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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.**

**Anonymous Referee #1**

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This paper describes chamber experiments investigating the influence of NO<sub>x</sub> (=NO<sub>2</sub> + NO) on halogen activation from salt aerosol. Gas-phase halogen and nitrogen oxide species were measured using a differential optical absorption spectrometer (DOAS, for BrO, ClO, OClO), a chemical ionization mass spectrometer (CIMS, for Br<sub>2</sub>, Cl<sub>2</sub>, BrCl, HOBr, HOCl, ClNO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, HONO) and a chemilluminescence detector (CLD, for NO<sub>2</sub>, NO<sub>x</sub>). The DOAS and CIMS measurements provide complementary data and hence a more complete description of the complex chemistry. The experimentally observed mixing ratios were compared to simulated mixing ratios, obtained using the CABA/MECCA chemical box model, which contains multi-phase halogen chemistry. The observations are fairly well captured by the model, and the observed ozone destruction is shown to have a strong relationship to [NO<sub>x</sub>].

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## GENERAL COMMENTS

The paper could be explained better. Given the complexity of the chemistry and the large range of variables (LWC, particle size, concentration, light conditions etc.) it is very important that the experiment/results/discussion be presented in a very clear, logical fashion. Currently, it is fairly difficult to follow. More specific suggestions for improvement are given in 'Specific Comments'. It does not help that the experiments were seemingly performed under different, not comparable conditions, with an unclean chamber. Can you compare the model NO<sub>x</sub> and O<sub>3</sub> (or rate of O<sub>3</sub> destruction) directly to the experimental observations? Only a comparison to BrO is given (Fig 4, left), and this is only given for the Low NO<sub>x</sub> case. Why not show the direct comparison of XO, OXO for the High NO<sub>x</sub> case too? Importantly, why is the observed O<sub>3</sub> loss rate not plotted against the modelled O<sub>3</sub> loss rate? Especially given that this is ultimately the metric that you use (in Fig 8) to determine the influence of NO<sub>x</sub> on halogen activation. I think this comparison would strengthen the paper a lot.

The discussion fails to focus on the particular role of light in accelerating the chemistry. Especially since R16-R18 and R7 and R19 do not involve light (these reaction are focused on a lot). R16-R18, R7 also require an initial source of BrO. Where does this come from? It was also suggested that for the high NO<sub>x</sub> case, the dark buildup of ClNO<sub>2</sub> and BrNO<sub>2</sub> which photolyze to give halogen radicals, initiates chemistry? However, the CIMS data only shows a slow loss of ClNO<sub>2</sub> with lights on. There is not a very clear discussion of the cycling between the gas and condensed phase. Potentially a schematic of the chemistry could be more useful than a list of reactions.

Furthermore, there is no discussion of the possibility of OH chemistry, despite the presence of HONO and other HO<sub>x</sub> precursors. The role/importance of hydrocarbons (other than for the radical clock) is not really addressed (e.g., for HO<sub>2</sub>). It is also difficult to follow when they are/are not present and what the implication is. Please address this. The LWC varies for model and between experiments. The role of surface area and LWC should be addressed in the discussion.

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Summary and discussion of implications is hard to follow. From the discussion, the main points are not clear; synthesis of the observations/model results could be improved. Ultimately Fig 8 shows how NO<sub>x</sub> influences the rate of ozone destruction, which is related in a complex way to halogen activation. The data in this figure is compelling, but deserved more discussion. The discussion really seems to trail off.

#### SPECIFIC COMMENTS

P10137, L7: Note that Pratt et al., 2013 did not observe chlorine species

P10140: NOCl?? Is this a very significant species?

P10141: Sedimented aerosol contributes to the chemistry? How do you know this?

P10143: How was the wall loss of O<sub>3</sub> determined?

P10143: Dilution rate?? What is the flow through the chamber?

P10143: Very few details are provided here about the CIMS. What is the reagent ion? What was the pressure in the ion-molecule reaction zone? What are the detection limits? Although a reference is provided, these details should be given in this paper.

P10143-10144: HC radical clock method. This is described in detail here. However, the experimentally measured HC traces are not shown. Nor are the 'calculated' OH and Cl concentrations. The [OH] and [Cl] are not addressed in the context of the halogen activation mechanism (in the discussion of results) – although this section makes it sound as if they will be. It seems that the purpose here was only to calculate the solar simulator's actinic photon flux. More information/data from the HC radical clock measurements and calculations should appear in the Supplement. Since there is clearly chlorine chemistry occurring (other than involving the HCs), the validity of using this method should also be discussed in greater detail. On P10147, L17 it also states that 'the difference to the observed ozone loss...might because by chlorine atoms, which were not monitored during the experiment'. But no comment is given about calculated chlorine atom concentration. Later on P10148, L14 there is finally mention

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of 'high OH levels' and then typical OH values are given, but this information seems out of context and tacked on.

P10145: Why was the model initialized with more liquid water content? What are the implications for comparison to experiment?

P10145, L15: Is lamp intensity decay with time linear?

P10145: Wall source of halogens? Please comment on the relative contribution of this chemistry to the modelled halogen concentrations.

P10146: It would be very helpful to have a table with the initial conditions of the 4 example runs (e.g., with categories RH%, mean particle diameter, LWC, initial [O<sub>3</sub>], [Br-], [Cl-], Br:Cl-, initial [NO<sub>x</sub>], presence/concentration/identity of any HCs including methane). This would make the comparisons much easier, and would take out a lot of repetition of experimental detail in the results section (the chamber cleaning procedure should probably just go in the experimental details, to also simplify things). The beginning of Section 3 could have a better overview of the experiments that were performed and a clearer indication that the detailed experiments are examples. How reproducible were the experiments? Please comment. It was also not clear if the majority of runs were done only with DOAS with only a few CIMS experiments? At the beginning of Section 3.1 and 3.2 the initial [NO<sub>x</sub>] should be stated at the outset, rather than leaving reader to figure out much farther into the paragraph.

P10147, L3-5: Stable BrO source of 200 ppt??? This is 2/3 of the 'measured' BrO mixing ratio. Please comment on the implications of this large source.

P10147, L20: R16-R18 require an initial source of XO, as does R7. Where does the BrO come from? Furthermore R16-R18 can occur in the dark. Lack discussion of dark reaction of O<sub>3</sub> to form Br<sub>2</sub> leading to BrO (although dark Br<sub>2</sub> production is observed using the CIMS, and mentioned later). However, the model results of Fig 4 and 6 do not show any dark production of Br<sub>2</sub> or Cl<sub>2</sub>. . .

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P10147, L25: You refer to Figure 4, but it has two parts. This should be made clearer (A and B). It is also not clear why in this case ONLY you plotted data as a function of gaseous Brx species. Figure 4 does not show a trace for calculated ClO, although the result is mentioned. It would be useful to have the ClO result on the figure as well (especially due to the previously mentioned significance of the BrO + ClO cross reaction).

P10148: The last section about HO<sub>2</sub>, methane and OH seems tacked on to the end and its significance is not included in the discussion. It is especially hard to follow since no data for methanol, formaldehyde or OH is given. . . maybe this could go in the Supplement.

P10148, Section 3.2: These experiments were performed with approx. 10× higher LWC than the ‘Low NO<sub>x</sub>’ case. Significance of this? The initial [O<sub>3</sub>] (770 ppb) is also higher than the “Low NO<sub>x</sub>’ case (508 ppb). Significance of this? These values seem quite different, granted the initial [NO<sub>x</sub>] is approx. 300x higher.

Why does the NO<sub>x</sub> mixing ratio recover? (from XNO<sub>2</sub> photolysis?) This is not captured in the model.

P10149-50, comparison to model: The model seems to have a 5min delay compared to the experiment. Is this significant? Please comment on this (why is this only addressed in the Figure caption?). There is a lot of information on Figure 6, but the discussion is actually quite brief. Also, how much dark N<sub>2</sub>O<sub>5</sub>, BrNO<sub>2</sub> and ClNO<sub>2</sub> is made in the dark in the low NO<sub>x</sub> case? That model result was not provided. If those species are not produced in the low NO<sub>x</sub> case due to limiting NO<sub>x</sub>, that is significant and should be mentioned. It should be stated more explicitly that consumption of O<sub>3</sub> starts by reaction with NO<sub>2</sub> to form NO<sub>3</sub>, which then reacts via R1 to form N<sub>2</sub>O<sub>5</sub>. Why is the photodissociation of XNO<sub>3</sub> to X and NO<sub>3</sub> not listed with reactions in the introduction? Is the main fate of XNO<sub>3</sub> photodissociation or R18 (formation of HOX)? It is stated that R16 replenishes the bromide in the aerosols by uptake and dissociation, how?

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Seems strange to talk about 'two experiments' but really display as one experiment with two parts. LWC, Bromide content, initial  $[\text{NO}_x]$  and  $[\text{O}_3]$  not given for the two experiments. Why was the chamber not cleaned? If, as stated,  $\text{NO}_x$  is converted to HONO on the droplet surface once the aerosol are injected (via which reaction? You should also provide it – you mean  $\text{H}_2\text{O} + 2\text{NO}_2?$ ), why is this not also considered in the overall mechanism (for all cases)? Then OH radical activation of the halogens should be addressed (upon photolysis of HONO). There is no discussion of OH chemistry (for all cases), although you apparently could calculate OH. The CIMS measurement of HONO (and HOX too) is given in arbitrary units (Fig 7). Can you relate these to concentrations?

You mention that R4-R8 as dark source of  $\text{Br}_2$  and  $\text{Cl}_2$ . But this is not captured at all by the model (Fig 4 or 6). Please comment. Is it possible that in the experiment the high HONO led to OH which liberated the halogens?

I don't follow the argument about NOCl (R23). Also, did you actually measure the bigger particles?

The gas phase HOCl you measured is significant. It indicates that ClO is reacting with  $\text{HO}_2$  to form HOCl, which probably is taken up by the salt aerosol to further liberate halogens. This result should be emphasised. But where does the dark HOCl come from?

## Summary and Conclusions

P10152. Why give an expression for the logarithmic curve?

P10152, L12: Comparison to salt pan experiments. No mention of role of surface area is given.

P10152: How can you definitely say that bromide and chloride is activated utterly by  $\text{NO}_x$  mechanisms? I don't think the experiments prove this. The discussion about chlorine activation is confusing. Previously there had been no discussion about the

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bromide concentration dependence on chlorine activation. The road salt halogen data is not given (Fig 8 only has ozone loss rate data), so this result needs to be presented more compellingly.

## TECHNICAL CORRECTIONS

It would be better to be consistent about expressing the bromide concentration always in mmol L<sup>-1</sup> or in mol L<sup>-1</sup> but not switching between both.

P10139, L1: 'aquatic' uptake should probably be changed to 'aqueous' or 'aqueous phase'

P10139, L6-7: sentence about pKa's needs to be fixed, it does not make sense as written

P10139, L26: subscript needed on ClNO<sub>2</sub>

P10141, L27: should be neglecting a coagulation loss for the largest particle sizes? (not these large)?. Should also say 'for the given particle size distribution'

P10141, L29: remove 'to' from 'volume equals the liquid water content'

P10143, L7: would be better for k<sub>1</sub> to be k<sub>11a</sub> since it corresponds to R<sub>11a</sub>, less confusing

P10144, L11: what are the I reactions? Should be n?

P10145, L10: should say 'included chlorine and bromine multi-phase...' rather than activated

P10147, L27: 'in term of the ozone decay', instead of 'in terms like the ozone decay...'

P10150, L27: reference to incorrect figure, should be Fig 6?

P10151, L13: Do you mean HOX? Or HOx?

P10162, Figure 4: Change so all unique colours (e.g. right now BrO and Br<sub>2</sub> are the

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same colour, NO<sub>2</sub> and BrCl are the same colour). Same with Figure 6, P10164.

P10164, Figure 6: Mistake 'In the logarithmic scale is the photolysis. . .' (remove 'is')

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