Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem

Tomás Sherwen1, Johan A. Schmidt2, Mat J. Evans1,3, Lucy J. Carpenter1, Katja Großmann4,a, Sebastian D. Eastham5, Daniel J. Jacob5, Barbara Dix6, Theodore K. Koenig6,7, Roman Sinreich6, Ivan Ortega6,7, Rainer Volkamer6,7, Alfonso Saiz-Lopez8, Cristina Prados-Roman8,b, Anoop S. Mahajan9, and Carlos Ordóñez10

1Wolfson Atmospheric Chemistry Laboratories (WACL), Department of Chemistry, University of York, York, YO10 5DD, UK
2Department of Chemistry, University of Copenhagen, Universitetsparken, 2100 Copenhagen O, Denmark
3National Centre for Atmospheric Science (NCAS), University of York, York, YO10 5DD, UK
4Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany
5School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA
6Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA
7Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309-021, USA
8Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rosalano, CSIC, Madrid, 28006, Spain
9Indian Institute of Tropical Meteorology, Maharashtra, 411008, India
10Dpto. Física de la Tierra II, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

anow at: Joint Institute For Regional Earth System Science and Engineering (JIFRESSE), University of California Los Angeles, Los Angeles, CA, 90095, USA
bnow at: Atmospheric Research and Instrumentation Branch, National Institute for Aerospace Technology (INTA), Madrid, Spain

Correspondence to: Tomás Sherwen (tomas.sherwen@york.ac.uk)

Received: 18 May 2016 – Published in Atmos. Chem. Phys. Discuss.: 20 May 2016
Revised: 12 September 2016 – Accepted: 16 September 2016 – Published: 29 September 2016

Abstract. We present a simulation of the global present-day composition of the troposphere which includes the chemistry of halogens (Cl, Br, I). Building on previous work within the GEOS-Chem model we include emissions of inorganic iodine from the oceans, anthropogenic and biogenic sources of halogenated gases, gas phase chemistry, and a parameterised approach to heterogeneous halogen chemistry. Consistent with Schmidt et al. (2016) we do not include sea-salt debromination. Observations of halogen radicals (BrO, IO) are sparse but the model has some skill in reproducing these. Modelled IO shows both high and low biases when compared to different datasets, but BrO concentrations appear to be modelled low. Comparisons to the very sparse observations dataset of reactive Cl species suggest the model represents a lower limit of the impacts of these species, likely due to underestimates in emissions and therefore burdens. Inclusion of Cl, Br, and I results in a general improvement in simulation of ozone (O3) concentrations, except in polar regions where the model now underestimates O3 concentrations. Halogen chemistry reduces the global tropospheric O3 burden by 18.6 %, with the O3 lifetime reducing from 26 to 22 days. Global mean OH concentrations of $1.28 \times 10^6$ molecules cm$^{-3}$ are 8.2 % lower than in a simulation without halogens, leading to an increase in the CH4 lifetime (10.8 %) due to OH oxidation from 7.47 to 8.28 years. Oxidation of CH4 by Cl is small (~2 %) but Cl oxidation of other VOCs (ethane, acetone, and propane) can be significant (~15–27 %). Oxidation of VOCs by Br is smaller, representing 3.9 % of the loss of acetaldehyde and 0.9 % of the loss of formaldehyde.
1 Introduction

To address problems such as air-quality degradation and climate change, we need to understand the composition of the troposphere and its oxidative capacity. A complicated relationship exists between key chemical families and species such as ozone (O$_3$), HO$_x$ (HO$_2$ + OH), NO$_x$ (NO$_2$ + NO), and organic compounds which include carbon monoxide (CO), methane (CH$_4$), hydrocarbons, and oxygenated volatile organic compounds (VOCs) (for example, see Monks et al., 2015). The most important tropospheric oxidant is OH, which is itself produced indirectly through photolysis of O$_3$. Oxidants control the concentrations of key climate and air-quality gases and aerosols (including O$_3$, methane, sulfate aerosol, and secondary organic aerosols) (Monks et al., 2009; Prather et al., 2012; Unger et al., 2006). O$_3$ itself is not directly emitted, and its tropospheric burden is controlled by its sources through chemical production from NO$_x$ and organic compounds, transport from the stratosphere, and loss via deposition and chemical reactions (Monks et al., 2015).

Halogens (Cl, Br, I) are known to destroy O$_3$ through catalytic cycles, such as that shown in Reactions (R1)–(R3) (Chameides and Davis, 1980). Tropospheric halogens have also been shown to change OH concentrations (Bloss et al., 2005) and perturb OH to HO$_2$ ratios towards OH (Chameides and Davis, 1980). Halogens perturb the NO to NO$_2$ ratio and reduce NO$_x$ concentrations by hydrolysis of XNO$_3$. These perturbations also indirectly decrease O$_3$ formation (von Glasow et al., 2004). Halogens directly oxidise organics species, with Cl radical reactions proceeding the fastest (Atkinson et al., 2006; Sander et al., 2011). This can cause significant O$_3$ formation through increased RO$_2$ concentrations (Knipping and Dadub, 2003), notably in regions with elevated ClNO$_2$ (Sarwar et al., 2014). Halogens also play an important role in determining the chemistry of mercury (Holmes et al., 2009; Parrella et al., 2012; Wang et al., 2015; Coburn et al., 2016). The literature on tropospheric halogens has been the topic of several recent reviews, which cover the background in more detail (Simpson et al., 2015; Saiz-Lopez et al., 2012b). However, many uncertainties still exist, notably with heterogeneous halogen chemistry (Abbatt et al., 2012; Simpson et al., 2015) and gas phase iodine chemistry (Saiz-Lopez et al., 2014; Sommariva and von Glasow, 2012).

$$\text{O}_3 + X \rightarrow \text{XO} + \text{O}_2 \quad (\text{R1})$$
$$\text{HO}_2 + \text{XO} \rightarrow \text{HOX} + \text{O}_2 \quad (\text{R2})$$
$$\text{HOX} + h\nu \rightarrow \text{OH} + X \quad (\text{R3})$$
$$\text{Net: HO}_2 + \text{O}_3 \rightarrow 2\text{O}_2 + \text{OH} \quad (\text{R4})$$

Tropospheric halogen chemistry has been studied in box model studies (see Simpson et al., 2015, and citations within) and more recently in global models (e.g. Parrella et al., 2012; Saiz-Lopez et al., 2012a, 2014; Schmidt et al., 2016; Sherwen et al., 2016a). Modelling has sought to quantify emissions budgets and evaluate these on a global scale (Bell et al., 2002; Ziska et al., 2013; Hossaini et al., 2013; Ordóñez et al., 2012). Global studies have considered impacts of halogens in the troposphere (Parrella et al., 2012; Saiz-Lopez et al., 2012a, 2014; Schmidt et al., 2016; Sherwen et al., 2016a) and reported reductions in the tropospheric O$_3$ burden by up to ~ 15%. However, this field of research is quickly evolving, with new halogen sources such as inorganic ocean iodine (Carpenter et al., 2013; MacDonald et al., 2014) and ClNO$_2$ produced from N$_2$O$_5$ hydrolysis on sea salt (Roberts et al., 2009; Bertram and Thornton, 2009; Sarwar et al., 2014) now appearing to be globally important.

Previous studies of halogen chemistry within the GEOS-Chem (http://www.geos-chem.org) model have focussed on either bromine or iodine chemistry. Parrella et al. (2012) presented a bromine scheme and its effects on oxidants in the past and present atmosphere. Eastham et al. (2014) presented the Unified tropospheric–stratospheric Chemistry eXtension (UCX), which added a stratospheric bromine and chlorine scheme. This chlorine scheme was then employed in the troposphere with an updated heterogeneous bromine and chlorine scheme by Schmidt et al. (2016). An iodine scheme was employed in the troposphere to consider present-day impacts of iodine on oxidants (Sherwen et al., 2016a), which used the representation of bromine chemistry from Parrella et al. (2012). Up to this point, the coupling of chlorine, bromine, and iodine in the GEOS-Chem model and its subsequent impact on the simulated present-day composition of the atmosphere have not been described.

Here we present such a coupled halogen model built within the GEOS-Chem framework and consider the present-day tropospheric impacts of halogens. The model presented here includes recent updates to chlorine (Eastham et al., 2014; Schmidt et al., 2016), bromine (Parrella et al., 2012; Schmidt et al., 2016), and iodine (Sherwen et al., 2016a) chemistry with further updates and additions described in Sect. 2. In Sect. 3 we describe the modelled distribution of inorganic halogens (Sects. 3.1–3.3) and compare with observations (Sect. 3.4). We then outline the impact on oxidants (Sects. 4.1–4.2), organic compounds (Sect. 4.3), and other species (Sect. 4.4).

2 Model description

This work uses the GEOS-Chem chemical transport model (http://www.geos-chem.org, version 10) run at 4° × 5° spatial resolution. The model is forced by assimilated meteorological and surface fields from NASA’s Global Modelling and Assimilation Office (GEOS-5). The model chemistry scheme includes O$_3$, HO$_2$, NO$_x$, and VOC chemistry as described in Mao et al. (2013). Dynamic and chemical time steps are 30 and 60 min, respectively. Stratospheric chemistry is modelled using a linearised mechanism as described by Murray et al. (2012).
Table 1. Additional halogen reactions included in this simulation that are not described in previous work (Eastham et al., 2014; Schmidt et al., 2016; Sherwen et al., 2016a). The full reaction scheme is given in Appendix B (Tables B2–B5). The rate constant is calculated using a standard Arrhenius expression $A \times \exp(-E_a/R)$.

| Rxn ID | Reaction | $A$ (cm$^3$ molecules$^{-1}$ s$^{-1}$) | $-E_a/R$ (K) | Citation |
|--------|----------|--------------------------------------|--------------|----------|
| M29    | IO + ClO → I + OCIO | 2.59 × 10$^{-12}$ | 280 | Atkinson et al. (2007) |
| M30    | IO + ClO → I + Cl + O$_2$ | 1.18 × 10$^{-12}$ | 280 | Atkinson et al. (2007) |
| M31    | IO + ClO → Cl + O$_2$ | 9.40 × 10$^{-13}$ | 280 | Atkinson et al. (2007) |
| M32    | Cl + HCOOH → HCl + CO$_2$ + H$_2$O | 2.00 × 10$^{-13}$ | – | Sander et al. (2011) |
| M33    | Cl + CH$_3$O$_2$ → ClO + CH$_3$O + HO$_2$ | 1.60 × 10$^{-10}$ | – | Sander et al. (2011) |
| M34    | Cl + CH$_3$O → HCl + CH$_3$O$_2$ | 5.70 × 10$^{-11}$ | – | Sander et al. (2011) |
| M35    | Cl + C$_2$H$_6$ → HCl + C$_2$H$_4$O$_2$ | 7.20 × 10$^{-11}$ | – | Sander et al. (2011) |
| M36    | Cl + C$_2$H$_5$O$_2$ → ClO + HO$_2$ + ALD | 7.40 × 10$^{-11}$ | – | Sander et al. (2011) |
| M37    | Cl + EOCl → HCl + ALD$_2$ | 9.60 × 10$^{-11}$ | – | Sander et al. (2011) |
| M38    | Cl + CH$_3$C(O)OH → HCl + CH$_3$O$_2$ + CO$_2$ | 2.80 × 10$^{-14}$ | – | Sander et al. (2011) |
| M39    | Cl + C$_3$H$_8$ → HCl + A$O_2$ | 7.85 × 10$^{-11}$ | –80 | Sander et al. (2011) |
| M40    | Cl + C$_3$H$_7$ → HCl + B$O_2$ | 6.54 × 10$^{-11}$ | – | Sander et al. (2011) |
| M41    | Cl + ACET → HCl + ATO2 | 7.70 × 10$^{-11}$ | –1000 | Sander et al. (2011) |
| M42    | Cl + ISOP → HCl + RIO2 | 7.70 × 10$^{-11}$ | 500 | Sander et al. (2011) |
| M43    | Cl + MOH → HCl + CH$_2$O$_2$ + HO$_2$ | 5.50 × 10$^{-11}$ | – | Sander et al. (2011) |
| M61    | Cl + ALK4 → HCl + R4O2 | 2.05 × 10$^{-10}$ | – | Atkinson et al. (2006) |
| M62    | Br + PRPE → HBr + PO2 | 3.60 × 10$^{-12}$ | – | Atkinson et al. (2006) |
| M63    | Cl + PRPE $\rightarrow$ HCl + PO2 | 2.80 × 10$^{-10}$ | – | Atkinson et al. (2006) |
| H1     | N$_2$O$\gamma$ → HNO$_3$ + ClNO$_2$ | – | – | (see table footnote) |
| H2     | HOI → 0.85Cl + 0.15Br$^f$ | – | – | (see table footnote) |
| H3     | INO$_2$ → 0.85Cl + 0.15Br$^f$ | – | – | (see table footnote) |
| H4     | INO$_2$ → 0.85Cl + 0.15Br$^f$ | – | – | (see table footnote) |
| P1     | ICl $\rightarrow$ I + Cl | – | – | Sander et al. (2011) |
| P2     | IBr $\rightarrow$ I + Br | – | – | Sander et al. (2011) |
| P3     | BrCl $\rightarrow$ Cl + Br | – | – | Sander et al. (2011) |

$^a$ Reaction from JPL, only considering the major channel (Daele and Poulet, 1996); product of CH$_3$O reacts to form CH$_3$O + HO$_2$ (CH$_3$O + O$_2$ → CH$_3$O + HO$_2$), $^b$ Only the first channel from JPL was considered. The second channel forms a triatomic (HCl + CH$_2$O$_2$) and therefore cannot be represented by reduced GEOS-Chem chemistry scheme. $^c$ Reaction defined by JPL and interpreted as proceeding via hydrogen abstraction; therefore the acetaldehyde product is assumed. $^d$ K(infinity) rate given in table. K(0) rate = 4.00 × 10$^{-28}$ with Fe = 0.6 as shown in Table B3. $^e$ Reaction only proceeds on sea-salt aerosol, with $\gamma$ value as described in Evans and Jacob (2005). $^f$ Reactions which were included in previous work (Sherwen et al., 2016a), but dihalogen products have been updated, split between ICl and Br (see Sect 2), and these reactions only proceed on acidic sea-salt aerosol following McFiggans et al. (2000). Acidity of aerosol is calculated as described in Alexander (2005). $\gamma$ values for uptake of halogen species are given in Table B4. Abbreviations for tracers are expanded in Appendix C.

We update the standard model chemistry to give a representation of chlorine, bromine, and iodine chemistry. We describe this version of the model as “Cl+Br+I” in this paper. It is based on the iodine chemistry described in Sherwen et al. (2016a) with updates to the bromine and chlorine scheme described by Schmidt et al. (2016) and Eastham et al. (2014). We have made a range of updates beyond these. Updated or new reactions not included in Sherwen et al. (2016a), Schmidt et al. (2016), or Eastham et al. (2014) are given in Table 1 with a full description of the halogen chemistry scheme used given in Appendix B Tables B2–B5.

For the photolysis of I$_2$O$_4$ (x = 2, 3, 4) we have adopted the absorption cross sections reported by Gómez Martín et al. (2005) and Spietz et al. (2005) and used the I$_2$O$_2$ cross section for I$_2$O$_4$. A quantum yield of unity was assumed for all I$_2$O$_4$ species. It is noted that recent work has used an unpublished spectrum for I$_2$O$_4$ that is much lower than that of I$_2$O$_3$ (Saiz-Lopez et al., 2014), but this is not expected to have a large effect on conclusions presented here.

The parameterisation for oceanic iodide concentration was changed from Chance et al. (2014), as used in Sherwen et al. (2016a), to MacDonald et al. (2014) because the latter resulted in an improved comparison with observations (see Sect. 7.5 of Sherwen et al., 2016a).

The product of acid-catalysed dihalogen release following $^1$ (HOI, INO, INO$_3$) uptake was updated from I$_2$ as in Sherwen et al. (2016a) to yield IBr and ICI following McFiggans et al. (2002). Acidity is calculated online through titra-
tion of sea-salt aerosol by uptake of sulfur dioxide (SO₂), nitric acid (HNO₃), and sulfuric acid (H₂SO₄) as described by Alexander (2005). Re-release of IX (X = Cl, Br) is only permitted to proceed if the sea salt is acidic (Alexander, 2005). Thus aerosol cycling of IX in the model is not a net source of IX (and may be a net sink on non-acidic aerosol) but alters the speciation (Sherwen et al., 2016a). The ratio between IBr and ICl was set to be 0.15 : 0.85 (IBr : ICl), instead of the 0.5 : 0.5 used previously (Saiz-Lopez et al., 2014; McFiggans et al., 2000). A ratio of 0.5 : 0.5 gives a large overestimate of bromine monoxide (BrO) with respect to the observations used in Sect. 3.4.2 (Read et al., 2008; Volkamer et al., 2015). We attributed this reduction to the debromination of sea salt, which we do not consider here, and the potential for the model to overestimate the BrO lifecycle. This is discussed further in the next section but future laboratory and field studies of these heterogenous process are needed to help constrain these parameters.

Iodine on aerosol is represented in the model with separate tracers based on the aerosol on which irreversible uptake occurs (see Table B4). We include three iodine aerosol tracers to represent iodine on accumulation and coarse-mode sea salt and on sulfate aerosol. The physical properties of the iodine aerosol tracers are assumed to be the same as their parent aerosol, as previously described for sulfate (Alexander et al., 2012) and sea-salt aerosol (Jaegle et al., 2011). As in Sherwen et al. (2016a), no nucleation of iodine species is considered in this work, with only photolytic and heterogeneous loss being treated.

We have added to the chlorine chemistry scheme described by Eastham et al. (2014) to include more tropospheric relevant reactions based on the JPL 10-6 compilation (Sander et al., 2011) and IUPAC (Atkinson et al., 2006). The heterogenous reaction of N₂O₅ on aerosols was updated to yield products of ClNO₂ and HNO₃ (Bertram and Thornton, 2009; Roberts et al., 2009) on sea salt and 2HNO₃ on other aerosol types. Reaction probabilities are unchanged (Evans and Jacob, 2005).

Deposition and photolysis of dihalogen species (ICl, BrCl, IBr) and the reaction between ClO and iodine monoxide (IO) were also included (Sander et al., 2011).

### 3 Model results

We run the model for 2 years (1 January 2004 to 1 January 2006), discarding the first year as a “spin-up” period and using the second year (2005) for analysis. Non-halogen emissions are described in Sherwen et al. (2016a). A reference simulation without any halogens (“NOHAL”) was also performed. Where comparisons with observations are shown, the model is run for the appropriate year with a 3-month “spin-up” before the observational dates, unless explicitly stated otherwise. The appropriate month from the 2005 simulation is used as the initialisation for these observational comparisons to account for interannual variations. The model is sampled at the nearest timestamp and grid box. The model only calculates chemistry in the troposphere. To avoid confusion we do not show results above the tropopause (lapse rate of temperature falls below 2 K km⁻¹).

#### 3.1 Emissions

The emissions fluxes of chlorine, bromine, and iodine species are shown in Fig. 1 with global totals in Table 2. We do not consider the Cl and Br contained within sea salt as emitted in our simulation, following Schmidt et al. (2016), until a chemical process liberates them into the gas phase. These liberation processes are the uptake of N₂O₅ on sea salt and uptake of I⁺ species on sea salt. We do not include explicit sea-salt debromination for reasons described in Schmidt et al. (2016).

| Sources | Iₓ (Tg I year⁻¹) | Brₓ (Tg Br year⁻¹) | Clₓ (Tg Cl year⁻¹) |
|---------|-----------------|--------------------|-------------------|
| CHₓX    | 0.26            | 0.06               | 2.10              |
| CHₓ₂X   | 0.33            | 0.09               | 0.57              |
| CHₓX    | –               | 0.41               | 0.25              |
| HOX     | 1.97            | –                  | –                 |
| X₂      | 0.14            | –                  | –                 |
| LX      | –               | 0.30*              | 0.73*             |
| XNO₂    | –               | –                  | 0.65              |
| Stratosphere | 0.00            | 0.06               | 0.43              |
| Total source* | 2.70            | 0.91               | 4.72              |

* Acid-catalysed sea-salt dihalogen IX (X = Cl, Br) flux is only stated for Clₓ and Brₓ as it does not represent a net Iₓ source.
The organic iodine (CH$_3$I, CH$_2$I$_2$, CH$_2$ICl, CH$_2$IBr) emissions are from Ordóñez et al. (2012) as described in Sherwen et al. (2016a). Inorganic iodine emissions (HOI, I$_2$) (Carpenter et al., 2013; MacDonald et al., 2014) are 30 % lower here than reported by Sherwen et al. (2016a) due to use of the MacDonald et al. (2014) parameterisation for ocean surface iodide rather than that of Chance et al. (2014). Heterogeneous iodine aerosol chemistry (Sects. 2 and B1 in Appendix B4) does not lead to a net release of iodine, instead just recycling it from less active forms (INO$_2$, INO$_3$, HOI) into more active forms (ICl/IBr).

The organic bromine (CH$_3$Br, CHBr$_3$, CH$_2$Br$_2$) emissions have been reported previously (Parrella et al., 2012; Schmidt et al., 2016) and our simulation is consistent with this work. A further source of 0.031 Tg Br year$^{-1}$ (3.5 % of total) is included here from CH$_2$IBr photolysis. The heterogeneous cycling for Br$_y$ (family defined in Appendix C) has been updated here from Schmidt et al. (2016), as described in Sect. 2/Appendix B1. An additional Br$_y$ source not considered by Schmidt et al. (2016) is iodine-activated IBr release from sea salt, which amounts to 0.30 Tg Br year$^{-1}$ and the majority (67 %) of this is tropical (22°N–22°S).

The organic chlorine emission (CH$_3$Cl, CHCl$_3$, CH$_2$Cl$_2$) for this simulation (Table 2) has been described previously Schmidt et al. (2016) and set using fixed surface concentrations. An additional source of 0.046 Tg Cl year$^{-1}$ (0.96 % of total) is present from CH$_2$ICl photolysis (Sherwen et al., 2016a). ClNO$_2$ production from the heterogeneous uptake of N$_2$O$_5$ provides a source of 0.66 Tg Cl year$^{-1}$ (14 % of total) with the vast majority (95 %) being in the Northern Hemisphere, with strongest sources in coastal regions north of 20°N. For June we calculate a global source of 21 Gg Cl month$^{-1}$, which is substantially less than the 62 Gg Cl month$^{-1}$ (Sarwar Golam, personal communication, 2016) calculated in a previous study (Sarwar et al., 2014). The difference in N$_2$O$_5$ concentrations due to differences in model resolution may contributes to this. Uptake of HOI, INO$_2$, and INO$_3$ to sea-salt aerosol leads to the emission of ICl, giving an additional source of 0.76 Tg Cl year$^{-1}$ (15.7 % of total) mostly (67 %) in tropical (22°N–22°S) locations.

Most of the emissions of Br and I species in our simulation occur in the tropics. It is notable that the chlorine emissions are more widely distributed (Fig. 1). This is a result of longer lifetimes of chlorine precursor gases, which moves their destruction further from their emissions, and the ClNO$_2$ source being primarily in the northern extratropics.
3.2 Deposition of halogens

Figure 2 shows the global annual integrated wet and dry deposition of inorganic $X_y$ ($X = \text{Cl, Br, I}$). Much of the deposition of the halogens occurs over the oceans (70, 73, and 90% for Cl$_y$, Br$_y$, and I$_y$ respectively). It is high over regions of significant tropical precipitation (Intertropical Convergence Zone, Maritime continents, Indian Ocean) and much lower at the poles, reflecting lower precipitation and emissions.

We find that the major Cl$_y$ depositional sink is HCl (94%), with HOCl contributing 5.1% and ClNO$_3$ 1.1%. The Br$_y$ sink is split between HBr, HOBr, and BrNO$_3$ with fractional contributions of 33, 30, and 28% respectively. The major I$_y$ sink is HOI deposition, which represents 59% of the deposi-
Figure 3. Tropospheric distribution of Cl<sub>y</sub>, Br<sub>y</sub>, and I<sub>y</sub> (defined in Appendix C) concentrations. Upper plots show surface and lower plots show zonal values. Only boxes that are entirely tropospheric are included in this plot. The Cl<sub>y</sub> colour bar is capped at 20 pmol mol<sup>-1</sup>, with a maximum plotted value of 116 pmol mol<sup>-1</sup> at the surface over the North Sea. The I<sub>y</sub> colour bar is capped at 10 pmol mol<sup>-1</sup>, with a maximum plotted value of 16.4 pmol mol<sup>-1</sup> at the surface over the Red Sea.

Figure 4. Tropospheric distribution of IO, BrO, and Cl concentrations. Upper plots show surface and lower plots show zonal values. Only boxes that are entirely tropospheric are included in this plot.

3.3 Halogen species concentrations

Figure 3 shows the surface and zonal concentration of annual mean I<sub>y</sub>, Br<sub>y</sub>, and Cl<sub>y</sub>, with Fig. 4 showing the same for IO, BrO, and Cl, key halogen compounds in the atmosphere. Figure 5 shows the global molecule weighted mean vertical profile of the halogen speciation.

Inorganic iodine concentrations are highest in the tropical marine boundary layer, consistent with their dominant emission regions. The highest concentrations are calculated in the coastal tropical regions, where enhanced O<sub>3</sub> concentrations...
from industrial areas flow over high predicted oceanic iodine concentrations and lead to increased oceanic inorganic iodine emissions. Within the vertical there is an average of ~0.5–1 pmol mol$^{-1}$ of I$_y$, consistent with previous model studies (Saiz-Lopez et al., 2014; Sherwen et al., 2016a). The lowest concentrations of I$_y$ are seen just above the marine boundary layer, where I$_y$ loss via wet deposition is most favourable due to partitioning towards water-soluble HOI. At higher altitudes, lower temperature and high photolysis rates push the I$_y$ speciation to less-water-soluble compounds (IO, INO$_3$) and hence the I$_y$ lifetime is longer. IO concentrations (Fig. 4) follow those of I$_y$, with high values in the tropical marine boundary layer. IO increases into the upper troposphere, reflecting a partitioning of I$_y$ in this region towards IO (and INO$_3$) and away from HOI. The global mean tropospheric lifetimes of I$_y$ and IO$_x$ (IO + I) are 2.2 days and 1.3 min, respectively. IO$_x$ loss proceeds predominately via reaction of IO with HO$_2$ (78%), with smaller losses via IO + BrO (7.9%) and IO + NO$_2$ (7.4%).

Total reactive bromine is more equally spread through the atmosphere than iodine. This reflects the longer lifetime of source species with respect to photolysis, which gives a more significant source higher in the atmosphere. The highest concentrations are still found in the tropics. Unlike I$_y$, Br$_y$ increases significantly with altitude, with BrNO$_3$ and HOBr being the two most dominant species. BrO concentrations (Fig. 4) follow those of inorganic bromine. In the boundary layer the highest concentrations are found in the tropics. BrO and IO do not strongly correlate in the tropical marine boundary layer reflecting their differing sources. BrO concentrations increase towards the upper troposphere associated with the increase in total Br$_y$. The global annual-average (molecule weighted) tropospheric BrO mixing ratio in our simulation is 0.49 pmol mol$^{-1}$ (Br$_y$ = 3.25 pmol mol$^{-1}$). When previous implementations (Parrella et al., 2012; Schmidt et al., 2016) are run for the same year and model version as this work (GEOS-Chem v10), the modelled BrO concentrations are found to be 11% higher than Schmidt et al. (2016) and 33% higher than Parrella et al. (2012). We calculate tropospheric lifetimes of 18 days for Br$_y$ and 8.1 min for BrO$_x$ (BrO + Br). Similarly
to IO\textsubscript{x}, BrO\textsubscript{x} loss proceeds predominately via reaction of BrO with HO\textsubscript{2} (71 %) and NO\textsubscript{2} (18 %).

Total inorganic chlorine has a highly non-uniform distribution at the surface, reflecting the ClNO\textsubscript{2} source from N\textsubscript{2}O\textsubscript{5} uptake on sea salt. At the surface ClNO\textsubscript{2}, HCl, BrCl, and HOCl represent around 25 % of the total Cl\textsubscript{x} each. Away from the surface the ClNO\textsubscript{2} concentrations drop off rapidly due to the short lifetime of sea salt. HCl concentrations increase significantly into the middle and upper troposphere and dominates the Cl\textsubscript{x} distribution. This suggests that stratospheric chlorine freed from CFCs and organic chlorine strongly contributes to free tropospheric concentrations of Cl\textsubscript{x}. Cl mixing ratios are very low (∼0.075 fmol mol\textsuperscript{-1} or ∼2000 cm\textsuperscript{-3}) in the marine boundary layer. Reactive Cl (i.e. Cl\textsubscript{x} excluding HCl) drops from the surface to around 10 km, where it then increases again towards the stratosphere. Cl shows a wider distribution than IO and BrO, reflecting the source wider distribution of Cl\textsubscript{x}. We calculate tropospheric lifetimes of 5 days for Cl\textsubscript{x} and 3.8 h for ClO\textsubscript{x} (Cl + ClO + ClOO + 2Cl\textsubscript{2}O\textsubscript{2}). A global tropospheric mean inorganic chlorine (Cl\textsubscript{y}) concentration of 71 pmol mol\textsuperscript{-1} is seen in our simulation. ClO\textsubscript{x} loss proceeds through reaction of Cl with CH\textsubscript{4} (27 %), ClO reaction with HO\textsubscript{2} (21 %), and ClO reaction with NO\textsubscript{2} (10 %). The longer \(X\textsubscript{O}\textsubscript{x}\) lifetime of ClO\textsubscript{x}, compared to BrO\textsubscript{x} and IO\textsubscript{x}, can be explained through the importance of the relatively slow dominant loss route through reaction with CH\textsubscript{4}.

The chemistry of halogens and sea salt is highly uncertain (Simpson et al., 2015; Saiz-Lopez et al., 2012b; Abbatt et al., 2012). Estimates for sea-salt debromination range from 0.51 Tg year\textsuperscript{-1} (Parrella et al., 2012, implemented in GEOS-Chem v10 and v9-2) to 2.9 Tg year\textsuperscript{-1} (Fernandez et al., 2014). Other studies have not included sea-salt debromination (von Glasow et al., 2004; Schmidt et al., 2016) as we do not in this work. Schmidt et al. (2016) found that including debromination of sea-salt aerosol improved the simula-
tion of the BrO and HOBr observations reported during the “Combined Airborne Studies in the Tropics” (CAST; Harris et al., 2016) campaign but resulted in overprediction of the “Tropical Ocean tRoposphere Exchange of Reactive halogen and Oxygenated VOC” campaign (TORERO; Volkamer et al., 2015; Wang et al., 2015) BrO observations. Arguably this work provides a lower estimate of bromine and chlorine sources in the troposphere, with further work needed to understand the Br$_y$ budget.

The difference in lifetimes of inorganic halogen families ($X_y$) can be understood from the change in loss routes, which shifts $HX$ to HOX following the order of group 17 in the periodic table ($\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$).

Figure 6 shows column-integrated BrO and IO, which are the major halogen species for which we have observations (see Sect. 3.4). Tropospheric ClO concentrations are small (see Fig. 5) and are therefore not shown in Fig. 6. Tropical maxima are seen for both BrO and IO, with BrO concentrations decreasing towards the equator. For IO a localised maximum is seen in the Arabian Sea. The IO maximum in Antarctica reported from satellite retrievals (Schönhardt et al., 2008) is not reproduced in our model, potentially reflecting the lack of polar-specific processes in the model.

### 3.4 Comparison with halogen observations

The observational dataset of tropospheric halogen compounds is sparse. Previous studies that this work is based on have shown comparisons for the oceanic precursors for chlorine (Eastham et al., 2014; Schmidt et al., 2016), bromine (Parrella et al., 2012; Schmidt et al., 2016), and iodine (Bell et al., 2002; Sherwen et al., 2016a; Ordóñez et al., 2012). The model performance in simulating these compounds has not changed since these previous publications so we focus here on the available observations of concentrations of IO, BrO, and some inorganic chlorine species (CINO$_3$, HCl, and Cl$_2$).

#### 3.4.1 Iodine monoxide

A comparison of IO to a suite of recent remote surface observations is shown in Fig. 7. The model shows an overall negative bias of 23 %. This compares with the 90 % positive bias previously reported in Sherwen et al. (2016a). This reduction in bias to IO observations is due to the use of the MacDonald et al. (2014) iodide parameterisation over that of Chance et al. (2014) which has reduced the inorganic emission of iodine, along with the restriction of iodine recycling to acidic aerosol.

Figure 8 shows a comparison between modelled IO with altitude against observations in the eastern Pacific.
Figure 9. Seasonal variation of zonal mean tropospheric BrO columns in different latitudinal bands. Observations from the GOME-2 satellite instrument in 2007 (Theys et al., 2011) are compared to GEOS-Chem values at the GOME-2 local overpass time (09:00–11:00).

(Volkamer et al., 2015; Wang et al., 2015). In general, the model agreement with observations is good. There is an average bias of +37% in the free troposphere (350 hPa < p < 900 hPa), which increases to +54% in the upper troposphere (350 hPa > p > tropopause). As with the surface measurements, the model bias when comparing to IO observations (Volkamer et al., 2015; Wang et al., 2015) in the free and upper troposphere is decreased from previously reported positive biases of 73 and 96%, respectively (Sherwen et al., 2016a).

3.4.2 Bromine monoxide

Comparisons of BrO against seasonal satellite tropospheric BrO observations from GOME-2 (Theys et al., 2011) are shown in Fig. 9. As shown previously (Parrella et al., 2012; Schmidt et al., 2016) the model has some skill in capturing both the latitudinal and monthly variations in tropospheric BrO columns. However, it underestimates the column BrO in the lower southern latitudes (60–90° S) and to a smaller degree also in lower northern latitudes (60–90° N), which may reflect the lack of bromine from polar (blown snow, frost flowers, etc.) sources and sea-salt debromination processes.

As shown in Fig. 10, comparisons between the model and observations of BrO made at Cape Verde (Read et al., 2008; Mahajan et al., 2010) show a negative bias of 22%. We attribute this to the high local sea-salt loadings at this site (Carpenter et al., 2010), which is situated in the surf zone. This may locally increase the BrO concentrations. The model concentrations of ~1 pmol mol⁻¹ are, however, consistent with other ship-borne observations made in the region (Leser et al., 2003).

Figure 11 shows modelled vertical BrO concentrations against observations in the eastern Pacific (Volkamer et al., 2015; Wang et al., 2015) in the subtropics (left) and tropics (right). Model and observations are in red and black, respectively. Observations and modelled values at the same location and time (as described in Sect. 2) are shown side-by-side around the midpoint of each bin. Measurements were taken aboard the NSF/NCAR GV research aircraft by the University of Colorado airborne multi-axis DOAS instrument (CU AMAX-DOAS) in the eastern Pacific in January and February 2012 (Volkamer et al., 2015; Wang et al., 2015). Locations of observations are shown in Fig. 20.
We find a reasonable agreement within the free troposphere (350 hPa < p < 900 hPa) in both the tropics and subtropics, with an average bias of −3.5 and +4.2 %, respectively. A similar comparison is seen in the upper troposphere (350 hPa < p > tropopause) with negative biases for the tropics and subtropics, of 6.3 and 9.7 %, respectively. The decrease in agreement seen in the TORERO comparison (Fig. 11) relative to that previously presented in Schmidt et al. (2016) is due to reduced BrCl and BrO production from slower cloud multiphase chemistry (see Sects. B1–B3 in Appendix B). We model higher BrO concentrations in the tropical marine boundary layer which are above those observed (Volkamer et al., 2015). Our modelled concentrations are lower than those reported previously (Miyazaki et al., 2010; Volkamer et al., 2015). We find that the model does reasonably well in coastal regions or regions with very high NOx, but does not reproduce observations in continental regions or with very high NOx.

3.4.3 Nitryl chloride (ClNO2), hydrochloric acid (HCl), hypochlorous acid (HOCl), and molecular chlorine (Cl2)

Very few constraints on the concentration of tropospheric chlorine species are available, but an increasing number of ClNO2 observations are becoming available. Table 3 shows a comparison between the model an available observations. We find that the model does reasonably well in coastal regions but does not reproduce observations in continental regions or regions with very high NOx.

Lawler et al. (2011) reports measurements of HOCl and Cl2 at Cape Verde for a week in June 2009. For the first 4 days of the campaign, HOCl concentrations were higher and peaked at ~100 pmol mol−1 with Cl2 concentrations peaking at ~30 pmol mol−1. For the later days, HOCl concentrations dropped to around 20 pmol mol−1 and Cl2 concentrations to ~0–10 pmol mol−1. We calculate much lower concentrations of Cl2 (~1 × 10−3 pmol mol−1) and slightly lower HOCl (~10 pmol mol−1). This is similar to findings of Long et al. (2014), who also found better comparisons with the later period of observations. Similar to the comparison with observed ClNO2, our model underestimated HOCl and Cl2.

The model does not include many sources of reactive chlorine. The failure to reproduce continental ClNO2 is likely due to a lack of representation of sources such as salt plains, direct emission from power station and swimming pools, and HCl acid displacement. The inability to reproduce the very high ClNO2 found in some cities (Pasadena) and industrialised regions (Texas) may be due to the coarse resolution of the model compared to the spatial inhomogeneity of these processes.
Table 4. Comparison between global tropospheric O₃ budgets of simulations “Cl+Br+I” (with halogen chemistry) and “NOHAL” (without halogen chemistry). Recent average model values from ACCENT (Young et al., 2013) are also shown for comparison. For the $X_1O + X_2O$ halogen crossover reactions where $X_1O \neq X_2O$, we split the O₃ loss equally between the two routes. Values are rounded to the nearest integer value.

|                          | “Cl+Br+I” | “NOHAL” | ACCENT       |
|--------------------------|-----------|---------|--------------|
| O₃ burden (Tg)           | 339       | 416     | 340 ± 40     |
| O₃ chemical sources (Tg yr) |           |         |              |
| NO + HO₂                 | 3436      | 3607    | –            |
| NO + CH₃O₂               | 1288      | 1316    | –            |
| NO + RO₂                 | 525       | 508     | –            |
| Total chemical O₃ sources (PO₃) | 5249   | 5431    | 5110 ± 606   |
| O₃ chemical sinks (Tg year⁻¹) |           |         |              |
| O₃ + H₂O $\rightarrow$ 2OH + O₂ | 1997   | 2489    | –            |
| O₃ + HO₂ $\rightarrow$ OH + O₂ | 1061   | 1432    | –            |
| O₃ + OH $\rightarrow$ HO₂ + O₂ | 562    | 737     | –            |
| HOBr $\rightarrow$ Br + OH | 285     | –       | –            |
| HOBr + HCl $\rightarrow$ BrCl | 54     | –       | –            |
| HOBr + HBr $\rightarrow$ Br₂ + H₂O (aq. aerosol) | 22   | –       | –            |
| BrO + BrO $\rightarrow$ 2Br + O₂ | 13    | –       | –            |
| BrO + BrO $\rightarrow$ Br₂ + O₂ | 4     | –       | –            |
| BrO + OH $\rightarrow$ Br + HO₂ | 12   | –       | –            |
| IO + BrO $\rightarrow$ Br + I + O₂ | 11   | –       | –            |
| ClO + BrO $\rightarrow$ Br + ClO₂/OCIO | 4     | –       | –            |
| Other bromine O₃ sinks | 0         | –       | –            |
| Total bromine O₃ sinks | 405       | –       | –            |
| HOI $\rightarrow$ I + OH | 438       | –       | –            |
| OIO $\rightarrow$ I + O₂ | 140       | –       | –            |
| IO + BrO $\rightarrow$ Br + I + O₂ | 11   | –       | –            |
| IO + ClO $\rightarrow$ I + Cl + O₂/ICl + O₂ | 1     | –       | –            |
| Other iodine O₃ sinks | 2         | –       | –            |
| Total iodine O₃ sinks | 591       | –       | –            |
| HOCI $\rightarrow$ Cl + OH | 27      | –       | –            |
| CH₃O₂ + ClO $\rightarrow$ ClOO | 6      | –       | –            |
| ClO + BrO $\rightarrow$ Br + ClO₂/OCIO | 4     | –       | –            |
| ClNO₃ + HBr $\rightarrow$ BrCl | 2     | –       | –            |
| IO + ClO $\rightarrow$ I + Cl + O₂/ICl + O₂ | 1     | –       | –            |
| Other chlorine O₃ sinks | 1         | –       | –            |
| Total chlorine O₃ sinks | 40        | –       | –            |
| Other O₃ sinks | 184       | 172     | –            |
| Total chem. O₃ sinks (LO₃) | 4841  | 4829    | 4668 ± 727   |
| O₃ PO₃ - LO₃ (Tg year⁻¹) | 408       | 602     | 618 ± 251    |
| O₃ dry deposition (Tg year⁻¹) | 799   | 980     | 1003 ± 200   |
| O₃ lifetime (days) | 22        | 26      | 22 ± 2       |
| O₃ STE (PO₃ - LO₃-Dry dep.) (Tg year⁻¹) | 391   | 378     | 552 ± 168    |
4 Impact of halogens

We now investigate the impact of the halogen chemistry on the composition of the troposphere. We start with O$_3$ and OH and then move onto other components of the troposphere.

4.1 Ozone

Figure 12 shows changes in column, surface, and zonal O$_3$ both in absolute and fractional terms between simulations with and without halogen emissions (“Cl+Br+I” vs. “NOHAL”). Globally the mass-weighted, annual-average
Figure 14. Comparison between annual modelled O\textsubscript{3} profiles and sonde data (2005). Profiles shown are the annual mean of available observations from World Ozone and Ultraviolet Radiation Data Centre (WOUDC, 2014) and model data for 2005 at given locations. Blue and red lines represent simulations without halogens (“NOHAL”) with halogens (“Cl+Br+I”), respectively. Observations (in black) show mean concentrations with upper and lower quartiles given by whiskers. Locations of observations are shown in Fig. 21.

Figure 15. Global annual-average tropospheric vertical odd oxygen loss (O\textsubscript{x}) through different reaction routes (Photolysis, HO\textsubscript{x}, IO\textsubscript{x}, BrO\textsubscript{x}, and ClO\textsubscript{x}).

mixing ratio is reduced by 9.4 nmol mol\textsuperscript{-1} with the inclusion of halogens and tropospheric burden decreases by 18.6% (“Cl+Br+I” – “NOHAL”)/ (“NOHAL” · 100). A much larger percentage decrease of 30.0% (8.5 nmol mol\textsuperscript{-1}) is seen over the ocean surface. Large percentage losses are seen in the oceanic Southern Hemisphere as reported previously (Long et al., 2014; Schmidt et al., 2016; Sherwen et al., 2016a), reflecting the significant ocean–atmosphere exchange in this region. The majority (65%) of the change in O\textsubscript{3} mass due to halogens occurs in the free troposphere (350 hPa < p < 900 hPa). The location of O\textsubscript{3} concentration decreases is noteworthy as the climate effect of O\textsubscript{3} is highly spatial and vertically variable (Myhre et al., 2013). Effects of halogens on tropospheric O\textsubscript{3} from preindustrial to present day are explored elsewhere (Sherwen et al., 2016b).

Comparisons of the model and observed surface and sonde O\textsubscript{3} concentrations are given in Figs. 13 and 14. In the tropics the fidelity of the simulation improves with the inclusion of halogens, as shown previously by Schmidt et al. (2016) and Sherwen et al. (2016a). Sonde and surface comparisons north of ~ 50° N and south of ~ 60° S, however, show that
the model now underestimates O$_3$. This is clearly the case for Neumayer and the South Pole (Fig. 13).

The global odd oxygen budget O$_3$ in the troposphere with (“Cl+Br+I”) and without (“NOHAL”) halogens is shown in Table 4. The O$_3$ loss through chlorine, bromine, and iodine represents 0.8, 8.4, and 12.2 % of the total O$_3$ loss respectively; thus halogens constitute 21.4 % of the overall O$_3$ loss. The sum of halogen-driven O$_3$ loss is 1036 Tg O$_3$ year$^{-1}$, which is similar to the magnitude of loss via reaction of O$_3$ with HO$_2$ of $\sim$1100 Tg O$_3$ year$^{-1}$ (21.9 % of total). Halogen cross-over reactions (BrO + IO, BrO + ClO, IO + ClO) contribute little to the overall O$_3$ loss. This number compares with $\sim$930 Tg O$_3$ year$^{-1}$ reported in GEOS-Chem previously by Sherwen et al. (2016a). Saiz-Lopez et al. (2014) found that, between 50$^\circ$S and 50$^\circ$N and over the ocean only, halogens are responsible for the loss of 640 Tg O$_3$ year$^{-1}$. We find a higher value of 827 Tg O$_3$ year$^{-1}$ with our model.

Halogens represent 39.6 and 33.0 % of O$_3$ loss in the upper troposphere (350 hPa > $\rho$ > tropopause) and marine boundary layer (900 hPa < $\rho$), respectively, as shown in Fig. 15. The marine boundary layer O$_3$ loss attributable to halogens is comparable to the 31 % reported by Prados-Roman et al. (2015a) previously, and it is higher than the 26 % reported solely for iodine (Sherwen et al., 2016a). The inter-reaction of halogen monoxide species is found to be less important here than previous studies (e.g. Read et al., 2008), which has been basis in locations of higher halogen monoxide concentrations. Inclusion of sea salt, which would increase BrO in the marine boundary layer, would increase the magnitude of contribution of these routes to total halogen-driven O$_3$ loss.

Although the partitioning of the O$_3$ loss processes is significantly different between the simulations with and without halogens (Table 4), the overall annual O$_3$ loss only increases by $\sim$0.25 % (4841 vs. 4829 Tg year$^{-1}$). The O$_3$ production term decreases by 3.4 %. This decrease is due to a reduction in NO$_x$ concentrations via hydrolysis of XNO$_3$ ($X$ = Cl, Br, I). Our tropospheric NO$_x$ burden decreases by 3.1 % to 167 Gg N (see Table A1) on inclusion of halogens consistent with previous model studies (Long et al., 2014; von Glasow et al., 2004; Parrella et al., 2012; Schmidt et al., 2016). Globally NO$_x$ losses through ClNO$_3$ and BrNO$_3$ hydrolysis are approximately equal (1 : 0.88) and overall proceed at a rate of $\sim$10 % of the NO$_x$ loss through the NO$_2$ + OH pathway. Iodine nitrite and nitrate (INO$_2$, INO$_3$) hydrolysis is much less significant ($\sim$0.2 % of rate of NO$_2$ + OH). Net O$_3$ is the difference
between the production and loss terms and the change here is much greater, leading to an overall decrease in net production of tropospheric $O_3$ ($PO_{ax} - LO_{ax}$) of 32% (194 Tg year$^{-1}$) and a resultant decrease in $O_3$ lifetime of 16%.

4.2 HO$_x$ (OH + HO$_2$)

We find that global molecule weighted average HO$_x$ (OH + HO$_2$) concentrations are reduced by 10.2% with the inclusion of halogens, with OH decreasing by 8.2% from $1.40 \times 10^6$ to $1.28 \times 10^6$ molecules cm$^{-3}$. Lower $O_3$ concentrations decreases the primary OH source ($O_3 \overset{h\nu}{\rightarrow} 2OH$) by 17.4% and the secondary OH source (HO$_2$ + NO) by 4.7%.

The reduction in the sources of OH is buffered by an additional OH source from the photolysis of HOX ($X = Cl, Br, I$) which acts to increase the conversion of HO$_2$ to OH. Previously, Sherwen et al. (2016a) showed an increase of 1.8% in global OH concentrations on inclusion of iodine. However, increased Br$_y$ and reduced I$_y$ concentrations in the simulations described here mean that the increased OH source from HOX photolysis does not compensate fully for the re-
duced primary source, resulting in an overall 8.2 % reduction in global mean OH. This buffering contributes to a change in OH smaller than the 11 % reported previously (Schmidt et al., 2016). As reported previously (Long et al., 2014; Schmidt et al., 2016), we also find the net effect of halogens on the OH:HO₂ ratio is a small increase (2.3 %).

4.3 Organic compounds

The oxidation of VOCs by halogens is included in this simulation (see Table B2 for reactions). The global fractional loss due to OH, Cl, Br, O₃, NO₃, and photolysis (hν) for a range of organics is shown in Fig. 16.

Globally, Br oxidation is small in our simulation and contributes 3.9 % to the loss of acetaldehyde (CH₃CHO), 0.8 % of the loss of formaldehyde (CH₂O), 0.63 % of the loss of ≥C₄ alkenes, and <0.001 % of the loss of other compounds. Recent work has suggested a significant source of oceanic oxygenated VOCs (oVOCs) (Coburn et al., 2014; Lawson et al., 2015; Mahajan et al., 2014; Millet et al., 2010; Myriokefalitakis et al., 2008; Sinreich et al., 2010; Volkamer et al., 2015), which we do not include in this simulation. Furthermore, although our modelled Brᵥ is broadly comparable to some previous work (Parrella et al., 2012; Schmidt et al., 2016), it is lower in the marine boundary layer than in other recent work (Long et al., 2014). The combination of these two factors suggests that our model provides a lower bounds of impacts of bromine on VOCs. Significantly higher concentrations of oVOC would decrease the BrO₃ concentrations in the model and might then allow an increased sea-salt source of reactive bromine.

The oxidation of VOCs by chlorine is more significant. In our simulation chlorine accounts for 27, 15, and 14 % of the global loss of ethane (C₂H₆), propane (C₃H₈), and acetone (CH₃(C(O)CH₃)), respectively. Loss of other VOCs is globally small. This increased loss due to Cl is to some extent compensated for by the reduction in the OH concentrations that we calculate. Thus the overall lifetime of ethane, propane, and acetone changes from 131, 38, and 85 days in the simulation without halogens to 113, 37, and 80 in the simulation with halogens. Notably the ethane lifetime without halogens is 16 % longer. Given that we consider the chlorine in the model to be a lower limit, ethane oxidation by chlorine may in reality be more significant than found here.

Methane is a significant climate gas, as it has the second-highest forcing amongst well-mixed greenhouse gases from preindustrial to present day (Myhre et al., 2013). In our simulation without halogens we calculate a tropospheric chemical lifetime due to OH of 7.47 years. With the inclusion of halogen chemistry the OH concentration drops, extending the methane lifetime due to OH to 8.28 years (an increase of 10.8 %). However, in our halogen simulations, chlorine radicals also oxidise methane (2.0 % of the total loss), shortening the lifetime to 8.16 years (1.52 %). As noted previously, the model’s chlorine concentrations appear to be underestimated. Allan et al. (2007) estimate a 25 Tg year⁻¹ sink for methane from Cl (~ 4 %), significantly higher than our estimate (4 Tg). Overall the model’s CH₄ lifetime still appears to be short compared to the observationally based estimation of 9.1 ± 0.9 from Prather et al. (2012), but halogens decrease this bias.
In our simulations, halogens (essentially chlorine) have a significant but not overwhelming role in the concentrations of hydrocarbons (from $\sim 1\%$ of methanol loss to $\sim 27\%$ of ethane loss). However, as discussed earlier, the low biases seen with the very limited observational dataset of chlorine compounds would suggest that the impacts calculated here are probably lower limits.

4.4 Other species

With the inclusion of halogens in the troposphere there are a large number of changes in the composition of the troposphere. Figure 17 illustrates the fractional global change in burden by species (for abbreviation see Appendix C). The spatial and zonal distribution of these changes by species family ($\text{HO}_x$, $\text{NO}_x$, $\text{SO}_x$ as defined in Appendix C) are shown in Fig. 18 and for a few VOCs ($\text{C}_2\text{H}_6$, $\text{CH}_3\text{CO}$, acetone, and $\geq \text{C}_4$ alkanes) in Fig. 19. A tabulated form of these changes is given within Appendix A (Table A1).

As discussed in Sects. 4.1 and 4.2, a clear decrease in oxidants ($\text{O}_3$, $\text{OH}$, $\text{HO}_2$, $\text{H}_2\text{O}_2$) is seen. This drives an increase in the concentrations of some VOCs (4.5% on a per carbon basis), including CO (6.1%) and isoprene (6.2%). However, as discussed, it also adds an additional Cl sink term which leads to an overall decrease in some species (e.g. $\text{C}_2\text{H}_6$, $\text{CH}_3\text{CO}$, $\text{C}_2\text{H}_3$) particularly in the northern hemispheric oceanic regions. The $\text{SO}_x$ burden increases slightly (0.5%), which can be attributed to decreases in oxidants.

5 Summary and conclusions

We have presented a model of tropospheric composition which has attempted to include the major routes of halogen chemistry impacts. Assessment of the model performance is limited as observations of halogen species are extremely sparse. However, given the available observations we conclude that the model has some useful skill in predicting the concentration of iodine and bromine species and appears to underestimate the concentrations of chlorine species.

Consistent with previous studies, our model shows significant halogen-driven changes in the concentrations of oxidants. The tropospheric $\text{O}_3$ burden and global mean OH decreases by 18.6 and 8.2%, respectively, on inclusion of halogens. The methane lifetime increases by 10.8%, improving agreement with observations.

There are a range of changes in the concentrations of other species. Direct reaction with Cl atoms leads to enhanced oxidation of hydrocarbons with ethane showing a significant response. Given that the model appears to provide a lower limit for atomic Cl concentrations, this suggests a major missing oxidation pathway for ethane which is currently not considered. NO$_x$ concentrations are reduced by aerosol hydrolysis of the halogen nitrates, which leads to reduced global $\text{O}_3$ production. Our simulation of BrO appears to be relatively consistent with observations, but we do not include a sea-salt debromination mechanism. This would suggest that either the cycling of bromine in our model is generally too fast or that we do not have sufficiently large BrO$_x$ sinks (potentially oVOCs). Both hypotheses warrant further research.

Significant uncertainties, however, remain in our understanding of halogens in the troposphere. The gas phase chemistry and photolysis parameters of iodine compounds are uncertain, together with the emissions of their organic and inorganic precursors (Sherwen et al., 2016a). For chlorine, bromine, and iodine heterogeneous chemistry, little experimental data exist and suitable parameterisations for the complex aerosols found in the atmosphere are unavailable (Abbatt et al., 2012). The uncertainties of this have been dis-
cussed in recent reviews (Saiz-Lopez et al., 2012b; Simpson et al., 2015) and considered in previous model studies (Schmidt et al., 2016; Sherwen et al., 2016a), and they still warrant further exploration.

Understanding fully the impact of halogens on tropospheric composition will require significant development of new experimental techniques and more field observations, new laboratory studies, and models which are able to exploit these developments.

6 Data availability

The model code used here will be made available to the community through the standard GEOS-Chem repository (http://www.geos-chem.org). Requests for materials should be addressed to Mat Evans (mat.evans@york.ac.uk).
Appendix A: Tabulated burden changes on inclusion of halogens

Table A1 gives the burdens with and without halogens and the fractional change.

**Table A1.** Tropospheric burden of species and families with (“Cl+Br+I”) and without halogens (“NOHAL”), and % change. Burdens are considered in elemental terms (e.g Gg S/N/C) and species masses for OH, HO$_2$, H$_2$O$_2$, and O$_3$. Families are defined in Appendix C.

| Species | “NOHAL” | “Cl+Br+I” | % Δ |
|---------|---------|-----------|-----|
| NO$_3$  | 1.49    | 1.14      | −23.57 |
| N$_2$O$_5$ | 9.38   | 7.48      | −20.22 |
| C$_2$H$_6$ | 3258.84 | 2628.05   | −19.36 |
| O$_3$   | 415 843.25 | 338 708.23 | −18.55 |
| HNO$_4$ | 19.84   | 16.84     | −15.14 |
| H$_2$O$_2$ | 3229.09 | 2764.27   | −14.39 |
| C$_3$H$_8$ | 609.76 | 524.31    | −14.01 |
| ≥C4 alkanes | 488.35 | 429.02    | −12.15 |
| PPN     | 15.82   | 14.31     | −9.55  |
| HO$_2$  | 27.55   | 24.95     | −9.44  |
| OH      | 0.28    | 0.26      | −6.31  |
| CH$_3$C(O)CH$_3$ | 7533.51 | 7085.23   | −5.95  |
| PAN     | 202.89  | 191.57    | −5.58  |
| NO$_2$  | 123.53  | 118.52    | −4.06  |
| CH$_2$O | 389.55  | 375.42    | −3.63  |
| NO$_x$  | 171.01  | 165.75    | −3.07  |
| SO$_4$ on SSA | 1.97   | 1.94      | −1.74  |
| PMN     | 0.68    | 0.67      | −1.27  |
| NO$_3$  | 1374.56 | 1367.26   | −0.53  |
| NO      | 47.48   | 47.24     | −0.50  |
| NH$_3$  | 126.61  | 126.42    | −0.15  |
| NH$_4$  | 270.93  | 270.88    | −0.02  |
| SO$_2$  | 398.98  | 400.80    | 0.46   |
| SO$_4$  | 397.01  | 398.86    | 0.47   |
| PROPNN  | 7.46    | 7.55      | 1.22   |
| Acetaldehyde | 184.93 | 187.23    | 1.25   |
| CH$_3$O$_2$NO$_2$ | 13.80 | 14.03    | 1.63   |
| HNO$_3$ | 463.49  | 471.53    | 1.74   |
| > C3 ketones | 186.99 | 190.49    | 1.87   |
| ≥C3 alkenes | 97.93  | 100.28    | 2.40   |
| SO$_2$  | 286.11  | 298.96    | 4.49   |
| VOCs   | 148 193.29 | 155 234.49 | 4.75   |
| MMN     | 3.15    | 3.32      | 5.17   |
| ≥ C4 alkyl nitrates | 64.60  | 68.00     | 5.26   |
| HNO$_2$ | 2.76    | 2.92      | 5.84   |
| CO      | 134 654.88 | 142 877.06 | 6.11   |
| Isoprene | 788.55 | 837.40    | 6.19   |
| ISOPN   | 0.65    | 0.71      | 9.40   |
Appendix B: Gas phase chemistry scheme

Here is described the full halogen chemistry scheme as presented in previous works (Bell et al., 2002; Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016a) and with updates as detailed in Sect. 2 and Table 1. The complete gas phase photolysis, bimolecular, and termolecular reactions are described in Tables B1, B2, and B3.

B1 Heterogenous reactions

The halogen multiphase chemistry mechanism is based on the iodine mechanism (“Br + I”) described in Sherwen et al. (2016a) and the coupled (Cl, Br) mechanism of Schmidt et al. (2016). The heterogenous reactions in the scheme are shown in Table B4 and with further detail individual detail on certain reactions below. The loss rate of a molecule X due to multiphase processing on aerosol is calculated following Jacob (2000).

\[
\frac{dn_X}{dt} = -\left(\frac{r}{D_g} + 4\frac{c}{\gamma}\right)^{-1} A n_X, \quad (B1)
\]

where \( r \) is the aerosol effective radius, \( D_g \) is the gas phase diffusion coefficient of \( X \), \( c \) is the average thermal velocity of \( X \), \( \gamma \) is the reactive uptake coefficient, \( A \) is the aerosol surface area concentration, and \( n_X \) is the gas phase concentration of \( X \).

B2 Aerosols

We consider halogen reactions on sulfate aerosols, sea-salt aerosols, and liquid and ice cloud droplets. The implementation of sulfate type aerosols in GEOS-Chem is described by Park et al. (2004) and Pye et al. (2009). Sulfate aerosols are assumed to be acidic with pH = 0.

The GEOS-Chem sea-salt aerosol simulation is as described by Jaeglé et al. (2011). The transport and deposition of sea-salt bromide follows that of the parent aerosol. Oxidation of bromide on sea salt produces volatile forms of bromine that are released to the gas phase. Sea-salt aerosol is emitted alkaline, but the alkalinity can be titrated in GEOS-Chem by uptake of HNO\(_3\) and assuming effective cloud droplet radii of 10 and 6 µm for marine and continental clouds, respectively. The ice cloud droplet surface area is modelled in a similar manner assuming effective ice droplet radii of 75 µm. We assume that ice cloud chemistry is confined to an unfrozen overlayer surrounding the ice crystal (see Schmidt et al. (2016) for details). Cloud water pH (typically between 4 and 6) is calculated locally in GEOS-Chem following Alexander et al. (2012).

The reactive uptake coefficients depend on the aerosol halide concentration. For sea-salt aerosol, the bromide concentration is calculated directly from the bromide content and the aerosol mass. Sea-salt aerosol chloride is assumed to be in excess (see below). For clouds and sulfate aerosol, the bromide and chloride concentration is estimated by assuming equilibrium between gas phase HX and aerosol phase \( X^- \).

B3 Reactive uptake coefficients

B3.1 HOBr + Cl\(^-\) / Br\(^-\)

The reactive uptake coefficient is calculated as

\[
\gamma = \left(\Gamma^{-1} + \alpha^{-1}\right)^{-1}, \quad (B2)
\]

where the mass accommodation coefficient for HOBr is \( \alpha = 0.6 \), and

\[
\Gamma = \frac{4H_{HOBr}RTk_{HOBr+X^-}[X^-][H^+]}{c f(l_r, r)}, \quad (B3)
\]

with \( k_{HOBr+Cl^-} = 5.9 \times 10^9 \text{ M}^{-2} \text{ s}^{-1} \) and \( k_{HOBr+Br^-} = 1.6 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1} \). In the equation above \( c \) is the average thermal velocity of HOBr, and \( f(l_r, r) \) is a reacto-diffusive correction factor,

\[
f(l_r, r) = \coth\left(\frac{r}{l_r}\right) - \frac{l_r}{r}, \quad (B4)
\]

with \( r \) being the radius of the aerosol. For sea-salt aerosol, HOBr + Cl\(^-\) is assumed to be limited by mass accommodation, i.e. \( \Gamma \gg \alpha \), due to high concentration of Cl\(^-\) in sea-salt aerosol. The reacto-diffusive length scale is

\[
l_r = \sqrt[4]{\frac{D_l}{k_{HOBr+X^-}[X^-][H^+]}}, \quad (B5)
\]

where \( D_l = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) is the aqueous phase diffusion coefficient for HOBr. The listed parameters are taken from Ammann et al. (2013), and \( k_{HOBr+Br^-} \) is from Beckwith et al. (1996).

B3.2 ClNO\(_3\) + Br\(^-\)

The reactive uptake coefficient is calculated as

\[
\gamma = \left(\Gamma^{-1} + \alpha^{-1}\right)^{-1}, \quad (B6)
\]

where the mass accommodation coefficient for ClNO\(_3\) is \( \alpha = 0.108 \), and

\[
\Gamma = \frac{4W RT \sqrt{[Br^-]D_l}}{c}, \quad (B7)
\]

where c is the average thermal velocity of ClNO\(_3\), \( D_l = 5.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) is the aqueous phase diffusion coefficient for ClNO\(_3\), and \( W = 10^6 \sqrt{\text{Ms bar}^{-1}} \).
Table B1. Photolysis reactions of halogens included in scheme. Photolysis is described in Eastham et al. (2014) (CINO₂, CINO₃, and ClOO), Sherwen et al. (2016a) (I₂, HOI, IO, OIO, INO, INO₂, INO₃, I₂O₂, I₂O₃, I₂O₄, CH₃I, CH₂I₂, CH₂ICl, and CH₂IBr), and Schmidt et al. (2016) (BrCl, Cl₂, ClO, HOCl, CINO₂, CINO₃, ClOO, Cl₂O₂, CH₃Cl, CH₂Cl₂, and CHCl₃). As stated in Sect. 2, we have used the I₂O₂ cross section for I₂O₄.

| ID | Reaction | Cross-section reference |
|----|----------|-------------------------|
| J1 | I₂ \(\text{hv}\) \(\rightarrow\) 2I | Sander et al. (2011) |
| J2 | HOI \(\text{hv}\) \(\rightarrow\) I + OH | Sander et al. (2011) |
| J3 | IO \((+ \text{O}_2)\) \(\text{hv}\) \(\rightarrow\) I \((+ \text{O}_3)\) | Sander et al. (2011) |
| J4 | OIO \(\text{hv}\) \(\rightarrow\) I + O₂ | Sander et al. (2011) |
| J5 | INO \(\text{hv}\) \(\rightarrow\) I + NO | Sander et al. (2011) |
| J6 | INO₂ \(\text{hv}\) \(\rightarrow\) I + NO₂ | Sander et al. (2011) |
| J7 | INO₃ \(\text{hv}\) \(\rightarrow\) I + NO₃ | Sander et al. (2011) |
| J8 | I₂O₂ \(\text{hv}\) \(\rightarrow\) I + OIO | Gómez Martín et al. (2005); Spietz et al. (2005) |
| J9 | CH₃I \(\text{hv}\) \(\rightarrow\) I | Sander et al. (2011) |
| J10 | CH₂I₂ \(\text{hv}\) \(\rightarrow\) 2I | Sander et al. (2011) |
| J11 | CH₂ICl \(\text{hv}\) \(\rightarrow\) I + Cl | Sander et al. (2011) |
| J12 | CH₂IBr \(\text{hv}\) \(\rightarrow\) I + Br | Sander et al. (2011) |
| J13 | I₂O₃ \(\text{hv}\) \(\rightarrow\) 2OIO | see caption |
| J14 | I₂O₃ \(\text{hv}\) \(\rightarrow\) OIO + IO | Gómez Martín et al. (2005); Spietz et al. (2005) |
| J15 | CHBr₃ \(\text{hv}\) \(\rightarrow\) 3Br | Sander et al. (2011) |
| J16 | Br₂ \(\text{hv}\) \(\rightarrow\) 2Br | Sander et al. (2011) |
| J17 | BrO \((+ \text{O}_2)\) \(\text{hv}\) \(\rightarrow\) Br \((+ \text{O}_3)\) | Sander et al. (2011) |
| J18 | HOBr \(\text{hv}\) \(\rightarrow\) Br + OH | Sander et al. (2011) |
| J19 | BrNO₂ \(\text{hv}\) \(\rightarrow\) Br + NO₂ | Sander et al. (2011) |
| J20 | BrNO₃ \(\text{hv}\) \(\rightarrow\) Br + NO₃ | Sander et al. (2011) |
| J21 | BrNO₃ \(\text{hv}\) \(\rightarrow\) BrO + NO₂ | Sander et al. (2011) |
| J22 | CH₂Br₂ \(\text{hv}\) \(\rightarrow\) 2Br | Sander et al. (2011) |
| J23 | BrCl \(\text{hv}\) \(\rightarrow\) Br + Cl | Sander et al. (2011) |
| J24 | Cl₂ \(\text{hv}\) \(\rightarrow\) 2Cl | Sander et al. (2011) |
| J25 | ClO \((+ \text{O}_2)\) \(\text{hv}\) Cl \((+ \text{O}_3)\) | Sander et al. (2011) |
| J26 | OCIO \((+ \text{O}_2)\) \(\text{hv}\) ClO \((+ \text{O}_3)\) | Sander et al. (2011) |
| J27 | Cl₂O₂ \(\text{hv}\) \(\rightarrow\) Cl + ClOO | Sander et al. (2011) |
| J28 | CINO₂ \(\text{hv}\) \(\rightarrow\) Cl + NO₂ | Sander et al. (2011) |
| J29 | CINO₃ \(\text{hv}\) \(\rightarrow\) Cl + NO₃ | Sander et al. (2011) |
| J30 | CINO₃ \(\text{hv}\) \(\rightarrow\) ClO + NO₂ | Sander et al. (2011) |
| J31 | HOCI \(\text{hv}\) \(\rightarrow\) Cl + OH | Sander et al. (2011) |
| J32 | ClOO \(\text{hv}\) \(\rightarrow\) Cl | Sander et al. (2011) |
| J33 | CH₂Cl \(\text{hv}\) \(\rightarrow\) Cl + CH₃O₂ | Sander et al. (2011) |
| J34 | CH₃Cl₂ \(\text{hv}\) \(\rightarrow\) 2Cl | Sander et al. (2011) |
Table B2. Bimolecular halogen reactions included in scheme. This includes reactions from previous updates to descriptions of halogen chemistry in GEOS-Chem (Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016a) and those described in Sect. 2. These are given in the Arrhenius form with the rate equal to $A \cdot \exp(-\frac{E_a}{R}T)$. Unknown values are represented by a dash and these set to 0 in the model, reducing the exponent to 1. The bi-molecular reactions with an $M$ above the arrow represent termolecular reactions where the pressure dependence is not known or are uni-molecular decomposition reactions. Abbreviations for tracers are expanded in Appendix C.

| Rxn ID | Reaction | $A \text{ cm}^3 \text{ molecules}^{-1} \text{s}^{-1}$ | $-E_a/R \text{ K}$ | Citation |
|--------|----------|---------------------------------|-----------------|----------|
| M1     | I + O$_3$ $\rightarrow$ IO + O$_2$ | 2.10 $\times$ $10^{-11}$ | -830 | Atkinson et al. (2007) |
| M2     | I + HO$_2$ $\rightarrow$ HI + O$_2$ | 1.50 $\times$ $10^{-11}$ | -1090 | Sander et al. (2011) |
| M3     | I$_2$ + OH $\rightarrow$ HOI + I | 2.10 $\times$ $10^{-10}$ | - | Atkinson et al. (2007) |
| M4     | HI + OH $\rightarrow$ I + H$_2$O | 1.60 $\times$ $10^{-10}$ | 440 | Atkinson et al. (2007) |
| M5     | HOI + OH $\rightarrow$ IO + H$_2$O | 5.00 $\times$ $10^{-12}$ | - | Riffault et al. (2005) |
| M6     | IO + HO$_2$ $\rightarrow$ HOI + O$_2$ | 1.40 $\times$ $10^{-11}$ | 540 | Atkinson et al. (2007) |
| M7     | IO + NO $\rightarrow$ I + NO$_2$ | 7.15 $\times$ $10^{-12}$ | 300 | Atkinson et al. (2007) |
| M8     | HO + CH$_3$I $\rightarrow$ H$_2$O + I | 4.30 $\times$ $10^{-12}$ | -1120 | Atkinson et al. (2008) |
| M9     | INO + INO $\rightarrow$ I$_2$ + 2NO | 8.40 $\times$ $10^{-11}$ | -2620 | Atkinson et al. (2007) |
| M10    | INO$_2$ + INO$_2$ $\rightarrow$ I$_2$ + 2NO$_2$ | 4.70 $\times$ $10^{-12}$ | -1670 | Atkinson et al. (2007) |
| M11    | I$_2$ + NO$_3$ $\rightarrow$ I + INO$_3$ | 1.50 $\times$ $10^{-12}$ | - | Atkinson et al. (2007) |
| M12    | INO$_3$ + I $\rightarrow$ I$_2$ + NO$_3$ | 9.10 $\times$ $10^{-11}$ | -146 | Kalsoyannis and Plane (2008) |
| M13    | I + BrO $\rightarrow$ IO + Br | 1.20 $\times$ $10^{-11}$ | - | Sander et al. (2011) |
| M14    | IO + Br $\rightarrow$ I + BrO | 2.70 $\times$ $10^{-11}$ | - | Bedjanian et al. (1997) |
| M15    | IO + BrO $\rightarrow$ Br + I + O$_2$ | 3.00 $\times$ $10^{-12}$ | 510 | Atkinson et al. (2007) |
| M16    | IO + BrO $\rightarrow$ Br + OIO | 1.20 $\times$ $10^{-11}$ | 510 | Atkinson et al. (2007) |
| M17    | OIO + OIO $\rightarrow$ I$_2$O$_4$ | 1.50 $\times$ $10^{-10}$ | - | Gómez Martín et al. (2007) |
| M18    | OIO + NO $\rightarrow$ NO$_2$ + IO | 1.10 $\times$ $10^{-12}$ | 542 | Atkinson et al. (2007) |
| M19    | IO + IO $\rightarrow$ I + OIO | 2.16 $\times$ $10^{-11}$ | 180 | Atkinson et al. (2007) |
| M20    | IO + IO $\rightarrow$ I$_2$O$_2$ | 3.24 $\times$ $10^{-11}$ | 180 | Atkinson et al. (2007) |
| M21    | IO + OIO $\rightarrow$ I$_2$O$_3$ | 1.50 $\times$ $10^{-10}$ | - | Gómez Martín et al. (2007) |
| M22    | I$_2$O$_3$ $\rightarrow$ IO + IO | 1.00 $\times$ $10^{-12}$ | -9770 | Ordóñez et al. (2012) |
| M23    | I$_2$O$_4$ $\rightarrow$ OIO + I | 2.50 $\times$ $10^{-14}$ | -9770 | Ordóñez et al. (2012) |
| M24    | I$_2$O$_4$ $\rightarrow$ 2OIO | 3.80 $\times$ $10^{-2}$ | - | Kalsoyannis and Plane (2008) |
| M25    | INO$_2$ $\rightarrow$ I + NO$_2$ | 9.94 $\times$ $10^{-17}$ | -11859 | McFiggans et al. (2000) |
| M26    | INO$_3$ $\rightarrow$ IO + NO$_2$ | 2.10 $\times$ $10^{-15}$ | -13670 | Kalsoyannis and Plane (2008) |
| M27    | IO + ClO $\rightarrow$ I + OCIO | 2.59 $\times$ $10^{-12}$ | 280 | Atkinson et al. (2007) |
| M28    | IO + ClO $\rightarrow$ I + Cl + O$_2$ | 1.18 $\times$ $10^{-12}$ | 280 | Atkinson et al. (2007) |
| M29    | IO + ClO $\rightarrow$ I + ClO$_2$ | 9.40 $\times$ $10^{-13}$ | 280 | Atkinson et al. (2007) |
| M30    | Cl + HCOOH $\rightarrow$ HCl + CO$_2$ + H$_2$O | 2.00 $\times$ $10^{-13}$ | - | Sander et al. (2011) |
| M31    | Cl + CH$_3$O$_2$ $\rightarrow$ ClO + CH$_2$O + HO$_2$ | 1.60 $\times$ $10^{-10}$ | - | Sander et al. (2011) |
| M32    | Cl + CH$_3$OOH $\rightarrow$ HCl + CH$_3$O$_2$ | 5.70 $\times$ $10^{-11}$ | - | Sander et al. (2011) |
| M33    | Cl + C$_2$H$_5$ $\rightarrow$ HCl + C$_2$H$_3$O$_2$ | 7.20 $\times$ $10^{-11}$ | -70 | Sander et al. (2011) |
| M34    | Cl + C$_2$H$_5$O$_2$ $\rightarrow$ ClO + HO$_2$ + ALD$_2$ | 7.40 $\times$ $10^{-11}$ | - | Sander et al. (2011) |
| M35    | Cl + EOH $\rightarrow$ HCl + ALD$_2$ | 9.60 $\times$ $10^{-11}$ | - | Sander et al. (2011) |
| M36    | Cl + CH$_3$C(O)OH $\rightarrow$ HCl + CH$_3$O$_2$ + CO$_2$ | 2.80 $\times$ $10^{-14}$ | - | Sander et al. (2011) |
| M37    | Cl + C$_2$H$_4$ $\rightarrow$ HCl + A3O2 | 7.85 $\times$ $10^{-11}$ | -80 | Sander et al. (2011) |
| M38    | Cl + C$_2$H$_4$ $\rightarrow$ HCl + B3O2 | 6.54 $\times$ $10^{-11}$ | - | Sander et al. (2011) |
| M39    | Cl + ACET $\rightarrow$ HCl + ATO2 | 7.70 $\times$ $10^{-11}$ | -1000 | Sander et al. (2011) |
| M40    | Cl + ISOP $\rightarrow$ HCl + RIO2 | 7.70 $\times$ $10^{-11}$ | 500 | Sander et al. (2011) |
| M41    | Cl + MOH $\rightarrow$ HCl + CH$_2$O + HO$_2$ | 5.50 $\times$ $10^{-11}$ | - | Sander et al. (2011) |

---

a Only first channel from JPL considered. The second channel forms a Criegee (HCl + C$_2$H$_4$O$_2$) and therefore cannot be represented by the reduced GEOS-Chem chemistry scheme. b Reaction defined by JPL and interpreted as proceeding via hydrogen abstraction; therefore, the acetaldehyde product is assumed.
Table B2. Continued.

| Rxn ID | Reaction                                                                 | $A$ (cm$^3$ molecules$^{-1}$ s$^{-1}$) | $-E_a/R$ (K) | Citation                           |
|--------|--------------------------------------------------------------------------|---------------------------------------|-------------|-----------------------------------|
| M42    | CHBr$_3$ + OH $\rightarrow$ 3Br + CO                                     | $1.35 \times 10^{-12}$               | $-600$      | Sander et al. (2011)             |
| M43    | CH$_2$Br$_2$ + OH $\rightarrow$ 2Br + CO                                 | $2.00 \times 10^{-12}$               | $-840$      | Sander et al. (2011)             |
| M44    | CH$_3$Br + OH $\rightarrow$ 3Br + CO                                     | $2.35 \times 10^{-12}$               | $-1300$     | Sander et al. (2011)             |
| M45    | Br + O$_3$ $\rightarrow$ BrO + O$_2$                                    | $1.60 \times 10^{-11}$               | $-780$      | Sander et al. (2011)             |
| M46    | Br + CH$_2$O $\rightarrow$ HO$_2$ + CO                                  | $1.70 \times 10^{-11}$               | $-800$      | Sander et al. (2011)             |
| M47    | Br + HO$_2$ $\rightarrow$ HBr + O$_2$                                   | $4.80 \times 10^{-12}$               | $-310$      | Sander et al. (2011)             |
| M48    | Br + CH$_3$CHO $\rightarrow$ CH$_3$CO$_3$                               | $1.30 \times 10^{-11}$               | $-360$      | Atkinson et al. (2007)           |
| M49    | Br + (CH$_3$)$_2$CO $\rightarrow$ CH$_3$C(O)CH$_2$OO                    | $1.66 \times 10^{-10}$               | $-7000$     | King et al. (1970)               |
| M50    | Br + C$_2$H$_6$ $\rightarrow$ C$_2$H$_5$OO                              | $2.36 \times 10^{-10}$               | $-6411$     | Seakins et al. (1992)            |
| M51    | Br + C$_3$H$_8$ $\rightarrow$ C$_3$H$_7$OO                              | $8.77 \times 10^{-11}$               | $-4330$     | Seakins et al. (1992)            |
| M52    | Br + BrNO$_3$ $\rightarrow$ Br$_2$ + NO$_3$                             | $4.90 \times 10^{-11}$               | 0           | Orlando and Tyndall (1996)       |
| M53    | Br + NO$_3$ $\rightarrow$ BrO + NO$_2$                                  | $1.60 \times 10^{-11}$               | 0           | Sander et al. (2011)             |
| M54    | HBr + OH $\rightarrow$ Br + H$_2$O                                      | $5.50 \times 10^{-12}$               | 200         | Sander et al. (2011)             |
| M55    | BrO + NO $\rightarrow$ Br + NO$_2$                                      | $8.80 \times 10^{-12}$               | 260         | Sander et al. (2011)             |
| M56    | BrO + OH $\rightarrow$ Br + HO$_2$                                      | $1.70 \times 10^{-11}$               | 250         | Sander et al. (2011)             |
| M57    | BrO + BrO $\rightarrow$ 2Br + O$_2$                                     | $2.40 \times 10^{-12}$               | 40          | Sander et al. (2011)             |
| M58    | BrO + BrO $\rightarrow$ Br$_2$ + O$_2$                                  | $2.80 \times 10^{-14}$               | 860         | Sander et al. (2011)             |
| M59    | BrO + HO$_2$ $\rightarrow$ HOBr + O$_2$                                 | $4.50 \times 10^{-12}$               | 460         | Sander et al. (2011)             |
| M60    | Br$_2$ + OH $\rightarrow$ HOBr + Br                                      | $2.10 \times 10^{-11}$               | 240         | Sander et al. (2011)             |
| M61    | Cl + Alk4 $\rightarrow$ HCl + R4O2                                      | $2.05 \times 10^{-10}$               | –           | Atkinson et al. (2006)           |
| M62    | Cl + PRPE $\rightarrow$ HCl + PO$_2$                                    | $3.60 \times 10^{-12}$               | –           | Atkinson et al. (2006)           |
| M63    | CH$_3$Cl + Cl $\rightarrow$ CO + 2HCl + HO$_2$                          | $2.17 \times 10^{-11}$               | $-1130$     | Sander et al. (2011)             |
| M64    | Cl + H$_2$O$_2$ $\rightarrow$ HO$_2$ + HCl                             | $1.10 \times 10^{-11}$               | $-980$      | Sander et al. (2011)             |
| M65    | Cl + HO$_2$ $\rightarrow$ O$_2$ + HCl                                   | $1.40 \times 10^{-11}$               | 270         | Sander et al. (2011)             |
| M66    | Cl + HO$_2$ $\rightarrow$ OH + ClO                                    | $3.60 \times 10^{-11}$               | $-375$      | Sander et al. (2011)             |
| M67    | Cl + O$_3$ $\rightarrow$ ClO + O$_2$                                   | $2.30 \times 10^{-11}$               | $-200$      | Sander et al. (2011)             |
| M68    | CINO$_3$ + Cl $\rightarrow$ Cl$_2$ + NO$_3$                             | $6.50 \times 10^{-12}$               | 135         | Sander et al. (2011)             |
| M69    | CIO + ClO $\rightarrow$ Cl$_2$ + O$_2$                                 | $1.00 \times 10^{-12}$               | $-1590$     | Sander et al. (2011)             |
| M70    | CIO + ClO $\rightarrow$ OCIO + Cl                                    | $3.50 \times 10^{-13}$               | $-1370$     | Sander et al. (2011)             |
| M71    | CIO + ClO $\rightarrow$ Cl + ClOO                                    | $3.00 \times 10^{-11}$               | $-2450$     | Sander et al. (2011)             |
| M72    | CIO + HO$_2$ $\rightarrow$ O$_2$ + HCl                                 | $2.60 \times 10^{-12}$               | 290         | Sander et al. (2011)             |
| M73    | CIO + NO $\rightarrow$ Cl + NO$_2$                                     | $6.40 \times 10^{-12}$               | 290         | Sander et al. (2011)             |
| M74    | ClOO + Cl $\rightarrow$ 2ClO                                          | $1.20 \times 10^{-11}$               | –           | Sander et al. (2011)             |
| M75    | ClOO + Cl $\rightarrow$ Cl$_2$ + O$_2$                                 | $2.30 \times 10^{-10}$               | –           | Sander et al. (2011)             |
| M76    | MO$_2$ + ClO $\rightarrow$ ClO$_2$ + HO$_2$ + CH$_2$O                  | $3.30 \times 10^{-12}$               | $-115$      | Sander et al. (2011)             |
| M77    | OH + CH$_3$Cl $\rightarrow$ Cl + HO$_2$ + H$_2$O                        | $3.90 \times 10^{-12}$               | $-1411$     | Sander et al. (2011)             |
| M78    | OH + Cl$_2$ $\rightarrow$ HOCI + Cl                                    | $2.60 \times 10^{-12}$               | $-1100$     | Sander et al. (2011)             |
| M79    | OH + Cl$_2$O$_2$ $\rightarrow$ HOCI + ClOO                              | $6.00 \times 10^{-13}$               | 670         | Sander et al. (2011)             |
| M80    | OH + CINO$_2$ $\rightarrow$ HOCI + NO$_2$                              | $2.40 \times 10^{-12}$               | $-1250$     | Sander et al. (2011)             |
| M81    | OH + CINO$_3$ $\rightarrow$ HOCI + NO$_3$                               | $1.20 \times 10^{-12}$               | $-330$      | Sander et al. (2011)             |
| M82    | OH + ClO $\rightarrow$ HCl + O$_2$                                     | $6.00 \times 10^{-13}$               | 230         | Sander et al. (2011)             |
| M83    | OH + ClO $\rightarrow$ HO$_2$ + Cl                                    | $7.40 \times 10^{-12}$               | 270         | Sander et al. (2011)             |
| M84    | OH + HCl $\rightarrow$ H$_2$O + Cl                                     | $1.80 \times 10^{-12}$               | $-250$      | Sander et al. (2011)             |
| M85    | OH + HOCl $\rightarrow$ H$_2$O + ClO                                   | $3.00 \times 10^{-12}$               | $-500$      | Sander et al. (2011)             |
| M86    | OH + OCIO $\rightarrow$ HOCl + O$_2$                                   | $1.50 \times 10^{-12}$               | 600         | Sander et al. (2011)             |
described by Atkinson et al. (2007).

\[ \gamma = \Gamma_b + \Gamma_s, \]

where \( \Gamma_b \) is the bulk reaction coefficient,

\[ \Gamma_b = \frac{4H_{O_3}RTk_{O_3+Br^-}[Br^-]f(r,l_r)}{c}, \]

with \( k_{O_3+Br^-} = 6.8 \times 10^8 \exp(-4450 K/T) \text{ M}^{-1} \text{s}^{-1} \). In the equation above \( c \) is the average thermal velocity of \( O_3 \), and \( f(l_r, r) \) is a reacto-diffusive correction factor,

\[ f(l_r, r) = \frac{\cosh \left( \frac{r}{l_r} \right) - 1}{r}, \]

with \( r \) being the radius of the aerosol. The reacto-diffusive length scale is

\[ l_r = \sqrt{\frac{D_l}{k_{O_3+Br^-}[Br^-]}}, \]

where \( D_l = 8.9 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} \) is the aqueous phase diffusion coefficient for \( O_3 \).

The surface reaction coefficient is calculated as

\[ \Gamma_s = \frac{4k_s[Br^-(surf)]K_{LangC}N_{\text{max}}}{c(1 + K_{LangC}[O_3(g)])}, \]

where the surface reaction rate constant is \( k_s = 10^{-16} \text{ cm}^2 \text{s}^{-1} \), the equilibrium constant for \( O_3 \) is \( K_{LangC} = 10^{-13} \text{ cm}^3 \), and the maximum number of available sites is taken as \( N_{\text{max}} = 3 \times 10^{14} \text{ cm}^{-2} \). The surface bromide concentration is estimated as

\[ [Br^-(surf)] = \min(3.41 \times 10^{14} \text{ cm}^{-2}\text{M}^{-1}[Br^-], N_{\text{max}}). \]
Table B4. Halogen multiphase reactions and reactive uptake coefficients ($\gamma$).

| ID | Reaction | Reactive uptake coefficient ($\gamma$) | Note | Reference |
|----|----------|--------------------------------------|------|-----------|
| 1  | HCl $\rightarrow$ Cl$^-$ (SSA)     | $4.4 \times 10^{-6} \exp(2989 \, K/T)$ | Sea salt only | Ammann et al. (2013) |
| 2  | HBBr $\rightarrow$ Br$^-$ (SSA)    | $1.3 \times 10^{-3} \exp(4290 \, K/T)$ | Sea salt only | Ammann et al. (2013) |
| 3  | HI $\rightarrow$ I(aerosol)        | 0.1                                   |      |           |
| 4  | ClNO$_3$ $\rightarrow$ HOCI + HNO$_3$ | 0.024                               | Hydrolysis | Deiber et al. (2004) |
| 5  | BrNO$_3$ $\rightarrow$ HOB + HNO$_3$ | 0.02                                 | Hydrolysis | Deiber et al. (2004) |
| 6  | INO$_3$ $\rightarrow$ 0.85Cl + 0.15Br + HNO$_3$ | 0.01                               | Sea salt only |           |
| 7  | INO$_2$ $\rightarrow$ 0.85Cl + 0.15Br + HNO$_3$ | 0.02                               | Sea salt only |           |
| 8  | HOB + Cl$^-$ (aq) $\rightarrow$ BrCl | See Sect. B3 in Appendix B | | Ammann et al. (2013) |
| 9  | HOB + Br$^-$ (aq) $\rightarrow$ Br$_2$ | See Sect. B3 in Appendix B | | Ammann et al. (2013) |
| 10 | HOI $\rightarrow$ 0.85Cl + 0.15Br | 0.01                               | Sea salt only |           |
| 11 | ClNO$_3$ + Br$^-$ (aq) $\rightarrow$ BrCl + HNO$_3$ | See Sect. B3 in Appendix B | | Ammann et al. (2013) |
| 12 | O$_3$ + Br$^-$ (aq) $\rightarrow$ HOB | See Sect. B3 in Appendix B | | Ammann et al. (2013) |
| 13 | I$_2$O$_2$ $\rightarrow$ I(aerosol) | 0.02                                | |           |
| 14 | I$_2$O$_3$ $\rightarrow$ I(aerosol) | 0.02                                | |           |
| 15 | I$_2$O$_4$ $\rightarrow$ I(aerosol) | 0.02                                | |           |

Table B5. Henry’s law coefficients and molar heats of formation of iodine species. Where Henry’s law constant equals infinity a very large values is used within the model ($1 \times 10^{20} \, \text{Matm}^{-1}$). The INO$_2$ Henry’s law constant is assumed equal to that of BrNO$_3$, from Sander (2015), by analogy. For I$_2$O$_X$ ($X = 2, 3, 4$) a Henry’s law constant of infinity is assumed by analogy with INO$_3$.

| No. | Species    | Henry’s law constant (H) at 298 K M atm$^{-1}$ | Reference                                  | d(ln $H$)/d(1/T) | Reference |
|-----|------------|-----------------------------------------------|--------------------------------------------|------------------|-----------|
| DX  | HOBr       | $6.1 \times 10^3$                             | Frenzel et al. (1998)                      | $6.01 \times 10^3$ | McGrath and Rowland (1994) |
| DX  | HBr*       | $7.1 \times 10^{13}$                          | Frenzel et al. (1998)                      | $1.02 \times 10^4$ | Schweitzer et al. (2000) |
| DX  | BrNO$_3$   | 0.3                                            | Frenzel et al. (1998)                      | –                | –         |
| DX  | BrNO$_3$   | $\infty$                                       | Sander (2015)                              | –                | –         |
| DX  | Br$_2$     | 0.76                                           | Dean (1992)                                | $3.72 \times 10^3$ | Dean (1992) |
| DX  | HOCI       | $6.5 \times 10^3$                             | Sander (2015)                              | $5.9 \times 10^3$ | Sander (2015) |
| DX  | HCl        | $7.1 \times 10^{13}$                          | Sander (2015)                              | $5.9 \times 10^3$ | Sander (2015) |
| DX  | ClNO$_3$   | $\infty$                                       | Sander (2015)                              | –                | –         |
| DX  | BrCl       | 0.97                                           | Sander (2015)                              | –                | –         |
| DX  | ICl        | $1.11 \times 10^4$                            | Sander (2015)                              | $2.11 \times 10^3$ | Sander et al. (2006) |
| DX  | IBr        | $2.43 \times 10^4$                            | Sander (2015)                              | $4.92 \times 10^3$ | Sander et al. (2006) |
| D1  | HOI        | $1.53 \times 10^4$                            | Sander (2015)                              | $8.37 \times 10^3$ | Sander et al. (2006) |
| D2  | HI*        | $7.43 \times 10^{13}$                         | Sander (2015)                              | $3.19 \times 10^3$ | Sander et al. (2006) |
| D3  | INO$_3$    | $\infty$                                       | Vogt et al. (1999)                         | $3.98 \times 10^4$ | Kaltsoyannis and Plane (2008) |
| D4  | I$_2$O$_2$ | $\infty$                                       | see caption text                           | $1.89 \times 10^4$ | Kaltsoyannis and Plane (2008) |
| D5  | I$_2$      | $2.63$                                         | Sander (2015)                              | $7.51 \times 10^3$ | Sander et al. (2006) |
| D6  | INO$_2$    | 0.3                                            | see caption text                           | $7.24 \times 10^3$ | Sander et al. (2006) |
| D7  | I$_2$O$_3$ | $\infty$                                       | see caption text                           | $7.70 \times 10^3$ | Kaltsoyannis and Plane (2008) |
| D8  | I$_2$O$_4$ | $\infty$                                       | see caption text                           | $1.34 \times 10^4$ | Kaltsoyannis and Plane (2008) |

* Effective Henry’s law of HX is calculated for acid conditions through $K_H^\infty(T) = K_H(T) \times (1 + \frac{K_w}{[H^+]}).$ A pH of 4.5 is assumed for a typical cloud droplet.
### Appendix C

**Table C1.** Abbreviations used in the document. Abbreviated species names used here are defined in the GEOS-Chem manual (http://acmg.seas.harvard.edu/geos/doc/man/appendix_6.html).

| Abbreviation | Expansion |
|--------------|-----------|
| PAN          | peroxyacetyl nitrate |
| PPN          | peroxypropionyl nitrate |
| MPN          | methyl peroxo nitrate |
| PMN          | peroxymethacryloyl nitrate |
| MOH          | methanol |
| EOH          | ethanol |
| ALD2         | acetaldehyde |
| ISOP         | isoprene |
| ALK4         | $\geq$ C4 alkanes |
| CH$_3$O$_2$  | methylperoxy radical |
| A3O2         | primary RO$_2$ from C$_3$H$_8$ |
| B3O2         | secondary RO$_2$ from C$_3$H$_8$ |
| ATO2         | RO$_2$ from acetone |
| R4O2         | RO$_2$ from $\geq$ C4 alkanes |
| RIO2         | RO$_2$ from acetone |
| HO$_x$       | OH + HO$_2$ |
| NO$_x$       | NO + NO$_2$ |
| SO$_x$       | SO$_2$ + SO$_4$ + SO$_4$ on sea salt |
| I$_x$        | I + 2I$_2$ + HOI + IO + OIO + HI + INO + INO$_2$ + 2INO$_2$ + 2INO + 2INO$_3$ + 2I$_2$O$_2$ + 2I$_2$O$_3$ + 2I$_2$O$_4$ |
| Br$_x$       | Br + 2Br$_2$ + HOB$_r$ + BrO + HBr + BrNO$_2$ + BrNO$_3$ + Br + BrCl |
| Cl$_x$       | Cl + 2Cl$_2$ + HCl + ClO + HCl + ClNO$_2$ + ClNO$_3$ + ClI + BrCl + ClOCl + OCIO + 2Cl$_2$O$_2$ |
| O$_x$        | O$_3$ + NO$_2$ + 2NO$_3$ + PAN + PMN + PPN + HNO$_4$ + 3N$_2$O$_5$ + HNO$_2$ + MPN + XO + HOX + XNO$_2$ + 2XNO$_3$ + 2OIO + 2I$_2$O$_2$ + 3I$_2$O$_3$ + 4I$_2$O$_4$ + 2Cl$_2$O$_2$ + 2OCIO (where X = Cl, Br, I) |
| PRPE         | $\geq$ C3 alkenes |
References

Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol: recent advances and remaining challenges, Chem. Soc. Rev., 41, 6555–6581, doi:10.1039/c2cs35052a, 2012.

Alexander, B.: Sulfate formation in sea-salt aerosols: Constraints from oxygen isotopes, J. Geophys. Res., 110, D10307, doi:10.1029/2004JD005659, 2005.

Alexander, B., Allman, D. J., Amos, H. M., Fairlie, T. D., Dachs, J., Hegg, D. A., and Sletten, R. S.: Isotopic constraints on the formation pathways of sulfate aerosol in the marine boundary layer of the subtropical northeast Atlantic Ocean, J. Geophys. Res., 117, D06304, doi:10.1029/2011JD016773, 2012.

Allan, W., Struthers, H., and Lowe, D. C.: Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: Global model results compared with Southern Hemisphere measurements, J. Geophys. Res.-Atmos., 112, D04306, doi:10.1029/2006JD007369, 2007.

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045–8228, doi:10.5194/acp-13-8045-2013, 2013.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and IUPAC Subcommittee: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625–4055, doi:10.5194/acp-6-3625-2006, 2006.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III – gas phase reactions of inorganic halogen compounds, Atmos. Chem. Phys., 7, 981–1191, doi:10.5194/acp-7-981-2007, 2007.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IV – gas phase reactions of organic halogen species, J. Phys. Chem. Ref. Data, 8, 4141–4496, 2008.

Bannan, T. J., Booth, A. M., Bacak, A., Muller, J. B. A., Leather, K. E., Le Breton, M., Jones, B., Young, D., Coe, H., Allan, J., Visser, S., Slowik, J. G., Furger, M., Prévôt, A. S. H., Lee, J., Dunmore, R. E., Hopkins, J. R., Hamilton, J. F., Lewis, A. C., Whalley, L. K., Sharp, T., Stone, D., Heidt, D. E., Fleming, Z. L., Leigh, R., Shallcross, D. E., and Percival, C. J.: The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation, J. Geophys. Res.-Atmos., 120, 5638–5657, doi:10.1002/2014JD022629, 2015.

Beckwith, R. C., Wang, T. X., and Margerum, D. W.: Equilibrium and Kinetics of Bromine Hydrolysis, Inorg. Chem., 35, 995–1000, doi:10.1021/ic950909w, 1996.

Bedjanian, Y., Le Bras, G., and Poulet, G.: Kinetic study of the Br+IO, I+BrO and Br+I2 reactions. Heat of formation of the BrO radical, Chem. Phys. Lett., 266, 233–238, doi:10.1016/S0009-2614(97)01530-3, 1997.

Bell, N., Hsu, L., Jacob, D. J., Schultz, M. G., Blake, D. R., Butler, J. H., King, D. B., Lobert, J. M., and Maier-Reimer, E.: Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models, J. Geophys. Res.-Atmos., 107, ACH 8-1–ACH 8-12, doi:10.1029/2001JD001151, 2002.

Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351–8363, doi:10.5194/acp-9-8351-2009, 2009.

Bloss, W. J., Evans, M. J., Lee, J. D., Sommariva, R., Heard, D. E., and Pilling, M. J.: The oxidative capacity of the troposphere: Coupling of field measurements of OH and a global chemistry transport model, Faraday Discuss., 130, 425–436, doi:10.1039/b419090d, 2005.

Carpenter, L. J., Fleming, Z. L., Read, K. A., Lee, J. D., Moller, S. J., Hopkin, J. R., Purvis, R. M., Lewis, A. C., Muller, K., Heinold, B., Herrmann, H., Fomba, K. W., van Pinxteren, D., Muller, C., Tegen, I., Wiedensohler, A., Muller, T., Niedermeier, N., Achterberg, E. P., Panev, M. D., Kozlova, E. A., Heinmann, M., Heidt, D. E., Plane, J. M. C., Mahajan, A., Oetjen, H., Ingham, T., Stone, D., Whalley, L. K., Evans, M. J., Pilling, M. J., Leigh, R. J., Monks, P. S., Karunaharan, A., Vaughn, S., Arnold, S. R., Tschritter, J., Pohler, D., Friess, U., Holla, R., Mendes, I. M., Lopez, H., Faria, B., Manning, A. J., and Wallace, D. R. W.: Seasonal characteristics of tropical marine boundary layer air measured at the Cape Verde Atmospheric Observatory, J. Atmos. Chem., 67, 87–140, doi:10.1007/s10874-011-9206-1, 2010.

Carpenter, L. J., MacDonald, S. M., Shaw, M. D., Kumar, R., Saunders, R. W., Partipan, R., Wilson, J., and Plane, J. M. C.: Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine, Nat. Geosci., 6, 108–111, doi:10.1038/ngeo1687, 2013.

Chameides, W. L. and Davis, D. D.: Iodine: Its possible role in tropospheric photochemistry, J. Geophys. Res.-Oceans, 85, 7383–7398, doi:10.1029/JC085iC12p07383, 1980.

Chance, R., Baker, A. R., Carpenter, L., and Jickells, T. D.: The distribution of iodide at the sea surface, Environ. Sci. Processes Impacts, 16, 1841–1859, doi:10.1039/C4EM00139G, 2014.

Coburn, S., Ortega, L., Thalman, R., Blomquist, B., Fairall, C. W., and Volkamer, R.: Measurements of diurnal variations and eddy
covariance (EC) fluxes of glyoxal in the tropical marine boundary layer: description of the Fast LED-CE-DOAS instrument, Atmos. Meas. Tech., 7, 3579–3595, doi:10.5194/amt-7-3579-2014, 2014.

Coburn, S., Dix, B., Edgerton, E., Holmes, C. D., Kinnison, D., Liang, Q., ter Schure, A., Wang, S., and Volkamer, R.: Mercury oxidation from bromine chemistry in the free troposphere over the southeastern US, Atmos. Chem. Phys., 16, 3743–3760, doi:10.5194/acp-16-3743-2016, 2016.

Daele, V. and Poulet, G.: Kinetics and products of the reactions of CH3O2 with Cl and ClO, J. Chem. Phys., 93, 1081–1099, 1996.

Dean, J. A.: Lage’s Handbook of Chemistry, McGraw-Hill, Inc., 1992.

Deiber, G., George, Ch., Le Calvé, S., Schweitzer, F., and Mirabel, At.: Global impacts of tropospheric halogens on oxidants and composition in GEOS-Chem (CAST), B. Am. Meteorol. Soc., doi:10.1175/BAMS-D-14-00290.1, online first, 2016.

Holmes, C. D., Jacob, D. J., Mason, R. P., and Jaffe, D. A.: Sources and deposition of reactive gaseous mercury in the marine atmosphere, Atmos. Environ., 43, 2278–2285, doi:10.1016/j.atmosenv.2009.01.051, 2009.

Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bónisch, H., Keber, T., Oram, D., Mills, G., Ordóñez, C., Saiz-Lopez, A., Warwick, N., Liang, Q., Peng, W., Moore, F., Miller, B. R., Marécal, V., Richards, N. A., Dorf, M., and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmos. Chem. Phys., 13, 11819–11838, doi:10.5194/acp-13-11819-2013, 2013.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmos. Environ., 34, 2131–2159, doi:10.1016/S1352-2310(99)00462-8, 2000.

Jaeglé, L., Quinn, P. K., Bates, T. S., Alexander, B., and Lin, J.-T.: Global distribution of sea salt aerosols: new constraints from in situ and remote sensing observations, Atmos. Chem. Phys., 11, 3137–3157, doi:10.5194/acp-11-3137-2011, 2011.

Kaltsoyannis, N. and Plane, J. M. C.: Quantum chemical calculations on a selection of iodine-containing species (IO, OIO, IO3, IO2, I2O3, IO3O and I3O4) of importance in the atmosphere, Phys. Chem. Chem. Phys., 10, 1723–1733, 2008.

Keene, W. C., Long, M. S., Pszenny, A. A. P., Sander, R., Maben, J. R., Wall, A. J., O’Halloran, T. L., Kerkweg, A., Fischer, E. V., and Schrems, O.: Latitudinal variation in the multiphase chemical processing of inorganic halogens and related species over the eastern North and South Atlantic Oceans, Atmos. Chem. Phys., 9, 7361–7385, doi:10.5194/acp-9-7361-2009, 2009.

King, K. D., Golden, D. M., and Benson, S. W.: Kinetics of the gas-phase thermal bromination of acetone. Heat of formation and stabilization energy of the acetyl radical, J. Am. Chem. Soc., 92, 5541–5546, doi:10.1021/ja00722a001, 1970.

Knipping, E. M. and Dabub, D.: Impact of Chlorine Emissions from Sea-Salt Aerosol on Coastal Urban Ozone, Environ. Sci. Technol., 37, 275–284, doi:10.1021/es052793a, 2003.

Lawler, M. J., Sander, R., Carpenter, L. J., Lee, J. D., von Glasow, R., Sommariva, R., and Saltzman, E. S.: HOCI and Cl2 observations in marine air, Atmos. Chem. Phys., 11, 7617–7628, doi:10.5194/acp-11-7617-2011, 2011.

Lawson, S. J., Selleck, P. W., Galbally, I. E., Keywood, M. D., Harvey, M. J., Lerot, C., Helmg, D., and Ristovski, Z.: Seasonal in situ observations of glyoxal and methylglyoxal over the temperate oceans of the Southern Hemisphere, Atmos. Chem. Phys., 15, 223–240, doi:10.5194/acp-15-223-2015, 2015.

Leser, H., Hönninger, G., and Platt, U.: MAX-DOAS measurements of BrO and NO2 in the marine boundary layer, Geophys. Res. Lett., 30, 1537, doi:10.1029/2002GL015811, 2003.

Long, M. S., Keene, W. C., Easter, R. C., Sander, R., Liu, X., Kerkweg, A., and Erickson, D.: Sensitivity of tropospheric chemical composition to halogen-radical chemistry using a fully coupled size-resolved multiphase chemistry-global climate system: halogen distributions, aerosol composition, and sensitivity of climate-relevant gases, Atmos. Chem. Phys., 14, 3397–3425, doi:10.5194/acp-14-3397-2014, 2014.
Millet, D. B., Guenther, A., Siegel, D. A., Nelson, N. B., Singh, H. B., de Gouw, J. A., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. L., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations, Atmos. Chem. Phys., 10, 3405–3425, doi:10.5194/acp-10-3405-2010, 2010.

Miyazaki, Y., Coburn, S., Uno, K., Ho, D. T., Pierce, R. B., Kawai-mura, K., and Volkamer, R.: Contribution of dissolved organic matter to submicron water-soluble organic aerosols in the marine boundary layer over the eastern equatorial Pacific, Atmos. Chem. Phys., 16, 7695–7707, doi:10.5194/acp-16-7695-2016, 2016.

Monks, P. S., Granier, C., Fuzzi, S., Stohl, A., Williams, M. L., Aki-moto, H., Amann, M., Balkanov, A., Baltensperger, U., Bey, I., Blake, N., Blake, R. S., Carslaw, K., Cooper, O. R., Dentener, F., Fowler, D., Fragkou, E., Frost, G. J., Generoso, S., Ginoux, P., Grewe, V., Guenther, A., Hannon, H. C., Henne, S., Hjorth, J., Hofzumahaus, A., Huntrieser, H., Isaksen, I. S. A., Jenkins, M. E., Kaiser, J., Kanakidou, M., Klimont, Z., Kulmala, M., Laj, P., Lawrence, M. G., Lee, J. D., Liouasse, C., Maione, M., McFiggans, G., Metzger, A., Mieville, A., Moussiopoulos, N., Orlando, J. J., O’Dowd, C. D., Palmer, P. I., Parrish, D. D., Petzold, A., Platt, U., Pöschl, U., Prévôt, A. S. H., Reeves, C. E., Reimann, S., Rudich, Y., Sellekri, G., Steinbrecher, R., Simpson, D., ten Brink, H., Theloke, J., van der Werf, G. R., Vautard, R., Vestreng, V., Vlachokostas, C., and von Glasow, R.: Atmospheric composition change – and global regional air quality, Atmos. Environ., 43, 5268–5350, doi:10.1016/j.atmosenv.2009.08.021, 2009.

Moortgat, G. K., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., de Gouw, J. A., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. L., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations, Atmos. Chem. Phys., 10, 3405–3425, doi:10.5194/acp-10-3405-2010, 2010.

MacDonald, S. M., Gómez Martín, J. C., Hay, T. D., Riemer, D. D., van der Werf, G. R., and Osthoff, H. D.: Heterogeneous formation of nitryl chloride and nitryl bromide in a Mid-Continental Urban Environment, Environ. Sci. Technol., 45, 8899–8906, doi:10.1021/es201955u, 2011.

McGrath, M. P. and Rowland, F., Jr.: The influence of natural and anthropogenic secondary sources on the glyoxal global distribution, Atmos. Chem. Phys., 12, 11609–11617, doi:10.5194/acp-12-11609-2012, 2012.

McGaff, G., Plane, J. M. C., Allan, B. J., Carpenter, L. J., Coe, H., and O’Dowd, C.: A modeling study of iodine chemistry in the marine boundary layer, J. Geophys. Res.-Atmos., 119, 6160–6169, doi:10.1002/2013JD020388, 2014.

Mao, J., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., Keller, C. A., Hudman, R. C., Barkley, M. P., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, J. Geophys. Res.-Atmos., 118, 11256–11268, doi:10.1029/2013JD020813, 2013.

McFiggans, G., Plane, J. M. C., Allan, B. J., Carpenter, L. J., Coe, H., and O’Dowd, C.: A modeling study of iodine chemistry in the marine boundary layer, J. Geophys. Res.-Atmos., 105, 14371–14385, doi:10.1029/1999JD901187, 2000.

McFiggans, G., Cox, R. A., Mossinger, J. C., Allan, B. J., and Plane, J. M. C.: Active chlorine release from marine aerosols: Roles for reactive iodine and nitrogen species, J. Geophys. Res.-Atmos., 107, ACH 10-1-ACH 10-13, doi:10.1029/2001jd000383, 2002.

McGraw, T. R. and Rowland, F. S.: The influence of natural and anthropogenic secondary sources on the glyoxal global distribution, Atmos. Chem. Phys., 10, 4611–4624, doi:10.5194/acp-10-4611-2010, 2010.

Woo, M., Ammann, M., Prados-Roman, C., Ordonez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. A., M愁e, H., and O’Dowd, C.: A modeling study of iodine chemistry in the marine boundary layer, J. Geophys. Res.-Atmos., 105, 14371–14385, doi:10.1029/1999JD901187, 2000.

Myhre, G., Shindell, D., Bréon, F.-M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D., Lamarque, J.-F., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G., Takemura, T., and Zang, H.: Anthropogenic and Natural Radiative Forcing In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Tech. rep., IPCC, 2013.

Mielke, L. H., Furgeson, A., and Ostrovsky, H. D.: Observation of Cl(p)O2 in a Mid-Continental Urban Environment, Environ. Sci. Technol., 45, 8899–8906, doi:10.1021/es201955u, 2011.

Mielke, L. H., Stutz, J., Tsai, C., Hurlock, S. C., Roberts, J. M., Veres, P. R., Froyd, K. D., Hayes, P. L., Cubison, M. J., Jimenez, J. L., Wagenfelder, R. A., Young, C. J., Gilman, J. B., de Gouw, J. A., Flynn, J. H., Grossberg, N., Lefer, B. L., Liu, J., Weber, R. J., and Ostrovsky, H. D.: Heterogeneous formation of nitryl chloride and its role as a nocturnal NO3 reservoir species during CalNex-LA 2010, J. Geophys. Res.-Atmos., 118, 10638–10652, doi:10.1029/2013JD020783, 2013.

Millet, D. B., Guenther, A., Siegel, D. A., Nelson, N. B., Singh, H. B., de Gouw, J. A., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. L., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations, Atmos. Chem. Phys., 10, 3405–3425, doi:10.5194/acp-10-3405-2010, 2010.
nitril chloride in the polluted subtropical marine boundary layer, Nat. Geosci., 1, 324–328, 2008.

Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, J. Geophys. Res.-Atmos., 109, D15204, doi:10.1029/2003JD004473, 2004.

Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickley, L. J., Miller, B., Evans, M. J., Yang, X., Pyle, J. A., Theye, N., and Van Roozendael, M.: Tropospheric bromine chemistry: implications for present and pre-industrial ozone and mercury, Atmos. Chem. Phys., 12, 6723–6740, doi:10.5194/acp-12-6723-2012, 2012.

Phillips, G. J., Tang, M. J., Thieser, J., Brickwedde, B., Schuster, G., Bohn, B., Lelieveld, J., and Crowley, J. N.: Significant concentrations of nitril chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, Geophys. Res. Lett., 39, L10811, doi:10.1029/2012GL051912, 2012.

Prados-Roman, C., Cuevas, C. A., Fernandez, R. P., Kinnison, D. E., Lamarque, J.-F., and Saiz-Lopez, A.: A negative feedback between anthropogenic ozone pollution and enhanced ocean emissions of iodine, Atmos. Chem. Phys., 15, 2215–2224, doi:10.5194/acp-15-2215-2015, 2015a.

Prados-Roman, C., Cuevas, C. A., Hay, T., Fernandez, R. P., Mahajan, A. S., Royer, S.-J., Gali, M., Simó, R., Dachs, J., Großmann, K., Kinnison, D. E., Lamarque, J.-F., and Saiz-Lopez, A.: Iodine oxide in the global marine boundary layer, Atmos. Chem. Phys., 15, 583–593, doi:10.5194/acp-15-583-2015, 2015b.

Prather, M. J., Holmes, C. D., and Hsu, J.: Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry, Geophys. Res. Lett., 39, L09803, doi:10.1029/2012GL051440, 2012.

Pszenny, A. A. P., Moldanová, J., Keene, W. C., Sander, R., Maben, J. R., Martinez, M., Crutzen, P. J., Perner, D., and Prinn, R. G.: Halogen cycling and aerosol pH in the Hawaiian marine boundary layer, Atmos. Chem. Phys., 4, 147–168, doi:10.5194/acp-4-147-2004, 2004.

Pye, H. O. T., Liao, H., Wu, S., Mickley, L. J., Jacob, D. J., Henze, D. K., and Seinfeld, J. H.: Effect of changes in climate and emissions on future sulfate-nitrate-ammonium aerosol levels in the United States, J. Geophys. Res., 114, D01205, doi:10.1029/2008JD010701, 2009.

Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J., and Plane, J. M. C.: Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, Nature, 453, 1232–1235, doi:10.1038/nature07035, 2008.

Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lermer, B. M., Vlasenko, A., Li, S.-M., Gilman, J., de Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S., and Thornton, J. A.: Nitril Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer, Environ. Sci. Technol., 46, 10463–10470, doi:10.1021/es204632r, 2012.

Riedel, T. P., Wagner, N. L., Dubé, W. P., Middlebrook, A. M., Young, C. J., Öztürk, F., Bahreini, R., VandenBoer, T. C., Wolfe, D. E., Williams, E. J., Roberts, J. M., Brown, S. S., and Thornton, J. A.: Chlorine activation within urban or power plant plumes: Vertically resolved ClNO2 and Cl2 measurements from a tall tower in a polluted continental setting, J. Geophys. Res.-Atmos., 118, 8702–8715, doi:10.1002/jgrd.50637, 2013.

Riffault, V., Bedjanian, Y., and Poulet, G.: Kinetic and mechanistic study of the reactions of OH with IBr and HOI, J. Photoch. Photobiol. A, 176, 155–161, doi:10.1016/j.jphotochem.2005.09.002, 2005.

Roberts, J. M., Osthoff, H. D., Brown, S. S., Ravishankara, A. R., Coffman, D. A., Quinn, P., and Bates, T.: Laboratory studies of products of N2O5 uptake on Cl containing substrates, Geophys. Res. Lett., 36, doi:10.1029/2009GL040448, 2009.

Saiz-Lopez, A., Lamarque, J.-F., Kinnison, D. E., Tilmes, S., Ordoñez, C., Orlando, J. J., Conley, A. J., Plane, J. M. C., Mahajan, A. S., Sousa Santos, G., Atlas, E. L., Blake, D. R., Sander, S. P., Schaufeller, S., Thompson, A. M., and Brasseur, G.: Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere, Atmos. Chem. Phys., 12, 3939–3949, doi:10.5194/acp-12-3939-2012, 2012a.

Saiz-Lopez, A., Plane, J. M. C., Baker, A. R., Carpenter, L. J., von Glasow, R., Martin, J. C. G., McFiggans, G., and Saunders, R. W.: Atmospheric Chemistry of Iodine, Chem. Rev., 112, 1773–1804, doi:10.1021/cr200029u, 2012b.

Saiz-Lopez, A., Fernandez, R. P., Ordoñez, C., Kinnison, D. E., Gómez Martín, J. C., Lamarque, J.-F., and Tilmes, S.: Iodine chemistry in the troposphere and its effect on ozone, Atmos. Chem. Phys., 14, 13119–13143, doi:10.5194/acp-14-13119-2014, 2014.

Sander, R.: Compilation of Henry’s law constants (version 4.0) for water as solvent, Atmos. Chem. Phys., 15, 4399–4981, doi:10.5194/acp-15-4399-2015, 2015.

Sander, S. P., Golden, D. M., Kurylo, M. J., Moortgat, G. K., Wine, P. H., Ravishankara, A. R., Kolb, C. E., Molina, M. J., Finlayson-Pitts, B. J., Huie, R. E., and Orkin, V. L.: Chemical kinetics and photochemical data for use in Atmospheric Studies Evaluation Number 15, NASA Jet Propulsion Laboratory, Pasadena, 2006.

Sander, S. P., Friedl, R. R., Abbatt, J. P. D., Barker, J. R., Burkholder, J. B., Golden, D. M., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Wine, P. H., Huie, R. E., and Orkin, V. L.: Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation Number 17, Tech. rep., NASA Jet Propulsion Laboratory, Pasadena, 2011.

Sarwar, G., Simon, H., Xing, J., and Mathur, R.: Importance of tropospheric CINO2 chemistry across the Northern Hemisphere, Geophys. Res. Lett., 41, 4050–4058, doi:10.1002/2014GL059962, 2014.

Schmidt, J. A., Jacob, D. J., Horowitz, H. M., Hu, L., Sherwen, T., Evans, M. J., Liang, Q., Suleiman, R. M., Oram, D. E., Breton, M. L., Percival, C. J., Wang, S., Dix, B., and Volkamer, R.: Modeling the observed tropospheric BrO background: Importance of multiphase chemistry and implications for ozone, OH, and mercury, J. Geophys. Res.-Atmos., doi:10.1002/2015JD024229, online first, 2016.

Schönhardt, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H. K., and Burrows, J. P.: Observations of iodine monoxide columns from satellite, Atmos. Chem. Phys., 8, 637–653, doi:10.5194/acp-8-637-2008, 2008.

Schweitzer, F., Mirabel, P., and George, C.: Uptake of Hydrogen Halides by Water Droplets, J. Phys. Chem. A, 104, 72–76, doi:10.1021/jp992621o, 2000.
Seakins, W. R., Pilling, M. J., Niiranen, J. T., Gutman, D., and Krasnoperov, L. N.: Kinetics and thermochemistry of R + HBr (R = CH₃, C₂H₅) reactions: determinations of the heat of formation of C₃H₇, i-C₃H₇, sec-C₄H₉, and t-C₄H₉, J. Phys. Chem., 96, 9847–9855, 1992.

Sherwen, T., Evans, M. J., Carpenter, L. J., Andrews, S. J., Lidster, R. T., Dix, B., Koenig, T. K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A. S., and Ordoñez, C.: Iodine's impact on tropospheric oxidants: a global model study in GEOS-Chem, Atmos. Chem. Phys., 16, 1161–1186, doi:10.5194/acp-16-1161-2016, 2016a.

Sherwen, T., Evans, M. J., Carpenter, L. J., Schmidt, J. A., and Mickely, L. J.: Halogen chemistry reduces tropospheric O₃ radiative forcing, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-688, in review, 2016b.

Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, Chem. Rev., 115, 4035–4062, doi:10.1021/cr5006638, 2015.

Sinreich, R., Coburn, S., Dix, B., and Volkamer, R.: Ship-based detection of glyoxal over the remote tropical Pacific Ocean, Atmos. Chem. Phys., 10, 11359–11371, doi:10.5194/acp-10-11359-2010, 2010.

Sofer, E. D., Bowdalo, D., Evans, M. J., Apadula, F., Bonasoni, P., Cupeiro, M., Ellul, R., Galbally, I. E., Gierzdienc, R., Lupp, S., Mimouni, M., Nahas, A. C., Saliba, M., and Torsseth, K.: Gridded global surface ozone metrics for atmospheric chemistry model evaluation, Earth Syst. Sci. Data, 8, 41–59, doi:10.5194/essd-8-41-2016, 2016.

Sommariva, R. and von Glasow, R.: Multiphase halogen chemistry in the tropical Atlantic Ocean, Environ. Sci. Technol., 46, 10429–10437, doi:10.1021/es3030209, 2012.

Spiezt, P., Gómez Martín, J. C., and Burrows, J. P.: Spectroscopic studies of the I₂/O₃ photochemistry: Part 2. Improved spectra of iodine oxides and analysis of the IO absorption spectrum, J. Photoch. Photobiol. A, 176, 50–67, doi:10.1016/j.jphotochem.2005.08.023, 2005.

Tham, Y. J., Yan, C., Xue, L., Zha, Q., Wang, X., and Wang, T.: Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, Chinese Sci. Bull, 59, 356–359, doi:10.1007/s11434-013-0063-y, 2014.

Theys, N., Van Roozendael, M., Hendrick, F., Yang, X., De Smedt, I., Richter, A., Begoin, M., Errera, Q., Johnston, P. V., Kreher, K., and De Mazière, M.: Global observations of tropospheric BrO columns using GOME-2 satellite data, Atmos. Chem. Phys., 11, 1791–1811, doi:10.5194/acp-11-1791-2011, 2011.

Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dubé, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, Nature, 464, 271–274, 2010.

Unger, N., Shindell, D. T., Koch, D. M., and Streets, D. G.: Cross influences of ozone and sulfate precursor emissions changes on air quality and climate, P. Natl. Acad. Sci. USA, 103, 4377–4380, doi:10.1073/pnas.0508769103, 2006.

Vogt, R., Sander, R., Von Glasow, R., and Crutzen, P. J.: Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, J. Atmos. Chem., 32, 375–395, doi:10.1023/a:1006179901037, 1999.

Volkmann, R., Baird, S., Campos, T. L., Coburn, S., DiGangi, J. P., Dix, B., Eloranta, E. W., Koenig, T. K., Morley, B., Ortega, I., Pierce, B. R., Reeves, M., Sinreich, R., Wang, S., Zondlo, M. A., and Romashkin, P. A.: Aircraft measurements of BrO, IO, glyoxal, NO₂, H₂O, O₂–O₃ and aerosol extinction profiles in the tropics: comparison with aircraft/ship-based in situ and lidar measurements, Atmos. Meas. Tech., 8, 2121–2148, doi:10.5194/amt-8-2121-2015, 2015.

von Glasow, R., von Kuhlmann, R., Lawrence, M. G., Platt, U., and Crutzen, P. J.: Impact of reactive bromine chemistry in the troposphere, Atmos. Chem. Phys., 4, 2481–2497, doi:10.5194/acp-4-2481-2004, 2004.

Wang, S.-Y., Schmidttd, J., Baird, S., Coburn, S., Dix, B., Koenig, T., Apel, E., Bowdalo, D., Campos, R., Eloranta, E., Evans, M., DiGangii, J., Zondlo, M., Gao, R.-S., Haggerty, J., Hall, S., Hornbrook, R., Jacob, D., Morley, B., Pierce, B., Reeves, M., Romashkin, P., ter Schure, A., and Volkamer, R.: Active and widespread halogen chemistry in the tropical and subtropical free troposphere, P. Natl. Acad. Sci. USA, 112, 9281–9286, doi:10.1073/pnas.1504121112, 2015.

WOUDC: WOUDC Ozone Monitoring Community, World Meteorological Organization-Global Atmosphere Watch Program (WMO-GAW)/World Ozone and Ultraviolet Radiation Data Centre (WOUDC) [Data], doi:10.14287/10000001, 2014.

Young, P. J., Archibald, A. T., Bowman, K. W., Lamarque, J.-F., Naik, V., Stevenson, D. S., Tilmes, S., Voulgarakis, A., Wild, O., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalstoen, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Horowitz, L. W., Josse, B., Lee, Y. H., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M., Rumbold, S. T., Skeie, R. B., Shindell, D. T., Strode, S. A., Sudo, K., Szopa, S., and Zeng, G.: Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmos. Chem. Phys., 13, 2063–2090, doi:10.5194/acp-13-2063-2013, 2013.

Ziska, F., Quack, B., Abrahamsson, K., Archer, S. D., Atlas, E., Bell, T., Butler, J. H., Carpenter, L. J., Jones, C. E., Harris, N. R., Hapich, H., Heumann, K. G., Hughes, C., Kuss, J., Krüger, K., Liss, P. A., Moore, R. M., Orlikowska, A., Raimund, S., Reeves, C. E., Reifenhäuser, W., Robinson, A. D., Schall, C., Tanhua, T., Tegtmeier, S., Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S., and Yokouchi, Y.: Global sea-to-air flux climatology for bromiform, dibromomethane and methyl iodide, Atmos. Chem. Phys., 13, 8915–8934, doi:10.5194/acp-13-8915-2013, 2013.