

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

Received and published: 27 May 2009

Reply Referee 1

Thank you very much for your comment and helpful suggestions to improve the manuscript.

I have only 2 major comments.

(1)
The first is one raised already in the 2nd short comment published by Eran Tas - i.e. the efficient hydrolysis of BrONO₂ on sulphate aerosol in even stratospheric conditions (Hanson and Ravishankara, 1995, 1996). This must be addressed.

For the discussion of the hydrolysis of BrONO_2 please see also our detailed reply to Eran Tas.

The heterogeneous reaction of BrONO_2 on sulphate and sea salt aerosols is explicitly calculated in our model as well as aqueous phase chemistry in sulphate (and sea salt) aerosol particles. We don't claim that this reaction is negligible but we come to the conclusion 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 of our study is, that the amount of bromide that is emitted into the atmosphere in salt aerosols is not sufficient to lead to BrO concentrations of 50-100 pmol/mol.

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

(2)
The second major comment is that the study makes no mention of the lifetime of HOBr against organics in seawater (nor in aerosols). Unless there are unusually small DOC concentrations in the Dead Sea (this should be discussed) , at such high HOBr concentrations (if they really do exist), I would expect rapid reactions with organics. Hypohalous acids are very reactive with a range of organic materials, especially humic acids, which are present in seawater. E.g. Jaworkse and Helz (1985), show that in estuaries, the halflife of bromine oxidants is only 7 ms.

We agree that the reaction between HOBr and DOM is an important issue that has to be included in the discussion in our manuscript. Below, we give a summary of the results of the sensitivity studies including the reaction of HOBr + DOM. This discussion was added in a similar way to the manuscript.

A high uncertainty is related to the actual rate constant for the reaction between HOBr and DOM as well as to the DOM (or DOC) concentrations in the Dead Sea water. No reliable literature values for the rate constant for this reaction is known to the authors. Furthermore, the only values for DOM (and DOC) in the Dead Sea water we found are from an unpublished PhD thesis from 1964 which are listed in Nissenbaum, 1975.

Thus we performed a series of sensitivity studies with different DOM concentrations and different rate coefficients in order to be able to discuss the potential impact of this reaction on our results.

No information is available about the sampling technique and analysis of the samples which were used to derive the DOM/DOC concentrations cited in Nissenbaum (1975). In addition the chemical composition of the Dead Sea water has changed over the last decades (Oren, 1999) as well as the salinity of the lake water (e.g. Anati and Shasha, 1989). Even though several microorganisms have been found in the Dead Sea water, their distribution does not seem to be homogeneous among the lake water and concentrations of bacteria seem to be comparatively low (Shimoni et al., 2002, Oren, 2008). Can we therefore also assume that DOM/DOC concentrations vary within the Dead Sea water, similar like the pH shows a gradient between the northern part of the lake and the southern part? Are there seasonal variations in DOM (or DOC) concentrations? We do not know where and when the samples were taken which were used for the creation of the dataset cited in Nissenbaum (1975). We further do not know if at that time e.g. algae were present in the lake water or had been present in

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

the weeks before the sampling took place.

Implications for the model results:

We varied DOM concentrations in the Dead Sea water between 0.0001 g/m^3 and 0.1 g/m^3 and the rate coefficient for the reaction between HOBr and DOM was varied between 10^4 and $10^6 \text{ M}^{-1}\text{s}^{-1}$ (based on Jaworkse and Helz (1985) as well as on Pechtl et al. (2007, and references therein) who performed a series of sensitivity tests for the reaction HOI+DOM).

If DOM concentrations exceed 0.01 g/m^3 , HOBr concentrations in the Dead Sea water decrease almost immediately by about two orders of magnitude. This results in negligibly small mixing ratios of BrO in scenario EXALL whereas they still increase up to at least about 15 pmol/mol (depending on the chosen rate coefficient) at 2 m altitude in scenario EXLIM. DOM concentrations for which at least several pmol/mol BrO build up in scenario EXLIM, are still smaller than reported in Nissenbaum (1975). Consequently, bromine species in the Dead Sea water become too small to degase in significant concentrations out of the Dead Sea water. Thus the question of additional bromine sources has to be addressed again. Surface reactions on the Dead Sea water could contribute to the gas phase bromine load as was suggested by Matveev (2001) but they are considered to be of minor importance. Crystallized surface salt deposits were discussed as a potential bromine source. However, no striking correlations regarding the existence of such salt deposits and high BrO mixing ratios were observed and are reported in the literature.

The sensitivity studies including reactions with DOM might further support the idea, that an inversion is necessary for the formation of high BrO levels (and an ODE).

We consider it as likely that DOM/DOC concentrations in the very shallow and highly concentrated evaporation ponds are lower than in the norther part of the lake which has a lower salinity such that concentrations of bromine species in the water of these ponds are high enough to supply a source of bromine to the gas phase.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Minor comments/typos:

(a)

P4528, L14: It has been suggested many times needs references.

(b)

P4531, L22: Give some detail on how threshold value of total water mass is calculated

(c)

P4544 L26: Although the explanation mark conveys the surprise regarding the large vertical gradients, it should be deleted.

(d)

P4545 L 26: Replace 'much stronger' with something like 'more rapidly'

(e)

P4549-4551: Latter half of discussion reads as a critique of the Tas et al. paper. I recommend to condense this discussion and present it purely in terms of major differences of this approach to that of Tas (maybe in bullet points/Table) with explanation of limitations of previous approach.

(f)

P 4550 L 30: Delete 'it happens' after 'show'

(g)

P4552 L9: 'extend' 'extent'

(h)

Figures - some of the grayscale ones look rather faint.

Thank you very much for pointing out the minor problems and typos, which we have corrected in the text.

We followed your suggestion from point (e). We will present the differences between the model approach by Tas et al. (2006) and our model approach in a tabular form with bullet points.

We further added the citations and described the aerosol activation in MISTRA with a

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



few more words.

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

ACPD

9, S2291–S2296, 2009

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

S2296

