

We thank the two reviewers for their thoughtful comments. Our responses are in blue. Trackable changes relative to the last manuscript are also attached at the end.

Referee #1

Sander (Referee)

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Received and published: 4 December 2018

Zhu et al. investigate the effect of sea-salt aerosol on tropospheric bromine chemistry. The study is very interesting and I recommend publication in ACP after considering several changes as described below.

Specific comments

Abstract: “We show, for the first time, observed levels of SSA debromination can be reproduced in a manner consistent with observed BrO concentrations.”

A key argument of your study is that acetaldehyde is “critical in moderating tropospheric BrO levels”. It should be noted, however, that this topic has already been studied in 2004 by Toyota et al. (doi 10.5194/ACP-4-1961-2004). They wrote: “Model calculations with the new chemical scheme reveal that the oceanic emissions of acetaldehyde (CH₃CHO) and alkenes (especially C₃H₆) are important factors for regulating reactive halogen chemistry in the MBL by promoting the conversion of Br atoms into HBr. . .”

The reaction HOBr + S(IV) has also been included in previous halogen studies, e.g., Long et al. (doi 10.5194/ACP-14-3397-2014).

Accepted. We have rephrased the words in the abstract. We now add Toyota et al. (2004) and Long et al. (2014) as references. Please see page 1 line 21.

To support your statement about HOBr and acetaldehyde, it would be good to add a table showing the relative importance of all reactions that convert reactive bromine back to HBr in your model.

Actually, we did give the relative importance of reactions converting bromine radical (Br) back to HBr in Figure 3 (term “B” at the top left corner) in the submitted manuscript. We agree with the reviewer, and add one sentence in the text to emphasize this point. Please see page 6 line 9-11.

Abstract: “Bromine radicals influence global tropospheric chemistry by depleting ozone and OH, and by oxidizing elemental mercury, sulfur species, and volatile organic compounds.”

In the main ozone-depleting cycle (Br → BrO → HOBr → Br), the OH radical is produced, not destroyed! If you see lower OH when you switch on Br chemistry in your model, this is more likely due to indirect effects. Maybe there is less OH production because of less ozone?

Indeed, the less OH production is due to less ozone. We have modified this sentence. Please see page 1 line 21 and page 2 line 2.

I don't think that VOCs are affected much by Br. The reactions with most VOCs (e.g. alkanes) are very slow. I agree that alkenes and aldehydes can be important for Br but this doesn't necessarily

imply that Br is important for them. Can you tell us what the relative contributions of OH and Br to the oxidation of aldehydes are in your model?

Accepted. We have removed “VOCs” from the sentence. Please see page 1 line 21 and page 2 line 2. In the model, OH accounts for 96.5% (Br 3.5%) of the total oxidation of HCHO within the troposphere. For acetaldehyde, OH accounts for 92.0% (Br 8.0%) of the total oxidation within the troposphere.

Page 5, lines 8-9: “Bry mobilized from coarse SSA is transferred to fine SSA as HBr. EF values drop further inland as Bry is remobilized from the fine SSA.” This is very interesting! However, so far you have only presented the overall EF. Can you calculate the EF for fine and coarse SSA individually? Then you can check if your statement is supported by the model.

Accepted. We now calculate and discuss the *EF* values for fine and coarse SSA separately. Please see page 14 for the revised Figure 1, and page 5 line 17-23 for discussion.

Page 4, lines 2-3: “SSA alkalinity is depleted by uptake of HNO₃ and SO₂.” The alkalinity is not depleted by SO₂. This happens only after it has been oxidized to S(VI).

Accepted. We have rephrased this. Please see page 4 line 14-15.

Page 6, lines 10-11: “The biases at high latitudes can be reduced by including a detail chlorine chemistry” At high latitudes, tropospheric ozone depletion events occur which dominate the halogen chemistry in those regions. Unless your model includes a good description of these events, I would not attempt to compare the model results with measurements here.

Accepted. We have included the comprehensive tropospheric chlorine chemistry from Wang et al. (2019) with some additional modifications, and have updated the manuscript accordingly. We also add one sentence to clarify the scope of the manuscript, please see page 3 line 20-22.

Technical Comments

Reactions occurring inside liquid aerosols should be called “multiphase”, not “heterogeneous” (see e.g., Ravishankara, doi 10.1126/science.276.5315.1058).

We appreciate the reviewer’s comment, but “heterogeneous” is a standard terminology in our field and people have used it in many previous studies. So, we prefer to use it in the manuscript.

According to the IUPAC Recommendations (page 1387 of Schwartz & Warneck “Units for use in atmospheric chemistry”, Pure & Appl. Chem., 67(8/9), 1377-1406, 1995, <https://www.iupac.org/publications/pac/pdf/1995/pdf/6708x1377.pdf>) the usage of “ppb” and “ppt” is discouraged for several reasons. Instead, “nmol/mol” and “pmol/mol” should be used for gas-phase mole fractions. I suggest to replace the obsolete units.

We appreciate the reviewer’s comment, but the term “ppb/ppt” is widely used in our field. We accept this comment by defining ppt as at its first appearance. Please see page 2 line 17.

Page 2, line 17 and elsewhere: “concentrations are typically of the order of 1 ppt” The physical properties “mixing ratio” and “concentration” are used as if they were identical. This is not the case! (for details, see <http://www.rolf-sander.net/res/vol1kg.pdf>) Please check all occurrences of the word “concentration” in the main text and check if it should read “mixing ratio” instead.

Accepted. We have replaced “concentration” with “mixing ratio” in multiple places in the text.

Data availability section: “Data are available upon request”. Obtaining data via personal request can be quite unsatisfactory, especially after a couple of years when it often becomes difficult to contact the authors. I suggest to present the most important data in the supplement to this article. This could include:

- The data files used to create the figures.
- The reaction mechanism (KPP equation file). Did you use Standard.eqn as supplied by GEOS-Chem 12.0.0, or did you modify the mechanism?

Accepted. We have uploaded the KPP files and data used to create figures, and have modified the Data availability section accordingly. Please see page 8 line 29-30.

Anonymous Referee #2

Received and published: 7 January 2019

In this work, Zhu and co-authors presented tropospheric bromine chemistry simulated using a global chemical transport model (GEOS-Chem), and the results are compared to sea salt bromide enrichment factor measurement compilation, GOME-2 tropospheric BrO column, as well as BrO measurements from recent aircraft campaigns. This paper is very interesting and scientifically sound to merit publication in Atmospheric Chemistry and Physics once the following concerns have been addressed.

The current form of the paper is very compact. However, I also feel that some essential information is missing. My major concerns are as follows:

1. The reactive uptake of HOBr onto bromide-containing particles is critical, which is very sensitive to acidity. However, in the present form of the manuscript, neither sea salt aerosol acidity nor the titration (by HNO₃, H₂SO₄, SO₂, etc) is justified by observations. This is the case for non-sea-salt aerosols and cloud droplets as well. Without proper justifications of modeled particle acidity and the acidic gases, such as HNO₃, H₂SO₄, SO₂, etc, I am not fully convinced that the modeled magnitude of sea salt debromination and bromide enrichment factors presented in the present form are necessarily for the right reason. I will get back to this later.

We agree with the reviewer that acidity is critical for the reactive uptake of HOBr in cloud and on sea salt aerosol. We have added one sentence to compare model cloud pH with observations reported in literatures. Please see page 4 line 15-17. We have also added a figure showing sea salt aerosol alkalinity in the Supplemental Materials (Figure S1).

2. The oceanic emission of acetaldehyde (Millet et al 2010) rapidly removes Br atoms in the remote troposphere and essentially shuts off chain propagation. However, the oceanic fluxes of acetaldehyde and the modeled acetaldehyde distributions in the remote troposphere remain untested, partially due to the known measurement artifacts for acetaldehyde in clean air (please see discussions in Millet et al 2010). This weakens one major conclusion of this work, that ocean emissions of aldehyde (especially acetaldehyde) plays a key role in reconciling the large debromination source with the relatively low BrO observations in the marine boundary layer. How does the modeled acetaldehyde compare to recent observations in the remote atmosphere?

Based on a recent study, GEOS-Chem acetaldehyde is 10% lower compared with observations over remote MBL from the ATom campaigns. By assuming such bias is uniform in the model, global tropospheric Br radical to HBr rate would be increased only by 4%. Please see page 6 line 12-14.

Specific comments:

3. This work does reproduce the mean bromide enrichment factors observed in ten surface sites around the globe, however the seasonality is only examined at one site. Any particular reason that the modeled seasonality is not examined against observations for the rest of the nine sites? Also, as shown in Figure 2, the modeled bromide enrichment factor shows almost the opposite annual trend, which appears to be inconsistent with the modeled alkalinity...? Anyway, this figure

certainly deserves more in-depth discussions. And I would suggest adding similar plots for other sites too (depending on data availability of course).

We appreciate the reviewer's comment, however, Gape Grim is the only site with seasonal *EF* observations we could find. We have rewritten this part to clarify. Please see page 5 line 17-27.

4. The authors claim that two types of sea salt aerosols are emitted in the model: coarse and fine modes. The lifetime of sea salt aerosol depends on size. Is the modeled vertical distributions of fine and coarse sea salt aerosols supported by observations?

GEOS-Chem sea salt aerosol simulation is based on Jaeglé et al. (2011) and has been evaluated with surface, cruise, satellite, and AERONET data. We think validation of sea salt aerosol profiles is beyond the scope of this study. However, we accept the reviewer's comment by adding "showed that it could reproduce successfully SSA observations over the oceans from ship cruises and coastal/island stations, as well as observations of aerosol optical depth (AOD) from the AERONET network and the MODIS satellite instrument" in the text. Please see page 4 line 8-10.

5. The author also mentioned that "Bry mobilized from coarse SSA to fine SSA as HBr", yet zero detail is given in the present form of the manuscript. Bry mobilizing from coarse SSA to fine SSA implies different enrichment factors between coarse and fine particles. Is this supported by observations? Come to think of it is this "enrichment factor" being discussed throughout the paper weighted between coarse and fine particle?

We calculated *EF* values using the total mass of bromide in SSA and the total mass of dry SSA, from both fine and coarse SSA. We state this in the text, please see page 5 line 4. We have accepted the reviewer's comment by calculating and discussing the *EF* values for fine and coarse SSA separately. Please see page 14 for the revised Figure 1, and page 5 line 17-23 for discussion.

6. The reported HOBr reactive uptake on tropospheric aerosols in the literature varies in magnitude. Roberts et al (2014) brought up a very interesting concern about the re-active uptake of HOBr on bromide-containing particles, that the widely used termolecular kinetic approach is strictly valid for a specific pH range, and the reactive uptake of HOBr on H₂SO₄-acidified particles may be substantially overestimated in current models. For the first time, Roberts et al (2014) reconciles the different reactive uptake coefficients reported from laboratory experiments. I understand that the evaluation of the new HOBr uptake framework (Roberts et al., 2014) in a global model may well be worth another paper. However, I feel this is not totally beyond the scope of the present work, given the profound impact of HOBr on the tropospheric bromine activation. Therefore I would strongly suggest at least a few sensitivity tests on different pH values for sea salt and non-sea-salt aerosols. This brings me back to my very first comment: What is the pH for fresh and aged sea salt aerosols? How much acidic gases (HNO₃, H₂SO₄) does the model predict and are these predictions supported by observations? How about non-sea-salt aerosols and cloud droplets?

We appreciate the reviewer's comment on possible overestimation of reactive uptake of HOBr in the model. However, our simulated BrO is generally toward the low end of the observed range of BrO (Figure 5 and Table 1). This implies that slowing down HOBr + Br⁻ may not help improve

the simulation. We have accepted the reviewer's comment by citing Roberts et al (2014) as a possible future direction. Please see page 8 line 20.

"SSA alkalinity is emitted at a ratio of 0.07 equivalents per kilogram of dry SSA, and is depleted by strong acids following Alexander et al. (2005)". We have added this sentence in the text to address the reviewer's comment. Please see page 4, line 14-15. Currently, the model only considers HOBr + Br⁻ reactions in cloud droplets, ice crystals, SSA, and sulfate aerosol. We have modified one sentence in the text to clarify this. Please see page 3 line 11.

7. Page 7 Line 4-5: It seems to me that the model predicts lower BrO in the free troposphere in the western tropical Pacific, which happens to be a hot spot for deep convection. Liang et al (2014) demonstrated that varying model deep convection strength can introduce a significant change in inorganic Bry scavenging and eventually the bromine product gas injection at the tropopause. How does the model handle convective transport and how may this affect the BrO (and Bry) predictions in this region?

Such bias is no longer the case. Please see page 7 line 19-21.

8. Page 7 Line 5: If "online aerosol pH" yields better pH, why don't you use it then? This is an issue throughout, that pH is so important yet virtually no detail is given in the present form of the paper. How much acidic gases does the model predict in the marine boundary layer and the free troposphere? How big of a difference does this "online pH calculation" make and how does this translate into the modeled BrO? To fully justify the findings (which are very interesting) in this work, I strongly suggest that the authors should get to the bottom of this. I am sure the readers will appreciate it, as it makes the paper much stronger.

Accepted. We have included the comprehensive tropospheric chlorine chemistry from Wang et al. (2019) with some additional modifications, and updated the manuscript accordingly.

Technical comments:

9. Page 1 Line 21 and Page 2 Line 2: I myself don't think "deplete" is the proper verb for OH radicals. Bromine chemistry converts HO₂ into OH but also destroys O₃ which itself is an OH precursor.

Accepted. We have modified this sentence. Please see page 1 line 21 and page 2 line 2.

10. Page 1 Line 24: define BrO.

Accepted. We have defined BrO as "bromine monoxide". Please see page 1 line 24.

11. Page 2 Line 26: I believe Millet et al (2010) only discussed acetaldehyde, not "oxygenated organics".

Accepted. We have modified the sentence. Please see page 2 line 27.

12. Page 4 Line 1: please define alkalinity and remind the readers how this is derived/calculated.

Accepted. We have rewritten this sentence. Please see page 4 line 14-15.

13. Page 5 Line 9-10: Does Bry also "mobilize" to non-sea-salt aerosols?

We now calculate and discuss the *EF* values for fine and coarse SSA separately. Please see page 14 for the revised Figure 1, and page 5 line 17-23 for discussion.

14. Page 5 Line 22 and Figure 3: please separate in-cloud processing from multiphase chemistry on sulfate aerosols.

We appreciate the reviewer's comment. Unfortunately, our current code doesn't allow separation of in-cloud processing between heterogenous chemistry on sulfate aerosols.

15. Page 6 Line 10-12: Please elaborate how does chlorine chemistry reduce the bias, and by how much.

We have updated the manuscript using the comprehensive tropospheric chlorine chemistry following Wang et al. (2019). Therefore, this part has been removed in the revised manuscript.

16. Page 7 Line 2-4: "The CONTRAST flight campaign took more readings over a region (near Guam) with higher SSA emission and load compared with CAST, resulting in higher level of BrO" this seems to be confusing to me. As described in the present form of the manuscript, it looks like CONTRAST and CAST were pretty much at the same time in the same region, i.e. they are sort of like different subsets of the same dataset. If more reading in one campaign leads to higher or lower values than the other, are you implying sampling bias in either or both?

CONTRAST took more observations near Guam where BrO level is higher due to higher SSA emissions. We have rewritten this sentence. Please see page 7 line 23-24. We have also modified Figure 6 (page 19) by showing aircraft observations for the closest season.

17. Page 7 Line 7-9: How much HOI and I₂ does the model predict in this region? And how much BrO does the model predict without iodine chemistry at this site? This is quite interesting.

Accepted. Such hotspot becomes weaker in the revised manuscript. We have rewritten this sentence. Please see page 7 line 25-27.

18. Figure 1: please add site names onto the map.

Accepted. Please see page 14 line 6-7.

19. I would love to see a vertical distribution of the inorganic Bry speciation plot. Can we do this as an update to the corresponding plot from Schmidt2016?

Accepted. Please see Figure S3 and S4 in the Supplemental Materials.

20. References

Roberts, T. J., Jourdain, L., Griffiths, P. T., and Pirre, M.: Re-evaluating the reactive uptake of HOBr in the troposphere with implications for the marine boundary layer and volcanic plumes, *Atmos. Chem. Phys.*, 14, 11185-11199, <https://doi.org/10.5194/acp-14-11185-2014>, 2014.

Liang, Q., Atlas, E., Blake, D., Dorf, M., Pfeilsticker, K., and Schauffler, S.: Convective transport of very short lived bromocarbons to the stratosphere, *Atmos. Chem. Phys.*, 14, 5781-5792, <https://doi.org/10.5194/acp-14-5781-2014>, 2014.

We now cite [Roberts et al. \(2014\)](#).

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Effect of sea-salt aerosol on tropospheric bromine chemistry

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Abstract. Bromine radicals influence global tropospheric chemistry by depleting ozone and by oxidizing elemental mercury, and reduced sulfur species. Observations typically indicate a 50% depletion of sea salt aerosol (SSA) bromide relative to seawater composition, implying that SSA debromination could be the dominant global source of tropospheric bromine. However, it has been difficult to reconcile this large source with the relatively low bromine monoxide (BrO) mixing ratios observed in the marine boundary layer (MBL). Here we present a new mechanistic description of SSA debromination in the GEOS-Chem global atmospheric chemistry model with a detailed representation of halogen (Cl, Br, and I) chemistry. We show that observed levels of SSA debromination can be reproduced in a manner consistent with observed BrO mixing ratios. Bromine radical sinks from the HOBr + S(IV) heterogeneous reactions and from ocean emission of acetaldehyde are critical in moderating tropospheric BrO levels. The resulting HBr is rapidly taken up by SSA and also deposited. Observations of SSA debromination at southern mid-latitudes in summer suggest that model uptake of HBr by SSA may be too fast. The model provides a successful simulation of free tropospheric BrO in the tropics and mid-latitudes summer, where the bromine radical sink from the HOBr + S(IV) reactions is compensated by more efficient HOBr-driven recycling in clouds compared to previous GEOS-Chem versions. Simulated BrO in the MBL is generally much higher in winter than in summer due to a combination of greater SSA emission and slower conversion of bromine radicals to HBr. An outstanding issue in the model is the overestimate of free tropospheric BrO in extratropical winter-spring, possibly reflecting an overestimate of the HOBr/HBr ratio under these conditions where the dominant HOBr source is hydrolysis of BrNO₂.

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1 Introduction

Bromine radicals ($\text{BrO}_x \equiv \text{Br} + \text{BrO}$) influence global tropospheric chemistry by depleting ozone and thus OH, and by oxidizing species such as elemental mercury, and dimethylsulfide (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015; Long et al., 2014). Tropospheric bromine radical chemistry is initiated by the production of reactive inorganic bromine (Br_y) from sea salt aerosol (SSA) debromination, decomposition of organobromines primarily of marine origin (CHBr_3 , CH_2Br_2 , and CH_3Br), and transport from the stratosphere. Within the Br_y family, bromine radicals cycle with non-radical reservoir species such as HBr, HOBr, BrNO_2 , BrNO_3 , Br_2 , BrCl , and IBr . Loss of Br_y is by wet and dry deposition to the surface, mainly as HBr which is highly soluble in water.

Sea salt aerosol (SSA) is thought to be the largest source of tropospheric bromine. Observations show extensive debromination of SSA relative to seawater composition (Sander et al., 2003; Newberg et al., 2005). Parrella et al. (2012) estimate a global Br_y source of $1420 \text{ Gg Br a}^{-1}$ from SSA debromination, as compared with 520 Gg a^{-1} from organobromines and 36 Gg a^{-1} from the stratosphere. Volatilization of bromide from SSA can take place by heterogeneous reactions with HOBr, HOCl, N_2O_5 , ozone, and ClNO_3 (Vogt et al., 1996; Hirokawa et al., 1998; Keene et al., 1998; Firkert et al., 1999; von Glasow et al., 2002a, b; Yang et al., 2005; Ordóñez et al., 2012; Saiz-Lopez et al., 2012; Long et al., 2014). A standing conundrum has been that observations of BrO in the marine boundary layer (MBL) do not show large enhancements relative to the free troposphere, where background mixing ratios are typically of the order of 1 ppt ($\text{ppt} \equiv \text{pmol mol}^{-1}$). Leser et al., 2003; Sander et al., 2003; Theys et al., 2011; Volkamer et al. 2015; Wang et al., 2015; Le Breton et al., 2017). Ozone observations in the MBL similarly do not show depletion that would be expected from high mixing ratios of BrO (de Laat and Lelieveld, 2000; Sherwen et al., 2016). This has led recent global models not to include SSA debromination as a source of Br_y (Schmidt et al., 2016; Sherwen et al., 2016).

Here we present a new mechanistic description of sea salt debromination in the GEOS-Chem global 3-D model of tropospheric chemistry including detailed representation of halogens (Cl, Br, and I) (Sherwen et al., 2016; Wang et al., 2019). We find that we can reproduce the observed levels of SSA debromination while also being consistent with the relatively low BrO mixing ratios observed in the MBL. This is because the previously-recognized fast production of Br_y from SSA debromination is offset by fast removal Br atoms by acetaldehyde emitted from the ocean (Toyota et al., 2004; Millet et al., 2010; Badia et al., 2019) and by fast removal of HOBr by dissolved SO_2 (S(IV)) in cloud (Long et al., 2014; Chen et al., 2017). We examine the implications for the global budget of tropospheric bromine and tropospheric oxidants.

2 Data and methods

We use GEOS-Chem 12.3.0 (<https://doi.org/10.5281/zenodo.2620535>), which includes a detailed representation of ozone- NO_x -VOC-aerosol-halogen tropospheric chemistry (Sherwen et al., 2016), to which we have added the comprehensive

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5 tropospheric chlorine chemistry of Wang et al. (2019) with some additional modifications as described below. The model is driven by assimilated meteorological data for 2011–2012 from the Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA2) produced by the NASA Global Modeling and Assimilation Office (Gelaro et al., 2017). The horizontal resolution of MERRA2 is $0.5^\circ \times 0.625^\circ$, and is degraded here to $4^\circ \times 5^\circ$ for input to GEOS-Chem. Dynamic and chemical time steps are 30 and 60 minutes, respectively. GEOS-Chem stratospheric chemistry (Eastham et al., 2014) is linearized following Murray et al. (2012) to serve as boundary conditions for stratospheric input to the troposphere. The model is spun up for 1 year and we use simulation results for 2012.

10 Tropospheric bromine chemistry in GEOS-Chem was first introduced by Parrella et al. (2012). Loss of Br_y from the troposphere is mainly by deposition of HBr, which is highly water-soluble, unlike HOBr or BrO. Parrella et al. (2012) found that the acid-catalyzed HOBr + Br^- reaction taking place in liquid-water clouds, ice crystal quasi-liquid surfaces, and aqueous aerosols was critical for recycling bromide and maintaining background tropospheric BrO at observed ~ 1 ppt levels:



20 The current standard version of the model (GEOS-Chem 12.3.0) includes more extensive heterogeneous bromine chemistry (Schmidt et al., 2016), coupling to other halogens (Sherwen et al. 2016), HOBr + S(IV) reactions in clouds (Chen et al., 2017), and oceanic emission of acetaldehyde which reacts rapidly with Br atoms (Toyota et al., 2004; Millet et al., 2010; Badia et al., 2019). Wang et al. (2019) more recently added a comprehensive treatment of tropospheric chlorine chemistry in GEOS-Chem including explicit accounting of SSA chloride volatilization and aerosol pH. The model does not attempt to simulate the fast but localized bromine chemistry taking place in the Arctic MBL in spring due to volatilization of bromine deposited on sea ice (Simpson et al., 2015).

25 Here we added several updates to the computation of heterogeneous chemistry recycling bromine radicals. Uptake of HOBr(aq) by clouds involves competition between reactions with Br^- , Cl^- , HSO_3^- , and SO_3^{2-} , as given by (R1), (R4), and (R5):



30 (R1) and (R4) recycle bromine radicals while (R5) is effectively a terminal sink because of HBr deposition. The standard GEOS-Chem code computes the reactive uptake coefficient (γ) independently for each pathway, which incorrectly assumes that other pathways do not affect mass transfer. Here we express the first-order aqueous-phase loss of HOBr as a sum of the four pathways to compute γ , and we then distribute the loss by pathways on the basis of the relative rates (see Supplemental

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 $\text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{HBr} + \text{CH}_2\text{CHO} \rightarrow \dots \rightarrow \text{R5}^\ddagger$
 This leads us to re-examine the impact of SSA debromination as a source of bromine radicals and the ability of the model to simulate relevant observations.†

† Emission of SSA to the atmosphere is through air bubbles bursting at the ocean surface, and positively depends on wind speed (Monahan et al., 1986; Gong, 2003).

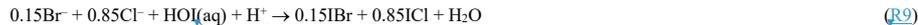
Materials Text S1). When calculating HOBr uptake by ice crystals, we assume a radius of 38.5 μm based on cloud observations (Fu, 1996) rather than 75 μm in the standard GEOS-Chem code, and further increase the effective surface area of ice crystals by a factor of 10 to account for their irregular shape (Schmitt and Heymsfield, 2005). Finally, we correct a registration error for SSA alkalinity in the standard GEOS-Chem code that caused underestimate of alkalinity titration (see Supplemental Materials Text S2). The overall result of our updates is to have more efficient heterogeneous recycling of bromine radicals, both in the MBL and in the free troposphere.

The GEOS-Chem SSA simulation is from Jaeglé et al. (2011), who showed that it could reproduce successfully SSA observations over the oceans from ship cruises and coastal/island stations, as well as observations of aerosol optical depth (AOD) from the AERONET network and the MODIS satellite instrument. The model separates fine ($\leq 0.5 \mu\text{m}$ radius) and coarse SSA as two separate transported species. The global dry SSA source in our simulation is 3140 Tg a^{-1} . We emit bromide as part of fine and coarse SSA with a seawater ratio of 2.11×10^{-3} kg Br per kg dry SSA (Sander et al., 2003; Lewis and Schwartz, 2004), since observations show that fresh SSA has a bromide content equals that of seawater (Duce and Woodcock, 1971; Duce and Hoffman, 1976; Turekian et al., 2003). SSA alkalinity is emitted at a ratio of 0.07 equivalents per kilogram of dry SSA, and is depleted by strong acids following Alexander et al. (2005). The cloud pH is calculated as described in Alexander et al. (2012) and is 3.5–6.5 for clean marine conditions, consistent with the observed range (3.8–6.1) reported in the literature (Gioda et al., 2009; Hegg et al., 1984; Lenschow et al., 1988; Vong et al., 1997; Watanabe et al., 2001).

Activation of SSA bromide takes place by heterogeneous reactions with HOBr, ozone, and ClNO₂ once alkalinity has been titrated and SSA is acidified (Hirokawa et al., 1998; Keene et al., 1998; Fickert et al., 1999):



We also consider parameterized SSA debromination by HOI(aq) following McFiggans et al. (2002), where HOI(aq) may be taken up from the gas phase or produced by hydrolysis of IONO₂ and IONO₃:



Inorganic oceanic iodine (HOI and I₂) emissions are from Carpenter et al. (2013). Unlike for chloride, SSA debromination does not take place by acid displacement because of the much stronger acidity of HBr than HCl or HNO₃ (Sander et al., 2003). On the contrary, uptake of gas-phase HBr can lead to bromine enrichment in SSA.

Sander et al. (2003) introduced the dimensionless enrichment factor (*EF*) as a measure of SSA debromination. *EF* is computed from aerosol measurements as:

$$EF = \frac{([\text{Br}^-]/[\text{Na}^+])_{\text{measured}}}{([\text{Br}^-]/[\text{Na}^+])_{\text{seawater}}} \quad (1)$$

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where aerosol $[\text{Na}^+]$ is assumed to be mainly from sea salt, a reliable assumption in marine air. In GEOS-Chem we treat 'SSA' as a chemically inert tracer, and account for sea-salt bromide as a separate species, therefore EF is computed as:

$$EF = \frac{([\text{Br}^-]/[\text{SSA}])_{\text{SSA aerosol}}}{([\text{Br}^-]/[\text{SSA}])_{\text{SSA emission}}} \quad (2)$$

We sum $[\text{Br}^-]$ and $[\text{SSA}]$ from both fine and coarse SSA to calculate EF . We will also present EF values for fine and coarse SSA separately.

3 Results and discussion

Figure 1 (top panel) shows the annual mean SSA bromine enhancement factors (EF) in surface air computed by GEOS-Chem and compares to annual mean observations compiled by Sander et al. (2003) and from Newberg et al. (2005). We consider 6 island and 4 coastal sites with bulk aerosol EF measurements available for more than one year. The observations are for different years than the GEOS-Chem simulation, but we assume that interannual variability is a minor source of error. The mean GEOS-Chem EF averaged over the sites is 0.75 ± 0.23 (± 1 standard deviation), compared with the observed value of 0.66 ± 0.32 . SSA bromide over the Southern Ocean in the model is less depleted ($EF \sim 0.9$) than over the northern mid-latitudes ($EF \sim 0.6$), because SSA tends to retain its alkalinity over the Southern Ocean (Alexander et al., 2005; Schmidt et al., 2016; Supplemental Materials Figure S1). Similarly in the observations, mean EF is 0.78 ± 0.08 over the Southern Ocean compared with 0.42 ± 0.11 at northern mid-latitudes. Most of the SSA debromination in the model is from (R1).

SSA mass in GEOS-Chem is dominated by the coarse component over the oceans and by the fine component over land (due to fast dry deposition of the coarse component). Thus the EF values for bulk SSA over the ocean are dominated by the coarse component. SSA debromination is more extensive for the fine component of SSA because the initial supply of bromide is less and loss of alkalinity is more extensive. Some areas of the ocean have weak SSA bromide enrichment ($EF > 1$) because of uptake of HBr. Over land the EF values are dominated by the fine SSA component because the coarse component deposits close to the coast. These EF values can be very large because Br_2 volatilized from the coarse SSA component is then taken up as HBr by the fine SSA after the coarse component has deposited.

The model overestimates the observed EF over the Southern Ocean. This appears to reflect a seasonal bias in the model. Figure 2 compares the simulated and observed seasonality at Cape Grim, Tasmania (Ayers et al., 1999; Sander et al., 2003). To our knowledge, this is the only site for which seasonal information is available in the observations. The observed EF is 0.6–0.8 for most of the year, consistent with the model, but decreases to below 0.4 in summer while the model does not. The summer minimum in the observations has been attributed to increased SSA acidity (Ayers et al., 1999; Sander et al., 2003). Indeed, Figure 2 shows that SSA alkalinity in the model is titrated in summer due to the combination of weaker SSA emission (lower winds) and larger photochemical production of strong acids (H_2SO_4 and HNO_3). This drives volatilization of Br_2 from SSA,

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but we find in the model that the resulting HBr mainly returns to SSA rather than deposits to the surface because SSA emission is still relatively high. Uptake of HBr by SSA proceeds in the model with a reactive uptake coefficient $\gamma = 1.3 \times 10^{-8} \exp(4290 \text{ K} / T)$ as recommended by IUPAC (Amman et al., 2013) but with large uncertainty, ranging from -90% to +860% at 278 K.

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Deleted: Inclusion of SSA debromination increases the tropospheric Br_y load by 60% (9.9 Gg Br) and the global annual mean tropospheric BrO by 45% (0.09 ppt). Global tropospheric annual mean ozone and OH is reduced by 4.0% (1.3 ppb) and 2.3%, respectively. The principal global sink of Br_y is uptake of HBr by SSA followed by SSA deposition. The dominant form of Br_y is HBr (21% of Br_y), unlike HOBr in Schmidt et al. (2016), due to the global effect of (R4) and (R5). Despite our inclusion of the SSA debromination source, the global mean tropospheric Br_y mixing ratio is decreased to 1.9 ppt as compared with 3.0 ppt in

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Deleted: (2016). This is caused by the larger fraction of Br_y present as HBr and therefore removed efficiently by uptake by SSA as well as by deposition. The global mean tropospheric BrO mixing ratio is 0.28 ppt as compared with 0.48 ppt in Schmidt et al. (2016). The daytime mixing ratio is about twice that value since BrO is depleted at night.*

Deleted: SSA debromination increases the global annual mean tropospheric BrO column in our model by 46%. The largest effect is at extratropical latitudes in winter and spring due to a combination of higher SSA emissions and more effective bromide recycling via (R1). We find in the model BrNO_3 hydrolysis becomes relatively more important in HOBr generation in winter and spring when BrNO_3 level is higher as a result of weaker photolysis. This leads to higher levels of HOBr, and therefore more effective recycling of bromide via (R1). Schmidt et al. (2016) previously found that their simulation including SSA debromination systematically overestimated the Theys et al. (2011) observations but we find the opposite because of (R4) and (R5) as discussed earlier. Chen et al. (2017) previously included (R4) and (R5) in GEOS-Chem with SSA debromination and found a mean low bias of 16% to 78% relative to the GOME-2 data depending on latitudes. Similarly, the global mean bias is -44% in our simulation. The biases at high latitudes can be reduced by including a detail chlorine chemistry (Wang et al., 2018), since high chloride in those regions accelerate HOBr recycling by serving as a catalyst.*

Figure 4 also shows tropospheric BrO columns measured in in Florida, USA (Coburn et al.,

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5 Figure 3 shows the global budget and speciation of tropospheric Br_y in our simulation. This updates a similar figure by Schmidt et al. (2016) to include SSA debromination, the HOBr + S(IV) reactions in clouds, oceanic emission of acetaldehyde, and full coupling with the other halogens. SSA debromination is the largest global source, mainly from (R1) and (R7) producing Br_2 and HOBr respectively. The dominant sink of Br_y is uptake of HBr by SSA, rather than deposition, emphasizing the importance of competition between these two processes in determining the extent of SSA debromination. Bromine radical (Br) is converted to HBr by formaldehyde, acetaldehyde, HO_2 radical, and $\geq \text{C}_3$ alkenes with relative contributions of 52%, 40%, 7%, and 1%, respectively. In the Schmidt et al. (2016) budget, acetaldehyde contributed only 17% of this bromine radical sink; the larger contribution in our simulation reflects its oceanic emission. Observations from the recent ATom aircraft campaign (Wofsy et al., 2018) over the remote Pacific and Atlantic show mean MBL acetaldehyde mixing ratios within 10% of those simulated by GEOS-Chem including the Millet et al. (2010) ocean source (Bates et al., 2018).

15 The global tropospheric loading of BrO in our simulation is 8.0 Gg Br, corresponding to a mean tropospheric mixing ratio of 0.86 ppt (1.7 ppt as daytime average). The BrO loading is higher than in previous GEOS-Chem versions starting with 3.8 Gg in Parrella et al. (2012), 5.7 Gg in Schmidt et al. (2016), 6.4 Gg in Sherwen et al. (2016), 3.6 Gg in Chen et al. (2017), and 4.2 Gg in Wang et al. (2019). Wang et al. (2019) described this evolution between versions. Our high BrO loading reflects our updates to HOBr uptake and correction of SSA alkalinity.

20 Figure 4 compares simulated tropospheric BrO columns with Global Ozone Monitoring Experiment (GOME)-2 satellite observations from Theys et al. (2011) as a function of season and for different latitudinal bands. Also shown are tropospheric columns from ground-based measurements in Florida, USA (Coburn et al., 2011) and derived from mean aircraft vertical profiles over the tropical Pacific from the TORERO (Volkamer et al., 2015; Wang et al., 2015; Dix et al., 2016) and CONTRAST (Koenig et al., 2017) campaigns. There is general consistency between these observations. Model results are from our standard simulation and from a sensitivity simulation without SSA debromination. The standard simulation provides a good fit to the observations in the tropics but is much too high at extratropical latitudes in winter and spring. High model mixing ratios under these conditions are due to high SSA emissions and fast bromide recycling via (R1), the latter due to a large HOBr source from BrNO_3 hydrolysis. BrNO_3 hydrolysis mainly takes place in cloud (droplets and ice crystals) rather than in aerosols. The dominant global sink for BrNO_3 is photolysis (Figure 3), but under extratropical winter-spring conditions we find that hydrolysis is more important because of weak radiation. Another reason for the high modeled BrO in extratropical winter-spring is that removal of Br_y via deposition of HBr becomes slower under these conditions, as described below.

Figure 5 compares simulated vertical profiles with aircraft BrO observations over the tropics in January and February. Schmidt et al. (2016) and Shermen et al. (2016) reported negative biases of 0.6–1.0 ppt in modeled BrO compared with TORERO observations in the upper free troposphere. Our standard simulation shows a much smaller bias (~ 0.3 ppt) because of the impact of faster HOBr uptake on cloud ice (Section 2). Figure 5 also shows BrO results from two sensitivity simulations not including SSA debromination or the HOBr + S(IV) reactions. Model-observation agreement in those two cases is generally not as good as in our standard simulation. As shown in Figure 5, the impact of SSA debromination extends through the depth of the troposphere by increasing BrO by 0.1–0.5 ppt with larger impact near the surface. This is generally seen in other seasons over the tropical latitudes as well (Supplemental Materials Figure S2). For the extratropical latitudes, the impact of SSA debromination on BrO is much larger (up to 3 ppt) especially in winter-spring, which is also reflected in BrO columns (Figure 4). Besides high SSA emissions and fast bromide recycling as described above, we also find that only ~ 15% of Br₂ there is present as HBr (Supplemental Materials Figure S3 and S4), reflecting the relatively lower Br/BrO ratio (~ 0.02 at winter while ~ 0.08 at summer) when radiation is weak. Br₂ has then a longer lifetime because non-HBr species are much less water-soluble (Parrella et al., 2012) and can be effectively transported to the free troposphere.

Figure 6 shows the simulated global distribution of BrO mixing ratios in surface air in January and July. We attribute the elevated marine surface BrO in winter time to a combination of greater SSA emission and slower removal of Br₂ via deposition of HBr. However, we fail to find enough information in previous studies to evaluate the modeled seasonality in marine surface BrO. Only Cape Verde has seasonal information (Read et al., 2008; Mahajan et al., 2010) and shows insignificant seasonal variation consistent with the model, but this is for the tropics. Observations are compiled in Table 1 with corresponding model values. The model is generally consistent with observations in showing daytime mixing ratios in the range 0.5–2 ppt, including low BrO (0.3–0.6) in the MBL measured from aircraft campaigns. The low level of BrO (~ 0.3 ppt) over the eastern tropical Pacific Ocean (Volkamer et al., 2015; Wang et al., 2015; Dix et al., 2016) observed during the TORERO flight campaign is driven by weak SSA emission in the austral summer. The higher BrO in CONTRAST than in CAST is reproduced by the model where it is due to regional variations in SSA emission. The tropical North Atlantic is enhanced with BrO (1–3 ppt) relative to other tropical oceans, both in the model and observations (Tenerife, Cape Verde). This is due in the model to slow removal of Br₂ via dry deposition of BrNO₂, resulting in elevated Br₂ (and BrO through Br₂ cycling). We find the production rate of BrNO₂ by BrO + NO₂ in this region is ~ 76% slower than over the surrounding Atlantic. Isolated hotspots near India (July) and the Caribbean (January and July) in the model correspond to localized hotspots of SSA emissions.

4 Conclusions

Observations of sea salt aerosol (SSA) debromination over oceans worldwide imply a large source of bromine radicals in the marine boundary layer (MBL), yet measured BrO mixing ratios in the MBL are relatively low. Here we attempted to reconcile

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[these observations with a global simulation of tropospheric bromine chemistry in the GEOS-Chem model including detailed representation of processes.](#)

We find that we can successfully simulate the observations of SSA debromination in the literature as measured by the SSA bromine enrichment factor (*EF*). Most of the debromination in the model is by the $\text{HOBr(aq)} + \text{Br}^- + \text{H}^+$ and $\text{O}_3(\text{aq}) + \text{Br}^- + \text{H}^+$ reactions taking place in acidified SSA. Debromination is more extensive at northern than southern latitudes because of higher acidity. Observations at southern mid-latitudes show extensive debromination in summer that is not captured by the model and we attribute this to model competition for HBr between uptake by SSA and deposition, where HBr uptake by SSA (taken from the IUPAC recommendation) may be too fast. The model predicts large bromide enrichments for fine SSA over land ($EF > 1$) as bromine lost from the coarse SSA transfers as HBr to the fine SSA that is transported inland.

Our model simulation improves over previous GEOS-Chem versions in the simulation of surface, aircraft, and satellite observations of BrO mixing ratios in the tropics and summertime mid-latitudes. Previous model versions including SSA debromination overestimated BrO in the MBL and underestimated it in the free troposphere. Our lower BrO in the MBL reflects the inclusion of radical sinks to HBr from the $\text{HOBr} + \text{S(IV)}$ and $\text{CH}_3\text{CHO} + \text{Br}$ reactions. Our higher BrO in the free troposphere reflects more efficient recycling of bromine radicals by HOBr reactions in clouds. However, the model appears to generate excessive free tropospheric BrO in the extratropics in winter-spring. A distinctive feature of these conditions in the model is a HOBr/HBr ratio in excess of unity, reflecting a large source of HOBr from BrNO_3 hydrolysis and the inefficient production of HBr in the MBL, allowing MBL bromine to be transported to the free troposphere. Further investigation into the chemistry mechanism and uncertainty may be needed, including uptake of HBr by SSA, uptake of HOBr by aerosols (Roberts et al., 2014), BrNO_3 hydrolysis, unexplained observations of oxygenated VOCs in the free troposphere (Volkamer et al., 2015; Andersen et al., 2017; Badia et al., 2019), and oxidation of bromide by ozone involving the BrOOO^- ozonide (Artiglia et al., 2017).

5 Acknowledgments

This work was supported by the NSF Atmospheric Chemistry Program. We acknowledge contributions from the TORERO, CONTRAST, and CAST science team. We thank Dexian Chen for the CONTRAST BrO observations. Q.C. and B.A. acknowledge support from NSF AGS 1343077. R.V. and T.K.K. acknowledge funding from NSF AGS-1620530.

6 Data availability

The GEOS-Chem model is available at <http://acmg.seas.harvard.edu/geos/>. GEOS-Chem chemistry mechanism and monthly bromine simulation output used in this study are available at <https://doi.org/10.7910/DVN/BADJDE>.

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7 Author contributions

L.Z. and D.J.J. designed the research and wrote the paper; L.Z., D.J.J., S.D.E., M.P.S., X.W., T.S., M.J.E., Q.C., and B.A. led the model development; T.K.K., R.V., L.G.H., M.L., T.J.B., and C.J.P. provided BrO observations.

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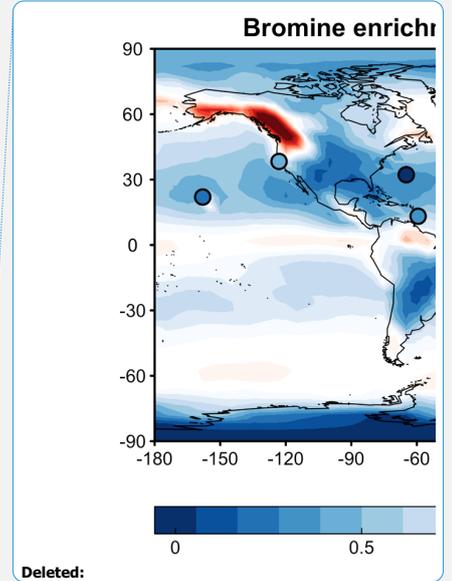
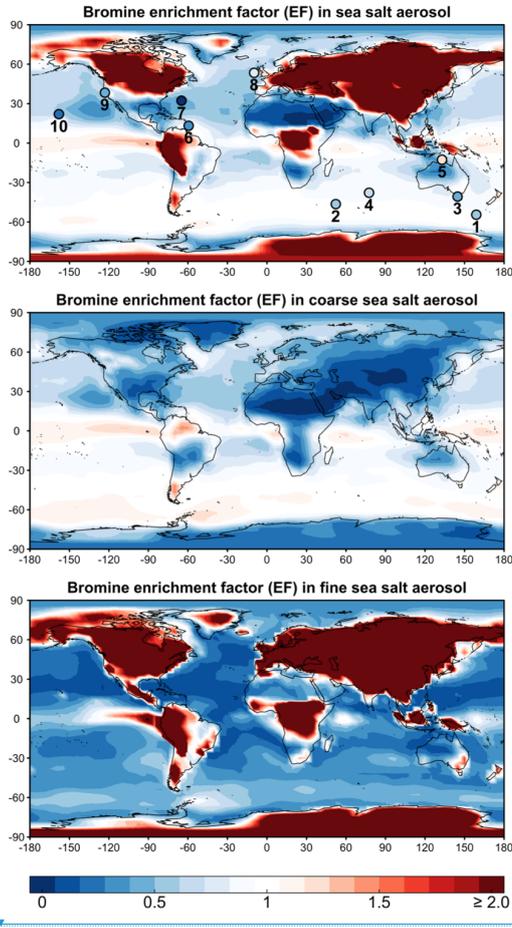
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Figure 1: Annual mean bromine enrichment factor (EF) of sea salt aerosol (SSA) in surface air. GEOS-Chem model results (contours) are compared to observations (circles in top panel). The top panel shows results for total SSA (fine + coarse), the middle panel is for coarse SSA ($> 0.5 \mu m$ radius), and the bottom panel is for fine SSA ($< 0.5 \mu m$ radius). Observations at 10 sites compiled by Sander et al. (2003) and from Newberg et al. (2005) are superimposed as circles and labeled in order 1–10: Macquarie Island, Crozet Islands, Cape Grim, Amsterdam Island, Jabiru, Barbados, Bermuda, Mace Head, Bodega Bay, and Hawaii, respectively. The simulation is for 2012 and the observations are for different years. Color bar saturates at 2.0. Maximum modeled EF is 25.0.

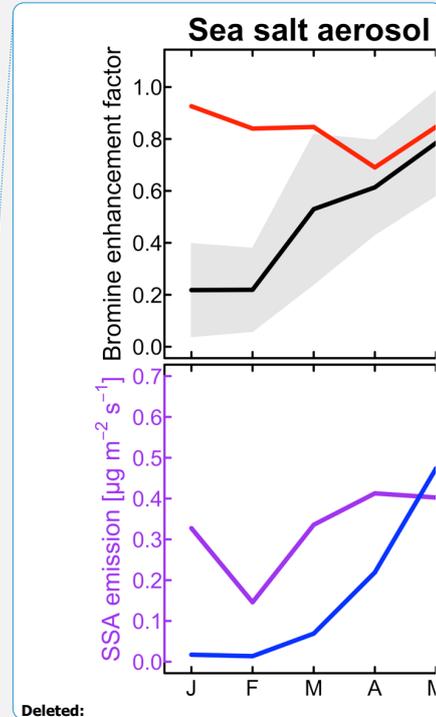
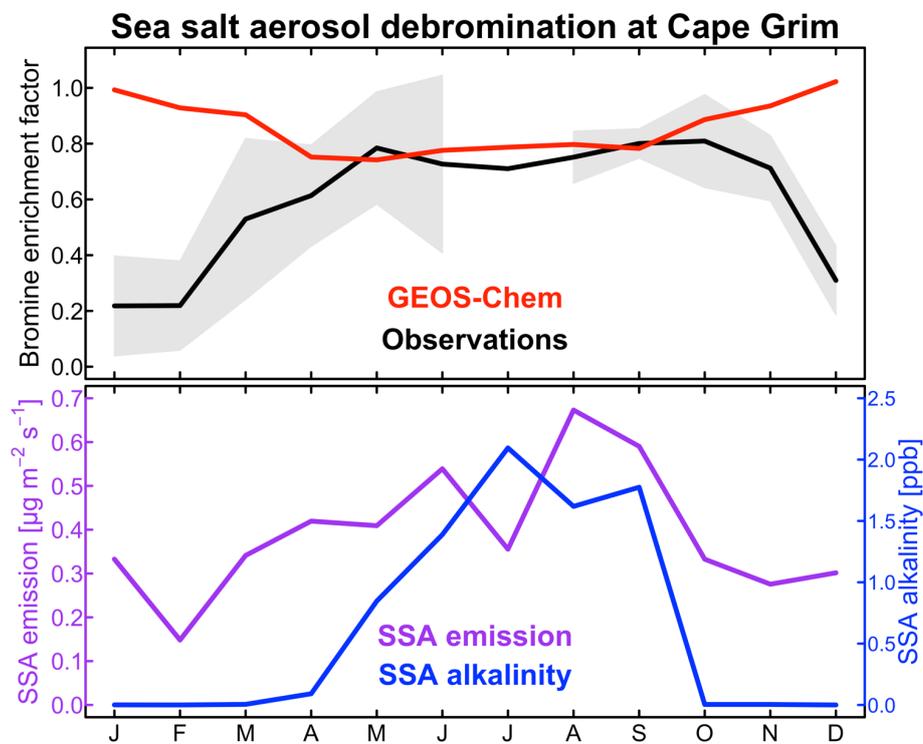
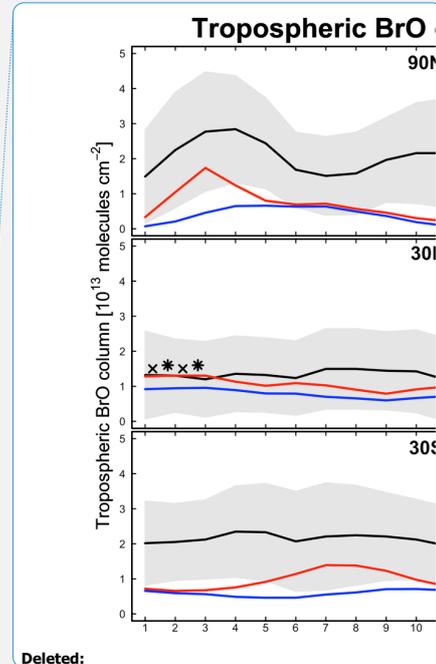
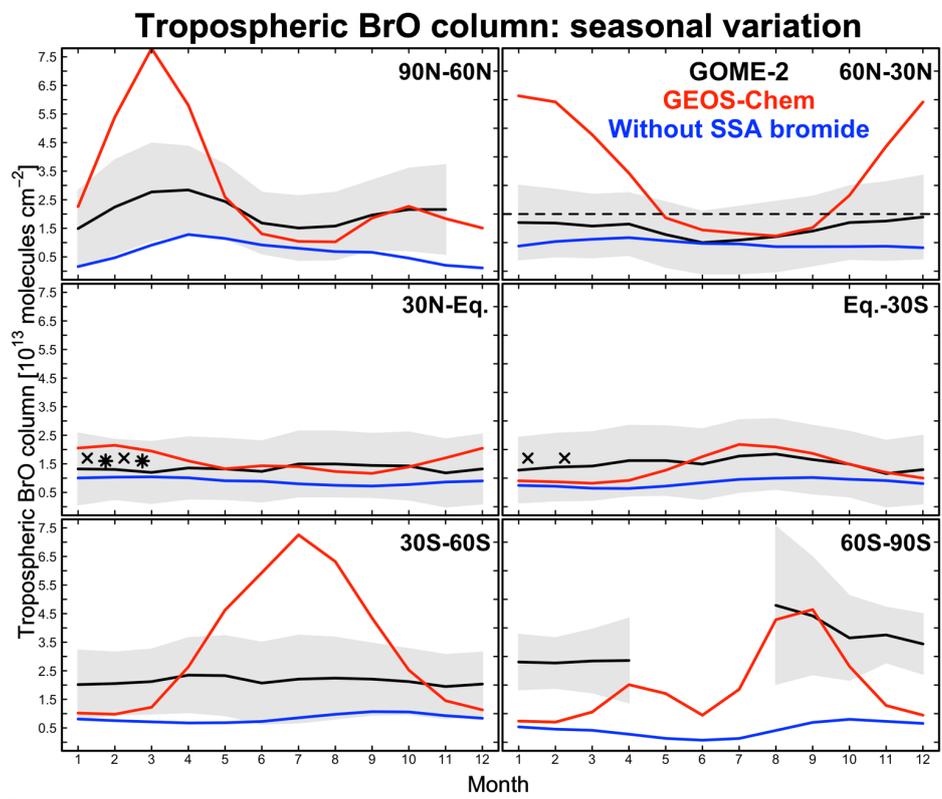


Figure 2. Seasonal variation of sea salt aerosol (SSA) debromination at Cape Grim, Tasmania (40.7°S, 144.7°E). The top panel shows the bromine enrichment factors (*EFs*) of [monthly mean](#) SSA in surface air. Observations from Ayers et al. (1999) and Sander et al. (2003) for 1996–1998 are compared to GEOS-Chem model values for 2012. Shading gives the interannual standard deviation in the [observations](#). The bottom panel shows the GEOS-Chem monthly SSA emission flux at Cape Grim ([Site 3 in Figure 1](#)) and the SSA alkalinity. The SSA emission flux is for the oceanic fraction of the Cape Grim gridsquare.

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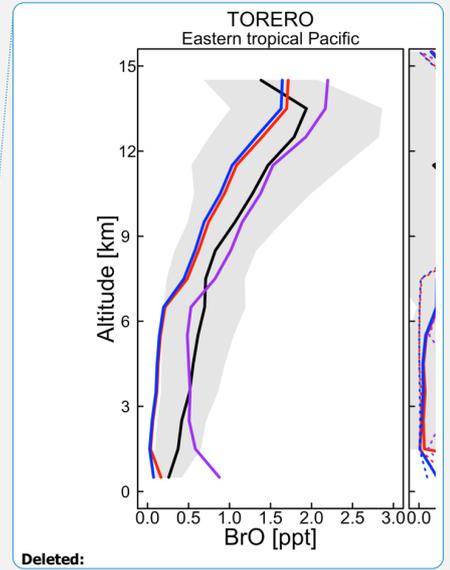
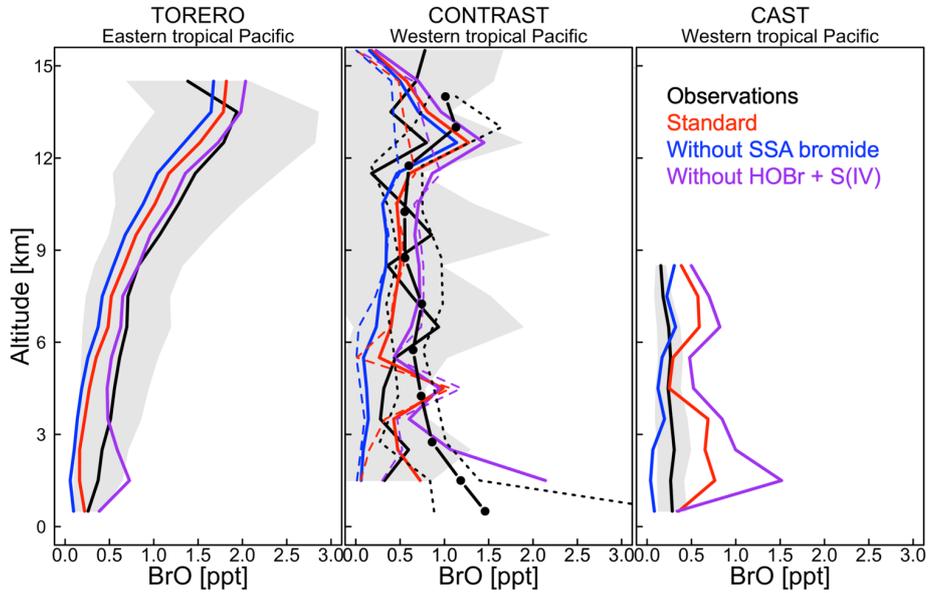
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Figure 4. Seasonal variation of zonal mean tropospheric BrO columns in different latitudinal bands. Monthly GOME-2 BrO observations are for 2007 and taken from Theys et al. (2011); shading represents one standard deviation about the monthly mean GOME-2 BrO columns. GEOS-Chem BrO columns are sampled at the GOME-2 local overpass time (09:00–10:00). Red lines are from our standard simulation including sea salt aerosol (SSA) debromination, blue lines are from a sensitivity simulation without SSA debromination. The black dashed line indicates observations for 2009–2011 reported by Coburn et al. (2011) in Florida, USA without seasonality information. Black crosses and stars represent average BrO columns measured during aircraft campaigns over the eastern tropical Pacific (Volkamer et al., 2015; Wang et al., 2015; Dix et al., 2016) and western tropical Pacific (Koenig et al., 2017), respectively.

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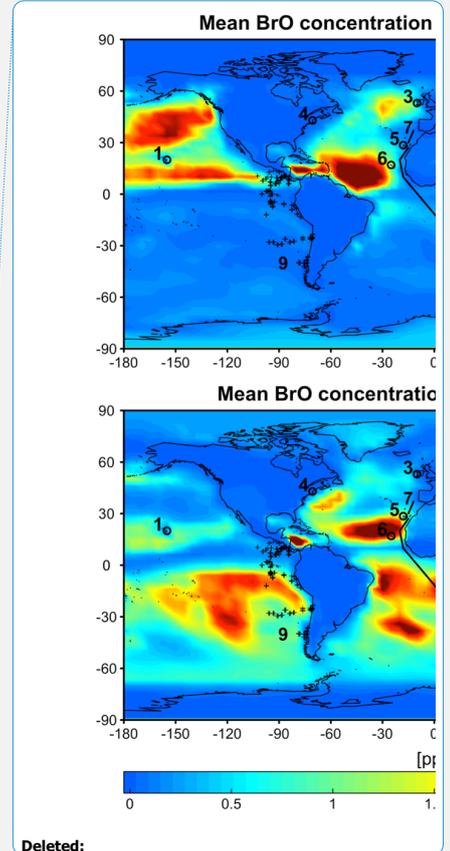
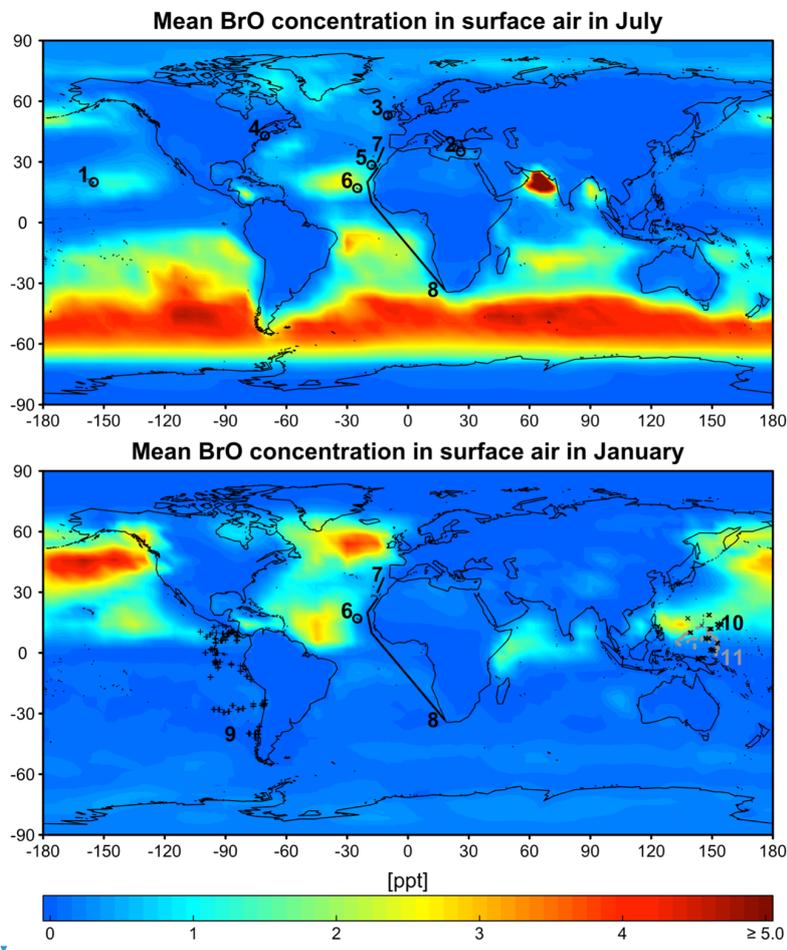


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Figure 5. Vertical profiles of BrO mixing ratios over the tropical Pacific. Observations from the TORERO (Volkamer et al., 2015; Wang et al., 2015; Dix et al., 2016), CONTRAST (Chen et al., 2016; Koenig et al., 2017), and CAST (Le Breton et al., 2017) aircraft campaigns are compared to model values. Solid black lines indicate mean observed values in 1-km vertical bins and with standard deviations (shading). We use two independent CONTRAST BrO data sets. The black line with dots shows the median values (dashed lines are 50% and 75% quantiles) as reported in Koenig et al. (2017). The solid line denotes the mean values from Chen et al. (2016). GEOS-Chem is sampled along the flight tracks at the time of the measurements. Model results are shown from our standard simulation including sea salt aerosol debromination (red lines), and sensitivity simulations not including SSA debromination (blue lines) and HOBr + S(IV) reactions (purple lines). Solid lines are mean values, dotted lines are median values.



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Figure 6. GEOS-Chem mean BrO mixing ratios in surface air in July (top) and January (bottom). Locations of BrO observations in Table 1 are shown as symbols for the closest season. Open circles are ground sites and solid lines are ship tracks. Flight tracks in the marine boundary layer (< 2 km) during the TORERO (Volkamer et al., 2015; Wang et al., 2015; Dix et al., 2016), CONTRAST (Chen et al., 2016), and CAST (Le Breton et al., 2017) aircraft campaigns are shown as pluses, crosses, and dots (gray), respectively. Daytime BrO mixing ratios are about double the values shown here since BrO drops to near zero at night. Color bar saturates at 13 ppt near India.

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Table 1. Daytime mixing ratios (ppt) of BrO in the marine boundary layer ^a

No.	Location	Time	Observed ^b	Simulated ^c	Reference ^d
Ground-based measurements					
1	Hawaii (20°N 155°W)	Sep. 1999	< 2.0	<u>1.1</u>	1
2	Crete (35°N 26°E)	Jul.–Aug. 2000	< 0.7–1.5	<u>0.48</u>	1
3	Mace Head (53°N 10°W)	Apr.–Oct. ^e	< 0.3–2.5	<u>2.1</u>	1, 2, 3
4	Maine (43°N 71°W)	Jul.–Aug. 2004	< 2.0	<u>0.49</u>	4
5	Tenerife Island (29°N 17°W)	Jun.–Jul. 1997	3.0	<u>1.0</u>	1
6	Cape Verde (17°N 25°W)	Nov. 2006–Jun. 2007	2.5 ± 1.9	<u>1.4</u>	5, 6
Ship-based measurements					
7	Atlantic Ocean (30°N–37°N)	Feb. and Oct. ^f	~ 1.0	<u>0.96</u>	7, 8, 9
8	Atlantic Ocean (33°S–27°N)	Oct. 2000	< 1.0–3.6	<u>0.97</u>	7
Aircraft-based measurements					
9	Eastern tropical Pacific Ocean (TORERO)	Jan.–Feb. 2012	0.26 ± 0.15	<u>0.22</u>	10, 11, 12
10	Western tropical Pacific Ocean (CONTRAST)	Jan.–Feb. 2014	0.63 ± 0.74	<u>0.66</u>	13
11	Western tropical Pacific Ocean (CAST)	Jan.–Feb. 2014	0.28 ± 0.16	<u>0.36</u>	14

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^a Locations of measurements are shown in **Figure 6**.

5 ^b Values reported as ranges, means, and means ± standard deviations depending on availability. The symbol “<” indicates that BrO is below the corresponding detection limit.

^c Mean values for the simulated model year of 2012. The observations are for different years. Model values are sampled at the location and time of year of the observations.

10 ^d 1 Sander et al. (2003), 2 Saiz-Lopez et al. (2004), 3 Saiz-Lopez et al. (2006), 4 Keene et al. (2007), 5 Read et al. (2008), 6 Mahajan et al. (2010), 7 Leser et al. (2003), 8 Martin et al. (2009), 9 Saiz-Lopez et al. (2012), 10 Volkamer et al. (2015), 11 Wang et al. (2015), 12 Dix et al., (2016); 13 Chen et al. (2016), and 14 Le Breton et al. (2017)

^e from 1996, 1997 and 2002.

^f from 2000 and 2007.

