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RESEARCH LETTER

10.1002/2017GL073812

Key Points:

- Inclusion of HOBr + S(IV) reactions in the model reduces global tropospheric Br<sub>y</sub> burden by 50%
- Large fraction of sulfate is produced via HOBr oxidation in the presence of clouds and high HOBr abundance over low-latitude oceans
- In-cloud sulfate production via HOBr oxidation does not necessarily result in less gas-phase SO<sub>2</sub> oxidation

Supporting Information:

- Supporting Information S1

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## Sulfate production by reactive bromine: Implications for the global sulfur and reactive bromine budgets

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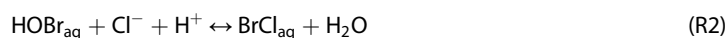
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**Abstract** Sulfur and reactive bromine (Br<sub>y</sub>) play important roles in tropospheric chemistry and the global radiation budget. The oxidation of dissolved SO<sub>2</sub> (S(IV)) by HOBr increases sulfate aerosol abundance and may also impact the Br<sub>y</sub> budget, but is generally not included in global climate and chemistry models. In this study, we implement HOBr + S(IV) reactions into the Goddard Earth Observing System-Chem global chemical transport model and evaluate the global impacts on both sulfur and Br<sub>y</sub> budgets. Modeled HOBr mixing ratios on the order of 0.1–1.0 parts per trillion (ppt) lead to HOBr + S(IV) contributing to 8% of global sulfate production and up to 45% over some tropical ocean regions with high HOBr mixing ratios (0.6–0.9 ppt). Inclusion of HOBr + S(IV) in the model leads to a global Br<sub>y</sub> decrease of 50%, initiated by the decrease in bromide recycling in cloud droplets. Observations of HOBr are necessary to better understand the role of HOBr + S(IV) in tropospheric sulfur and Br<sub>y</sub> cycles.

### 1. Introduction

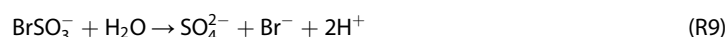
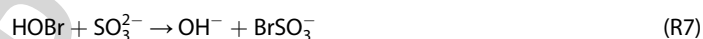
Reactive bromine (Br<sub>y</sub> = BrO + Br + Br<sub>2</sub> + HOBr + BrCl + HBr + BrNO<sub>3</sub> + BrNO<sub>2</sub>) has multiple impacts on tropospheric chemistry, including O<sub>3</sub> depletion, HO<sub>x</sub> and NO<sub>x</sub> perturbations, and oxidation of reduced sulfur species, volatile organic compounds (VOCs), and mercury [Vogt *et al.*, 1996; von Glasow *et al.*, 2004; Parrella *et al.*, 2012; Simpson *et al.*, 2015; Schmidt *et al.*, 2016]. The O<sub>3</sub> destruction driven by Br<sub>y</sub> and the oxidation of SO<sub>2</sub> and VOCs by Br<sub>y</sub> to produce sulfate and organic aerosols have implications for the radiative balance of the atmosphere and thus climate [von Glasow *et al.*, 2002; Saiz-Lopez *et al.*, 2012; Ofner *et al.*, 2012]. Box and 1-D modeling studies suggest that aqueous-phase oxidation of dissolved SO<sub>2</sub> (S(IV) = HSO<sub>3</sub><sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) by HOBr accounts for ~20% of sulfate production in the marine boundary layer (MBL) [Vogt *et al.*, 1996; von Glasow *et al.*, 2002]. This reaction is not included in global models of atmospheric chemistry due to uncertainties in reaction rates, which stem mainly from uncertainties in the abundance of HOBr [Chen *et al.*, 2016]. Recently, Chen *et al.* [2016] provided the first observational constraint on the importance of HOBr/HOCl + S(IV) for sulfate production in the remote, Southern Hemisphere MBL in spring and summer and found that hypohalous acids are responsible for 33–50% of sulfate formation. No studies have examined the implications of these reactions on the tropospheric Br<sub>y</sub> budget.

The main sources of tropospheric Br<sub>y</sub> are oxidation (by OH) and photolysis of bromocarbons (CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, and CHBr<sub>3</sub>) and sea salt aerosol (SSA) debromination [Parrella *et al.*, 2012; Carpenter *et al.*, 2014]. In polar regions, debromination has been proposed to occur on halide surface such as frost flowers [Rankin *et al.*, 2002], first-year sea ice [Simpson *et al.*, 2007a], blowing snow [Yang *et al.*, 2008], and snowpacks above tundra and first-year sea ice [Pratt *et al.*, 2013]. In addition, Br<sub>y</sub> is transported from the stratosphere to the troposphere, but this source is minor globally [Schmidt *et al.*, 2016]. SSA debromination is thought to occur via uptake of HOBr followed by acid-catalyzed heterogeneous reaction with sea salt Br<sup>-</sup> and Cl<sup>-</sup> (R1)–(R6) [Fan and Jacob, 1992; Vogt *et al.*, 1996] to produce Br<sub>2</sub> (~90%) and BrCl (~10%) [Fickert *et al.*, 1999]. Br<sub>y</sub> is mainly removed from the troposphere via wet and dry deposition to the Earth's surface and uptake by SSA to form Br<sup>-</sup> [Schmidt *et al.*, 2016].





HOBr serves as one of the most abundant Br<sub>y</sub> reservoirs in the troposphere during daytime, with modeled global tropospheric annual mean mixing ratio on the order of 0.1–1 parts per trillion (ppt = pmol/mol) [Fernandez *et al.*, 2014; Schmidt *et al.*, 2016]. Observations of HOBr abundance in the troposphere are sparse, with daytime concentrations ranging from 2 ppt (flight tracks over the tropical Western Pacific) [Le Breton *et al.*, 2017] to 10 ppt (surface observations in Alaska) [Liao *et al.*, 2012]. The effective Henry's law constant of HOBr ( $H_{\text{HOBr}}$ ) is estimated to be between 93 and 6100 M atm<sup>-1</sup> [Sander, 2015; Chen *et al.*, 2016], so that >90% of HOBr is present in the gas phase even in the cloudy MBL. The small fraction of HOBr dissolved in aerosol or cloud liquid water reacts with Cl<sup>-</sup> and Br<sup>-</sup> to produce Br<sub>2</sub> and BrCl, rapidly recycling reactive bromine (R1)–(R6), and with S(IV) to produce sulfate (R7)–(R9) [Troy and Margerum, 1991; Liu, 2000].



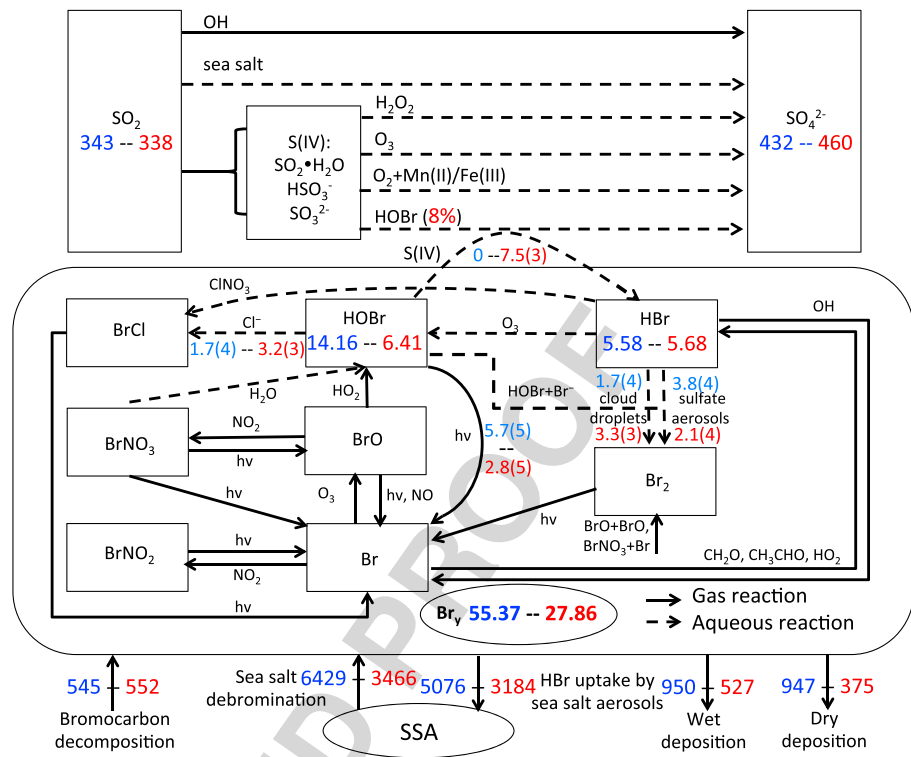
In this study, we implement HOBr + S(IV) in Goddard Earth Observing System (GEOS)-Chem to investigate the effects of these reactions on both the sulfur and Br<sub>y</sub> budgets.

## 2. GEOS-Chem Model

The model used in this study, GEOS-Chem v9-02, driven by GEOS-5 assimilated meteorological data from the NASA Goddard Earth Observing System, is a global three-dimensional chemical transport model (<http://www.geos-chem.org/>) of coupled aerosol-oxidant chemistry containing detailed HO<sub>x</sub>-NO<sub>x</sub>-VOC-ozone-BrO<sub>x</sub> tropospheric chemistry [Schmidt *et al.*, 2016]. All simulations were performed at 4° × 5° horizontal resolution and 47 vertical levels up to 0.01 hPa. In order to compare the reactive bromine results presented in this study with those in Parrella *et al.* [2012] and Schmidt *et al.* [2016], we run all simulations for the year 2007, after spinning up the model for 1 year (2006). We run two main simulations: (i) without HOBr + S(IV) reactions, (ii) with HOBr + S(IV) reactions, and several sensitivity simulations by modifying sulfur emissions, SSA, and cloud properties to examine the effects of model uncertainties on the impacts of HOBr + S(IV) on tropospheric sulfur and Br<sub>y</sub> budgets (Table S3 in the supporting information).

In the model, sulfate is produced via gas-phase oxidation of SO<sub>2</sub> by OH; in-cloud aqueous-phase oxidations of S(IV) by H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and O<sub>2</sub> catalyzed by the transition metals iron and manganese [Park *et al.*, 2004; Alexander *et al.*, 2009, 2012]; and oxidation of S(IV) by O<sub>3</sub> on SSA [Alexander *et al.*, 2005]. The bulk cloud water pH is calculated as described in Alexander *et al.* [2012]. In this study, we have added in-cloud HOBr + S(IV) reactions to the model assuming first-order loss of HOBr via uptake by cloud droplets:

$$-\frac{d[\text{SO}_4^{2-}]}{dt} = \frac{d[\text{HOBr}]}{dt} = -\frac{c\gamma}{4} S[\text{HOBr}]$$



**Figure 1.** The global model budgets of tropospheric sulfur and Br<sub>y</sub> for simulations without (blue color) and with (red color) HOBr + S(IV). Inventories (inside the boxes) are in units of Gg S for sulfur and Gg Br for Br<sub>y</sub>. The solid arrows represent gas-phase reactions, while the dashed arrows represent aqueous-phase reactions. Production rates and loss rates of Br<sub>y</sub> (below the big box) are in units of Gg Br a<sup>-1</sup>. Loss rates for HOBr (next to the arrows) are in units of Gg Br a<sup>-1</sup>. Read 7.5(3) as 7.5 × 10<sup>3</sup>. HOBr + S(IV) accounts for 8% of sulfate production.

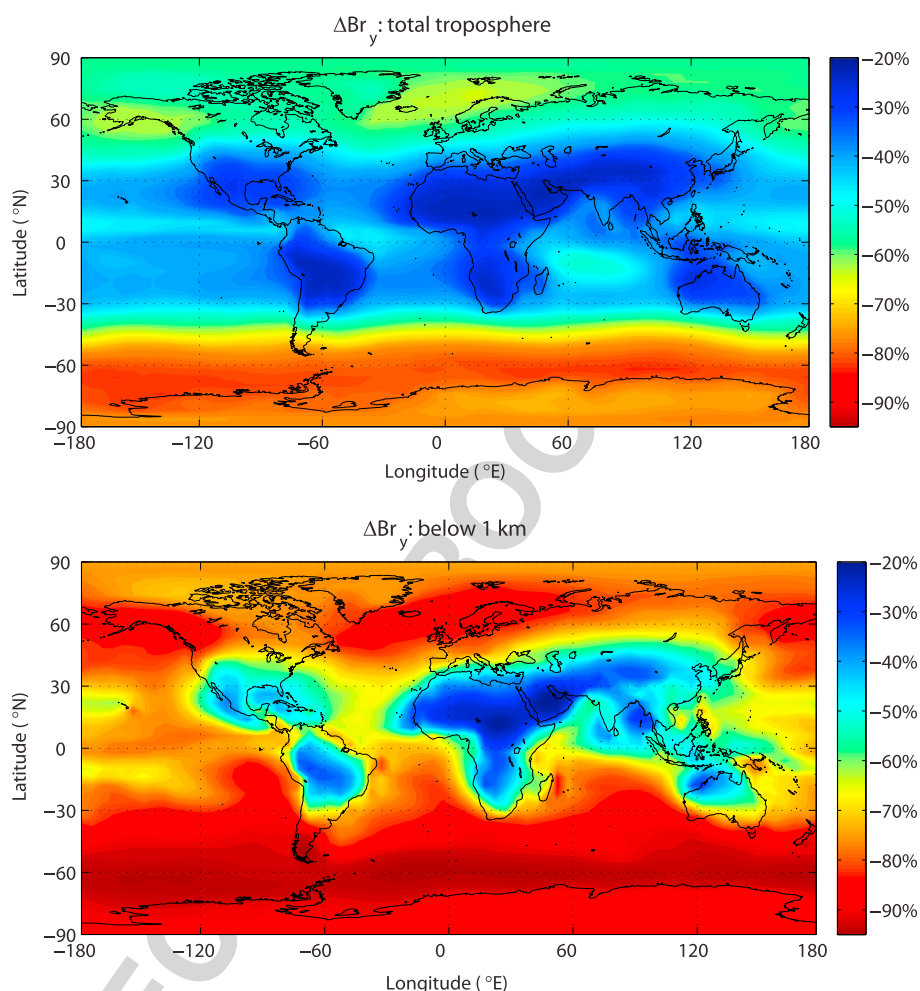
where  $\gamma$  (unitless) is the reactive uptake coefficient of HOBr that involves gas diffusion, mass accommodation, and chemical reaction in the cloud droplets;  $c$  is the average thermal velocity of HOBr (unit: cm s<sup>-1</sup>);  $S$  is the total surface area concentration of cloud droplets (unit: cm<sup>2</sup> cm<sup>-3</sup>). The reaction rate coefficient for the HOBr + HSO<sub>3</sub><sup>-</sup> reaction ( $k_{\text{HOBr}+\text{HSO}_3^-}$ ) and the HOBr + SO<sub>3</sub><sup>2-</sup> reaction ( $k_{\text{HOBr}+\text{SO}_3^{2-}}$ ) is 3.2 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> [Liu, 2000] and 5.0 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> [Troy and Margerum, 1991], respectively. More details about the implementation of HOBr + S(IV) in the model are shown in the supporting information. We neglect HOBr + S(IV) on SSA since most HOBr will react with Cl<sup>-</sup> in SSA due to the much higher aqueous-phase concentration of Cl<sup>-</sup> (SI).

We use the tropospheric bromine mechanism described by Schmidt et al. [2016]. SSA debromination via oxidation of Br<sup>-</sup> by HOBr, O<sub>3</sub>, and ClNO<sub>3</sub> on SSA was enabled as a sensitivity study in Schmidt et al. [2016] and is used in this study. There is no snow source of Br<sub>y</sub> in the model.

### 3. Results and Discussion

#### 3.1. Effects of HOBr + S(IV) Reactions on the Tropospheric Br<sub>y</sub> Budget

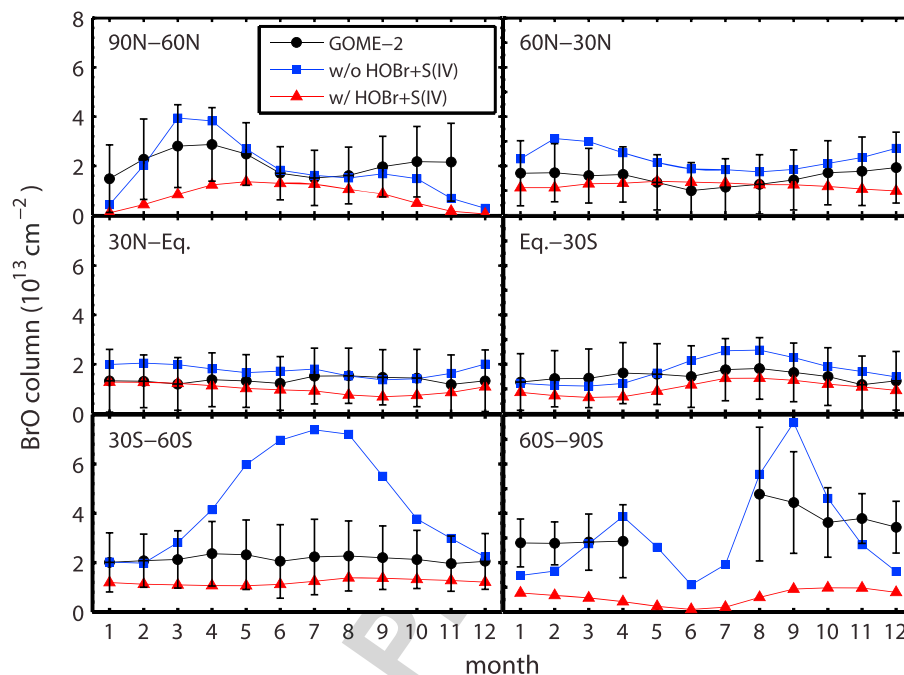
Figure 1 shows the comparison of the tropospheric Br<sub>y</sub> budgets between simulations with and without HOBr + S(IV). The modeled Br<sub>y</sub> burden decreases by 50% after adding HOBr + S(IV) (additional sink of HOBr), initiated by the large (55%) decrease in HOBr abundance. The decrease in HOBr abundance in turn decreases SSA debromination, as more than 90% of SSA debromination occurred via reaction of HOBr with Br<sup>-</sup> in sea salt aerosols (Br<sub>SSA</sub><sup>-</sup>) (R1)–(R6) before adding HOBr + S(IV) to the model. The global Br<sub>y</sub> production rate from SSA debromination is 6429 Gg Br a<sup>-1</sup> and 3466 Gg Br a<sup>-1</sup> for simulations without and with HOBr + S(IV), respectively, with the latter magnitude closer to previous modeling estimates of 1150–2900 Gg Br a<sup>-1</sup> [Yang et al., 2005; Parrella et al., 2012; Fernandez et al., 2014; Schmidt et al., 2016]. Global



**Figure 2.** Percentage decrease in modeled annual mean  $Br_y$  burden in the (top) troposphere and (bottom) below 1 km after adding HOBr + S(IV).

bromocarbon decomposition rates are  $545 \text{ Gg Br a}^{-1}$  and  $552 \text{ Gg Br a}^{-1}$  for simulations without and with HOBr + S(IV), respectively, which is similar to recent global estimates ( $520\text{--}550 \text{ Gg Br a}^{-1}$ ) [Parrella *et al.*, 2012; Schmidt *et al.*, 2016]. The small difference between the two simulations is due to higher OH concentrations in the model after adding HOBr + S(IV) due to lower  $Br_y$ , as discussed below. The decrease in HBr uptake by SSA, despite the slight increase in tropospheric burden of HBr, is because this process occurs mainly in the MBL where HBr abundance decreases (Figure S1 in the supporting information).

The addition of HOBr + S(IV) in the model lowers the burdens of all  $Br_y$  species, except HBr, by 28–75% (Table S1). The slight increase in HBr burden is due to the decrease in HBr removal by HOBr and the production of HBr (which is in equilibrium with  $Br^-$  in cloud droplets) from HOBr + S(IV) (R7)–(R9). HOBr + S(IV) competes with HOBr +  $Br^-$  in cloud droplets such that less HOBr is available for oxidizing  $Br^-$  to produce  $Br_2$ . In our simulation with HOBr + S(IV), the amount of HOBr removed by reactions with S(IV) is 4.5 times that removed by reaction with  $Br^-$  in cloud droplets. This lowers the Br radical production rate, resulting in reductions in BrO and HOBr abundance. The lower HOBr abundance results in slower bromide recycling in both cloud droplets and sulfate aerosols. The lower HOBr abundance also results in even lower debromination from SSA, which is the largest source of  $Br_y$  in the lower troposphere. Previous studies have also shown that the bromine recycling on aerosols and cloud droplets (HOBr +  $Br^-$ ) is critical for sustaining high  $Br_y$  levels in the troposphere [von Glasow *et al.*, 2004; Yang *et al.*, 2010; Parrella *et al.*, 2012; Schmidt *et al.*, 2016]. In particular, Parrella *et al.* [2012] reported a factor of 2 decrease in BrO mixing ratios when they turned off the HOBr +  $Br^-$  heterogeneous reaction in the model.



**Figure 3.** Comparison of modeled tropospheric BrO column with GOME-2 satellite observations of tropospheric BrO column (09:00–10:00) from *Theys et al.* [2011]. The error bars in the observations represent one standard deviation of spatial averaging.

Figure 2 shows the global annual mean distribution of percentage decreases in  $Br_y$  burden ( $\Delta Br_y$ ) in the total troposphere (Figure 2, top) and below 1 km (Figure 2, bottom) after adding HOBr + S(IV). The spatial pattern of the magnitude of the decrease in  $Br_y$  depends mainly on the amount of clouds for HOBr + S(IV) to occur and SSA abundance for debromination. In general, cloud fraction and cloud liquid water content (LWC) are high over the equator and high-latitude oceans such as Southern Ocean and low over the subtropics [*Molod et al.*, 2012; *Sud et al.*, 2013], while SSA burden is high over subtropics and high-latitude oceans and lower elsewhere [*Jaeglé et al.*, 2011]. Consequently, large decreases in  $Br_y$  occur over high-latitude oceans, especially Southern Ocean. A large decrease of  $Br_y$  over high-latitude oceans results in a large decrease of  $Br_y$  in polar regions from where  $Br_y$  is mainly transported. Note that there is no snow source of  $Br_y$  in the model. In the subtropics,  $Br_y$  is not as sensitive to HOBr + S(IV) because of low cloud amount, regardless of the high SSA abundance. In the lower troposphere (below 1 km), the decrease in  $Br_y$  is more significant, as HOBr + S(IV) mainly occur in the lower troposphere where clouds are present. The difference in  $\Delta Br_y$  between low-latitude oceans and high-latitude oceans for the total troposphere is larger than that for MBL below 1 km, as upper troposphere  $Br_y$  reduction is smaller at low latitudes due to higher bromocarbon decomposition rates.

Figure 3 shows a comparison of modeled tropospheric BrO column with Global Ozone Monitoring Experiment (GOME)-2 satellite observations of tropospheric BrO column from *Theys et al.* [2011]. The addition of HOBr + S(IV) lowers modeled tropospheric BrO column globally throughout the year, with the impact increasing with increasing latitude. At low latitudes (30°S–30°N), the modeled BrO column is generally biased high for simulation without HOBr + S(IV) and biased low for the simulation with HOBr + S(IV), although both simulations are within the range of the observations. The addition of HOBr + S(IV) improves agreement with observations at midlatitudes (30°–60°). At high latitudes (60°–90°), the addition of HOBr + S(IV) causes the model to underestimate the observations by 60–80% (annual mean), where prior to adding HOBr + S(IV) the model underestimated the observations by only 7% at 90°–60°N and overestimated the observations by 2% at 60°S–90°S (annual mean). We expect the model to significantly underestimate observed BrO at high latitudes due to the lack of debromination in polar regions [*Simpson et al.*, 2007b]. We also note that the model does not include reactive iodine chemistry and includes very simple gas phase reactive chlorine



chemistry. Addition of reactive iodine and chlorine chemistry to the model will likely increase modeled BrO (and Br<sub>y</sub>) abundances through Cl-Br-I interactions such as reactions of HOCl, HOI, ICl, and IBr with Br<sup>-</sup> in aerosols and cloud droplets to sustain more efficient Br<sub>y</sub> recycling [Vogt *et al.*, 1999; Ammann *et al.*, 2013; Sherwen *et al.*, 2016]. We expect this impact to be larger over midlatitude and high-latitude oceans where SSA abundance is high and clouds are frequent.

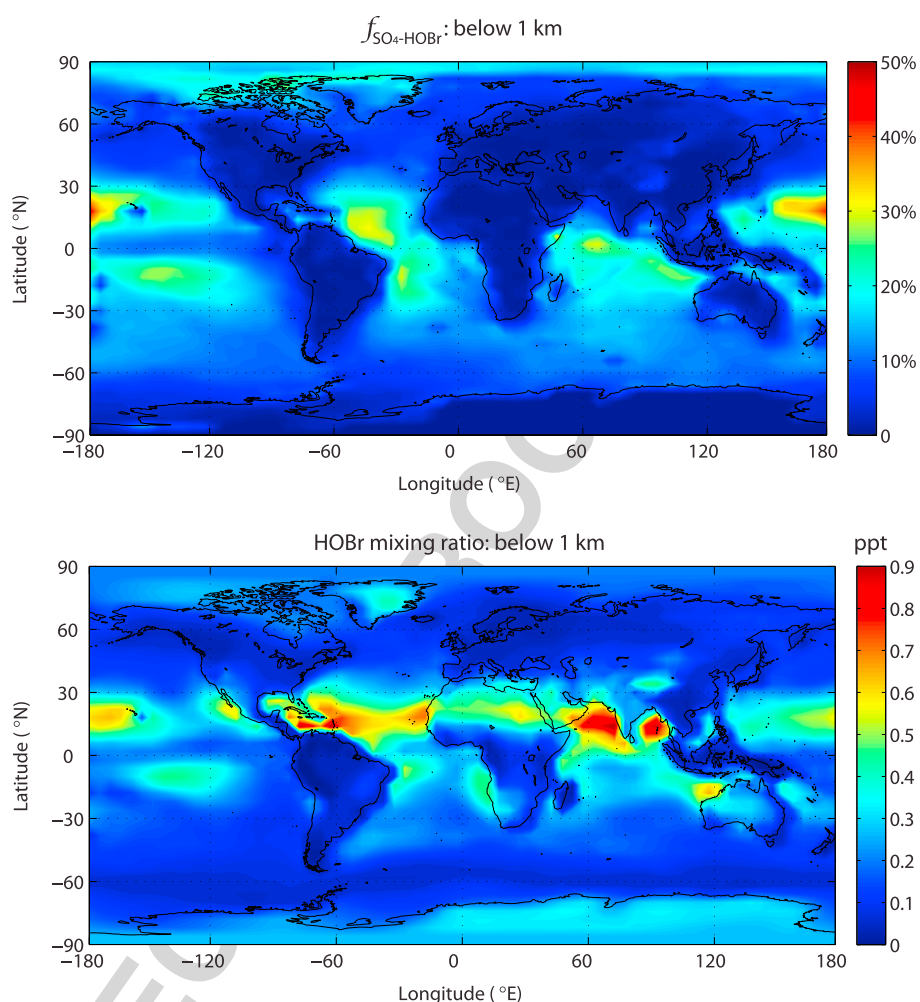
### 3.2. Effects of HOBr + S(IV) Reactions on the Tropospheric Sulfur Budget

Adding HOBr + S(IV) to the model increases both the global sulfate production rate and global sulfate burden by 6% (Figure 1). The global SO<sub>2</sub> burden decreases by only 2%, owing to the enhanced SO<sub>2</sub> production from oxidation of dimethyl sulfide (DMS) by OH. The global annual mean tropospheric OH concentration increases by 5% in the simulations with HOBr + S(IV) due to reductions in Br<sub>y</sub>, resulting in an increase in the DMS oxidation rate by 6%. Vogt *et al.* [1996] suggested that oxidation of S(IV) by HOBr and HOCl on preexisting particles reduces the amount of SO<sub>2</sub> available for gas-phase oxidation and the formation of new cloud-condensation nuclei (CCN). The increase of OH abundance caused by reductions in Br<sub>y</sub> after adding HOBr + S(IV) to the model, which was not considered in Vogt *et al.* [1996], could mitigate this CCN reduction effect via enhancing the SO<sub>2</sub> production rate from oxidation of DMS by OH. In our study, the change in the global sulfate production rate via the gas-phase reaction SO<sub>2</sub> + OH is negligible (<1%) after adding HOBr + S(IV) in the model.

For the model simulation with HOBr + S(IV), oxidation of S(IV) by HOBr accounts for 8% of sulfate production globally, mostly 96% via the HOBr+HSO<sub>3</sub><sup>-</sup> channel as HSO<sub>3</sub><sup>-</sup> is the dominant S(IV) species (>93%) in clouds at typical marine cloud pH between 3 and 6 [Faloona, 2009]. The corresponding tropospheric mean HOBr mixing ratio is about 0.4 ppt. In contrast, using the coupled chemistry-global climate model Community Atmosphere Model v4.6.33, Long *et al.* [2014] found that HOBr + S(IV) accounts for <1% of tropospheric sulfate formation globally (0.8% in clouds and 0.2% on SSA), despite similar HOBr mixing ratios (~0.3 ppt). A possible reason that Long *et al.* [2014] shows a small HOX + S(IV) contribution to sulfate formation could be that cloud chemistry is computed after gas phase chemistry in their model so that there is not a continuous supply of HOBr from the gas to the aqueous phase within the chemistry time step, as shown in their companion paper [Long *et al.*, 2013]. HOBr + S(IV) in cloud droplets in our study is coupled with gas phase chemistry, allowing for a continuous supply of HOBr produced from gas-phase reactions (e.g., BrO + HO<sub>2</sub>). To confirm this explanation, we performed one sensitivity study in which HOBr + S(IV) in clouds was computed separately after gas phase chemistry and found that HOBr + S(IV) accounts for about 1% of sulfate formation globally, consistent with Long *et al.* [2014].

The percentage of sulfate produced from HOBr + S(IV) ( $f_{\text{SO}_4\text{-HOBr}}$ ) varies from 0 to 45% (Figure 4a) in the lower troposphere, depending on a variety of factors including the abundance of different oxidants (mainly OH, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and HOBr), cloud fraction, cloud pH, and the concentrations of Cl<sup>-</sup> and Br<sup>-</sup> in cloud droplets that compete with HOBr + S(IV). In general,  $f_{\text{SO}_4\text{-HOBr}}$  is smaller than 5% over the continents due to relatively low cloud fraction, high H<sub>2</sub>O<sub>2</sub>, and relatively low HOBr mixing ratios. Over the tropical oceans,  $f_{\text{SO}_4\text{-HOBr}}$  reaches up to 45% where HOBr mixing ratios are high (Figure 4b). Higher HOBr mixing ratios do not guarantee higher  $f_{\text{SO}_4\text{-HOBr}}$  however. Over the Arabian Sea west of India, the HOBr mixing ratio reaches about 0.8 ppt, but  $f_{\text{SO}_4\text{-HOBr}}$  is only about 10% due to the limited amount of clouds. Over the South Atlantic Ocean west of Angola ([0°–20°S, 0°–20°E]), the HOBr mixing ratio reaches about 0.5 ppt, but  $f_{\text{SO}_4\text{-HOBr}}$  is only about 15% due to relatively high H<sub>2</sub>O<sub>2</sub> abundance.

Observations and calculations from Chen *et al.* [2016] suggested that 33–50% of sulfate in the Southern Hemisphere MBL during austral spring and summer (November–March) is produced via oxidation of S(IV) by HOBr and HOCl, suggesting daily mean HOBr + HOCl mixing ratio on the order of 0.01–0.1 ppt. In comparison, our model results show that only 7% of sulfate is produced via HOBr + S(IV) over the Southern Hemisphere MBL below 1 km during austral spring and summer, with a daily mean HOBr mixing ratio of 0.15 ppt. The difference in the calculated importance of S(IV) oxidation by hypohalous acids in these two studies, despite similar order-of-magnitude estimates of hypohalous acid abundance, is due to the fact that the gas-phase diffusion limitation of HOBr and HOCl was not considered in Chen *et al.* [2016] when calculating aqueous-phase production rates. Aqueous-phase reactions of HOBr with Cl<sup>-</sup>, Br<sup>-</sup>, and S(IV) are very rapid so that uptake of HOBr on the cloud droplets is limited by gas diffusion. Additionally, after HOBr enters the cloud droplets, Cl<sup>-</sup> and Br<sup>-</sup> remove HOBr and limit the availability of HOBr available for S(IV) oxidation.



**Figure 4.** Global distribution of the percentage of annual mean sulfate produced via (top) HOBBr oxidation ( $f_{\text{SO}_4\text{-HOBr}}$ ) and (bottom) HOBBr mixing ratio below 1 km for the model simulations with HOBr + S(IV).

The modeled underestimate of BrO (Figure 3), especially in the high southern latitudes, suggests that the modeled underestimate of the fraction of sulfate produced from HOBr and HOCl is due to a modeled low bias in HOBr, in addition to the lack of S(IV) oxidation by HOCl in the model.

#### 4. Implications

The large impacts of HOBr + S(IV) on the reactive bromine budget in the model have further implications for the oxidation capacity of the atmosphere via its impacts on the burden of  $\text{O}_3$  and the partitioning of  $\text{HO}_x$  ( $\text{OH} + \text{HO}_2$ ) and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) [von Glasow *et al.*, 2004]. Reactive bromine destroys  $\text{O}_3$  through the Br-BrO cycle. A 50% reduction of  $\text{Br}_y$  burden after adding HOBr + S(IV) results in a 5 ppb increase in global mean tropospheric  $\text{O}_3$  (up to 10 ppb over Southern Ocean and Antarctica). Reactive bromine perturbs  $\text{HO}_x$  partitioning via  $\text{BrO} + \text{HO}_2$  to produce HOBr and subsequent photolysis of HOBr to produce Br and OH. Based on this, a reduction of  $\text{Br}_y$  burden after adding HOBr + S(IV) should result in a decrease in OH. However, this effect is compensated by the increase in  $\text{O}_3$ . As such, tropospheric OH abundance increases by 5% after adding HOBr + S(IV). This is consistent with the previous finding that the impact of  $\text{Br}_y$  on OH occurs mainly via the  $\text{O}_3$  destruction channel rather than the  $\text{HO}_2$  conversion by BrO channel [Parrella *et al.*, 2012; Wang *et al.*, 2015]. Reactive bromine removes  $\text{NO}_x$  via  $\text{BrO} + \text{NO}_2$  to produce  $\text{BrNO}_3$  and subsequent hydrolysis of  $\text{BrNO}_3$  to produce nitrate. After adding HOBr + S(IV), tropospheric  $\text{NO}_x$  burden



increases by 3% globally, up to 90% over Southern Ocean, although the absolute abundance of  $\text{NO}_x$  is very low in this region (several parts per trillion).

The important role of  $\text{HOBr} + \text{S(IV)}$  on the  $\text{Br}_y$  budget suggests that changes in sulfur emissions could impact the oxidative capacity of the troposphere. We conduct two sensitivity studies using our model simulations with  $\text{HOBr} + \text{S(IV)}$  to examine potential impacts of changes in sulfur emissions on  $\text{Br}_y$  and oxidant budgets. First, we examine the impacts of anthropogenic emissions of sulfur by switching off anthropogenic sulfur emissions in the model, which reduces the total emissions of sulfur ( $\text{SO}_2 + \text{DMS}$ ) by 73%. The change in the  $\text{Br}_y$  burden is less than 1% globally, with regional increases up to 5% over China and regional decrease up to 4% over the north Indian Ocean. The change in tropospheric  $\text{O}_3$  mixing ratio is less than 1.1 ppb everywhere. The small change in  $\text{Br}_y$  and oxidant budgets when turning off anthropogenic sulfur emissions is due to the fact that most anthropogenic emissions occur over continents where  $\text{HOBr}$  is relatively low and clouds are few, and because the resulting increase in cloud pH due to a reduction in  $\text{SO}_2$  emissions slows down the acid-catalyzed  $\text{HOBr} + \text{Br}^-$  reaction in cloud droplets. In a second sensitivity simulation, we examine the impact of changing sulfur emissions on tropospheric  $\text{Br}_y$  and oxidant budgets during preindustrial times by doubling DMS emission together with turning off anthropogenic sulfur emissions in the model. The change in  $\text{Br}_y$  burden is also less than 1% globally, with regional increases up to 3% over Southern Ocean where pH decreases by 0.4 and regional decrease up to 2% over some Northern Hemisphere ocean regions where pH decreases by less than 0.2. Thus, changes in sulfur emissions have a small impact on the global  $\text{Br}_y$  budget due to compensating effects of changes in the sink of  $\text{HOBr}$  (via  $\text{HOBr} + \text{S(IV)}$ ) and changes in the acid-catalyzed production rate of  $\text{Br}_y$  (R1)–(R6). This emphasizes the importance of explicitly considering changes in cloud pH when evaluating potential impacts on changing emissions on the global  $\text{Br}_y$  budget. It should be noted from Figure 1 that a change in cloud pH after adding  $\text{HOBr} + \text{S(IV)}$  in the model is negligible in this study as the sulfate burden change is only 6%.

Other sensitivity scenarios (Table S3) examining the importance of model uncertainties on the impacts of  $\text{HOBr} + \text{S(IV)}$  include doubling SSA emission, doubling SSA bromide concentrations ( $[\text{Br}_{\text{SSA}}^-]$ ), reducing coarse-mode SSA pH by two units, reducing  $k_{\text{HOBr}+\text{HSO}_3^-}$  by 2 orders of magnitude, doubling cloud LWC, reducing cloud pH by one unit, and increasing both  $[\text{Cl}^-]$  and  $[\text{Br}^-]$  concentrations in clouds by 1 order of magnitude. For all these scenarios, the percentage increase in annual mean tropospheric sulfate burden ( $\Delta\text{SO}_4$ ) varies from 6% to 8%, the percentage decrease in  $\text{Br}_y$  ( $\Delta\text{Br}_y$ ) varies from  $-42\%$  to  $-57\%$ , and the fraction of sulfate abundance formed from  $\text{HOBr} + \text{S(IV)}$  ( $f_{\text{SO}_4\text{-HOBr}}$ ) varies from 7% to 11% after adding  $\text{HOBr} + \text{S(IV)}$ , which do not differ significantly from the standard model runs ( $\Delta\text{SO}_4 = 6\%$ ;  $\Delta\text{Br}_y = -50\%$ ;  $f_{\text{SO}_4\text{-HOBr}} = 8\%$ ). Doubling SSA emissions does not result in a doubling of  $\text{Br}_y$  abundance (only 18–38% increase) because SSA also provides a surface for uptake of  $\text{HBr}$ , which partially compensates for the increased SSA emissions flux by reducing the lifetime of  $\text{HBr}$ . Additionally, SSA is not the only source of  $\text{Br}_y$  in the troposphere. Doubling  $[\text{Br}_{\text{SSA}}^-]$  and reducing coarse-mode SSA pH by two units do not result in significant changes in tropospheric  $\text{Br}_y$  burden ( $<5\%$ ) because the uptake of  $\text{HOBr}$  by SSA is limited by gas phase diffusion of  $\text{HOBr}$  in the MBL (SI).  $f_{\text{SO}_4\text{-HOBr}}$  remains small (8%–9%) when doubling  $[\text{Br}_{\text{SSA}}^-]$  and reducing coarse-mode SSA pH because of the small changes in  $\text{Br}_y$  abundance. Tropospheric sulfate and  $\text{Br}_y$  burdens are not very sensitive to the changes in  $k_{\text{HOBr}+\text{HSO}_3^-}$  (and  $H_{\text{HOBr}}$ ), cloud LWC, cloud pH, and  $\text{Cl}^-$  and  $\text{Br}^-$  concentrations in cloud droplets because uptake of  $\text{HOBr}$  by cloud droplets is limited by gas diffusion of  $\text{HOBr}$  and  $\text{HOBr} + \text{S(IV)}$  is much faster (up to 5 orders of magnitude) than  $\text{HOBr} + \text{Cl}^-/\text{Br}^-$  in cloud droplets (SI). In sum, the impact of adding  $\text{HOBr} + \text{S(IV)}$  to the model is not highly sensitive to the varied model parameters. We note that missing processes in the model such as interactions with reactive iodine or  $\text{Br}_y$  sources in polar regions could significantly impact  $\text{Br}_y$  abundance and  $f_{\text{SO}_4\text{-HOBr}}$ .

## 5. Conclusions

It has been proposed that hypohalous acids such as  $\text{HOBr}$  could be responsible for a large fraction of sulfate production in the MBL [Vogt *et al.*, 1996; von Glasow *et al.*, 2002; Chen *et al.*, 2016]. Here we implemented  $\text{HOBr} + \text{S(IV)}$  reactions into GEOS-Chem for the first time to investigate the global impact of these reactions on both tropospheric sulfur and reactive bromine budgets. Adding  $\text{HOBr} + \text{S(IV)}$  increased the global sulfate production rate by 6% and decreased the global  $\text{Br}_y$  burden by 50%. About 8% of sulfate is produced via

HOBr oxidation globally, under a global mean HOBr mixing ratio of 0.4 ppt. The reduction in Br<sub>y</sub> resulting from adding HOBr + S(IV) to the model led to an increase in O<sub>3</sub>, OH, and NO<sub>x</sub> abundances. Increases in OH resulted in an increased production rate of SO<sub>2</sub> from DMS + OH, compensating for reductions in SO<sub>2</sub> from faster removal by HOBr + S(IV), leading to negligible change in the gas-phase sulfate production rate from SO<sub>2</sub> + OH. Changes in sulfur emissions after adding HOBr + S(IV) did not significantly impact the global Br<sub>y</sub> and oxidant budgets on the global scale because of compensating effects of cloud pH on acid-catalyzed reactive bromine production. This study, combined with our previous study on Δ<sup>17</sup>O of sulfate in the MBL [Chen *et al.*, 2016], suggests that reactive halogens could play an important role in sulfate production in the MBL, even with HOBr mixing ratios as low as sub-ppt levels. Due to the large impacts of HOBr + S(IV) reactions on tropospheric sulfur and reactive bromine budgets, we recommend including HOBr + S(IV) reactions in global models of tropospheric chemistry and climate and prioritizing observations of tropospheric HOBr abundance.

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