

## ***Interactive comment on “Measurement-based modeling of bromine-induced oxidation of mercury above the Dead Sea” by E. Tas et al.***

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We would like to thank very much the reviewer for the relevant and important comments. Below we outline a point by point detailed description of the modifications that will be incorporated in the revised version.

1. Some discussion regarding how mercury chemistry was implemented in the MECCA simulation will be useful. Was the oxidant generation simulated on-line or off-line? This could make a significant difference of the model results because the resulted oxidant concentrations would be different. Also, the generation of reactive halogen species is highly dependent on the aerosol generation scheme and associated meteorology (i.e., wind and sunlight), and should be made clear. Finally, a table summarizing the initial conditions and the atmospheric environment for the chemical modeling will be

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extremely helpful, as it would significantly affect the model results.

- The oxidants formation was calculated online based on chemical in-situ measurements of NO<sub>x</sub> and O<sub>3</sub> and BrO (used for model validation) plus in-situ measurements of meteorological parameters (Sect. 2.1). The concentrations of sea salt (initial composition was based on the Dead Sea water composition, Sect. 2.2) and sulphate aerosols modes were determined as follows: dependency of average sea salt aerosol number concentrations on wind speed was taken into account using Eq. 4 in Gong et al. (1997) on 5 minutes time resolution (see also Tas et al., 2006); average sulphate aerosol number concentrations were determined based on in situ measurements, using reported densities (Karg et al., 1995) and radius dependency on RH (Yue, 1979) (Sect. 2.2) and updated on time resolutions of 5 minutes. Photochemical rate constants were updated at each time step (1 minute) as described in Landgraf and Crutzen. (1998). Notice that simulation days showed dominant daytime wind directions from the east (i.e., i.e., from Dead Sea) so that no significant advected sources from land were expected to be present during AMDEs simulations. Aerosol activity was shut down for RH<28%, which was determined based on measurements (see Obrist et al., 2011). Measured temperature and relative humidity were updated on a 5 minutes time step. In MECCA, gas-aerosol partitioning is based on kinetic limitations for the Henry's law, by using transfer coefficients (Sander et al., 1996). The averaged mass transfer coefficient for each aerosol mode in MECCA is based on integration over a lognormal shape distribution of the particle radius, for each aerosol mode (compare e.g. Sander (1999), Eq. 113). The mercury mechanism was implemented into MECCA based on the reaction rates which are presented in tables 1-4 in the supplemental section. We will make sure that any missing information of the above will be included in the revised paper including a table which will present the typical concentrations and average values of the measured chemical and meteorological parameters.

2. The entire simulation has a strong emphasis on bromine species (Section 3.1). Although the authors stated that other reactive halogen species were also included

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in the modeling, it is not clear to what extent this was done. MECCA is capable of calculating a wide range of odd oxygen and reactive halogen species, and therefore it is possible to compute the relative importance of various oxidants. Depending on the atmospheric conditions, the role of reactive chlorine and iodine species could be important. There is a need for the author to make a stronger case that the contribution of the reactions involving other oxidants can be ruled out.

- Our simulations in fact included all reactions of halogen species which are included in the default MECCA mechanism (<http://www.mpch-mainz.mpg.de/~sander/messy/mecca/>). Our model results indicated that the role of chlorine and iodine species were unimportant for Hg0 to HgII conversion at the Dead Sea and that bromine species were the main oxidants (see Fig. 7). The results are in agreement with an expected dominance of bromine chemistry at the Dead Sea: previous studies showed that the bromine explosion mechanism is the most probable mechanism for bromine release from Dead Sea water (e.g., Matveev et al., 2001; Tas et al., 2005; Tas et al., 2005, 2006; Smoydjini and von Glasow). Laboratory studies also indicate dominant release of Br<sub>2</sub> from seawater for [Br<sup>-</sup>]/[Cl<sup>-</sup>] ratios of 1/2000, (Fickert et al., 1999). while the [Br<sup>-</sup>]/[Cl<sup>-</sup>] ratio in Dead Sea water is about 50 times higher (Tas et al., 2005), resulting in much higher dominance of Br<sub>2</sub> release over BrCl. This is likely the reason that any attempt to measure ClO at the Dead Sea have failed. The relatively low contribution of reactive chlorine species at the Dead Sea was reinforced by our model simulations (Fig. 7) as model simulations indicate that the ClO concentrations were always in the sub-ppt level (at least two orders of magnitude than BrO concentrations). Fig. 7 also shows that iodine species were unlikely oxidants for mercury. In addition, iodine species, which at the Dead Sea have been measured as iodine oxide (IO) up to 10 pptv (IO), appear to be inactive at high BrOx levels based on the observation that BrO peaks only in the absence or at low levels of IO (Zingler et al., 2005). This fact, together with the exact temporal correspondence between Hg(II) production, Hg(0) depletion, and high BrO levels, show that IO does not play any significant role in AMDE of the Dead Sea (see also Obrist et al., 2011). The above

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points will be made clearer in the revised version.

3. Was there any measurement performed for Br to suggest that the simulated concentration is representative? What was the cause for the sudden peak for the BrO/Br ratio?

- There are no direct measurements of Br available. However, we believe that both ozone (see new figure 1 below which will be added to the revised manuscript in response to comments by referee#2) and BrO (Figs. 1,2 and Supplement Figs. 1 and 2 for BrO) are well represented in our model. Br concentrations can be well approximated using concentrations of O<sub>3</sub> and BrO (e.g., Wayne et al., 1995). The reason for the sudden peak for the BrO/Br is sudden increase in measured O<sub>3</sub> concentrations after the termination of RBS activity and AMDE's. This increase was also represented in the model with an O<sub>3</sub> advection source term (as discussed in detail in Sect. 2.3 and as extensively described in our responses to referee # 2).

4. From Figures 1-9, the authors only showed the concentration changes or depletion rate of gaseous elemental mercury (GEM). Since reactive gaseous mercury (RGM) was also measured during the campaign, would it be possible to show the corresponding RGM production from the measurement and model simulation to better illustrate the fate of mercury during the depletion events?

- We focused on GEM in our simulations since converted RGM will undergo immediate and strong deposition. Hence, to accurately simulate RGM concentrations, good knowledge of oxidized mercury deposition velocities are needed which are currently not well determined. For this reason, we selected to focus on GEM. However, in our previous manuscript focused on experimental measurements (Obrist et al., 2011), we show a graph how GEM depletions relate to RGM concentrations and infer about the immediate deposition of RGM (30 – 60%, depending on season) during AMDEs.

References

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- Calvert, J. G. and Lindberg, S. E.: A modeling study of the mechanism of the halogen-ozonemercury homogeneous reactions in the troposphere during the polar spring, *Atmos. Environ.*, 37, 4467–4481, 2003.
- Gong, S.L., Barrie, L.A., and Blachey, J.-P.: Modelling sea-salt aerosols in the atmosphere. 1. Model development. *J. Geophys. Res.* 102 (D3), 3805, 1997.
- Karg, E., Uhl, J., and Heyder, J.: Particle Density of Sulfite and Sulfate Test Aerosols, *J. Aerosol Sci.*, 26, S611–S612, 1995.
- Landgraf, J. and Crutzen, P. J.: An efficient method for online calculations of photolysis and heating rates, *J. Atmos. Sci.*, 55(5), 863–878, 1998.
- Lindberg, S. E., Brooks, S., Lin, C.-J., Scott, K. J., Landis, M. S., Stevens, R. K., Goodsite, M., and Richter, A.: Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise, *Environ. Sci. Technol.*, 36, 1245–1256, 2002.
- Matveev, V., Peleg, M., Rosen, D., Tov-Alper, D. S., Hebestreit, K., Stutz, J., Platt, U., Blake, D., and Luria, M.: Bromine oxide-ozone interactions over the Dead Sea, *J. Geophys. Res.*, 106, 10375–10387, 2001.
- Obrist, D., Tas, E., Peleg, M., Matveev, V., FaĀĀsn, X., Asaf, D., and Luria, M.: Bromine-induced oxidation of mercury in the mid-latitude atmosphere, *Nature Geosci.*, 4, 22–26, 2011.
- Smoydzin, L. and von Glasow, R.: Modelling chemistry over the Dead Sea: Bromine and ozone chemistry, *Atmos. Chem. Phys.*, 9, 5057-5072, doi:10.5194/acp-9-5057-, 2009.
- 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: 1. Bromine chemistry at the Dead Sea, *Atmos. Chem. Phys.*, 6, 5589–5604, doi:10.5194/acp-6-5589-2006, 2006.

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- 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.
- Vogt, R., Crutzen, P. J., and Sander, R.: A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature*, 383, 327–330, 1996.
- Wayne, R. P., Poulet, G., Biggs, P., Burrows, J. P., Cox, R. A., Crutzen, P. J., Haymann, G. D., Jenkin, M. E., Bras, G. L., Moortgat, G. K., Platt, U., and Schindler, R. N.: Halogen oxides: Radicals, sources and reservoirs in the laboratory and in the atmosphere, *Atmos. Environ.*, 29, 2675–2884, 1995.
- Xie, Z.-Q., Sander, R., PĀĀoschl, U., and Slemr, F.: Simulation of atmospheric mercury depletion events (AMDEs) during polar springtime using the MECCA box model, *Atmos. Chem. Phys.*, 8, 7165–7180, doi:10.5194/acp-8-7165-2008, 2008. 5 Yue, G. K.: On the Characteristics of Sulfate Aerosols formed
- Yue, G. K.: On the Characteristics of Sulfate Aerosols formed in the Presence of Ion Sources, *J. Aerosol Sci.*, 10, 387–393, 1979.
- Zingler, J. and Platt, U.: Iodine oxide in the Dead Sea Valley: Evidence for inorganic sources of boundary layer IO, *J. Geophys. Res.*, 110, D07307, doi:10.1029/2004JD004993, 2005.

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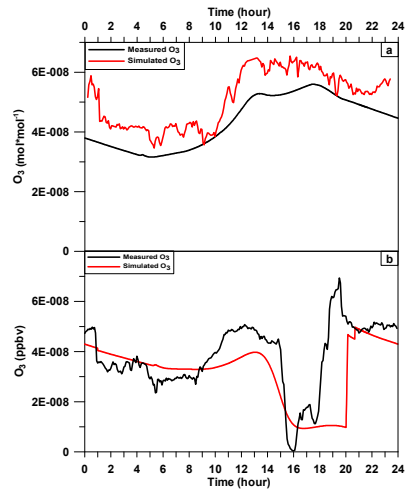


Figure 1. Simulated and measured O<sub>3</sub> concentrations. Comparisons are shown for Julian days 201 (panel a) and 188 (panel b).

Fig. 1.

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