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A. Saiz-Lopez, J. M. C. Plane, A. S. Mahajan, P. S. Anderson, S. J.-B. Bauguitte, A. E. Jones, H. K. Roscoe, R. A. Salmon, W. J. Bloss, J. D. Lee, et al.

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# 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

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## Abstract

A one-dimensional chemical transport model has been developed to investigate the vertical gradients of bromine and iodine compounds in the Antarctic coastal boundary layer. The model has been applied to interpret recent year-round observations of iodine and bromine monoxides (IO and BrO) at Halley Station, Antarctica. The model requires an equivalent I atom flux of  $\sim 10^9$  molecule  $\text{cm}^{-2} \text{s}^{-1}$  from the snowpack in order to account for the measured IO levels, which are up to 20 ppt during spring. Using the current knowledge of gas-phase iodine chemistry, the model predicts significant gradients in the vertical distribution of iodine species. However, recent ground-based and satellite observations of IO imply that the radical is well-mixed in the boundary layer, indicating a longer than expected atmospheric lifetime for the radical. This can be modelled by including photolysis of the higher iodine oxides ( $\text{I}_2\text{O}_2$ ,  $\text{I}_2\text{O}_3$ ,  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_5$ ), and rapid recycling of HOI and  $\text{INO}_3$  through sea-salt aerosol. The model also predicts significant concentrations (up to 25 ppt) of  $\text{I}_2\text{O}_5$  in the lowest 10 m of the boundary layer, which could lead to the formation of ultrafine iodine oxide aerosols. Heterogeneous chemistry involving sea-salt aerosol is also necessary to account for the vertical profile of BrO. Iodine chemistry causes a large increase (typically more than 3-fold) in the rate of  $\text{O}_3$  depletion in the BL, compared with bromine chemistry alone. Rapid entrainment of  $\text{O}_3$  from the free troposphere is required to account for the observation that on occasion there is little  $\text{O}_3$  depletion at the surface in the presence of high concentrations of IO and BrO. The halogens also cause significant changes to the vertical profiles of HO and  $\text{HO}_2$  and the  $\text{NO}_2/\text{NO}$  ratio. The average  $\text{Hg}^0$  lifetime against oxidation is also predicted to be about 10 h during springtime. Overall, our results show that halogens profoundly influence the oxidizing capacity of the Antarctic troposphere.

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## 1 Introduction

Reactive halogen species (RHS= X, X<sub>2</sub>, XY, XO, OXO, HOX, XNO<sub>2</sub>, XONO<sub>2</sub> where X, Y is a halogen atom: Br, Cl, or I) play important roles in a number of atmospheric processes. One major impact is the depletion of ozone through catalytic cycles involving halogen radicals (e.g. Br, IO, BrO, Cl). In the 1970s, interest was focused mainly on stratospheric ozone depletion (e.g. Molina and Rowland, 1974; Stolarsky and Cicerone, 1974), whereas since the 1980s there have been reports of complete O<sub>3</sub> depletion events (ODEs) in the polar tropospheric boundary layer (BL) of both the Arctic and Antarctic (e.g., Bottenheim et al., 1986; Oltmans and Komhyr, 1986; Murayama et al., 1992; Kreher et al., 1997; Tuckermann et al., 1997; Wessel et al., 1998; Spicer et al. 2002; Brooks et al. 2006; Jones et al., 2006). These events occurred at polar sunrise in the spring and were explained by the influence of bromine-catalyzed chemical cycles (e.g. Barr et al., 1988; McConnell et al., 1992; Tuckermann et al., 1997; Kreher et al., 1997; Friess et al., 2004; Kaleschke et al., 2004). Bromine chemistry also plays a central role in the oxidation of atomic mercury (Hg<sup>0</sup>) in the polar atmosphere (Schroeder et al., 1998; Brooks et al., 2006), which seems to provide an important pathway for this element to enter the Arctic food chain (Scott, 2001). It has been suggested that the presence of iodine can trigger this bromine chemistry and enhance the removal of ozone and mercury (Calvert and Lindberg, 2004a, b; O' Driscoll et al., 2006; Saiz-Lopez et al., 2007a).

Major components of the atmospheric chemistry of bromine and iodine in the polar BL are illustrated in Fig. 1. The release of bromine-containing compounds proceeds through the so-called “bromine explosion”, which involves bromide ions in brine-coated sea ice or snow being converted to gas-phase inorganic bromine (Br, BrO, HOBr etc.) in the BL (Honninger and Platt, 2002). The presence of BrO has been reported by several groups such as Tuckermann et al. (1997) at Ny Alesund, Honninger et al. (2004a) at Hudson Bay, Canada and Brooks et al. (2006) at Barrow, Alaska. Some measurements of BrO were also made in coastal Antarctica using a passive DOAS instrument

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(e.g. Friess et al., 2004). Satellite observations have shown the presence of BrO in both the northern and southern polar regions (Richter et al., 1998; Wagner and Platt, 1998; Wagner et al., 2001; Richter et al., 2002; Hollwedel et al., 2004).

The vertical extent of bromine chemistry has been studied using a combination of the long path DOAS and multi-axis DOAS measurement techniques (Tuckermann et al., 1997; Martinez et al., 1999; Honninger et al., 2004b). These studies showed that the enhanced BrO during ODEs was confined to the BL. It was also concluded that there was a very small vertical gradient of BrO within the BL (Honninger and Platt, 2002; Honninger et al., 2004b). These observations of BrO being well-mixed within the BL are consistent with a one-dimensional model study by Lehrer et al. (2004), which concluded that ODEs in the Arctic are caused by halogen chemistry confined to the BL by an inversion layer. This study also showed that emission from brine-covered sea ice was not sufficient to explain the observed ODEs, and suggested that recycling of halogen radicals through heterogeneous chemistry on aerosols was also required.

Besides removing  $O_3$ , RHS can also affect the oxidizing capacity of the troposphere in other ways. X and XO radicals reach a photochemical steady state during the day, essentially governed by reaction with  $O_3$  and photolysis (Fig. 1). The X atoms can react with non-methane hydrocarbons (NMHC), leading to hydrogen atom abstraction (analogous to OH). In fact, indirect measurements of the vertical extent of RHS have been carried out by measuring hydrocarbon destruction patterns (Solberg et al., 1996; Ramacher et al., 1999). Br atoms also recombine with  $Hg^0$  to produce HgBr, which is relatively stable at the low temperatures of the polar spring BL; HgBr can then add a further radical (Br, I etc.) to yield mercury in its stable 2+ oxidation state (Goodsite et al., 2004). Halogen oxides such as BrO and IO can also act directly as oxidizing radicals. For example, the rate of oxidation of dimethyl sulphide by XO can be up to an order of magnitude higher than the oxidation by OH (Saiz-Lopez et al., 2004).

RHS also affect the  $HO_x$  (i.e.,  $[HO_2]/[OH]$ ) and  $NO_x$  ratios (i.e.,  $[NO_2]/[NO]$ ) (e.g. von Glasow and Crutzen, 2003; Saiz-Lopez and Plane, 2004a; Bloss et al., 2005). XO radicals oxidize NO to  $NO_2$ , thus increasing the  $NO_x$  ratio. In contrast, they react with

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HO<sub>2</sub> to yield HOX, which then photolyses efficiently to OH (particularly in the case of HOI), thus decreasing the HO<sub>x</sub> ratio (Bloss et al., 2005).

Lastly, the role of iodine oxides in forming ultra-fine aerosol has been investigated by laboratory, field and modeling experiments (e.g. O'Dowd et al., 1998; Hoffmann et al., 2001; O'Dowd et al., 2002; Jimenez et al., 2003; Saiz-Lopez and Plane, 2004b; McFiggans et al., 2004; Burkholder et al., 2004; Sellegri et al., 2005; Saunders and Plane, 2005 & 2006; Saiz-Lopez et al., 2006). The process of iodine oxide particle (IOP) production is thought to involve the recombination reactions IO + IO, IO + OIO, and OIO + OIO to yield I<sub>2</sub>O<sub>y</sub>, where y=2, 3 or 4, respectively. Further oxidation with O<sub>3</sub> may then produce the most stable higher oxide, I<sub>2</sub>O<sub>5</sub>, which can then polymerize to form solid particles of I<sub>2</sub>O<sub>5</sub> (Saunders and Plane, 2005, 2006). Thus the presence of IO in the atmosphere points to the possibility of IOP formation; these particles could then provide condensation nuclei for other condensable vapours and grow to the point of becoming cloud condensation nuclei.

In Antarctica, the vertical column of IO has been measured using a ground-based differential optical absorption spectrometer (DOAS) (Friess et al., 2001), and very recently from the SCIAMACHY instrument on the ENVISAT satellite (Saiz-Lopez et al., 2007b; Schoenhardt et al., 2007). However, the most comprehensive data set on Antarctic IO (and BrO) in the BL was obtained during the Chemistry of the Antarctic Boundary Layer and Interface with Snow (CHABLIS) field measurement campaign at Halley Station, shown on the map in Fig. 2 (Saiz-Lopez et al., 2007a). In the present paper we investigate, using a 1-D model, the sources and likely vertical distributions of halogens within the Antarctic BL. The effects of the combined iodine and bromine chemistry on O<sub>3</sub> depletion, the HO<sub>x</sub> and NO<sub>x</sub> ratios and the lifetime of Hg within the BL are then investigated.

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## 2 Model description

The Tropospheric Halogen Chemistry model (THAMO) is a one-dimensional chemical and transport model that uses time-implicit integration (Shimazaki, 1985). It has three main components: i), a chemistry module that includes photochemical, gas-phase and heterogeneous reactions; ii), a transport module that includes vertical diffusion, and sedimentation of particles; and iii), a radiation scheme which calculates the solar irradiance as a function of altitude, wavelength and solar zenith angle. The continuity equations to account for the change in concentration  $n_i$  of a species  $i$  at an altitude  $z$  and a time  $t$  are given by:

$$\frac{\partial n_i}{\partial t} = P_i - L_i n_i - \frac{\partial \phi_i}{\partial z} \quad (1)$$

where  $P_i$  and  $L_i$  are the production and loss rates of  $i$ , respectively.  $\phi_i$  is the vertical flux due to eddy diffusion:

$$\phi_i = K_z \left[ \frac{\partial n_i}{\partial z} + \left( \frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{\bar{H}} \right) n_i \right] \quad (2)$$

where  $\bar{H}$  is the scale height of the atmosphere and  $K_z$  is the eddy diffusion coefficient. These equations are solved in the model with an integration time step of 2 min. In this study, the model extends from the ground up to the upper boundary at 200 m with a spatial resolution of 1 m. To account for the downward convective transport of free tropospheric  $O_3$ , an additional flux at the upper boundary is estimated using the following expression (Shimazaki, 1985):

$$\phi_i = K_z [O_3] \left( \frac{1}{\bar{H}} - \frac{1}{H_{O_3}} \right) \quad (3)$$

where  $H_{O_3}$  is the scale height of  $O_3$  at the top of the BL, typically 7.5 km. Sensitivity studies are run for different flux strengths and for a scenario where the flux across the

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upper boundary is set to zero (i.e. a neutral BL). The lower boundary is the snowpack surface, where deposition from the gas phase and an upward trace gas flux from the snowpack can occur.

## 2.1 Vertical transport parameterization

5 This is described by the turbulent diffusion coefficient  $K_z(z, t)$ , which will usually be a function of time  $t$  and height  $z$ . Near the surface, the layer where there is minimal change in momentum flux, turbulence is generated predominantly by wind shear. This “surface layer” is well described by Monin-Obhukov similarity theory, from which a function for the diffusion coefficient can be derived (Stull, 1988):

$$10 \quad K_z(z, t) = \kappa \cdot z \cdot u^*(t) \quad (4)$$

where  $\kappa$  is the Von Karmen constant = 0.4,  $z$  is the height above the surface and  $u^*(t)$  is the surface friction velocity. In the neutral BL, where buoyancy can be neglected,  $u^*$  can be derived to a good approximation from:

$$15 \quad \frac{\kappa U}{u^*} = \ln \left( \frac{z}{z_0} \right) \quad (5)$$

where  $U$  is wind speed,  $z$  is the measurement height of the wind, and  $z_0$  is the surface roughness length. For Halley, long-term measurements indicate that  $z_0 \sim 5 \times 10^{-5}$  m (King and Anderson, 1994). Note that this form of  $K_z(z, t)$  is relevant to the surface layer, where  $u^*(t)$  is virtually constant. Equation (4) implies that  $K_z(z, t)$  is linearly dependent on  $z$ , and tends to zero at the surface. This in turn would imply that a trace gas released at the surface,  $z=0$ , would never diffuse upwards, a situation which is clearly unrealistic. Hence, a surface condition is used which assumes that this form of  $K_z(z, t)$  is only valid for  $z \geq z_0$  (Stull, 1988).

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## 2.2 Chemical scheme

In addition to halogen chemistry, the THAMO model contains a set of odd-hydrogen, odd-nitrogen and methane chemical reactions, and a limited treatment of non-methane hydrocarbon (NMHC) chemistry. It also includes a detailed chemical scheme of reduced sulphur oxidation. Specific details of the iodine and bromine chemistry schemes are given in Sects. 4.1 and 4.2, respectively. A simplification of the chemistry described in the model is illustrated in Fig. 1, whereas the full reaction scheme is listed in Table 1 of the supplementary material (<http://www.atmos-chem-phys-discuss.net/7/9385/2007/acpd-7-9385-2007-supplement.pdf>). The model is constrained with typical measured values of other chemical species via a time-step method to simulate the fluctuations of species; with diurnal mixing ratio profiles peaking at  $[\text{CO}] = 35 \text{ ppb}$ ;  $[\text{DMS}] = 80 \text{ ppt}$ ;  $[\text{SO}_2] = 100 \text{ ppt}$ ;  $[\text{CH}_4] = 2000 \text{ ppb}$ ;  $[\text{CH}_3\text{CHO}] = 150 \text{ ppt}$ ;  $[\text{HCHO}] = 150 \text{ ppt}$ ;  $[\text{isoprene}] = 60 \text{ ppt}$ ;  $[\text{propane}] = 25 \text{ ppt}$ ;  $[\text{propene}] = 15 \text{ ppt}$ . The concentrations of the constrained species were then read in at the appropriate simulation time and interpolated for each integration step. The model is also updated at every simulation time-step with measurements of temperature and relative humidity made during CHABLIS.

## 2.3 Photochemistry

The rate of photolysis of species is calculated on-line using an explicit two-stream radiation scheme from Thompson (1984). The irradiance reaching the surface is computed after photon attenuation through 50 1-km layers in the atmosphere as a function of solar zenith angle (SZA), location and time-of-year. The absorption cross-section and quantum yield data used in this model are summarized in Table 1 (supplementary material <http://www.atmos-chem-phys-discuss.net/7/9385/2007/acpd-7-9385-2007-supplement.pdf>). The rate of photolysis of species is computed by including snowpack albedo measurements (typical measured albedo = 0.85) made with an actinic flux spectrometer during the CHABLIS campaign.

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## 2.4 Sea ice surface and aerosol uptake

Here, it is assumed that species such as HOBr, HOI, HBr, HI, IONO<sub>2</sub> and BrONO<sub>2</sub> are dry deposited to the surface snowpack and, through heterogeneous reactions involving Br<sup>-</sup>, I<sup>-</sup> and Cl<sup>-</sup> ions, recycle back to the gas phase in the form of photolabile halogen species XY (X = I, Br; Y = I, Br, Cl). Similarly, the uptake onto sea-salt aerosol surfaces is estimated for a number of species including HOBr, HOI, HBr, HI, IONO<sub>2</sub>, BrONO<sub>2</sub>, OH, HO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, CH<sub>3</sub>O<sub>2</sub>, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The uptake of a gas species onto an aerosol surface is computed using the volumetric aerosol surface area (ASA) and the free molecular transfer approximation (Fuchs, 1964). The ASA used in this work is 10<sup>-7</sup> cm<sup>2</sup> cm<sup>-3</sup> (von Glasow et al., 2002) chosen to be typical of remote oceanic conditions, and is assumed constant in each vertical level of the model (i.e. the aerosol is well-mixed in the BL). The uptake coefficients are taken from the recommendations of Sander et al. (2006) and Atkinson et al. (2000), unless otherwise stated.

## 3 DOAS observations at Halley Station

BL observations of IO and BrO were carried out at Halley Station from Jan. 2004 to Feb. 2005 using the technique of long-path differential optical absorption spectroscopy (DOAS) (Plane and Saiz-Lopez, 2006). The measurements were performed during the CHABLIS campaign at Halley Station (75° 35' S, 26° 30' W) situated on the Brunt Ice Shelf, about 35 m above sea level (Fig. 2). The ice edge is some 12 km north, 30 km west and 20 km south-west of the station. A detailed description of the CHABLIS campaign can be found elsewhere in this issue (Jones et al., 2007a<sup>1</sup>).

The instrument was located in the Clean Air Sector Laboratory (CASLAB). An effective light path of 8 km at a height of 4 to 5 m above the snowpack (varying through the

<sup>1</sup>Jones, A. E., Wolf, E. W., Salmon, R. A., et al.: Chemistry of the Antarctic Boundary Layer and the Interface with Snow: An overview of the CHABLIS campaign, in preparation, 2007a.

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year as a result of snow accumulation) was set up between the CASLAB and a retro-reflector array positioned 4 km to the east. Further information on the instrumental design and spectral de-convolution procedures can be found in Plane and Saiz-Lopez (2006).

5 The measurements provide the first comprehensive observations of the diurnal and seasonal trends of both radicals in coastal Antarctica (Saiz-Lopez et al., 2007a). The IO and BrO concentrations exhibit a diurnal cycle with a clear dependence on solar irradiance. Higher concentrations were also measured in air that had passed over sea ice within the previous 24 h. However, even in continental air that had spent at least four  
10 days over the interior of Antarctica, both radicals were still measured at mixing ratios up to ~6 ppt during sunlit periods, significantly above the detection limit of the instrument (1–2 ppt). This striking finding implies that halogen activation is not restricted to close proximity to the ice edge, and is widespread in the Antarctic coastal BL. This conclusion is strongly supported by satellite observations of the tropospheric BrO column, where  
15 it was assumed that most of the BrO was confined to the BL (e.g., Hollwedel et al., 2004).

The seasonal trends of both radicals are remarkably similar, both in timing and absolute concentration. The radicals first appeared above the DOAS detection limit during twilight (August), and were then present throughout the sunlit part of the year. The peak  
20 mixing ratios of IO and BrO (20 ppt) were measured in springtime (October), followed by a possible smaller peak in autumn (March–April).

Regarding the DOAS detection of OIO, the molecule was not conclusively measured above its DOAS detection limit (6–7 ppt) during 21 days of observations between January 2004 and February 2005. For more details about the DOAS measurements and  
25 correlation with meteorology during CHABLIS, see Saiz-Lopez et al. (2007a).

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## 4 Results and discussion

### 4.1 Iodine chemistry

The major objective of this modelling study is to simulate the IO observations, and thus explore the impact of iodine chemistry in the polar BL. The THAMO *standard model* contains the gas-phase iodine chemistry scheme we have used in previous modeling studies (McFiggans et al., 2000; Saiz-Lopez et al., 2006). Heterogeneous chemistry is treated in the following way. The uptake and subsequent hydrolysis of IONO<sub>2</sub>, HOI and INO<sub>2</sub> on aerosols produces HOI, which equilibrates between gas and aqueous phase according to its Henry's law solubility. The processing of aqueous HOI to IBr, ICl and I<sub>2</sub>, via reaction with Br<sup>-</sup>, Cl<sup>-</sup> and I<sup>-</sup>, respectively, takes only between 10 and 15 min in fresh sea-salt aerosol (McFiggans et al., 2000). The di-halogen molecules are insoluble and will then be released rapidly to the gas phase. Hence, uptake of the inorganic iodine species onto aerosols is the rate-limiting step of the process (McFiggans et al., 2000). Note, however, that aged sea-salt aerosols will become depleted in Br<sup>-</sup> and Cl<sup>-</sup>, and progressively acidified by uptake of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and SO<sub>2</sub> (e.g. Fickert et al., 1999; von Glasow et al., 2002): both effects will slow down the aerosol processing time.

The gas-phase chemistry of IO in very clean air (NO<sub>x</sub> < 30 ppt) is dominated by the reactions of IO with itself to form I<sub>2</sub>O<sub>2</sub> and OIO + I (Sander et al., 2006), IO + OIO to form I<sub>2</sub>O<sub>3</sub> (Martin et al., 2005), and that of OIO + OIO to form I<sub>2</sub>O<sub>4</sub> (Martin et al., 2005). These reactions proceed rapidly in the gas phase with rate coefficients of  $1 \times 10^{-10}$ ,  $5 \times 10^{-11}$  and  $1 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The model also includes the formation of gas-phase I<sub>2</sub>O<sub>5</sub> through a series of oxidation reactions of I<sub>2</sub>O<sub>2</sub>, I<sub>2</sub>O<sub>3</sub> and I<sub>2</sub>O<sub>4</sub> by O<sub>3</sub> up to the +5 oxidation state; we adopt a lower limit to the rate coefficients of these reactions of  $6 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Saunders and Plane, 2005). We also assume in the standard model that I<sub>2</sub>O<sub>2</sub>, I<sub>2</sub>O<sub>3</sub>, I<sub>2</sub>O<sub>4</sub> and I<sub>2</sub>O<sub>5</sub> do not undergo photolysis or other reactions which would reduce them to IO or OIO, and that these molecules are

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lost by dry deposition to the snowpack, uptake onto pre-existing aerosol surfaces, and polymerization to form IOPs. Hence, any newly formed IO and OIO will be rapidly converted into higher-order iodine oxides, effectively limiting the atmospheric lifetime of both radicals.

5 Here we use the model to investigate two important questions. First, what is the iodine source strength required to simulate the IO mixing ratios observed at the height of the DOAS measurements (i.e., 4–5 m above the snowpack)? Second, what is the vertical extent of the iodine chemistry in this environment: is its impact limited to the near surface or throughout the entire BL. During the CHABLIS campaign, the highest  
10 mixing ratios of IO, up to 20 ppt, were observed in springtime, following enhanced activation mechanisms that, for the case of iodine, are not yet well understood. Figure 3 shows the modelled mixing ratios of IO and OIO in spring using the standard model of iodine chemistry, with an I atom flux out of the snowpack of  $1 \times 10^{10}$  molecule  $\text{cm}^{-2} \text{s}^{-1}$ . The calculated IO mixing ratio maximum of 16–18 ppt is in good accord with the DOAS  
15 observations. For OIO the mixing ratios are below 6 ppt, which was the instrumental detection limit during the CHABLIS campaign. The diurnally-averaged lifetime for  $\text{I}_x\text{O}_y$  is  $\sim 2$  h. The modelled summer IO mixing ratio at midday peaking at 6 ppt, in accord with the DOAS observations, requires an I atom flux out of the snowpack of  $1 \times 10^9$  molecule  $\text{cm}^{-2} \text{s}^{-1}$ .

20 Figures 3a and 3b show that both IO and OIO exhibit a strong vertical gradient in the BL: the concentration of IO at a height of 30 m is only 10% of that at 5 m. In the standard model, the transport of reactive iodine to the top of the BL occurs only via iodine recycling through sea-salt aerosol. However, the result of such a steep IO gradient is that the column abundance of the radical is predicted to be only  
25  $7 \times 10^{11}$  molecule  $\text{cm}^{-2}$  for the springtime simulation in Fig. 3. This is very much smaller than satellite observations of IO by SCIAMACHY in October 2005, where vertical columns  $> 3 \times 10^{13}$  molecule  $\text{cm}^{-2}$  were observed over Antarctic sea ice (Saiz-Lopez et al., 2007b), or zenith-pointing DOAS measurements of the IO slant columns up to  $1 \times 10^{14}$  molecule  $\text{cm}^{-2}$  made at the coastal Antarctic station of Neumayer (Friess et al.,

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2001). Hence, vertical column measurements strongly suggest that IO does *not* have a steep gradient within the BL. The most likely explanation is that the standard model is missing a recycling mechanism from the higher iodine oxides to IO, which would increase the IO lifetime and allow it to be well-mixed in the BL.

5 The most likely recycling mechanism is photodissociation of  $I_xO_y$ . This would have two effects: i) increase the lifetime of  $IO_x$  and therefore impact on the vertical distribution of inorganic iodine, ii) reduce the required atomic I flux from the snowpack into the gas phase to sustain the observed levels of IO. The model was therefore run with the photolysis of  $I_2O_2$ ,  $I_2O_3$ ,  $I_2O_4$  and  $I_2O_5$ , set to a frequency at noon of  $1 \times 10^{-2} \text{ s}^{-1}$ .  
10 This photodissociation frequency is 2–3 times faster than  $J(\text{IONO}_2)$  at this location in spring, calculated using a new measurement of the  $\text{IONO}_2$  photolysis cross section (J. M. C. Plane and S. H. Ashworth, personal communication). Preliminary measurements of the absorption cross sections of these higher iodine oxides indicate that their magnitudes and long wavelength thresholds are similar to those of  $\text{IONO}_2$  (Martin et al., 2005). Nevertheless, further laboratory work on the photochemistry of  $I_xO_y$  species is urgently needed to advance our understanding of this aspect of atmospheric iodine chemistry.

The inclusion of  $I_xO_y$  photolysis is now referred to as the *revised model*. Figure 4a shows the computed IO mixing ratio for the springtime scenario using the revised model  
20 (note the different height scale with respect to Fig. 3). The calculated IO at the top of the BL (200 m) is now 20% of that close to the surface, and the vertical column of  $5 \times 10^{12} \text{ molecule cm}^{-2}$  is now approaching reasonable accord with the satellite column measurement. Thus,  $J(I_xO_y) = 1 \times 10^{-2} \text{ s}^{-1}$  is the lower limit required to sustain high IO levels throughout the boundary layer.

25 Figure 4b shows vertical profiles of the major gas-phase iodine species throughout the BL. Note that the main reservoir of iodine is  $I_2O_5$  with mixing ratios ranging from 25 ppt to 8 ppt from the surface to the top of the BL, respectively. Figure 5 shows the modelled diurnal variation of the  $I_2O_5$  mixing ratio. Since the formation rate of IOPs is highly non-linear in  $I_xO_y$  mixing ratio (Saunders and Plane, 2005), most ultra-

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fine particles are predicted to form in the first 10 m above the snowpack, in the early afternoon (12:00–16:00 LT). This may be the source of ultra-fine particles that have been measured over sea-ice around Antarctica (Davison et al., 1996). Once IOPs form, there will be a competition between uptake onto pre-existing aerosol and further growth by the uptake of condensable vapours and coagulation.

IO was also observed at mixing ratios up to 6 ppt in air masses that had been over the continent for several days. This indicates an efficient iodine recycling mechanism capable of sustaining iodine radical chemistry over the snowpack. One possibility is the transport of sea-salt aerosol, and frost-flower fragments coated with sea-salt, from the ice front into the interior of the continent followed by deposition onto the snowpack; subsequent heterogeneous reactions would then recycle photolabile iodine to the gas phase. In fact, recent satellite measurements show that IO is widespread around coastal Antarctica, including areas over the snowpack (Saiz-Lopez et al., 2007b).

## 4.2 Bromine chemistry

Figure 6a shows a two-day model simulation of the BrO vertical profile in springtime. The initial Br<sub>2</sub> flux from the snowpack is set to be only  $1 \times 10^9$  molecule  $\text{cm}^{-2} \text{s}^{-1}$  (i.e. a factor of 5 smaller than the I atom flux (see above)), because of the effect of the bromine autocatalytic mechanism. It can be seen that on the second day of the simulation the BrO mixing ratios at the height of the DOAS measurements are similar to the observations, peaking at  $\sim 20$  ppt. During this season it is predicted that BrO will be better mixed within the boundary layer than IO (cf. Figs. 3 and 4). Figure 6b shows the noon vertical profiles of gas-phase bromine species during spring. Note that significant concentrations of inorganic bromine species reach the top of the BL, suggesting that BL ventilation under convective conditions may provide a source of inorganic bromine to the free troposphere. The predicted BrO column abundance for a 200 m BL height is  $1 \times 10^{13}$  molecule  $\text{cm}^{-2}$ , while satellite observations have reported averaged tropospheric vertical columns of  $4 \times 10^{13}$  molecule  $\text{cm}^{-2}$  in the austral spring over coastal Antarctica (Hollwedel et al., 2004). The difference could arise from the presence of a

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free tropospheric component in the satellite column measurement (Salawitch, 2006).

For the summertime case, a modelled BrO peak mixing ratio of 6 ppt at 4–5 m, in accord with the DOAS measurements, requires a Br<sub>2</sub> flux of  $2 \times 10^8$  molecule cm<sup>-2</sup> s<sup>-1</sup>. For both summer and spring model runs the predicted concentrations essentially track the solar irradiance profile and therefore peak at local noon when photodissociation of photolabile bromine (e.g. Br<sub>2</sub>, BrCl) is most efficient. In summer the BrO mixing ratio for SZA >90° does not decrease to zero since there is enough solar radiation reaching the surface during twilight for halogen activation to occur.

If heterogeneous reprocessing of bromine on sea-salt aerosol is switched off in the model, only a small fraction (~10%) of BrO at the surface will be transported by convection to the top of the BL, producing a pronounced vertical gradient. In contrast, including heterogeneous processing of bromine yields a vertical distribution of BrO that is well-mixed through the BL, in good accord with observations in the Arctic which have shown elevated levels of BrO at heights tens of meters above the snow surface (e.g. Tuckermann et al., 1997; Martinez et al., 1999; Honninger et al., 2004). This shows that aerosols have a significant effect on the vertical distribution of inorganic bromine, although the actual efficiency of the halogen aerosol processing will depend on the vertical profile of the aerosol size distribution and chemical composition (in particular, the degree of halide ion depletion and the pH of the aerosol).

#### 4.3 Impact of bromine and iodine chemistry on ozone

For a case where the noon peak of BrO is 10 ppt, a simple photochemical box model shows the diurnally-averaged O<sub>3</sub> loss rate is 0.14 ppb h<sup>-1</sup> arising from bromine chemistry alone (the averaged background O<sub>3</sub> level during spring was ~20 ppb). An O<sub>3</sub> depletion rate of 0.25 ppb h<sup>-1</sup> is calculated for a noon peak of IO = 10 ppt due to iodine chemistry only. When the halogens couple through the cross reaction



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the total O<sub>3</sub> loss rate is 0.55 ppb h<sup>-1</sup>, more than the sum of each component in isolation (Saiz-Lopez et al., 2007a). Thus, the O<sub>3</sub> depletion rate is almost four times as fast as that predicted from bromine chemistry alone, demonstrating the central role that iodine plays in O<sub>3</sub> depletion during Antarctic polar sunrise.

Figure 7a illustrates a THAMO run during springtime, for the case of a strong temperature inversion and neutrally buoyant BL, with no O<sub>3</sub> entrainment from the free troposphere. It can be seen that after 36 h the computed O<sub>3</sub> levels in the BL drop to below the instrumental detection limit (~1 ppb) due to the combined impact of iodine and bromine chemistry. This is similar to the complete removal of O<sub>3</sub>, which has been reported in the Arctic when a strong temperature inversion and high levels of BrO occur (e.g. Barrie et al., 1988; McConnell et al., 1992; Honninger and Platt, 2002).

However, during the CHABLIS campaign it was observed that elevated levels of IO and BrO occurred without complete removal of O<sub>3</sub>. We now use the THAMO model to examine whether the occurrence of high halogen oxide concentrations for a prolonged period of time without complete O<sub>3</sub> destruction can be explained by entrainment of O<sub>3</sub>-rich air from aloft. The transport of O<sub>3</sub> from the free troposphere into the BL was described using Eq. (4). Figure 7b shows the calculated O<sub>3</sub> profile with a downward flux from the free troposphere of O<sub>3</sub> of 3×10<sup>11</sup> molecule cm<sup>-2</sup> s<sup>-1</sup>, and a convective BL. The predicted O<sub>3</sub> levels after 36 h have now only decreased by 20%, consistent with the observations. Note also that the O<sub>3</sub> is well-mixed throughout the BL, without a pronounced vertical gradient, as observed by Arctic and Antarctic ozonesonde observations during ODEs (e.g. Wessel et al., 1998; Tarasick and Bottenheim, 2002).

#### 4.4 Impact of halogens on HO<sub>x</sub>, NO<sub>x</sub> and the Hg lifetime

During January and February 2005 (austral summer), in situ measurements of OH and HO<sub>2</sub> were performed using the FAGE technique (Bloss et al., 2007). The measurements were made at the same height above the snowpack (~5 m) as the DOAS beam. Typical peak noon values of 4×10<sup>-2</sup> ppt and 1.50 ppt were measured for OH and HO<sub>2</sub>

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respectively. IO and BrO react with HO<sub>2</sub> to form HOI and HOBr, whose subsequent photolysis produces OH, thus reducing the HO<sub>2</sub>/OH ratio. In order to model the OH and HO<sub>2</sub> mixing ratios, we use the  $J(O^1D)$  values measured during CHABLIS (typical noon photolysis frequency of  $4 \times 10^{-5} \text{ s}^{-1}$ ) and the measured mixing ratios of relevant species (see Sect. 2.2). Figures 8a and 8b show the effect of halogen chemistry on the vertical distributions of OH and HO<sub>2</sub>, respectively, for runs with the standard model, the revised model, and no halogens. At the height of the measurements, the model runs without halogen chemistry over-predict HO<sub>2</sub> by ~3 times the measured concentration, and underpredict OH by ~40%. Thus, the modeled HO<sub>x</sub> (HO<sub>2</sub>/OH) ratio is 115, compared with the measured ratio of 37. When halogen chemistry is included (i.e. typical summer noon BrO and IO mixing ratios of 5 ppt), the calculated OH and HO<sub>2</sub> levels and diurnal profile are in very good agreement with the observations: the modeled ratio is now 33. Figure 8 also shows that above about 10 m height there is a significant difference in the modeled OH and HO<sub>2</sub> profiles depending on whether I<sub>x</sub>O<sub>y</sub> photochemistry is included.

NO and NO<sub>2</sub> were also measured during the Antarctic summer period with noon average mixing ratios of 14 ppt and 7.5 ppt, respectively, so that the NO<sub>x</sub> (NO<sub>2</sub>/NO) ratio was 0.5 (Bauguitte et al., 2007<sup>2</sup>). IO and BrO increase the NO<sub>2</sub>/NO ratio by converting NO to NO<sub>2</sub>. NO<sub>x</sub> production in the model is from photochemistry of snowpack nitrate ions – entrainment from the free troposphere is not included. The model was constrained with summer  $J(\text{NO}_2)$  (typical noon maximum values of  $0.015 \text{ s}^{-1}$ ) values measured with an actinic flux spectrometer during CHABLIS. The photochemical flux of NO<sub>x</sub> from the snowpack required to simulate the NO<sub>x</sub> measurements at 5 m height is  $3 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$ , which is in sensible accord with a previous estimate of the summer NO<sub>x</sub> flux of  $\sim 2 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$  during CHABLIS (Jones et al., 2007b).

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<sup>2</sup>Bauguitte, S. J.-B., Bloss, W. J., Evans, M. E., Jones, A. E., Lee, J. D., Mills, G. P., Saiz-Lopez, A., Salmon, R. A., Roscoe, H. K., and Wolff, E. W.: An overview of multi-seasonal NO<sub>x</sub> measurements during the CHABLIS campaign: Can sources and sinks estimates unravel observed diurnal cycles?, in preparation, 2007.

Without halogens in the model, the NO<sub>x</sub> ratio at noon is only 0.3, whereas when halogens are included the ratio is 0.54.

Lastly, we use the THAMO to assess the impact of bromine and iodine chemistry on the lifetime of elemental mercury (Hg<sup>0</sup>) over coastal Antarctica. To calculate the lifetime of Hg<sup>0</sup> against oxidation to Hg<sup>II</sup>, we use the formalism given in Goodsite et al. (2004):

$$\tau = \frac{(k_{-2} + k_3[Br] + k_4[I])}{k_2[Br](k_3[Br] + k_4[I])} \quad (6)$$

where, at a pressure of 1 bar in air,

$$k(\text{Hg} + \text{Br} \rightarrow \text{HgBr}, 180\text{--}400 \text{ K}) = 1.1 \times 10^{-12} (T/298 \text{ K})^{-2.37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{R2})$$

$$k(\text{HgBr} \rightarrow \text{Hg} + \text{Br}, 180\text{--}400 \text{ K}) = 1.2 \times 10^{10} \exp(-8360/T) \text{ s}^{-1} \quad (\text{R-2})$$

$$k(\text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2, 180\text{--}400 \text{ K}) = 1.4 \times 10^{-10} + 2.6 \times 10^{-13} T - 8.6 \times 10^{-16} T^2 \quad (\text{R3})$$

$$k(\text{HgBr} + \text{I} \rightarrow \text{HgBrI}, 180\text{--}400 \text{ K}) = 1.2 \times 10^{-10} + 4.2 \times 10^{-13} T - 1.0 \times 10^{-15} T^2 \quad (\text{R4})$$

During springtime, the model shows that the diurnally-averaged mixing ratio of BrO of ~8 ppt measured by DOAS would have coexisted in steady state with a Br mixing ratio of ~0.7 ppt for a springtime diurnally-averaged O<sub>3</sub> mixing ratio of 12 ppb. The computed lifetime of Hg<sup>0</sup>, against oxidation by bromine chemistry alone (Reactions 2–3) is then about ~13 h at an average temperature of 260 K. The average IO measured by DOAS during springtime (~8 ppt) would have coexisted with a calculated I mixing ratio of ~5 ppt. The larger IO/I ratio, compared to that of BrO/Br, arises from the self-reaction of IO to form OIO + I and I<sub>2</sub>O<sub>2</sub> (Sander et al., 2006), and from the thermal decomposition of I<sub>2</sub>O<sub>2</sub> to OIO + I and IO + IO. Including the role of atomic I through reaction R4 leads to a 40% reduction of the Hg lifetime. In addition, iodine chemistry decreases the calculated BrO/Br ratio from 11 to 5 via conversion of BrO back to Br through Reaction (R1).

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The  $\text{Hg}^0$  lifetime is predicted to be reduced to only 2 h under conditions of high XO mixing ratios (i.e. 20 ppt), as observed as Halley during springtime, when the Br and I mixing ratios would have been 4 ppt and 13 ppt, respectively. Note that these calculations are made for high levels of halogens *without* severe  $\text{O}_3$  depletion, as observed on occasion during CHABLIS (Saiz-Lopez et al., 2007a). If  $\text{O}_3$  were completely removed, then the BrO/Br and IO/I ratios would decrease to 0.15 and 0.01, respectively, and the  $\text{Hg}^0$  lifetime would be reduced to  $\sim 10$  min. Our measurements of BrO and IO therefore indicate that there should be sustained removal of Hg into the snowpack throughout the sunlit period in coastal Antarctica.

## 5 Summary and conclusions

The THAMO chemical transport model has been used to investigate the vertical gradients of halogens in the Antarctic coastal BL with a parameterization of the vertical transport under neutral and convective BL conditions. The standard iodine chemistry model predicts a very steep gradient of iodine gas-phase species in the first 20 m of the BL. This does not explain evidence from measurements of IO by boundary layer DOAS during the CHABLIS campaign, and column abundance measurements from the ground and satellites, that IO is well-mixed in the BL. We have therefore revised the standard model to including the photolysis of the higher iodine oxides  $\text{I}_2\text{O}_y$ , where  $y=2-5$ . These reactions recycle IO efficiently throughout the BL, producing much better agreement between the model and observations. The photochemistry of these species needs to be studied in the laboratory.

The revised THAMO model was then used to explain the surprising occurrence of close-to-average  $\text{O}_3$  concentrations in the presence of high levels of IO and BrO, by replenishment of  $\text{O}_3$  through entrainment from the free troposphere. The model predicts a well-mixed vertical profile for  $\text{O}_3$  within the BL, which is in agreement with ozonesonde observations.

Finally, the model is able to account for the measured perturbations in the  $\text{HO}_x$  and

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NO<sub>x</sub> ratios by the observed concentrations of IO and BrO, and demonstrates that the presence of high atomic I concentrations leads to a significant enhancement in the oxidation rate of elemental Hg<sup>0</sup> by atomic Br.

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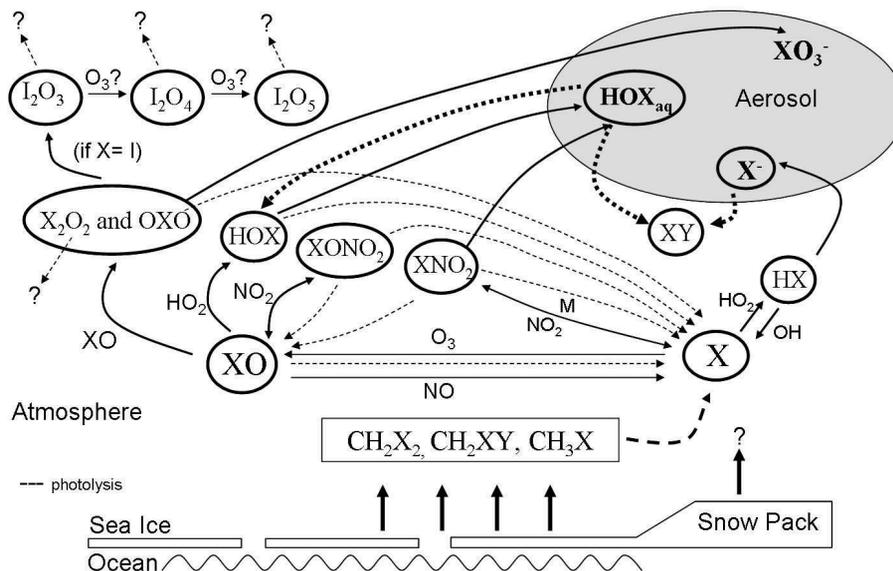
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**Fig. 1.** Simplified scheme of bromine and iodine chemistry in the Antarctic boundary layer.

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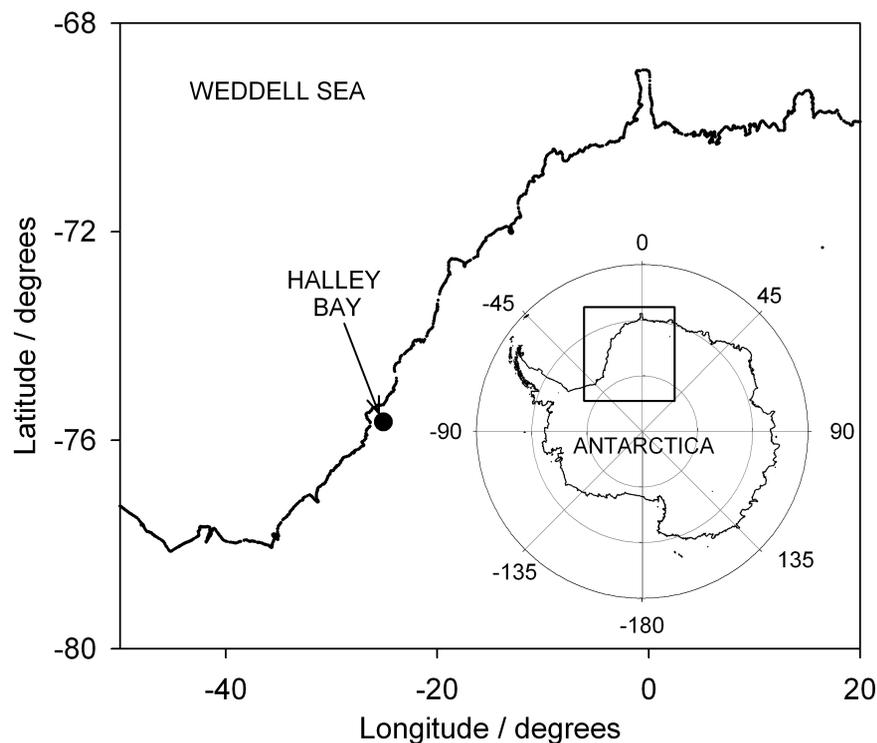
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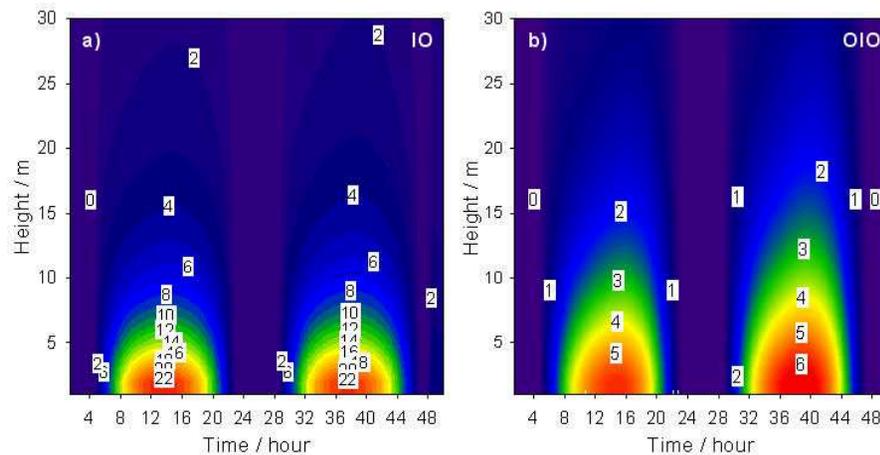
**Fig. 2.** Map showing the location of Halley Station on the Brunt Ice Shelf in Antarctica during 2005. Antarctic coastline generated using the Coastline Extractor page hosted by the National Oceanic & Atmospheric Administration (NOAA) /National Geophysical Data Center, Marine Geology and Geophysics Division.

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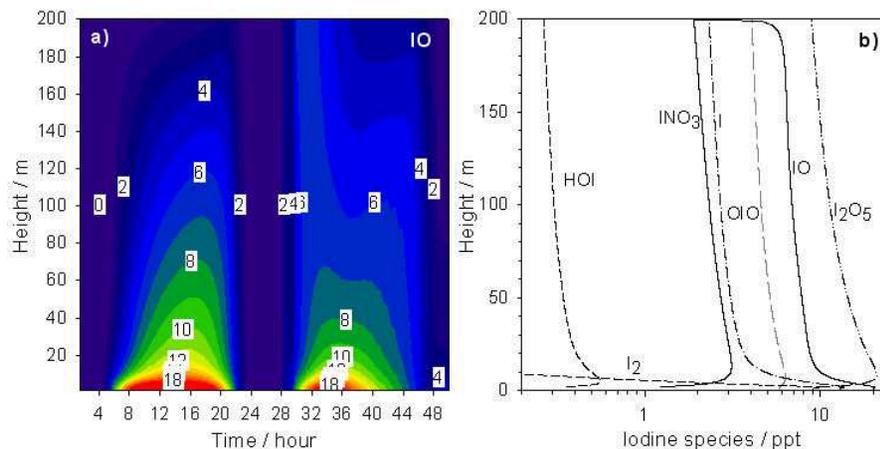


**Fig. 3.** Modelled diurnal variations of (a), the IO mixing ratio profile, and (b), the OIO mixing ratio profile during the austral summer at Halley, using the standard model (see text for details).

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**Fig. 4.** (a) Modelled diurnal IO mixing ratio profile during the austral spring at Halley, and (b) vertical profiles at noon of the main gas-phase iodine species, using the revised model (photolysis of  $I_xO_y$ ).

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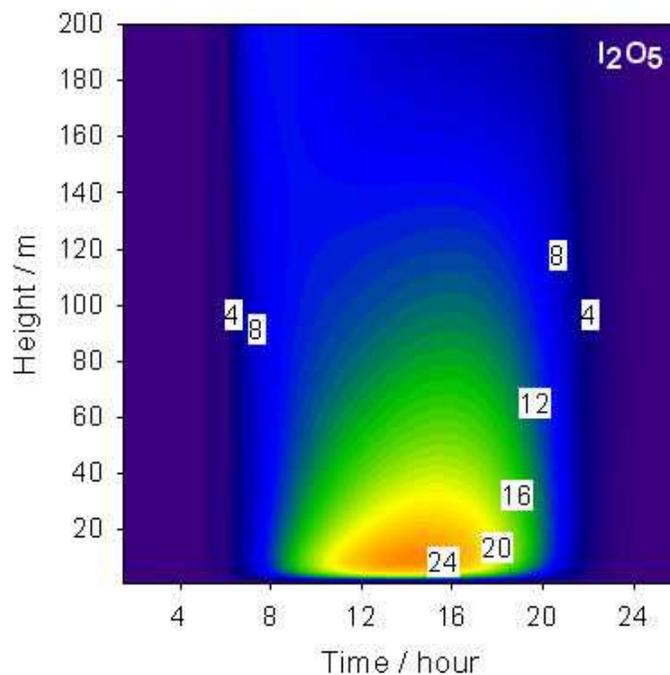
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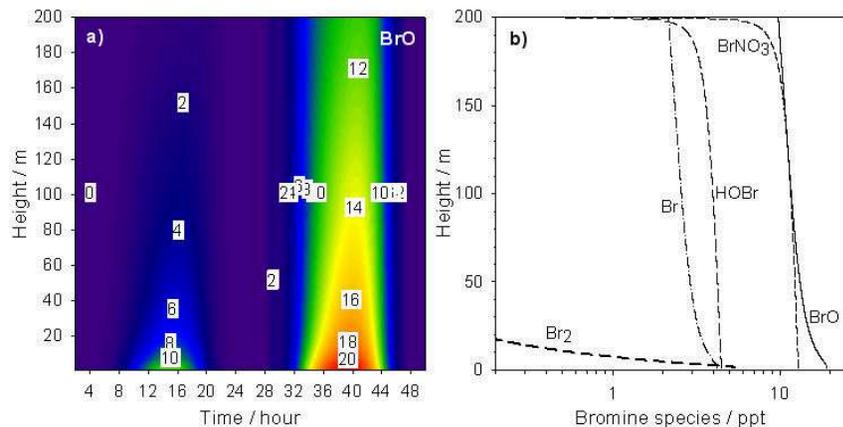


**Fig. 5.** Modelled diurnal  $I_2O_5$  mixing ratio profile during the Antarctic springtime, using the revised model.

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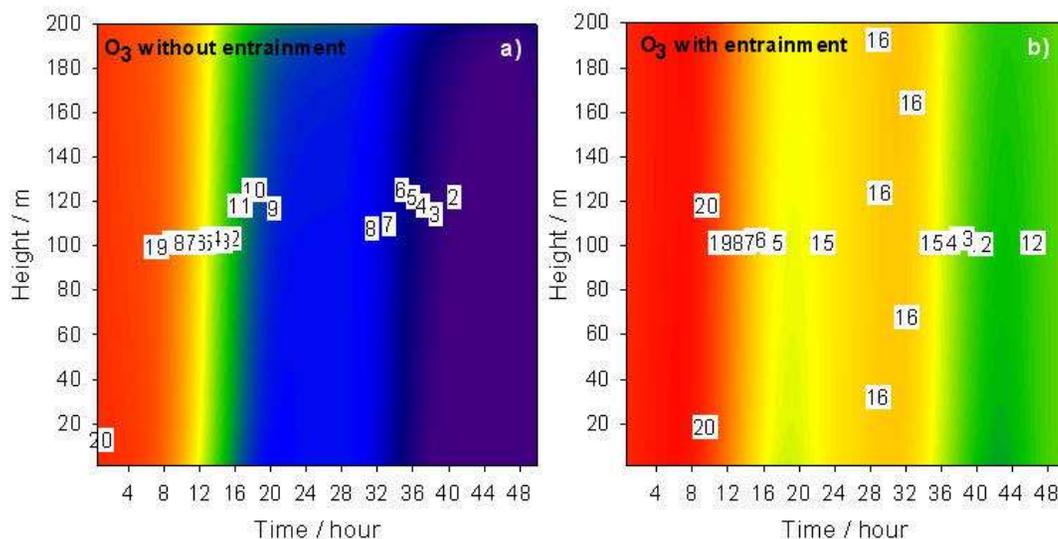


**Fig. 6.** (a) Two-day simulation of the boundary layer distribution of BrO during Antarctic spring-time; (b), vertical profiles of the major gas-phase bromine species at noon on day 2.

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**Fig. 7.** Diurnal variation of the boundary layer O<sub>3</sub> profile in the presence of springtime BrO and IO levels for two scenarios: **(a)** no entrainment of O<sub>3</sub> and **(b)** entrainment of O<sub>3</sub> from the free troposphere.

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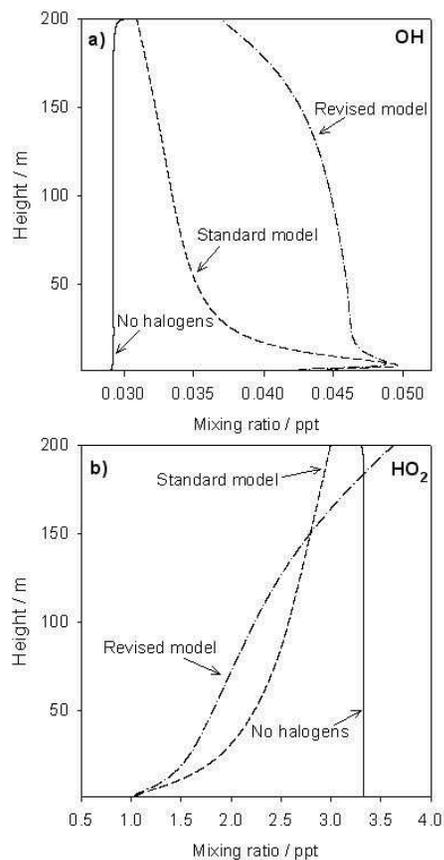
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**Fig. 8.** Vertical profiles of (a) modelled OH and (b) modelled HO<sub>2</sub> for three scenarios: without halogen chemistry, with halogens (standard model), and including photolysis of I<sub>x</sub>O<sub>y</sub> species (revised model).

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