

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.

E. Tas et al.

Received and published: 1 October 2006

We would like to thank very much the reviewer for his efforts and the relevant and detailed comments. Several comments raised by the reviewer indicate that a number of points presented in our paper were not entirely clear. Our responses to the reviewer's comments clarify these issues point by point, and most of these explanations will be incorporated into the revised version.

1. We agree that the paper needs to be restructured. The revised manuscript is being severely edited to improve clarity and in order to prevent repetitions. Most of section 3.2 (Chemical Mechanisms) will be removed to the Introduction. It was thought that separating section 3 into subsections might be more helpful for the reader. However,

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

based on the comments of the two referees we agree now that some of the subsections should be removed, especially in section 3. The results and discussion sections will be reorganized. We agree that cycles 1 and 2 should be included in the introductory section. However, we contend that the chemical mechanism we present as Cycle 3 belongs in the results and discussion section, because it presents for the first time a coherent cyclical unit of RBS chemistry, and, furthermore, it is shown to be a central component of this chemistry in a physical location.

To the best of our knowledge, this combination of reactions was not yet presented as an integrated process. It emphasizes the combined effect of H1 and H2 on the production of Br, the sensitivity of this combined process to anthropogenic NO₂, and enables us to establish a variety of chemical parameters: the rate limiting step, the net of the reaction cycle, and those parameters to which this process is sensitive. Beyond the theoretical contribution to the understanding of RBS chemistry, our paper demonstrates the validity of this cycle in a physical location - the Dead Sea - that happens to provide the conditions that enhance the importance of this cycle, in particular the levels of NO₂ which are high relative than at other RBS activity locations. One of the purposes of this paper is to present this process so that it may be considered for studies of other areas with RBS activity, especially in mid-latitudes.

2. In the reply for the first comment in this document we have demonstrated the importance of including reactions H1 and H2 as part of Cycle 3b. By doing so we were able to better characterize these processes and the factors to which they are sensitive. In the revised manuscript we will change the emphasis in the presentation of the mechanism of Cycle 3. Instead of introducing the two heterogeneous processes (reactions H1 and H2) in the existing form, we will present the integrated cycle in the Results and discussion section as part of the RBS chemistry at the Dead Sea, while clarifying the previously known importance of the reactions themselves.

3. We agree that additional information regarding the one-dimensional model should be provided. The revised manuscript will reflect the explanations provided in the following

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

sub-sections as appropriate.

-We believe that the paper provides a clear explanation about what chemistry occurs in the gas phase (see section 2.1, P.4933, lines 17-20), and which is a heterogeneous process (see section 2.1, P.4934, lines 10-16). However, we will make sure that the differentiation between the gas and aqueous phases is as clear as possible in the revised manuscript.

-The total surface area of the sulfate aerosols was estimated based on measured concentrations of sulfate aerosols (Matveev et al., 2001), the average value for the sulfate aerosols density and the average radius of the sulfate aerosol. The total surface area values used are in the range of 50-65 $\mu\text{m}^2/\text{cm}^3$. It should be remarked that the concentrations of sulfate aerosols measured at the Dead Sea by Matveev et al. (2001) were 'similar to other values that were reported for this area (Andrea et al., 2002; Wanger et al., 2000; Formenti et al, 2001)' (P. 4935, lines 2-4). Sensitivity analysis showed a relative small change (<20% average for all time points) in BrO concentrations for different values of ASA's in the range of 40 to 75 $\mu\text{m}^2/\text{cm}^3$, and no effect on the trends in BrO concentrations.

The only species that were allowed to be taken up onto aerosol surfaces are BrONO₂ on sulfate aerosols and HOBr on sea salt aerosols, since reactions H1 and H2 are the only two heterogeneous reactions that were included in the model. This will be emphasized in the text. The reason for that is explained in the reply to the comments of referee # 1 (methodical problems, comment no.1 in the two documents). 'A value of 0.75 was assumed for (H1) based on literature data (Atkinson et al., 2004; Hanson et al., 1996) and a comparison of model simulations with relevant measurements' (P. 4935, lines 12-14). No specific uptake coefficient for reaction H2 was used in the model, because the rate constant for reaction H2 was determined as a degree of freedom in the model based on comparison of model simulations and measurements (see our reply to the comments of referee #1, Methodical problems, comments 2 and P. 4936, lines 12-15). It should be remarked that 'The average rate obtained for reaction H2 was $\sim 1.35 \cdot 10^{-6}$

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ppb/s, in a good agreement with reported values' (P. 4936, lines 14-15).

The photolysis rate of BrONO₂ is given in Table 2 representing the value for 150 zenith angle. Please notice that the rates of photolysis reactions were not constant and were changed according the magnitude of the calculated actinic flux (see P.4934, lines 1-9). The values for DH1 / Dt and DH2 / Dt are provided for Julian Day 221 (see Fig. 8). The average rate for reaction H1 will be provided in the revised version, and we may also compare it to the photolysis rate of BrONO₂.

In the model only the uptake of BrONO₂ on sulfate aerosol and the uptake of HOBr on sea salt aerosols were considered. One of the major contributions of this paper is to demonstrate that the addition of only these two heterogeneous reactions is not only necessary but also sufficient to reconstruct the BrO time-series measured at the Dead Sea (see section 3.1.2, Figs. 3 and 4). Other heterogeneous reactions may take place at the Dead Sea, but our simulations suggest that their role in the RBS chemistry at this area is expected to be less significant (see our reply to the comments of referee #1, methodical problems, comment no. 1). A more detailed comparison of the processes that take place at the Dead Sea is beyond the scope of this paper, and should definitely be a priority for future research.

We will comment in the paper about the possible involvement of BrCl and its potential effect on our results. The influence of chlorine species at the Dead Sea should not be ruled out, although it is expected to be low relative to the contribution of bromine species due to the low Cl/Br ratio (about 40) at the Dead Sea. This is because the production of Br₂ is expected to be more efficient than the production of BrCl for T=<295 K in a factor greater than 10 (Fickert et al., 1999) and because the production of Cl is dominant only for a [Cl-]/[Br-] ratio of greater than 2000 (Behnke et al., 1999).

As was already explained in this reply, other heterogeneous reactions may take place at the Dead Sea, although our simulations suggest that their role in the RBS chemistry at this area is expected to be less significant (see our reply to the comment of referee

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

#1, methodical problems, comment no. 1).

- The model that was used is certainly not constrained by NOX and hydrocarbons fluxes. The NOX and hydrocarbons fluxes were determined based on measurements. This was done by performing dozens of preliminary simulations that were based on these days in which no significant activity of Reactive Halogen Species (RHS) was detected at the evaporations ponds. In these preliminary simulations the Reactive Bromine Species (RBS) mechanism was not included. At the end of this stage a reasonable agreement was obtained between the measured and simulated time series of ground level NOX and hydrocarbons for these days in which no RBS activity was detected. Only at the next stage, the RBS mechanism was included, but the fluxes were not changed. Thus, once these fluxes were determined for these days in which no RBS activity was observed, they were not changed and the same fluxes were used for each of the simulations that included bromine chemistry. More information about the physical meaning and additional information about how they were calculated can be found in the reply to referee #1 comments, methodical problems, comment no.3 In addition to the NOX and hydrocarbons also ozone fluxes were included as explained in detail in sections 3.1.1 and 3.4 and in the reply to the comments of referee #1, methodical problems, comment no.4. The time series of these fluxes was determined based on direct measurements of ozone concentrations at the site of the evaporation ponds at the Dead Sea. These fluxes should have been included in every model that would aimed at describing the RBS activity at the Dead Sea, due to the entrainment of ozone fluxes into the area of the evaporation ponds (see sections 3.1.1 and 3.4). In addition to that, 'a very small flux of Br₂ of 10 molecules*cm⁻² s⁻¹ was added only for initiation of the bromine species activity, from ground level upwards'(P. 4936, lines 22-24).

Since the inclusion of the heterogeneous processes and the ozone fluxes were sufficient in order to obtain a good agreement between simulations and measurements (see Fig. 4 and section 3.1.2), there was no need to use the model with constraining fluxes. We will include additional information on the fluxes used in the model in the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

revised version.

-The height of planetary boundary layer in each of the simulations was changed continuously as a result of the dynamic atmospheric processes. The planetary boundary layer height was calculated by running the 1 d Meteorological model (McNider and Pielke, 1981) (see P. 4936, lines 26-27).

The model simulations describe the chemical species at a height of 2 meters above ground level. This information together with the information about the vertical resolution of the model will be provided in the revised version. The description of the vertical profiles was beyond the scope of the present study.

If required, details regarding the vertical parameters used in the model can be provided.

4. In this paper we refer only to gaseous HOBr. In section 3.3 we refer to the rate of decomposition of BrONO₂ which yields gaseous phase HOBr via the formation of HOBr(aq) (e.g., Hanson and et al., 1996; Atkinson et al., 2003). We should make this point clearer.

The average mixing ratios of OH and HO₂ will be given in the revised version. In the paper, the formation of HOBr by reaction between HO₂ and BrO (reaction G6, Table. 1) was compared to the rate of formation by the heterogeneous decomposition of BrONO₂ (H1). The implications of the ratio between the two reactions rate was further discussed in the light of the significance of reaction H1 (see P. 4949, lines 7-13). We think that a more detailed discussion about the influence of HO₂ is beyond the scope of this paper. We may, however, discuss this issue in the paper if asked to do so. The concentrations of NO_x and HO_x were not kept constant. Their concentrations were changed by the model throughout the model runs.

5. The changes in Br concentrations with time serve as a chemical regulator for the entrainment of ozone fluxes in the transition area between the outside of the evaporation ponds to their center. It does not mean that these changes in time of Br concentrations

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

influence the entrainment of air masses, but that they influence the levels of ozone in these advected air masses in the transition zone. This issue is explained in detail in section 3.4. We certainly agree that the paragraph in section 3.4 that describe the influence of the change of Br concentrations in time on O₃ concentrations should be reworded.

6. In the paper we explain the conversion of NO₂ to NO_z by the heterogeneous decomposition of BrONO₂ (reaction H1) leading to the formation of HNO₃ (see section 3.6 P. 4949, lines 14-28 and P. 4950, lines 1-8). All of the 166 reactions that represent the basic photochemical mechanism were included in all of the simulations that were presented in our study. Thus, other chemical channels that lead to the formation and destruction of HNO₃ were taken into account in the analysis presented in figure 9, including the reaction between NO₂ and OH. The analysis showed that only the inclusion of reaction H1 could account for the sharp decrease in NO₂ concurrent with an equivalent increase of ~1 to 2 ppb in NO_z, as was frequently observed by the measurements.

In the revised version we will clearly state that this analysis includes all of the other gas phase reactions that influences the concentrations of HNO₃.

7. The morning peak in BrO will be discussed although this peak (Figs. 3 c,d) is not a special interest at the Dead Sea, because in this area the BrO profile contains several other peaks during the length of the day. This is due the cyclic periodic process described in section 3.4 which leads alternately to the efficient production of BrO and then to its fast destruction. We will include a short discussion regarding this point in the revised version. It should also be remarked that the peak which is strongly evident in figure 3a and 3b does not appear in the measurements, and only appeared for incomplete stages of the model simulations.

References:

Andrea, T. W., Andrea, M. O., Ichoku, C., Maenhaut, W., Cafmeyer, J., Karnieli, A., and

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

orlovsky, L.: Light scattering by dust and anthropogenic aerosol at remote site in the Negev desert, Israel, *J. Geophys. Res.*, 107(D2), doi:10.1029/2001JD900252, 2002.

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, 2003. <http://www.iupac-kinetic.ch.cam.ac.uk/>.

Behnke, W., C., George, V. Scheer, and Zetzsch, C.: Production and decay of CINO₂ from the reaction of gaseous N₂O₅ with NaCl solution: bulk and aerosol experiments. *J. Geophys. Res.*, 102, 3795-3804, 1997.

Fickert, S., Adams, J. W., and Crowley, J. N.: Activation of Br₂ and BrCl via uptake of HOBr onto aqueous salt solutions, *J. Geophys. Res.*, 104 (D19), 23,719-23,727, 1999.

Formenti, P., Andrea, M. O., Andrea, 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), 4871- 4890, 2001.

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), 9063-9069, 1996.

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, 2001.

McNider, R. T., and Pielke, R. A.: Diurnal boundary-layer development over sloping terrain, *J. Atmos. Sci.*, 38, 2198-2212, 1981.

Wanger, A., Peleg, M., Sharf, G., Mahrer, Y., Dayan, U., Kallos, G., Kotroni, V., Lagourdou, K., Varinou, M., Papadopoulos, A., and Luria, M.: Some observational and modeling evidence of long-range transport of air pollutants from Europe toward Israeli

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

coast, J. Geophys. Res., 105 (D6), 7177-7186, 2000.

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

ACPD

6, S3443–S3451, 2006

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

S3451

EGU