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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 #1

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The goal of this manuscript is an understanding of the bromine chemistry in the Dead Sea with the help of a one-dimensional model. The model studies are based on and compared with measurements that were performed in the Dead Sea area. An investigation of the chemical and physical processes in this unique region of the world is certainly highly interesting and fits well into current reseach interests. However, I somewhat doubt that the model approach the authors use is adequate for a thorough comparison with available field data. In my opinion, it contains some serious deficiencies, which I will describe in detail below. Further, several model assumptions are not sufficiently explained and/or justified. Finally, the paper is lengthy, not really well-organized and contains too many repetitions. In my opinion, the paper cannot be published with-

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out major modifications both in content and style, and therefore I suggest rejection of the manuscript in the present from.

Methodical problems:

1. The authors investigate the importance of two heterogeneous processes with a model that does not include chemistry on and in aerosol particles. They only include the two heterogeneous processes (their reactions H1 and H2) they are interested in. This strategy is questionable since it does not allow to investigate the importance of these reactions compared to others that might also be important but which are not included in the model.

2. The two heterogeneous reactions are implemented in a highly simplified / parameterized manner which is not well-explained. The authors do not provide important details such as the aerosol surface area (and where the information about aerosol surface area is taken from). Information such as "this relationship was included in the parameterization of the rate of Reaction H2, according to Eq. 4" (p.4935, lines 25/26) is not precise enough: Is this relationship used to derive $[Br^-]$ (based on typical Br^- concentrations in seasalt) which is then used to calculate the rate of reaction H2? Equally, it does not become clear how wind direction is "parameterized into the rate of reaction H2" (p.4936, line 11).

3. Fluxes of NOx, hydrocarbons and ozone are "entered into the model at heights between ground level and the base of the planetary boundary layer, based on actual measurements performed at the dead sea" (p.4936, lines 16-18). How are these fluxes justified from a physical point of view? How exactly are the fluxes determined? Are they constant or variable with time? If NOx measurements were taken from Metzoke Dragot as described later in the paper (p.4938, last paragraph): How can you expect these values to resemble NOx values near the evaporation ponds, which are located at a 400 m lower altitude and 50 km to the south?

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4. "The simulated ozone concentrations were approximately 3-fold lower than the measured ozone" (p.4940, lines 13/14). I am not convinced that the absolute magnitude of ozone concentrations is unimportant for BrO mixing ratios as claimed by the authors (Ozone destruction rates do normally depend on the magnitude of $[O_3]$): "The BrO concentrations were generally found to be relatively insensitive to the magnitude of the ozone levels" (p. 4940, lines 17/18). Is this statement really shown somewhere? I did not find respective model sensitivity studies in the manuscript. Generally, if the authors add ozone fluxes anyway, why don't they do it in a way the ozone levels are captured also quantitatively? Their explanation for lower O_3 concentrations "since the concentrations of RBS are expected to be lower at the edge of the evaporation ponds than over the ponds" is not valid: If the airmass that moves along the DOAS lightpath and over the ozone monitor is not the same, then a comparison is not possible anyway; if it is the same air mass, then how should ozone be reformed within some minutes? "The contribution of each reaction to the formation of its products was investigated by including an inert species as an additional product in the reaction. For example, Reaction G1 appeared in the model as $Br + O_3 \longrightarrow BrO + O_2 + X$, where X is an inert gas product specific to Reaction G1" (p.4937, lines 11-14). Why do you use this strange concept? What about simple budget calculations? If X is specific to a reaction, how can it be transported or deposited as stated by the authors (p. 4937, lines 18/19)?

5. The authors use a one-dimensional model (vertical column model), but do not provide any information about model resolution and model top. The model level for which they show and compare results is never given, nor are vertical profiles mentioned.

Further major points:

1. The presented chemical mechanism (including the two heterogeneous reactions

H1 and H2) is not new, but has already been presented in several other papers before. Therefore, the "chemical mechanisms" (section 3.2) should not be presented as part of the "Results" but should be discussed earlier.

2. The finding that "at the Dead Sea, O_3 can occasionally function as a limiting factor for the formation and recycling of BrOx" (p.4944, lines 23/24) is not really surprising. The threshold value of 1-2 ppb, below which ozone, according to the authors, becomes a limiting factor for BrOx production, is repeatedly mentioned, but it is never explained how this value was determined.

3. "The change of Br concentrations with time appears to play an important role in controlling the increase in O_3 concentrations due to advection" (p. 4946, lines 9/10) / "There is a high probability that the changes in Br concentrations with time serve as chemical regulator for the entrainment of O_3 fluxes" (p.4953, lines 16-18): How can chemical processes control advection? Advection is a physical process that cannot be affected by chemistry.

4. Several features in Figure 3 are not well-explained: What is the reason for the morning peak in 3a, b? Why does reaction H1 lead to such a strong structure in BrO (3c, d)? Further, the difference between Fig. 3c and 3d looks nearly negligible. Therefore, the conclusion "it is only when both of the heterogeneous reactions are added together that the simulations agree with both the BrO pattern and its magnitude" (p. 4941, lines 9-11) does not seem justified.

5. Figure 6: Why does the Sum(Br) have an initial value of about 400 ppt (at night)? The explanation for this initialization is missing.

6. Figure 8: BrOx production due to reactions H1 and H2 is, according to this Figure, max. 0.25 ppt/min, i.e., 15 ppt/h. This production rate is not high enough to explain BrO levels of 120 ppt that are formed within 2 h. What really is the source of bromine in the model?

7. I think the organisation of section 3 in so many subsections is more confusing than helpful and especially leads to many repetitions. Some subsection labels are even similar (e.g. "3.5.3 Heterogeneous reactions" and "3.6 The role of heterogeneous processes"). Especially the second half of section 3.6. (p. 4950 line 16ff) contains many repititions and already summarizes part of the paper (which I regard as not adequate in a "Results" chapter).

There are several minor points of which I mention only some in the following:

- The net reaction of Cycle 3b (p. 4944) is wrong: Correction: $2\ O_3 + NO_2 + H^+ + Br^- \longrightarrow BrO + HNO_3 + 2\ O_2$

- Figure 2b: Labels for O_3 and BrO are interchanged

- "The simulated results were relatively insensitive to the parameterization of wind speed" (p.4941, line 12): What is the reason for that? Shouldn't the amount of Br liberation depend on seasalt concentration and hence on wind speed?

- "This may imply that the seasalt aerosols are not the only source of airborne Br" (p.4941, lines 14-15): In the model, it has to be possible to clearly differentiate between the different sources.

- Section 3.3 and Figure 6: Why did you include OBrO? Couldn't it have been expected to be negligible?

- The expression "profiles" which is repeatedly used (e.g. p. 4939, line 1) is missleading: No "profiles", but time-series are shown.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 4929, 2006.

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