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A one dimensional model study of the mechanism of halogen liberation and vertical transport in the polar troposphere

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Abstract. Sudden depletions of tropospheric ozone during spring were reported from the Arctic and also from Antarctic coastal sites. Field studies showed that those depletion events are caused by reactive halogen species, especially bromine compounds. However the source and seasonal variation of reactive halogen species is still not completely understood. There are several indications that the halogen mobilisation from the sea ice surface of the polar oceans may be the most important source for the necessary halogens. Here we present a one dimensional model study aimed at determining the primary source of reactive halogens. The model includes gas phase and heterogeneous bromine and chlorine chemistry as well as vertical transport between the surface and the top of the boundary layer. The autocatalytic Br release by photochemical processes (bromine explosion) and subsequent rapid bromine catalysed ozone depletion is well reproduced in the model and the major source of reactive bromine appears to be the sea ice surface. The sea salt aerosol alone is not sufficient to yield the high levels of reactive bromine in the gas phase necessary for fast ozone depletion. However, the aerosol efficiently "recycles" less reactive bromine species (e.g. HBr) and feeds them back into the ozone destruction cycle. Isolation of the boundary layer air from the free troposphere by a strong temperature inversion was found to be critical for boundary layer ozone depletion to happen. The combination of strong surface inversions and presence of sunlight occurs only during polar spring.

1 Introduction

Reactive halogen species (RHS=X, X_2, XY, XO, OXO, HOX, XNO_2, $XONO_2$, where X, Y denotes a halogen atom) play a well recognised, central and largely understood role in the destruction of stratospheric ozone (e.g. Solomon, 1990). Initially chlorine was investigated, however since the suggestion of the BrO – ClO cycle by McElroy et al. (1986) and Yung et al. (1980) and the subsequent detection of stratospheric BrO by Brune and Anderson (1986) and Solomon et al. (1989) it is clear that reactive bromine species also contribute considerably to the loss of stratospheric ozone.

While it has been argued that the abundance of inorganic halogen species should be small in the troposphere due to wet removal of the water soluble species (e.g. HBr) in recent years it became clear that reactive halogen species can play a significant role also in the troposphere. In the mid-1980s, sudden, complete boundary layer O_3 depletion at polar sunrise was observed by Oltmans and Komhyr (1986) at Point Barrow, Alaska and by Bottenheim et al. (1986) at Alert, Canada. During the depletion events ground-based O_3 mixing ratios decrease within hours from the mid-winter mean of 30 to 40 ppb to <1 ppb (parts per billion denote volume mixing ratio of 10^{-9}=nmol/mol throughout this paper). The coincidence of the phenomenon with elevated particulate bromine at polar sunrise was subsequently noted by Barrie et al. (1988). Since then ground-based, balloon and aircraft observations have confirmed that O_3 depletion in the surface-based inversion layer over the Arctic Ocean is a widespread phenomenon (e.g. Hopper et al., 1998; Rasmussen et al., 1997; Solberg et al., 1996; Bottenheim et al., 2002).

As a common feature all observations of polar O_3 depletion events were made during the period mid-March to the end of May when sunlight is present at high latitudes and the Arctic Ocean is still frozen. This observation strongly suggests that photochemistry must play a key role in the

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responsible reaction schemes. On the other hand sunlight is also present during summer and fall, but no or only very weak ozone depletion is observed.

The vertical extend of O_3 depleted air masses typically range over the lowest 500 to 2000 m of the troposphere (Solberg et al., 1996; Tuckermann et al., 1997; Martinez et al., 1999; Bottenheim et al., 2002). The downward mixing of ozone rich air from aloft is mostly prevented due to strong temperature inversions at the top of the boundary layer.

An important step towards an understanding of the relevant destruction processes was achieved with the detection of enhanced levels of BrO during depletion events in polar regions. In the Arctic BrO was observed by ground based active and passive DOAS (Differential Optical Absorption Spectroscopy; Platt, 1994) at Alert (Hausmann and Platt, 1994; Hönninger and Platt, 2002) and at Ny Ålesund (Tuckermann et al., 1997; Martinez et al., 1999), in Antarctica measurements were made by passive DOAS (Kreher et al., 1997; Frieß, 2001; Frieß et al., 2004). Mixing ratios of up to 30 ppt BrO were detected simultaneous to complete ozone destructions (parts per trillion denote volume mixing ratio of 10^{-12}=pmol/mol throughout this paper). Those results strongly supported the theory of bromine catalysed ozone destruction in the polar troposphere.

In particular it could be shown that there is no detectable gradient in the BrO concentration inside the atmospheric boundary layer. Simultaneous measurements by two active long – path DOAS instruments at Ny Ålesund, one light path running horizontally at about 50 m above sea level (Tuckermann et al., 1997), the other one from near sea level (20 m a.s.l.) to 474 m altitude (Martinez et al., 1999) found no systematic difference in BrO. In addition, recent studies employing MAX-DOAS (Multi Axis DOAS, Hönninger et al., 2004a) also allowed to study the vertical profile of BrO in the lowest kilometres of the atmosphere. It was shown that the enhanced BrO during ozone depletion is confined to the boundary layer (Hönninger and Platt, 2002; Hönninger et al., 2004b). Simultaneous active long-path DOAS and passive MAX-DOAS measurements allowed an even better determination of the vertical BrO profile. Excellent agreement with long-path DOAS BrO mixing ratios was found for data derived from MAX-DOAS column density measurements in case of a constant BrO mixing ratio over the vertical extent of the boundary layer (Hönninger et al., 2004b).

Despite several attempts ClO in the polar boundary layer was not detected unambiguously to date. Estimates based on upper limits gained by differential optical absorption spectroscopy (Tuckermann et al., 1997) and on calculations via Cl atom concentrations deduced from hydrocarbon destruction patterns (Jobson et al., 1994; Solberg et al., 1996; Ramacher et al., 1997, 1999), from determination by chemical amplification (Perner et al., 1999), or from measurements of BrCl (Foster et al., 2001; Spicer et al., 2002) suggest ClO mixing ratios during depletion events of the order of a few ppt.

During springtime large parts of the Arctic basin are subject to ozone depletion. Satellite observations of tropospheric BrO column densities (Richter et al., 1998; Wagner and Platt, 1998; Wagner et al., 2001; Hollwedel et al., 2004) provided first information about the extension of the regions where ozone depletion is in progress. During spring areas exceeding 10^7 km^2 (about 2% of the earth's surface) might be affected at any given time.

There are strong indications that similar surface O_3 destruction also occurs at polar sunrise in Antarctica. Ozone depletion events during Austral spring were reported from Syowa, Neumayer Station and Arrival Heights (Murayama et al., 1992; Wessel et al., 1998; Kreher et al., 1997). The tropospheric BrO observations via satellite measurements support the ground based measurements at Antarctica. It is interesting to note, that the satellite measurements indicate that high BrO levels are restricted to coastal areas and the sea ice belt around Antarctica (e.g. Wagner et al., 2001; Hollwedel et al., 2004). To date this process appears to have only few parallels outside polar regions (Platt and Hönninger, 2003; Sander et al., 2003). However, even higher BrO mixing ratios (up to 172 ppt) were detected by optical absorption spectroscopy (DOAS) in the Dead Sea basin during summer (Hebestreit et al., 1999; Matveev et al., 2001). Recently significant BrO abundances were also reported from Great Salt Lake, Utah, USA (Stutz et al., 2002) and from Salar de Uyuni, Central Altiplano, Bolivia (Hönninger et al., 2004c). In addition, evidence is accumulating that BrO (at levels around 1–2 ppt) is also occurring in the free troposphere (in polar regions as well as at mid-latitudes) (McElroy et al., 1999; Ferlemann et al., 1998; Frieß et al., 1999; Fitzenberger et al., 2000; Pundt et al., 2000; van Roozendael et al., 2002).

2 The sources and effects of reactive halogen species (RHS)

A detailed discussion of the halogen catalysed ozone destruction mechanisms can be found in various publications in the literature, (see e.g. Platt and Hönninger, 2003). In brief, the mechanism of O_3 depletion can be explained by catalytic reaction cycles where the catalyst (mainly Br atoms) reacts with ozone forming BrO and O_2. Br atoms are recycled in the subsequent self-reaction of BrO radicals or in a second cycle via reaction of BrO with HO_2 followed by photolysis of HOBr. In contrast to processes in the stratosphere the McElroy cycle should only play a minor role in the troposphere. Bromine atoms can be lost by reaction with formaldehyde, HO_2, or olefins, yielding HBr. The BrO lifetime is controlled by its photolysis and is approximately 100 s. The calculated BrO_x lifetime is by far too short to explain the destruction of all ozone molecules within the boundary layer. With the mentioned gas phase reactions only a few ppt of ozone would be destroyed before bromine would accumulate as HBr. For a complete ozone depletion a constant level of 20 ppt BrO

for at least a day (or roughly 100 000 s) is required. Therefore an efficient and fast halogen recycling from unreactive HX to r-Br (reactive bromine) and r-Cl (reactive chlorine) is necessary to obtain a complete ozone loss. Heterogeneous reactions on aerosol surfaces can account for such necessary halogen recycling (Fan and Jacob, 1992; Abbatt, 1994, 1995; Mozurkewich, 1995; Tang and McConnell, 1996; Vogt et al., 1996; Borken, 1996; Kirchner et al., 1997; Abbatt and Nowak, 1997; Sander et al., 1997; Fickert et al., 1999; Lehrer, 1999; Michalowski et al., 2000).

Although the mechanism leading to O_3 depletion in the polar boundary layer can be well explained by catalytic cycles involving bromine (e.g. Platt and Hönninger, 2003), it is still unclear how reactive halogen species (RHS) originally enter the gas phase. As discussed previously (Barrie et al., 1988; Fan and Jacob, 1992; Tang and McConnell, 1996; Tuckermann et al., 1997) two possible sources of RHS during Arctic spring are:

(i) liberation from sea salt either in the aerosol or on the Arctic ocean ice surface, or

(ii) degradation of organohalogen compounds of anthropogenic or natural origin.

Due to the relatively long photolysis lifetime of the most abundant gaseous organohalogens (e.g. CH_3Br, $CHBr_3$, $CHBr_2Cl$) under polar springtime conditions, the latter source is unlikely. However, strong evidence has emerged, which shows that atmospheric reactions involving oxidants lead to auto-catalytic liberation of r-Br from sea salt reservoirs (sea salt containing by weight 55.7% Cl, 0.19% Br, and 0.00002% I), that can be released to the atmosphere as gaseous reactive halogen species (e.g. Cl_2, Br_2 or BrCl). Proposed reaction sequences involve NO_y species (Finlayson-Pitts et al., 1990) HOBr (Fan and Jacob, 1992; McConnell et al., 1992), HOCl, or other oxidants such as H_2O_2 (Wessel et al., 1997). However, measurements of NO_x in the Arctic seem to rule out nitrogen species (e.g. N_2O_5) as the oxidant. In principle those processes should work at both sea salt reservoirs: airborne sea salt aerosol particles and the surface of the sea ice. The differences and relative importance of both reservoirs will be discussed in the next section.

Several modelling studies (Fan and Jacob, 1992; Sander and Crutzen, 1996; Vogt et al., 1996), as well as laboratory studies (Abbatt, 1994; Fickert et al., 1999; Kirchner et al., 1997; Adams et al., 2002) indicate that autocatalytic processes via HOBr are responsible for halogen release:

$$HOBr + X^-_{seasalt} + H^+ \rightarrow BrX_{gas}(X=Br, Cl) + H_2O \quad (R1)$$

Once Br_2 or BrCl is in the gas phase it can be photolysed rapidly to release halogen atoms, which subsequently will start ozone destruction. This autocatalytic bromine release mechanism resulting in an exponential increase of gas phase bromine is referred to as "Bromine Explosion" (Platt and Lehrer, 1997 as quoted by Wennberg, 1999).
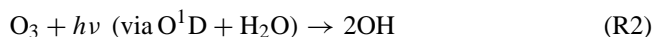
Table 1. List of input parameters

Typ. Levels (total weight) of sea salt aerosol	0.4–4 μgm^{-3}
Br – fraction thereof (0.19%)	0.8–8 ngm^{-3}
Equivalent gas phase mixing ratio (at $-15°C$)	0.2–2 ppt
Observed levels:	up to 30 ppt BrO
	up to 80 ppt total Br

The role of HOBr within the bromine explosion mechanisms is twofold: 1) HOBr drives the primary halogen activation out of the sea salt reservoir and 2) HOBr is responsible for the autocatalytical recycling of HX on the surface of aerosol particles. One Br_x is recycled via heterogeneous reactions on aerosol surfaces roughly 30 times before it can promote a new Br_x via the primary activation process to the atmosphere. In other words about 3% of total HOBr is available for the primary Br_x production. The surface uptake of HOBr and subsequent heterogeneous recycling of r-Br was found to be a prerequisite for ozone depletion (Lehrer, 1999; Michalowski et al., 2000).

HOBr is mainly produced by reactions of BrO with HO_2, CH_3O_2 and R'O_2 (R'=org. group, except CH_3). The production of HOBr therefore strongly depends on the availability of peroxy radicals RO_2 (R=H, CH_3, R'). The HO_2 production rate must therefore exceed the production of HBr. Assuming that the reaction of Br with HCHO or olefins leads to at least one HO_2 molecule, all HBr can be recycled back to r-Br.

Any HO_2, which is in excess, is available to promote new bromine into the destruction cycle by primary processes. The source strength of HO_2 (CH_3O_2–R'O_2) seems to be a critical point for halogen activation.

The major production pathways for HO_2 are initiated by ozone and formaldehyde photolysis.

$$O_3 + h\nu \text{ (via } O^1D + H_2O) \rightarrow 2OH \quad (R2)$$

$$OH + CO \rightarrow HO_2 + CO_2 \quad (R3)$$

$$HCHO + h\nu \rightarrow 2HO_2 + CO \quad (R4)$$

An estimation of the HO_2 production rate via this mechanism ($J_{R10}=4.7\times10^{-7}$ s^{-1}, branching ratio for OH production from O^1D+H_2O, v$=0.8\times10^{-2}$; $[H_2O]=2.2\times10^{16}$; $[O_3]=10^{12}$ cm^{-3}) provides 40 ppt HO_2 per day.

2.1 The primary halogen source: sea salt aerosol or sea ice

While it is very likely that bromine liberation from sea salt is the source of the observed BrO, no satisfying answer is presently available, whether the sea salt contained in the aerosol or on the sea ice surface (or snow pack) is the source of reactive bromine species during polar tropospheric ozone depletion.

Sander and Crutzen (1996) pointed out that liberation processes from sea salt aerosol might lead to ozone depletion in the remote marine atmosphere. However, the sea salt concentrations in polar regions are lower compared to those at open sea conditions. Aerosol measurements at Ny Ålesund/Spitsbergen (Langendörfer et al., 1999; Lehrer et al., 1997) provide typical concentration levels between 0.1 and 1 μg m^{-3} (see Table 1). The maximum concentrations were observed in winter and early spring together with maximum average wind speed. With an estimated atmospheric lifetime of sea salt aerosol particles of 2 days and under the assumption that the liberation of reactive halogen molecules by the above mentioned processes is fast compared to the residence time of the aerosol, the observed sea salt concentrations can account for up to few ppt of photolysable bromine. Impey et al. (1997) noted that aerosol alone is not sufficient to explain the high amounts of photolysable bromine measured during ozone depletion. To explain the observed levels of BrO (up to 30 ppt) or total bromine (up to 80 ppt) halogen release out of sea salt aerosol has to occur over a period of more than one week. This is not in accordance with estimates for the actual time period of an event of complete ozone depletion, which is in the range of 2–3 days (e.g. Sander et al., 1997).

Although maximum sea-salt aerosol concentrations can be several times the average levels the available amount of aerosol bromine is at least one order of magnitude too low to explain the observed BrO levels. Therefore it is unlikely that sea salt aerosol is the primary source of reactive bromine in the polar troposphere and sea-salt deposits on ice have to be considered in addition. Thus the "well-mixed atmosphere" picture used in earlier modelling studies focussing on the mid-latitude marine boundary layer (Sander and Crutzen, 1996; Vogt et al., 1996) cannot be correct for polar regions, since these studies base on the assumption that all primary halogen species are already airborne.

Tang and McConnell (1996) suggested that halogen liberation may be possible from halogen deposits on the snow pack. The mobilisation out of the snowpack can help to reactivate bromine, which was scavenged by snow flakes or aerosols and then deposited. However there is no reason, why the snow pack should serve as primary sea salt reservoir.

On the other hand the fresh sea ice surface is known to act as a huge reservoir of halogens (Perovich and Richter-Menge, 1994). The freezing process of sea water leads to a thin liquid film on top of the sea ice surface. This brine solution is highly enriched in sea salt and reaches typical salinity values up to 100 psu (3 times the salinity of sea water; 1 psu=1 g sea salt per liter sea water). Also the growing of crystals, which were enriched in sea salt was observed. Wolff and Martin (1998) suggested that frost flowers may serve as source for sea salt aerosol at Antarctic coastal areas.

Under typical Arctic conditions the vertical atmospheric column over the lowest 1000 m contains 10^{-3} cm^2 of reactive aerosol surface per cm^2 of ground surface (Staebler et al., 1999). In comparison the sea ice surface provides 1000 times the reactive surface compared to the sea salt aerosol. Taking into account that the sea ice surface is not flat, but may be covered by e.g. frost flowers it likely provides an even greater reaction surface for halogen liberation.

If all the bromine which is contained inside a 1 mm thick brine layer of 100 psu was released to the gas phase as reactive Br this would correspond to gas phase mixing ratios of up to 55 ppb Br in the lowest 1000 m. This mixing ratio is 2 orders of magnitude higher than the observed levels of reactive bromine during ozone depletion events. It is clear, that the sea ice surface provides a nearly inexhaustible source. On the other hand – in the case of a surface source – transport limitations between the phase boundary and the atmosphere have to be taken into account.

In their multiphase model study of Arctic boundary layer chemistry Michalowski et al. (2000) found that the mass transfer rate of HOBr to the surface is critical and the limiting factor for ozone depletion rates in the boundary layer. In this study it was also shown that aerosol particles are needed to achieve fast ozone depletion.

Several laboratory studies suggested that the HOX (X=Br, Cl) catalysed halogen mobilisation out of sea salt reservoirs requires a low pH of the reservoir. Fickert et al. (1999) pointed out, that below pH=6.5 sea salt solutions are very efficient bromine sources. Therefore no liberation from the ocean surface (pH=8.4) is to be expected. Aerosol measurements in the Arctic provide very acidic conditions, indicated by high sulfate concentration levels during Arctic Haze season (January–April). In Antarctica tropospheric ozone depletion and elevated levels of BrO are observed at sulfate concentrations which are at least one order of magnitude lower. However, although polar ozone depletion is believed to have natural causes, Arctic haze sulphate aerosols and gaseous pollutants advected from Europe, Russia and to a lesser extent, North America may also contribute.

There is only little information available on the pH of the fresh sea ice surface. Adams et al. (2002) performed laboratory investigations into halogen activation out of frozen sea salt solutions. Their results, that frozen sea salt surfaces prepared from alkaline solutions, and non-acidified dry surfaces both support activation, suggest that the requirement of acidification applies only to aqueous sea salt aerosol. This might be a simple solution why bromine explosion is also observed under non-acidic conditions at the Antarctic sea ice belt.

In summary, presently there exists no coherent theory that explains all observed features of the "Polar tropospheric ozone hole", in particular there are the following open questions:

– Does the bromine come from sea-salt deposits or aerosol?

– What is the role of chlorine?

Table 2. Parameters of liquid phase reactions in the aerosol phase used in the model after Abbatt and Co-workers (Abbatt, 1994, 1995; Abbatt und Nowak, 1997; Waschewsky und Abbatt, 1998). H^* is the effective Henry constant, calculated for pH=5 using $H^*=H\left(1+\frac{k_{diss}}{a_{H^+}}\right)$, D_{liq} is the liquid phase dissociation constant and k^{II} denotes the second order liquid phase rate constant.

	HBr	HOBr	HCl	HOCl
H^* [M atm^{-1}]	3×10^8	1.7×10^4	3×10^6	1.7×10^5
D_{liq} [cm^2 s^{-1}]	5×10^{-6}	5×10^{-6}	5×10^{-6}	5×10^{-6}
k^{II} [M^{-1} s^{-1}]	5.0×10^4 (HBr/HOBr)		1.0×10^5 (HCl/HOBr)	
	2.0×10^6 (HBr/HOCl)		Not included (HCl/HOCl)	

Table 3. List of chemical species in the model.

Family	Species
O_x	O_3 O_2
HO_x	H_2O OH HO_2 H_2O_2
NO_x	N_2 NO NO_2 NO_3 HNO_3 HONO HNO_4 PAN
VOC	CO CO_2 CH_4 C_2H_6 C_2H_5 C_2H_4 C_2H_2 C_3H_8
	HCHO CH_3CHO CH_3OO CH_3OOH CH_3OH CH_3CH_2OO
	CH_3CH_2OOH CH_3CO_3 CH_3CH_2O
Br_x	Br_2 Br BrO HBr HOBr $BrNO_2$ $BrONO_2$
Cl_x	Cl_2 Cl ClO OClO ClOO HCl HOCl Cl_2O_2 BrCl $ClONO_2$

– Why does it occur only in polar regions?

– Why is halogen activation related to ozone depletion only observed in springtime, i.e. after sunrise, but not during summer and fall?

– What causes the event-like pattern of the occurrence of ozone depletion?

To clarify these questions, we will discuss here available data from field measurements and present one dimensional model calculations of the key processes. Based on those results we present a consistent theory of the processes that gives satisfactory answers to the above questions.

Figure 1 shows the general picture of bromine chemistry including gas phase and heterogeneous reactions, but neglecting chlorine chemistry for the sake of simplicity.

3 Model description

The presented model was developed with the aim to obtain a quantitative understanding of the concurring liberation processes from sea salt reservoirs at the ground and in the aerosol and to help answering the question whether sea salt aerosol or the sea ice surface is responsible for bromine release in the polar springtime troposphere. This was attempted by including halogen activation processes from sea ice and from sea salt aerosol into the model and by comparing the respective time scales of both liberation mechanisms. In the case of the sea ice surface the transport of the relevant species between the upper part of the boundary layer and the phase boundary to the sea ice has to be implemented into the model.

The presented one dimensional model was written in FACSIMILE developed by the British Atomic Energy Agency (FACSIMILE, 1992), which was previously also used by Vogt et al. (1996) and Sander and Crutzen (1996) for their box model studies.

3.1 Vertical transport in the model

The transport limitations between sea ice and lower troposphere are realized by defining a vertical model structure and dividing the virtual boundary layer into 8 stacked vertical boxes (see Fig. 2). The major assumption bases on a boundary layer of 1000 m height, which is stably stratified and topped by an inversion layer. The height of the boxes is growing from the surface in a logarithmic scale, with the lowest box 0.09 μm high and the top box 900 m high. The inversion situation above the boundary layer was represented in the model by not allowing exchange between the top box and the layer above (i.e. free troposphere) in the base run of the model.

Within each individual box all included species (compare Table 3) are assumed to be well mixed and the exchange between individual boxes was characterized by respecting turbulent mixing $K(z)$ as well as molecular diffusion D:

$$J_{\downarrow,\uparrow} = -\left(K(z) + D\right)\frac{\Delta\,[X]}{\Delta z} \tag{1}$$

where $J_{\downarrow,\uparrow}$ is the upward or downward directed flux between the boxes, $\Delta[X]=[X_{i+1}]-[X_i]$ (i=number of box) the concentration difference between neighbouring boxes and Δz the vertical distance between the centres of two neighbouring boxes. In case of neutral stratification the coefficient of turbulent diffusion $K(z)$ is known to be a linear function of height z. The used values for $K(z)$ and D for all boxes are given in Table 4.

The concentration change for each box i per time step is calculated as the sum of the volume source strength P_i and the volume sink D_i, together with upward and downward directed flux $J_\uparrow$ and $J_\downarrow$ divided by the height l_i of box i.

$$\frac{d\,[X]_i}{dt} = P_i - D_i + \frac{J_\downarrow}{l_i} + \frac{J_\uparrow}{l_i} \tag{2}$$

P_i and D_i denote volume sources (P_i) and sinks (D_i) by chemical (gas phase and heterogeneous) reactions.

Table 4. List of turbulent and molecular diffusion parameters $K(z)$ and D.

Box No	Bottom [cm]	Top [cm]	Box height [cm]	$K(z)$ [cm^2/s]	D [cm^2/s]
1	0	0.01	0.01	0.078	0.2
2	0.01	0.1	0.09	0.7	0.2
3	0.1	1	0.9	7	0.2
4	1	10	9	70	0.2
5	10	100	90	700	0.2
6	100	1000	900	7000	0.2
7	1000	10 000	9000	70 000	0.2
8	10 000	100 000	90 000	700 000	0.2

Fig. 1. Scheme of bromine explosion with neglected chlorine chemistry. See text for details. The thickness of the black arrows indicate the Br$_x$ fluxes.

3.2 Representation of the aerosol in the model

Aerosol particles can serve as substrate for heterogeneous reactions. The model includes the heterogeneous reactions of HOBr+Br$^-$, HOBr+Cl$^-$ and HOCl+Br$^-$ on aerosol surfaces. It is assumed that the recycling surface is provided only by sulfate particles, which contributes more than 95% of the total aerosol surface under typical Arctic springtime conditions (Staebler et al., 1999). The typical parameters of the sulfate aerosol were normalized according to the results of Staebler et al. (1999) where a=0.45 μm denotes the aerosol radius, A=100 μm^2 cm^{-3} the aerosol surface and V=10 μm^3 cm^{-3} the aerosol volume.

According to Hanson et al. (1994) the uptake-coefficient γ is calculated as:

$$\frac{1}{\gamma_{spherical}} = \frac{1}{\alpha} + \left[\frac{4RTH\sqrt{D_{liq}k_{liq}^I}}{v_{therm}} \left(\coth\left(\frac{a}{l}\right) - \frac{l}{a} \right) \right]^{-1} \quad (3)$$

Here R and T denote the universal gas constant and the absolute temperature, respectively. The Henry-coefficients H have to be replaced by effective Henry coefficients H^*. The first order liquid phase rate constants k_{liq}^I, and liquid diffusion coefficients D_{liq} were taken from the work of Abbatt and co-workers (see Table 2). According to those studies an accommodation coefficient α=1 was assumed. Halogen uptake was corrected for the curved aerosol surface by the last term in the brackets of Eq. (3) with the help of the aerosol radius a and the diffusive-reaction length $l = \sqrt{\frac{D_{liq}}{k_{liq}^I}}$.
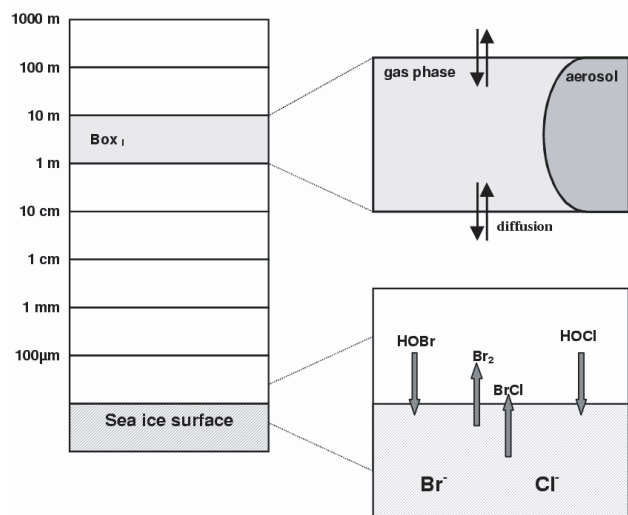
Fig. 2. Vertical structure of the model as used for the model calculations.

The thermal velocity v_{therm} for a compound of molecular mass $m_{molecule}$ is calculated according to $v_{therm} = \sqrt{\frac{8kT}{\pi m_{molecule}}}$.

The production rate of the di-halogen molecules Y_{gas} (Br_2 or BrCl) is calculated according to Schwartz (1986), with X_{gas} being the limiting reaction partner (HOX or HX) in the liquid phase.

$$\frac{d[Y_{gas}]}{dt} = -\frac{d[X_{gas}]}{dt} = \left(\frac{a}{D_g} + \frac{4}{v_{therm}\gamma}\right)^{-1} A_{surface}[X_{gas}] \tag{4}$$

Here, D_g denotes the gas phase diffusion coefficient, which is set in the model to a typical value of $0.2\,cm^2/s$; $A_{Surface}$ is the aerosol surface. An HOBr uptake coefficient $\gamma=0.12$ is calculated from Eq. (3) at gas phase mixing ratio of 10 ppt HBr. Together with 10 ppt HOBr this corresponds to a HOBr loss rate (or Br_2 production rate) of 1.8×10^5 molecules $cm^{-3}\,s^1$.

In the base run of the model sea salt aerosol as a primary halogen source was not considered. A variant of the model to test for the potential of the aerosol source is described in Sect. 4.3.

3.3 Representation of the sea ice surface in the model

The sea ice surface is coupled to the model by allowing exchange between a sea salt reservoir and the lowest box of the model. Included are all reactions between HOBr and HOCl and sea salt. The halogen content in the sea ice layer is assumed to be an inexhaustible source. The uptake coefficient of HOX onto the sea ice surface was chosen $\gamma=0.06$ after Sander and Crutzen (1996).

Table 5. Constants for reactions used in the model, which are not taken from Atkinson et al. ([a] MOCCA Ice (Sander et al., 1997), [b] (Borken, 1996), [c] (Barnes et al., 1993), [d] (DeMoore et al., 1997), [e] (Sander and Crutzen, 1996), [f] (Aranda et al., 1997)). A summary of all gas phase reactions is included as supplemental material.

$C_2H_4+O_3$	$\rightarrow$	$HCHO+CO$	4.33×10^{-19}	[a]
$C_2H_5O+O_2$	$\rightarrow$	$CH_3CHO+HO_2$	7.44×10^{-15}	[a]
$C_2H_5O+O_2$	$\rightarrow$	CH_3O_2+HCHO	7.51×10^{-17}	[a]
$C_2H_5OOH+OH$	$\rightarrow$	$C_2H_5O_2+H_2O$	8.21×10^{-12}	[a]
$C_2H_5OOH+Cl$	$\rightarrow$	$C_2H_5O_2+HCl$	5.70×10^{-11}	[a]
$C_2H_5OOH+Br$	$\rightarrow$	$C_2H_5O_2+HBr$	5.19×10^{-15}	[a]
$BrO+CH_3O_2$	$\rightarrow$	$Br+HCHO+HO_2$	1.60×10^{-12}	[f]
$BrO+CH_3O_2$	$\rightarrow$	$HOBr+HCHO$	4.10×10^{-12}	[f]
$Br+C_2H_2$	$\rightarrow$	$2CO+2HO_2+Br$	4.20×10^{-14}	[b]
$Br+C_2H_2$	$\rightarrow$	$2CO+HO_2+HBr$	8.92×10^{-14}	[b]
$Br+C_2H_4$	$\rightarrow$	$2CO+2HO_2+Br$	2.52×10^{-13}	[c]
$Br+C_2H_4$	$\rightarrow$	$2CO+HO_2+HBr$	5.34×10^{-13}	[c]
$Cl+C_2H_2$	$\rightarrow$	$2CO+2HO_2+Cl$	2.00×10^{-11}	[b]
$Cl+C_2H_2$	$\rightarrow$	$2CO+HO_2+HCl$	4.24×10^{-11}	[b]
$OClO+NO$	$\rightarrow$	NO_2+ClO	2.44×10^{-13}	[d]
Br_2+Cl	$\rightarrow$	$BrCl+Br$	1.20×10^{-10}	[e]
$BrCl+Br$	$\rightarrow$	Br_2+Cl	3.30×10^{-15}	[e]
$Br+Cl_2$	$\rightarrow$	$BrCl+Cl$	1.10×10^{-15}	[e]
$BrCl+Cl$	$\rightarrow$	$Br+Cl_2$	1.50×10^{-11}	[e]

The most important products of the heterogeneous HOX reactions at the sea ice surface are Br_2 and BrCl. Due to the small abundance of HOCl, the production of Cl_2 is negligible. Therefore the branching ratio between Br_2 and BrCl production plays a key role. The branching ratio of Br_2 to BrCl activation was chosen 40 to 60%, respectively. This ratio is in accordance with the results of Kirchner et al. (1997) and provides a very conservative assumption in regard to the studies of Fickert et al. (1999) and Adams et al. (2002). The latter found in their more representative experiments that Br_2 is almost exclusively produced by the primary production processes at the sea ice surface as long as bromide on the surface is not significantly depleted. If the salt surface is well aged and therefore depleted in bromide, BrCl release becomes more important.

3.4 Gas phase chemistry

The gas phase species included in the model are listed in Table 3. Reaction rates were calculated assuming a temperature of 258 K. Most of the reaction constants were calculated using the data published in (Atkinson et al., 1997). Reaction constants which were not documented there are listed together with the literature citation in Table 5. A complete list of gas phase reactions in the model is included as a supplement.
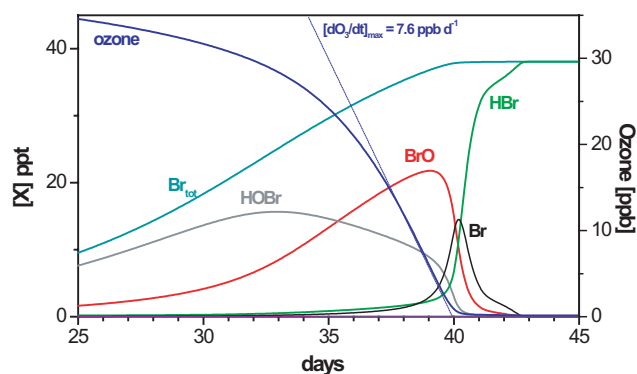
Fig. 3. Basic run (initially 0.6 ppt of Br and Cl; SZA fixed at 80°) – time series (day 25–day 45) of bromine species and ozone inside the top box (100–1000 m).

3.5 Photochemistry

All presented runs of the model were calculated by assuming a fixed solar zenith angle (SZA=80°). The photolysis frequencies were calculated using the model of Röth et al. (1996) and are listed in Table 6. A comparison of results with a model run under the simulation of diurnal and monthly SZA variations provided no substantial difference in time scale of ozone depletion and absolute concentration levels of relevant species.

3.6 Initial mixing ratios

The initial mixing ratios used for the simulation are listed in Table 7. The hydrocarbon mixing ratios are adapted to the results of Ramacher et al. (1997). Initial bromine and chlorine mixing ratios are present in their molecular form, which guarantees via photolysis a rapid distribution into all gaseous halogen species included in the model. The (unrealistic) assumption of equal amounts of bromine and chlorine in the model was made to compare the respective role of each halogen.

4 Results and Discussion

The concentration records for ozone and the most important bromine species are demonstrated for the model box representing the upper part of the boundary layer (100–1000 m) as shown in Fig. 3. The onset of a fast ozone depletion occurs around day 35 of the simulation and within 5 days the ozone concentration drops to immeasurable low values. Other simulations with different initial halogen concentrations demonstrate that higher or lower initial halogen concentrations results in a shorter or longer initial period, respectively, but the time scale in which most of the ozone is destroyed remains almost the same.

Fig. 4. Vertical concentration profiles for ozone and bromine species, according to simulation model basic run.

The maximum ozone destruction rate of 7.6 ppb per day is observed during the end of the depletion process. 90% of initial 40 ppb O_3 are destroyed within 5 days. This value lies in the range of previous assumptions but at the upper end of previous suggestions (compare Hausmann and Platt, 1994) and it compares well with a previous modelling study by Michalowski et al. (2000) who also found ozone to be depleted in ~5 days.

During the initial phase HOBr is the dominating bromine species. Shortly after the onset of rapid ozone destruction BrO takes over the role as major bromine species. With decreasing ozone BrO production slows down and finally at $O_3 < 2$ ppb, the probability of BrO production is negligible compared to the HBr channel. The maximum BrO levels of 20 ppt are comparable to field measurements at Alert (Hausmann and Platt, 1994; Hönninger and Platt, 2002) and at Spitsbergen (Tuckermann et al., 1997; Martinez et al., 1999).

At the end of the depletion process all Br is accumulated in form of HBr. This was already suggested by Langendörfer et al. (1999) and supported by their aerosol measurements, where high levels of filterable bromide, possibly represented by additional HBr, were found on aerosol filters.

This model run also provides information on the vertical gradients of the key species (see Fig. 4). The ozone

Table 6. Photolysis reactions in the model and photolysis rates calculated for SZA=80° after the model of Roeth (1996).

	J [s⁻¹]		J [s⁻¹]		J [s⁻¹]
$O_3 \rightarrow O(^1D)$	4.7×10^{-7}	H_2O_2	2×10^{-6}	C_2H_5OOH	1.2×10^{-6}
BrO	1.4×10^{-2}	NO_2	3.5×10^{-3}	Cl_2	8.5×10^{-4}
Br_2	2.1×10^{-2}	$NO_3 \quad \rightarrow \quad NO_2 + O$ $\rightarrow NO + O_2$	1.4×10^{-1} 1.7×10^{-2}	ClO	5.0×10^{-7}
$BrONO_2$	3.4×10^{-4}	HNO_3	4.4×10^{-8}	HOCl	8.6×10^{-5}
HOBr	3.0×10^{-4}	$HCHO \rightarrow CO + H_2$ $\rightarrow CHO + H$	9.6×10^{-6} 5.5×10^{-6}	$ClONO_2$	1.3×10^{-2}
BrCl	5.7×10^{-3}	CH_3CHO	6.9×10^{-7}	OClO	3.6×10^{-2}
$BrNO_2$	9.3×10^{-5}	CH_3OOH	1.2×10^{-6}		

Table 7. Initial mixing ratios of base run of the model.

Species	$[X]_0$	Species	$[X]_0$	Species	$[X]_0$
O_3	40 ppb	CO	132 ppb	C_2H_2	600 ppt
Br_2	0.3 ppt	HCHO	100 ppt	C_3H_8	1.2 ppb
Cl_2	0.3 ppt	CH_3CHO	100 ppt	NO	5 ppt
CH_4	1.9 ppm	C_2H_6	2.5 ppb	NO_2	10 ppt
CO_2	371 ppm	C_2H_4	100 ppt		

Fig. 5. Basic run (initially 0.6 ppt of Br and Cl; SZA fixed at 80°) – time series (day 25–day 45) of chlorine species and ozone inside the top box (100–1000 m).

concentration is distributed homogeneously inside the whole column throughout the depletion process. This is consistent with findings from ozone soundings, which suggest that the ozone concentration is almost constant within the boundary layer (e.g. Bottenheim et al., 2002).

The simulated BrO profile (Fig. 4) suggests a small concentration gradient between the lowest meter and all layers above, which is consistent with the fact that no significant gradient was found above one meter during several field studies as discussed in the introduction.

According to our model appreciable amounts of Br_2 should only be present in the lowest meter above the sea ice (Fig. 4, lowest panel). While ascending from the phase boundary up to the free atmosphere most of the Br_2 is photolysed within the lowest centimetres. The first measurements of Br_2 and BrCl during polar sunrise 2000 by Foster et al. (2001) actually confirmed up to 25 ppt Br_2 and 35 ppt BrCl, respectively at 125 cm above the snow pack. As the solar zenith angle during these measurements was close to 90°, photolysis is significantly slower resulting in higher concentrations of photolabile species. On the other hand almost all HOBr is consumed by reactions on the sea ice surface. Therefore HOBr mixing ratios in the order of several ppt are observed only in the upper box (Fig. 4, second to lowest panel).

4.1 The role of chlorine

An important question in the chemical processes of ozone destruction is the role of chlorine atom chemistry. Unlike the stratosphere chlorine atom chemistry plays a minor role in direct destruction of boundary layer ozone. However, Rudolph et al. (1999) suggested that chlorine atom chemistry might be important for HO_2 production. Presently no method has been able to directly detect chlorine atoms. The best estimates of chlorine atom concentrations are deduced from the destruction patterns of specific hydrocarbons (hydrocarbon clock). Rudolph et al. (1999) and Ramacher et al. (1999) found time integrated chlorine atom concentrations of 10^{10} s cm^{-3}. With an assumed time period for ozone depletion process of 1 day this corresponds to a chlorine atom concentration of 1.2×10^5 cm^{-3} (2.3×10^4 cm^{-3} for 5 days).

The model results for chlorine species for the base run are shown in Fig. 5. The model provides maximum chlorine atom concentrations of 1.2×10^3 cm^{-3} and integrated chlorine atom concentration over the whole depletion process of 1.1×10^9 s cm^{-3}. The chlorine atom concentrations in the model are at least one order of magnitude lower than field observations suggest. The role of chlorine chemistry is
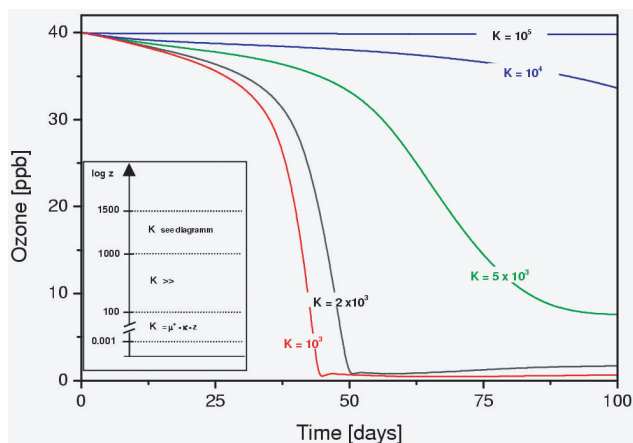
Fig. 6. Model results of ozone time series in the top box (100 m–1000 m) including turbulent diffusion of ozone of various strengths from the free troposphere into the boundary layer (see insert).
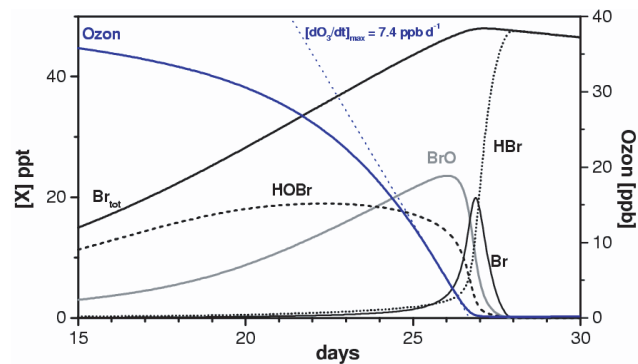

Fig. 7. Model run under the assumption of an additional halogen release out of sea salt aerosol (initially 0.6 ppt of Br and Cl; SZA fixed at 80°) – time series (day 15–day 30) of bromine species and ozone inside the top box (100–1000 m).

underestimated within this model. Therefore the loss of alkanes due to chlorine atoms chemistry is only 1/3 of which is observed under Arctic conditions (Ramacher et al., 1999).

One possible reason might be the unrealistic low initial chlorine concentration or the decomposition of organochlorine compounds which are not implemented in the model. The consequences might be that peroxy radical formation due to chlorine atom reactions could be more important in reality, as suggested by Rudolph et al. (1999). However, the model results support the results of Fickert et al. (1999), which concluded, that the observed levels of chlorine atoms in the marine boundary layer are very unlikely due to chlorine activation out of sea salt via heterogeneous reaction of HX/HOX. In order to explain the observed levels of chlorine during polar sunrise, clearly an additional chlorine source is necessary as also noted by Grannas et al. (2002). Spicer et al. (2002) concluded from the comparison of their $Br_2/BrCl$ measurements with modelled [Cl]/[Br] ratios that an additional sink for Br atoms or an additional source for Cl atoms has to be assumed.

However it is noteworthy that in our model additional HO_2 production by chlorine atom chemistry is not necessary in order to explain the observed BrO levels and degree of O_3 depletion. The model results show that higher chlorine levels are not a prerequisite for bromine catalysed ozone depletion.

4.2 Role of boundary layer inversions

Additional model runs allowing turbulent diffusion from the free troposphere into the boundary layer were performed and are summarized in Fig. 6. It is clear that significant entrainment of ozone-rich air from the free troposphere prevents complete ozone depletion in the boundary layer. While turbulent diffusion coefficients up to $2 \times 10^3 \, \mathrm{cm^2 \, s^{-1}}$ only slow down ozone loss in the boundary layer, for K exceeding

$5 \times 10^3 \, \mathrm{cm^2 \, s^{-1}}$ no complete ozone depletion in the boundary layer appears.

Therefore we conclude that complete ozone depletion in the boundary layer can only be observed if dilution of the reactive bromine and down-mixing of ozone rich air from aloft are prevented by a strong inversion at top of the boundary layer. The standard simulation of the model does not allow any transport across the top of the surface based inversion layer.

4.3 Aerosol as additional halogen source

In order to study the role of aerosol in an additional model run it was assumed that sea salt aerosol production and the subsequent deposition of those particles leads to a constant bromine content in the aerosol equalling the amount contained in 1 $\mu g \, m^{-3}$ sea salt. The production rates were identical inside each box. To simplify the calculations the sea salt aerosol halogen content was put into the model in its inactive form either as HBr or HCl, respectively:

$$\frac{d\,[\mathrm{HX}]}{dt} = + \frac{1}{\tau_{aerosol}} \, [\mathrm{HX}]_{seasalt} - \frac{1}{\tau_{aerosol}} \, [\mathrm{HX}]_{aq} \qquad (5)$$

The first term on the right side of Eq. (5) describes the formation of sea salt aerosol, the second term, the deposition of HX, which is scavenged in the aerosol. $[\mathrm{HX}]_{aq}$ was calculated over the phase ratio between liquid and gaseous fraction of HX using effective Henry coefficients (see Table 2). The aerosol lifetime $\tau_{aerosol}$ was assumed to be 2 days.

These assumptions might overestimate the influence of the halogen source strength due to sea salt aerosol. This is due to the simplification that all fresh halogens which are transported via the sea salt aerosol into the upper layers of the boundary layer are transferred into the autocatalytic recycling mechanism.

Therefore the results of this modification shown in Fig. 7 indicate the maximum influence of the sea salt aerosol as source.

Under the same initial conditions as used in the standard simulation, complete ozone depletion occurs after 25 days. But no differences are observed in the amount of released bromine and in the time scale of the last part of the depletion process.

4.4 Comparison of different model runs

To investigate in the importance of each individual step of the bromine explosion cycle the base run (variation A – sea ice surface sole halogen source) was compared to the other model runs (Fig. 8): variation B: aerosol plus surface source but halogen recycling on aerosol surface excluded; variation C: only sea salt aerosol as source for RHS implemented; variation D: sea salt aerosol plus sea ice surface as potential halogen source.

The fastest ozone depletion was obtained under the assumption that both – the sea ice surface and sea salt aerosol particles – serve as source for reactive halogen species (D). However, the maximum rate of ozone destruction was not slower without the consideration of the aerosol source (A), but only a slower buildup of total bromine was observed, resulting in a lag in the rapid ozone depletion compared to case (D). The amount of total gas phase Br within the boundary layer at the end of the depletion process is almost equal for both assumptions (A and D). On the other hand halogen activation out of sea salt aerosol particles (C) alone is by far too slow to account for a fast ozone depletion.

The importance of halogen recycling on aerosol particles was studied in case (B). It clearly shows, that without halogen recycling at the surface of aerosol particles (B) no exponential growth of the bromine species can be obtained.

5 Conclusions

The presented model compared the role of the two concurring halogen sources: activation out of sea salt aerosol and out of the sea ice surface. The model calculations together with information about typical sea salt aerosol concentrations in the Arctic boundary layer demonstrated that sea salt aerosol is a minor source compared to the potential of the sea ice surface source strength.

Halogen activation from the (brine layer on the) sea ice surface as single source leads to an exponential growth of reactive halogen species in the boundary layer. 90% of initial 40 ppb ozone are destroyed within the last 5 days of the depletion process. The duration of the initial depletion phase depends on the amount of reactive bromine available at the beginning of the simulation. A Br or Cl threshold concen-
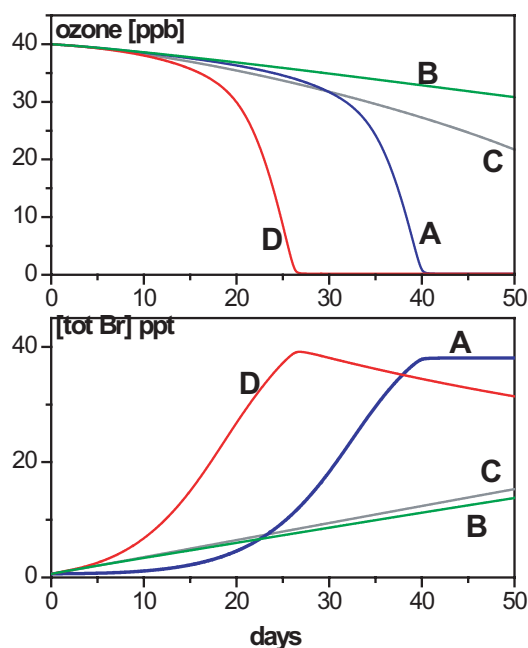

Fig. 8. Comparison of ozone record and the mixing ratio of total bromine under different simulation conditions (A: only surface source; B: no halogen recycling at aerosol surfaces; C: only aerosol source; D: surface plus aerosol source). Only the top box (100 m–1000 m) is shown.

tration to trigger a bromine explosion is not necessary. For 0.6 ppt of initial Br_x and Cl_x the initial phase lasts 35 days.

As a critical point for the success of a bromine explosion the significance of pH<6.5 for the primary sea salt reservoir is not completely proven. There are indications that the sea salt aerosol might be sufficiently acidified. The conditions of the sea ice surface are presently not well characterized. Here we suggest field experiments to investigate in the ionic composition of young and aged sea ice surfaces as well as frost flowers.

Strong gradients in the lowest meter above the surface are found for HOBr, Br_2 and BrCl, with the first species not at all and the others exclusively observed in the lowest meter of the atmosphere.

It is demonstrated that halogen recycling at aerosol surfaces is necessary to keep enough bromine in the active reservoir. A bromine atom is recycled about 30 times before it can activate a new Br atom via the primary processes.

Prerequisites for a polar bromine explosion are:

– Availability of sea salt surface (brine, dry salt, or possibly frost flowers) on sea ice

– Sun light

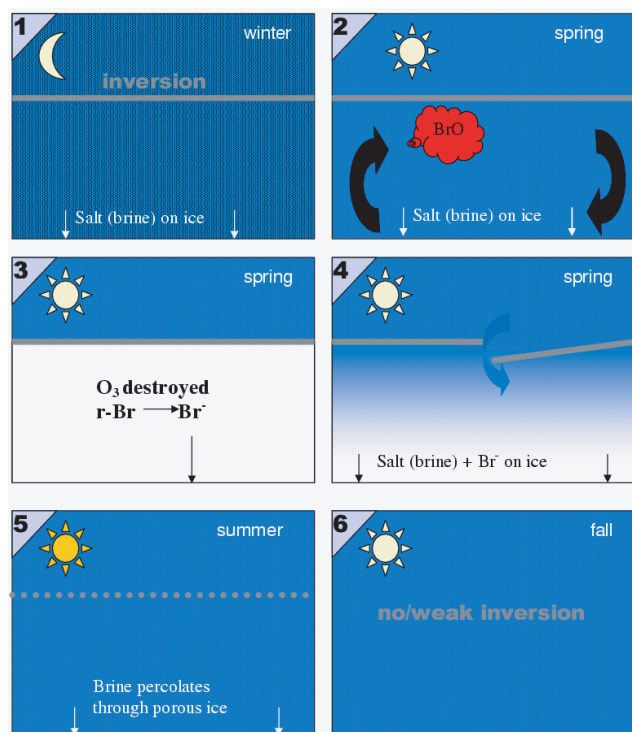– Strong temperature inversion at top of the boundary layer

Fig. 9. Seasonal changes of the factors influencing bromine explosions and ozone depletion events. Only in spring all prerequisites are fulfilled (panel 3). See text for details.

The seasonal changes of the prerequisites for bromine explosions and ozone depletions are summarised in Fig. 9. In polar regions all three prerequisites are only fulfilled after polar sunrise during polar spring. Ozone depletion events in the polar boundary layer are not seen in winter (i.e. the polar night), summer, and fall. The sea ice surface not only decreases strongly during polar summer, but also the amount of sea salt on the ice surface decreases as melt water efficiently transports surface salt through cracks back into the ocean. Strong temperature inversions are also only typical for polar spring as continuous solar radiation enhances convection during the summer months. Polar fall is typically very short and – although new sea ice starts forming during this time – areas of open ocean prevent strong temperature inversions.

However, as discussed above, conditions favourable for bromine explosions appear in certain areas outside polar regions, where large salt deposits provide surfaces from which reactive bromine can be released. The role of temperature inversions (and topography) in these cases remains to be investigated.

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