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Interactive Comment

Interactive comment on "Measurement-based modeling of bromine chemistry at the Dead Seaboundary layer – Part 2: The influence of NO₂ on bromine chemistryat mid-latitude areas" by E. Tas et al.

E. Tas et al.

Received and published: 14 July 2008

We are very grateful to the reviewer for the level of attention given to our paper, and for the comments that are very helpful in improving the paper

Scientific comments:

We have edited the new version of the manuscript according to the reviewers comments. We refer here to all cases in which further clarification or details are needed.

- According the reviewers comment we will add the following as the first sentence in the experimental section (Sec. 2.1):



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The model used for the present study is essentially the same as used for a companion paper (Tas et al., 2006).

In addition to that, according the reviewers suggestion, the assumptions underlying the treatment of the heterogeneous reactions H1 and H2 including the used surface area of aerosols and the uptake coefficients will be added to the revised version.

- We agree with the referee that the discussion about the significance of reactions H3 and H4, under the condition of the present study, should be based on their rates compared to other reactions that were included in the mechanism. Therefore, the following will be included (replacing lines 2-8, page 7741):

In order to investigate the effect of these reactions on the analysis described in the present paper, their potential influence on BrOX levels should be evaluated, based on the NO2 fluxes used in the present study. For this purpose the rate of reactions H3 and H4 should be compared with these of the rate limiting step reactions of cycles 3a, 3b, 4 and 5. The rate of reaction H2 is the slowest of all limiting rate reactions of these cycles. The rate of reaction H2 was compared to the calculated rates of reactions H3 and H4, assuming uptake coefficients (γ for reactions H3 and H4 of 0.16 (Seisel et al., 1997) and 0.023, respectively. The calculations show that the daily average rates (06:00 and 20:00 LT) of reactions H3 and H4 are lower than the rates of reaction H2, by at least 1.5 and 3.5 orders of magnitude, respectively, for all of the simulations described in the present study. Thus, it appears that the influence of reactions H3 and H4 on BrOx production can be neglected, under the conditions used for the present study. However, it should be remarked that reactions H3 and H4 are expected to have higher influence on BrOx production and NO₂ lost during nighttime, and also in cases that the available salt surface area is large enough for significant surface reactions.

- It may appear that a comparison between the periodic two stage cyclic process described in the present paper and the cyclic behavior of ozone-RBS-NO_x as discussed by Evans et al., 2003, is beyond the scope of the present study. However, we think

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that such a discussion may be both interesting and helpful for a better understanding of RHS activity in other areas, both in mid-latitude and Polar Regions. Thus, we have decided to include the following:

It should be remarked that the relationship between BrO_r , ozone and NO_r during ozone depletion events, as described by the two stages periodic process, are not limited only to the Dead Sea area. A similar relationship between these species, during ozone depletion events at the Arctic boundary layer, was discovered by Evans et al. 2003 and was defined as An Oscillatory System in Bromine-Catalyzed O_3 depletion. Because of the relatively small area of the evaporation ponds, and the high intensity of RBS activity, the time period and the magnitude of these oscillations at this area are expected to be small, in comparison with other areas. Thus, Evans et al. 2003 reported a much larger time period (3 days) for the oscillations at the Arctic, compared to the 1 to 3 hours time period of the oscillations described in the present paper. The time period in the first case was long enough, so that a photochemical recovery of ozone occurred. Advection of ozone is expected to be the main cause for ozone recovery in cases that the time period is short enough, as was evident at the Dead Sea evaporation ponds. It is also could be that the recovery of ozone by advection may be limited only to the more outer parts of the area at which RHS activity occur. This may be the case, when the area at which RHS activity occurs is big enough, that the traveling time of fresh ozone from outside of this area is high enough.

Literature cited:

-A reference to the paper by Fan and Jacob (1992) was added.

-The original references for the work carried out in Polar Regions, is replaced by reference of Simpson et al. (2007).

Definition: RHS and RBS will be defined in the new manuscript (at the beginning of sect. 1).

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An information about the location, relevant features and the potential influence of the Dead Sea Works on RBS activity, will be included in the section describes the model simulations (currently Sect. 2.1). Page 7731, lines 21 to 25: We have rephrased the original sentence by dividing it into two sentences as follows:

All of the results and discussion presented in Sect. 3.1 are directly based on the FULL simulation. The results and discussion presented in Sect. 3.2 refer to a set of simulations based on the FULL simulation and on the NOB simulation, changing only the NO2 fluxes, as described in more detail in Sect. 3.2.

Page 7736, line 13:

The average values of ozone and BrO_x , as well as all other species that were discussed in this section, are taken only over the time of RBS activity (i.e., between 6:00 and 20:00 LT). Since this was not clear, the following will replace the original sentence:

In this section the investigation is limited only to the influence of NO₂ mixing ratios on the average mixing ratios of BrO, Br, BrO_x and O_3 obtained during daytime RBS activity (6:00-20:00 LT). Its influence on the diurnal profile of these species is ignored.

Page 7736, line 23: We have changed the original two sentences (page 7736, lines 20-24) in a way that is less redundant, but still emphasizes that fact that for each simulation only a single multiplication factor, n, was used:

For each of these 11 simulations, the value of the NO_2 flux obtained in the FULL scenario, was multiplied by a single multiplication factor, n, at each update time (every 15 min). For each simulation, a different value for n was used, varying from 0.1 to 100.

- Page 7739, line 24: The sentence was rephrased according the reviewers comment:

For example, several studies (e.g., Beine et al., 1997; Sander et al., 1999; Ridley and Orlando., 2003) have showed that an increase in the concentrations of NO_x impedes the destruction of ozone due to an increase in the concentrations of bromine-containing nitrogen reservoirs.

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Page 7741, line 12:

According the referee comment, the sentence will be rephrased:

The influence of NO $_2$ on both the diurnal profiles and daily average production of Br and BrO was investigated in this study, based on measurements performed at the Dead Sea evaporation ponds.

Figures and Tables:

Table 1: The title will be changed according the referee suggestion: Average mixing ratios of various species obtained for different NO_2 flux values over the time period 8230;.

We apologize for the mistake in the unit of the average flux of NO₂ during FULL simulation. The value was checked again and the formats of the number and units were changed as follows: The average NO₂ flux used for FULL simulation is 3.61 $^{\circ}$ 1013 molec $^{\circ}$ m-2 $^{\circ}$ s-1 during RBS activity (06:008211;20:00 LT).

Figure 3 :caption: A description of the link between reactions G2, G7 and G9 will be given in the legend of Fig. 3. In addition to that, the caption of Fig. 3 was edited to include the connection between reactions G2, G7 and G9.

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Fig.4: caption: last sentence:

The referee advise is accepted.

References:

Andreae, T. W., Andreae, M. O., Ichoku, C., Maenhaut, W., Cafmeyer, J., Karnieli, A., and Orlovsky, L.: Light scattering by dust and anthropogenic aerosol at remote site in the Negev desert, Israel, J. Geophys. Res., 107(D2), 4008, doi:10.1029/2001JD900252, 2002.

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8, S4742-S4748, 2008

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Interactive Discussion



Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Kerr, J. A., Rossi, M. J., and Troe, J.: Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, Web Version, http://www.iupac-kinetic.ch.cam.ac.uk/, 2004.

Fan, S.-M. and Jacob, D. J.: Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols, Nature, 359, 5228211;524, 1992.

Formenti, P., Andreae, M. O., Andreae, T. W., Ichoku, C., Schebeske G., Kettle, J., Maenhaut, W., Ptasinsky, J., Karnieli A., and Leliveld, J.: Physical and chemical characteristics of aerosols over the Negev Desert (Israel) during summer 1996, J. Geophys. Res., 106(D5), 48718211;4890, 2001.

Hanson, D. R. and Ravishankara, A. R.: Heterogeneous chemistry of Bromine species in sul25 furic acid under stratospheric conditions, J. Geophys. Res., 22(4), 3858211;388, 1995.

Hanson, D. R., Ravishankara, A. R., and Lovejoy, E. R.: Reaction of BrONO2 with H2O on submicron sulfuric acid aerosol and implications for the lower stratosphere, J. Geophys. Res., 101(D4), 90638211;9069, 1996.

Hebestreit, K., Stutz, J., Rosen, D., Matveev, V., Peleg, M., Luria, M., and Platt, U.: First DOAS Measurements of Tropospheric Bromine Oxide in Mid Latitudes, Science, 283, 558211;57, 1999.

Matveev, V., Hebestreit, K., Peleg, M., Rosen, D. S., Tov-Alper, D., Stutz, J., Platt, U., Blake, D., and Luria, M.: Bromine Oxide-Ozone interaction over the Dead Sea, J. Geophys. Res., 106, D10, 10 3758211;10 387, 2001.

Siesel, S., Caloz, F., Fenter, F. F., van den Bergh, H., and Rossi, M. J.: The Heterogeneous Reaction of NO3 with NaCl and KBr: A Nonphotolytic Source of Halogen Atoms, J. Geophys. Res., 24(D22), 27578211;2760, 1997.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J.,

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8, S4742–S4748, 2008

Interactive Comment

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Burrows, J., Carpenter, L. J., Friess, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and their role in polar boundary layer ozone depletion, Atmos. Chem. Phys., 7, 43758211;4418, 2007,

[ERAN: you should give the entire list of authors, without et al.]

Tas, E., Peleg, M., Matveev, V., Zingler, J., and Luria, M.: Frequency and extent of bromine oxide formation over the Dead Sea, J. Geophys. Res., 110(D11), D11304, doi:10.1029/2004JD005665, 2005.

Tas, E., Peleg, M., Pedersen, D. U., Matveev, V., Pour Biazar, A., and Luria, M.: Measurement-based modeling of bromine chemistry in the boundary layer - Part 1 : Bromine chemistry at the Dead Sea, Atmos. Chem. Phys., 6, 5889 8211; 5604, 2006.

von Glasow, R., Sander, R., Bott, A., and Crutzen, P. J.: Modeling halogen chemistry in the marine boundary layer 1. Cloud-free MBL, J. Geophys. Res., 107(D17), 43418211;4352, 2002.

Wanger, A., Peleg, M., Sharf, G., Mahrer, Y., Dayan, U., Kallos, G., Kotroni, V., Lagouvardos, K., Varinou, M., Papadopoulos, A., and Luria, M.: Some observational and modeling evidence of long-range transport of air pollutants from Europe toward Israeli coast, J. Geophys. Res., 105(D6), 71778211;7186, 2000.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7725, 2008.

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8, S4742-S4748, 2008

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