

Interactive comment on “The influence of nitrogen oxides on the activation of bromide and chloride in salt aerosol” by S. Bleicher et al.

Anonymous Referee #2

Received and published: 6 June 2014

Bleicher et al present a combination of DOAS and CIMS measurements in a reaction chamber and numerical model studies to investigate the importance of nitrogen oxides on the release of halogens (bromine and chlorine) from salt aerosols. This is a novel study which shows the influence of NO_x on halogen release under high NO_x conditions and a logarithmic relationship for O_3 destruction as function of initial NO_x mixing ratios was shown to fit the data. However the conclusions could and should be stronger and only few attempts are made to discuss the atmospheric relevance of this study which is surprising given the name of the journal that this manuscript was submitted to. The ability of the model to reproduce the measurements is much poorer than stated and implied in the manuscript and it remains somewhat unclear whether the main processes and reaction cycles are really quantitatively reproduced and understood. Many details

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of the experiment and modeling remain unclear.

Specific comments

Abstract: Please explain the atmospheric relevance of this study. Lines 13-18 contain very little information and it is unclear what “reasonable” agreement is and how this provides “important information”. Please strengthen the key conclusions.

p. 10138, l. 21: How important is this reaction? It does not seem to be included in the model, which – according to the supplement – only has photolysis as loss for OClO. Under the very high chlorine loadings in the chamber the reaction of ClO + OClO might be important too as it is only a slightly slower than Cl + OClO but the ClO concentrations are much higher than [Cl]. These reactions only lead to interversion of ClO_x species but this could help to address the problems with ClO_x mixing ratios in the model compared to the measurements and the timing of peaks (see below).

p. 10139, l. 26: Missing subscript in ClNO_2 .

p. 10139, l. 27: Sentence incomplete.

p. 10140, l. 13: How important is NOCl in the atmosphere? To my knowledge it has never been observed and it doesn't seem to be included in the model used here.

p. 10141, l. 7: Is the overpressure really only 0.5 Pa and not 0.5 hPa? Is that sufficient to achieve what is mentioned in the next few lines?

p. 10141, l. 26: Reference is missing in bibliography.

p. 10141, l.27-29: At these relative humidities there is a substantial contribution of the volume of the aerosol constituents to the total particle volume so their total volume is greater than the liquid water content.

p. 10142, l. 7-9: Does the concentration of Br^- really have a measurable impact on Mie scattering? The total aerosol volume of course but the Br^-/Cl^- ratio surely doesn't.

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p. 10142, l. 16: A 4σ statistical error appears quite conservative as estimate of the detection limit especially given the results presented in Figure 3 which seems to show substantial OCIO levels.

p. 10143, eq (1): This seems to be a rather drastic simplification of the O_3 loss rate. Under what conditions is it valid? Surely the parameter c has to be a function of $[O_3]$ as most O_3 loss reaction are at least linear in O_3 .

p. 10143 Radical clock method: given that the hydrocarbons constitute losses for OH and Cl – how easy is it to use the concentrations derived for these radicals this way in chamber experiments without injection of the hydrocarbons? What are the derived [OH] and [Cl] concentrations? How does HO_x radical chemistry influence the reactions cycles discussed here? It is surprising how little use is made of the radical clock results in this paper.

p. 10144, chlorine actinometry: How did you test that [Cl] levels are only affected by Cl_2 photolysis and not by other photochemistry occurring in the chamber with UV lights turned on?

p. 10145, l. 15: What is this scaling factor and how did you chose it? According to your explanation the change in light output depends on the age of the lamps and that probably varies between the chamber experiments so why is a constant scaling factor appropriate for the simulation of all chamber experiments?

p. 10145, l. 26 - , p. 10146, l. 2: These assumed reactions are very fast (about 100x the respective photolytical loss of HOX) and hence are probably the main sink reactions for HOX in the model which adds a lot of uncertainty. This approach might be conserving mass but is it really a conservative estimate of what is happening? It is conceivable that the chamber walls are net sources of halogens from previous experiments – then mass conservation would not be appropriate. See also next point. The need to include these very fast reactions seems to suggest that the chemistry in the chamber is not really understood.

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p. 10146, l. 13, caption figure 3, p. 10147, l. 3-7, l. 15-16: The subtraction of a background of 200 ppt of BrO requires a stronger justification. Any bromine left over from previous experiments or released from the walls will take part in photochemical cycles so it is not clear why a constant value should be subtracted from the measured mixing ratio of BrO. Such a large change in [BrO] will affect how much of the observed $d[O_3]/dt$ can be explained by halogen chemistry. Given that the calculated ozone loss of 12 ppt/s is much less than the measured value of 55 ppt/s this could be a major issue. Please explain this in more detail.

p. 10148, l., 4 (see also p. 10142, l. 16): The measured OCIO (see figure 3) is obviously below the detection limit that you defined but can the measured values of about 100 ppt of OCIO really be completely discounted and are they really consistent with the modeled values of less than 3ppt? Please discuss this in more detail.

p. 10149, l. 5: What is this assumption based on?

p. 10149, model vs data discussion: The model does not seem to reproduce the measurements very well: BrO is too low in the model, ClO is far too high and in the model $[ClO] \gg [OCIO]$ whereas in the experiment the opposite is the case. Furthermore the evolution with time of BrO, ClO and OCIO looks quite different in the model compared to the experiment. Please explain why you think that based on this the simulated and measured mixing ratios are “quite comparable”. Also (l. 17-19): it should be easy to show that the shape of BrO is caused by your assumption, this should be added.

p. 10150, model vs data discussion: The figure references appear to be wrong, please check. The sequence in which XY peak is different in observations (fig 7: first Br_2 , then BrCl, then Cl_2) and model results (fig. 6: first Br_2 , then Cl_2 , BrCl not shown). How does this “verify” the model results?

p. 10151, discussion of potential importance of reactions R20-22: What is the source of NOCl and has it ever been measured in the atmosphere? Why is it not included in the model if you think that this is the most important reaction cycle? Please show a

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mass balance that proves that addition of Cl^- to the particles leads to a measurable growth of the aerosol.

p. 10151, l. 13-15: Please expand this explanation as it is too brief.

p. 10151, l. 18; p. 10152, l. 3: This presumably refers to Fig 8?

p. 10152, l. 9-10: Surely 1ppt of chlorine is not going to make a difference on ozone in a semi-polluted environment. Please explain this comment in more detail.

p. 10151-10152: The overall conclusions and atmospheric relevance need to be discussed in more detail. The first few lines on p. 10152 for example only list conclusions that had already been drawn in previous studies. The model does not seem to be able to reproduce the measurements quantitatively so the last paragraph is quite a strong exaggeration. It remains somewhat unclear what the conclusions of this study are and how the atmospheric community is supposed to use the outcomes.

Fig. 6: The time evolution of bromide looks quite intriguing – it drops by about 8 orders of magnitude in 1 min and then jumps up again by 3 orders of magnitude. Please explain the reason for this.

Fig. 8: There appears to be a local minimum around 4ppb of NO_x in the case depicted with pink diamonds – is this an artifact or is there a physical explanation for this?

Other comments

The modeled $[\text{O}_3]$ is never shown. It would increase the confidence of the reader in the model runs if this were to reproduce the observations. Please add this to the model figures.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 10135, 2014.