Atmospheric
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Discussions

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

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Ref. 2 wrote: 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 O3 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

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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 of the experiment and modelling remain unclear.

Answer: We like to express our gratitude to the referee for valuable comments and questions on our paper. We have tried to answer all the questions and apply comments to our manuscript.
We think this work provides an important piece of information especially for a journal like ACP, with focus on field measurement. Detection of halogen oxides in medium to strong polluted areas are still rare and we feel it is important to raise awareness of the possible enhancement of BrO and even ClO formation by NO_X emission in those areas. We like to express our faith in understanding most chemical processes, especially the NO_X dependent bromine and chlorine release. We tried to state clearly, where the lack of understanding currently is and help to point into the direction for future research.
All changes have been addressed and pages and lines are indicated, where the paper has been changed.

Ref. 2 wrote: Abstract: Please explain the atmospheric relevance of this study.

Answer: We add to the abstract: P10136, l2: The influence of nitrogen oxides on halides is controversial discussed in the scientific community, since measurements of halogens in polluted areas are rare. This proofs that nitrogen oxides have a significant influence on the activation of halides. Since halides are omnipresent in the environment, the rising emissions of nitrogen oxides could have an impact on the oxidation capacity of the lower atmosphere.
Additionally we add to the introduction on p10137, l5: . . .discussion. Recently, Morin et al. (2012) indirectly linked the presence of reactive halogen species with emissions of NO_X from snowpack under arctic clean air conditions. Laboratory studies by Lopez-Hilfiker et al. (2012) and Wren et al. (2013) confirm the production of gaseous chlorine and bromine molecules from NaCl/NaBr-doped and acidified ice surfaces. The forma-

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tion of molecular bromine species was also observed in Arctic surface snowpacks by Pratt and coworkers (2013). The acidification of....

We also like to add to the introduction on p10136: ...is anthropogenic (Thornton et al.,2010). Minor sources such as the salt pans in arid continental areas and road salts are now coming into the spotlight of scientific discussion (e.g. Buxmann et al. 2012). Although...

Ref. 2 wrote: 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.

Answer: We like to replace p10136, l13-18 (Measurements ... aerosol pH.) with: This is a novel study where complex experiments close to environmental conditions are performed and directly compared to computer simulations by a multiphase model. Our main question was: "are halogen oxides observable if high loads of nitrogen oxides are present?" Here, the model predicted a consumption of NO_X before any XO radicals are observable. Moreover, the model calculations showed a strong correlation between the initial NO_X and the activation of halogens, especially chlorine. Our experimental results prove this. A way to summarize the effects of the complex reaction mechanism is the comparison of the consumption of ozone. The model shows a good agreement in consumption of ozone with the experiments over a wide range of different initial conditions. On the other hand, the model is not able to reproduce the duration of the induction period and the exact shape of the time profile of BrO, which has a direct influence on the time profiles of OClO and ClO. In the experiment we observed higher BrO mixing ratios than the model predicts. We think that the chamber walls are accelerating the chemistry by providing additional surface where heterogeneous reactions can occur. Although the quantitative overlay is not perfect, the model provides a detailed insight into the activation cycles and illuminates the chemistry of the aerosol phase. For a wide range of initial NO_X mixing ratios, the simulated ozone depletion rate matches the observations. Moreover, as in the experiments, the major consumption of ozone

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begins after the total loss of NO_X. Indeed, in direct comparison of the time profiles, the model calculation is by some minutes delayed; this is explainable by light leaks into the chamber, which start the day time chemistry earlier than in the model.

Ref. 2 wrote: 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 ClOx species but this could help to address the problems with ClOx mixing ratios in the model compared to the measurements and the timing of peaks (see below).

Answer: The product of the ClO + OClO reaction is Cl2O3, which is an intermediate with a fast unimolecular decay of $1.8 \times 10^5 s^{-1}$ back to ClO + OClO (Atkinson et al., 2007). This fast back reaction is the reason why it is not considered here.

Indeed, the addition of the OClO + Cl → 2 Cl (5.66 $\times 10^{-11}$) reaction does not change the system in a substantial way. Therefore, we removed R13 from the manuscript (Atkinson, R., Baulch, D.L., Cox, R.A.Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III - gas phase reactions of inorganic halogens, Atmos. Chem. Phys., 7, 981 – 1191, 2007).

Ref. 2 wrote: p. 10142, l. 16: A 4 σ statistical error appears quite conservative as estimate of the detection limit especially given the results presented in Figure 3 which seems to show substantial OClO levels.

Answer: We agree that Fig. 3 shows substantial OClO levels. We substituted the previous fig.3 and fig. 4 with only one figure 3 which shows a direct comparison of the experiment and the model run (here Fig.1). To reproduce the OClO mixing ratio we increased the initial NO_2 value to 1 ppb which led to a better reproduction of the experimental observation of the ozone depletion (here Fig. 1). The simulation repro-

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duces the experimental measurements well during the main part of the experiment. This main part is the activation and the release of halogens from the liquid phase. After the maximum values are reached, the modelled mixing ratios of the halogen oxides remain in a plateau, which is caused by the simplified wall reactions which do not allow a deactivation of halogens. See also the answer to referee 1.

Ref. 2 wrote: p. 10139, l. 26: Missing subscript in ClNO$_2$.

Answer: We correct this.

Ref. 2 wrote: p. 10139, l. 27: Sentence incomplete.

Answer: We remove "It alters".

Ref. 2 wrote: 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.

Answer: Since we are not able to give a direct prove, we decided to remove all reference to NOCl from this manuscript.

Ref. 2 wrote: 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?

Answer: Yes; the sensor for differential pressure (Kalinsky Elektronik, DS1, measurement range 0-25 Pa), although uncalibrated, worked in the lower range of its scale. The flow into the chamber was typically between 6-10 L/min, while the flow out of the chamber was typically between 2-5 L/min. The chamber walls were firmly inflated (except for the CIMS measurements, when this overpressure control had not yet been installed).

Ref. 2 wrote: p. 10141, l. 26: Reference is missing in bibliography.

Answer: p. 10157, l. 20: Siekmann, F.: Freisetzung von photolabilen und reaktiven Halogenverbindungen aus salzhaltigen Aerosolen unter simulierten und troposphärischen Reinluftbedingungen in einer Aerosol-Smogkammer, University of

Bayreuth, 2008.

Ref. 2 wrote: 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 that the liquid water content.

Answer: We agree with the reviewer, that the salt itself contributes to the volume of the aerosol. We have corrected the paragraph and the liquid water content at the respective pages as follows: p. 10141, l 27: The total volume of the particles equals to the liquid water content (LWC, given in m^3/m^3) plus the volume of the salt ions. The volume of dissolved sodium chloride is 2.9×10^{-29} m^3, which is the sum of the volume of both ions assuming spherical ions with a radius of Cl$^-$ of 181 pm and Na$^+$ of 102 pm [R. D. Shannon (1976)]. At 6100 mmol L^{-1} NaCl, the volume of the ions is 0.1 m^3/m^3, and the LWC is 90% of the total aerosol volume.
p.10146, l.17: ...containing 6.2×10^{-11} m^3/m^3 of liquid water and 0.8×10^{-11} m^3/m^3 dissolved sodium chloride.
p.10148, l. 22: with a LWC of 4.5×10^{-10} m^3/m^3 and 0.5×10^{-10} m^3/m^3 dissolved sodium chloride.
p.10160, Fig 2 caption:...in run A (6.2×10^{-11} m^3/m^3) compared to run B (5.5×10^{-10} m^3/m^3).
p.10166, Fig8 caption:... LWC 4.5×10^{-10}, red circles – 300 mmol L^{-1} bromide and LWC 4.5×10^{-10} and additional VOC injected, blue triangles – 1.6 mmol L^{-1} (road salt) bromide and LWC 4.5×10^{-10}, green triangles – salt pan experiments from Buxmann et al., 2012, pink diamonds – 30 mol L^{-1} bromide and LWC 4.5×10^{-9}, cyan dots – 5.2 mmol L^{-1} bromide and LWC 4.5×10^{-9}, orange asterisks – 52 mmol L^{-1} bromide and LWC 4.5×10^{-9}. The open symbols are model runs with initial parameters corresponding to the experiments.... R. D. Shannon (1976). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides". Acta Cryst A32: 751–767. Bibcode:1976AcCrA..32..751S. doi:10.1107/S0567739476001551.

Ref. 2 wrote: 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.

Answer: The concentration of bromide surely has no impact on the Mie scattering, but the size of the particles and concentration do have an impact During DOAS experiments, the aerosol concentration was lowered, and the bromide concentration in the aerosol was increased as a compensation in order to obtain a significant bromine activation.
For a better understanding we changed p. 10142, l. 7-9 to: ...(b) as compensation for a lower aerosol concentration during DOAS experiments due to Mie scattering of the aerosol, the bromide concentration of the aerosol phase was increased to 300 mmol L^{-1}.

Ref. 2 wrote: p. 10143, eq (1): This seems to be a rather drastic simplification of the O3 loss rate. Under what conditions is it valid? Surely the parameter c has to be a function of [O3] as most O3 loss reaction are at least linear in O3.

Answer: Eq. (1) is only valid under conditions where bromine is the main ozone consumer; it is not valid in the presence of high mixing ratios of chlorine in the gaseous phase. Such "high chlorine conditions" occur in our system at initial NO$_X$ mixing ratios higher than 3 ppb. However, the stated wall loss of 0.02 ppb s^{-1} is a maximum value at typical ozone mixing ratios in our system. Of course, the wall loss is a first order reaction with an inverse life time of ozone of $\tau \approx 10^{-5}$ s^{-1}.

Ref. 2 wrote: 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?

Answer: Since hydrocarbons are a sink for OH and Cl, the concentration of these radical species must be higher without injected hydrocarbons. One can calculate the

source Q of the radical species by following equation:

$$Q_Y = \int_0^\tau \sum_i k_{Y,i}[HC]_{t,i}[Y]_t dt \tag{1}$$

where Y is either OH or Cl derived from eq. (2). In fact the upper equation is a simplification of eq. (3), where we assume that d[X]/dt = 0. The calculated value of Q is independent of hydrocarbons if all hydrocarbon species and their time profiles are known. In fact we may only follow the original species but not their reaction products, which are also a sink for radicals. Using the known hydrocarbon concentrations, the upper equation gives an lower limit for Q. Typical values for the Cl source are 10^{11} cm^{-3} and 10^{12} cm^{-3} for the OH source after an hour of light exposure ($\tau =$1 h) in an high NO$_X$ experiment.

Ref. 2 wrote: 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.

Answer: Typically, we observe OH concentrations below 10^7 molec cm^{-3} with injected hydrocarbons, as it is shown in both figures below. However, we expect a higher concentration of both radical species if HC are not present, as it is also stated in the answer to referee 1. The reaction of OH with hydrocarbons leads to a production of aldehydes, which are an important source of hydroperoxyl radical.

Ref. 2 wrote: 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?

Answer: Since we injected pure Cl$_2$ into a clean, ozone and NO$_X$ free chamber, we assume that the Cl$_2$ photolysis was the major source of chlorine radicals in this experiment. Other sources, as the photolysis of HCl were neglected.

Ref. 2 wrote: 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?

Answer: Our repeated measurements of j(NO_2) show that the lamp intensity decreases exponentially during the first 600 operating hours, afterwards this intensity loss slows down to a plateau (see Bleicher 2012). Here we assumed that the spectrum of the lamps does not change in time (which is a simplification). The intensity of a new lamp is circa four times higher than of an aged lamp (with over 600 operating hours). The solar simulator consist of seven lamps, each of them in a different condition. The lamp age is logged in a lab book. To make all simulation runs comparable, we set the scaling to a value of 2. From empirical experience, this represents the mean state of the solar simulator very well.

Ref. 2 wrote: p. 10145, l. 26 - , p. 10146, l. 2: These assumed reactions are very fast (about 100x the respective photolytic 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.

Answer: The assumption of an HOX → X reaction is literary conservative, since it does not add any X into the system. Indeed, the chemistry of the chamber is not understood. Especially the walls need to be considered as a condensed phase with a huge surface. However, many parameters of the wall like the LWC, the pH, the halide concentration etc. are unknown and would need to be assumed. In that case the model results would be dependent on the unknowns. This exceeds the possibilities of this novel study.

Ref. 2 wrote: 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[O3]/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.

Answer: We agree that the difference between simulation and observation is too big to be neglected. Therefore we recalculated the model run by raising the initial NO_2 value to 1 ppb. This led to a better reproduction of the experiment, as it is shown in the answer to referee 1., where we also stated that the background signal of 200 ppt of BrO during the dark phase was detected by the DOAS and remained as a stable offset throughout the experiment. We assume it is an interference either formed from a previous high ozone chamber purge without aerosol or some other artefact due to wall effects. But since the level remained stable in the dark, we think the implication on the chemistry is minor. However, we do not have a method to test this.

We will change the paragraph as follows p.10146, l13: A fraction of the observed BrO seemed to be released by the chamber walls during a previous high ozone chamber purge with light and without aerosol. It remained as a stable background signal of 200 ppt of BrO in the chamber during the dark phase. Since up to date there is no known process to explain dark phase BrO, further investigation including extensive experiments and model studies would be necessary, which is beyond the scope of the present study. Thus, from the BrO-mixing ratio an offset of 200 ppt was subtracted, since it was obviously an artefact remaining after the previous chamber purge.

Ref. 2 wrote: p. 10148, l., 4 (see also p. 10142, l. 16): The measured OClO (see figure 3) is obviously below the detection limit that you defined but can the measured values of about 100 ppt of OClO really be completely discounted and are they really consistent with the modelled values of less than 3ppt? Please discuss this in more
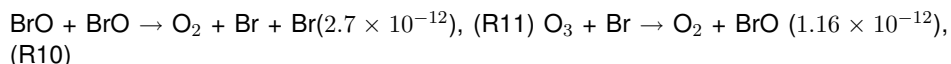
detail.

Answer: An activation of chlorine is possible, and would explain the ozone depletion. We increased the modelled initial NO_2 value to 1 ppb. This led to 100 ppt of $OClO$ and a better reproduction of the ozone depletion (see above).

Ref. 2 wrote: p. 10149, l. 5: What is this assumption based on?

Answer: We observe a rapid depletion of NO_2. This is highly related to the aerosol halide load. Reactions which consume NO_2 and involve bromine atoms are:

NO_2 + BrO → $BrONO_2$ (1.176×10^{-11}), (R16) Br + NO_2 → $BrNO_2$ (1.03×10^{-11})
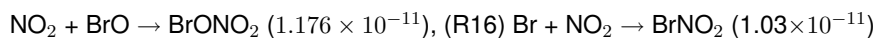
and we don't observe any rise in $BrNO_2$

BrO + BrO → O_2 + Br + Br(2.7×10^{-12}), (R11) O_3 + Br → O_2 + BrO (1.16×10^{-12}), (R10)

Ref. 2 wrote: 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] > [OClO] whereas in the experiment the opposite is the case. Furthermore the evolution with time of BrO, ClO and OClO 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.

Answer: Indeed, the model does not reproduce the exact quantitative time profiles of the experiment. However, one needs to keep in mind that the model is an approximation of a complex system. Moreover, the experiment itself is not perfect; the chamber has stray light from the laboratory and from the DOAS instrument. The chamber is also not perfectly clean, HONO and NO_3 and N_2O_5 are not observable with our instruments, but these species have a strong impact on the experimental result. In detail, the model does not reach the observed BrO mixing ratios, which affects the ClO/OClO

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ratio directly (R12). The most likely reason is the influence of the chamber walls, which is poorly understood. However, the model reproduces the consumption of NO_2 and the decay of ozone very well, see also Fig.8. It is also able to reproduce experiments with a wide range of Br-/Cl- ratios in the aerosol phase (e.g. the road salt experiments). Moreover the model confirms the experiment that no XO is observable in the gaseous phase as long NO_X is still available.

We also changed the caption of Fig.5 in the paper: Direct comparison of high NO_X scenario with a large activation of chloride in the experiment and in the model (dashed lines). The loss of NO_2 begins in the dark and can be explained by the production of N_2O_5 and XNO_2. A rapid loss of ozone was observed after the consumption of NO_2 under light conditions, thus forming the observable XO_X species. The time delay of the model in terms of ozone decay and halogen activation may be caused by light leaks during the experiment. The model BrO (green dashed line) underestimates the experimental values (green circles), probably due to bromine released from the wall in the experiment. Therefore, higher OClO (blue squares) and lower ClO (black triangles) mixing ratios were observed during the experiment as compared to the model. Note that the statistical error of the spectral fits is smaller than the size of the symbols in most (if not all) DOAS measurements.

Ref. 2 wrote: 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 Br2, then BrCl, then Cl2) and model results (fig. 6: first Br2, then Cl2, BrCl not shown). How does this "verify" the model results?

We change the text on p. 10150, l 25: Both maxima occurred while NO_X (originating from the photolysis of HONO) was still present in high mixing ratios. This verifies the model calculation in Fig. 6, where a big fraction of chlorine and bromine was already present in the gaseous phase as NO_X was still available. However, the shown model run is not a simulation of the CIMS runs. We assume that the measured dark Br_2 is activated by processes which are not included into the model yet.

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

Answer: Since we are not able to give a direct proof on the involvement of NOCl in our experiments, we decided to remove our speculations from the manuscript.

Ref. 2 wrote: p. 10151, l. 13-15: Please expand this explanation as it is too brief.

p. 10151, l. 13-15: The relatively low CIMS-signals of both HOX species and the high XO mixing ratios measured by DOAS led us to introduce the previously mentioned HOX to X+OH wall reactions.

Answer: Although we are not able to give absolute concentrations of both HOX species, we may assume that their concentrations are relatively low, which is based on the observed low CIMS counts. The model, in its original state, gave HOX mixing ratios in the ppb range. Therefore, we assume that a HOX chemistry must going on by converting HOX back to active halogens on the chamber walls. Following this assumption, we introduced the said simplified wall reactions.

Ref. 2 wrote: p. 10151, l. 18; p. 10152, l. 3: This presumable refers to Fig 8?

Answer: Yes, we correct this.

Ref. 2 wrote: 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.

Answer: We stated: Following the model calculations one can define a noticeable release of chlorine in a ppt range from 0.5 ppb of NO_X, which results in an accelerated consumption of ozone.

In a semi-polluted environment we expect NO_X mixing ratios in a 5-15 ppb range,

which would yield to chlorine mixing ratios above 1 ppb.

Ref. 2 wrote: 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.

Answer: We add to the discussion: According to our experimental results, nitrogen oxides have a strong impact on the activation of bromide and chloride. This fact was topic of current scientific discussion, since BrO/OClO in polluted areas are rare Also, by using the model we showed that under day time conditions the activated species are present as XNO_3. The scientific community should take both halogen species into focus. Moreover, we showed that road salts, which contain only low bromide fractions, are able to emit high chlorine amounts into the gaseous phase, if high loads of nitrogen oxides are present. An activation of chloride is also possible without bromide, as model calculations show.

Ref. 2 wrote: 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.

Answer: First bromide is activated by NO_2 to $BrNO_2$ during night time. This process consumes the available bromide very fast, since NO_2 is in excess. As the light is switched on, $BrNO_3$ is produced. The solubility and disassociation of $BrNO_3$ is very fast, which replenishes the bromide into the aerosol. The same can be said about chloride, if even more NO_X is present.

Ref. 2 wrote: Fig. 8: There appears to be a local minimum around 4ppb of NO_X in the case depicted with pink diamonds – is this an artefact or is there a physical explanation for this?

Answer: This is an artefact.

Ref. 2 wrote: The modelled $[O_3]$ 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.

Answer: We added these curves, see answer to referee 1.

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