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# A global model study of natural bromine sources and the effects on tropospheric chemistry using MOZART4

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**Abstract** Halogens in the atmosphere chemically destroy ozone. In the troposphere, bromine has higher ozone destruction efficiency than chlorine and is the halogen species with the widest geographical spread of natural sources. We investigate the relative strength of various sources of reactive tropospheric bromine and the influence of bromine on tropospheric chemistry using a 6-year simulation with the global chemistry transport model MOZART4. We consider the following sources: short-lived bromocarbons ( $\text{CHBr}_3$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ , and  $\text{CH}_2\text{Br}_2$ ) and  $\text{CH}_3\text{Br}$ , bromine from airborne sea salt particles, and frost flowers and sea salt on or in the snowpack in polar regions. The total bromine emissions in our simulations add up to 31.7 Gmol(Br)/yr: 63 % from polar sources, 24.6 % from short-lived bromocarbons and 12.4 % from airborne sea salt particles. We conclude from our analysis that our global bromine emission is likely to be on the lower end of the range, because of too low emissions from airborne sea salt. Bromine chemistry has an effect on the oxidation capacity of the troposphere, not only due to its direct influence on ozone concentrations, but also by reactions with other key chemical species like  $\text{HO}_x$  and  $\text{NO}_x$ . Globally, the impact of bromine chemistry on tropospheric  $\text{O}_3$  is comparable to the impact of gas-phase sulfur chemistry, since the inclusion of bromine chemistry in MOZART4 leads to a decrease of the  $\text{O}_3$  burden in the troposphere by 6 Tg, while we get an increase by 5 Tg if gas-phase sulfur chemistry is switched off in the standard model. With decreased ozone burden, the simulated oxidizing capacity of the atmosphere decreases thus affecting species associated with the oxidation capacity of the atmosphere ( $\text{CH}_3\text{OOH}$ ,  $\text{H}_2\text{O}_2$ ).

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## 1 Introduction

After roughly two decades of research on the role of halogens in tropospheric ozone chemistry (for example Tarasick and Bottenheim 2002; Harder et al. 1998; McElroy et al. 1999; Van Roozendaal et al. 2002; Matveev et al. 2001; Bobrowski et al. 2007; von Glasow et al. 2004; Yang et al. 2005), their direct impact on ozone concentrations is understood on a regional scale. To date, the consensus is that the background level of BrO in the troposphere is in the range of 1–2 pptv, which implies a significant effect on ozone in polluted regions as shown by von Glasow et al. (2004). He reported a decrease of up to 40 % in the ozone concentration. However, according to the study of Yang et al. (2005), it may be unlikely that these average BrO concentrations really occur in polluted regions. Nevertheless, Yang et al. (2005) considered two recognized global sources of bromine in the troposphere only, namely short-lived halocarbons and sea salt formed from sea spray, but did not incorporate the polar sources. In this work, we analyze the global impact of these three sources.

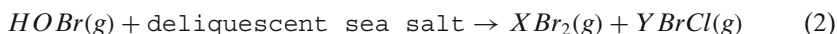
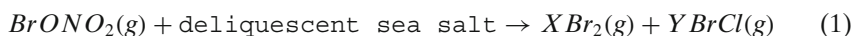
Bromocarbons are important contributors to the bromine burden in the troposphere. They are mainly produced in the oceans, at locations with high primary biological productivity (Quack and Wallace 2003; Schauffler et al. 1999; Carpenter and Liss 2000; Gribble 2000; World Meteorological Organization 2010). The main destruction pathways for bromocarbons is by photolysis and oxidation by OH (World Meteorological Organization 2010), with the resulting release of bromine into the atmosphere. Additional bromine production then follows through heterogeneous chemical reactions on sea salt particles in the marine boundary layer. Frost flowers and sea salt incorporated in the snowpack of polar regions represent the most important and first discovered source of Br in polar regions (McElroy et al. 1999; Koop et al. 2000; Rankin et al. 2002; Kaleschke et al. 2004). Frost flowers generally last for some days before being blown away or being covered by snow (Perovich and Richter-Menge 1994). Sea salt aerosols from the ocean and the blown frost flowers serve as bromine source when they are incorporated in the snowpack (Tang and McConnell 1996). Frost flowers have higher salinity levels and lower ratios of  $\text{Cl}^-/\text{Br}^-$  than sea salt aerosols produced from the ocean spray (Koop et al. 2000; Perovich and Richter-Menge 1994; Rankin et al. 2002), and thus potentially produce more bromine than sea salt particles (Rankin et al. 2002 calculated a value of bromide concentration in the snowpack of 3.29 ng/g, while the value measured by them in frost flowers was  $5 \times 10^4$  times higher). However, even if frost flowers seem to serve as an important polar bromine source, recent field studies argue that sea salt in the snowpack may have higher relevance than expected (Simpson et al. 2007a; Jones et al. 2009).

## 2 Model and simulations

To assess the effect of bromine on tropospheric chemistry on a global scale, we use the three-dimensional global chemistry transport model MOZART4 designed

to simulate tropospheric ozone and its precursors (Emmons et al. 2010). MOZART4 simulates the concentrations of 80 chemical trace species from the surface up to the middle/upper stratosphere (2 hPa), comprising a detailed chemistry scheme for tropospheric ozone, nitrogen oxides and hydrocarbon chemistry. The model simulations were performed at a  $2.8^\circ \times 2.8^\circ$  horizontal grid (128 longitude  $\times$  64 latitude grid boxes), 28 vertical levels extending up to approximately 42 km, and with a 20 minutes integration timestep. The meteorological fields for driving the dynamical core of the model are taken from the National Center for Environmental Prediction (NCEP) and NCAR Reanalysis (Kistler et al. 2001) and are interpolated from a 6-hour time resolution to the 20-min timestep of the simulations. The emissions are taken from the European Union project POET (Precursors of Ozone and their Effects in the Troposphere, Granier et al. 2005). The dimethyl sulfide (DMS) emissions are monthly means from the marine biogeochemistry model HAMOCC5, representative of the year 2000 (Kloster et al. 2006). The global emission is equal to 27.4 Tg(DMS)/yr, which means a global burden of 0.093 Tg(S) in DMS. The sea salt source term applied by MOZART4 is that described by Gong et al. (1997), which results in an annual average production of 3435 Tg(NaCl)/yr.

We developed a modified version of MOZART4 that is expanded by bromine chemistry comprising photolysis, gas-phase reactions, and reactions on aerosol surfaces of sulfate,  $\text{NH}_4\text{NO}_3$ , organic carbon, and sea salt. The compilation of reactions was accomplished through a literature review (e.g. Sander and Crutzen 1996; McGivern et al. 2000, 2002; National Aeronautics and Space Administration (NASA) 2006; Hanson et al. 1994, 1996; Hanson 2003; Larichev et al. 1995; Vogt et al. 1996; Lehrer et al. 2004; von Glasow et al. 2004; Lary 1996; Wachsmuth et al. 2002; Iraci et al. 2005; Friess et al. 2004; Simpson et al. 2007b). A detailed description of the extended model version of MOZART4 is given by Santos (2008). Dry and wet deposition are also included. We introduced as bromine sources: (1) interactively calculated oceanic emissions of bromocarbons in which the emission parameterization in the tropical region is dependent on phytoplankton concentrations in the ocean. Furthermore, the emissions are 2.5 times higher in coastal regions than in the open ocean areas. This parameterization is partly used in recent studies by Ordóñez et al. (2012) and Saiz-Lopez et al. (2012), (2) emissions from airborne sea salt aerosols, and (3) frost flowers and sea salt in or on the snowpack. Bromine itself is then released through chemical reactions. The bromocarbons are destroyed by photolysis and by reaction with OH releasing all their bromine atoms in one step (the chemical kinetic parameters were taken from the JPL Publication 06-02 (National Aeronautics and Space Administration (NASA) 2006)). The emission of bromine from airborne sea salt occurs by the following heterogeneous chemical reactions:



where X and Y are the yields, which differ between the Northern and Southern Hemisphere based on assumptions regarding the acidity of the particles. In the Northern Hemisphere, we assume that acidifying agents are present in sufficient quantities to render the particles acid, because of air pollution by  $\text{SO}_2$  and  $\text{NO}_x$  that will be oxidized to  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , respectively. The Southern Hemisphere is comparatively clean. We adopted a relative yield of 0.2 for  $\text{Br}_2$  and 0.8 for  $\text{BrCl}$

in the Southern Hemisphere and of 0.9 for Br<sub>2</sub> and 0.1 for BrCl in the Northern Hemisphere as obtained by Fickert et al. (1999) for newly formed sea salt particles and acidified particles, respectively. The assumption of a weak acidification in the Southern Hemisphere was made after a sensitivity study that will be discussed in Section 3.1. Therefore, we do not directly include the seasonality of bromine depletion from sea salt particles found at several measurement stations in the Southern Hemisphere (Sander et al. 2003).

The reaction rate  $k$  associated with Eqs. 1 and 2, considering a first order rate constant, the kinetic gas theory, and that the concentration of the reactant in the droplet only depends on the distance from the center of the droplet in steady state, is given by the equation:

$$k = \frac{\bar{v}}{4} \cdot \Gamma \cdot \mathcal{A} \quad (3)$$

where  $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$  ( $R$  being the molar gas constant,  $M$  the molar mass, and  $T$  the temperature),  $\mathcal{A}$  is the available sea salt surface per volume, and  $\Gamma$  gives the fraction of molecules that collide on the surface and react (a “success factor”).

The source function by Gong et al. (1997) calculates the mass of sea salt that is produced per m<sup>2</sup> of ocean surface and for a size range of radii between 0.1 and 10 μm. This mass is then summed into four bins that have the ranges (in μm): 0.1–0.5, 0.5–1.5, 1.5–5.0, 5.0–10. For the conversion of sea salt mass into sea salt surface per volume, we consider a sphere with density 1.236 g/cm<sup>3</sup> (Millero 1996), the average radius of each bin being (in cm)  $0.3 \times 10^{-4}$ ,  $1. \times 10^{-4}$ ,  $3.2 \times 10^{-4}$ ,  $7.5 \times 10^{-4}$ , and finally a growth factor due to atmospheric humidity from the empirical relationship by Gerber (1985). We also consider that the steady state for the heterogeneous reactions is reached in the 20 minutes timestep.

The total reactive uptake  $\Gamma$  for spherical particles, considering the ideal gas law, Fickian diffusion and a first order reaction in the liquid phase, is:

$$\frac{1}{\Gamma} = \frac{1}{\alpha} + \frac{\bar{v}}{4 k_H RT D^{(l)} \sqrt{K} \left( \coth(\sqrt{K} a) - \frac{1}{\sqrt{K} a} \right)} \quad (4)$$

Here,  $\alpha$  is the accommodation coefficient, which gives the extent to which a collision leads to absorption in the substrate. With  $k_H$  we denote the Henry law coefficient,  $R$  is the molar gas constant,  $T$  is the temperature,  $D^{(l)}$  is the diffusion coefficient in the liquid phase,  $K = \frac{k^{(l)}}{D^{(l)}}$ , the ratio between the reaction rate and the diffusion coefficient in the liquid phase, and  $a$  is the radius of the particle.

The choice of the total reactive uptake  $\Gamma$  for the heterogeneous reactions was based on literature and sensitivity simulations. Few experiments were found that are closer to real conditions using salt with a composition similar to that of natural sea salt and spherical particles under wet conditions. From these studies (Pratte and Rossi 2006; Deiber et al. 2004; Abbatt and Waschewsky 1998), we conclude that the  $\Gamma$  values are in the range of 0.01–0.02 for BrONO<sub>2</sub> and 0.1–0.2 for HOBr (for a more detailed discussion of the literature see Santos 2008). We chose three different scenarios (maximum scenario with  $\Gamma_{\text{BrONO}_2} = 0.02$  and  $\Gamma_{\text{HOBr}} = 0.2$ , intermediate scenario with  $\Gamma_{\text{BrONO}_2} = 0.02$  and  $\Gamma_{\text{HOBr}} = 0.1$ , and a minimum scenario with  $\Gamma_{\text{BrONO}_2} = 0.01$  and  $\Gamma_{\text{HOBr}} = 0.1$ ) as a basis for our sensitivity studies. Our sensitivity simulation for the maximum scenario resulted in large regions at the surface between 40 °N and

60 °N in the North Atlantic and Northeast Pacific monthly averages for the volume mixing ratio of  $\text{Br}_x$  ( $= \text{Br} + \text{BrO} + \text{HOBr} + \text{HBr} + \text{BrONO}_2 + \text{BrCl} + 2 \times \text{Br}_2$ ) between 10 and 65 pptv. These are very high values and still do not account for the third source of bromine in the polar regions that would already have an effect at 60 °N. In our minimum scenario, the results of the surface volume mixing ratio for  $\text{Br}_x$  was overall too low and dominated by the organic emissions (maxima over the Indian Ocean of 0.9 pptv). Finally, the intermediate scenario gave the best  $\text{Br}_x$  distribution with  $\Gamma$  values close to the range for natural substrates reported in the literature.

The emissions from frost flowers and sea salt incorporated in the snowpack occurs according to the following equations:



where the production of  $\text{Br}_2$  is calculated by the equation:

$$\frac{dC_{\text{Br}_2}}{dt} = 2 \times (k_{\text{max}}^a \cdot C_{\text{BrONO}_2} + k_{\text{max}}^b \cdot C_{\text{HOBr}}) \times f_{\text{ice}} \quad (7)$$

We assume that each molecule  $\text{BrONO}_2$  or  $\text{HOBr}$  containing one Br atom produces one  $\text{Br}_2$  molecule. The values  $k_{\text{max}}^a$  and  $k_{\text{max}}^b$  were chosen with the help of sensitivity simulations with the objective of estimating a maximum possible effect of emissions from frost flowers and sea salt incorporated in the snowpack. The values were chosen such that the patterns of tropospheric BrO concentrations observed by satellite were approximated by the simulation in polar areas. The values are  $k_{\text{max}}^a = 4.0 \times 10^{-3} \text{ s}^{-1}$  and  $k_{\text{max}}^b = 2.5 \times 10^{-3} \text{ s}^{-1}$ , respectively. The factor  $f_{\text{ice}}$  is the fractional sea ice in the respective surface gridbox. For a detailed description of the parameterization see Santos (2008).

We performed two computer simulations from January 1997 to December 2003: one using the standard MOZART4 model and another including bromine chemistry. We discuss the results for the years 1998 to 2003. We performed an additional third simulation from January 1997 to December 1998 without gas-phase sulfur chemistry, in order to compare the relative effect of sulfur and bromine chemistry on tropospheric ozone in MOZART4. We only consider the year 1998 in comparisons with this simulation.

### 3 Discussion

#### 3.1 Bromine emissions

We first consider emissions from halocarbons. We obtained global emissions of 7.3 Gmol(Br)/yr in form of halocarbons (including  $\text{CH}_3\text{Br}$  and the very-short lived species<sup>1</sup>  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ , the last ones accounting for 4.7 Gmol(Br)/yr, which is on the lower end of the range of values reported

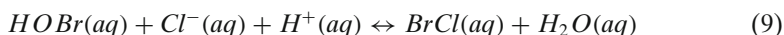
<sup>1</sup>Very-short lived species are species with lifetimes lower than half an year according to definition of the World Meteorological Organization (2010).

in the literature of 2.5–20 Gmol(Br)/yr (Quack and Wallace 2003)). Yang et al. (2005) obtained very similar global halocarbon emissions of 7.8 Gmol(Br)/yr using the model p-TOMCAT.

Secondly, we discuss sea salt as a source of bromine. This source is much more uncertain. It depends on the production rate of sea salt from sea spray and the physico-chemical properties of the particles that determine its bromine depletion. In global models, the production rate of sea salt from sea spray is modelled using empirical equations that link the number or mass production of particles with the wind speed (however, there are other dependencies, such as fetch, whitecap cover or wave spectrum). Normally the sea salt production is proportional to surface winds cubed, thus making it very sensitive to wind speed. This sensitivity may be part of the fact that the predictions from different source functions can range over six orders of magnitude at a given particle radius (Andreas 1998 cited by Schulz et al. 2004). Yang et al. (2005) obtained an emission flux of 2060 Tg(NaCl)/yr using the parameterization by Monahan et al. (1986) and 1150 Tg(NaCl)/yr using that of Smith et al. (1993). MOZART4 applies the source function described in the article of Gong et al. (1997), and results in an annual average production of 3435 Tg(NaCl)/yr.

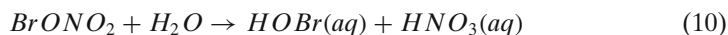
Bromine emissions from sea salt also depend on the size of the particles and on their physico-chemical properties, in particular their acidity. Sander et al. (2003) made a comprehensive analysis of field data observations for several measurement campaigns and found that large particles show a bromine content similar to sea water, medium sized particles (few micrometers in diameter) show bromine depletions and submicrometer particles showed enrichment in bromine. Large particles have short lifetimes and a ratio of surface area to volume, which do not promote the acidification of the particles and the removal or addition of bromine prior to deposition. The enrichment of submicrometer particles in bromine is not yet understood. Whereas Sander et al. (2003) give a chemical explanation, Enami et al. (2007) propose a physical mechanism. We did not account for the effects of particle size in our simulations.

If all bromine contained in the sea salt particles would be released into the atmosphere we would obtain an emission flux of 90.7 Gmol(Br)/yr assuming a mass ratio of Br to Cl of 0.00348 kg/kg as it was done by Sander et al. (2003). In general, only a small fraction of Br contained in sea salt particles is released into the atmosphere. This fraction largely depends on the pH of the particles. Although some authors did not find any impact of the pH on the reaction of HOBr on NaCl/NaBr surfaces (Adams et al. 2002), other studies found that the acidification of the particles promotes the activation of the chemistry, not only in the laboratory (Abbatt and Waschewsky 1998; Huff and Abbatt 2002; Deiber et al. 2004; Pratte and Rossi 2006), but also in the field (Ayers et al. 1999; Sander et al. 2003). The reason for this is that chemical reactions in the particle need the presence of protons:



Also BrONO<sub>2</sub> can be at the origin of the activation of Br from sea salt particles since the hydrolysis of BrONO<sub>2</sub> is fast even in experiments with very low gas phase humidity (Aguzzi and Rossi 1999). In the field, the high importance of bromine

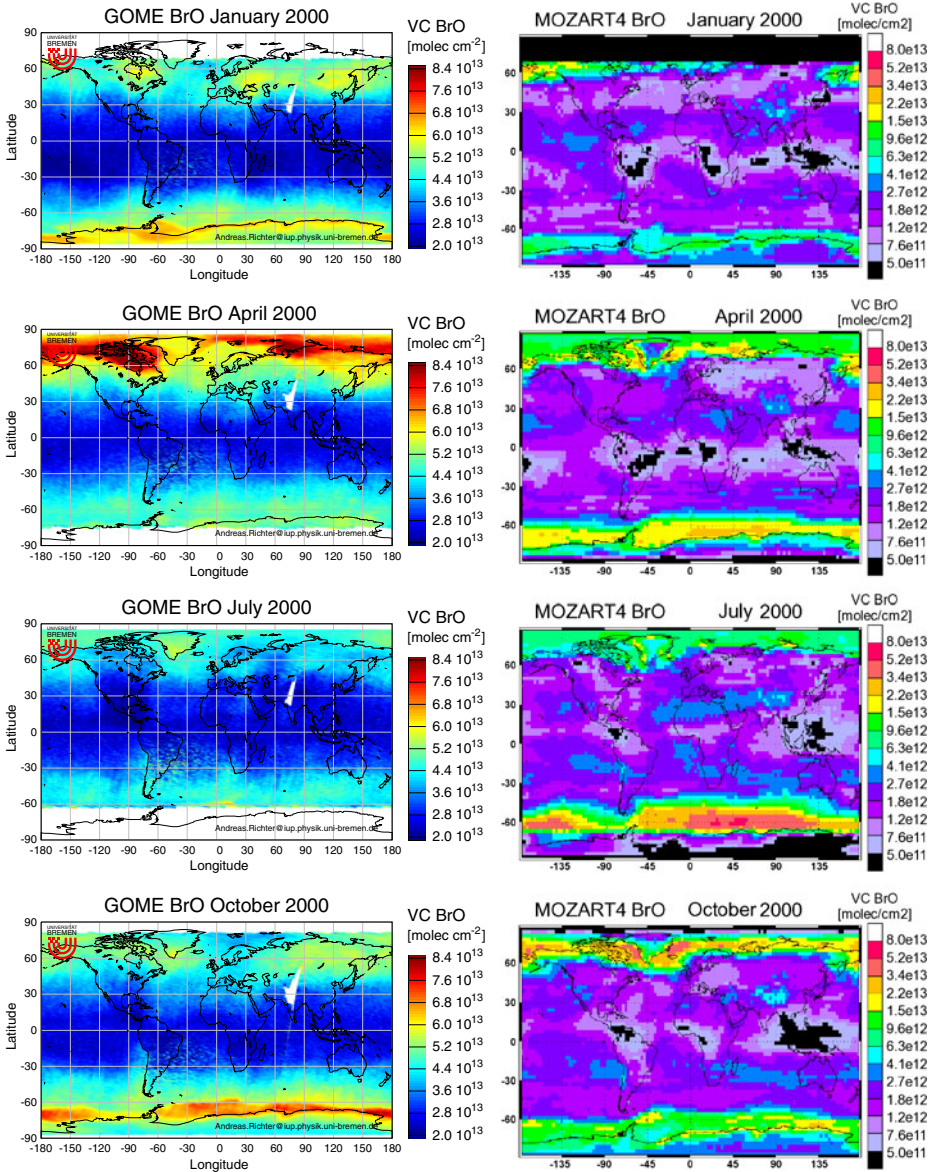
nitrate hydrolysis during ozone depletion events was observed for example by Morin et al. (2007). The hydrolysis of  $\text{BrONO}_2$  also means a cycling of the acidity in the particle through the formation of  $\text{HNO}_3$  as follows:



In this case,  $\text{BrONO}_2$  is transformed into  $\text{HOBr}$  and Eqs. 8 and 9 apply. Thus, we can choose the same yields as in Eqs. 1 and 2 for the Br activation via  $\text{BrONO}_2$ .

The uncertainty in the Br emissions from sea salt is likely to be lower in the Northern Hemisphere, as the pollution by  $\text{SO}_2$ ,  $\text{NO}_x$ , and their oxidation products will promptly acidify the sea salt particles. Sander et al. (2003) report depletion of sea salt particles in bromine all over the ocean including the Southern Ocean, therefore even if the Southern Hemisphere is relatively clean, the sea salt particles are still a source of atmospheric bromine. In the Southern Hemisphere, DMS is the main source of acidifying  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  (Davis et al. 1998). DMS shows prominent seasonal variation at extra-tropical latitudes (Kloster et al. 2006). Consequently, the availability of acidifying agents in the cleaner oceanic regions depends on the season and adds to the uncertainty in the degree of acidification of the particles. The highest atmospheric concentration of DMS in the Southern Hemisphere is observed in southern hemispheric summer and the minima in southern hemispheric winter (see Kloster et al. 2006 and observations by Sciare et al. 2000 and Putaud et al. 1992 and references therein). Therefore, the bromine depletion in sea salt particles in the Southern Hemisphere has a positive correlation with the DMS seasonal cycle (Sander et al. 2003; Ayers et al. 1999). However, this effect is not taken into account in our study.

We obtain the maximum possible bromine emissions from sea salt, if we assume strong acidification ( $X = 0.9$  and  $Y = 0.1$  in Eqs. 1 and 2) of sea salt particles globally. In that case, our simulation gives global emissions of 8.4 Gmol(Br)/yr and high BrO column densities of  $4\text{--}8 \times 10^{13}$  molecules/cm<sup>2</sup> over large areas of the Southern Ocean between 50 °S and 65 °S during the months with the highest wind speeds in that region (May to August). However, the high levels of BrO detected by GOME are always over or near areas with frozen salt water (Wagner and Platt 1998; Wagner et al. 2001) and never surpass roughly the value of  $6.3 \times 10^{13}$  molecules(BrO)/cm<sup>2</sup> (see Fig. 1). This finding is corroborated by measurements on the ground: BrO observations performed on board of a ship that travelled near the Antarctic coast in the winter of 2006 (Wagner et al. 2007), show that enhanced concentrations of BrO up to 50 pptv are found in areas of young sea ice, but outside these areas BrO concentrations are below 3.7 pptv. We have monthly concentrations of BrO at the surface in the region between 50 °S and 65 °S higher than 7 pptv in the southern hemispheric winter months in the simulation with strong acidification globally. This is also due to the dynamic conditions around 58 °S during the southern hemispheric winter months, which produce high sea salt emissions and trap the bromine molecules in the belt promoting a strong chemical feedback. Due to the circumpolar pattern of the winds there is no region where this feedback may break down. Consequently, this leads us to the conclusion that the acidification of sea salt particles and subsequent release of bromine must be weaker in the cleaner Southern Hemisphere. In this way, we assumed weak acidification and used the yields  $X = 0.2$  and  $Y = 0.8$  in Eqs. 1 and 2 found by Fickert et al. (1999) for newly formed sea



**Fig. 1** Tropospheric BrO vertical column density [molecules/cm<sup>2</sup>] retrieved by GOME and from the MOZART4 simulation for 2000 (monthly averages of daily instantaneous results at 10:30 h local time)

salt particles. Therefore, we set a lower limit of bromine emissions in the Southern Hemisphere.

In this way, our setup simulates two extreme conditions: strong acidification in the Northern Hemisphere and weak acidification in the Southern Hemisphere. The inclusion of information about the effect of size and aging of sea salt particles on their



degree of acidification and the dependency of the yields and uptake coefficients on particle acidity would modulate the bromine emissions. To accomplish this task we need more information about acidification and its influence on the yields and uptake coefficients (Sander et al. 2003). However, it seems that strong acidification is a good approximation even for large particles in remote areas of the Northern Hemisphere (Alexander et al. 2005).

Yang et al. (2005) obtained a flux of 14 and 26 Gmol(Br)/yr (for two different sea salt source functions, respectively), considering variable pH in the Southern Hemisphere. However, the parameterization of the Br emission flux  $E_{\text{Br}}$  from sea salt used by Yang et al. (2005) and in this work are very different. Yang et al. (2005) use the equation  $E_{\text{Br}} = P \times R_a \times DF$ , where  $P$  is the sea salt mass production (particles with a dry radius  $< 10 \mu\text{m}$ ),  $R_a$  is the sea salt Br/NaCl ratio, and  $DF$  is the fraction of bromine in sea salt aerosol which is released in gaseous form into the atmosphere. The latter quantity takes into account the particle acidity in the Southern Hemisphere and is set to 0.5 in the Northern Hemisphere and at latitudes below  $30^\circ\text{S}$ . A  $DF$  of 0.5 as considered by Yang et al. (2005) is too high, because most sea salt particles have radii in the supermicrometer range, for which  $DF$  is close to zero (Sander et al. 2003). In this way, for the bulk aerosol samples compiled by Sander et al. (2003)  $DF = 0.5$  is shown as a higher limit for most of the campaigns. In this work, bromine emissions from sea salt use the MOZART4 chemical scheme applying Eqs. 1 and 2. This means that the gas phase concentrations of the reactants and feedback processes are taken into account in our study.

The emissions from frost flowers and sea salt incorporated in the snowpack of polar regions are interactively calculated. From these sources, we obtain  $(20 \pm 0.64)$  Gmol(Br)/yr. From sea salt aerosol, we obtain only 3.9 Gmol(Br)/yr whereas Yang et al. (2005) had emissions as high as 14 or 26 Gmol(Br)/yr depending on their sea salt model. In contrast to our model, Yang et al. (2005) do not include any explicit emissions from frost flowers but seem to include those in the sea salt emissions. Although our total emissions from frost flowers and sea salt of 24 Gmol(Br)/yr is near the maximum of the range of the emissions reported by Yang et al. (2005), we feel that only 3.9 Gmol(Br) from sea salt aerosols is likely on the low side. Consequently, Yang et al. (2005) obtained a homogeneous distribution of tropospheric BrO over the globe in the range of 0.2 to  $1.2 \times 10^{13}$  molecules/cm<sup>2</sup>, however, their maxima are generally located over the open ocean, which is not correct (Wagner and Platt 1998; Wagner et al. 2001). The location of our maxima fit better with satellite observations as we will see later.

Our bromine sources lead to a tropospheric<sup>2</sup> BrO global annual mean of 0.42 pptv (instantaneous output at 10:30 h local time), that is a factor of 2–4 lower than the expected 1–2 pptv. We suppose that the emissions from sea salt are at the origin of this gap.

In polar regions, we obtained an ozone destruction rate at the surface of about 34 ppbv/h when BrO was around 16 pptv. These ozone destruction values are similar to those reported from other studies. Lee et al. (2005) observed in volcano plumes ozone destruction rates of 31 ppbv/h when BrO was around 20 pptv and ClO 1 ppbv.

<sup>2</sup>For simplicity, we use a tropopause at 100 hPa throughout our study.

In the Arctic region, Tuckermann et al. (1997) observed rates of 1.3 to 2.4 ppbv/h (30 pptv BrO and 35 pptv ClO) and at the Dead Sea Basin, Hebestreit et al. (1999) observed 10–20 ppbv/h of ozone destroyed at the very high BrO volume mixing ratio of 176 pptv. In our simulations, the spots with highest bromine emissions from airborne sea salt aerosols showed maximum ozone destruction rates 100 times lower than the rates caused by polar source emissions.

### 3.2 Comparison of model results with satellite observations

Satellite retrieval permits to measure the vertical tropospheric column density of BrO globally.<sup>3</sup> The comparison of the model results with GOME retrievals is difficult, because of the uncertainties in the satellite derived BrO vertical column density in the troposphere. These uncertainties mainly arise from a lack of the exact knowledge of the BrO concentration in the stratosphere and surface albedo effects (personal communication by Andreas Richter). The detection limit of ERS-2 at GOME is roughly  $1\text{--}2 \times 10^{13}$  molecules/cm<sup>2</sup> (Richter et al. 1998; Hegels et al. 1998), but because of the uncertainties we are not able to know the absolute column densities. Moreover, according to personal communication by Andreas Richter, the dark blue colour of the left hand side of Fig. 1 represents some arbitrary reference value. We can only compare the pattern of the maxima and seasonal cycle in the high latitude regions. During polar spring the chemical activation gives rise to an increase of the vertical column densities to about  $6 \times 10^{13}$  molecules/cm<sup>2</sup>. Therefore, from March to May high column densities are retrieved over the North Polar region, and similarly over the South Polar region during September–December. This results from the unique one-day/one-night light regime. Very recently, a more accurate analysis of the tropospheric BrO column using satellite data is available (Choi et al. 2012), but it is for April 2008 only.

We have a satisfactory representation of global patterns of tropospheric BrO vertical column densities over the polar regions compared with satellites (Fig. 1). In our model, we have a maximum in spring and fall, the one in fall being higher. This is mainly due to the sea ice cover in the model in the Arctic, which has a too large extension during the summer months.<sup>4</sup> This is even truer for the later years in this study, as observations show a rapid decline in Arctic sea-ice extent, especially in the summer months (Hassol 2004). However, a smaller maximum in fall is expected due to polar emissions being fuelled by sea salt emissions and has been observed in the Southern Hemisphere by Saiz-Lopez et al. (2007).

In the South Polar region, we also see that the tropospheric BrO vertical column density annual maxima given by the model deviates from the observations. This is due to the high sea salt concentration and production of bromine from May to August. During this period of southern hemispheric winter, strong winds course around the Antarctic producing large amounts of sea salt, which are transported to the coast. Nonetheless, we still observe a strong gradient in the tropospheric

<sup>3</sup>Products from the Satellite GOME can be visualized at [http://www.doas-bremen.de/bro\\_from\\_gome.htm](http://www.doas-bremen.de/bro_from_gome.htm). Last accessed February 5, 2011.

<sup>4</sup>See <http://arctic.atmos.uiuc.edu/cryosphere/>. Last accessed February 17, 2011.

BrO vertical tropospheric column density during the transition from polar day to polar night. As mentioned above, a quantitative analysis is not possible due to limitations of the satellite retrievals (a more detailed explanation is given by Santos 2008, p. 74).

### 3.3 Comparison of model results with ground-based observations

In Table 1 we show values of BrO and Br<sub>x</sub> from ground-based observations and from the model experiments. At stations affected by polar emissions, the model simulates BrO concentrations that are characteristic of polar BrO enhancements. BrO observations performed on board of a ship that traveled near the Antarctic coast in the winter of 2006 (Wagner et al. 2007), show that enhanced concentrations of BrO are found in areas of young sea ice, but outside these areas BrO concentrations are below 3.7 pptv, with a ratio of 5 between measurements within and outside sea ice covered regions. In our results, we have a ratio of 4. However, the values reported by Wagner et al. (2007) for winter are surprisingly high for this period of low solar irradiation. Saiz-Lopez et al. (2007) detected a maximum in October/November followed by a decrease in summer and an apparent small maximum in March. The model reproduces this seasonal cycle. This demonstrates the high importance of the seasonal cycle in solar irradiation and wind for BrO concentrations in high latitudes. Moreover, we get the same twin peaks in the Northern high latitudes, in May and September/October. Our parameterization of bromine emissions in polar regions produces continuous emissions as soon as there is sunlight. However, in reality there are emission pulses. A better spatio-temporal description of the emissions would improve our comparisons.

At low and mid-latitudes, our modelled BrO has the tendency to be low when compared with observations (cf. Table 1). Nevertheless, there is a good agreement with the measurements of Schofield et al. (2004) and Leser et al. (2003), but at Cape Verde and Reunion the model values are too low by roughly one order of magnitude. We suppose that our low bromine concentrations are due to low bromine emissions from airborne sea salt particles. In areas highly influenced by both, sea salt and bromocarbon sources, the BrO monthly mean volume mixing ratio follows sea salt concentrations closer than bromocarbon concentrations. At Cape Verde, this means that BrO volume mixing ratio increases to the West from Cape Verde, especially from March to June and increases to the North from July to September when the trade winds are weaker.

In the Southern Hemisphere, the low bromine concentrations are probably linked to the fact that we consider yields for reactions (1) and (2) typical of low particle acidification. The uptake coefficients can not be the sole cause of this underprediction since an increase of  $\Gamma_{\text{HOBr}}$  by a factor of 2 led to an increase in the BrO column densities by only 73 % and 163 % at Cape Verde and Reunion, respectively. Therefore, this  $\Gamma_{\text{HOBr}}$  value still does not lead to an increase by one order of magnitude in those two locations but produces too high BrO column densities elsewhere. Moreover, the emission of sea salt particles themselves from the ocean surface is very uncertain, with predictions from different source functions ranging over six orders of magnitude at a given particle radius as mentioned before. Furthermore, we only take wind speed into account whereas Jaeglé et al. (2011) showed that sea salt emissions depending on sea surface temperatures can improve

**Table 1** Ground-based measurements of bromine chemical species ordered from South to North. SCHOF06: Schofield et al. (2006), SCHOF04: Schofield et al. (2004), THEYS07: Theys et al. (2007), MARTIN09: Martin et al. (2009), READ08: Read et al. (2008), PSZENNY04: Pszeny et al. (2004), LESER03: Leser et al. (2003), STURGES90: Sturges (1990), HENDRICK07: Hendrick et al. (2007), FITZEN00: Fitzenberger et al. (2000)

Station	Species	Observed concentration	Model	Units	Period	Reference
Arrival Heights	BrO	Background: $0.3 \pm 0.3 \times 10^{13}$ High: $1.8 \pm 0.1 \times 10^{13}$	$1.5 \times 10^{13}$	molecules/cm <sup>2</sup>	Obs: 07.09–27.10.2002 Model: 09 and 10.2002★	SCHOF06
Antarctica	BrO	High: 7	High: $24 \pm 2.5$	pptv	Obs: 01.2004–02.2005 Model: 1998–2003★	SAIZLOPEZ07
Coast of Antarctica	BrO	Typical: 25 High: 50	Mean: $8 \pm 2$	pptv	Obs: 24.06–15.08.2006 Model: 06–08.1998–2003★	WAGNER07
Lauder, NZ	BrO	$0.2 \pm 0.4 \times 10^{13}$	$0.18 \pm 0.051 \times 10^{13}$	molecules/cm <sup>2</sup>	Obs: 03.2001–04.2003(n=72) Model: 03.2001–04.2003★	SCHOF04
South Pacific	BrO	$1.1 \pm 0.45 \times 10^{13}$	$0.19 \pm 0.085 \times 10^{13}$	molecules/cm <sup>2</sup>	Obs: 08.2004–06.2005 Model: 1998–2003	THEYS07
Reunion	BrO	Background: $< 1.2 \times 10^{13}$ High: $3.6 \pm 1.3 \times 10^{13}$	$0.19 \pm 0.050 \times 10^{13}$	molecules/cm <sup>2</sup>	Obs: 02.2007 Model: 02.1998–2003	MARTIN09
S-Indian Ocean	BrO	ca.2	$0.084 \pm 0.071$	pptv	Obs: 10.2006–10.2007 Model: 1998–2003★	READ08
Cape Verde Atlantic	BrO		0.8	pptv	Obs: 09.1999 Model: 09.1999♦	PSZENNY04
Canary Islands Atlantic	BrO	Mean: $0.17 \pm 0.06 \times 10^{13}$ Max: $0.59 \pm 0.53 \times 10^{13}$	$0.2 \times 10^{13}$	molecules/cm <sup>2</sup>	Obs: 2 days in 10.2000 Model: 10.2000★	LESER03
Isle of Harris North Sea	Br <sub>X</sub>	8▲	$2.6 \pm 1.5$	pptv	Obs: 26.04–05.05.1987 Model: 04 and 05.1998–2003	STURGES90
Harestua Norway	BrO	Mean: $0.92 \pm 0.38 \times 10^{13}$ Max: $1.52 \pm 0.62 \times 10^{13}$	$0.23 \pm 0.16 \times 10^{13}$	molecules/cm <sup>2</sup>	Obs: 2000–2006 Model: 1998–2003	HENDRICK07
Kiruna Sweden	BrO	Feb: $5 \times 10^6$ Aug: $< 1 \times 10^5$	Feb: $6.7 \times 10^6$ Aug: $4.8 \times 10^5$	molecules/cm <sup>3</sup>	Obs: 10.02.1999, 19–20.08.1998 Model: 02.1999, 08.1998	FITZEN00

Notes:

★ - Monthly average of daily instantaneous output for 10h30 local time

♦ - Monthly average

■ - Br<sub>X</sub> = Br + BrO + HOBr + HBr + BrONO<sub>2</sub> + BrCl + 2 × Br<sub>2</sub>

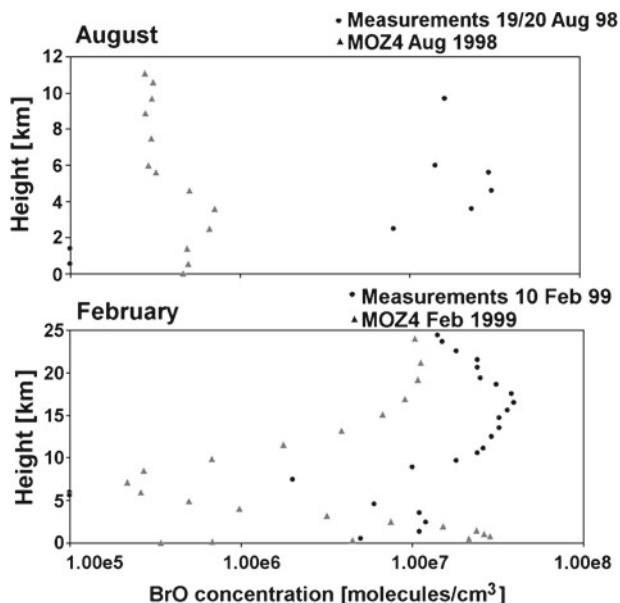
▲ - Original measurement is 28 ng(Br<sub>X</sub>)/m<sup>3</sup>. We considered standard atmospheric conditions for the transformation

the sea salt concentrations, especially in the tropics. It is less likely that the bromine production from short-lived bromocarbons is at the origin of our low BrO values since their emissions and chemical degradation are less uncertain (Santos 2008; Ordóñez et al. 2012) than the bromine flux from airborne sea salt particles (cf. our discussion in Section 3.1).

We now discuss the altitude profiles measured in the Northern hemisphere at Kiruna (67.1 °N, 22.5 °E) by Fitzenberger et al. (2000). In Fig. 2 we compare the profiles obtained by Fitzenberger et al. (2000) (circles) and the ones resulting from our simulation (triangles). For February and below 10 km, we observe a striking agreement in the shape of the curves. The profiles show an S shape, with a maximum at around 2 km altitude and a minimum between 6 and 7.5 km altitude. From 7.5 km to circa 10 km, the modelled values do not increase as sharply as shown in the observations. Above 10 km, the main cause for the lower model results is most probably the lack of long-lived halocarbon emissions in the model simulations. In the boundary layer, the agreement is good for the February measurements. Annual averages of BrO concentrations at Kiruna from simulations including different sets of sources (not shown) reveal that the S shape profile observed in February is a signal of the polar bromine emissions. Indeed, the maximum at 2 km does not appear if we only include sea salt and halocarbon emissions. Furthermore, the halocarbon emissions give rise to annual mean concentrations in the order of  $10^5$  molecules/cm<sup>3</sup>. This number is increased by one order of magnitude if we include the emissions from airborne sea salt particles.

We need more long-term measurements and especially measurements that allow to discern between open ocean background conditions in bromine concentrations and the effect from biogenic emissions in coastal areas to further improve the evaluation of the relative influence of the various bromine sources.

**Fig. 2** BrO concentration profiles [molecules/cm<sup>3</sup>] resulting from measurements (circles, Fitzenberger et al. (2000)) and from MOZart4 simulations (triangles) at Kiruna (model grid: 67.1 °N, 22.5 °E); monthly averages of daily instantaneous outputs at 10:30 h local time. Symbols on the Y-axis represent small values below  $1 \times 10^5$ . The standard deviation of the measurements is roughly 30 %

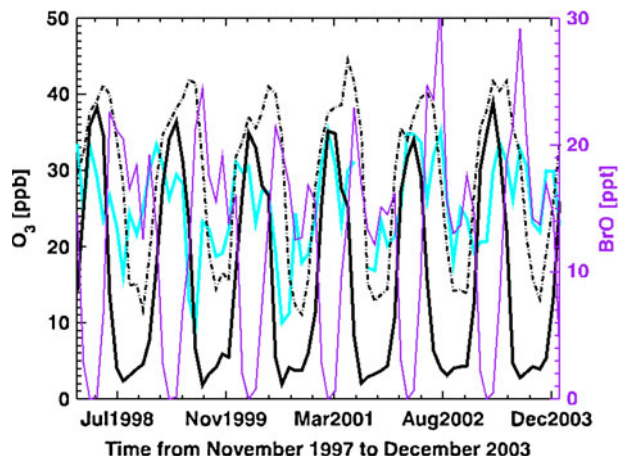


### 3.4 Effect on ozone and its precursors

From our simulations, we conclude that the global effect of bromine on tropospheric ozone is small: less than 10 % ozone decrease at the surface compared to the Base Run (without bromine chemistry), unless the high emissions in the polar regions are taken into account. In this case, tropospheric BrO column densities reach values of the order of  $10^{13}$  molecules/cm<sup>2</sup> at day time (Fig. 1), which leads to decreases of 60 % to nearly 100 % of ozone relative to the Base Run. In Fig. 3, we show the time evolution of ozone and bromine at Barrow, Alaska. The O<sub>3</sub> time series from the Base Run is represented by the dashed black line. Ozone oxidizes Br to BrO (purple line) and leads to decreased O<sub>3</sub> (solid black line). The decrease in ozone in the simulation including bromine chemistry during spring time starts earlier in the year at first sunlight and ozone concentrations stay lower until the end of the summer compared to the simulation without bromine chemistry. Although the ozone concentrations resulting from the simulations including bromine chemistry are closer to the observations (blue line), the model fails to predict the high variability of the observations in time. This is due to the fact that the bromine emissions are constant in time in the simulations whereas the bromine emissions from frost flowers are highly variable in time (Perovich and Richter-Menge 1994; Kaleschke et al. 2004). The date and depth of ozone minima is less well captured than the maxima by the simulations. We explain this deficiency, at least in part, by the general underestimation of ozone in the Northern Hemisphere mid-troposphere (30 °N–90 °N, at 650 hPa and 400 hPa) by MOZART4 as shown by Emmons et al. (2010). They indicate as the most likely reason the weak transport from the stratosphere into the troposphere at low vertical resolution. According to the comparisons in their study, the underestimation in the mid-troposphere extends down to the 900 hPa level, therefore contributing to our end of the summer underestimation of ozone.

In terms of annual global burdens, the destruction of ozone due to the introduction of bromine chemistry leads to, in average, 6 Tg ozone less in the troposphere (an average ozone burden of  $(312.5 \pm 1.90)$  Tg in the base run and  $(306.4 \pm 1.94)$  Tg in the simulation including bromine chemistry). Similarly, switching off gas-phase

**Fig. 3** Model results at Barrow, Alaska (71.3 °N, 156.6 °W): surface ozone volume mixing ratio [ppbv] resulting from the model MOZART4 without (*dashed black line*) and including bromine chemistry (*solid black line*). The *blue line* depicts ozone observations [ppbv] of NOAA (Oltmans et al. 1998). Simulated surface bromine oxide [pptv] is shown in *purple* (right axis)



sulfur chemistry in MOZART4 leads to an increase of 5 Tg in the ozone burden. Therefore, the effect of gas-phase sulfur chemistry on tropospheric ozone is comparable to that of bromine chemistry. This is remarkable since sulfur-containing compounds are prominent in atmospheric gas-phase and heterogeneous chemistry (Warneck 1999; Seinfeld and Pandis 1998; Pozzoli et al. 2008) being emitted from anthropogenic and natural sources (volcanos, ocean) whereas Br species are present in lower concentrations.

Bromine chemistry leads to a global average decrease of the  $\text{HO}_2/\text{OH}$  ratio of  $5.3 \pm 0.52\%$  at the surface, that reaches  $37.2 \pm 3.0\%$  in the North Polar region and  $55.1 \pm 7.0\%$  in the South Polar region during local Spring. It also leads to lower destruction rates of species reacting with odd hydrogen. This decrease reaches 28.6% for the reaction of CO with OH and 26.7% for the reaction of  $\text{CH}_4$  with OH in the polar troposphere, but the global effect is 1% only. In contrast to that, in the simulation excluding gas-phase sulfur chemistry a global increase of 14.6% for CO and 3.7% for  $\text{CH}_4$  is reached, which transforms into a reduction of the  $\text{CH}_4$  atmospheric lifetime from 8.46 to 8.36 years. The difference in the impact of sulfur and bromine chemistry on CO and  $\text{CH}_4$  is related to the fact that gas-phase sulfur chemistry directly acts on OH concentrations in polluted areas whereas bromine chemistry acts on  $\text{O}_3$  concentrations in polar regions primarily. Consequently, gas-phase sulfur chemistry directly influences the oxidation rate of ozone precursors like  $\text{CH}_4$  or CO in polluted areas whereas bromine chemistry changes the oxidation capacity of the atmosphere mainly in remote areas. Therefore, the effect of gas-phase sulfur chemistry on ozone precursors is stronger than that of bromine chemistry.

Bromine chemistry also leads to a decrease in tropospheric  $\text{NO}_x$  burden by  $128 \pm 51.5$  Mmol ( $-1.3\%$ ). This effect is due to the heterogeneous chemistry of  $\text{BrONO}_2$  and  $\text{ClONO}_2$ , and was already reported by Pszenny et al. (2004). Due to gas-phase sulfur chemistry, there is an increase by  $67.5 \pm 63.4$  Mmol (0.69%).

In the simulation with bromine chemistry, the Leighton ratio ( $[\text{NO}_2]/[\text{NO}]$ ) increases in average by  $(9.0 \pm 1.9)\%$  globally at the surface, and increases during local Spring by  $(126 \pm 36.3)\%$  and  $(83.4 \pm 13.4)\%$  in the North and South Polar regions, respectively. The increases in the Leighton ratio may lead to an impairment of ozone formation. Both effects on  $[\text{HO}_2]/[\text{OH}]$  and  $[\text{NO}_2]/[\text{NO}]$  just reported are in the opposite direction when heterogeneous chemistry on ice particles is present. This is because OH and  $\text{NO}_2$  are removed from the atmosphere by the proxy heterogeneous equations (5) and (6). Probably, in reality there is a degree of regeneration of these species (Piot and von Glasow 2008). The simulation results show a very pronounced effect in polar regions on both ratios going from the region with sea ice cover, the region with no ice cover but high concentrations of bromine reactive species until roughly  $45^\circ$ – $50^\circ$  latitudes in both hemispheres at the month of higher activity (April in the North Polar region and September in the South Polar region).  $[\text{HO}_2]/[\text{OH}]$  shows a decrease of 20–80% even when there is no sea ice, because  $\text{HO}_2$  is more efficient than OH reacting with the bromine species. As bromine concentrations decrease, OH oxidizing chemistry takes over and results in  $\text{HO}_2/\text{OH}$  increasing by 10–20% in neighboring regions until dropping to very low values.  $[\text{NO}_2]/[\text{NO}]$  decreases by 20–60% over sea ice covered regions and abruptly increases in neighboring areas because of reaction  $\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$ , and again decreases abruptly to low ratio values. Platt and Hoenninger (2003), discuss the effects of tropospheric bromine chemistry on the  $[\text{HO}_2]/[\text{OH}]$  and the Leighton

ratio. They expect a decrease of the  $[\text{HO}_2]/[\text{OH}]$  and an increase of the  $[\text{NO}_2]/[\text{NO}]$  ratios, as we have in our simulations in areas with high concentrations of bromine species but no heterogenous reactions (5) and (6). Wennberg et al. (1998) observed such changes in the upper troposphere.

The effect of bromine natural emissions on tropospheric chemistry is important at polar regions, where we have a decrease of about 16 % in  $\text{CH}_3\text{OOH}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{NO}_x$ .

#### 4 Conclusion

In terms of annual global burdens, the destruction of ozone due to bromine species leads to 6 Tg less ozone in the troposphere. On the other hand, if we switch off the gas-phase sulfur chemistry in MOZART4 this leads to an increase of the ozone burden of 5 Tg. Therefore, the global effect of gas-phase sulfur chemistry on tropospheric ozone is of comparable global importance as that of bromine species. However, the impact on ozone and its precursors is restricted to the polar regions where the simulations indicate decreases of 60 to 100 % in  $\text{O}_3$ , and 16 % in  $\text{CH}_3\text{OOH}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{NO}_x$ .

All three sources of bromine in the troposphere are relevant to bromine concentrations in the troposphere, with bromocarbons contributing especially in tropical regions and higher altitudes, sea salt in the global marine boundary layer, and frost flowers and the snowpack in high latitudes.

Global bromine emissions of 3.9 Gmol(Br)/yr from sea salt are too low as expected and implied by the ground-based measurements. This is true even in the Northern Hemisphere where strong acidification was assumed. In order to improve the accuracy of bromine emissions from airborne sea salt particles, we need a better source function for sea salt aerosols. Following the work of Jaeglé et al. (2011) would allow higher sea salt emissions at low latitudes by adding to the source function a dependency on sea surface temperature. Consequently, the bromine emission would increase in regions where the observations hint at low concentrations of bromine at the surface.

A second important source of uncertainty is the effect of particles size and aging on their acidity state and therefore the bromine release from those particles. We need more information about acidification and its influence on the yields and uptake coefficients (Sander et al. 2003). Furthermore, to constrain the sea salt source further we need more ground-based measurements over longer time periods and with a higher spatial coverage.

Our simple parameterization of bromine emissions from frost flowers and sea salt in or on sea ice using sea ice as a proxy depends on the availability of sunlight and the concentration of the reactants only. This means that there are continuous surface emissions of bromine from polar sources during polar-day, leading to too high BrO concentrations and subsequent too high impact on ozone. On the other hand, BrO concentrations near the polar regions are sensitive to the exact spatio-temporal variation of the source. Since it is still under discussion whether frost flowers or 1-year sea-ice are the most important source for bromine emissions (Kaleschke et al. 2004; Rankin et al. 2002; Simpson et al. 2007b; Jones et al. 2009) a model study investigating both sources may help to decide this question in the future.



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