Impacts of S(IV) oxidation by HOBr on the global sulfur and reactive bromine budgets

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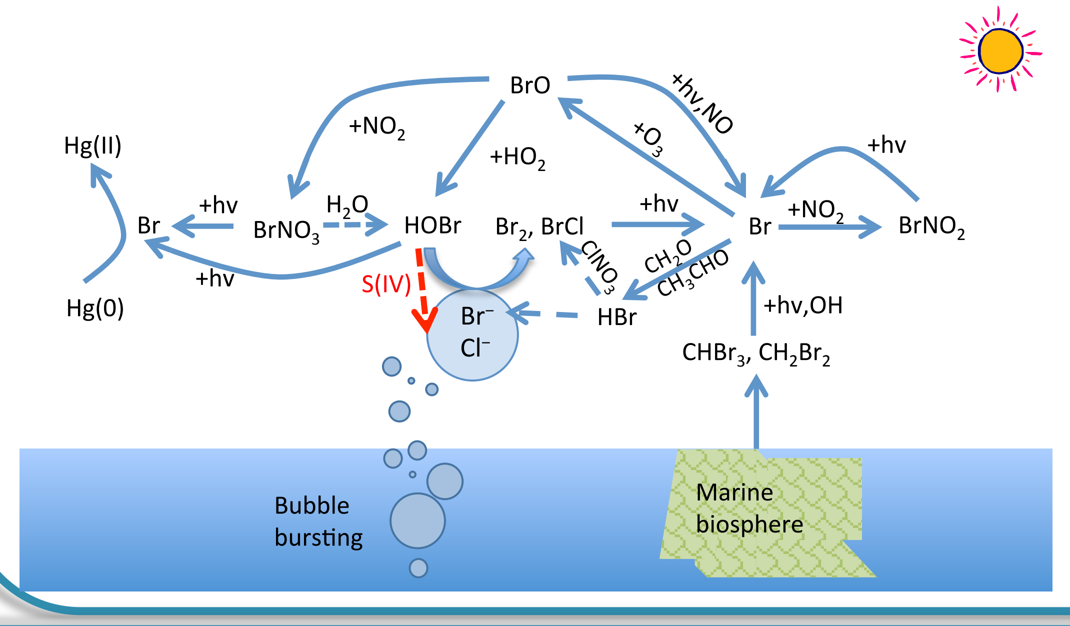
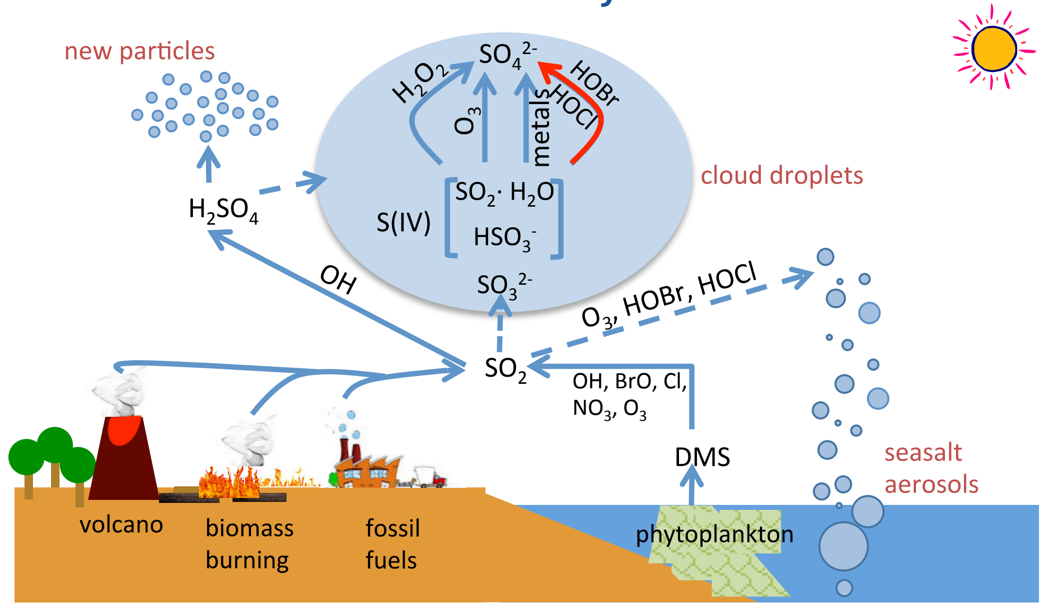
Overview

Tropospheric sulfur and reactive bromine (Br_y = BrO + Br + Br_2 + HOBr + BrCl + HBr + $BrNO_3$ + $BrNO_2$) play vital roles in tropospheric chemistry and the global radiation budget. Previous studies suggest oxidation of S(IV) (HSO_3^- and SO_3^{2-}) by HOBr in atmospheric aerosols accounts for a large fraction of sulfate production in the marine boundary layer (Vogt et al., 1996; von Glasow et al., 2002; Chen et al., 2016). The "HOBr+S(IV)" reaction could also impact the Br_y budget, as it converts HOBr into Br^- in cloud droplets and slows down the Br_y cycle. Regardless of its importance, this reaction is generally not included in global climate and chemistry models due to large uncertainties in reaction rates. In this study, we implement the "HOBr+S(IV)" reaction into a global chemical transport model GEOS-Chem, based on the updated Br_y simulation from Schmidt et al. (2016), and evaluate the global impacts on both the sulfur and Br_y budgets.

Reactive bromine cycle

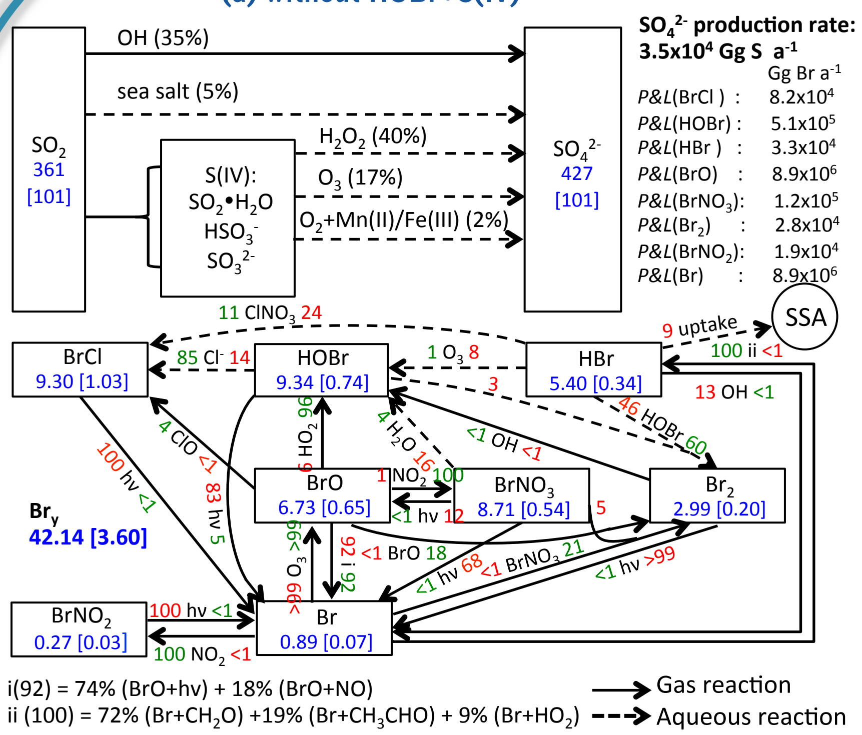


Sulfur cycle

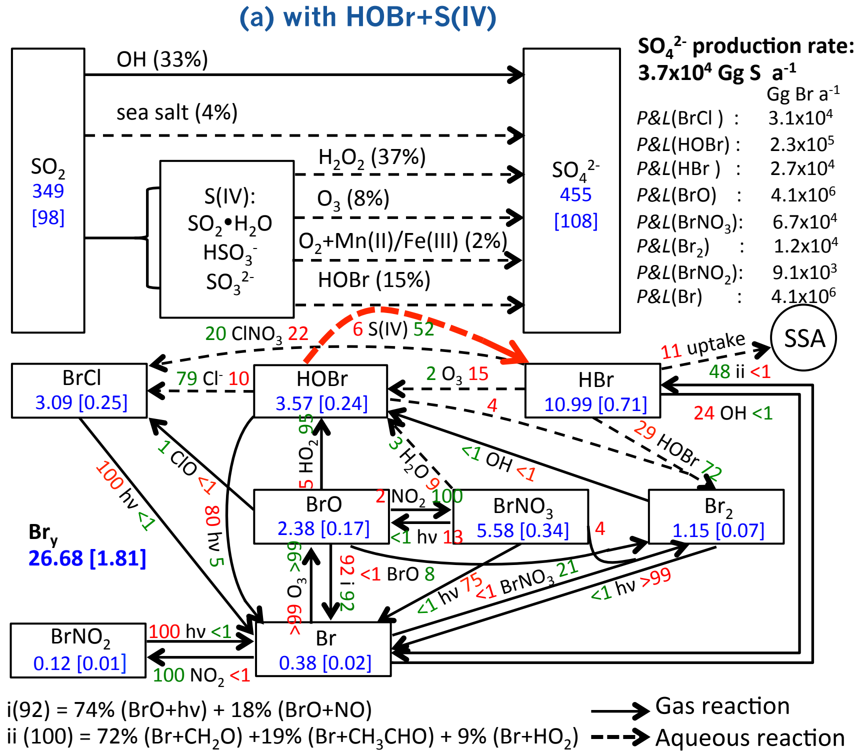


Tropospheric Sulfur and Br_y budgets

(a) without HOBr+S(IV)



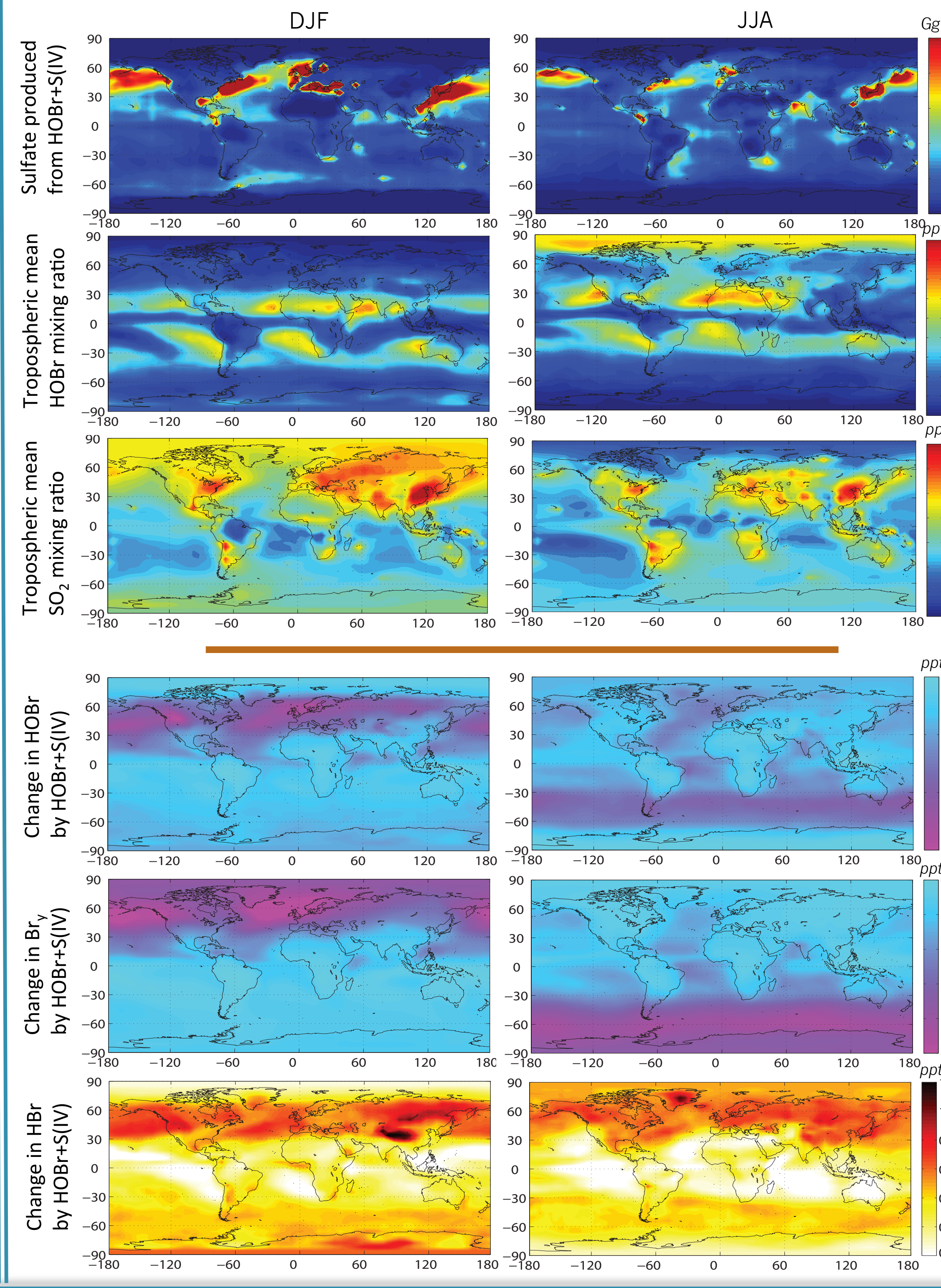
(a) with HOBr+S(IV)



Inventories (blue color) are in unit of Gg S for sulfur and Gg Br for Br_y, and numbers in brackets are mean tropospheric mixing ratios in units of ppt. Numbers in red are percentages of removal of each Br_y species and numbers in green are percentages of production of each Br_y species.

- **Inclusion of HOBr+S(IV) reaction in the model increases sulfate production rate by 6% and reduces Br_y burden by 37%.**
- **The fraction of sulfate produced from HOBr+S(IV) pathway is 15% globally.**

Spatial distribution and seasonality



- **In subtropics, high HOBr mixing ratio does not guarantee high sulfate production rate via HOBr+S(IV) reaction due to the limit of SO_2 and clouds.**
- **Sulfate production rate via HOBr+S(IV) reaction is highest over Northern Hemisphere mid-latitudes ocean**
- **Decrease in Br_y mixing ratio is largest in the winter Hemisphere where chemical recycling of HBr is slow.**
- **Decrease in HOBr results in decrease in sea salt debromination, which results in decrease in Br_y and larger decrease in HOBr.**
- **Change of HBr mixing ratio is determined by both chemical production (via HOBr or Br) and removal (via OH, ClNO3, HOBr and O_3) of HBr.**
- **Back of envelop calculation suggests that removal of HOBr by cloud droplets via "HOBr+S(IV)" reaction is most likely diffusion-limited, as the reaction proceeds very fast.**

Summary

- Preliminary results show that the "HOBr+S(IV)" reaction increases global sulfate production rate by 6%, with most of the increase occurring over the oceans, and reduces the global tropospheric Br_y burden by 37%.
- Due to the importance of this reaction for tropospheric sulfate aerosol production and the burden of reactive bromine, it should be included in global models of tropospheric chemistry and climate.

Reference

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