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Supplement of

Bromine partitioning in the tropical tropopause layer: implications for stratospheric injection

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1 Updates on the bromine chemistry scheme

Heterogeneous recycling of halogen species over stratospheric sulfate aerosol, tropospheric ice-crystals and sea-salt aerosols are shown in (Table S1), while the Henry law's constants for wet deposition of each independent inorganic species is presented in Table S2.

2 Uncertainty of box-model results

Figure 9 in the main text presents estimates of the uncertainty of calculated values of Br, BrO, and HBr in the tropical tropopause layer. The figure includes a representation of the uncertainty due to gas phase processes, plus a total overall uncertainty found considering heterogeneous and gas phase processes. Here, we describe how these uncertainties were found. The baseline sensitivity simulation (*Run_1a*) was run using JPL-2010 kinetics (Sander et al., 2011). The simulations were repeated many times, allowing each time for a single change in a kinetics parameter relative to the baseline simulation. Rate constants for $Br+O_3$, BrO+NO, $Br+H_2CO$, and $Br+HO_2$ were varied according to the uncertainties given by JPL-2006. Similarly, the *J-value* for BrO was varied, allowing for an uncertainty of ±8 % as reported by Wilmouth et al., (Wilmouth et al., 1999), because JPL-2010 does not give an uncertainty for the BrO cross-section. The model was run for variations allowing for both increases and decreases of each parameter. The results of Figure 9 are focused on daytime chemistry. These 5 kinetic parameters were determined, based on analysis of model output, to be the primary determinants of the daytime partitioning of Br, BrO, and HBr. The dashed lines in Figure 9 were found based on a root mean sum of squares (RSS) combination of the fractional differences between results of the baseline simulation and results of each of the individual uncertainty analysis runs, accounting for the direction of the shift of each molecule (i.e., the lower limit for Br represents all simulations that resulted in reduced values of Br relative to the baseline run). The dashed lines represent the combined uncertainty due to the 5 gas phase kinetic parameters described above.

Consideration of uncertainties in heterogeneous processes leads to additional uncertainty, particularly for HBr and Br. For calculation of these uncertainties, two additional model runs were folded into the analysis (see Table 2): *Run_0*, which results in higher values of HBr and lower values of Br relative to the baseline (due to a reaction probability of zero for the

HOBr+HBr heterogeneous reaction); and, *Run_2b*, which results in decreased HBr and increased Br, due to the very efficient heterogeneous processing associated with the combination of ice and chlorine. The dotted lines in Figure 9 represent incorporation, into a RSS analysis, of fractional differences resulting from *Run_0* and *Run_2b* plus the perturbations to gas phase kinetics. The dotted lines therefore represent an overall uncertainty due to both gas phase and heterogeneous processes.

Table S1. Heterogeneous reactions involving bromine and chlorine in CAM-Chem.

	Reactions	Reactive uptake	Comments
	Stratospheric sulfate aerosol reactions		
H1.	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	f(wt%)	a
H2.	$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	f(T,P,HCl,H2O,r)	a
H3.	$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$	f(T,P,H2O,r)	a
H4.	$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	f(T,P,HCl,H2O,r)	a
H5.	$HOCl + HCl \rightarrow Cl_2 + H_2O$	f(T,P,HCl,HOCl,H2O,r)	a
H6.	$HOBr + HCl \rightarrow BrCl + H_2O$	f(T,P,HCl,HOBr,H2O,r)	a
	Nitric acid tri-hydrate reactions		
H7.	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	$\gamma = 4.0 \times 10^{-4}$	b
H8.	$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	$\gamma = 4.0 \times 10^{-3}$	b
H9.	$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	$\gamma = 0.2$	b
H10.	$HOCl + HCl \rightarrow Cl_2 + H_2O$	$\gamma = 0.1$	b
H11.	$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$	$\gamma = 0.3$	b
	ice crystals reactions		
H12.	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	$\gamma_{strat} = 0.02$	b
H13.	$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	$\gamma_{trop} = \gamma_{strat} = 0.3$	b
H14.	$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$	$\gamma_{trop} = 0.1^{\dagger}$; $\gamma_{strat} = 0.3$	b
H15.	$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	$\gamma_{strat} = 0.3$	b
H16.	$HOCl + HCl \rightarrow Cl_2 + H_2O$	$\gamma_{trop} = \gamma_{strat} = 0.2$	b
H17.	$HOBr + HCl \rightarrow BrCl + H_2O$	$\gamma_{trop} = \gamma_{strat} = 0.3$	b
H18.	$HOCl + HBr \rightarrow BrCl + H_2O$	$\gamma_{trop} = 0.2^{\dagger}$	b
H19.	$HOBr + HBr \rightarrow Br_2 + H_2O$	$\gamma_{trop} = 0.12^{\dagger}$	b
	Sea-salt aerosol reactions		
HSS0.	$BrONO_2 \rightarrow 0.65\ Br_2 + 0.35\ BrCl$	$\gamma = 0.08$	c
HSS1.	$BrNO_2 \rightarrow 0.65\ Br_2 + 0.35\ BrCl$	$\gamma = 0.04$	c
HSS2.	$HOBr \rightarrow 0.65\ Br_2 + 0.35\ BrCl$	$\gamma = 0.1$	c
HSS3.	$ClONO_2 \rightarrow Cl_2$	$\gamma = 0.02$	c
HSS4.	$ClNO_2 \rightarrow Cl_2$	$\gamma = 0.02$	c
HSS5.	$HOCl \rightarrow Cl_2$	$\gamma = 0.1$	c

[a] gamma computed online following (Kinnison et al., 2007).
[b] values taken from JPL-2010 (Sander et al., 2011).
[c] values based on the THAMO model (Saiz-Lopez et al., 2008) adjusted to the CAM-Chem implementation following (Ordóñez et al., 2012).
† the tropopause level computed online in CAM-Chem was used to differentiate the troposphere and the stratosphere.

Table S2. Henry's Law constants for relevant halogen species in CAM-Chem.

Species	k_0 (M atm^{-1})	c (K)	Ice-uptake	Comments
$ClONO_2$	1.0 x 10^6		YES	a
$ClNO_2$	3.5 x10^{-2}		YES	b
HCl	1.54 x10^0	9000	YES	c, †
HOCl	9.3 x10^2		YES	C
$BrONO_2$	1.0 x 10^6		YES	A
$BrNO_2$	3.0 x10^{-1}		YES	
HOBr	1.9 x10^3		NO	B
HBr	7.2 x10^{-1}	6100	NO	c, †
BrCl	9.4 x10^{-1}	5600	YES	c
Br_2	7.6 x10^{-1}	4100	YES	c

All values were taken from the Henry's Law Constant Compilation of Dr. Rolf Sander (Sander, 1999).
[a] Virtually infinite solubility is represented in the model using a very large but arbitrary number.
[b] Within the range of values given in the corresponding reference.
[c] Other values are also reported in the corresponding reference.
† An effective Henry's Law constant (K_H^{eff}) is computed considering an acid dissociation constant of $K_a = 1.3 \times 10^{6}$ for HCl, $K_a = 1.0 \times 10^{9}$ for HBr and pH = 5 (Ordóñez et al., 2012). Values at 298 K are $K_H^{eff}(HCl) = 2.0 \times 10^{11}$ M atm^{-1} and $K_H^{eff}(HBr) = 7.2 \times 10^{13}$ M atm^{-1}.

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