

***Interactive comment on “On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for O<sub>3</sub>, HO<sub>x</sub>, NO<sub>x</sub> and the Hg lifetime” by A. Saiz-Lopez et al.***

**A. Saiz-Lopez et al.**

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We would like to thank both reviewers for their detailed comments on the paper. The revised version of the paper is considerably improved as a result. The responses to the reviewers' comments are given below

Reviewer #1:

The model and its description

R1.1) ...the reader might get the impression that the chemistry within aerosols is treated in detail.

RESPONSE: We do not explicitly treat the aqueous phase chemistry in the bulk of

the aerosol. We assume that the limiting step for halogen heterogeneous recycling on aerosols is the first-order rate of uptake which we compute, using the free-regime approximation, for a number of gas-phase species. This is now clarified in the revised paper.

R1.2) The authors speculate about the role of iodine oxides in new particle formation.

RESPONSE: The precise mechanism by which IO and OIO form iodine oxide particles (IOPs) is unknown, though the subject of ongoing research. Hence, IOP formation cannot be modelled with a great degree of confidence. There are two problems. The first is that the solid particles produced in the laboratory have the stoichiometry of  $I_2O_5$ , but it is not clear whether this is produced in the gas phase by  $O_3$  oxidising  $I_2O_y$  ( $y < 5$ ), or by the polymerization of these lower oxides into particles which then rearrange and eject  $I_2$  (see Saunders and Plane, 2005). The second is that although IOP production in the laboratory is very rapid, there may be free energy barriers to nucleation which are not apparent at the relatively high concentrations of IO employed (compared with the atmosphere). The influence of humidity and other condensable vapours in the marine environment (e.g.  $H_2SO_4$ ) also remains to be explored.

Since there were no aerosol measurements during CHABLIS, we have not explicitly examined IOP production in this study, other than to point out that a significant build up of  $I_xO_y$  is predicted even if the  $I_xO_y$  species photolyse quite rapidly, and so IOP production may be possible. We have made this clear in the revised paper.

R1.3) Equation 1

RESPONSE: The terms in equation 1 are defined after the equation; eddy diffusivity is the last term in the equation.

R1.4) According to p. 9390. I. 15-18 the model time step is 2 min and the vertical resolution 1 m.

RESPONSE: In the present study we choose a 2 minute time-step as a compromise

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between the computation time efficiency and compliance with the Courant criterion. Confirmation of this is that when the time step is reduced to 15 s, the calculated IO and BrO after 48 hours change by less than 1 %. This has now been added to the revised paper.

R1.5) Fluxes of what species are prescribed at the surface and what are the source strengths (p. 9391, l. 1-3)?

RESPONSE: The species whose fluxes are prescribed at the surface are I2 and Br2: the fluxes are  $1.0E10$  molecule  $cm^{-2} s^{-1}$  and  $1.0E9$  molecule  $cm^{-2} s^{-1}$  during spring, respectively. In addition, summer and spring NO<sub>x</sub> fluxes of  $2.0E8$  and  $1.2E7$  molecule  $cm^{-2} s^{-1}$ , respectively, which were measured during CHABLIS (Jones et al., 2007b), are prescribed in the model. This is now stated more clearly in the revised paper.

R1.6) Constrained modeling (section 2.2) and NO<sub>x</sub>.

RESPONSE: We use the NO<sub>x</sub> fluxes measured during CHABLIS (Jones et al., 2007). The lowest box in the model is constrained with the measured NO<sub>x</sub> fluxes  $2.0E8$  and  $1.2E7$  molecule  $cm^{-2} s^{-1}$  for summer and spring, respectively. The model contains standard NO<sub>x</sub> photochemistry (gas-phase and heterogeneous reactions), and snow-pack deposition of N species (e.g. HNO<sub>3</sub>). Exchange of NO<sub>x</sub> between the boundary layer and the free troposphere is not included. The N-mass balance is preserved throughout the model runs. This is now clarified in the revised paper.

R1.7) p. 9392, l. 11: how is the diurnal variation determined?

RESPONSE: The diurnal profiles of these species were constrained from measurements made during the campaign. This is now clarified in the revised paper.

R1.8) p. 9393, l. 1-2: The deposition velocities for these compounds are not listed in the supplement. How do you calculate/determine them?

RESPONSE: Dry deposition to the surface occurs in the lowermost level of the model. The deposition flux within this level is calculated as  $V_d/C_i$ , where  $V_d$  is the deposition

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velocity and  $C_i$  is the concentration of species  $i$ . The deposition velocities used in the model were all set to  $0.5 \text{ cm s}^{-1}$ . This is now explained in the revised paper.

R1.9) p. 9393, l. 11 Is a marine aerosol surface area really appropriate for these conditions?

RESPONSE: Halley Station is only a few km from the Weddell Sea. Therefore, in the absence of actual measurements at the site we consider that the aerosol surface area of remote marine conditions is the most appropriate approximation for a remote coastal location such as Halley. This is now stated in the revised paper.

R1.10) p. 9395, l. 14 - 17: Many halogen related reactions in the aqueous phase are dependent on acidity.

RESPONSE: This typographical error has now been corrected in the revised paper.

R1.11) p. 9395, l. 19 - 22: Are the rate coefficients of these reactions really known?

RESPONSE: The rate coefficients of  $\text{IO} + \text{OIO}$  and  $\text{OIO} + \text{OIO}$  were obtained from careful fitting of simultaneous decays of  $\text{I}$ ,  $\text{IO}$  and  $\text{OIO}$  in a laboratory experiment (Gomez Martin et al., 2007). Although this was a challenging exercise, the results are convincing (the reference has now been added correctly).

R1.12) Discussion on p. 9397: I feel you should phrase this a bit more cautiously as the chemistry of higher iodine oxides is, to my knowledge, not very well understood and you had to make quite a few assumptions.

RESPONSE: The reviewer is right that we still lack good understanding of the chemistry of higher order iodine oxides. However, on pages 11 and 12 we only describe sensitivity runs incorporating possible reaction channels for the iodine oxides. We do not make firm statements about the chemistry but rather test several possibilities. Also, to ensure that the uncertainties in iodine chemistry are clear we have added a paragraph in the revised paper.

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R1.13) p. 9397, l. 23-24: In order to show that the chosen photolysis rate is a "lower limit" you should present or at least discuss model runs with lower rates.

RESPONSE: The gas-phase rate coefficients for the formation of I<sub>2</sub>O<sub>3</sub> and I<sub>2</sub>O<sub>4</sub> are now reasonably well established from the lab study of Gomez Martin et al. (2007). We do not yet know whether the oxides can be oxidized to I<sub>2</sub>O<sub>5</sub> by O<sub>3</sub>. However, by lumping I<sub>x</sub>O<sub>y</sub> together with a single photolysis rate, our purpose here is to show that there must be a reasonably fast photochemical turnover of these species back to IO, on a time scale of ~100 s. This turnover time could only be longer (or the photolysis rate slower than 0.01 s<sup>-1</sup>), if the rate coefficients measured by Gomez et al. are significant over-estimates, which we have no reason to believe.

R1.14) Source of iodine (p. 9398, l. 8-12): In sea water and therefore also in brine etc the concentration of iodide and iodate is very small, so in order for the sea salt to be a relevant source for it would have to be highly enriched.

RESPONSE: The reviewer is right about the iodine levels in brine, and iodine would actually recycle mostly as interhalogen compounds (IBr or ICl), rather than I<sub>2</sub>. Organo-iodine compounds may also make a contribution. But since these sources are so poorly understood, we don't want to speculate further on the nature of the source. Rather, we use the model to estimate the size of the source strength necessary to sustain the dynamic halogen chemistry observed in the atmosphere over Halley. We now emphasise this in the revised paper.

R1.15) p. 9402, l. 20: You mention the thermal decomposition of I<sub>2</sub>O<sub>2</sub>.

RESPONSE: These rates were mistakenly omitted from Table 1 and have now been added (Reaction A96 and A97)

Conclusions: I don't really think that your model can reproduce measured O<sub>3</sub> concentrations including an entrainment term.

RESPONSE: Reproducing measured O<sub>3</sub> in the presence of high halogen oxide con-

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centrations is indeed a challenge. In the constraints of a 1D model, the only way to match the observation of high O<sub>3</sub> in the presence of IO and BrO is by including entrainment from aloft. We have changed the conclusion to ensure that this point is clear in the revised paper.

R1.17) p. 9390, l. 17: Do you really mean "downward convective transport" or rather entrainment?

RESPONSE: Corrected: this should have been "entrainment".

R1.18) p. 9390, l. 21: What is a "scale height at the top of the BL"?

RESPONSE: In fact, equation 3 was not used to estimate the O<sub>3</sub> entrainment flux (instead, the entrainment flux was simply specified into the top box). We have therefore removed equation 3 and this sentence from the revised paper.

R1.22) p. 9399, l. 13-15: These measurements were made at a constant height and therefore do not show a rather homogeneous distribution.

RESPONSE: We agree that the vertical distribution of BrO is probably not very homogeneous, as indicated by our revised model which sees only about 50% of the surface concentrations at the top of the boundary layer. In the paper by Avallone et al. they measured higher concentrations of BrO closer to the snow pack than in the DOAS light path indicating that the snow could be acting as a source. If the release of BrO in CHABLIS was from a nearby local source we should have seen some incidences where the BrO concentrations dropped below the detection limit for certain wind directions. This was not seen to happen. We have included the Avallone et al. reference and discussion in the revised paper.

R1.24) p. 9400, l. 19-20: Maybe you should also mention that after 48h O<sub>3</sub> has decreased by about 50%.

RESPONSE: Added to the revised paper.

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R1.25) p. 9401, l. 19-20: The reader might get the impression that you actually calculated the production of NO<sub>x</sub> from the photolysis of nitrate in the snowpack.

RESPONSE: No, the flux of NO<sub>x</sub> was constrained to the measured value, and this is now stated clearly in the revised paper.

R1.26) p. 9402, l. 3-5: I would rather say that you used XO concentrations and XO:X ratios from the model to calculate the lifetime.

RESPONSE: That is now clarified in the revised paper.

R1.27) p. 9403, l. 1: Are there any mercury measurements available to compare your data with? With these lifetimes there should basically be no Hg<sup>0</sup> present during daytime.

RESPONSE: Unfortunately, Hg measurements were not made during the campaign. This is now mentioned in the revised paper.

Reviewer #2:

R2.1) If ozone rich air is mixed downward from the free troposphere, also dilution of the constituents in the boundary layer must occur, and it is not clear to what extent this is considered in the model.

RESPONSE: We only include an O<sub>3</sub> entrainment from the free troposphere (FT) into the BL to account for the episodes of simultaneous high halogens and moderately high O<sub>3</sub> levels. We do not include a parameterization of the BL-FT exchange of halogens because BL ventilation is a complex problem that is beyond the scope of this work. For instance, the concentrations of the halogens in the lower FT are needed to properly quantify BL-FT exchange, and these are not well known. Hence, since we do not include BL ventilation, the halogen flux used in the model can be considered a lower limit under convective boundary layer conditions. This is now stated in the revised paper.

R2.2) The representation of heterogeneous and liquid phase chemistry in the model is only described very briefly, and no rate constants for liquid phase reactions are provided in the supplemental.

RESPONSE: Refer to comment (R1.1)

R2.3) The model study presented here neglects horizontal transport of halogen-rich air masses from the sea ice to the coast.

RESPONSE: The reviewer's points about the halogen sources are justified. The results of the CHABLIS campaign do indeed raise important questions about how these high halogens in the Antarctic boundary layer can be maintained. However, we reiterate that the focus of this paper is not on the sources but on the impacts of such high halogen concentrations in the Antarctic boundary layer. The main reason for considering the snow pack as a possible secondary source is the fact that moderate concentrations of IO and BrO were observed even when air masses had been over continental Antarctica for several days (Saiz-Lopez et al., 2007a). This shows that there has to be some way of recycling halogens very efficiently. The absence of IO and BrO at night indicates that solar radiation is required for the emission of halogens to take place efficiently from the snowpack: if the halogens were stored as gas-phase reservoirs during the night (HOI, INO<sub>3</sub> etc), then "pulses" of IO and BrO would be seen after sunrise. This behaviour was not observed. Hence, even though oceanic air that has crossed the sea ice zone is most likely the primary source, snowpack recycling can be treated as a secondary source. Assuming this to be the case, the flux of halogens was tuned to reproduce the levels of IO and BrO seen during the campaign. Though these fluxes are certainly high, the observed levels of IO and BrO require such high fluxes to sustain them. We do not consider iodo-carbons as the main source of halogens in the model, because these high concentrations of halogen oxides cannot be produced from halocarbons at concentrations that have been observed previously (by groups mentioned by the reviewer), although these species were not measured during CHABLIS. Hence, we parametrise the halogen flux using using a flux of I<sub>2</sub> and Br<sub>2</sub>. A full treatment of the

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different possible sources of halogens is well beyond the scope of this paper. These points have now been added in the revised paper.

R2.4) As a result of the assumption that halogens are exclusively emitted in situ from the snowpack, the modelled BrO and IO mixing ratios exhibit strong vertical gradients

RESPONSE: The measurements made during the CHABLIS campaign found up to 6 ppt of BrO and IO when the air came from the continent and was not of oceanic influence (Saiz-Lopez et al., 2007a). This was the main difference between the CHABLIS observations and previous measurements, and indicates a possible local (or continental) source in Antarctica. This was the main reason for considering the snowpack as a source, which then generates a gradient of BrO. However, this gradient is not very steep, so that the modeled column density is in accord with the previous MAX-DOAS column measurements of BrO. Frieß et al. (2004) mention that the average concentration in the boundary layer would be about 13 ppt, which is the concentration of BrO at the top of the boundary layer in figure 6b. Furthermore, there have been previous studies which have shown a gradient in BrO (Avallone et al., 2003). Nevertheless, we emphasize that our knowledge of the sources that lead to the high BrO and IO observed at Halley is still rather poor. Since horizontal transport is not considered in this study we simply use the 1D vertical model to estimate the source strength needed to account for the observed IO and BrO. These points have now been added in the revised paper.

R2.5) The coincident presence of high levels of BrO and ozone is explained by the downward mixing of ozone-rich air from the free troposphere into the boundary layer.

RESPONSE: Please see the response to comment R2.1. The range of  $K_z$  values used in the model are now given in the revised paper. It is likely that the transport of air from nearby sea ice is the source of the highest levels of halogens observed during CHABLIS. However, this does not explain the measurement of up to 6 ppt when the air comes from the continent. The authors agree that the oceanic sector is the primary

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source (see Saiz-Lopez et al., 2007), but a secondary source of halogens is needed to explain the presence of halogens at such high levels.

R2.6) It would therefore be very interesting to extend the model calculations to the autumn and summer period in order to assess the overall impact of halogens on the boundary layer chemistry.

RESPONSE: We certainly agree that halogens will affect the boundary layer chemistry throughout the sunlit part of the year. However, the reason for running the model for spring time was to explore the greatly enhanced effects of the halogens during this season. Knowledge of the halogen sources is still very uncertain, especially in summer when the sea ice-covered area in the proximity of Halley Station is smallest. Further work is needed to properly assess the sources and impacts of halogens through this part of the year, but this is beyond the scope of this first study.

R2.7) The modelled IO concentrations (Fig. 3 and 4) show a pronounced diurnal cycle, whereas previous model studies (Vogt et al., 1999) come to the conclusion that the IO concentrations are quite constant whenever sunlight is present because a photochemical steady state is quickly established after sunrise. What is the explanation for this diurnal cycle?

RESPONSE: We considered the emission of iodine and bromine from the snowpack to be dependant on actinic flux. Since the actinic flux follows a roughly Gaussian profile, the same would apply for emissions. This was done to match the diurnal profiles seen during the campaign. We have tried to word this more clearly in the revised paper.

How do the model results compare to the measurements made during Chablis?

RESPONSE: The halogen fluxes in the model were tuned to provide good agreement with the measured values at a height of 5 m (the DOAS beam height) that are reported in Saiz-Lopez et al., 2007a. So the agreement is by definition very good, and we do not wish to add a further figure to the present paper. Instead, we have cited the

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measurements in the captions for figures 3, 4 and 6.

R2.8) A surface albedo of 0.85 is used for the determination of actinic fluxes and photolysis rates.

RESPONSE: The surface albedo was measured during the campaign; the reference has now been provided in the revised paper.

R2.9) It is stated in the abstract that an I atom flux from the snow pack of 109 molecules cm<sup>-2</sup> s<sup>-1</sup> is necessary to account for up to 20 ppt, whereas a 10 times higher flux is mentioned in Section 4.1.

RESPONSE: This has now been corrected in the Abstract (the summertime flux was listed in error).

R2.10) Frieß et al. (2004) have analysed and interpreted springtime BrO measurements at Neumayer station during two years (1999 and 2000), covering a longer time period than the Chablis campaign.

RESPONSE: We agree with the reviewer that the reference to the earlier work was poorly phrased. By "comprehensive" measurements we meant that this was the most comprehensive measurement campaign, not only in terms of halogens measurements. Changes have been made in the revised paper.

R2.11) P. 9388, L25: The impact of halogens on DMS oxidation has been studied in detail by von Glasow et al. (2004). This publication should be cited here.

RESPONSE: Inserted in the revised paper.

R2.13) It is stated that acidification of aerosols will slow down the aerosol processing time (P. 9395, L. 14).

RESPONSE: See response to comment R1.10

R2.14) The model scenarios need to be described in more detail.

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RESPONSE: The model is run for springtime conditions where the air mass is of oceanic influence. Sunrise is at 0430 and sunset is at 2330 GMT. The days matching these conditions are 20th and 21st October 2004, which are presented in Saiz-Lopez et al. (2007a). These details are now added in the revised paper.

R2.16) In the chemical scheme shown in Fig. 1, the conversion of XO to X occurs only via the reaction with NO.

RESPONSE: In figure 1, the photolysis of XO is now shown with a dotted arrow. The reaction of XO with YO was omitted, but has now been added to the figure. The photolysis of BrO is included in the model, and has not been added to Table 1 (J25 in the list of reactions).

R2.17) References are required for the mixing ratios of the chemical species to which the model is constrained (Section 2.2).

RESPONSE: We thank the reviewer for spotting these errors: the concentrations were wrongly transcribed from a sensitivity analysis. The correct values, measured during the campaign and used in the normal model runs, are listed in the revised paper.

R2.18) What is a time-step method (P. 9392, L. 10)?

RESPONSE: We use a time-step method to incorporate the fluctuations of constrained species. This requires that the field data (constrained species) are first averaged or interpolated to the two-minute frequency. Then, the concentrations of the constrained species were read in at the appropriate integration time step. Hence, these species were not assigned continuity equations and integrated, and their fluctuations do not determinate the size of the integration time-step. This is now explained on in the revised paper.

R2.20) How can satellite measurements of slant columns provide evidence that IO is well mixed in the boundary layer as mentioned in the summary?

RESPONSE: The long-path DOAS makes measurements at the base of the boundary

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layer. If the boundary layer is horizontally homogeneous over the DOAS pathlength (as it is at Halley Bay), and the height of the boundary layer is known, then the IO column abundance can be computed assuming the IO is well mixed. This can then be compared with satellite measurements of the (slant) column density. Good agreement indicates (though does not prove) that the species is well mixed. This is now explained more clearly in the revised paper.

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