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Comment

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

E. Tas et al.

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We would like to thank very much the reviewer Referee 2 for his efforts and the important comments.

In response to the referees comment, an additional section (Sect 2.1 - Model description) will be added in order to include a description of the model and its evaluation in the paper, as follows:

2.1 Model description

The core of the research analysis was done by a one dimensional Chemical Transport

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Interactive Discussion

Discussion Paper



Model, UAHCTM 1D (Biazar, 1995). This model and its settings for the present study are essentially the same as used for a companion paper (Tas et al., 2006). A brief description of the model and its settings are presented here. The model includes an explicit gas phase chemical mechanism and takes into account the vertical motion of the different species based on diffusion and advection calculations and on deposition velocity values. For the present study the model used 27 levels from the surface to a height of 10 km with variable spacing in order to represent the boundary layer with greater vertical resolution. Results are presented only for a height of 2 m, at which the chemical parameters were measured.

Fluxes were added for NO, NO₂ and 13 different hydrocarbons species, at heights between ground level and the base of the planetary boundary layer. The fluxes were determined from simulations based on measurements performed at the Dead Sea evaporation ponds on days when no significant activity of RHS was detected. Ozone fluxes were added in order to simulate the advection of fresh ozone into the evaporation ponds (see Sect. 3.1.1 in Tas et al. (2006)). A very small flux of Br₂ of 10 molecules cm⁻² s⁻¹ was added for initiation of the bromine species activity, from ground level upwards. Necessary meteorological parameters representative of real conditions, including the planetary boundary height, were obtained by running the 1 d Meteorological model (McNider and Pielke, 1981).

The deposition velocities of some bromine species were included based on Sander and Crutzen (1996). The deposition velocities for NO, NO₂, and 9 additional organic compounds were determined based on Trainer et al. (1987). The meteorological conditions, fluxes, solar data and heterogeneous parameterizations were updated every 15 min in all simulations.

In the model the basic photochemical processes are described by 166 gas-phase reactions based on the Trainer mechanism (Trainer et al., 1987), and updated according to Atkinson et al. (2003). Thirty-one reactions, including five photochemical reactions were added to describe the bromine gas phase mechanism. The rate constant of each

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photochemical reaction was calculated by running the Tropospheric Ultraviolet Visible Radiation model (Madronich et al., 1998). Two heterogeneous processes, the heterogeneous decomposition of BrONO₂ (H1) and the Bromine Explosion mechanism (H2) were also added.

In addition, a more detailed description of the parameterization of the two heterogeneous reactions (H1 and H2) will be included in Sect 2.1, according the comment of referee 1 regarding this issue.

The second comment of the reviewer refers to the usage of the counter species method. It appears that we have used for the present paper a method that is partially similar to the counter Species analysis that was originally described by Leone and Seinfeld. (1984). The purpose of the two methods is to quantitatively estimate the influence of a specific reaction, or chemical pathway, on a complex chemical mechanism. For both methods this goal is technically achieved by inclusion of a fictitious species as the reaction product. In the method we used the fictitious product is also subjected to the physical processes that were included in the model. This enables the isolation of the chemical effect from the physical effects in determining the contribution of this reaction to the formation of its products (see Sect. 2.2 in Tas et al., 2006). Due to the similarity between the two methods, we will add the relevant citation (Leone and Seinfeld, 1984) to the revised version in order to indicate it. It should be remarked that we believe that the reviewer referred in his comment to the above-mentioned paper, although in his comment the reviewer mentioned the work presented by the paper of Leone and Seinfeld. (1985). It should be noted here that a detailed description of the method used for the present paper is available in Tas et al. (2006).

According to the reviewers suggestion we have performed an additional analysis based on the counter species method, for cases for which we thought it may be relevant to include additional support to our conclusions based on this method. It should be remarked that most of our conclusions in the present manuscript were already supported by the counter species method, even if it was not specifically mentioned. Based on this

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Interactive Discussion

Discussion Paper



further analysis we will add the following to the revised version of the paper:

Page 7737, line 15: An analysis following the counter species method (Leone Seinfeld) showed that there is an overall increase of about a factor of 4.2 in the production of Br via Cycle 3b due to an increase of about a factor of 2 in the rate of reaction H2.

Page 7737, line 28: In the higher zone, the rate of reactions through Cycle 3b increases by about 10The first analysis emphasizes the significant contribution of Cycle 3b to the production of BrO_x and ozone destruction in the lower zone. The second analysis quantitatively support the fact that the decrease in the concentrations of BrOx in the higher zone is mainly the result of the increase in the rate of reactions through Cycle 5 relative the rates of reactions through Cycle 3b. The information supplied for the two zones supports our explanations for the difference between the influence of NO₂ on RBS activity, in the two zones, which is the chemical basis for the main conclusions presented by the paper.

References

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/>, 2003.

Biazar, A. P.: The role of natural nitrogen oxides in ozone production in the southern environment, Dissertation, The Department of Atmospheric Sciences, The University of Alabama in Huntsville, 1995.

Leone, J. A., and Seinfeld, J. H.: Analysis of the characteristics of complex chemical reaction mechanisms: application to photochemical smog chemistry, Environ. Sci. Technol. 1984, 18, 280-287.

Leone, J.A. and J.H. Seinfeld, Comparative analysis of chemical reaction mechanisms for photochemical smog, Atmos. Environ., 19, 437 - 464, 1985.

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Interactive Discussion

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McNider, R. T. and Pielke, R. A.: Diurnal boundary-layer development over sloping terrain, *J. Atmos. Sci.*, 38, 21988211;2212, 1981.

Michalowski, B. A., Francisco, J. S., Li, S. M., Barrie, L. A., Bottenheim, J. W., and Shepson, P. B.: A computer model study of multiphase chemistry in the Arctic boundary layer during polar sunrise, *J. Geophys. Res.*, 105, 15 1318211;15 145, 2000.

Mozurkewich, M.: Mechanisms for the release of halogens from sea-salt particles by free radical reactions, *J. Geophys. Res.*, 100(D7), 14 1998211;14 207, 1995.

Sander, R. and Crutzen, P. J.: Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea, *J. Geophys. Res.*, 101(D4), 91218211;9138, 1996.

Tas, E., Peleg, M., Pedersen, D. U., Matveev, V., Biazar, A. P., and Luria, M.: Measurementbased modeling of bromine chemistry in the boundary layer: 1. Bromine chemistry at the Dead Sea, *Atmos. Chem. Phys.*, 6, 55898211;5604, 2006.

Trainer, M., Williams, E. J., Parish, D. D., Buhr, M. P., Allwine, E. J., Westberg, H. H., Fehsenfeld, F. C., and Liu, S. C.: Models and observations of the impact of natural hydrocarbons on rural ozone, *Nature*, 329, 7058211;707, 1987.

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