including the implementation of other species such as iodine chemistry) is probably needed.

Again, we are presenting these sensitivity studies not to try to reproduce single measurements but to show what effects certain assumptions can have on our model results. The results can then be used to evaluate whether or not the assumptions are likely to be realistic for the chemistry at the Dead Sea or not. We don't claim to have solved all problems related to the chemistry at the Dead Sea but we would also like to point out that the absence of measurements of mixing ratios as high as resulting from this particular scenario is no evidence that they can't be that high.
The overestimation of BrO mixing ratios in scenario EXLIM is mainly related to the (potentially too) low inversion height and not to the missing iodine chemistry. If the

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same case is calculated including iodine chemistry, IO mixing ratios are as well (tremendously) overestimated.
We will point this out more clearly in the revised manuscript.

(11)
P4529 L20: Citation incorrect: Niemi et al. are the editors of the monograph. The article8217;s author should be given.
Sirkes et al., 1997, Surface currents and seiches in the Dead Sea. In: Niemi et al. (eds.), The Dead Sea, Oxford Monographs on Geology and Geophysics, 36, p. 104-113

We thank the reviewer for pointing out this oversight and have corrected our reference.

(12)
P4553 L4: Might it be less ambiguous to write "Austral. Meteorol. Mag."; instead of "Austr. Meteorol. Mag."?

The correct abbreviation is 'Aust. Met. Mag.'.
We have corrected this citation.

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