

# Observation and modelling of ozone-destructive halogen chemistry in a passive degassing volcanic plume

Surl et al.

## 1 Figures

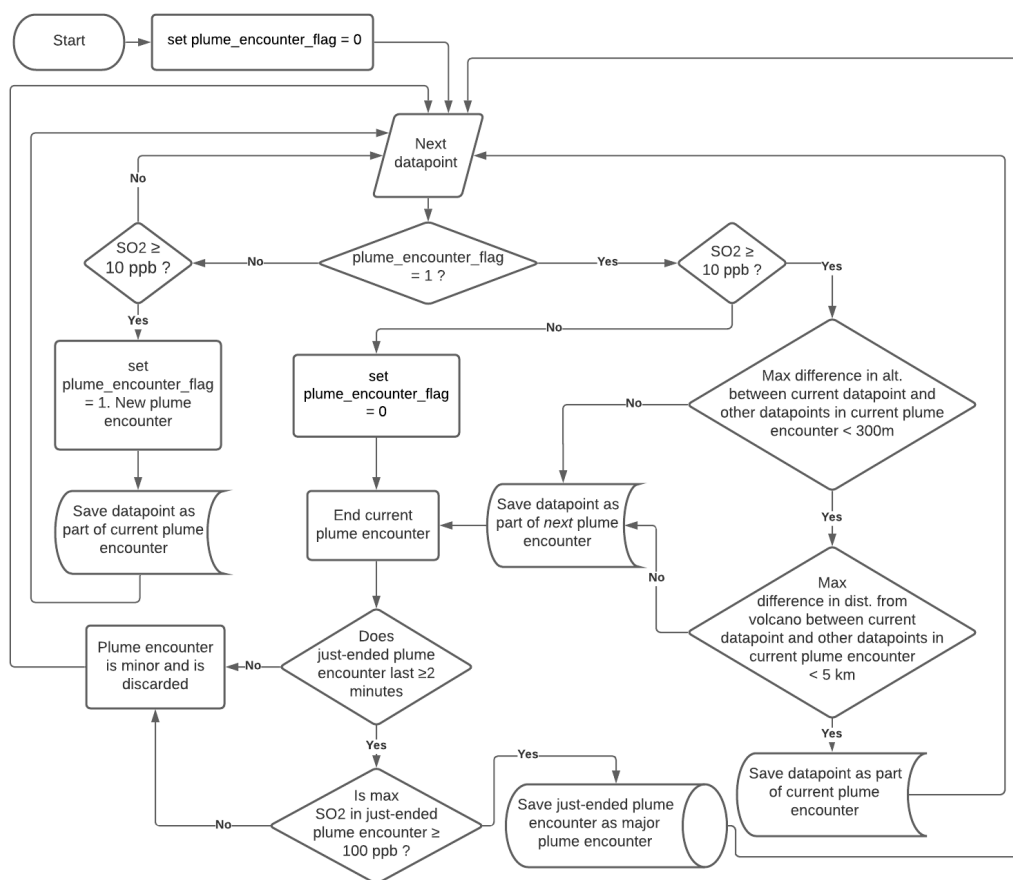
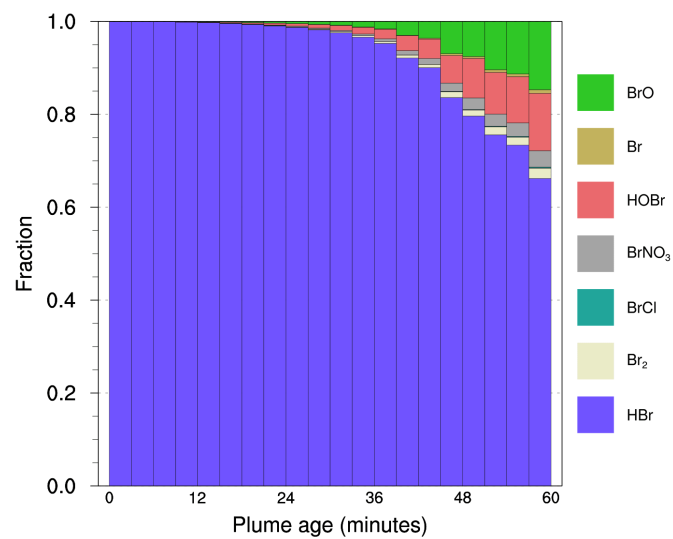
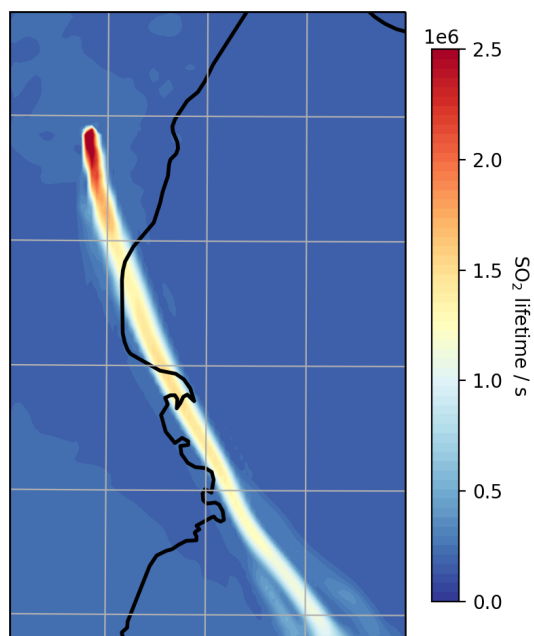


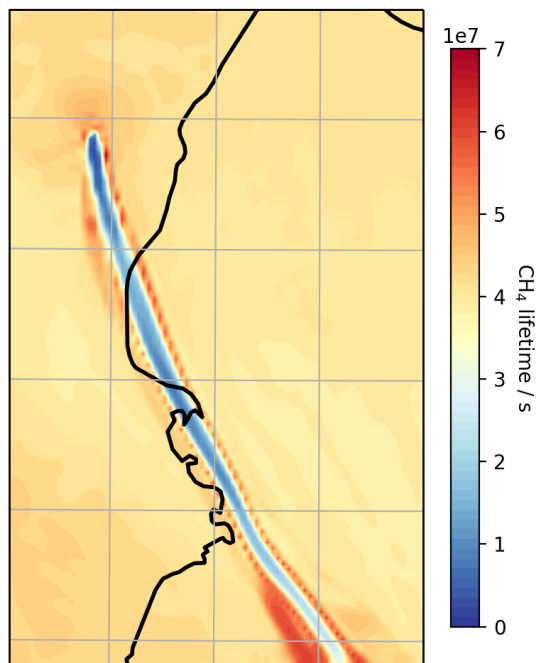
Figure S1. Flow chart representation of algorithm used to identify major plume encounters within the observational data.



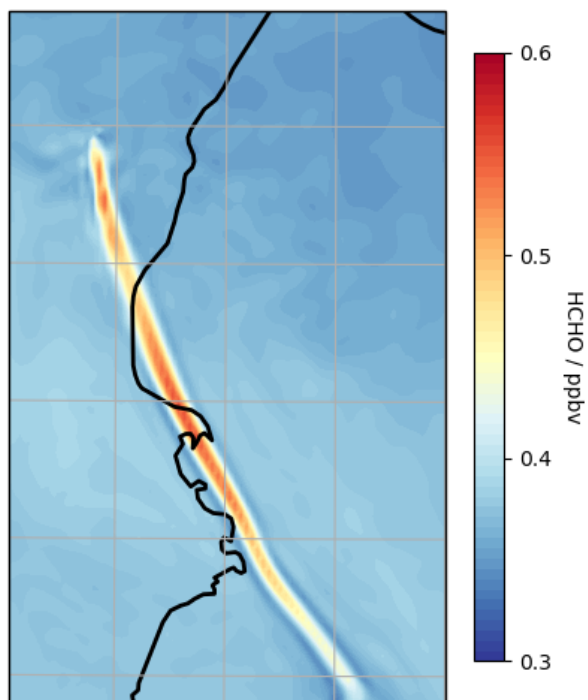
**Figure S2.** Differentiation of bromine between species for plume of different ages ranging from 0–60 minutes for 2012-08-01 using model output from the *noHighT* run.



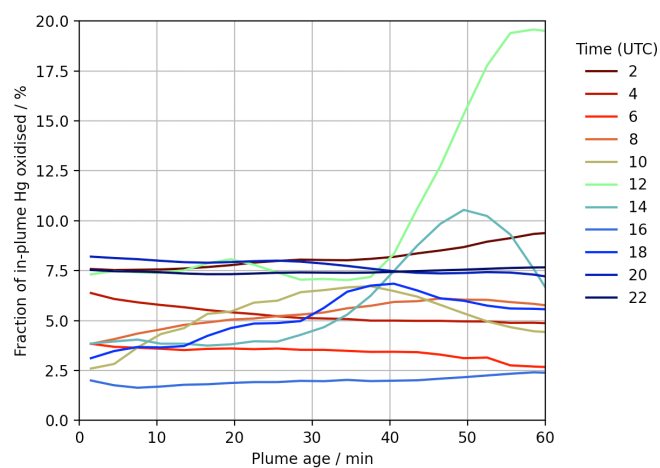
**Figure S3.** Modelled instantaneous lifetime of SO<sub>2</sub> at 3300mASL 0800 UTC on 2012-08-01.



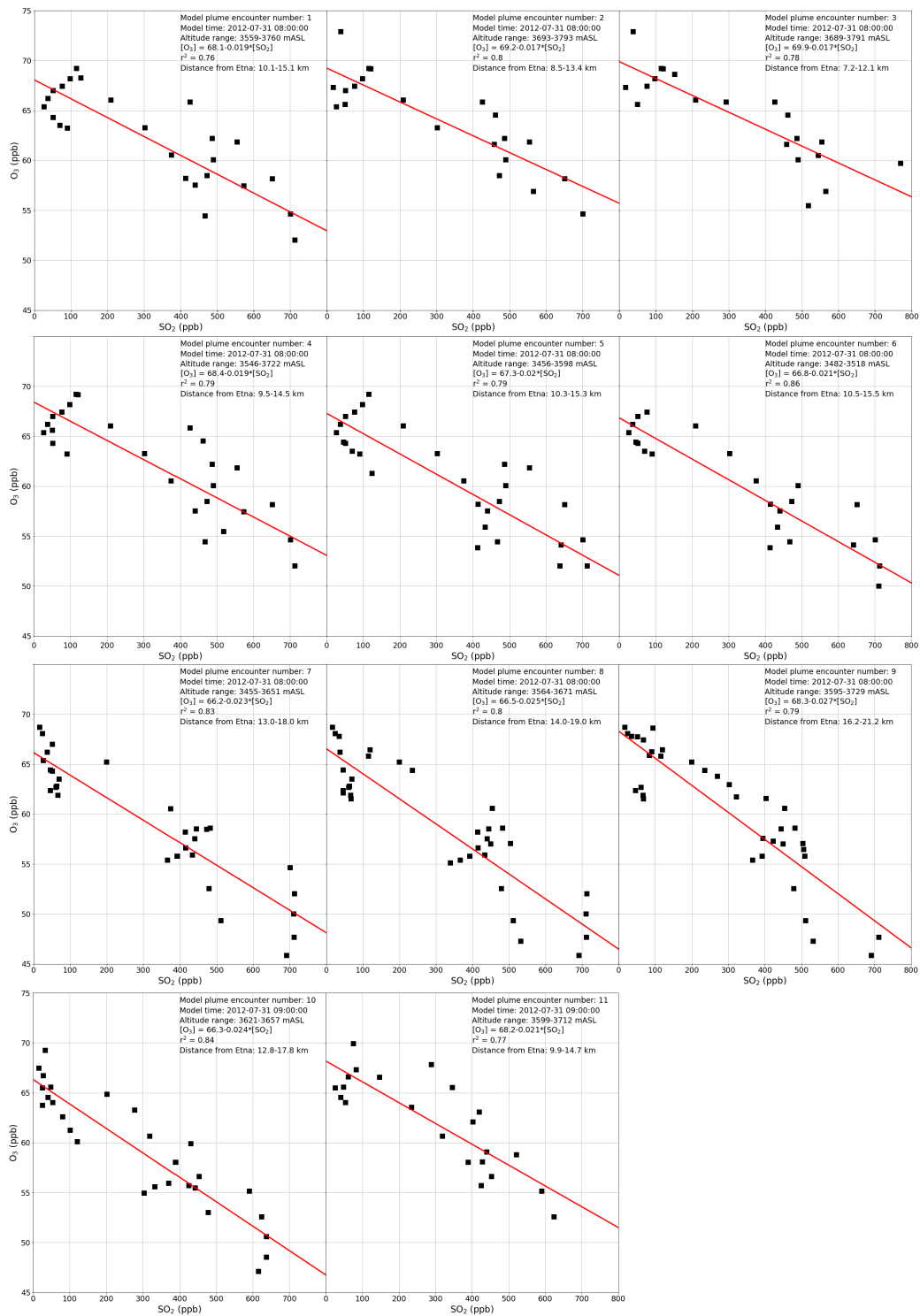
**Figure S4.** Modelled instantaneous lifetime of CH<sub>4</sub> at 3300mASL 0800 UTC on 2012-08-01.



**Figure S5.** Modelled mixing ratio of HCHO at 3300mASL 0800 UTC on 2012-08-01.



**Figure S6.** In-plume average percentage of Hg in oxidised forms for plume of different ages ranging from 0–60 minutes at several times on 2012-08-01. Note that these lines represent snapshots of the plume rather than Lagrangian traces



**Figure S7.** Modelled equivalent  $SO_2$  and  $O_3$  for the 11 major plume encounters on 2012-07-31.

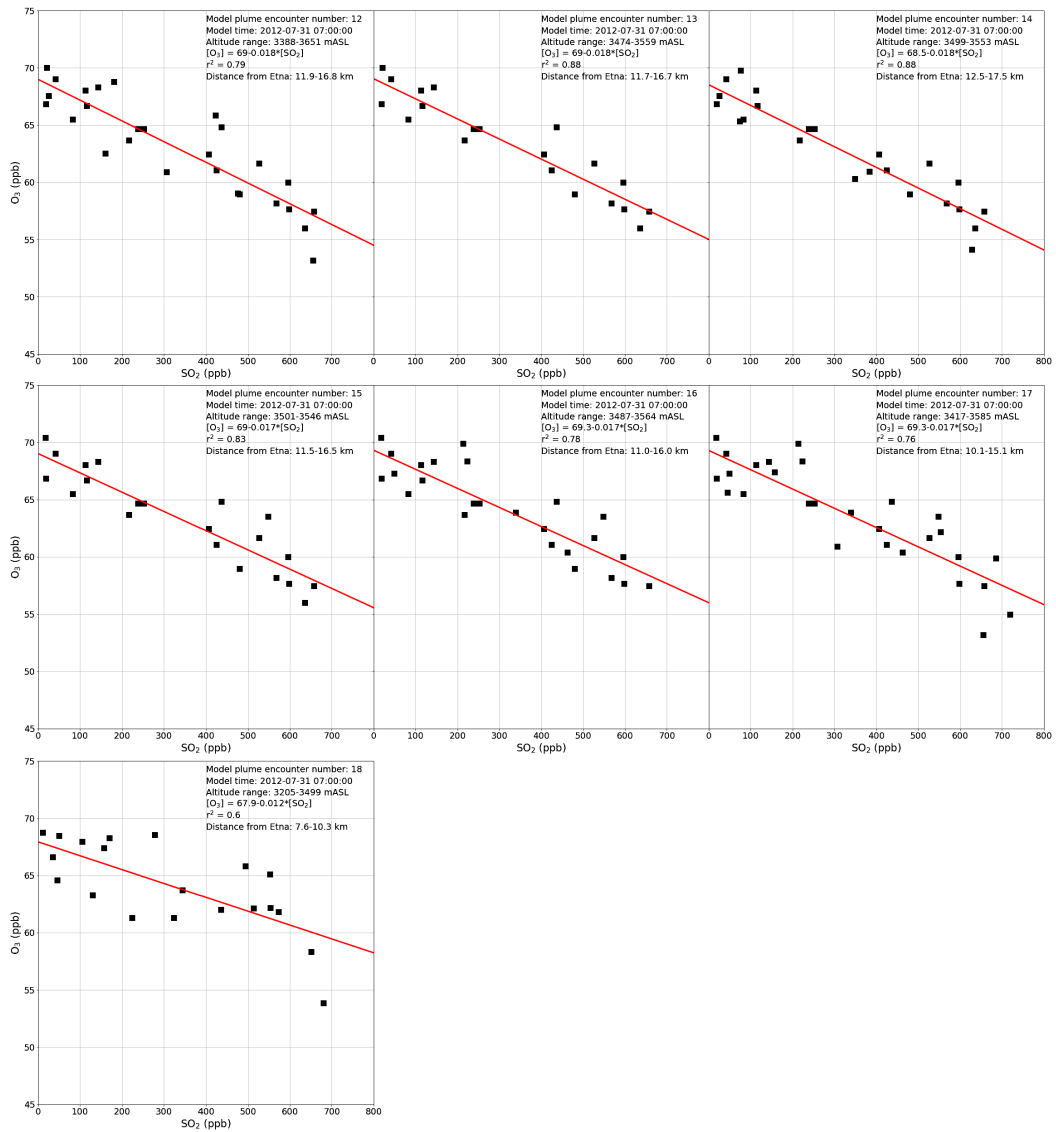


Figure S8. Modelled equivalent  $\text{SO}_2$  and  $\text{O}_3$  for the 8 major plume encounters on 2012-08-01.

## 2 Model chemical mechanism

The following tables list the reactions added to the CMBZ MOSAIC 8-bin mechanism to form the WCV mechanism. The main source for reaction rates are the values recommended by the IUPAC Task Group on Atmospheric Chemistry (<http://iupac.pole-ether.fr>: Atkinson et al., 2004, 2006, 2007, 2008; Crowley et al., 2010; Ammann et al., 2013), this source is referred to as "IUPAC" in the tables below.

Fractional quantities indicate reactions that account for multiple, branching reactions. O<sub>2</sub> is not included as a reaction product in the mechanism as it is not simulated by the model. Some short lived species, such as the H radical, are not expressly modelled; their products (e.g. H + O<sub>2</sub> → HO<sub>2</sub>) are considered to be formed directly by the mechanism. As such, some reactions do not balance stoichiometrically.

### 2.1 Photolysis

New photolysis reactions are tabulated in Table S1.  $h\nu$  indicates a photon.

Reactant		Products	Reference
BrO	$\xrightarrow{h\nu}$	Br + O <sub>3</sub>	IUPAC
Br <sub>2</sub>	$\xrightarrow{h\nu}$	2 Br	IUPAC
HOBr	$\xrightarrow{h\nu}$	Br + OH	IUPAC
BrNO <sub>2</sub>	$\xrightarrow{h\nu}$	Br + NO <sub>2</sub>	IUPAC
BrNO <sub>3</sub>	$\xrightarrow{h\nu}$	Br + NO <sub>3</sub>	IUPAC
OCIO	$\xrightarrow{h\nu}$	ClO + O <sub>3</sub>	IUPAC
Cl <sub>2</sub>	$\xrightarrow{h\nu}$	2 Cl	IUPAC
HOCl	$\xrightarrow{h\nu}$	Cl + OH	IUPAC
ClNO <sub>2</sub>	$\xrightarrow{h\nu}$	Cl + NO <sub>2</sub>	IUPAC
ClNO <sub>3</sub>	$\xrightarrow{h\nu}$	Cl + NO <sub>3</sub>	IUPAC
BrCl	$\xrightarrow{h\nu}$	Br + Cl	IUPAC
HgBr	$\xrightarrow{h\nu}$	Hg + Br	Saiz-Lopez et al. (2019)
HgCl	$\xrightarrow{h\nu}$	Hg + Cl	Saiz-Lopez et al. (2019)
HgBr <sub>2</sub>	$\xrightarrow{h\nu}$	HgBr + Br	Saiz-Lopez et al. (2018)
HgBrCl	$\xrightarrow{h\nu}$	HgCl + Br	<i>see below</i>

**Table S1.** Photolysis reactions of bromine and chlorine species in the WCV mechanism

To our knowledge no photolysis cross section has been published for HgBrCl. We assume photolysis rates of half that of HgBr<sub>2</sub> with Br radicals being produced as this is the weaker bond. Saiz-Lopez et al. (2018) report tropospheric lifetimes of HgCl<sub>2</sub> far in excess of the timescales of this study, we therefore exclude photolysis of this species.

## 2.2 Heterogenous

WCV's reaction mechanism includes heterogeneous reactions (Table S2) where the reaction is assumed to take place between a gas-phase species and a species adsorbed onto or into the aerosol. We do not compute these by calculating the bulk aqueous-phase chemistry, but instead employ a reaction probability approach wherein the rate of a heterogeneous reaction is considered to be proportional to the rate of reactive uptake of the gas-phase species to the aerosol phase. We use the mechanism developed by Marelle et al. (in review) which also accounts for gas-phase diffusion effects and the approach of Jourdain et al. (2016) to determine the products of HOBr reactive uptake.

Reactant		Products
$\text{N}_2\text{O}_5 + \text{H}_2\text{O}$	$\longrightarrow$	$2 \text{HNO}_3$
$\text{BrNO}_3 + \text{H}_2\text{O}$	$\longrightarrow$	$\text{HOBr} + \text{HNO}_3$
$\text{ClNO}_3 + \text{H}_2\text{O}$	$\longrightarrow$	$\text{HOCl} + \text{HNO}_3$
$\text{HOBr} + \text{HBr}$	$\longrightarrow$	$\text{Br}_2 + \text{H}_2\text{O}$
$\text{HOBr} + \text{HCl}$	$\longrightarrow$	$\text{BrCl} + \text{H}_2\text{O}$

**Table S2.** Heterogeneous reactions in the WCV mechanism

The various coefficients used to calculate heterogeneous reaction rates are tabulated in Table S3.  $\gamma$  are uptake coefficients; the probability that the specified molecule, upon impacting an aerosol surface, undergoes a reaction. The  $D$  values below are values for the diffusivity of these species in air, which is used in calculations that account for local depletion of these species in the air around aerosol particles.

The concentration of HBr and HCl in particles is calculated on-line from the gas-phase concentrations of these species and their effective Henry's law coefficients ( $H'$ ). Following HOBr uptake, the branching ratio between the  $\text{Br}_2^-$  and  $\text{BrCl}$ -producing pathways is calculated from these concentrations and the equilibrium constants of the  $\text{BrCl} + \text{Br}^- \xrightleftharpoons{K_2} \text{Br}_2\text{Cl}$  and  $\text{Br}_2\text{Cl}^- \xrightleftharpoons{K_3} \text{Br}_2 + \text{Cl}$  reactions (Wang et al., 1994; Jourdain et al., 2016).

For HOBr, the recommended value for the accommodation coefficient ( $\alpha$ ), the fraction of gas-phase HOBr molecules taken onto or into the particles after collision, is 0.6 (Ammann et al., 2013). Experiments on sea-salt aerosol suggest that the uptake coefficient, is very close to the accommodation coefficient for acidic particles (Ammann et al., 2013). As volcanic aerosol is highly acidic, we set  $\gamma$  to be 0.6.

At standard temperatures, the value of  $\frac{K_2}{K_3} \frac{H'_{\text{HCl}}}{H'_{\text{HBr}}}$  is about  $10^{-7}$ , meaning that the branching will strongly favour  $\text{Br}_2$  production unless HBr is nearly completely depleted within the plume.

Equivalent heterogeneous reactions for HOCl are not included in the model, as the uptake coefficient is reported to be  $<0.02$  (Crowley et al., 2010).



Parameter	Value	Reference
$\gamma_{\text{HOBr}}$	0.6	IUPAC
$\gamma_{\text{N}_2\text{O}_5}$	0.03	IUPAC
$\gamma_{\text{BrNO}_3}$	0.8	Burkholder et al. (2015)
$\gamma_{\text{ClNO}_3}$	0.11	IUPAC
$D_{0,\text{HOBr}}$	11000 Pa cm <sup>2</sup> s <sup>-1</sup>	Tang et al. (2014)
$D_{0,\text{N}_2\text{O}_5}$	8700 Pa cm <sup>2</sup> s <sup>-1</sup>	
$D_{0,\text{BrNO}_3}$	36000 Pa cm <sup>2</sup> s <sup>-1</sup>	Theoretical values calculated as per Tang et al. (2014)
$D_{0,\text{ClNO}_3}$	37000 Pa cm <sup>2</sup> s <sup>-1</sup>	
$H'_{\text{HCl}}$	$2.0 \times 10^4 e^{9000(\frac{1}{T} - \frac{1}{298})}$ mol <sup>2</sup> m <sup>-6</sup> Pa <sup>-1</sup>	Brimblecombe and Clegg (1988, 1989), as reported by Sander (2015)
$H'_{\text{HBr}}$	$1.3 \times 10^7 e^{10000(\frac{1}{T} - \frac{1}{298})}$ mol <sup>2</sup> m <sup>-6</sup> Pa <sup>-1</sup>	
$K_2$	1.3 M <sup>-1</sup>	Wang et al. (1994)
$K_3$	$1.8 \times 10^4$ M <sup>-1</sup>	

**Table S3.** Coefficients used to determine heterogeneous reaction rates and branching ratio of the HOBr reaction

## 2.3 Gas phase

- 40 Table S4 gives the other bromine, chlorine, and mercury reactions included in the WCV mechanism. T is temperature in K. [X] indicates the concentration of species X in molecules cm<sup>-3</sup>. [M] indicates the total air concentration.

Table S4: Br, Cl, and Hg gas-phase reactions in the WCV mechanism.

Reactants	Products	Rate equation / s <sup>-1</sup>	Reference
Br + O <sub>3</sub>	→ BrO	$1.7 \times 10^{-11} e^{\frac{-800}{T}} [\text{Br}][\text{O}_3]$	IUPAC
Br + HO <sub>2</sub>	→ HBr	$7.7 \times 10^{-12} e^{\frac{-450}{T}} [\text{Br}][\text{HO}_2]$	IUPAC
Br + HCHO	→ HBr + CO + HO <sub>2</sub>	$7.7 \times 10^{-12} e^{\frac{-580}{T}} [\text{Br}][\text{HCHO}]$	IUPAC
Br + CH <sub>3</sub> OOH	→ CH <sub>3</sub> O <sub>2</sub> + HBr	$2.7 \times 10^{-12} e^{\frac{-1610}{T}} [\text{Br}][\text{HCHO}]$	von Glasow et al. (2004)
BrO + HO <sub>2</sub>	→ HOBr	$4.5 \times 10^{-12} e^{\frac{500}{T}} [\text{BrO}][\text{HO}_2]$	IUPAC
BrO + CH <sub>3</sub> O <sub>2</sub>	→ 0.72 HOBR + 0.28 Br + 0.28 HO <sub>2</sub> + HCHO	$4.1 \times 10^{-13} e^{\frac{800}{T}} [\text{BrO}][\text{CH}_3\text{O}_2]$	von Glasow et al. (2004)
BrO + NO	→ Br + NO <sub>2</sub>	$8.7 \times 10^{-12} e^{\frac{260}{T}} [\text{BrO}][\text{NO}]$	IUPAC
BrO + NO <sub>2</sub>	→ BrNO <sub>3</sub>	$\frac{k_0}{1 + \frac{k_0}{k_\infty}} 0.6^{(1 + \log_{10}(\frac{k_0}{k_\infty}))^{-1}} [\text{BrO}][\text{NO}_2]$	IUPAC <sup>A</sup>

where:

$$k_0 = 5.2 \times 10^{-31} \left(\frac{T}{300}\right)^{-3.2} [\text{M}]$$

$$k_\infty = 6.9 \times 10^{-12} \left(\frac{T}{300}\right)^{-2.9}$$

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**Table S4 – continued from previous page**

Reactants	Products	Rate equation / s <sup>-1</sup>	Reference
BrO + BrO	→ 2 Br	$2.7 \times 10^{-12} [\text{BrO}][\text{BrO}]$	IUPAC
BrO + BrO	→ Br <sub>2</sub>	$2.9 \times 10^{-14} e^{\frac{840}{T}} [\text{BrO}][\text{BrO}]$	IUPAC
HBr + OH	→ Br + H <sub>2</sub> O	$6.7 \times 10^{-12} e^{\frac{155}{T}} [\text{HBr}][\text{OH}]$	IUPAC
BrO + OH	→ Br + HO <sub>2</sub>	$1.8 \times 10^{-11} e^{\frac{250}{T}} [\text{BrO}][\text{OH}]$	IUPAC
Br <sub>2</sub> + OH	→ HOBr + Br	$1.9 \times 10^{-11} e^{\frac{240}{T}} [\text{Br}_2][\text{OH}]$	IUPAC
Br + NO <sub>2</sub>	→ BrNO <sub>2</sub>	$\frac{k_0}{1 + \frac{k_0}{k_\infty}} 0.55^{(1 + \log_{10}(\frac{k_0}{k_\infty}))^{-1}} [\text{Br}][\text{NO}_2]$	IUPAC
where:			
$k_0 = 4.2 \times 10^{-31} (\frac{T}{300})^{-2.4} [\text{M}]$			
$k_\infty = 2.7 \times 10^{-11}$			
BrNO <sub>3</sub>	→ BrO + NO <sub>2</sub>	$2.8 \times 10^{13} e^{\frac{-12360}{T}} [\text{BrNO}_3]$	Orlando and Tyndall (1996)
Cl + O <sub>3</sub>	→ ClO	$2.8 \times 10^{-11} e^{\frac{-250}{T}} [\text{Cl}][\text{O}_3]$	IUPAC
Cl + HO <sub>2</sub>	→ 0.8 HCl + 0.2 ClO + 0.2 OH	$4.4 \times 10^{-11} [\text{Cl}][\text{H}_2\text{O}_2]$	IUPAC
Cl + H <sub>2</sub> O <sub>2</sub>	→ HCl	$1.1 \times 10^{-11} e^{\frac{-980}{T}} [\text{Cl}][\text{H}_2\text{O}_2]$	IUPAC
Cl + RO <sub>2</sub>	→ 0.5 ClO + 0.5 HCHO + 0.5 HO <sub>2</sub> + 0.5 HCl + 0.5 CO	$1.6 \times 10^{-10} [\text{Cl}][\text{RO}_2]$	Burkholder et al. (2015) <sup>B</sup>
Cl + CH <sub>4</sub>	→ HCl + CH <sub>3</sub> O <sub>2</sub>	$6.6 \times 10^{-12} e^{\frac{-1240}{T}} [\text{Cl}][\text{CH}_4]$	IUPAC
Cl + C <sub>2</sub> H <sub>6</sub>	→ HCl + RO <sub>2</sub>	$7.1 \times 10^{-11} e^{\frac{-60}{T}} [\text{Cl}][\text{C}_2\text{H}_6]$	IUPAC
Cl + HCHO	→ HCl + HO <sub>2</sub> + CO	$8.1 \times 10^{-11} e^{\frac{-34}{T}} [\text{Cl}][\text{HCHO}]$	IUPAC
Cl + ClNO <sub>3</sub>	→ Cl <sub>2</sub> + NO <sub>3</sub>	$6.2 \times 10^{-12} e^{\frac{145}{T}} [\text{Cl}][\text{ClNO}_3]$	IUPAC
ClO + HO <sub>2</sub>	→ HOCl	$2.2 \times 10^{-12} e^{\frac{340}{T}} [\text{ClO}][\text{HO}_2]$	IUPAC
ClO + CH <sub>3</sub> O <sub>2</sub>	→ Cl + HCHO + HO <sub>2</sub>	$3.2 \times 10^{-12} e^{\frac{-110}{T}} [\text{ClO}][\text{CH}_3\text{O}_2]$	IUPAC <sup>C</sup>
ClO + NO	→ Cl + NO <sub>2</sub>	$6.2 \times 10^{-12} e^{\frac{295}{T}} [\text{ClO}][\text{NO}]$	IUPAC
ClO + NO <sub>2</sub>	→ BrNO <sub>2</sub>	$\frac{k_0}{1 + \frac{k_0}{k_\infty}} 0.4^{(1 + \log_{10}(\frac{k_0}{k_\infty}))^{-1}} [\text{ClO}][\text{NO}_2]$	IUPAC
where:			
$k_0 = 1.6 \times 10^{-31} (\frac{T}{300})^{-3.4} [\text{M}]$			
$k_\infty = 7.0 \times 10^{-11}$			
ClO + ClO	→ Cl <sub>2</sub>	$1.0 \times 10^{-12} e^{\frac{-1590}{T}} [\text{ClO}][\text{ClO}]$	IUPAC
ClO + ClO	→ OCIO + Cl	$3.5 \times 10^{-13} e^{\frac{-1370}{T}} [\text{ClO}][\text{ClO}]$	IUPAC
ClO + ClO	→ 2 Cl	$3.0 \times 10^{-11} e^{\frac{-2450}{T}} [\text{ClO}][\text{ClO}]$	IUPAC

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**Table S4 – continued from previous page**

Reactants	Products	Rate equation / s <sup>-1</sup>	Reference
HCl + OH	→ H <sub>2</sub> O + Cl	$1.7 \times 10^{-12} e^{\frac{-230}{T}} [\text{HCl}][\text{OH}]$	IUPAC
ClNO <sub>2</sub> + OH	→ HOCl + NO <sub>2</sub>	$2.4 \times 10^{-12} e^{\frac{-1250}{T}} [\text{ClNO}_2][\text{OH}]$	IUPAC
ClNO <sub>3</sub> + OH	→ 0.5 ClO + 0.5 HNO <sub>3</sub> + 0.5 HOCl + 0.5 NO <sub>3</sub>	$1.2 \times 10^{-12} e^{\frac{-330}{T}} [\text{ClNO}_3][\text{OH}]$	IUPAC
BrO + ClO	→ Br + OClO	$1.6 \times 10^{-12} e^{\frac{430}{T}} [\text{BrO}][\text{ClO}]$	IUPAC
BrO + ClO	→ BrCl	$5.8 \times 10^{-13} e^{\frac{170}{T}} [\text{BrO}][\text{ClO}]$	IUPAC
BrO + ClO	→ Br + Cl	$2.9 \times 10^{-12} e^{\frac{220}{T}} [\text{BrO}][\text{ClO}]$	IUPAC
Hg + Br	→ HgBr	$1.4 \times 10^{-32} (T/298)^{-1.86} [\text{Hg}][\text{Br}][\text{M}]$	Horowitz et al. (2017)
Hg + Cl	→ HgCl	$1.8 \times 10^{-11} [\text{Hg}][\text{Cl}]$	Sun et al. (2016)
HgBr + Br	→ HgBr <sub>2</sub>	$3.0 \times 10^{-11} [\text{HgBr}][\text{Br}]$	Horowitz et al. (2017)
HgBr + Cl	→ HgBrCl	$\frac{k_0}{1 + \frac{k_0}{k_\infty}} 0.6^{(1 + \log_{10}(\frac{k_0}{k_\infty}))^2} [\text{HgBr}][\text{Cl}]$ where: $k_0 = 2.27 \times 10^{-29} (\frac{T}{300})^{-4.37} [\text{M}]$ $k_\infty = 7.0 \times 10^{-11} (\frac{T}{300})^{-2.37}$	Horowitz et al. (2017)
HgCl + Br	→ HgBrCl	$3.0 \times 10^{-11} [\text{HgCl}][\text{Br}]$	Horowitz et al. (2017)
HgCl + Cl	→ HgCl <sub>2</sub>	$\frac{k_0}{1 + \frac{k_0}{k_\infty}} 0.6^{(1 + \log_{10}(\frac{k_0}{k_\infty}))^2} [\text{HgCl}][\text{Cl}]$	Horowitz et al. (2017)
HgBr + Br	→ Hg + Br <sub>2</sub>	$3.9 \times 10^{-11} [\text{HgBr}][\text{Br}]$	Horowitz et al. (2017)
HgCl + Cl	→ Hg + Cl <sub>2</sub>	$1.2 \times 10^{-11} e^{\frac{-5942}{T}} [\text{HgCl}][\text{Cl}]$	Horowitz et al. (2017)
HgBr	→ Hg + Br	$1.6 \times 10^{-9} \frac{T}{298}^{-1.86} e^{\frac{-7801}{T}} [\text{HgBr}][\text{M}]$	Horowitz et al. (2017)

*A* - for  $F_c = 0.6$

*B* - rate of Cl + CH<sub>3</sub>O<sub>2</sub> reaction

*C* - reaction channel 1 only

*D* - midpoint of narrowest range of rates in table 1 of Si and Ariya (2018)

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