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Atmospheric Chemistry and Physics Discussions



# *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.

**Anonymous Referee #2**

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The authors present a modeling study to assess the remarkable high levels of BrO and to investigate the relations between the radical and O3 within the context of the bromine chemistry at the Dead Sea basin. The importance of the heterogeneous halogen recycle on aerosol surfaces, via uptake of BrONO2, and the necessity of constraining the model with entrainment of O3-rich fluxes is highlighted in order to reconcile the field observations with the model predictions. The paper's goal which is to bring together chemistry and transport, in a one-dimensional manner, to explain the bromine activation at this location fits well within the scope of ACP and should be of interest to its audience. However, in my opinion, the authors need to thoroughly address some serious issues in a revised version before the paper can be published. I therefore



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recommend major revisions which take account of the following points:

1. The paper can be better structured. Some of the sub-sections can be removed and grouped into fewer ones since some of the statements are repetitive and do not add extra information. In particular, the results and discussion section (Section 3) would need to be re-organized. More importantly, in this section, point 3.2 (Chemical mechanisms) would fit better in the introductory section since the chemical reactions are not results of this work but rather well studied and reported chemical processes involving bromine species.

2. The authors claim to present a “chemical mechanism which can account for the observed chemical activity at the Dead Sea” via introducing “two heterogeneous processes: the Bromine Explosion and the heterogeneous decomposition of BrONO2”. These two mechanisms have been suggested for quite some time now and are well documented in the literature. In particular, the role of bromine nitrate in the halogen recycle on aerosols is not new, previously reported studies have suggested the importance of this mechanism (e.g. see Sander et al., 1999; Evans et al., 2003; von Glasow et al., 2004; Saiz-Lopez et al., 2006). Therefore, the authors should remove the emphasis on the novelty of this approach to explain the observed levels and diurnal variation of BrO.

3. In general, the description of the one-dimensional model utilized in this work is insufficient:

-There is no clear information regarding what chemistry occur in the aqueous phase and which in the gas phase.

-Details about what effective available aerosol surface area (ASA) is considered in the calculations are not given, either its justification from previous measurements or whether sensitivity studies have been carried out with different ASAs. Similarly, no information is provided on what species are allowed to be taken up onto aerosol surfaces and what uptake coefficients are employed, for instance how does photolysis of



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BrONO2 compare with the first order loss rate of the molecule onto aerosols?. If only BrONO2 is considered, why neglecting the contribution to aqueous bromine from the uptake of species such as HOBr, HBr, BrNO2 ?. The authors should comment on how gas phase equilibration of other species such as BrCl would affect their results. Certainly, including only one heterogeneous process does not represent a full treatment of the bromine activation. This, in turn, influences the fluxes of chemical species needed in the model to match the observations.

-The fluxes with which the model is constrained are not clearly described. What are the numbers?, besides, how are they calculated and what is their physical meaning in this context?. Further information needs to be provided on this regard.

-What planetary boundary layer height is considered?. Also, what is the vertical resolution of the model and at which height in the model the authors try to quantitatively investigate the chemical species mixing ratios?.

4. In section 3.3 the authors should clarify if they refer to gaseous or aqueous HOBr since the paragraph is confusing, relating the formation and photolysis of HOBr with the rate of decomposition of BrONO2 (H1). In addition, mixing ratios of other species (e.g. HO2, OH) used in the model should be given, likewise commenting on the impact of the HO2 diurnal profile upon the formation of gas phase HOBr and subsequent uptake and recycle of bromine atoms. Are HOx and NOx species kept constant or calculated throughout the model runs?.

5. In section 3.4, the authors appear to relate the Br atom concentration change with time with the advection of O3. This paragraph has to be re-worded since surely the bromine chemistry should not affect the physical process of advection of O3.

6. In the conclusions, a final point is given regarding the formation of HNO3 through the heterogeneous processing of BrONO2. If the idea is to study the quantitative conversion of NO2 to NOz other chemical channels need to be considered/added, such as the reaction of NO2 + OH, etc.



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7. Finally, there is no mention to a clear feature visible in both the model and the measured BrO diurnal variation plots as it is the evidence for a sudden post sunrise bromine activation peak being most likely the result of build-up of precursors during the preceding night. This feature has also been noticed in reports from the mid-latitude marine boundary layer (e.g. Saiz-Lopez et al., 2006).

Minor points:

- The citation to Sander, Rudich and von Glasow is repeated in the Reference section

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