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Supplement of

Effect of sea salt aerosol on tropospheric bromine chemistry

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Text S1. Updated parameterization of first-order loss of gas-phase HOBr in cloud

In the model, HOBr(g) is uptaken by cloud water (clouds droplets and ice crystal quasi-liquid surfaces), and then reacts with $Br^-/Cl^-/HSO_3^-/SO_3^{2-}$ in the aqueous phase.

$HOBr(aq) + Br^- + H^+ \rightarrow Br_2(g) + H_2O$ (R1)

$HOBr(aq) + Cl^- + H^+ \rightarrow BrCl(g) + H_2O$ (R4)

$HOBr(aq) + HSO_3^- \rightarrow H_2O + BrSO_3^-$ (R5a)

$HOBr(aq) + SO_3^{2-} \rightarrow OH^- + BrSO_3^-$ (R5b)

Here we number the four reactions in the same order as in the manuscript. Chen at al. (2017) computed the overall reactive uptake coefficient of HOBr in cloud (γ) using following parameterization:

$$\gamma = \left(\frac{1}{\gamma_d} + \frac{1}{a_b} + \frac{1}{\Gamma}\right)^{-1} \quad (1)$$

$$\Gamma = \Gamma_1 + \Gamma_4 + \Gamma_{5a} + \Gamma_{5b} \quad (2)$$

where γ_d is gas-phase diffusion coefficient (unitless), calculated following Schmidt et al. (2016) and Sherwen et al. (2016); a_b (0.6, Ammann et al., 2013) is mass accommodation coefficient (unitless); and Γ is bulk reaction coefficient (unitless). Γ is the sum of reaction coefficients of the four reactions (Γ_1, Γ_4, Γ_{5a}, and Γ_{5b}), which are calculated as:

$$\Gamma_1 = 4HRT\sqrt{D_l k_1 [\mathrm{H^+}][\mathrm{Br^-}]}\frac{f_r}{c} \quad (3)$$

$$\Gamma_4 = 4HRT\sqrt{D_l k_4 [\mathrm{H^+}][\mathrm{Cl^-}]}\frac{f_r}{c} \quad (4)$$

$$\Gamma_{5a} = 4HRT\sqrt{D_l k_{5a} [\mathrm{HSO_3}^-]}\frac{f_r}{c} \quad (5)$$

$$\Gamma_{5b} = 4HRT\sqrt{D_l k_{5b} \left[\mathrm{SO_3}^{2-}\right]}\frac{f_r}{c} \quad (6)$$

where H (1300 M atm^{-1} × exp[6014 K^{-1} × (1/T – 1/298.15)], Sander, 2015) is the Henry's law constant of HOBr; T is air temperature (K); R (8.31×10^{-2} L bar mol^{-1} K^{-1}) is the universal gas constant; D_l (1.4×10^{-5} cm^2 s^{-1}, Ammann et al., 2013) is the liquid phase diffusion coefficient for HOBr; f_r and c is the reacto-diffusive correction term (Ammann et al., 2013) and the mean thermal velocity (cm s^{-1}), respectively, calculated following Schmidt et al. (2016) and Sherwen et al. (2016); k_1 (1.6×10^{10} M^{-2} s^{-1}, Beckwith et al., 1996), k_4 (2.3×10^{10} M^{-2} s^{-1}, Liu and Margerum, 2001), k_{5a} (3.2×10^{9} M^{-1} s^{-1}, Liu, 2000), and k_{5b} (5.0×10^{9} M^{-1} s^{-1}, Troy and Margerum, 1991) is the reaction rate coefficient for (R1), (R4), (R5a), and (R5b), respectively.

However, such parameterization subjects to the assumption that physical uptake of HOBr, including diffusion in the gas phase, accommodation on the liquid surface, and diffusion in the aqueous phase, occurs independently and separately for each pathway. We argue that such assumption does not hold. Instead, aqueous HOBr(aq) + $Br^-/Cl^-/HSO_3^-/SO_3^{2-}$ reactions should all follow the same physical uptake of HOBr. We express the first-order aqueous-phase loss of HOBr(aq) as a sum of the four pathways. We update the parameterization of HOBr(aq) + $Br^-/Cl^-/HSO_3^-/SO_3^{2-}$ reaction system as described in Chen at al. (2017) by computing bulk reaction coefficient Γ using the sum (R^I) of the first order loss rate coefficient of HOBr(aq) via (R1), (R4), (R5a), and (R5b).

$$\Gamma = 4HRT\sqrt{D_l R^I}\frac{f_r}{c} \tag{7}$$

$$R^I = k_1[\mathrm{H^+}][\mathrm{Br^-}] + k_4[\mathrm{H^+}][\mathrm{Cl^-}] + k_{5a}[\mathrm{HSO_3}^-] + k_{5b}[\mathrm{SO_3}^{2-}] \tag{8}$$

Then the overall reactive uptake coefficient of HOBr in cloud (γ) is computed using equation (1). The updated parameterization tends to have greater impact on the bulk reaction coefficient (Γ) and thus on γ at a lower cloud pH. Following Chen at al. (2017), we consider the condition with a temperature of 283 K, cloud liquid water content of 0.2 g m^{-1}, cloud droplet radius of 10 μm, gas-phase SO_2, HCl and HBr concentrations to be 100 ppt, 1 ppt and 1 ppt, respectively. For cloud pH of 3, we estimate that Γ is 0.11 following Chen at al. (2017), but 0.06 (decreased by 41%) with the updated parameterization. Accordingly, γ decreases from 0.018 to 0.016 (by 10%). For cloud pH of 6, Γ decreases from 6.4 to 5.1 (by 20%) with the updated parameterization, but γ remains almost the same (0.021).

The overall first-order loss rate of HOBr(g) R_{HOBr} (molecules cm^{-3} s^{-1}) is computed as:

$$R_{\mathrm{HOBr}} = \frac{1}{4}c\gamma S[\mathrm{HOBr}] \tag{9}$$

Where S is the total surface area concentration of cloud droplets and ice crystals (cm^2 cm^{-3}). We distribute the loss by the above four pathways on the basis of their relative aqueous rates.

For (R1) and (R4), we also consider the dependence of Br_2 production yield (Y) on $[Br^-]$ and $[Cl^-]$ following Fickert et al. (1999), Chen at al. (2017), and Wang et al. (2019).

$$Y = 0.41\log_{10}\left(\frac{[\mathrm{Br^-}]}{[\mathrm{Cl^-}]}\right) + 2.25 \qquad \text{for } [\mathrm{Br^-}] / [\mathrm{Cl^-}] < 5\mathrm{x}10^{-4} \tag{10}$$

$$Y = 0.90 \qquad \text{for } [\mathrm{Br^-}] / [\mathrm{Cl^-}] \geq 5\mathrm{x}10^{-4} \tag{11}$$

Finally, we compute the loss rate of HOBr(g) via (R1), or the production rate of Br_2(g), R_{Br2} as:

$$R_{\mathrm{Br2}} = \frac{k_1[\mathrm{H^+}][\mathrm{Br^-}]+k_4[\mathrm{H^+}][\mathrm{Cl^-}]}{R^I} Y R_{\mathrm{HOBr}} \tag{12}$$

The loss rate of HOBr(g) via (R4), or the production rate of BrCl(g), R_{BrCl} is:

$$R_{\mathrm{BrCl}} = \frac{k_1[\mathrm{H^+}][\mathrm{Br^-}]+k_4[\mathrm{H^+}][\mathrm{Cl^-}]}{R^I}(1-Y)R_{\mathrm{HOBr}} \tag{13}$$

The loss rate of HOBr(g) via (R5a) R_{HSO3} is:

$$R_{\mathrm{HSO3}} = \frac{k_{5a}[\mathrm{HSO_3}^-]}{R^I} R_{\mathrm{HOBr}} \quad (14)$$

And the loss rate of HOBr(g) via (R5b) R_{SO3} is:

$$R_{\mathrm{SO3}} = \frac{k_{5b}[\mathrm{SO_3}^{2-}]}{R^I} R_{\mathrm{HOBr}} \quad (15)$$

Text S2. Correction a registration error for SSA alkalinity in the standard GEOS-Chem code

In the standard GEOS-Chem code, SSA alkalinity was incorrectly registered as cloud pH in Headers/state_chem_mod.F. By doing so, the code generally assigned higher values (than the debromination threshold) for SSA alkalinity, thus largely prevented SSA debromination from happing. We corrected this error in our simulations.

Around line 1049 in state_chem_mod.F, we changed the following line

```
CALL Register_ChmField( am_I_Root, chmID, State_Chm%pHCloud, State_Chm, RC )
```

to

```
! Fix the typo

CALL Register_ChmField( am_I_Root, chmID, State_Chm%SSAlk, State_Chm, RC )
```

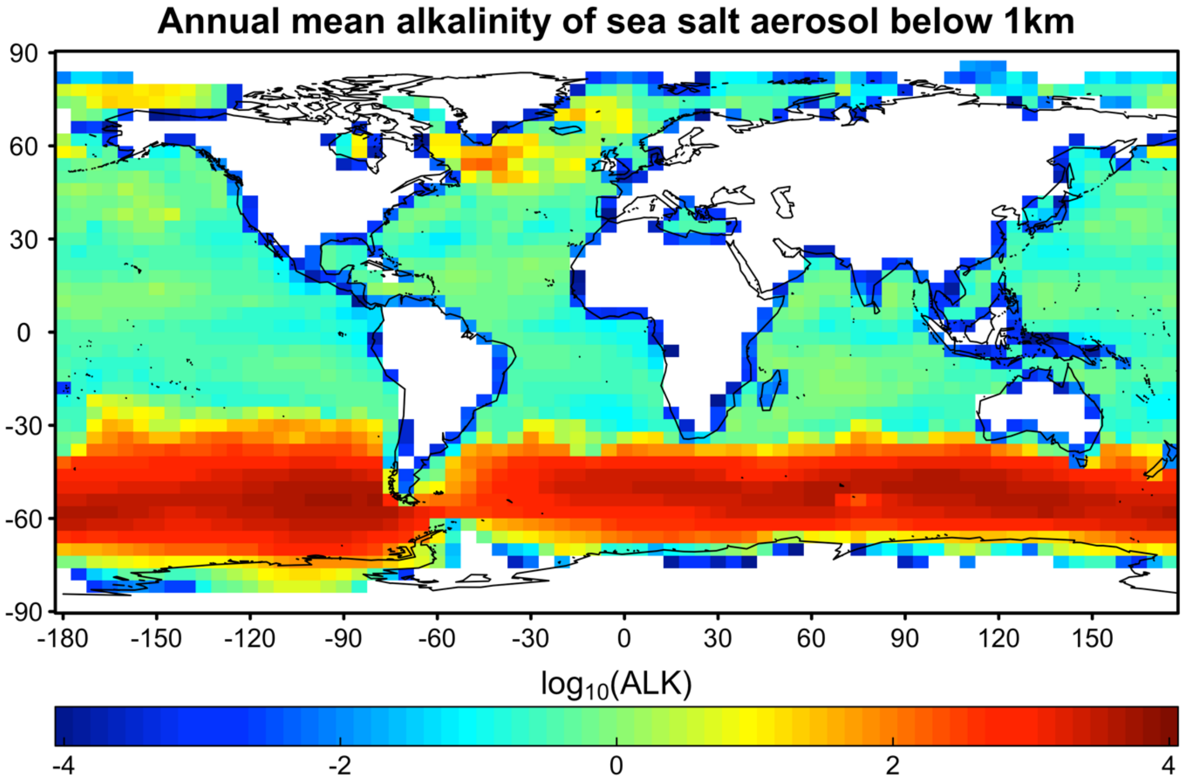

Figure S1. Annual mean alkalinity of sea salt aerosol (SSA) below 1km simulated by GEOS-Chem. Alkalinity (ALK) is in the unit of ppt. Results are shown as $\log_{10}$(ALK). White color means ALK is zero.

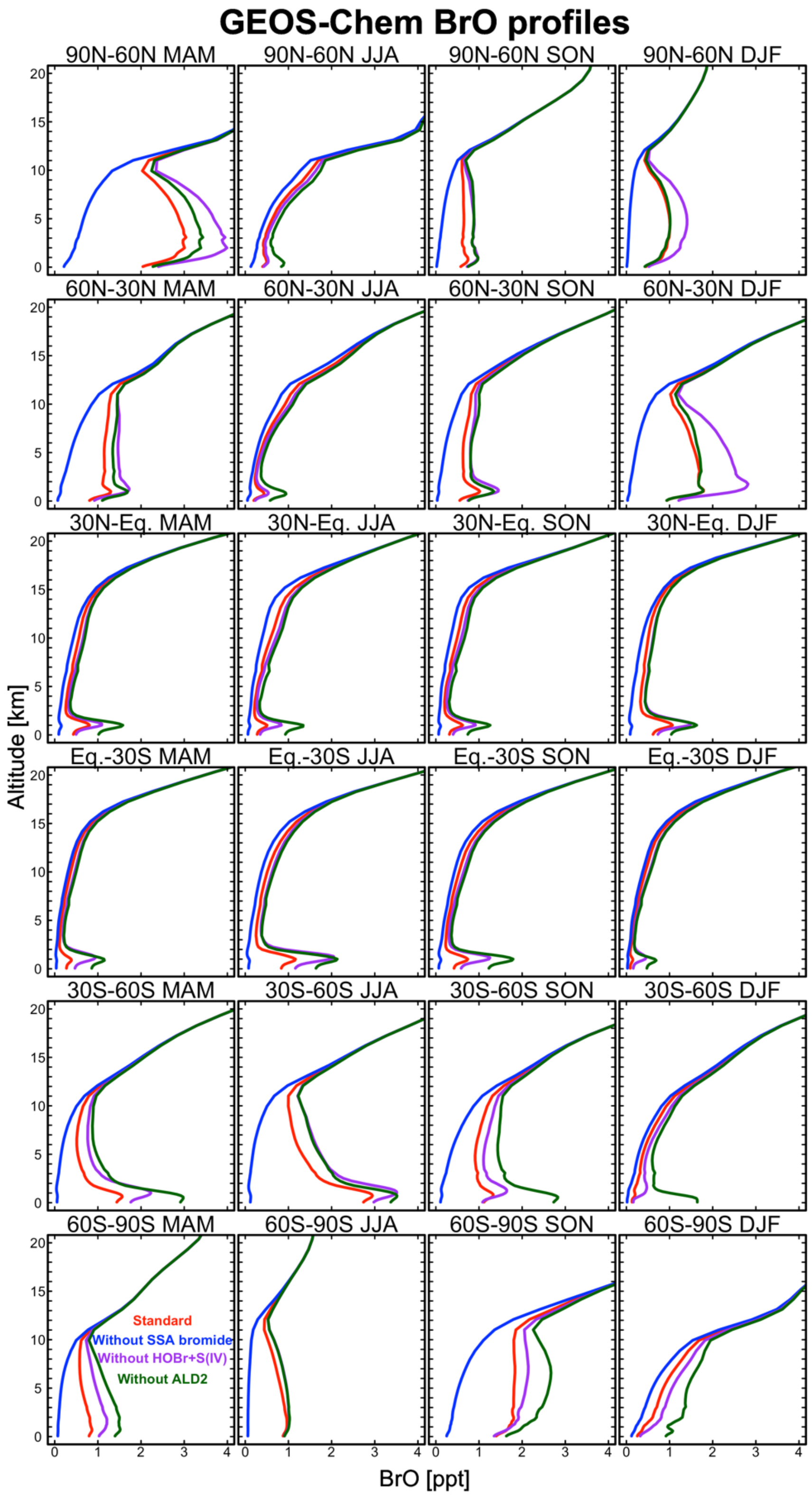

Figure S2. GEOS-Chem BrO vertical profiles averaged over different seasons and latitudinal bands. Model results are shown from our standard simulation including sea salt aerosol debromination (red lines), and sensitivity simulations not including SSA debromination (blue lines), HOBr + S(IV) reactions (purple lines), and oceanic acetaldehyde emissions (green lines).

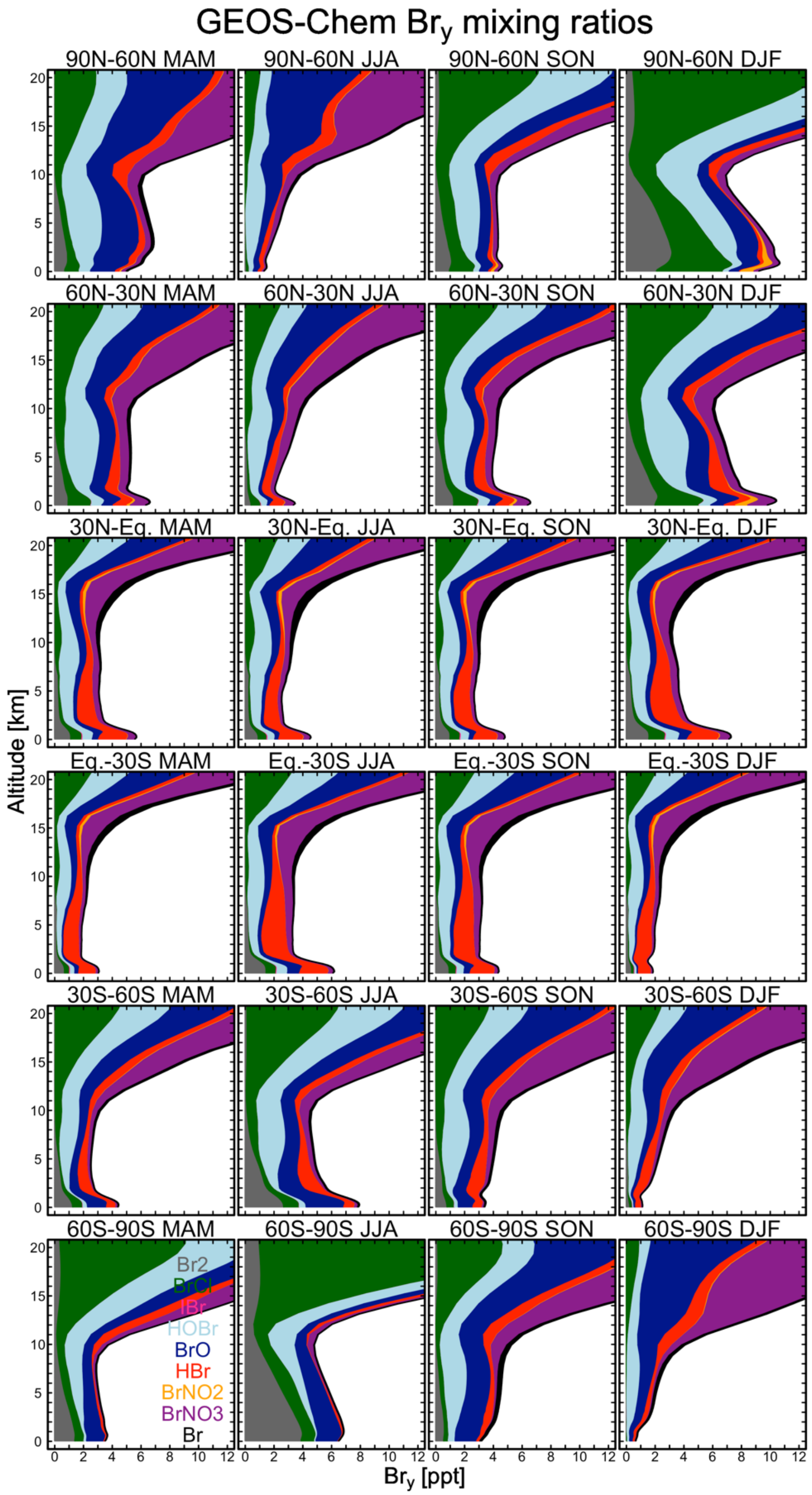

Figure S3. GEOS-Chem Br$_y$ vertical profiles over different seasons and latitudinal bands. Model results are shown from our standard simulation including sea salt aerosol debromination.

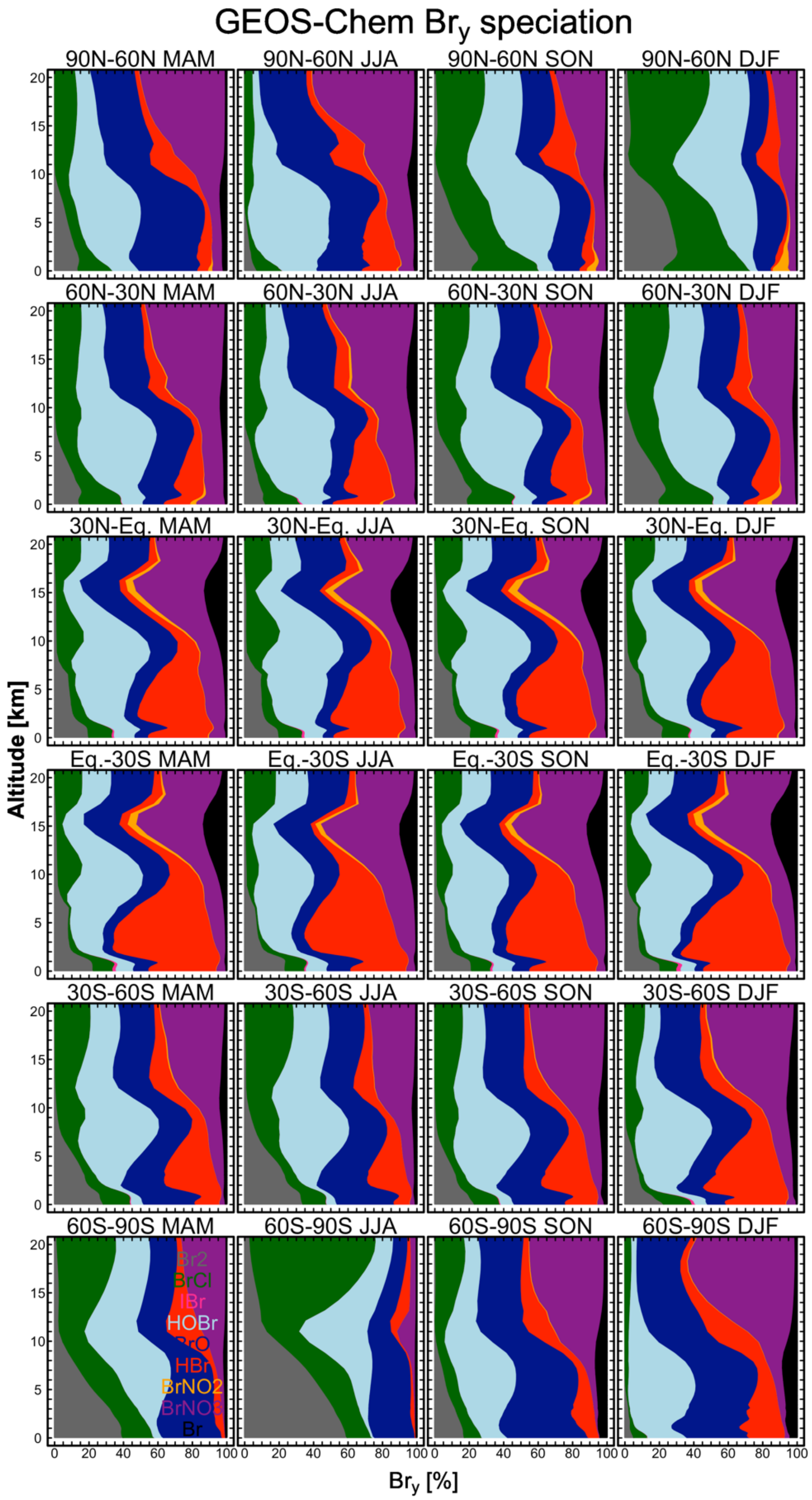

Figure S4. GEOS-Chem Br$_y$ speciation over different seasons and latitudinal bands. Model results are shown from our standard simulation including sea salt aerosol debromination.

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