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A mechanism for biologically-induced iodine emissions from sea-ice

A. Saiz-Lopez and C. S. Boxe

Earth and Space Science Division, NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA

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Correspondence to: A. Saiz-Lopez (alfonso.saiz-lopez@jpl.nasa.gov)

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Abstract

Only recently, ground- and satellite-based measurements have reported high concentrations of IO in coastal Antarctica. The sources of such a large iodine burden in the Antarctic atmosphere remain unknown. We propose a novel mechanism for iodine release from sea-ice surfaces. The release is triggered by the biological production of iodide (I^-) and hypoiodous acid (HOI) from marine algae, contained within and underneath sea-ice, and their diffusion through sea-ice brine channels to accumulate in the quasi-liquid layer on the surface of sea-ice. A multiphase chemical model of polar atmospheric chemistry has been developed to investigate the biology-ice-atmosphere coupling in the polar environment. Model simulations were conducted to interpret recent observations of elevated IO in the coastal Antarctic springtime. The results show that the levels of inorganic iodine (i.e. I_2, IBr, ICl) released from sea-ice through this mechanism account for the observed IO concentrations in the Antarctic springtime environment. The model results also indicate that iodine may trigger the catalytic release of bromine from sea-ice through phase equilibration of IBr. Considering the extent of sea-ice around the Antarctic continent, we suggest that the resulting high levels of iodine may have widespread impact on catalytic ozone destruction and aerosol formation in the Antarctic lower troposphere.

1 Introduction

Over the past two decades, the role of atmospheric iodine in the catalytic destruction of ozone has been extensively studied (e.g. Chameides and Davis, 1980; Solomon et al., 1994; Vogt et al., 1999; McFiggans et al., 2000; Calvert and Lindberg, 2004a). In the mid-latitudes marine boundary layer (MBL) iodine decreases the HO_x ratios (i.e., HO_2/OH) via the reaction of IO and HO_2 to form HOI, which then photolyzes efficiently to OH, whereas the NO oxidation to NO_2 by IO increases the NO_x ratios (i.e., NO_2/NO) (e.g. Bloss et al., 2005).

Recently, considerable attention has been given to the role of iodine oxides in the formation of ultra-fine aerosol (i.e. 3–10 nm diameter) and its potential to contribute to cloud condensation nuclei (CCN) formation (e.g. O'Dowd et al., 1998; Hoffmann et al., 2001; O'Dowd et al., 2002; Jimenez et al., 2003; Saiz-Lopez and Plane, 2004; McFiggans et al., 2004; Burkholder et al., 2004; Sellegri et al., 2005; Saunders and Plane, 2005, 2006; Saiz-Lopez et al., 2006). In the polar atmosphere iodine has also been suggested to impact the depletion of gaseous elemental mercury (Hg°) by oxidation to reactive gaseous mercury (Hg^{II}) (Calvert and Lindberg, 2004b; Saiz-Lopez et al., 2007a).

IO is formed following photolysis of photolabile reactive iodine precursors and the subsequent reaction of I atoms with atmospheric O_3. In the polar boundary layer IO has so far only been detected in coastal Antarctica by ground- (Friess et al., 2001; Saiz-Lopez et al., 2007b) and satellite-based instrumentation (Saiz-Lopez et al., 2007c; Schönhardt et al., 2007). These studies have shown iodine to be very abundant (e.g. up to 20 pptv during Antarctic springtime) and widespread around coastal Antarctica. In addition, it has recently been suggested, using a one-dimensional chemical transport model, that iodine profoundly impacts the chemistry and vertical distribution of O_3, HO_x, NO_x and Hg in the coastal Antarctic marine boundary layer (Saiz-Lopez et al., 2007a).

Hence, the striking high levels of iodine observed in coastal Antarctica together with its relevance for the atmospheric chemistry in this environment opens the question about the release mechanisms and source strength required to account for such large burden of gas phase iodine.

In the polar regions, the source of reactive inorganic bromine and chlorine has been proposed to be heterogeneous reactions involving sea-salt bromide on sea-ice, snowpack, or marine aerosol surfaces (e.g. Barrie et al., 1988; Vogt et al., 1996; von Glasow and Crutzen, 2007). These heterogeneous reactions take part in an autocatalytic cycle that destroys ozone, while preserving atomic halogen radicals. However, these mechanisms do not result in significant iodine release to the gas phase due to the compar-

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atively much smaller content of iodide in sea-salt. In addition, in coastal Antarctica, biological emissions of iodocarbons are unlikely to be sufficient to account for the high concentrations of gas phase iodine due to their comparatively long photolytic lifetimes and small concentrations (Carpenter, 2003). Therefore, the sources and mechanisms of iodine release over ice-covered areas in coastal Antarctica still remain unknown.

In this study a hypothesis for iodine release from sea-ice surfaces is presented. The coupling between biology, sea-ice and overlying atmosphere is investigated using a newly developed multiphase chemical model.

2 Model description

In order to study the link between Antarctic marine algae iodine emissions and the potential for inorganic iodine release from sea-ice, we developed a multiphase chemical model CON-AIR (Condensed Phase to Air Transfer Model). CON-AIR incorporates the multi-component aspect of sea-ice (e.g., ice, quasi-liquid layer (QLL), brine channels, macro and microalgae), interfaced with overlying atmospheric boundary layer chemistry.

It is structured in three main components: i) algae emissions and transport through sea-ice brine channels; ii) explicit aqueous phase chemistry regime in the QLL; iii) gas phase chemistry scheme comprising photochemical, thermal and heterogeneous reactions.

Brine channels are defined as vertically-elongated tubular systems containing fluid, with diameters of less than a few millimeters to several centimeters and up to 50 cm in vertical extent (Thomas and Dieckmann, 2003). The typical brine channels density is in the order of one larger channel per 10 cm^2 and the convective contribution to the total heat transfer through the ice column can be of several Wm^{-2}. Experimental and numerical modeling evidence suggest that the density and morphology of individual channels is determined by a combination of hydrodynamic processes and microstructural controls (Thomas and Dieckmann, 2003). The QLL is defined as a thin layer on the surface of sea-ice where water molecules are not in a rigid solid structure, yet not in the random order of liquid (Petrenko and Whitworth, 1999).

The aqueous phase component treats 14 species and comprises 25 condense phase reactions, representing iodine, bromine, and chlorine chemistry in the QLL. The gas phase chemistry includes 41 chemical species, 154 reactions representative of the standard O_3-NO_x-HO_x-S and halogen gas phase chemistry, along with a treatment of the halogen recycle on deliquesced airborne sea-salt aerosols. It also incorporates 12 processes of heterogeneous uptake and wet/dry deposition, and 38 photochemical reactions. The complete scheme of gas-phase and QLL reactions employed in the model is summarized in Tables 1 and 2, respectively, of the supplementary material http://www.atmos-chem-phys-discuss.net/8/2953/2008/acpd-8-2953-2008-supplement.pdf.

The exchange of halogen species between the liquid (QLL) and gas phase is treated via phase equilibration as well as deposition of gas phase molecules onto the sea-ice surface. For iodine species, the liquid-gas phase exchange depends upon the Henry's law constants of species including I_2, IBr and ICl. The gas phase equilibrating species, Henry's law solubility constants and temperature dependences are shown in Table 3 of the supplementary material http://www.atmos-chem-phys-discuss.net/8/2953/2008/acpd-8-2953-2008-supplement.pdf. The temperature dependence of the solubility of species is taken into account by including a diurnal variation of the typical temperature profile during springtime (i.e., $250 \leq T/K \leq 265$).

2.1 Aqueous phase scheme and QLL parameterizations

The initial concentrations of I^-, Br^- and Cl^- in the QLL are assumed to be that of the ions in seawater 1.3×10^{-7} M, 8×10^{-4} M and 0.545 M respectively (Wayne, 2000). This model assumes that all ions and molecular species reside in the QLL. In order to account for the concentration effect on the aqueous phase reaction rates the volume of the QLL needs to be calculated. Using a mean thickness for the Southern Ocean sea-ice and density of 50 cm and 0.91 g m^{-3} (Thomas and Dieckmann, 2003), respectively, the total potential liquid content in a snow column of 1 cm^2 cross-sectional area of sea-ice can be computed as:

$$\text{total potential liquid content} = \frac{50\,\text{cm} \times 0.91\,\text{g}\,\text{cm}^{-3}}{1\,\text{g}\,\text{cm}^{-3}} = 45.5\,\text{cm}^3\,\text{cm}^{-2} \tag{1}$$

The mean mass fraction of liquid water in ice between 265 and 250 K is 1×10^{-3} (Conklin and Bales, 1993). We calculate a mean QLL thickness=500 μm by: sea-ice thickness×sea-ice crosssectional area×mass fraction of liquid water=50 cm×1 $\text{cm}^2\times10^{-3}$=0.05 cm^3; then, 0.05 cm^3/1 cm^2=500 μm. The QLL volume in sea-ice can now be calculated as:

$$\text{QLL volume} = 45.5\,\text{cm}^3\,\text{cm}^{-2} \times 1 \times 10^{-3} = 0.0455\,\text{cm}^3\,\text{cm}^{-2} \tag{2}$$

For an atmospheric boundary layer height of 400 m (40 000 cm) a volumetric factor is obtained:

$$\text{volumetric} = \frac{0.0455\,\text{cm}^3\,\text{cm}^{-2}}{40,000\,\text{cm}} = 1.14 \times 10^{-6}\,\left(\frac{\text{cm}^3\,(\text{QLL})}{\text{cm}^3\,(\text{atmosphere})}\right) \tag{3}$$

Accordingly, the reaction rates are quantified incorporating the volumetric factor. We find that this enhancement in model concentrations and reaction rates due to the concentration effect of ions and molecular species in the QLL is necessary to provide ample gas-phase concentrations. The rate constants for the QLL reactions are then expressed as:

$$k[1\,\text{cm}^3\,(\text{atmosphere})]/[1.14 \times 10^{-6}\,(\text{QLL})] \tag{4}$$

$$k[1\,\text{cm}^3\,(\text{atmosphere})]^2/[1.14 \times 10^{-6}\,(\text{QLL})]^2 \tag{5}$$

where k are the actual literature aqueous phase rate constants in units of $\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ and $\text{cm}^6\,\text{molecule}^{-2}\,\text{s}^{-1}$, for second- and third-order rate constants, respectively.

The rate of transfer of halogen species from the QLL into the boundary layer air is calculated using an approximation for the first-order rate constant, $k_t = 1.25 \times 10^{-5}\,\mathrm{s}^{-1}$, previously suggested by (Gong et al., 1997; Michalowski et al., 2000):

$$k_{\mathrm{mix}} = k_t \times \frac{40,000\,\mathrm{cm}^3\,(\mathrm{atmosphere})}{0.0455\,\mathrm{cm}^3\,(\mathrm{QLL})} \tag{6}$$

However, the rate of transfer of species will depend on the concentration and Henry's law constants for solubility of the corresponding species. Hence, the complete expression for the phase equilibration of species from the QLL to the atmosphere is:

$$k_{(\mathrm{QLL}\rightarrow\mathrm{Atmosphere})} = (k_{\mathrm{mix}} \times [\text{species concentration}] \times \text{volumetric})/\,(H') \tag{7}$$

where H' is the dimensionless Henry's law constant. H' is accordingly defined as $H' = (\mathrm{HRT})$, where H is a species' Henry's law constant, R is the gas constant, $0.082058\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}$, and T is the temperature (K).

2.2 Radiation and gas phase scheme

Photolysis rates are calculated off-line from reported absorption cross-sections and quantum yields using a 2-stream radiative transfer code (Thompson, 1984), where the irradiance reaching the surface is computed after photon attenuation through fifty 1 km layers in the atmosphere.

Some species in the model are constrained to their typical values measured during the Chemistry of the Antarctic Boundary Layer and Interface with Snow (CHABLIS) measurement field campaign that took place at Halley Bay in coastal Antarctica (Jones et al., 2008; Read et al., 2007), with diurnal mixing ratio profiles peaking at [CO]=35 ppb; [DMS]=80 ppt; [SO_2]=15 ppt; [CH_4]=1750 ppb; [CH_3CHO]=150 ppt; [HCHO]=150 ppt; [isoprene]=60 ppt; [propane]=25 ppt; [propene] =15 ppt. During the model simulations all other species are allowed to vary. The model is solved using a variable step-size fourth-order Runge-Kutta integrator.

Assuming that the limiting step for halogen heterogeneous recycling on aerosols is the first-order rate of uptake we compute the heterogeneous recycle rate of a species on airborne sea-salt aerosols using the free molecular transfer approximation $k_t = 0.25\gamma c\ A$, where γ are the uptake coefficients whose values for the different species are taken from Atkinson et al. (2005), c is the root mean square molecular speed, and A is the effective available surface area, 10^{-7} cm^2 cm^{-3} (von Glasow et al., 2002) chosen to be typical of remote oceanic conditions. The dry deposition of a species i is computed as $V_i C_i(t)/H$, where C is the concentration of a gaseous species at a given time and V_i is the deposition velocity of species over a fixed boundary layer over time with a depth H of 400 m.

3 Proposed mechanism for iodine release from sea-ice

The mechanism is broadly illustrated in Fig. 1. Briefly, the process includes: release of iodine, in the equilibrium form of $HOI+I^-+H^+ \leftrightarrow I_2+H_2O$ from sea-ice algae; thereafter, diffusion through brine channels to accumulate in the QLL of the ice surface accompanied by deposition and recycle of atmospheric iodine species on the QLL. Figure 2 shows a simplified quantitative schematic of the mechanism and model structure. The mechanism is based on three characteristics that separately have been reported to occur in the Antarctic springtime environment:

(i) The Southern Ocean contains the largest quantity of macro and microalgae (phytoplankton bloom) in the world. The Antarctic sea-ice covers an extensive portion of the Earth's surface (e.g., maximum extent ∼4%=19×10^6 km^2 in winter and minimum extent ∼1%=5×10^6 km^2 in summer) and is accompanied to a significant degree by biological activity (e.g., macro and microalgae), therefore it represents one of the principal biomes on Earth (Thomas and Dieckmann, 2003). It is known that algae populations colonize the underside of sea-ice (at the seawater-sea-ice interface) and within the brine channels of sea-ice (Thomas and Dieckmann, 2003). Via pre-concentration processes, these organisms contain enhanced concentrations of iodine up to 30 000 times the iodine levels in the surrounding seawater (e.g. $[I^-]_{seawater}$ $\sim 10^{-7}$M) (Küpper et al., 1998). Iodide (I^-) accumulates to these high concentrations by way of a facilitated-diffusion process, by which efficient transport and iodine uptake from natural seawater into macro and microalgal cells occurs, independent of its electrochemical potential gradient (Küpper et al., 1998). Additionally, in the extracellular domain, haloperoxidases, membrane-bound enzymes or cell wall oxidases, along with probable intracellular sources, produce a constant flow of H_2O_2 in the apoplast of cells. Therefore, within the cells, haloperoxidases act as catalysts for the physiological oxidation of I^- into I^+ (i.e. HOI) (Vilter, 1995), Reaction (1), which can then cross the plasma membrane. The oxidative formation of HOI in the apoplast leads to a strong iodine solution in free diffusive contact with the surrounding seawater. HOI can then form I_2 via further reaction with I^-, as shown in Reaction (2), until equilibrium (2, −2) is achieved (e.g. Lobban et al., 1985; Küpper et al., 1998):

$$I^- + H_2O_2 \leftrightarrow HOI + OH^- \tag{R1}$$

$$HOI + I^- + H^+ \leftrightarrow I_2 + H_2O \tag{R2}$$

There has been a number of laboratory studies reporting that algae releases inorganic (e.g. I_2) and organic iodine after light-, chemical- and oxidative-induced stress (e.g. McFiggans et al., 2004 and references therein; Palmer et al., 2005).

During the springtime, solar radiation can penetrate through the relatively thin Southern Ocean's sea-ice layer (see below) and sea-ice fractures reaching the algae colonies that populate underneath and within sea-ice. In order to account for a diurnal pattern in the light-induced iodine emissions from marine algae the model includes a parameterization of the iodine flux from the algae colonies following the diurnal variation in actinic flux.

(ii) The brine channels within sea-ice and the QLL at the sea-ice-air interface. Following solar radiation incidence upon the algae colonies and subsequent light-induced stress, intracellular iodine, equilibrated between HOI, I^- and I_2, effluxes into brine channels of sea-ice, and then diffuses up to the QLL, where it accumulates. The upward diffusion through the brine channels is driven by an iodine concentration gradient. This gradient arises from the concentration difference between the iodine emission point (e.g. algae colonies) and the iodine content in the QLL, which is that in seawater. For example, the upper limit for the concentration gradient can be up to $\sim 10^{-4}$ M between the QLL ($[\mathrm{I}^-] \sim 10^{-7}$ M) and the iodine source in the algae colonies ($[\mathrm{I}^-]$ up to 10^{-3} M) (Küpper et al., 1998).

Note that algae populations colonize the brine channel surfaces well into the interior of the sea-ice, close to the top of the sea-ice layer (Thomas and Dieckmann, 2003). Hence, due to the occurrence of sea-ice fractures, following springtime warming, it is also likely that during the process of sea-ice thinning and breakage the algae colonies in the upper part of the sea-ice layer will only be covered by a thin water film or be directly exposed to air.

(iii) The comparatively thin Antarctic sea-ice (mean sea-ice thickness ~ 0.5 m) (Thomas and Dieckmann, 2003) allows for the relatively fast diffusion (see below) of iodine through sea-ice brine channels and further release of $\mathrm{I}_{2(g)}$ from the QLL to the atmosphere. In the model we use the Fick's laws of diffusion to compute the diffusion coefficient, D, and the strength of the iodine flux, J, as a function of iodine concentration gradient variability with time:

$$J = -D\frac{\partial \phi}{\partial x} \tag{8}$$

$$\frac{\partial \phi}{\partial t} = D\frac{\partial^2 \phi}{\partial x^2} \tag{9}$$

where D is the diffusion coefficient, ϕ is the concentration, x is the sea-ice thickness and t is time. Using Eq. (9) at t=1 s, we calculate a maximum $D \sim 10^{-2}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ for initial $\phi = 6.0\times 10^{15}$ molecules cm^{-3} (10^{-5} M) and x=50 cm. The initial iodine flux $J \sim 10^{12}$ molecules $\mathrm{cm}^2\,\mathrm{s}^{-1}$ is then obtained by incorporating D into Eq. (8). Hence, for the typical Antarctic sea-ice thickness we calculate an initial diffusion timescale of ∼6 h. However, according to Eqs. (8) and (9), the iodine flux and the diffusion coefficient will decrease with time as the iodine concentration gradient decreases due to accumulation of iodine in the QLL.

Note that we initialize the model using a biological iodine pre-concentration of 10^{-5} M which is much smaller than the reported range detected in algae of up to ~10^{-3} M (Küpper et al., 1998). We have used an algae's iodine concentration of 10^{-5} M to account for possible losses of iodine via reaction with organic material in seawater before and/or during diffusion through brine channels. Therefore, even though our conservative model conditions show to be sufficient for significant iodine release, it is possible that the iodine concentration gradient between algae colonies and QLL is larger than that used in this study. One factor that can influence the concentration gradient is the vertical extent of the alga populations within the brine channels. For instance, the closer the algae colonies are to the sea-ice surface the lesser the possible losses of iodine from reaction with organics in seawater during diffusion through brine channels.

4 Model simulations and discussion

The model is initialized in October at local midnight at 75° S in the southern hemisphere springtime. Figure 3 shows simulations of iodine exchange between the QLL and the atmosphere as a function of time. The simulations in Fig. 3a show that the nocturnal gas-phase I_2 can reach concentrations of 7×10^{8} molecule cm^{-3} over the course of six days, whereas daytime I_2 concentrations are much smaller due to its fast rate of photolysis to form I atoms (Saiz-Lopez et al., 2004). Figure 3b shows that the predicted I^- concentration in the QLL increases by 2 orders of magnitude after six days of simulation due to the upward flux of iodine from the algal colonies and the accumulation in the QLL. $I_{2(aq)}$ increases at a similar rate to I^- since it forms primarily from Reaction (2). Following Equation (7), for a $[I_{2(aq)}] \sim 2 \times 10^{-8}$ M we estimate a transfer rate of I_2 from the QLL to the gas phase of ~1.5×10^{5} molecules cm^{-3} s^{-1}. The concentration of $IBr_{(aq)}$, which forms from the reaction of Br^- with HOI, also increases in the QLL in step with the increase of HOI.

Model simulations were run with a QLL pH value of 8, similar to ocean water. We have also assumed acidification of the QLL and model runs for pH 4 have shown a small enhancement in the release of gas phase I_2. As the model simulation evolves with time, the strength of the iodine flux from the phytoplankton and the iodine concentration increase in the QLL will be the major drivers determining the timescale as well as the concentrations of photolabile reactive iodine precursors released from sea-ice.

Also note that as the Antarctic springtime progresses, there are two factors enhancing the accumulation of I^- in the QLL: i) the phytoplankton bloom associated with high iodine emissions and increase in solar irradiance reaching the sea-ice surface, ii) the thinning of the sea-ice and more frequent occurrence of brine channels favoring faster upward transport through the ice.

Figure 4 shows an example of the gas phase chemistry resulting from I_2 release to the atmosphere, following the model run conditions shown in Fig. 3. Atomic iodine reacts with atmospheric O_3 to form IO, and this radical then self-reacts to yield OIO. The calculated concentrations of IO can reach 2×10^8 molecules cm^{-3}; these levels are in good agreement with average boundary layer concentrations of the molecule recently measured at coastal Antarctica (Saiz-Lopez et al., 2007b). The computed O_3, also plotted in Fig. 4a, shows a substantial rate of depletion due to iodine chemistry of 0.25 ppb h^{-1}. This is almost twice as fast as that calculated from bromine-mediated chemistry alone (0.14 ppb h^{-1} for typical Antarctic springtime boundary layer BrO mixing ratios of 10 ppt). Fig 4b shows the diurnal profiles of gas-phase HOI, HI and $IONO_2$ as a result of the reactions of IO with HO_x and NO_x. These three species can be deposited back from the gas phase onto the sea-ice surface and subsequently converted to aqueous HOI. The set of reactions involved is summarized as follows (iodine species are in the gas phase unless indicated):

$$HOI \rightarrow HOI_{(aq)} \qquad \text{(R3)}$$

$$HOI_{(aq)}+I^{-}+H^{+}\rightarrow I_{2(aq)}+H_2O \tag{R4}$$

$$I_{2(aq)}\rightarrow I_2 \tag{R5}$$

$$I_2+h\nu\rightarrow 2I \tag{R6}$$

$$2(I+O_3)\rightarrow 2(IO+O_2) \tag{R7}$$

$$2(IO+HO_2)\rightarrow 2HOI+2O_2 \tag{R8}$$

Another point to consider is that this mechanism potentially establishes a synergy between the biologically-induced emissions of iodine and the trigger of bromine release from Antarctic sea-ice. The model results show that the increase in iodine content in the QLL will also trigger the catalytic release of bromine from sea-ice via formation and subsequent release of IBr to the gas phase (see Fig. 3), which following photolysis will provide a source of reactive bromine in the Antarctic atmosphere.

We also propose that similar to the inorganic iodine release mechanism, algal emissions of iodocarbons followed by transport and accumulation in the top of the sea-ice layer may arise in phase equilibration of organic iodine from ice-covered ocean areas to the atmosphere.

Finally, we suggest that this mechanism is more efficient for the Antarctic sea-ice environment than for the Arctic due to physical constraints such as greater mean sea-ice thickness (e.g., ~3 m) and smaller algal population in the Arctic (Thomas and Dieckmann, 2003). Due to the non-linearity in the system (see Eqs. 8 and 9), our calculations show that the diffusion timescale of iodine species through Arctic sea-ice is ~40 times slower than that in the Antarctic. This is an upper limit for Arctic iodine emissions through the proposed mechanism since algal colonies are less predominant in the Arctic than in the Antarctic and propagation of solar irradiance through ice will also be largely limited due to thicker sea-ice. This will greatly limit the overall metabolic production of iodine species. However, it cannot be ruled out that when the Arctic sea-ice melts the phytoplankton colonies will be directly exposed to air and therefore constitute a potential source of iodine in the Arctic atmosphere.

5 Summary and conclusions

A mechanism for iodine release from sea-ice has been proposed. This mechanism incorporates the coupling between stress-induced biological emissions of iodine, diffusion of iodine through sea-ice and phase equilibration to the atmosphere. In order to quantitatively investigate the feasibility of the mechanism a multiphase chemical model has been developed. Model simulations for the coastal Antarctic springtime show that the release of photolabile inorganic iodine (i.e. I_2, IBr, ICl) accounts for the recent observations of elevated IO in this environment. This process may also trigger reactive bromine release from sea-ice via gas phase equilibration and subsequent photolysis of IBr. In addition, following the same mechanism, organic iodine may also be released from sea-ice to the atmosphere. We suggest that the efficiency of iodine release from sea-ice would be less in the Arctic than in the Antarctic due to environmental differences (e.g. ice thickness, algae populations) between both polar regions.

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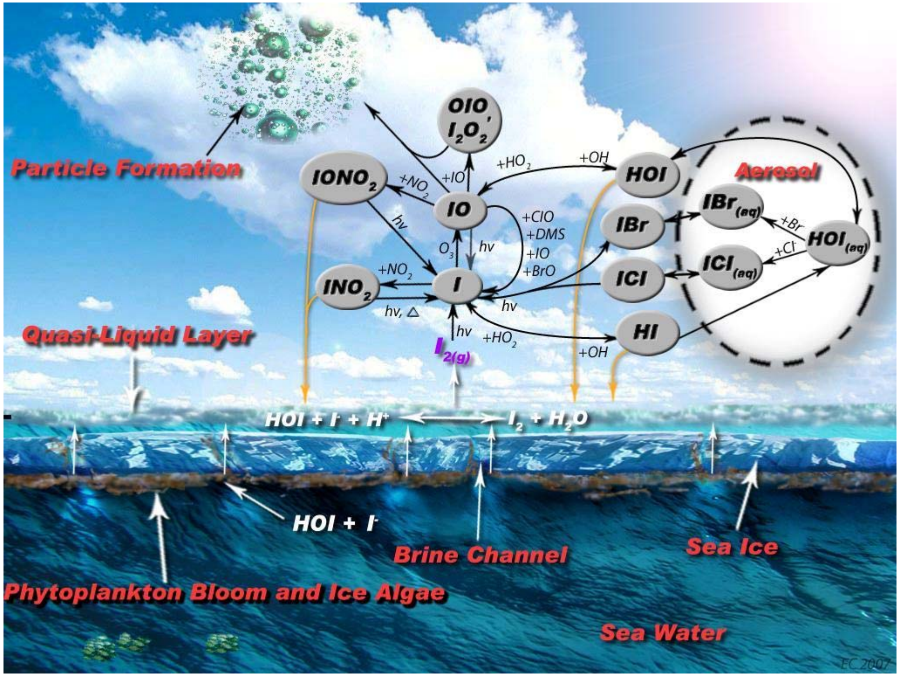

Fig. 1. A simplified scheme of iodine cycling in and over Antarctic sea-ice. In and on the underside of Antarctic sea-ice the biological release of iodine into brine channels occurs. Subsequently diffusion of iodine through brine channels allows for the accumulation of these species in the QLL, releasing $I_{2(g)}$ to the atmosphere via gas phase equilibration. Thereafter transformations of compounds occur in the gas phase, and in deliquesced sea-salt aerosol.

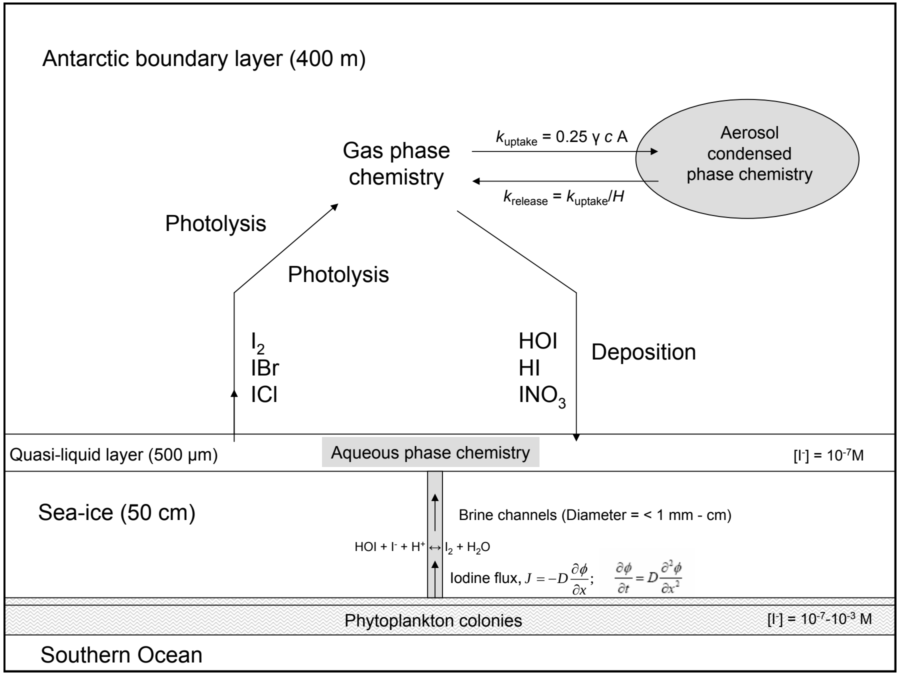

Fig. 2. A simplified quantitative schematic of the proposed mechanism and the CON-AIR model structure. Note that the dimensions are not at real scale.

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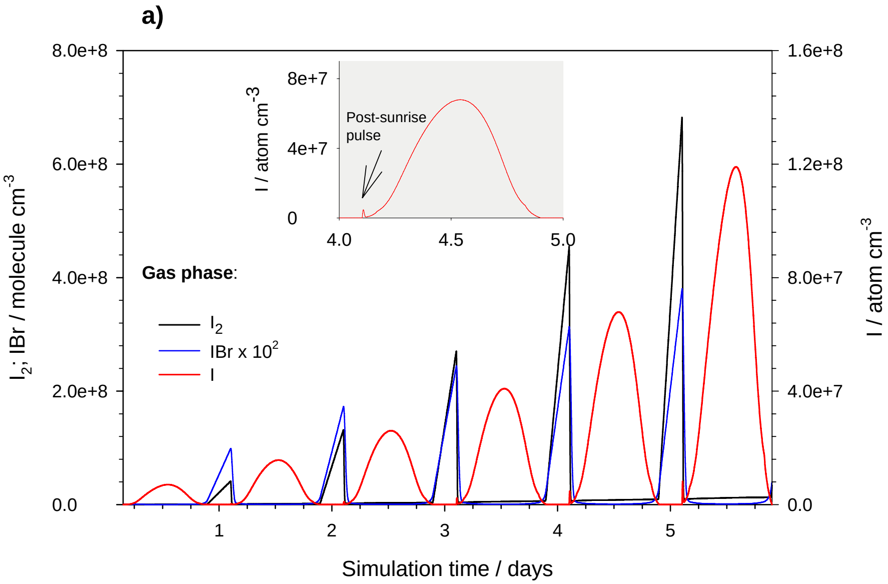

Fig. 3. Iodine exchange from Antarctic sea-ice to the atmospheric boundary layer. **(a)** gas phase I, I_2, and IBr. **(b)** aqueous I^-, I_2, and IBr in the QLL. The post-sunrise pulse of I, shown in greater detail in the insert of Fig 2a, is the result of the nighttime buildup of atmospheric I_2. Note that the emission of these species into the gas phase at night is slower than their production rates in the condensed phase. With time, the I^- concentration becomes comparable to that of Br^- and the reaction of HOI with I^-, to form I_2, competes with that of the acid with Br^-. The differences in the $I_{2(aq)}$ and $IBr_{(aq)}$ concentration profiles are due to the fact that the reverse rate constant to form HOI+Br^-, starting from $IBr_{(aq)}$, is orders of magnitude faster than that for formation of HOI+I^-, starting from $I_{2(aq)}$ (see supplementary text http://www.atmos-chem-phys-discuss.net/8/2953/2008/acpd-8-2953-2008-supplement.pdf).

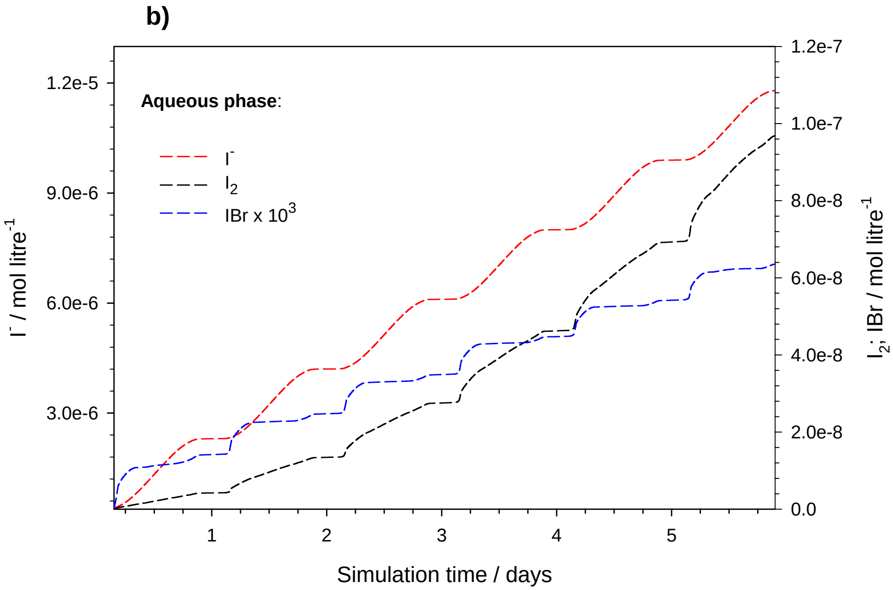

Fig. 3. Continued.

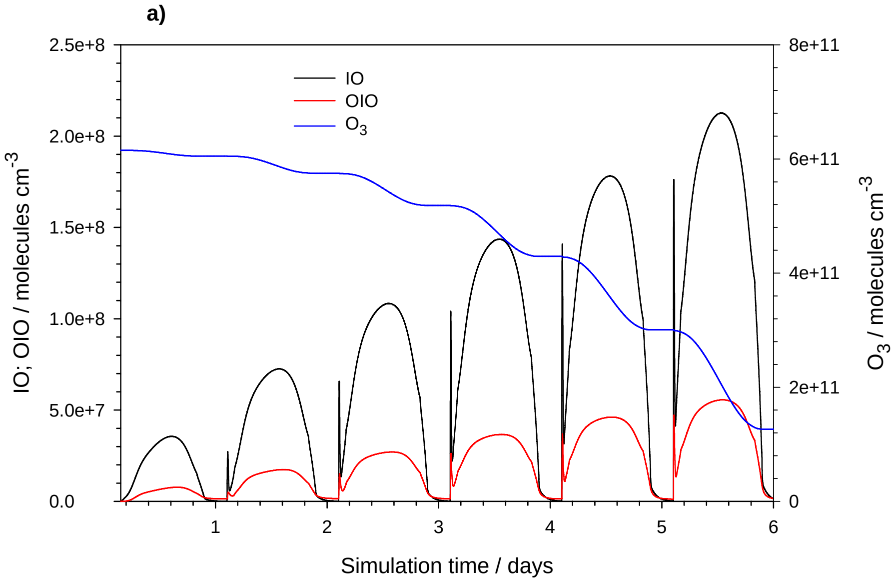

Fig. 4. Modelled concentrations of gas phase iodine species resulting from the emission of I_2 from sea ice over six days from the start of the simulation. Following the buildup of I_2 during the preceding night, the model predicts a post-sunrise pulse of IO followed by a diurnal cycle shaped by solar radiation. The HOI (from $IO+HO_2$) and HI (from $I+HO_2$) profiles track the diurnal cycle of HO_2 and solar radiation. By contrast, $IONO_2$ will photolize very efficiently during the day yielding its typical diurnal cycle with maxima in mid-morning and late afternoon.

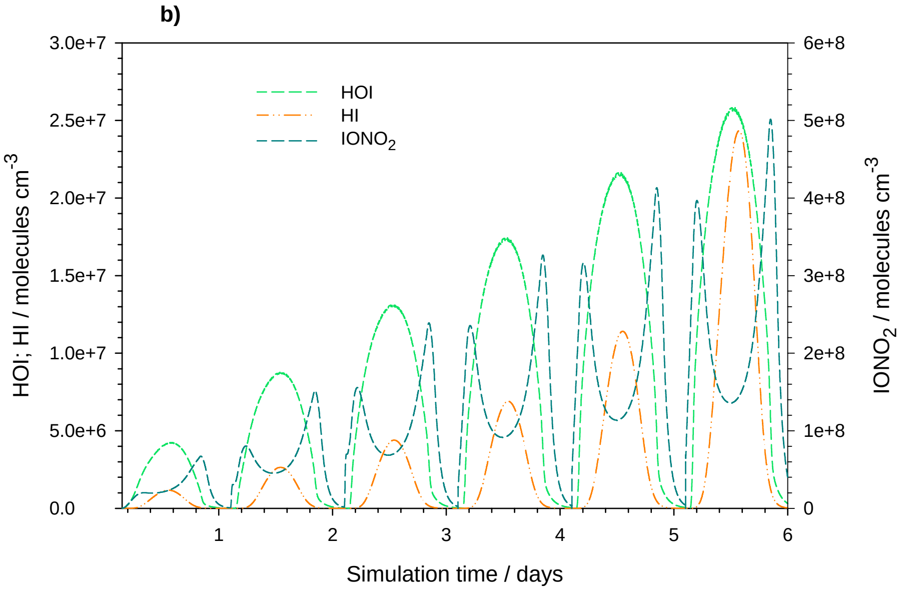

Fig. 4. Continued.