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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement-based modeling of bromine chemistry at the Dead Seaboundary layer – Part 2: The influence of NO_2 on bromine chemistryat mid-latitude areas" *by* E. Tas et al.

Anonymous Referee #1

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Tas et al. (2008) contribute to the understanding of the interactions between bromine chemistry and that of nitrogen oxides and ozone, at mid-latitudes. The key point of this work, following-up an earlier study focused on the modeling of ozone depletion events occurring at the Dead Sea (Tas et al., 2006), is the study of the effects of varying NO_2 fluxes into the modeled volume of atmosphere, and to compare the differences in terms of the production of reactive bromine species (RBS, BrO_x = Br + BrO) through different recycling pathways. Overall the manuscript is well written and is appropriately supported by the figures. Therefore, given the high significance of the assessment of

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RBS chemistry in polluted area, this manuscript should be published in ACP. Before this, the authors are asked to clarify a few scientific issues, and perform a few fixes aimed at making their manuscript easier to read and understand.

Scientific comments

It is the reviewer's understanding that the model used for the present study is essentially the same as for the Tas et al. (2006) paper. However, it may appear necessary to briefly state the assumptions underlying the treatment of the heterogeneous reactions H1 and H2 (in particular the used surface area of aerosols and the uptake coefficients (γ values)), even though the reader can be referred to Tas et al. (2006) for details with respect to the justification of the choices made by the authors.

Discussion of H3 and H4 : the conclusions that these two reactions play a minor role, backed by the observation that NO_3 and N_2O_5 are present in small amounts, is not convincing : for instance the OH radical is present in tiny amounts, but still plays an outstanding role in atmospheric chemistry ! The discussion should be based on the rate of these two reactions in comparison to other Br- or $BrNO_2$-forming reactions, by either adding these two reactions into the model (for instance using the work of Sander et al. (1999)), or finding a way to quantitatively assess its role even if not quantitatively included in the present model study.

Cyclic behavior of the ozone-RBS-NO_x system : it may be interesting to compare the cyclical nature of the interactions within this system with the model results of Evans et al. (2003), suggesting that periodic oscillations (with a period of about 3 days) could take place in this system in the Arctic atmosphere in spring.

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Literature cited

Overall the research findings are well connected to other scientific studies performed on similar topics. Useful additions could include the pioneering paper by Fan and Jacob (1992) (e.g. page 7728, line 10-15, where the need for heterogeneous reactions is mentioned). Also, references to work carried out in polar regions could be summarized by mentioning the recent review of Simpson et al. (2007).

Minor revisions

Title : please replace 'at' by 'in' (i.e., 'in the Dead Sea boundary layer').
Throughout the manuscript, the authors should refer to atmospheric levels of chemical species in a consistent manner. The term 'concentrations' is inappropriate if levels are expressed as molar mixing ratios (i.e. ppbv or pptv). In some occurrences the authors use the term 'mixing ratio', which is better, and should be used throughout the whole paper.
Definition : There is apparently no definition of neither Reactive Halogen Species (RHS) nor Reactive Bromine Species (RBS) in this manuscript. It would be useful to give an unambiguous definition for each of those terms. Also, no account is given to what 'Dead Sea Works' refers to, which should be fixed.
Page 7731, line 21 to 25 : this sentence should be rephrased (possibly split in two) as it is currently hard to follow.
Page 7736, line 12 : 'enhance' $\rightarrow$ 'enhances'
Page 7736, line 13 : it is not clear whether the average values of ozone and BrO_x species mixing ratios are taken over the whole day or only over the time of RBS activity. This should be clarified.
Page 7736, line 23 : the part of sentence starting with 'where n is ...' is redudant with

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the previous sentences.
Page 7739, line 21 : 'continues' → 'continuous' ?
Page 7739, line 24 : this sentence should be rephrased, as currently 'its' grammatically refers to 'ozone' even though it appears to refer to 'the increase of the concentrations of NO_x' instead.
Page 7740, line 21 : 'should' → 'could'
Page 7740, line 23 : 'did' → 'would'
Page 7740, line 26 : 'led' → 'would lead'
Page 7741, line 12 : 'at' → 'of'
Page 7744, line 11 : 'Hoeninger' → 'Hoenninger'.

Figures and Tables

Table 1 : the caption is misleading. A suggested alternative caption could be : 'Average (...) mixing ratios of various species obtained for different NO_2 flux values'. Also, the value of the base flux, indicated at the bottom of the table, could be checked (the number format is currently pretty awkward), as well as its unit (why isn't the flux given as a quantity of NO_2 per unit surface per unit time ?)
Figure 1 : caption : ratioss → ratios
Figure 2 : panel a : the double arrow indicating RS activity should match the shaded area, as it is currently no the case.
Figure 3 : caption : in the text, a link should be made between cycles 3, 4 and 5 and the reactions G2, G5 and G9, which is currently not obvious and hard to properly understand. The same indication could be given in the legend of the graph.
Figure 4 : caption : last sentence : it is not clear what is meant by $n <= 1$. This could be replaced by $n \leq 1$ if this is what is meant.
Figure 6 : x-axis : FUL → FULL ; legend : FUL → FULL

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Sander, R., Rudich, Y., von Glasow, R., and Crutzen, P. J.: The role of $BrNO_3$ in marine tropospheric chemistry: A model study, Geophys. Res. Lett., 26, 2857 – 2860, 1999.

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