

The Impact of BrO on Dimethylsulfide in the Remote Marine Boundary Layer

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We have used a global three-dimensional chemical transport model coupled to a detailed size-resolved aerosol microphysics module to study the impact of BrO on dimethylsulfide (DMS) in the remote marine boundary layer. Our model results suggest BrO contributes 16% of the global annual DMS oxidation sink. This effect is most profound over the SH oceans where low NO_x concentrations and a high sea salt aerosol source, coupled with high DMS concentrations, drives a large contribution of BrO to DMS oxidation (>20%). Bromine chemistry also results in an 18% reduction in the global DMS burden and lifetime. In addition, when we use an alternative DMS source parameterization resulting in a factor 2 increase in DMS flux the release of bromine from sea salt aerosol increases by 50-60% in the southern hemisphere summer because of additional aerosol acidity. This suggests a possible DMS-SO₂-sea salt-BrO marine aerosol feedback mechanism that acts to reduce the sensitivity of the DMS lifetime to increases in DMS emission.

1. Introduction

Dimethylsulfide (DMS) emitted by phytoplankton over the oceans is an important precursor to aerosol formation in remote marine regions [Charlson et al., 1987]. Model studies and observations have found a clear correlation between DMS emission and cloud condensation nuclei (CCN) number concentrations [Ayers and Gillet, 2000].

Understanding the chemical sinks of DMS is key to quantifying its impact on the climate system. Global model studies have reported an overprediction of DMS [Spracklen et al., 2005] possibly due to missing oxidants in the model or an overprediction of emissions. Most global sulfur models currently only use OH and NO₃ as DMS oxidants [e.g. Berglen et al., 2002; Spracklen et al., 2005].

The primary source of BrO in the remote MBL is sea salt aerosol. Measurements of aged sea salt often show a significant bromide depletion compared to fresh sea salt implying a net atmospheric source of bromine from the aerosol [Sander et al., 2003]. Bromocarbons such as bromoform and dibromomethane emitted from macroalgae provide an additional source of reactive bromine to the troposphere [Warwick et al., 2006].

Bromine species may impact DMS oxidation either via direct reaction [Toumi, 1994]



or indirectly through changes to oxidative capacity via effects on O₃, HO_x and NO_x [Jenkin, 1992]. Observations of BrO in the remote MBL suggest mixing ratios of between 1 and 2.5 pmol mol⁻¹ during the daytime [Read et al., 2008]. If BrO is present at this

level throughout the remote MBL it would contribute significantly to DMS oxidation on a global scale.

The first global model study of BrO and DMS used a global sulfur cycle model in a GCM with fixed oxidants and a constant BrO mixing ratio of 1 pmol mol^{-1} in the lowest 1.3 km of the atmosphere [Boucher et al., 2003]. This study estimated that BrO could contribute up to 29% of the DMS sink. Von Glasow et al., [2004b] used a 3D chemical transport model (CTM) with a comprehensive treatment of tropospheric gas-phase chemistry including a bromine scheme to study the impact of $0.5\text{-}2 \text{ pmol mol}^{-1}$ of BrO on DMS and ozone in the free troposphere. They found up to a 26% reduction in the tropospheric DMS burden due to bromine chemistry. However, this study did not explicitly account for a sea salt or short-lived organohalogen source of bromine in the MBL.

In this study we have coupled a detailed tropospheric chemistry model, which includes a description of bromine chemistry, with a size-resolved aerosol model. To our knowledge this is the first global model study to calculate a bromine source from explicit sea salt emissions to quantify the contribution of BrO to DMS oxidation. Our coupled approach also enables us to improve the quantification of the effect of bromine on DMS and to address possible marine aerosol feedbacks between DMS emission and bromine release from sea salt aerosols and the impact on DMS lifetime.

2. Model Description

We use the TOMCAT global 3-D CTM [Chipperfield, 2006; Arnold et al., 2005] coupled to the GLOMAP-BIN size-resolved aerosol microphysics module [Spracklen et al., 2005]. The chemistry scheme in TOMCAT includes Ox-NO_y-HO_x-C₁-C₃ NMHCs and isoprene.

A full description of the chemical scheme used in the coupled TOMCAT-GLOMAP model is provided in the auxiliary material. Large-scale transport and meteorology is specified from 6-hourly European Centre for Medium-Range Weather Forecasts (ECMWF) analyses. For the runs used here the model has a horizontal resolution of $5.6^\circ \times 5.6^\circ$ with 31 levels from the surface to 10 hPa.

In our chemical scheme we allow DMS oxidation by OH, NO₃ and BrO. DMS emissions are calculated from DMS seawater concentrations [Kettle and Andreae, 2000] and the sea-to-air transfer velocity of Liss and Merlivat [1986].

The bromine chemistry scheme follows that published in Yang et al., [2005]. We include three heterogeneous reactions;



Heterogeneous reaction rate coefficients are calculated from Schwarz [1986]. Reactions 2 and 3 occur on aerosol particles and cloud droplets, reaction 4 only occurs on aerosols. We use the uptake coefficients (γ) specified in Yang [manuscript in preparation, 2009] for N₂O₅, BrONO₂, HOBr and HBr. Aerosol surface areas are calculated in GLOMAP from the aerosol size distribution.

Oceanic bromocarbon emission distributions from macroalgae and phytoplankton are taken from Warwick et al., [2006].

To calculate the source of bromine from sea salt we have extended the parameterization used in Yang et al., [2008] to include the scheme published in Alexander et al., [2005]. Br_2 is emitted from sea spray aerosol size bins that have been "acidified" by uptake of SO_2 and HNO_3 . As in Alexander et al., [2005] we calculate the alkalinity flux (due to freshly emitted sea salt) and the acidity flux (due to SO_2 and HNO_3) in each sea salt size bin. The uptake coefficient for SO_2 on sea salt is taken from Song and Carmichael [2001]. We only assume the size bin has been acidified if the alkalinity flux is exceeded by the acidity flux during the model chemical timestep of 30 minutes or the lifetime of the sea salt aerosol in the bin, whichever is shorter. The particle lifetime is calculated according to the rate of wet and dry deposition.

If the aerosol size bin has been acidified the emission of Br_2 into the lowest model grid box is calculated using equation 5, where SSMF is the sea salt mass flux (kg NaCl/timestep), MR is the sea salt Br/NaCl mass ratio (0.00223 g/g) and DF is a size-dependent bromine depletion factor (see auxiliary material). The DF value is calculated by segregating the data in Sander et al., [2003] into a series of size bins and then interpolating the median DF in each bin onto the GLOMAP aerosol size grid. Sub-micron sea salt size bins have a negative DF down to -1.98. For super-micron size bins DF varies from 0.21 to 0.51. We use the sea salt emission parameterizations of Gong [2003] for sizes below $1.5\mu\text{m}$ dry radius and Smith and Harrison [1998] for sizes larger than $1.5\mu\text{m}$ dry radius.

$$\text{BR}_{\text{flux}} = \text{SSMF} \times \text{MR} \times \text{DF} \quad (5)$$

We have performed 5 model runs. Run **Br** was the basic model with organic and sea-salt bromine emissions and the DMS flux parameterization scheme of Liss and Merlivat [1986]. Run **NOBr** did not include any bromine emissions. Run **ORGBr** included organic bromine emissions only. Finally, runs **BrNi** and **NOBrNi** were the same as runs **Br** and **NOBr**, respectively, but used the higher DMS flux scheme of Nightingale et al., [2000].

3. Results

3.1. DMS and BrO Distributions

For 2004, the global DMS source is $10.3 \text{ Tg S yr}^{-1}$ which is lower than published in Berglen et al., [2004] who reported a source of $11.95 \text{ Tg S yr}^{-1}$. The annual mean surface DMS mixing ratio is shown in Figure 1. The high DMS source regions in the SH oceans can be seen, as can the lower DMS mixing ratios in coastal areas.

Figure 2 compares model DMS and observations at Cape Grim and Amsterdam Island. Run **Br** shows good agreement with the observations at Amsterdam Island with the exception of a large underprediction in January (Figure 2a). At Cape Grim run **Br** overpredicts the monthly mean DMS mixing ratios during the summer and autumn (Figure 2b).

The model predicts an annual bromine source from sea salt of $0.57 \text{ Tg Br yr}^{-1}$ for run **Br**. This source is distributed with 0.29 Tg Br in the NH and 0.28 Tg Br in the SH. Sea salt emissions are much higher in the SH, hence the release of bromine is greater per kg of sea salt emitted in the NH because of the high available acidity from anthropogenic NO_x and SO_2 sources.

Figure 3 shows the total column of BrO in the troposphere in January. The model estimates roughly $0.5\text{-}1.25\times 10^{13}$ cm^{-2} of troposphere column BrO in the mid-latitudes, which is in agreement with GOME observations of 1.0×10^{13} cm^{-2} of BrO in the troposphere [Van Roozendael et al., 2002]. At high latitudes the model underestimates tropospheric column BrO ($0.5\text{-}0.75\times 10^{13}$ cm^{-2}) compared to GOME ($2.0\text{-}3.0\times 10^{13}$ cm^{-2}). This is because we do not include a sea-ice source of bromine [Yang et al., 2008]. In the SH low latitudes the model appears to overestimate the troposphere column BrO possibly due to an underestimate in wet deposition in these regions. Figure 3c shows the model January mean surface BrO mixing ratio at 10:30am local time. The model estimates 0.2 to 1.0 pmol mol^{-1} BrO throughout the open oceans, with maximum a mixing ratio of 1.2 pmol mol^{-1} in the SH oceans.

3.2. Impact of BrO on DMS

As a global annual average (for 2004) we find that BrO contributes 16% of the total DMS sink in run **Br**. This is comparable to NO_3 (24%), but less than OH (60%). We observe a decrease in the global DMS burden of 18% from 0.041 Tg S in run **NOBr** to 0.034 Tg S in run **Br**. Both burden values are lower than the 0.063 Tg S estimated by Berglen et al., [2004]. This difference can be explained mainly by the larger DMS source in the Berglen et al., [2004] study.

The BrO + DMS reaction is most active in the MBL due to surface sources of bromine and DMS. We find oxidation of DMS at the surface increases by 18% in run **Br** and the global mean DMS lifetime decreases from 1.47 days in run **NOBr** to 1.21 days in run **Br**.

Figure 4 shows the annual mean contribution of OH abstraction, OH addition, NO_3 and BrO to the total DMS oxidation in run **Br**. Panel 4d shows that in coastal areas and in the high NO_x outflow areas of the North Atlantic, BrO contributes less than 10% of the annual DMS oxidant sink. Around coastlines the low contribution of BrO to DMS oxidation is explained by the simulated low BrO mixing ratios (Figure 3c). In the NO_x outflow regions of the NH, high NO_3 concentrations represent the dominate sink for DMS (Figure 4c).

In the tropics we find BrO contributes approximately 11% of the annual DMS oxidation sink. In this region the increased abundance of water vapour and ample year-round sunlight supports higher OH concentrations. The high OH and the presence of increased levels of NO_3 from primary NO_x sources out compete BrO for reaction with DMS. Figure 4a shows that in the tropics, outside coastal areas, DMS oxidation is dominated by OH.

Figure 4d shows the largest contribution from BrO is in the SH south of 40° . Throughout the $40^\circ - 70^\circ\text{S}$ latitude band over 20% of the annual DMS sink is due to BrO. In high DMS regions ($70^\circ\text{S}, 135^\circ\text{W}$) (Figure 1) this can be up to 50%. This large BrO oxidation of DMS is in agreement with von Glasow et al., [2004b], who also found the largest BrO contribution in regions of high DMS emission.

At Amsterdam Island and Cape Grim we observe a decrease in monthly mean DMS mixing ratios of 10-20% in run **Br** compared to run **NOBr** in the summer and autumn (Figure 2). The small difference between runs **NOBr** and **ORGBr** in Figure 2, suggests that non-local emissions of organic bromine are not important for DMS oxidation at these

two sites. Throughout the SH oceans monthly mean DMS mixing ratios are 10-20% lower in the SH summer and autumn in run **Br** compared to run **NOBr**.

There are a number of factors why BrO is more important for DMS oxidation in the SH remote ocean. First, the low NO_x levels do not make NO_3 a competitive sink for DMS south of 40°S (Figure 4c). Second, the nighttime bromine reservoir Br_2 is photolysed at longer wavelengths than O_3 . Under low NO_x conditions BrO concentrations are sustained for a longer period than OH [von Glasow et al., 2002]. A third factor is that DMS source regions may also be areas of elevated bromine emission from sea salt. As wind speeds are high in the SH remote ocean there is an abundant source of sea salt. The limiting factor is the available acidity. In clean remote marine regions away from anthropogenic and volcanic emissions, the dominant source of SO_2 is DMS. Hence, the emission of DMS may control the release of bromine from the aerosol. This could represent a mechanism through which DMS regulates its own lifetime by controlling its oxidation sink. Clearly this marine aerosol feedback could have important implications for our understanding of DMS and its impact on CCN.

To assess the importance of this mechanism we can compare the sea salt bromine source between runs **Br** and **BrNi**. Run **BrNi**, has a higher DMS source by a factor 2 than run **Br** and gives a global DMS burden of 0.1 Tg S and DMS lifetime 1.70 days which is within the range of published values [Spracklen et al., 2005]. In the SH summer the sea salt bromine source is 50 - 60% larger in the **BrNi** simulation. Only a small increase was simulated during the rest of the year. No sensitivity was simulated in the NH and tropics which can be explained by the DMS source of SO_2 representing only a small

fraction of the available gas phase acidity in these regions. In run **BrNi** the annual mean contribution of BrO to the DMS sink increased to 22%. Interestingly, the $\text{NO}_3 + \text{DMS}$ pathway decreased to 19% as higher DMS concentrations increased removal of NO_3 via HNO_3 deposition. Increased BrO in the **BrNi** simulation also decreases surface O_3 by 2-3% over the SH oceans. The resulting reduction in OH formation from O_3 photolysis decreases surface OH by 2-3%. The perturbation in OH from this BrO/ O_3 /OH feedback is of minor importance for DMS compared to the large increase in BrO.

In addition we find the inclusion of bromine chemistry reduces the sensitivity of the DMS lifetime to increases in the DMS flux. The globally averaged DMS lifetime increased by 60% between runs **NOBr** and **NOBrNi** compared to only a 40% increase between run **Br** and run **BrNi**.

4. Discussion and Summary

Overall our model simulations show a significant impact of bromine chemistry on the DMS distribution, burden and lifetime. We find BrO contributes up to 50% of the DMS sink in the SH remote oceans. The model results show BrO is less important around coastlines due to low surface BrO mixing ratios. Also, we find the importance of BrO for DMS is low in the NH because of high NO_x pollution and in the tropics due to high OH concentrations.

Our study also shows when the DMS source is increased by a factor 2, SH sea salt bromine emissions increase by up to 60% because of the extra aerosol acidity. We find because of this feedback the inclusion of bromine chemistry reduces the sensitivity of the DMS lifetime to increases in the DMS flux. Model studies that ignore the DMS-BrO

feedback will likely overestimate the DMS lifetime and transport of DMS to the free troposphere, particularly in high DMS source regions in the remote SH oceans.

These results emphasize the need for an improved network of seawater and atmosphere DMS concentrations. A wider network of measurements of BrO concentrations and sea salt bromide depletions is required to improve our understanding of reactive bromine chemistry. There also remains potential for improvement in aerosol phase cycling and treatment of bromine release from sea salt.

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Figure 1. Annual mean surface DMS mixing ratio (pmol mol^{-1}) for 2004 from simulation **Br**.

Figure 2. Monthly mean observed and modeled DMS mixing ratio (pmol mol^{-1}) at (a) Amsterdam Island (37.83°S , 77.50°E) [Nguyen et al., 1992] and (b) Cape Grim (40.68°S , 144.68°E) [Ayers et al., 1991]. Observations indicated by crosses.

Figure 3. BrO troposphere total column density ($\times 10^{13}$ molecules cm^{-2}) at 10:30am local time from (a) GOME satellite (Jan 2000) and (b) model run **Br** (Jan 2004). Panel (c) shows January mean surface BrO mixing ratio (pmol mol^{-1}) at 10:30am local time.

Model Simulation	DMS Burden (Tg S)	DMS lifetime (days)
Br	0.034	1.21
NOBr	0.041	1.47
ORGBr	0.040	1.42
BrNi	0.100	1.70
NOBrNi	0.130	2.34

Table 1. 2004 annual mean global DMS burden and DMS lifetime for each simulation

Figure 4. Annual mean % contribution to DMS oxidation in run **Br** from (a) OH abstraction, (b) OH addition, (c) NO₃ and (d) BrO.







