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Interactive comment on "On the vertical distribution of boundary layer halogens over coastalAntarctica: implications for O_3, HO_x, NO_x and the Hg lifetime" *by* A. Saiz-Lopez et al.

Anonymous Referee #2

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Based on photochemical model calculations, the manuscript entitled 'On the vertical distribution of boundary layer halogens over coastal Antarctica: Implications for O_3, HO_x, NO_x and the Hg lifetime' by Saiz-Lopez et al. aims to investigate the sources and impacts of halogen radicals (BrO and IO) observed in the coastal boundary layer of Antarctica. The model study is based on recently published year-round DOAS measurements at Halley Station during the Chablis campaign, from which mixing ratios of up to 20 ppt were reported both for BrO and IO. To my knowledge, these are the highest IO levels ever reported in the atmosphere, whereas similar BrO mixing ratios where found previously during bromine explosion events.

A one-dimensional photochemical and dynamical scheme is used for the modeling of halogen chemistry. The model covers the lowermost 200 m of the atmosphere. The manuscript describes boundary conditions at the top of the model only for ozone, but not for the other constituents considered in the model. 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. It is stated that the downward flux of ozone from the free troposphere is set to zero for a neutral boundary layer. This is not correct since there is still some vertical mixing under neutral conditions, e.g. due to wind shear. An almost complete suppression of vertical mixing occurs only under stable conditions, mainly due to a strong inversion layer which is frequently present at the top of the boundary layer in the Antarctic. A turbulent diffusion coefficient of zero at the surface does not imply that there is no 'diffuse' (diffusive?) upward flux from the surface as stated in Section 2.1: the flux at the surface is dominated by molecular diffusion.

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. A much more detailed description of the heterogeneous chemistry scheme implemented in the model is necessary, also in comparison to other state of the art models (e.g., Vogt et al., 1999; von Glasow et al., 2002; Lehrer et al., 2004; Piot and von Glasow, ACPD, 2007).

The model scenarios presented in the manuscript appear to be over-simplified and also in contradiction to the current knowledge of the mechanisms leading to the bromine explosion phenomenon. Numerous ground-based and space borne observations (e.g., Kreher et al., 1997; Kaleschke et al., 2004; Frieß et al., 2004; Hönninger et al., 2004; Hollwedel et al., 2004) have shown that reactive bromine is produced over the polar sea ice by release from highly saline surfaces, such as frost flowers and brine. Bromine activated air is then transported to the coastal measurement sites. The model study presented here neglects horizontal transport of halogen-rich air masses from the sea ice to the coast. Instead, it is assumed that the observed BrO and IO amounts are produced and sustained exclusively by emission from the snowpack. This requires unrealistically high fluxes out of the snowpack: 10^9 molecules cm^{-2} s^{-1} in case of bromine and even up to 10^{10} molecules cm^{-2} s^{-1} in case of iodine. Distributed over the lowermost 200 m of the atmosphere, this value corresponds to an input of inorganic iodine of about 1500 ppt day^{-1} which is clearly an unrealistic value. An explanation how the snowpack can serve as a continuous source for such high amounts of reactive halogens is lacking. Model studies (Lehrer et al., 2004) have shown that sea salt aerosols, either airborne or deposited on the snow, cannot be a sufficient source due to their limited bromide and even smaller iodide content (although they are of importance for bromine recycling). A recently published model study (Piot and von Glasow, ACPD, 2007) shows that the deposition flux of bromine compounds in bromine-activated air (about 10^7 molecules cm^{-2} s^{-1}, from which 75% are assumed to be re-emitted into the gas phase) is 2-3 orders of magnitude smaller than the fluxes back from the snow to the atmosphere assumed here. Organohalogens in the snowpack are also unlikely to be a sufficient source for up to 20 ppt of gaseous IO and BrO. The total abundance of organoiodides in polar regions is typically in the order of 3.5 ppt (Reifenhäuser and Heumann, 1993; Carpenter et al., 1999). The authors argue themselves in their recently published Science paper that IO is not emitted by (but possibly recycled on) the snow pack, but that high concentrations of phytoplankton, which colonize the underside of sea ice, produce iodocarbons which then provide a source of inorganic iodine in the boundary layer, and that ’the concentrations of BrO and IO were strongly correlated with the local wind direction as well as the air mass origin predicted by back trajectory calculations. Enhanced concentrations of both radicals were observed when the wind was from the open ice front sector, in air masses that had been over sea ice within the previous 24 hours’. How can the snowpack be considered as the main source for reactive halogens in the face of these findings? It is neither mentioned in the manuscript that organohalogens are considered in the model nor are any photolysis rates for these source gases listed in the supplemental. Why are they ignored if the authors assume that iodocarbons are the main source for inorganic iodine?

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 with high concentrations near the surface (e.g., decrease in BrO mixing ratios by a factor of two in the first 200 m, as shown in Fig. 6a). The more likely transport of halogen-rich air from the sea ice to Halley Station would instead lead to a mixing of reactive halogens within the boundary layer. Indeed, trajectory calculations have shown that BrO detected by a DOAS instrument at Neumayer station, Antarctica, is likely to be well mixed within the boundary layer and that even uplifted layers of bromine-enriched air occur under certain meteorological conditions (Frieß et al., 2004). This study also shows that bromine activation only occurs if air masses come from the sea ice. Hönninger et al. (2004) come to the same conclusion on the basis of MAX-DOAS measurements of BrO at Hudson Bay and determine a BrO layer height of 1 km.

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. This is represented in the model by a downward flux of ozone of 3×10^{11} molecules cm^{-2} s^{-1} and a convective BL (values for the turbulent diffusion coefficient K_z are not provided anywhere in the manuscript). Only the temporal and vertical distribution of ozone, but not of the inorganic bromine and iodine compounds is shown. Turbulent diffusion does not only lead to a downward flux of ozone, but must also cause an upward flux of air from the boundary layer into the free troposphere and thus a dilution of reactive halogens. Is this considered in the model? No values for the measured BrO, IO and ozone concentrations are provided in the manuscript for this event. How is it possible to keep the IO and BrO mixing ratios at ≈ 15 ppt (as it is the case on October 21st 2004 as shown in the Science paper) in a convective boundary layer, and what would be the necessary surface emission rates? The modeled ozone loss rate in the presence of 10 ppt BrO and IO is 0.55 ppb h^{-1}, corresponding to a lifetime of ≈ 1.5 days. Isn't the transport of air in which bromine release has occurred very recently (i.e., over the sea ice close to the measurement site), and in which ozone levels are still high, a more likely explanation?

Apart from the extremely high IO concentrations, the presence of significant levels of IO and BrO throughout the sunlit period is one of the most interesting aspects of the Chablis data. To my knowledge, the presence of a BrO background of up to 5 ppt in summer and autumn has not been measured before. However, the model calculations only deal with the bromine explosion period in polar spring when very high BrO and IO amounts are present. The presence of halogen radicals throughout the sunlit period is expected to have a significant impact on the photochemistry in the Antarctic boundary layer. 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.

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? Is the iodine emission rate from the snowpack kept constant or has it a Gaussian distribution peaking at noon, as for the model calculations in the Science paper?

How do the model results compare to the measurements made during Chablis? For a quantitative comparison, provide figures with the diurnal variations of modelled and measured BrO and IO at the altitude of observation.

A surface albedo of 0.85 is used for the determination of actinic fluxes and photolysis rates. This value, on which the photochemical reactions critically depend, is surprisingly low and requires explanation, since other measurements determined an albedo of the Antarctic snowpack very close to one throughout the UV-Vis spectral range (typically 0.99, see e.g. Grenfell et al., JGR, 1994, DOI:10.1029/94JD01484).

It is stated in the abstract that an I atom flux from the snow pack of 10^9 molecules cm^{-2} s^{-1} is necessary to account for up to 20 ppt, whereas a 10 times higher flux is mentioned in Section 4.1.

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. Describing these as ’Some measurements’ (P. 9387, L. 27) is therefore inappropriate. Explain why the data set obtained during Chablis is the ’most comprehensive’ (P. 9389, L. 18), and the ’first comprehensive’ (P 9394, L5) if year-round measurements of IO and two years of springtime BrO observations in the Antarctic coastal boundary layer have been published before (Frieß et al., 2001; Frieß et al., 2004).

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.

The first two paragraphs of Section 4.1 should be moved to Section 2 since they describe features of the photochemical model.

It is stated that acidification of aerosols will slow down the aerosol processing time (P. 9395, L. 14). This is in contradiction to previous model studies (e.g., Mozurkewich, 1995; Tang and McConnell, 1996; Vogt et al., 1996), which show that acidification is a necessary prerequisite for the release of reactive bromine and will instead accelerate the halogen release.

The model scenarios need to be described in more detail. For example, for which days are the results shown in Fig. 3-7 shown? At what time are sunset and sunrise?

What is a ’scale height at the top of the boundary layer’ (P. 9390, L. 21)?

In the chemical scheme shown in Fig. 1, the conversion of XO to X occurs only via the reaction with NO. This reaction should be of minor importance due to the low NO$_x$ concentrations. Instead, the XO + YO reactions (A.114, A.117, A.118) and the photolysis of XO (J22) are expected to dominate in the Antarctic boundary layer. The photolysis of BrO to Br + O is not listed in the supplement. Is this important reaction not implemented?

References are required for the mixing ratios of the chemical species to which the model is constrained (Section 2.2). A methane mixing ratio of 2000 ppb is too high, the contemporary value is around 1700 ppb. The mixing ratio of SO_2 is very high (100 ppt), typical background values in polar regions are 10 times smaller (Barrie and Hoff, 1984; Bottenheim et al., 1990).

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

First sentence of Section 3: Since the DOAS technique is a well established method, an original publication should be cited (e.g. Platt 1994) instead of Plane and Saiz-Lopez (2006).

How can satellite measurements of slant columns provide evidence that IO is well mixed in the boundary layer as mentioned in the summary? How can this be concluded from long-path DOAS observations, which measure the average concentration of trace gases along a horizontal light path?

No adequate care has been taken in the preparation of the reference list. Numerous publications cited in the text are not listed (e.g., Richter et al., 1998; Wagner and Platt, 1998; Wagner et al., 2001; Richter et al., 2002; Frieß et al., 2001; Thompson, 1984). Barrie is cited as ’Barr’ (P. 9387, L. 13). Hönninger is cited as ’Honninger’ and Frieß as ’Friess’ throughout the paper. The pioneer in aerodynamics was Theodore von Kármán and not ’Von Karmen’ (P. 9391, L. 11).

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9385, 2007.