

Interactive  
Comment

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

**S. Bleicher et al.**

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Ref. 1 wrote: Can you compare the model  $\text{NO}_x$  and  $\text{O}_3$  (or rate of  $\text{O}_3$  destruction) directly to the experimental observations? Only a comparison to  $\text{BrO}$  is given (Fig 4, left), and this is only given for the Low  $\text{NO}_x$  case. Why not show the direct comparison of  $\text{XO}$ ,  $\text{OXO}$  for the High  $\text{NO}_x$  case too? Importantly, why is the observed  $\text{O}_3$  loss rate not plotted against the modelled  $\text{O}_3$  loss rate? Especially given that this is ultimately the metric that you use (in Fig 8) to determine the influence of  $\text{NO}_x$  on halogen activation. I think this comparison would strengthen the paper a lot.

Answer: The new version of Fig. 3 (here Fig 1.) substitutes the previous fig. 4 as well and shows a direct comparison of the experiment and the model run. We think that

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the measured OCIO values during the low  $\text{NO}_x$  experiment are substantial. Since the initial  $\text{NO}_x$  mixing ratio is correlated to the amount of activated halides (see Fig. 8), we increased the initial  $\text{NO}_2$  mixing ratio to 1 ppb in the model run. Now the model is able to reproduce the observed OCIO and BrO to the point of maximal ozone consumption. After passing this point the modelled curves remain in plateaus, while the observed curves of halogen oxides are decreasing. This is caused by the simplified wall reactions in the model, which do not allow a deactivation of halogens ( $\text{X} \rightarrow \text{X}^-$ ).

The experiment of the high  $\text{NO}_x$  case (150 ppb of  $\text{NO}_2$ ) was shown in Fig. 5 of our manuscript, and the corresponding model calculation was shown in fig. 6. We include the model calculations as direct comparison in Fig. 5 (Fig. 2 here). More species from the model run are shown in Fig. 6 of the manuscript, those species are important to understand the underlying chemical mechanisms. The model is c. a. 2.5 minutes delayed in terms in comparison to the experiment, which is probably reasoned by light leaks during the dark part of the experiment. Moreover, the model BrO does not reach the experimental values, which also results in lower OCIO and higher ClO mixing ratios. We think that this is reasoned by bromide impurities on the chamber walls. In contrast to the “low  $\text{NO}_x$ ” experiment, the halogen oxides disappear after the maximum ozone decay was reached, since ozone was fully consumed here.

Fig. 8 in the paper clearly shows general agreement above 1 ppb of  $\text{NO}_X$  for the majority of the experiments and a discrepancy between model (red curve) and experiment (black curve) at very low  $\text{NO}_x$  levels in the ppt range (where experiments become extremely difficult in view of the detection limit of the  $\text{NO}_x$  analyzer of 200 – 500 ppt).

Ref. 1 wrote: 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  $\text{NO}_X$  case, the dark buildup of  $\text{ClNO}_2$  and  $\text{BrNO}_2$  which photolyze to give halogen radicals, initiates chemistry? However, the CIMS data only shows a slow loss of  $\text{ClNO}_2$  with lights on. There is not a very clear discussion of the cycling between the gas and condensed

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phase. Potentially a schematic of the chemistry could be more useful than a list of reactions.

Answer: Indeed, R16-R18 and R7 and R19 do not involve light, but light is needed to form the involved XO molecules (see R9-R10), and to photolyse  $XNO_2$ . This is the reason why the upper reactions actually need light to proceed, they do not occur under typical night time conditions.

If  $NO_x$  is available, R16-R18 is the main mechanism to activate halides. It requires only minor mixing ratios of XO to start a fast conversion of condensed phase to gaseous phase halogen species, as model calculations show.

Ref. 1 wrote: Furthermore, there is no discussion of the possibility of OH chemistry, despite the presence of HONO and other  $HO_x$  precursors. The role/importance of hydrocarbons (other than for the radical clock) is not really addressed (e.g., for  $HO_2$ ). 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. 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  $NO_x$  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.

Answer: Both DOAS-experiments shown here, as well as the experiments marked by the full black circles in Fig. 8 are experiments without hydrocarbons, despite the 500 ppb of methane. The model runs, which are discussed in detail, were performed exactly under the measured starting conditions of the related experiments; the LWC value was the measured volume of the aerosol. The general influence of LWC and the surface area, as well as the influence of the bromide concentration in the aerosol, is shown in Fig. 3 here.

We would like to add to the discussion at p10151 l.17: 'One effect of halogen activation

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is the depletion of ozone. This depletion rate summarizes the strength of the activation of both regarded halide species in a brief and clear way. In our context, the main parameter to release halogens from halide aerosol is the initial  $\text{NO}_x$  mixing ratio. Other parameters, such as the LWC, the aerosol surface, the bromide content or the initial ozone mixing ratio, have limited impact on release of halogens in the our system.'

Ref. 1 wrote: P10137, L7: Note that Pratt et al., 2013 did not observe chlorine species

We revised the paragraph: p10137, l5: discussion. Recently, Morin et al. (2012) indirectly linked the presence of reactive halogen species with emissions of  $\text{NO}_x$  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 formation of molecular bromine species was also observed in Arctic surface snowpacks by Pratt and coworkers (2013). The acidification of....

Ref. 1 wrote: P10140: NOCl?? Is this a very significant species?

Answer: We cancel lines 11-18 and all reference to NOCl in the manuscript.

Ref. 1 wrote: P10141: Sedimented aerosol contributes to the chemistry? How do you know this?

Answer: We are sorry for the confusion caused by this sentence. As we wrote, the effect of sedimented aerosol is neither measurable nor included in the model. However, since we perform several experiments in the same Teflon chamber before changing the Teflon foil, there might be remainders from former experiments. We try to minimize that effect by rinsing the chamber with water between experiments. However, we cannot exclude a memory effect of the Teflon chamber completely and feel that this is an important piece of information for the reader.

We changed the paragraph at p 10141: The same chamber set up is used for multiple experiments. Between two experiments the whole chamber is purged with distilled wa-

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ter and further cleaned photochemically by introducing high levels of humidity (>60 %) and ozone (700 ppb) and irradiating by the solar simulator.

We have to note that sedimented aerosol and memory effects of the wall, although not quantifiable, might contribute to the chemistry, which results in a considerable uncertainty for the computer modelling applied in this study. Only the wall loss of ozone is well characterized and included in the model, as described below.

Ref. 1 wrote: P10143: How was the wall loss of O<sub>3</sub> determined?

We add to the text in the manuscript on p10143, l12: The wall loss of ozone was determined in a dark measurement by injecting high mixing ratios of ozone (>1 ppm) into a NO<sub>x</sub> free chamber (<0.5 ppb). The data was corrected for dilution (3 - 8 L/min, determined by a mass flow controller).

Ref. 1 wrote: P10143: Dilution rate?? What is the flow through the chamber?

Answer: The flow through the chamber was set constant to 3 - 8 L/min by a flow controller, dependent on the attached instruments to the chamber.

Ref. 1 wrote: 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.

Answer: We added the following description of the CIMS instrument: The CIMS uses iodide and its clusters with water as a reagent ion. Chamber air is sampled through a critical orifice at 2 l/min) into the ionization region held at 60 Torr total pressure. Iodide ions are generated by passing trace CH<sub>3</sub>I from a permeation device in 2.5 l/min of ultrahigh purity N<sub>2</sub> through a commercially available Po-210 ionizer directly attached to the ionization region. The sample and ion source flows mix for 60 ms during transit through a 2 cm ID stainless steel flow tube before a fraction is sampled into the differentially pumped chamber housing the mass spectrometer and transfer optics. Most

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species of interest are detected at the mass to charge ratio corresponding to the cluster of that species with iodide, e.g.,  $\text{ClNO}_2$  is detected as  $\text{I}(\text{ClNO}_2)$ . Detection limits are not uniform and depend upon the species of interest, but for most halogen species the detection limits approach 5 ppt in a 1 second time average.

Ref. 1 wrote: 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 of 'high OH levels' and then typical OH values are given, but this information seems out of context and tacked on.

Answer: As reported in the manuscript, typical OH concentrations are below  $10^7 \text{ cm}^{-3}$  in a purged (HONO free) chamber with hydrocarbons injected. This can be seen in the two figures below. Both experiments employed a comparable amount of injected HCl (n-pentane, 2,2-dimethylbutane and toluene). Although the mixing ratio of  $\text{NO}_x$  is not known in the first experiment, we expect the total amount of reactive nitrogen species to be below 3 ppb. The values of Cl show a plateau around  $10^6 \text{ cm}^{-3}$ , which is consistent with the measured OCIO values according to the following equation, the

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photostationary state of OCIO:

$$0 = \frac{d[OCIO]}{dt} = -k_1[ClO][BrO] - k_2[OCIO][Cl] - j(OCIO)[OCIO] - k_3[OH][OCIO] \quad (1)$$

where  $k_1[ClO][BrO] = k_4[O_3][Cl]$ , represents the photo-stationary steady state of ClO. With higher initial  $NO_x$  mixing ratios, we observe a stronger activation of chloride. This is also observable with the radical clock. The concentration of Cl atoms is higher than  $10^6 \text{ cm}^{-3}$  and rises during the experiment. After ozone is totally consumed, the concentration of OH decreases, since ozone is the major source. The concentration of Cl atoms rises since  $ClO_x$  species are decomposed to Cl and  $O_2$ . The hydrocarbons constitute a sink for OH and Cl radicals, so we expect higher radical concentrations in a HC free chamber ( $OH > 10^8 \text{ cm}^{-3}$ ). By using

$$Q_Y = \int_0^\tau \sum_i k_{Y,i}[HC]_{t,i}[Y]_t dt \quad (2)$$

with  $Y = OH, Cl$ , we can calculate the sources  $Q$  of OH and Cl.  $Q$  is independent of  $[HC]$ . Typical values for the Cl source are  $10^{11} \text{ cm}^{-3}$  and  $10^{12} \text{ cm}^{-3}$  for the OH source after an hour of light exposure in an high  $NO_x$  experiment.

However, model calculations show that the concentration of  $HO_2$  is in the same order of magnitude (lower ppt range) in all runs.

Ref. 1 wrote: P10145: Why was the model initialized with more liquid water content? What are the implications for comparison to experiment?

Answer: This is a typo, the default initial value was  $5 \times 10^{-10} \text{ cm}^3/\text{cm}^{-3}$ . We corrected that in the paper.

Ref. 1 wrote: P10145, L15: Is lamp intensity decay with time linear?

Answer: The intensity of the lamps decreases exponentially during the first 800 operating hours by a factor of four, then the intensity enters a quite stable plateau (measured

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by NO<sub>2</sub> actinometry, see Bleicher 2012). As a simplification, we assume that the spectrum does not change. The solar simulator consists of seven lamps in different conditions, we experienced that a scaling factor of two represents a typical mixed condition well. A constant scaling allows also a direct comparison between simulation runs.

Ref. 1 wrote: P10145: Wall source of halogens? Please comment on the relative contribution of this chemistry to the modelled halogen concentrations.

Answer: We observed no to little active halogen species in a purged chamber. However, fresh aerosol can moisten the chamber wall, which could lead to activation. Those wall effects are poorly understood and would require a separate study. In an optimal case, the walls should be treated as a fluid phase with a huge surface and a shrinking LWC. Also, parameters such as the pH and the halide content etc. need to be known, which exceeds the possibilities of this study. Therefore, we introduced the HOX → X + OH reactions (for all simulation runs) after lots of testing. These reactions are literally conservative, they do not add halogens to the chemistry and they represent the experiments quite well (see Fig. 8). The model can not reproduce the experimentally observed XO or OXO without these reactions. This leads to the question whether the chamber is generally able to reproduce atmospheric conditions. By excluding the HOX → X + OH reactions in the model, we can simulate the conditions without walls, and such simulations are now added to Fig. 8 (red crosses).

Ref. 1 wrote: 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 ma-

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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.

Table 1: Initial parameters for the shown experiments

	Low NO <sub>x</sub>	High NO <sub>x</sub>	CIMS1	CIMS2
LWC	$6.3 \times 10^{-11}$	$4.5 \times 10^{-10}$	n.a. <sup>1</sup>	n.a.
Mean particle diameter injected HC <sup>2</sup>	300 nm	300 nm	n.a.	n.a.
RH	–	–	–	100 ppb
Initial O <sub>3</sub>	60% (20 °C)	60% (20°C)	75% (10°C)	75% (10°C)
Initial NO <sub>x</sub>	508 ppb	767 ppb	322 ppb	360 ppb
[Br <sup>-</sup> ]	0.5 ppb	152 ppb	25 ppb	17 ppb
[Cl <sup>-</sup> ]	515 ppt	3.6 pp	n.a.	n.a.
	10.9 ppb	78 ppb	n.a.	n.a.

<sup>1</sup> not applicable, <sup>2</sup> excluding 500 ppb CH<sub>4</sub> from zero air

Ref. 1 wrote: 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.

Answer: 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, 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: 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. 1 wrote: 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>.

Answer: As mentioned above we do not have an explanation for BrO in the dark and do not know about any possible mechanism. This would need further investigation. R7 is not strictly dependent on gaseous XO, HOX can also be formed by dissolved ozone as R4-R6 show. This mechanism can provide initial gaseous Br<sub>2</sub> from a slightly acidic fluid phase. R16-R18 need only a minor amount of XO to start a catalytic activation cycle, which can be provided by a photolysis of XNO<sub>2</sub>. This implies that these reactions can occur only during daytime.

Ref. 1 wrote: 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 Br<sub>x</sub> 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).

Answer: We substituted fig.4 with the new version of fig.3 (here fig.1), as shown above.

Ref. 1 wrote: 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.

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Answer: The total amount of methane is 500 ppb. Our model predicts a minor methanol formation of up to 6 ppt, which is about two orders of magnitude lower than typically observed over the ocean (e.g. Yang, M., Nightingale, P., Beale, R., Liss, P., Blomquist, B., and Fairall, C.: Atmospheric deposition of methanol over the Atlantic Ocean, P. Natl. Acad. Sci., doi:10.1073/pnas.1317840110, 110, 20034–20039).

p.10148: One important oxidation product of methane is formaldehyde, since it is a main sink for bromine atoms to form HBr. The HCHO mixing ratio was calculated to be at a plateau of 300 ppt. The high OH levels are explained by the low amounts of sinks in the surrounding air. Typical OH values in our chamber are below 0.5 ppt in a low  $\text{NO}_x$  case and between 0.5 and 2 ppt in a moderate  $\text{NONO}_x$  atmosphere, measured by RCM with injected HCs. Model calculations give OH mixing ratios of 5-10 ppt in a HC free air.

Ref. 1 wrote: P10148, Section 3.2: These experiments were performed with approx.  $10\times$  higher LWC than the ‘Low  $\text{NO}_x$ ’ case. Significance of this? The initial  $[\text{O}_3]$  (770 ppb) is also higher than the “Low  $\text{NO}_x$ ’ case (508 ppb). Significance of this? These values seem quite different, granted the initial  $[\text{NO}_x]$  is approx.  $300\times$  higher. Why does the  $\text{NO}_x$  mixing ratio recover? (from  $\text{XNO}_2$  photolysis?) This is not captured in the model.

Answer: In low  $\text{NO}_x$  experiments, the LWC has no influence on the activation of halides. It is obvious that in high  $\text{NO}_x$  experiments the activation of halides is limited by the LWC. The initial ozone mixing ratio has minor influence on the activation of halides. According to model studies, a higher ozone concentration at the initial phase would allow a faster depletion rate if enough halogen radicals are present. Actually the model does capture the regeneration of  $\text{NO}_x$ , this is shown in Fig. 6 of our manuscript. The source is  $\text{HNO}_3$  which degasses from aerosol and reacts back to  $\text{NO}_x$ .

Ref. 1 wrote: P10149-50, comparison to model: The model seems to have a 5 min delay compared to the experiment. Is this significant? Please comment on this (why is

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this only addressed in the Figure caption?).

Answer: Unlike the experiments the model runs are quite optimal. During the experimental runs, there is straylight from the solar simulator before the blockage is removed and probably a minor contribution from the DOAS instrument .. This can lead to a release of X<sub>2</sub> during “dark” experiments and may accelerate the experimental runs compared to the model.

We added in the text p. 10149: The simulated mixing ratios of the halogen oxide species are quite comparable to the experiment, although the OClO values are lower. This may be caused by a higher supply of bromine in the experiment, probably by the chamber walls. Furthermore, the model shows a time delay of about 2.5 minutes. As mentioned above, light leaks may have started the photochemistry before the shutter was removed. Therefore, NO<sub>2</sub> was consumed faster in the experiment, and halogen oxide formation occurred earlier than in the model.

Ref. 1 wrote: 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.

Answer: The concentrations of the said species are in the ppt range in the low NO<sub>x</sub> experiment. The bromine species are enhanced over the chlorine counterparts. Fig. 6 of our manuscript gives background information to the not observable parameters, such as the aerosol pH and the chloride and bromide concentrations in the aerosol phase. It shows that the NO<sub>x</sub> mixing ratio is sufficient almost fully activate both halide species by forming XNO<sub>2</sub>. This is interesting, since no light is involved here. Such activations may also occur on deiced roads in the wintertime when high NO<sub>x</sub> and halides are present. After the ignition of the lamps we observe a photostationary state between X<sub>2</sub>, X and XO for a period when enough ozone is available. After ozone is fully consumed, the XO species disappear and form X atoms.

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Ref. 1 wrote: 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>.

Answer: We add this reaction.

Ref. 1 wrote: 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)?

Answer: The photolysis frequencies are quite fast for ClNO<sub>3</sub> and even faster for BrNO<sub>3</sub>:  $J(\text{ClNO}_3) = 4 \times 10^{-5} \text{ s}^{-1}$ ,  $J(\text{BrNO}_3) = 10 \times 10^{-3} \text{ s}^{-1}$ . However, according to our findings, their uptake into the liquid phase dominates the process as long as enough aerosol is available.

Ref. 1 wrote: It is stated that R16 replenishes the bromide in the aerosols by uptake and dissociation, how?

BrNO<sub>3</sub> is very soluble in the liquid phase, it may dissociate to bromide.

Ref. 1 wrote: Seems strange to talk about ‘two experiments’ but really display as one experiment with two parts. LWC, Bromide content, initial [NO<sub>x</sub>] and [O<sub>3</sub>] not given for the two experiments. Why was the chamber not cleaned?

Answer: In this experiment we had lot of water condensation on the chamber walls, due to forced cooling to 10°C. Therefore, the measured LWC is not true and cannot be given. [NO<sub>x</sub>] and [O<sub>3</sub>] are given in Tab. 1.

We are sorry for the confusion; actually, the chamber was cleaned but had no overpressure. It was contaminated by ambient air during the experiment.

Ref. 1 wrote: If, as stated, NO<sub>x</sub> is converted to HONO on the droplet surface once the aerosol are injected (via which reaction? You should also provide it – you mean H<sub>2</sub>O + 2 NO<sub>2</sub>?), 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

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calculate OH. The CIMS measurement of HONO (and HOX too) is given in arbitrary units (Fig 7). Can you relate these to concentrations?

Answer: The levels of OH are highly correlated to the availability of precursors such as ozone and HONO. Since instruments for HONO measurements, such as the long path absorption photometer (LOPAP, e.g. Kleffmann, J., J. Heland, R. Kurtenbach, J. Lorzer, and P. Wiesen (2002). A new instrument (LOPAP) for the detection of nitrous acid (HONO). Environ. Sci. Pollut. R., Vol. 4, 48-54) were not available for everyday use, we purged the chamber before every experiment for all cases except the CIMS run. A typical chamber purge is shown in Fig.1, where a LOPAP was used to measure the HONO mixing ratio (note that the used  $\text{NO}_x$  instrument detects HONO too). After such chamber purge we observe HONO in the lower ppt range, which excludes it from being a major OH source. We are not able to give the absolute concentration of HONO and HOX in the CIMS measurement.

During the CIMS experiment the injection of aerosol lasted 2x45 min ( $\text{LWC} > 10^{-9} \text{ m}^3/\text{m}^3$ ), which is enough to produce HONO in the ppb range via the slow  $\text{H}_2\text{O} + 2 \text{NO}_2$  conversion. This is in contrast to the DOAS experiments, where the aerosol injection was very short ( 5 min) and the lamps were ignited shortly after. Moreover,  $\text{NO}_x$  was already present in the chamber during the long aerosol injection time of the CIMS experiment, since the chamber was not purged before. This explains why HONO is not considered in the DOAS runs.

Ref. 1 wrote: 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.

Answer: This is a first observation of dark source of  $\text{Br}_2$  in a complex system. The observations have to be included into the model in upcoming work.

Ref. 1 wrote: Is it possible that in the experiment the high HONO led to OH which liberated the halogens?

Answer: Additional modelling with high initial HONO mixing ratios (20 ppb) showed

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the typical  $\text{XNO}_3$  activation path after the photolysis of HONO. The simulation did not change when we suppressed the  $\text{HO}_2$  production from OH.

Ref. 1 wrote: I don't follow the argument about NOCl (R23).

Answer: We removed all statements regarding NOCl from the paper since we are not able give a direct proof.

Ref. 1 wrote: Also, did you actually measure the bigger particles?

Answer: Particles were measured between 30-1200 nm diameter.

Ref. 1 wrote: P10152. Why give an expression for the logarithmic curve?

Answer: This expression summarizes the findings of the paper.

Ref. 1 wrote: P10152, L12: Comparison to salt pan experiments. No mention of role of surface area is given.

Answer: Our measurements on salt pans and aerosol show that despite its larger surface area, salt pans have a lower ability to release halogens. This is reasoned by a faster evaporation of the liquid phase from the irradiated salt pan surface.

Ref. 1 wrote: 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.

Answer: We are definitely able to say that bromide and chloride are activated almost utterly by  $\text{NO}_x$  mechanisms due to the following reasons:

- In our experiments we used bi-distilled water and almost pure salts (NaCl, NaBr).
- In clean conditions we do not observe a fast depletion of ozone, neither we observe high mixing ratios of halogen oxides.
- Our model calculations predict only minor halogen activations in clean conditions.

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Ref. 1 wrote: Previously there had been no discussion about the 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.

Answer: We have no systematic experimental data on the activation of chloride vs. a varying concentration of bromide. However, our experiments show a faster consumption of ozone if the bromide concentration is raised (Fig. 8 here). As it can be seen in the figure, the max. ozone depletion is no longer rising at a point which is set by the initial  $\text{NO}_x$  mixing ratio. Moreover, we would like to add an experiment on road salt, which had low concentrations of bromide to the supplement (Fig. 9 here). The road salt sample contained  $470\mu\text{g/g}$  NaBr (Asbit GmbH). The nebulized solution contained  $1\text{g/l}$  salt, which resulted in  $1,6 \times 10^{-3}$  mol/l bromide in the liquid phase. We observed high mixing ratios of OClO and almost no BrO during illumination. This is caused by an excess of ClO, which consumes BrO and forms OClO.

Ref. 1 wrote: It would be better to be consistent about expressing the bromide concentration always in  $\text{mmol L}^{-1}$  or in  $\text{mol L}^{-1}$  but not switching between both.

Answer: We will switch to  $\text{mmol L}^{-1}$ .

Ref. 1 wrote: P10139, L1: ‘aquatic’ uptake should probably be changed to ‘aqueous’ or ‘aqueous phase’

Answer: Yes, aqueous-phase

Ref. 1 wrote: P10139, L6-7: sentence about pKa’s needs to be fixed, it does not make sense as written

Answer: Yes, we remove “and a” from line 7

Ref. 1 wrote: P10139, L26: subscript needed on  $\text{ClNO}_2$

Answer: Yes

Ref. 1 wrote: P10141, L27: should be neglecting a coagulation loss for the largest par-

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ticle sizes? (not these large)?. Should also say 'for the given particle size distribution'

Answer: Yes

Ref. 1 wrote: P10141, L29: remove 'to' from 'volume equals the liquid water content'

Answer: Yes

Ref. 1 wrote: P10143, L7: would be better for k1 to be k11a since it corresponds to R11a, less confusing

Answer: Yes

Ref. 1 wrote: P10144, L11: what are the I reactions? Should be n?

Answer: Should be i

Ref. 1 wrote: P10145, L10: should say 'included chlorine and bromine multi-phase. . .' rather than activated

Answer: Yes

Ref. 1 wrote: P10147, L27: 'in term of the ozone decay', instead of 'in terms like the ozone decay. . .'

Answer: Yes

Ref. 1 wrote: P10150, L27: reference to incorrect figure, should be Fig 6?

Answer: Yes

Ref. 1 wrote: P10151, L13: Do you mean HOX? Or HOx?

Answer: HOX

Ref. 1 wrote: P10162, Figure 4: Change so all unique colours (e.g. right now BrO and Br<sub>2</sub> are the 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. . .'

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(remove 'is')

Answer: Yes, we change that

Additional comment: We would like to add Fig.4, Fig.5 and Fig.9 of this answer to the manuscripts supplement.

Figure captions:

Figure 1: Direct comparison of a "low-NO<sub>x</sub>" experiment with a model calculation. After the maximum of the ozone depletion is reached the model in its current state cannot render the experimental data. This is probably caused by the simplified wall reactions in the model.

Figure 2: Direct comparison of high NO<sub>x</sub> scenario with a large activation of chloride in the experiment and in the model (dashed lines). The loss of NO<sub>2</sub> begins in the dark and can be explained by the production of N<sub>2</sub>O<sub>5</sub> and XNO<sub>2</sub>. A rapid loss of ozone was observed after the consumption of NO<sub>2</sub> under light conditions, thus forming the observable XO<sub>x</sub> 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

Figure 3: Shown is the comparison of the ozone depletion and the aerosol surface at similar experimental conditions (initial NO<sub>x</sub> < 1 ppb). We do not observe a correlation here. The influence of the aerosol surface and the LWC on the depletion of ozone is

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limited by the initial  $\text{NO}_x$  mixing ratio.

Figure 4: Low  $\text{NO}_x$  experiment with DOAS and radical clock. It shows the typical concentrations of OH and Cl in our system with injected hydrocarbons.

Figure 5: Measurement of a high  $\text{NO}_x$  halide activation with radical clock. The concentration of OH is nearly constant as long as ozone is available; it decreases to the detection limit after ozone was consumed. The concentration of chlorine atoms rises after the ozone has been consumed, since the intermediate sinks ClO and OClO cannot be formed.

Fig 6: New Figure 8: The figure now includes model runs without the wall reactions ( $\text{HOX} \rightarrow \text{X} + \text{OH}$ , red crosses).

Figure 7: A chamber purge to reduce the HONO mixing ratio without a prior injection of ozone. The ozone mixing ratio increases due to the  $\text{RO}_2\text{-NO}_x$  mechanism.

Figure 8: Shown is the max. ozone depletion in dependence on the concentration of bromide in aerosol (all other parameters were nearly equal). The activation of bromide is limited by the initial  $\text{NO}_x$  mixing ratio.

Figure 9: Experiment on road salt. The concentration of bromide in the aerosol was  $1.5 \text{ mmol L}^{-1}$ , the LWC was  $2 \times 10^{-10} \text{ m}^3/\text{m}^3$ . The BrO mixing ratio was suppressed due to the excess of ClO by the reaction of  $\text{BrO} + \text{ClO} \rightarrow \text{OClO}$ .

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C6381/2014/acpd-14-C6381-2014-supplement.zip>

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

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14, C6381–C6409, 2014

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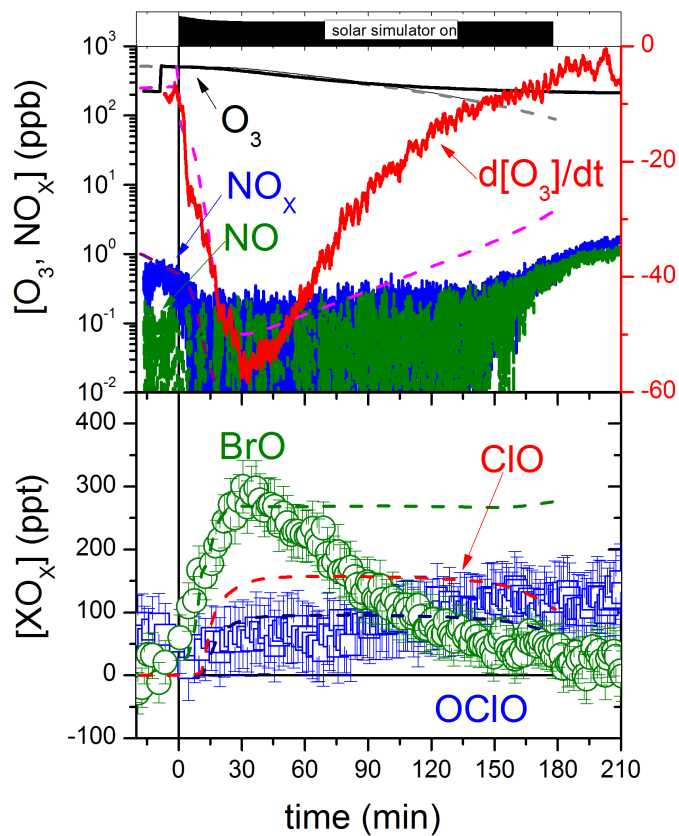
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Fig. 1.

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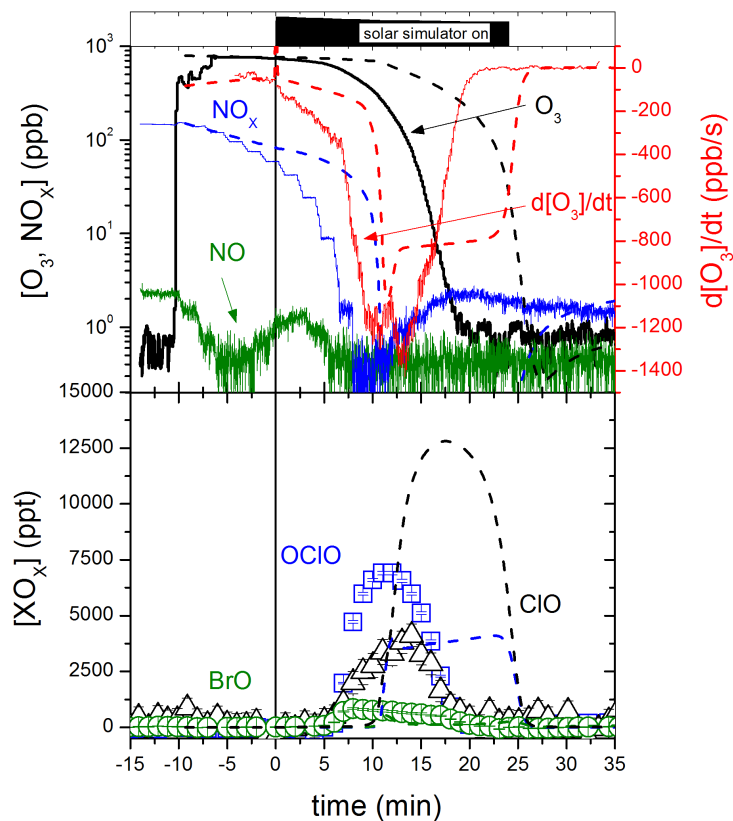
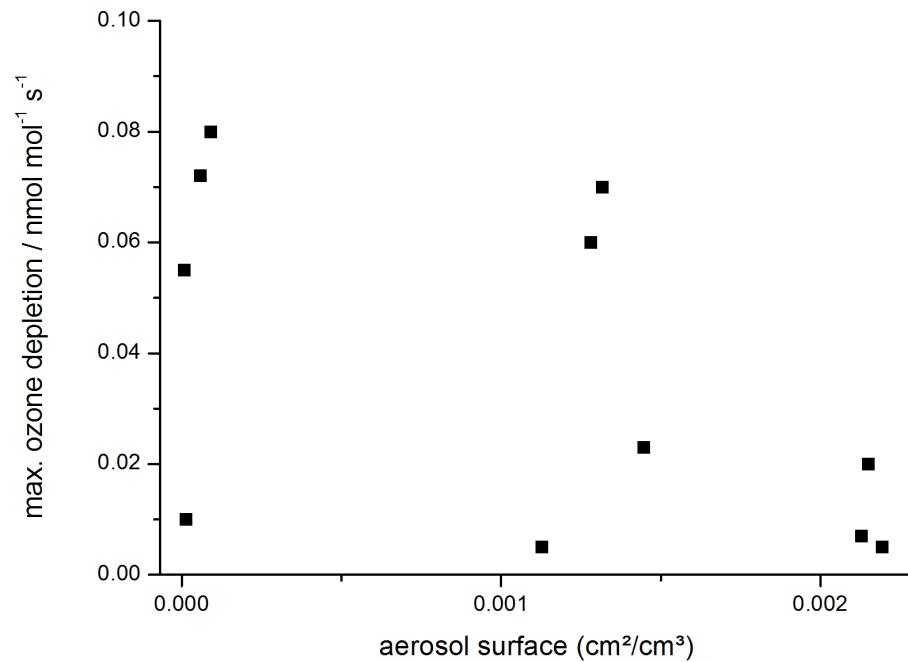
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Fig. 2.

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[Interactive  
Comment](#)**Fig. 3.**

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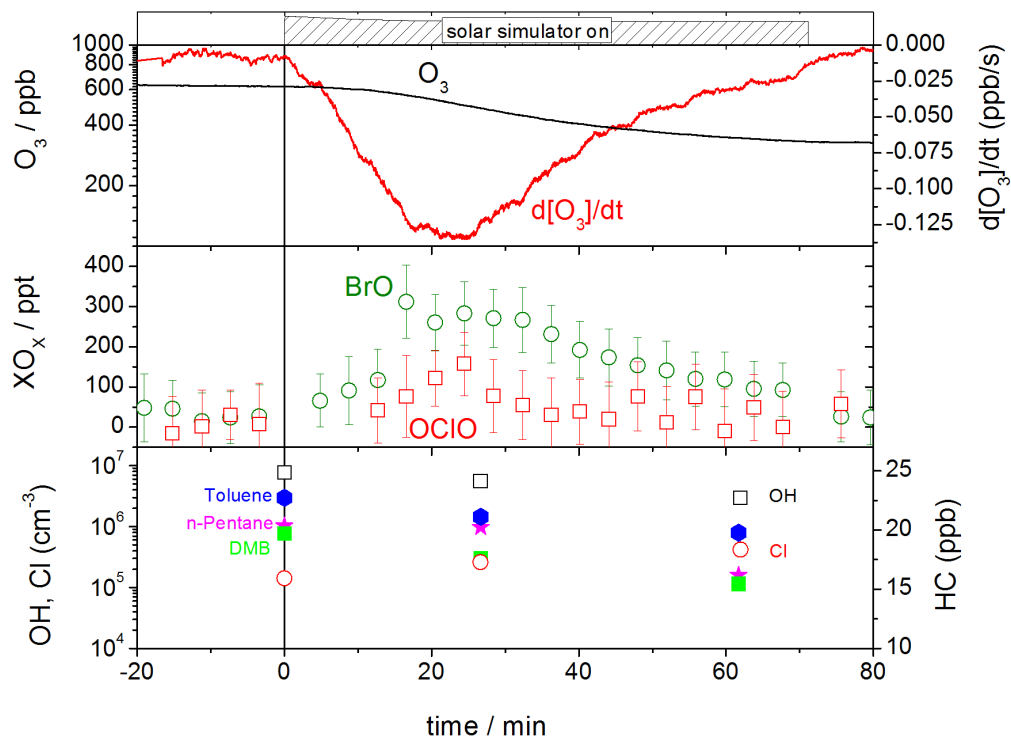
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Fig. 4.

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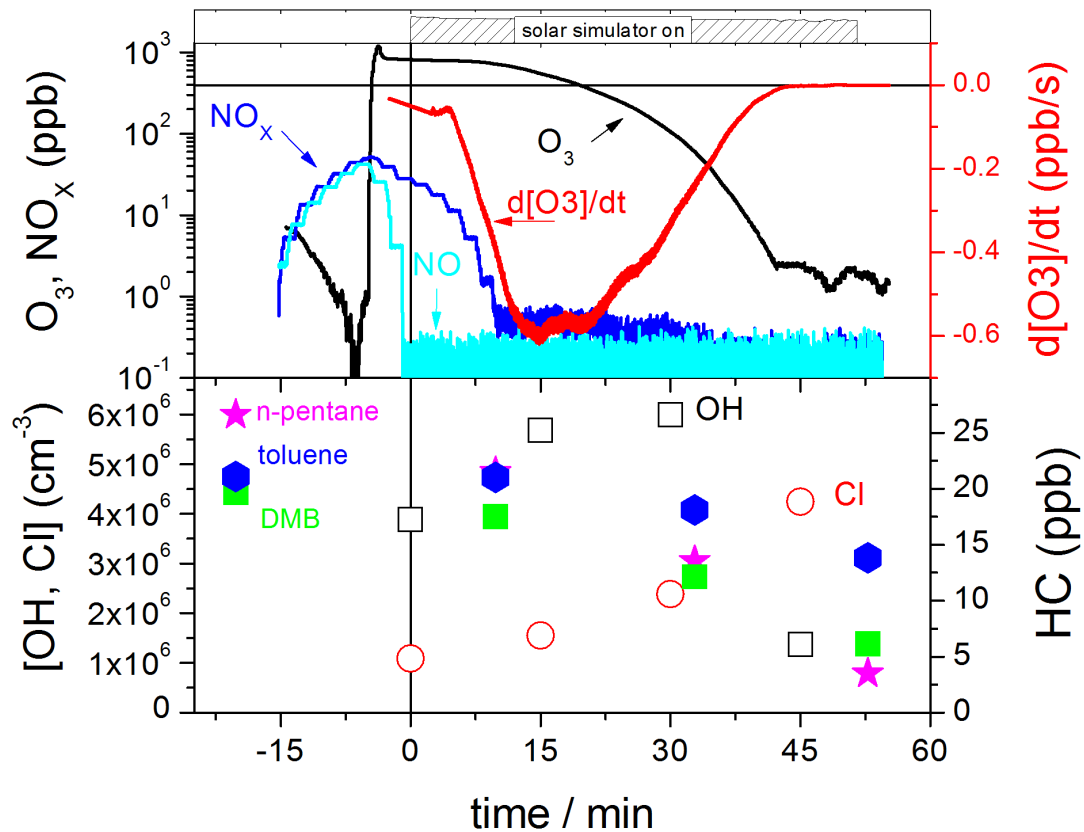
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Fig. 5.

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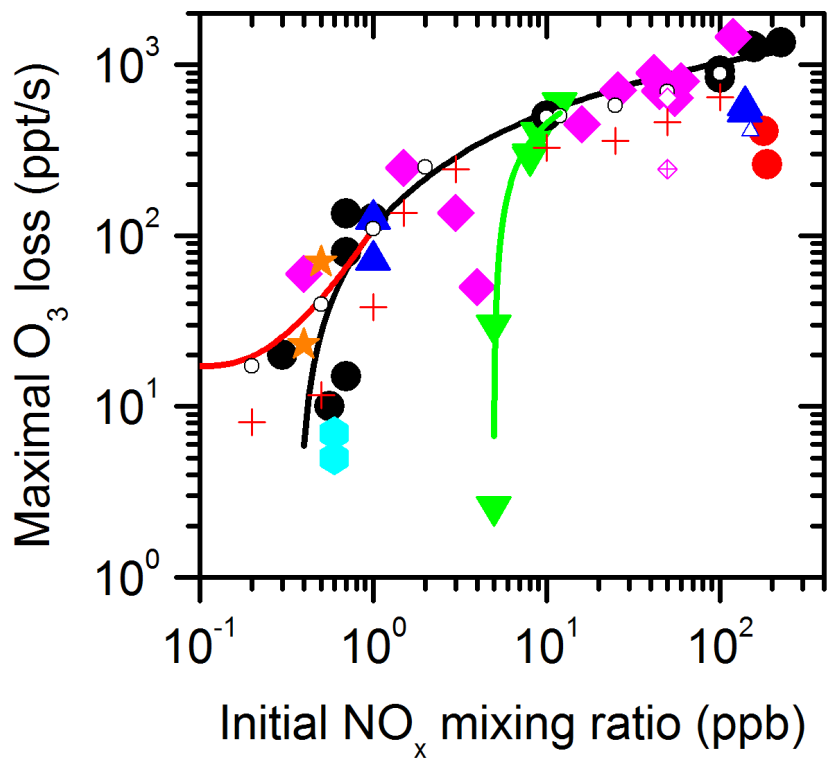
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Fig. 6.

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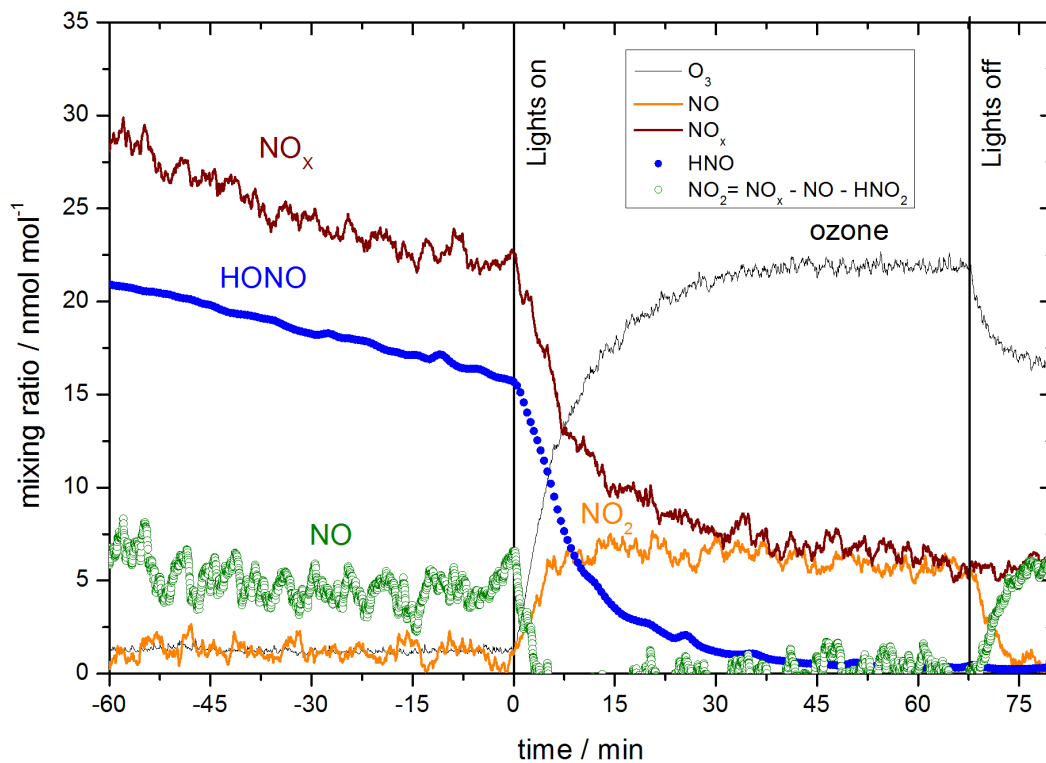
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Fig. 7.

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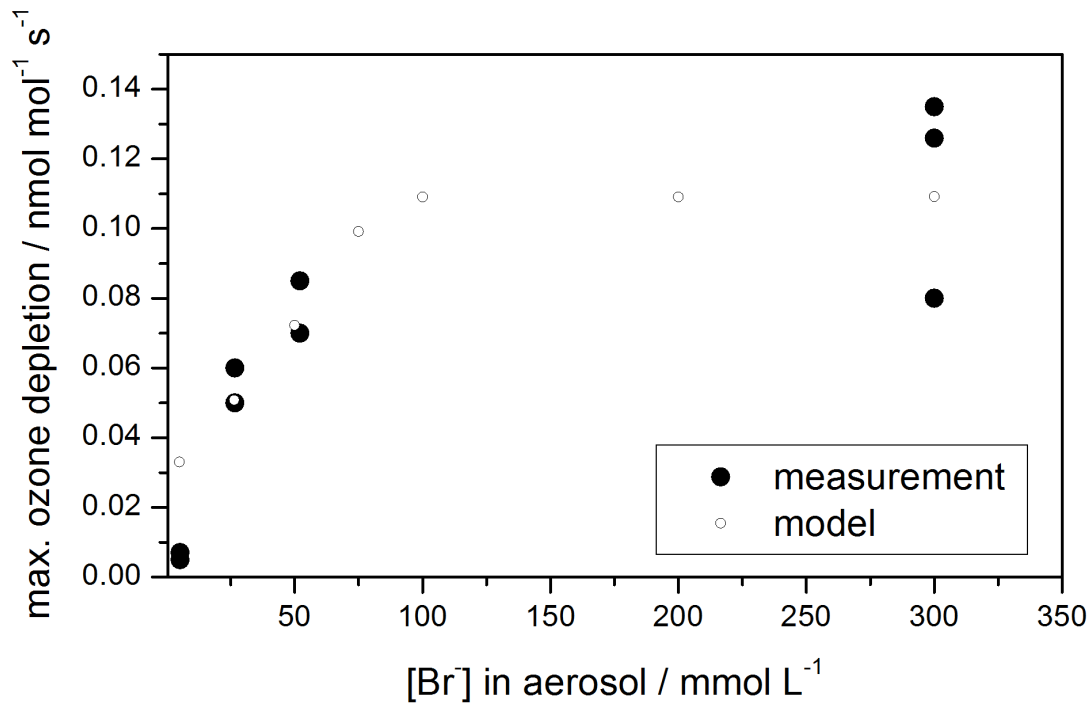
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Fig. 8.

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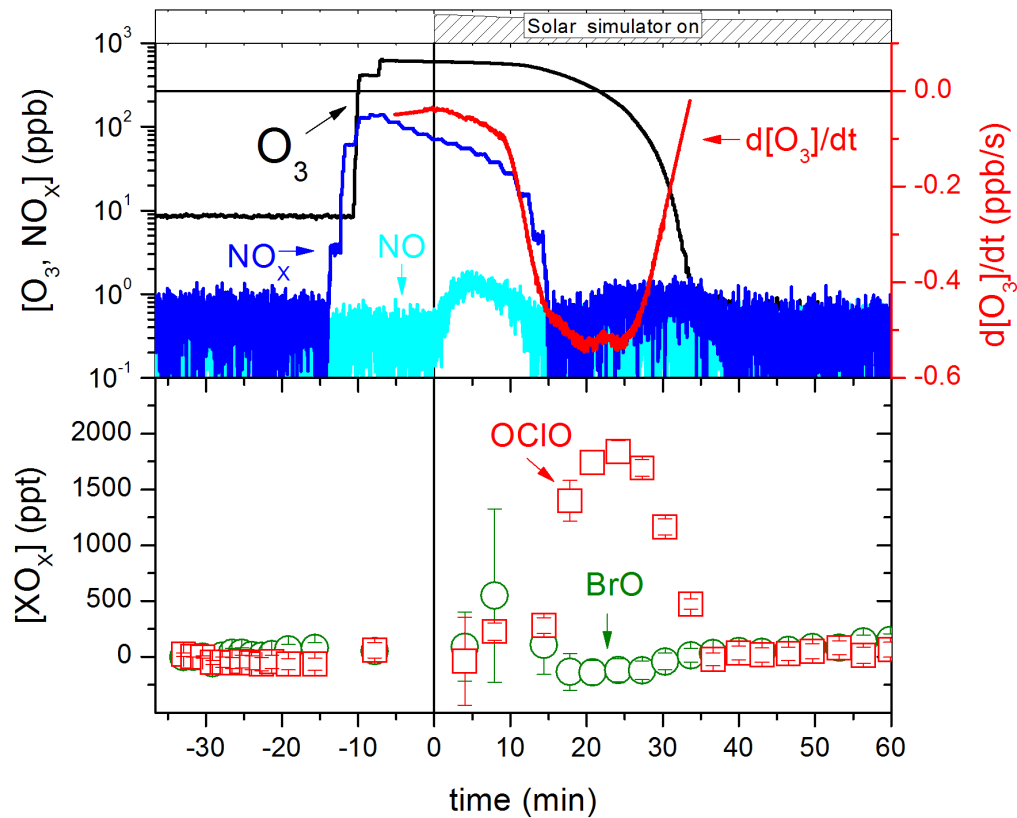


Fig. 9.

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