Supplementary online material

Bromine and iodine in a global chemistry-climate model: Description, very short-lived oceanic sources and evaluation

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Chemistry of VSL halogen species in CAM-Chem

An introduction to the tropospheric halogen chemistry scheme in CAM-Chem is given in Section 3 of the main text. That section also describes the breakdown of very short-lived (VSL) halocarbons into their products. Here we focus on the main gas phase reactions involving reactive bromine and iodine in the model, in particular those which are relevant for tropospheric ozone (O_3) depletion. We will also briefly summarise other processes of importance for the troposphere, following the review by von Glasow and Crutzen (2007). The bimolecular, termolecular and photolytic reactions involving halogen species in the model are summarised in Tables 1, 2 and 3, respectively. Information on heterogeneous reactions, Henry's Law constants and dry deposition velocities of halogen species is included in Tables 4, 5 and 6, respectively. In the following, X represents Cl, Br or I. If two halogen species are present in the same reaction then we use X and Y to design both of them.

In addition to the photochemical breakdown of halocarbons, halogen radicals (X, Y) can be formed in the troposphere by the photolysis of dihalogens (X_2 or XY) or other inorganic halogen species like HOX (Table 3). They react with O_3 producing halogen oxides (XO). If these oxides photolyse, both O_3 and the halogen radical X are formed again; however they can also undergo chemical reactions that lead to net O_3 destruction. One of the main O_3 destruction paths includes the reaction of XO with HO_2, which is also responsible for reducing the HO_x (HO_2/OH) ratio:

$$X + O_3 \rightarrow XO + O_2 \qquad \text{(R38, R65)}$$

$$XO + HO_2 \rightarrow HOX + O_2 \qquad \text{(R46, R68)}$$

$$HOX + h\nu \rightarrow X + OH \qquad \text{(J25, J41)}$$

$$Net{:}\ HO_2 + O_3 \rightarrow OH + 2O_2$$

BrO and IO self-reactions are also of importance for tropospheric ozone destruction:

$$2(Br + O_3 \rightarrow BrO + O_2) \qquad \text{(R38)}$$

$$BrO + BrO \rightarrow 2Br + O_2 \qquad \text{(R54)}$$

$$Net:\ 2O_3 \rightarrow 3O_2$$

$$2(I + O_3 \rightarrow IO + O_2) \qquad \text{(R65)}$$

$$IO + IO \rightarrow OIO + I \qquad \text{(R69)}$$

$$OIO + h\nu \rightarrow I + O_2 \qquad \text{(J36)}$$

$$Net:\ 2O_3 \rightarrow 3O_2$$

When two halogen oxides are present in the troposphere, cross reactions such as

$$BrO + ClO \rightarrow Br + Cl + O_2 \qquad \text{(R49)}$$

$$IO + BrO \rightarrow I + Br + O_2 \qquad \text{(R84)}$$

can make O_3 destruction very efficient. Photochemical box model calculations of observations in coastal Antarctica (Saiz-Lopez et al., 2007) and the tropical Atlantic Ocean (Read et al., 2008) have shown that the effect of IO and BrO together is greater than the sum of their individual contributions, because the reaction IO + BrO increases the rate at which the halogen oxides are converted back to I and Br atoms. Other reaction paths for the BrO + ClO reaction produce OClO (R48) and BrCl (R50), while an additional channel of the IO + BrO reaction yields OIO (R85).

In very clean air (NOx<30 ppt), the gas-phase chemistry of IO is dominated by the reactions of IO with itself to form I_2O_2 and OIO + I, IO + OIO to form I_2O_3, and OIO + OIO to form I_2O_4 (Table 1). These reactions proceed rapidly in the gas phase, with rate coefficients of ~10^{10}–10^{11}. In the current version of CAM-Chem we do not include the formation of gas phase I_2O_5 through oxidation of I_2O_4 by O_3. We also assume that, with the only exception of the very rapid thermal decomposition of I_2O_2 (R73 and R74), I_2O_x (x=2, 3, 4) do not undergo photolysis or other reactions which would reduce them to IO or OIO. Hence, the rapid conversion of IO and OIO into higher order iodine oxides limits the atmospheric lifetime of both radicals in the model. 1-D model calculations strongly suggest that the photolysis of I_2O_2, I_2O_3, I_2O_4 and I_2O_5 would be required to explain the vertical distribution of IO in the Antarctic boundary layer (Saiz-Lopez et al., 2008). However further laboratory work on the photochemistry of these species is needed.

The formation of halogen nitrates and nitrites can be important in semi-polluted environments:

$$XO + NO_2\ (+M) \rightarrow XONO_2\ (+M) \qquad \text{(T4, T7)}$$

$$X + NO_2\ (+M) \rightarrow XNO_2\ (+M) \qquad \text{(T5, T6)}$$

Depending on conditions, these species can either photolyse

$$XONO_2 + h\nu \rightarrow X + NO_3 \qquad \text{(J26, J40)}$$

$$XONO_2 + h\nu \rightarrow XO + NO_2 \qquad \text{(J27)}$$

$$XNO_2 + h\nu \rightarrow X + NO_2 \qquad \text{(J28, J38)}$$

$$XNO_2 + h\nu \rightarrow XO + NO \qquad \text{(J29, J39)}$$

thermally decompose

$$INO_2 \rightarrow I + NO_2 \qquad \text{(R81)}$$

undergo oxidation (see Table 1) or react on surfaces (Table 4). Some of these reactions can also lead to O_3 depletion.

Sea salt is also an important source of reactive bromine and iodine in the troposphere. Typical diameters of sea salt particles are > 0.1 μm, which limits their relevance to the marine boundary layer due to fast removal by sedimentation and wet scavenging. In CAM-Chem, the heterogeneous recycling of halogens on sea salt aerosols is treated as follows. The uptake and subsequent hydrolysis of $XONO_2$, HOX and XNO_2 on marine aerosols produces HOX, which equilibrates between gas and aqueous phase according to its Henry's law solubility. The processing of aqueous HOX to Br_2, BrCl, IBr, ICl and Cl_2 via reaction with Br^-, Cl^- and I^- takes only between 10 and 15 min on fresh sea-salt aerosols (McFiggans et al., 2000). Since di-halogen molecules are insoluble they are rapidly released to the gas phase. As a consequence, uptake of inorganic bromine and iodine species onto aerosols is the rate-limiting step of the process (McFiggans et al., 2000). Aged sea-salt aerosols become depleted in Br^- and Cl^- thus slowing down the halogen recycling on aerosols (e.g. Fickert et al., 1999; von Glasow et al., 2002). Additionally, aged particles become progressively acidified by uptake of HNO_3, H_2SO_4 and SO_2, which in turn increases the rate of processing. In CAM-Chem we do not explicitly treat the aqueous phase chemistry in the bulk of the sea salt aerosols. Instead, we assume that the limiting step for halogen recycling on sea salt aerosols is the firstorder rate of uptake computed for a number of gaseous species using the free molecular transfer regime approximation (see Table 4). CAM-Chem simulations indicate that heterogeneous processing of bromine on sea-salt aerosol is needed to reproduce the observed BrO in the marine boundary layer, but the full description of all the processes which release halogens from sea-salt aerosols is out of the scope of this paper. Note that the photochemical processing of bromocarbons provides the main source of mid- and upper tropospheric reactive bromine due to their longer lifetimes relative to those of most inorganic bromine species, as already pointed out by Yang et al. (2005) and Warwick et al. (2006).

The halogen species removed in CAM-Chem by washout and scavenging in clouds are listed in Table 5 together with the corresponding Henry Law's coefficients. In addition, dry deposition to the surface occurs from the lowermost level of the model for the following reactive halogen species: HCl, HBr, HOCl, $ClONO_2$, HOBr, $BrONO_2$, HI, I_2O_2, HOI, $IONO_2$, INO_2 (see Table 6 of the Supplementary Material). The deposition flux of each gaseous species is calculated as the product of the deposition velocity and the concentration.

Table 1. Halogen chemistry scheme in CAM-Chem. Bimolecular and thermal decomposition reactions.

	Reactions	**Rate Constants (cm^3 $molecule^{-1}$ s^{-1})**	**Notes**
R1.	$CH_3Cl + Cl \rightarrow HO_2 + CO + 2HCl$	3.20 x 10^{-11} $e^{(-1250/T)}$	1
R2.	$CH_3Cl + OH \rightarrow Cl + H_2O + HO_2$	2.40 x 10^{-12} $e^{(-1250/T)}$	2
R3.	$CH_3CCl_3 + OH \rightarrow H_2O + 3Cl$	1.60 x 10^{-12} $e^{(-1520/T)}$	1
R4.	$HCFC22 + OH \rightarrow Cl + H_2O + CF_2O$	4.00 x 10^{-12} $e^{(-1400/T)}$	1
R5.	$CH_3Br + OH \rightarrow Br + H_2O + HO_2$	2.35 x 10^{-12} $e^{(-1300/T)}$	2
R6.	$CH_2BrCl + OH \rightarrow Br + Cl$	2.40 x 10^{-12} $e^{(-920/T)}$	2
R7.	$CH_2Br_2 + OH \rightarrow 2Br$	2.00 x 10^{-12} $e^{(-840/T)}$	2
R8.	$CHBr_3 + OH \rightarrow 3Br$	1.35 x 10^{-12} $e^{(-600/T)}$	2
R9.	$CHBrCl_2 + OH \rightarrow Br + 2Cl$	9.00 x 10^{-13} $e^{(-600/T)}$	3
R10.	$CHBr_2Cl + OH \rightarrow 2Br + Cl$	9.00 x 10^{-13} $e^{(-600/T)}$	3
R11.	$OH + CH_3I \rightarrow CH_2I + H_2O$	2.9 x 10^{-12} $e^{(-1100/T)}$	2
R12.	$OH + CF_3I \rightarrow HOI + CF_3$	2.5 x 10^{-11} $e^{(-2070/T)}$	2
R13.	$Cl + O_3 \rightarrow ClO + O_2$	2.30 x 10^{-11} $e^{(-200/T)}$	1
R14.	$Cl + H_2 \rightarrow HCl + H$	3.70 x 10^{-11} $e^{(-2300/T)}$	1
R15.	$Cl + H_2O_2 \rightarrow HCl + HO_2$	1.10 x 10^{-11} $e^{(-980/T)}$	1
R16.	$Cl + HO_2 \rightarrow HCl + O_2$	1.80 x 10^{-11} $e^{(170/T)}$	1
R17.	$Cl + HO_2 \rightarrow OH + ClO$	4.10 x 10^{-11} $e^{(-450/T)}$	1
R18.	$Cl + HCHO \rightarrow HCl + HO_2 + CO$	8.10 x 10^{-11} $e^{(-30/T)}$	1
R19.	$Cl + CH_4 \rightarrow CH_3O_2 + HCl$	9.60 x 10^{-12} $e^{(-1360/T)}$	1
R20.	$ClO + O(^3P) \rightarrow Cl + O_2$	3.00 x 10^{-11} $e^{(+70/T)}$	1
R21.	$ClO + OH \rightarrow Cl + HO_2$	7.40 x 10^{-12} $e^{(270/T)}$	1
R22.	$ClO + OH \rightarrow HCl + O_2$	6.0 x 10^{-13} $e^{(230/T)}$	1
R23.	$ClO + HO_2 \rightarrow O_2 + HOCl$	2.7 x 10^{-12} $e^{(220/T)}$	1
R24.	$ClO + NO \rightarrow NO_2 + Cl$	6.40 x 10^{-12} $e^{(290/T)}$	1
R25.	$ClO + ClO \rightarrow 2Cl + O_2$	3.00 x 10^{-11} $e^{(-2450/T)}$	1
R26.	$ClO + ClO \rightarrow Cl_2 + O_2$	1.00 x 10^{-12} $e^{(-1590/T)}$	1
R27.	$ClO + ClO \rightarrow Cl + OClO$	3.50 x 10^{-13} $e^{(-1370/T)}$	1
R28.	$HCl + OH \rightarrow H_2O + Cl$	2.60 x 10^{-12} $e^{(-350/T)}$	1
R29.	$HCl + O(^3P) \rightarrow Cl + OH$	1.00 x 10^{-11} $e^{(-3300/T)}$	1
R30.	$HOCl + O(^3P) \rightarrow ClO + OH$	1.70 x 10^{-13}	1
R31.	$HOCl + Cl \rightarrow HCl + ClO$	2.50 x 10^{-12} $e^{(-130/T)}$	1
R32.	$HOCl + OH \rightarrow H_2O + ClO$	3.00 x 10^{-12} $e^{(-500/T)}$	1
R33.	$ClONO_2 + O(^3P) \rightarrow ClO + NO_3$	2.90 x 10^{-12} $e^{(-800/T)}$	1
R34.	$ClONO_2 + OH \rightarrow HOCl + NO_3$	1.20 x 10^{-12} $e^{(-330/T)}$	1
R35.	$ClONO_2 + Cl \rightarrow Cl_2 + NO_3$	6.50 x 10^{-12} $e^{(135/T)}$	1
R36.	$ClNO_2 + OH \rightarrow HOCl + NO_2$	2.40 x 10^{-12} $e^{(-1250/T)}$	1
R37.	$Cl_2 + OH \rightarrow HOCl + Cl$	1.4 x 10^{-12} $e^{(-900/T)}$	1
R38.	$Br + O_3 \rightarrow BrO + O_2$	1.7 x 10^{-11} $e^{(-800 / T)}$	1
R39.	$Br + HO_2 \rightarrow HBr + O_2$	1.5 x 10^{-11} $e^{(-600 / T)}$	1
R40.	$Br + HCHO \rightarrow HBr + HO2 + CO$	1.7 x 10^{-11} $e^{(-800 / T)}$	2
R41.	$Br + CH_3CHO \rightarrow HBr + CH_3CO_3$	1.3 x 10^{-11} $e^{(-360 / T)}$	11
R42.	$Br + NO_3 \rightarrow BrO + NO_2$	1.6 x 10^{-11}	2
R43.	$Br + OH \rightarrow HOBr$	4.2 x 10^{-11}	11

R44.	$BrO + O(^3P) \rightarrow Br + O_2$	$1.9 \text{ x } 10^{-11}\ e^{(230/T)}$	1
R45.	$BrO + OH \rightarrow Br + HO_2$	$7.5 \text{ x } 10^{-11}$	1
R46.	$BrO + HO_2 \rightarrow HOBr + O_2$	$3.4 \text{ x } 10^{-12}\ e^{(540/T)}$	1
R47.	$BrO + NO \rightarrow Br + NO_2$	$8.8 \text{ x } 10^{-12}\ e^{(260/T)}$	2
R48.	$BrO + ClO \rightarrow Br + OClO$	$9.5 \text{ x } 10^{-13}\ e^{(550/T)}$	2
R49.	$BrO + ClO \rightarrow Br + Cl + O_2$	$2.3 \text{ x } 10^{-12}\ e^{(260/T)}$	2
R50.	$BrO + ClO \rightarrow BrCl + O_2$	$4.1 \text{ x } 10^{-13}\ e^{(290/T)}$	2
R51.	$BrO + CH_3O_2 \rightarrow Br + HCHO + HO_2$	$1.6 \text{ x } 10^{-12}$	4
R52.	$BrO + CH_3O_2 \rightarrow HOBr + HCHO$	$4.1 \text{ x } 10^{-12}$	4
R53.	$BrO + CH_3CO_3 \rightarrow Br + CH_3O_2$	$1.7 \text{ x } 10^{-12}$	11
R54.	$BrO + BrO \rightarrow 2Br + O_2$	$1.5 \text{ x } 10^{-12}\ e^{(230/T)}$	2
R55.	$HBr + OH \rightarrow Br + H_2O$	$5.5. \text{ x } 10^{-12}\ e^{(200/T)}$	2
R56.	$HBr + O(^3P) \rightarrow OH + Br$	$5.8 \text{ x } 10^{-12}\ e^{(-1500/T)}$	1
R57.	$HBr + O(^1D) \rightarrow 0.2O + 0.2HBr + 0.8OH + 0.8Br$	$1.5 \text{ x } 10^{-10}$	2
R58.	$Br_2 + OH \rightarrow HOBr + Br$	$2.1 \text{ x } 10^{-11}\ e^{(240/T)}$	1
R59.	$BrONO_2 + O(^3P) \rightarrow BrO + NO_3$	$1.91 \text{ x } 10^{-11}\ e^{(215/T)}$	1
R60.	$BrONO_2 + Br \rightarrow Br_2 + NO_3$	$1.78 \text{ x } 10^{-11}\ e^{(365/T)}$	5
R61.	$BrONO_2 + Cl \rightarrow BrCl + NO_3$	$6.28 \text{ x } 10^{-11}\ e^{(215/T)}$	5
R62.	$BrO + DMS \rightarrow Br + DMSO$	$1.4 \text{ x } 10^{-14}\ e^{(950/T)}$	2
R63.	$I_2 + O_3 \rightarrow IO + I + O_2$	$3.8 \text{ x } 10^{-18}$	5
R64.	$I_2 + O_3 \rightarrow OIO + IO$	$3.8 \text{ x } 10^{-18}$	5
R65.	$I + O_3 \rightarrow IO + O_2$	$2.1 \text{ x } 10^{-11}\ e^{(-830/T)}$	6
R66.	$I + HO_2 \rightarrow HI + O_2$	$1.5 \text{ x } 10^{-11}\ e^{(-1090/T)}$	2
R67.	$IO + NO \rightarrow I + NO_2$	$7.15 \text{ x } 10^{-12}\ e^{(300/T)}$	6
R68.	$IO + HO_2 \rightarrow HOI + O_2$	$1.4 \text{ x } 10^{-11}\ e^{(540/T)}$	6
R69.	$IO + IO \rightarrow OIO + I$	$1.6 \text{ x } 10^{-11}\ e^{(180/T)}$	6
R70.	$IO + IO \rightarrow I_2O_2$	$3.7 \text{ x } 10^{-11}\ e^{(180/T)}$	6
R71.	$IO + OIO \rightarrow I_2O_3$	$5.0 \text{ x } 10^{-11}$	7
R72.	$OIO + OIO \rightarrow I_2O_4$	$1.5 \text{ x } 10^{-10}$	7
R73.	$I_2O_2 \rightarrow OIO + I$	$2.5 \text{ x } 10^{14}\ e^{(-9770/T)}$	8
R74.	$I_2O_2 \rightarrow IO + IO$	$1 \text{ x } 10^{12}\ e^{(-9770/T)}$	8
R75.	$I_2 + OH \rightarrow HOI + I$	$1.8 \text{ x } 10^{-10}$	2
R76.	$I_2 + NO_3 \rightarrow IO + INO_2$	$1.5 \text{ x } 10^{-12}$	6
R77.	$I + NO_3 \rightarrow IO + NO_2$	$4.5 \text{ x } 10^{-10}$	9
R78.	$OH + HI \rightarrow I + H_2O$	$3.0 \text{ x } 10^{-11}$	2
R79.	$HOI + OH \rightarrow IO + H_2O$	$2.0 \text{ x } 10^{-13}$	10
R80.	$IO + DMS \rightarrow DMSO + I$	$1.2 \text{ x } 10^{-14}$	2
R81.	$INO_2 \rightarrow I + NO_2$	$(2.4 / 0.005) \text{ x } 2.07 \text{ x } 10^{15}\ e^{(-11859/T)}$	10
R82.	$INO + INO \rightarrow I_2 + 2NO$	$8.4 \text{ x } 10^{-11}\ e^{(-2620/T)}$	2
R83.	$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	$2.9 \text{ x } 10^{-11}\ e^{(-2600/T)}$	2
R84.	$IO + BrO \rightarrow Br + I + O_2$	$0.30 \text{ x } 10^{-11}\ e^{(510/T)}$	6
R85.	$IO + BrO \rightarrow Br + OIO$	$1.20 \text{ x } 10^{-11}\ e^{(510/T)}$	6
R86.	$I + BrO \rightarrow IO + Br$	$1.2 \text{ x } 10^{-11}$	2
R87.	$IO + ClO \rightarrow I + OClO$	$5.1 \text{ x } 10^{-12}\ e^{(280/T)}$	2

[1] JPL 02-25 (Sander et al., 2003); [2] JPL 06-02 (Sander et al., 2006); [3] estimated (see main text of the paper); [4] Aranda et al. (1997); [5] NIST (2010); [6] Atkinson et al. (2007b); [7] Gómez Martín et al. (2007); [8] calculated using RRKM theory; [9] Chambers et al. (1992); [10] McFiggans et al. (2000); [11] Estimated.

Table 2. Halogen chemistry scheme in CAM-Chem. Termolecular reactions.

Termolecular reactions	$\mathbf{k = (k_0\ [M] / (1 + k_0 [M] / k_\infty)) \times F_c^n}$ $\mathbf{n = \{1 + (\log_{10}(k_0\ [M] / k_\infty))^2\}^{-1}}$ $\mathbf{F_c = 0.6}$
T1. $ClO + NO_2 (+ M) \rightarrow ClONO_2 (+ M)$	$k_0 = 1.8 \times 10^{-31} \times (T / 300)^{-3.4}$
	$k_\infty = 1.5 \times 10^{-11} \times (T / 300)^{-1.9}$
T2. $Cl + NO_2 (+ M) \rightarrow ClNO_2 (+ M)$	$k_0 = 1.8 \times 10^{-31} \times (T / 300)^{-2}$
	$k_\infty = 1.0 \times 10^{-10} \times (T / 300)^{-1}$
T3. $ClO + ClO (+ M) \rightarrow Cl_2O_2 (+ M)$	$k_0 = 1.6 \times 10^{-32} \times (T / 300)^{-4.5}$
	$k_\infty = 2.0 \times 10^{-12} \times (T / 300)^{-2.4}$
T4. $BrO + NO_2 (+ M) \rightarrow BrONO_2 (+ M)$	$k_0 = 5.2 \times 10^{-31} \times (T / 300)^{-3.2}$
	$k_\infty = 6.9 \times 10^{-12} \times (T / 300)^{-2.9}$
T5. $Br + NO_2 (+ M) \rightarrow BrNO_2 (+ M)$	$k_0 = 4.2 \times 10^{-31} \times (T / 300)^{-2.4}$
	$k_\infty = 2.7 \times 10^{-11}$
T6. $I + NO_2 (+ M) \rightarrow INO_2 (+ M)$	$k_0 = 3 \times 10^{-31} \times (T / 300)^{-1}$
	$k_\infty = 6.6 \times 10^{-11}$
T7. $IO + NO_2 (+ M) \rightarrow IONO_2 (+ M)$	$k_0 = 6.5 \times 10^{-31} \times (T / 300)^{-3.5}$
	$k_\infty = 7.6 \times 10^{-12} \times (T / 300)^{-1.5}$
T8. $I + NO (+ M) \rightarrow INO (+ M)$	$k_0 = 1.8 \times 10^{-32} \times (T / 300)^{-1}$
	$k_\infty = 1.7 \times 10^{-11}$
T9. $Cl_2O_2 + M \rightarrow ClO + ClO + M$	$K_{T9} = K_{T3} / [\ 9.3 \times 10^{-28} \times e^{(8835 / T)}]$

k_0 is given in cm^6 $molecule^{-2}$ s^{-1}
k_∞ is given in cm^3 $molecule^{-1}$ s^{-1}
All expressions taken from JPL 06-02 (Sander et al., 2006).

Table 3. Photochemical reactions for halogen species in CAM-Chem.

	Photochemical reactions of halogen species
J1.	$CH_3Cl + h\nu \rightarrow Cl + CH_3O_2$
J2.	$CCl_4 + h\nu \rightarrow 4Cl$
J3.	$CH_3CCl_3 + h\nu \rightarrow 3Cl$
J4.	$CFC11 + h\nu \rightarrow 3Cl$
J5.	$CFC12 + h\nu \rightarrow 2Cl$
J6.	$CFC113 + h\nu \rightarrow 3Cl$
J7.	$HCFC22 + h\nu \rightarrow Cl$
J8.	$Cl_2 + h\nu \rightarrow 2Cl$
J9.	$OClO + h\nu \rightarrow O + ClO$
J10.	$Cl_2O_2 + h\nu \rightarrow 2Cl$
J11.	$HOCl + h\nu \rightarrow OH + Cl$
J12.	$HCl + h\nu \rightarrow H + Cl$
J13.	$ClONO_2 + h\nu \rightarrow Cl + NO_3$
J14.	$ClONO_2 + h\nu \rightarrow ClO + NO_2$
J15.	$CH_3Br + h\nu \rightarrow Br + CH_3O_2$
J16.	$CF_3Br + h\nu \rightarrow Br$
J17.	$CF_2ClBr + h\nu \rightarrow Br + Cl$
J18.	$CHBr_3 + h\nu \rightarrow 3Br$
J19.	$CH_2Br_2 + h\nu \rightarrow 2Br$
J20.	$CH_2BrCl + h\nu \rightarrow Br + Cl$
J21.	$CHBr_2Cl + h\nu \rightarrow 2Br + Cl$
J22.	$CHBrCl_2 + h\nu \rightarrow Br + 2Cl$
J23.	$BrCl + h\nu \rightarrow Br + Cl$
J24.	$BrO + h\nu \rightarrow Br + O$
J25.	$HOBr + h\nu \rightarrow Br + OH$
J26.	$BrONO_2 + h\nu \rightarrow Br + NO_3$
J27.	$BrONO_2 + h\nu \rightarrow BrO + NO2$
J28.	$BrNO_2 + h\nu \rightarrow Br + NO_2$
J29.	$BrNO_2 + h\nu \rightarrow BrO + NO$
J30.	$CH_3I + h\nu \rightarrow CH_3 + I$
J31.	$CH_2I_2 + h\nu \rightarrow CH_2 + 2I$
J32.	$CH_2IBr + h\nu \rightarrow CH_2Br + I$
J33.	$CH_2ICl + h\nu \rightarrow CH_2Cl + I$
J34.	$I_2 + h\nu \rightarrow 2I$
J35.	$IO + h\nu \rightarrow I + O$
J36.	$OIO + h\nu \rightarrow I + O_2$
J37.	$INO + h\nu \rightarrow I + NO$
J38.	$INO_2 + h\nu \rightarrow I + NO_2$
J39.	$INO_2 + h\nu \rightarrow IO + NO$
J40.	$IONO_2 + h\nu \rightarrow I + NO_3$
J41.	$HOI + h\nu \rightarrow I + OH$
J42.	$IBr + h\nu \rightarrow I + Br$
J43.	$ICl + h\nu \rightarrow I + Cl$

Photolysis rates are computed online from absorption cross-sections and quantum yields reported in Atkinson et al. (2000, 2007a) and JPL 06-02 (Sander et al., 2006), and the actinic flux calculation in CAM-Chem.

Table 4. Heterogeneous reactions involving halogens in CAM-Chem.

	Reactions	Comments
	Sulfate aerosol reactions	
H1.	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	*
H2.	$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	*
H3.	$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$	*
H4.	$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	*
H5.	$HOCl + HCl \rightarrow Cl_2 + H_2O$	*
H6.	$HOBr + HCl \rightarrow BrCl + H_2O$	*
	Nitric acid tri-hydrate reactions	
H7.	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	*
H8.	$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	*
H9.	$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	*
H10.	$HOCl + HCl \rightarrow Cl_2 + H_2O$	*
H11.	$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$	*
	Water-ice aerosol reactions	
H12.	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	*
H13.	$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	*
H14.	$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$	*
H15.	$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	*
H16.	$HOCl + HCl \rightarrow Cl_2 + H_2O$	*
H17.	$HOBr + HCl \rightarrow BrCl + H_2O$	*
	Sea-salt aerosol reactions	
HSS0.	$BrONO_2 \rightarrow 0.65\ Br_2 + 0.35\ BrCl$	$\gamma = 0.08$
HSS1.	$BrNO_2 \rightarrow 0.65\ Br_2 + 0.35\ BrCl$	$\gamma = 0.04$
HSS2.	$HOBr \rightarrow 0.65\ Br_2 + 0.35\ BrCl$	$\gamma = 0.1$
HSS3.	$ClONO_2 \rightarrow Cl_2$	$\gamma = 0.02$
HSS4.	$ClNO_2 \rightarrow Cl_2$	$\gamma = 0.02$
HSS5.	$HOCl \rightarrow Cl_2$	$\gamma = 0.1$
HSS6.	$IONO_2 \rightarrow 0.5\ IBr + 0.5\ ICl$	$\gamma = 0.01$
HSS7.	$INO_2 \rightarrow 0.5\ IBr + 0.5\ ICl$	$\gamma = 0.02$
HSS8.	$HOI \rightarrow 0.5\ IBr + 0.5\ ICl$	$\gamma = 0.06$

(*) As in Table A4 from Auxiliary Material in Kinnison et al. (2007)

Following McFiggans et al. (2000) we applied the free molecular transfer approximation for the uptake of gas-phase halogen species on sea-salt aerosols. That is, the transfer coefficient (s^{-1}) is given by

$$K = \frac{\gamma}{4} < c > A$$

where γ is the uptake coefficient,$< c >$ is the root-mean-square molecular speed, and A is the total available sea-salt surface area density (cm^2/cm^3). $< c >$ is given by:

$$< c >= 100 \sqrt{\frac{8\,R\,T}{\pi M}}$$

with R = 8.3145 J mol^{-1} K^{-1}, T is the temperature and M the molecular mass of the species (in Kg mol^{-1}). The factor 100 converts to cm s^{-1}.

Table 5. Henry's Law constants for relevant halogen species in CAM-Chem.

Species	k_0 (M atm^{-1})	c (K)	Reference
$ClONO_2$	1.0×10^6		1, a
$BrONO_2$	1.0×10^6		1, a
HCl	1.9×10^1	9000	1, b
HOCl	9.3×10^2		1, b
HOBr	1.9×10^3		1, c
HBr	7.2×10^{-1}	6100	1, b
BrCl	7.0×10^{-2}	4000	3
IBr	2.4×10^1		1
ICl	1.1×10^2		1
$BrNO_2$	3.0×10^{-1}		1
$ClNO_2$	4.0×10^{-2}		1, c
HI	2.5×10^1	9800	3
HOI	4.5×10^2		2

Temperature dependent Henry's law constants are calculated as:

$$k_H = k_0 \times \exp\left[c\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

where

k_0 = value of k_H at standard conditions
T_0 = 298.15 K

[1] Sander (1999)
[a] Virtually infinite solubility is represented in the model using a very large but arbitrary number.
[b] Other values are also reported in the corresponding reference.
[c] Within the range of values given in the corresponding reference.
[2] Chemical mechanism of MECCA (Sander et al., 2011).
[3] Estimated.

Table 6. Dry deposition velocities of relevant halogen species in CAM-Chem.

Species	**Deposition velocity (cm s^{-1})**
HCl, HBr	2.00
HOCl, $ClONO_2$	1.00
HOBr	1.60
$BrONO_2$	0.50
HI	1.00
I_2O_2	1.00
HOI , $IONO_2$, INO_2	0.75

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