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

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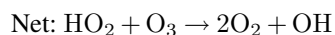
Abstract. We present a simulation of the global composition of the troposphere which includes the chemistry of halogens (Cl, Br, I). Building on previous work within the GEOS-Chem model we include emissions of inorganic iodine from the oceans, anthropogenic and biogenic sources of halogenated gases, gas phase chemistry, and a parameterised approach to heterogeneous halogen chemistry. Consistent with Schmidt et al. (2016) we do not include sea-salt de-bromination. Observations of halogen radicals (BrO, IO) are sparse but the model has some skill in reproducing these. IO shows both high and low biases in different datasets, BrO concentrations though appear to be modelled low. Comparisons to the very sparse observations dataset of reactive Cl species suggests the model represents a lower limit on impacts due to likely underestimates in emissions and therefore burdens. Inclusion of Cl, Br, 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 ~15 %, with the O₃ lifetime reducing from 26 days to 22 days. Global mean OH concentrations of 1.34 x 10⁶ molecules cm⁻³ are 4.5 % lower than in a simulation without halogens, leading to an increase in the CH₄ lifetime (6.5 %) due to OH oxidation from 7.48 years to 7.96 years. Oxidation of CH₄ by Cl is small (~1 %) but Cl oxidation of other VOCs (ethane, acetone, and propane) can be significant (~9-18 %). Oxidation of VOCs by Br is smaller, representing 2.1% of the loss of acetaldehyde and 0.6% 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) (see for example Monks et al. (2015)). The most important of tropospheric oxidants 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 productions 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 1-3 (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). They 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), and gas-phase iodine chemistry (Saiz-Lopez et al., 2014; Sommariva and von Glasow, 2012).



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. 2016). 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., 2016) and reported reductions in the tropospheric O_3 burden by up to $\sim 15\%$. 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_2O_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 (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
5 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., 2016), which used the representation of bromine chemistry from Parrella et al. (2012). Up this point, however, the coupling of chlorine, bromine, and iodine in the GEOS-Chem model and its subsequent impact on the simulated composition of the atmosphere has not been described.

Here we present such a coupled halogen scheme within GEOS-Chem and consider tropospheric impacts of halogens. This
10 simulation 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., 2016) chemistry with further updates and additions described in Section 2. In Section 3 we describe the modelled distribution of inorganic halogens (Section 3.1-3.3), and compare with observations (Section 3.4). We then outline the impact on oxidants (Section 4.1-4.2), organic compounds (Section 4.3), and other species (Section 4.4).

15 2 Model Description

This work uses the GEOS-Chem chemical transport model (www.geos-chem.org, version 10) run at $4^\circ \times 5^\circ$ 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_x , HO_x , NO_x , and VOC chemistry as described in Mao et al. (2013). Dynamic and chemical time-step are 30 and 60 minutes, respectively. Stratospheric chemistry is modelled using a linearised
20 mechanism as described by Murray et al. (2012).

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. (2016) 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. (2016), Schmidt et al. (2016), or
25 Eastham et al. (2014) are given in Table 1 with a full description of the halogen chemistry scheme used given in Appendix Tables 6-9.

For the photolysis of I_2O_X ($X=2,3,4$) we have adopted the absorption cross-sections reported by Gómez Martín et al. (2005) and Spietz et al. (2005) and used the I_2O_2 cross-section for I_2O_4 . A quantum yield of unity was assumed for all I_2O_X species. It is noted that recent work has used an unpublished spectrum for I_2O_4 that is much lower than I_2O_3 Saiz-Lopez et al. (2014),
30 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) to MacDonald et al. (2014) as the latter resulted in an improved comparison with observations (see Section 7.5 of Sherwen et al. 2016).



The product of acid catalysed di-halogen release following I^+ (HOI, INO_2 , INO_3) uptake was updated from I_2 as Sherwen et al. (2016) to yield IBr and ICl following McFiggans et al. (2002). Acidity is calculated online through titration of sea salt aerosol by uptake of sulfate dioxide (SO_2), nitric acid (HNO_3) and sulfuric acid (H_2SO_4) 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 I_Y (and may be a net sink on non-acid aerosol) but alters the speciation (Sherwen et al., 2016). 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 BrO with respect to the observations used in Section 3.4.2 (Read et al., 2008; Volkamer et al., 2015). We attributed this reduction to the de-bromination of sea-salt which we do not consider here, and the potential for the model to over estimate the BrOx lifetime. 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 8). We include 3 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 its parent aerosol as previously described for sulfate (Alexander et al., 2012) and sea-salt aerosol (Jaeglé et al., 2011).

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 N_2O_5 on aerosols was updated to yield products of $ClNO_2$ and HNO_3 (Bertram and Thornton, 2009; Roberts et al., 2009) on sea salt, and $2HNO_3$ on other aerosol types. Reaction probabilities are unchanged (Evans and Jacob, 2005).

Deposition and photolysis of inter-halogen species (ICI, BrCl, IBr) and the reaction between ClO and IO were also included (Sander et al., 2011).

3 Model results

We run the model for two years (1/1/2004 to 1/1/2006), 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. (2016). 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 months “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 inter-annual 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).

3.1 Emissions

The emissions fluxes of chlorine, bromine, and iodine species are shown in Figure 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 processes are the uptake of N_2O_5 on sea-salt and uptake of I^+ species on sea-salt. We do not include explicit sea-salt de-bromination for reasons described in Schmidt et al. (2016).

The organic iodine (CH_3I , CH_2I_2 , CH_2ICl , CH_2IBr) emissions are from Ordóñez et al. (2012) as described in Sherwen et al. (2016). Inorganic iodine emissions (HOI , I_2) (Carpenter et al., 2013; MacDonald et al., 2014) are 28 % lower here than reported by Sherwen et al. (2016), 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 (Section 2 and Appendix Section B1) 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_3Br , $CHBr_3$, CH_2Br_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 $0.031 \text{ Tg Br yr}^{-1}$ (3.4 % of total) is included here from CH_2IBr photolysis. The heterogeneous cycling for Br_Y (defined in footnote below¹) has been updated here from Schmidt et al. (2016), as described in Section 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 $0.31 \text{ Tg Br yr}^{-1}$ and the majority (67 %) of this is tropical ($22^\circ N$ - $22^\circ S$). With all these updates, the tropospheric mean daytime (07:00-19:00) BrO concentration is $1.1 \text{ pmol mol}^{-1}$ ($0.64 \text{ pmol mol}^{-1}$ 24 hr average), which is 13 % higher than reported in Schmidt et al. (2016).

The organic chlorine emission (CH_3Cl , $CHCl_3$, CH_2Cl_2) for this simulation (Table 2) has been described previously Schmidt et al. (2016) and set using fixed surface concentrations. An additional source of $0.046 \text{ Tg Cl yr}^{-1}$ (0.94 % of total) is present from CH_2ICl photolysis (Sherwen et al., 2016). $ClNO_2$ production from the heterogeneous uptake of N_2O_5 provides a source of $0.66 \text{ Tg Cl yr}^{-1}$ (14 % of total) with the vast majority (95 %) being in the northern hemisphere, with strongest sources in coastal regions north of $20^\circ N$. For June we calculate a global source of $21 \text{ Gg Cl month}^{-1}$ which is substantially less than the $62 \text{ Gg Cl month}^{-1}$ (Pers. com. Sarwar Golam 2016) calculated in a previous study (Sarwar et al., 2014). The difference in NO_x concentrations due to differences in model resolution probably 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 $0.78 \text{ Tg Cl yr}^{-1}$ (17.6 % of total) mostly (67 %) in tropical ($22^\circ N$ - $22^\circ S$) 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. This is as a result of longer lifetimes of chlorine precursor gases which moves their destruction further from their emissions and that the $ClNO_2$ source is primarily in the northern extra tropics.

3.2 Deposition of halogens

Figure 2 shows the global annual integrated wet and dry deposition of inorganic X_Y ($X=Cl, Br, I$). Much of the deposition of the halogens occurs over the oceans (69 %, 83 %, and 90 % for Cl_Y , Br_Y and I_Y respectively). It is high over regions of significant tropical precipitation (ITCZ, Maritime continents, Indian Ocean) and much lower at the poles reflecting lower precipitation and emissions.

We find that the the major Cl_Y depositional sink is HCl (85 %), with $HOCl$ contributing 11 % and $ClNO_3$ 3.2 %. The Br_Y sink is split between HBr , $HOBr$ and $BrNO_3$ with fractional contributions of 38, 30 and 24 % respectively. The major I_Y sink

¹Here X_Y ($X=Cl, Br, I$) is the sum of gas-phase inorganic species of a given halogen in units of that halogen



is HOI deposition which represents 59 % of the depositional flux. The two next largest sinks are deposition of INO_3 and iodine aerosol (22 % and 15 %).

3.3 Halogen species concentrations

Figure 3 shows the surface and zonal concentration of annual mean I_y , Br_y , Cl_y , with Figure 4 showing the same for IO, BrO and Cl, key halogen compounds in the atmosphere. Figure 5 showing 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 emissions regions. The highest concentrations are calculated in the coastal tropical regions, where enhanced O_3 concentrations from industrial areas flow over high predicted oceanic iodide concentrations and lead to increased oceanic inorganic iodine emissions. Within the vertical there is an average of $\sim 0.5\text{--}1$ pmol mol^{-1} of I_y consistent with previous model studies (Saiz-Lopez et al., 2014; Sherwen et al., 2016). 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 (Figure 4) follow the concentrations of I_y with high concentrations in the tropical marine boundary layer. The IO concentration increases into the upper troposphere reflecting a partitioning of I_y in this region towards IO (and IONO_2) and away from HOI. The global mean tropospheric lifetimes of I_y and IO_x are 2.3 days and 1.3 minutes, respectively.

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 (Figure 4) follows the concentration of inorganic bromine. In the boundary layer the highest concentrations are found in the tropical marine boundary layer concentrations are in the tropical marine boundary. 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 0.64 pmol mol^{-1} ($\text{Br}_y=4.5$ 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 12 % lower than Schmidt et al. (2016), but 17 % higher than Parrella et al. (2012). We calculate a tropospheric lifetime of Br_y of 17 days and a BrO_x lifetime of 15 minutes.

Total inorganic chlorine has a highly non-uniform distribution at the surface reflecting the dominance of the ClNO_2 source from N_2O_5 uptake on sea-salt. At the surface ClNO_2 , HCl, BrCl and HOCl represent around 25 % of the total Cl_y each. Away from the surface the ClNO_2 concentrations drop off rapidly due to the short lifetime of sea salt. HCl concentrations increase significantly into the middle and upper troposphere and dominate the Cl_y distribution. This suggests that stratospheric chlorine freed from CFCs and organic chlorine strongly contributes to free tropospheric concentrations of Cl_y . However modelled Cl_y is likely a lower limit on the concentrations in the uppermost troposphere (Froidevaux et al., 2008). Cl mixing ratios are very low 0.075 fmol mol^{-1} or 2000 cm^{-3} in the marine boundary layer. Reactive Cl (ie not HCl) drop from the surface to around



10km where it then increases again towards to stratosphere. Cl shows a wider distribution than IO and BrO reflecting the source wider distribution of Cl_y . We calculate a tropospheric lifetime of Cl_y of 15 days, a ClO_x lifetime of 2 seconds, and a global tropospheric mean inorganic chlorine (Cl_y) concentration of 70 pmol mol^{-1} in our simulation.

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 de-bromination range from 0.51 Tg yr^{-1} (Parrella et al. 2012 implemented in GEOS-Chem v10 and v9-2) to 2.9 Tg yr^{-1} (Fernandez et al., 2014). Some studies have also not included sea-salt de-bromination (von Glasow et al., 2004; Schmidt et al., 2016) as we do not in this work. Arguably this work therefore provides a lower estimate of bromine and chlorine sources in the troposphere.

Figure 6 shows column integrated BrO and IO, which are the major halogen species for which we have observations (see Section 3.4). Tropospheric ClO concentrations within the troposphere are small (see Figure 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., 2016; 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 ($ClNO_3$, HCl and Cl_2).

3.4.1 Iodine monoxide (IO)

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 21 %. This compares with the 90 % positive bias previously reported in (Sherwen et al., 2016). This reduction in bias 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 (Volkamer et al., 2015; Wang et al., 2015). In general, the model agreement with observations is good. There is an average bias of +40 % in the free troposphere ($350 \text{ hPa} < p < 900 \text{ hPa}$), which increases to +58 % in the upper troposphere ($350 \text{ hPa} > p >$ 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., 2016).



3.4.2 Bromine monoxide (BrO)

Comparisons of BrO against seasonal satellite tropospheric BrO observations from GOME-2 (Theys et al., 2011) are shown in Figure 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°S-90°S), and to a smaller degree also in lower northern latitudes (60°N-90°N) which may reflect the lack of bromine from polar (blown snow, frost flowers etc.) sources and sea-salt de-bromination processes.

Figure 11 shows modelled vertical BrO concentrations against observations in the eastern Pacific (Volkamer et al., 2015; Wang et al., 2015). We find a reasonable agreement within the free troposphere (350 hPa < p < 900 hPa) in both the tropics and subtropics, with an average negative bias of 15 and 34 %, respectively. A similar comparison is seen in the upper troposphere (350 hPa > p > tropopause) show similar negative biases for the tropics and subtropics, of 20 and 24 %, 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 Sections B1-B3). We model higher BrO concentrations in the tropical marine boundary layer above those observed (Volkamer et al., 2015). Our modelled concentrations are lower than those reported previously (Miyazaki et al., 2016; Long et al., 2014; Pszenny et al., 2004; Keene et al., 2009).

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 50 %. 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 $\sim 1 \text{ pmol mol}^{-1}$ are however consistent with other ship borne observations made in the region (Leser et al., 2003).

Our model does not include sea-salt de-bromination and yet calculated roughly the correct concentrations of BrO. Inclusion of sea-salt de-bromination leads to excessively high BrO concentration in the model (Schmidt et al., 2016). Sea-salt de-bromination is well observed, thus the success of the model despite the lack of inclusion of this process suggest model failure in other areas. The BrO_x lifetime may be too long. This is dominated by the reaction between Br and organics to produce HBr. Oceanic sources of VOCs such as acetaldehyde have been proposed (Millet et al., 2010; Volkamer et al., 2015) and a significant increase in the concentration of these species would lead to lower BrO_x concentrations. Alternatively, a reduction in the efficiency of cycling of Br_γ through aerosol would also have a similar effect. The aerosol phase chemistry is complex and the parameterisations used here may be too simple or fail to capture key processes (e.g. pH, organics). These all require further study in order to help reconcile the rapidly growing body of observation of both gas and aerosol phase bromine in the atmosphere with models.

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.

An increasing number of ClNO₂ observations are available (Table 3). We find that the model does reasonably well in coastal regions, but does not reproduce observations in continental regions or regions with very high NO_x.



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 (1x10⁻³ pmol mol⁻¹) and slightly lower HOCl (10 pmol mol⁻¹) throughout the same days of the year in our analysis year (2005). This is similar to findings of Long et al. (2014), who also found better comparisons with the cleaner period of observations. Similar to the comparison with observed ClNO₂, our simulation underestimates 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 cities (Pasadena) and industrialised regions (Texas) may be due to the coarse resolution of the model compared to the spatial inhomogeneity of these observations. The failure to reproduce the Cape Verde observations may be due to the very simple aerosol phase chlorine chemistry included in the model. Overall we suggest that the model provides a lower limit estimate of the chlorine emissions and therefore burdens within the troposphere, but constraints at the surface concentrations are limited and vertical profiles are not available. Further laboratory work to better define aerosol processes and observations will be necessary to investigate the role of chlorine on tropospheric chemistry.

4 Impact of halogens

We now investigate the impact of the halogen chemistry on the composition of the troposphere. We start with O₃ and OH and then move onto other components of the troposphere.

4.1 Ozone (O₃)

Figure 12 shows changes in column, surface and zonal O₃ both in absolute and fractional terms between simulations with and without halogen emissions (“Cl+Br+I” vs “NOHAL”). Globally the mass-weighted, annual-average mixing ratio is reduced by 7.4 pmol mol⁻¹ (14.6%) with the inclusion of halogens (“Cl+Br+I”-“NOHAL”)/“NOHAL”*100). A much larger percentage decrease of 25.0 % (7.2 pmol mol⁻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., 2016) reflecting the significant ocean-atmosphere exchange in this regions. The majority (65 %) of the change in O₃ mass due to halogens occurs in the free troposphere (350 hPa < p < 900 hPa).

Comparisons of the model and observed surface and sonde O₃ concentrations are given in Figures 13 and 14. In the tropics the fidelity of the simulation improves with the inclusion of halogens (Schmidt et al., 2016; Sherwen et al., 2016). Sonde and surface comparisons north of ~50°N and south of ~60°S however show that the model now underestimates O₃.



The global odd oxygen budget (O_X , as defined in the footnote below²) in the troposphere with (“Cl+Br+I”) and without halogens (“NOHAL”) is shown in Table 4. The O_X loss through chlorine, bromine, and iodine represents 0.46, 5.8 and 12 % of the total O_X loss respectively, thus halogens constitute 18.2 % of the overall O_3 loss. The sum of halogen driven O_X loss is 900 Tg O_X yr⁻¹, which is similar to the magnitude of loss via reaction of O_3 with HO_2 of ~1100 Tg O_X yr⁻¹ (23 % of total).

5 Halogen cross-over reactions (BrO+IO, BrO+ClO, IO+ClO) contribute little to the overall O_3 loss. This number compares with ~930 Tg O_X yr⁻¹ reported in GEOS-Chem previously by Sherwen et al. (2016). Saiz-Lopez et al. (2014) found that, between 50°S-50°N and over ocean only, halogens are responsible for the loss of 640 Tg O_X yr⁻¹. We find a comparable value of 670 O_X yr⁻¹ with our model.

10 The majority of the halogen driven O_3 loss (58.1 %) occurs in the free troposphere (350 hPa<p<900 hPa). Halogens represent 34.9 and 31.0 % of O_X loss in the upper troposphere (350 hPa>p> tropopause) and marine boundary layer (900 hPa<p) respectively as shown in Figure 15. The marine boundary layer O_X loss attributable to halogens is equal to the 31 % reported by Prados-Roman et al. (2015a) previously, and it is slightly higher than that reported solely for iodine of 26 % (Sherwen et al., 2016).

15 Although the partitioning between the O_X loss processes is significantly different between the simulations with halogens and without (Table 4), the overall annual O_X loss only increases by 2.2 % (4933 vs 4829 Tg yr⁻¹). The O_X production term decreases by 1.0 %. This decrease is due to a reduction in NO_X concentrations due to hydrolysis of XNO_3 (X=Cl, Br, I). Our tropospheric NO_X burden decreases by 1.7 % to 168 Gg N (see table 10) on inclusion of halogens consistent with observations and previous model studies (Long et al., 2014; von Glasow et al., 2004; Parrella et al., 2012; Schmidt et al., 2016). Globally NO_X loss through $ClNO_3$ and $BrNO_3$ hydrolysis is approximately equal (1:0.86), and overall proceeds at a rate of ~10 %
 20 of the NO_X loss through the NO_2 +OH pathway. Iodine nitrite and nitrate (INO_2 , INO_3) hydrolysis is much less significant (~0.25 % of rate of NO_2 +OH). Net O_X 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_X - LO_X) of 26 % (159 Tg yr⁻¹), and a resultant in decrease O_3 lifetime of 14 %.

4.2 HO_X (OH+ HO_2)

25 We find that global molecule weighted average HO_X (OH+ HO_2) concentrations are reduced by 8.5 % with the inclusion of halogens, with OH decreasing by 4.5 % from 1.40×10^6 to 1.34×10^6 molecules cm⁻³. Lower O_3 concentrations decrease the primary OH source ($O_3 \xrightarrow{h\nu} 2OH$) by 15.5 %, and the secondary OH source from HO_2 +NO by 2.2 %.

30 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. (2016) 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 reduced primary source, resulting

²Here O_X is defined as $O_3 + NO_2 + 2NO_3 + PAN + PMN + PPN + HNO_4 + 3N_2O_5 + HNO_3 + MPN + XO + HOX + XNO_2 + 2XNO_3 + 2OIO + 2I_2O_2 + 3I_2O_3 + 4I_2O_4 + 2Cl_2O_2 + 2OClO$, where X=Cl, Br, I; PAN = peroxyacetyl nitrate; PPN = peroxypropionyl nitrate; MPN = methyl peroxy nitrate; and PMN = peroxyethacryloyl nitrate.



in an overall 4.5 % reduction in global mean OH. This buffering contributes to a smaller change in OH than report previously by Schmidt et al. (2016) of 11 %. 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 (4.4 %).

4.3 Organic Compounds

5 The oxidation of volatile organic compounds (VOCs) by halogens is included in this simulation (see Table 6 for reactions). The global fractional loss due to OH, Cl, Br, NO₃, and photolysis for a range of organics is shown in Figure 16.

Globally, Br oxidation is small in our simulation and contributes 2.0 % to the loss of acetaldehyde (CH₃CHO), 0.6 % of the loss of formaldehyde (CH₂O), 0.26 % of the loss of ≥C₄ alkenes, and < 0.001 % of the loss of other compounds. Recent work has suggests a significant source of oceanic oxygenated VOCs (Millet et al., 2010; Coburn et al., 2014; Sinreich
10 et al., 2010; Mahajan et al., 2014; Lawson et al., 2015; Volkamer et al., 2015; Myriokefalitakis et al., 2008) which we do not include in this simulation. Furthermore although our modelled Br_γ is broadly comparable to some previous work (Schmidt et al., 2016; Parrella et al., 2012), it is lower in the marine boundary layer than in other recent work (Long et al., 2014). The combination of these two factors suggest that our model provides a lower bounds of impacts of bromine on VOCs. Significantly higher concentrations of oVOC would decrease the BrO concentrations in the model and might then allow an increased sea-salt
15 source of reactive bromine.

The oxidation of Volatile Organic Compounds (VOCs) by chlorine is more significant. In our simulation chlorine accounts for 18, 9, and 9 % of the global loss of ethane (C₂H₆), propane (C₃H₈), and acetone (CH₃C(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, 85 days in
20 the simulation without halogens to 120, 37, 82 in the simulation with halogens. Notably the ethane lifetime without halogens is 10% longer than it is with. 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
25 due to OH of 7.48 years. With the inclusion of halogen chemistry the OH concentration drops, extending the methane lifetime due to OH of become to 7.96 years (an increase of 6.5 %). However, in our halogen simulations, chlorine radicals also oxidise methane (~1 % of the total loss) shortening the lifetime to 7.89 years (0.85 %). As noted previously, the model's chlorine concentrations appear to be underestimated. Allan et al. (2007) estimate a 25 Tg yr⁻¹ sink for methane from Cl (~4 %), significantly higher than our estimate. Overall the model's CH₄ lifetime still appears to be short compared to the observationally
30 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 ~1 % of methane loss to ~18 % 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 footnote³). The spatial and zonal distribution of these changes by species family (HO_x , NO_x , SO_x as defined in footnote⁴) are shown in Figure 18 and for a few VOCs (C_3H_8 , C_2H_6 , acetone, and $\geq\text{C}_4$ alkanes) in Figure 19. A tabulated form of these changes is given within the Appendix (Table 10)

As discussed in section 4.1 and 4.1, a clear decrease in oxidants (O_3 , OH, HO_2 , H_2O_2) is seen. This drives an increase in the concentrations of some VOCs (2.1 % on a per carbon basis), including CO (2.8 %) and Isoprene (3.4 %). However, as discussed, it also adds an additional Cl sink term which leads to an overall decrease in some species (e.g. C_2H_6 , $(\text{CH}_3)_2\text{CO}$, C_3H_8) particularly in the northern hemisphere oceanic regions. The SO_x burden increases slightly (0.7 %), 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 O_3 burden and global mean OH decreased by 14.6 %, and 4.5 % respectively, on inclusion of halogens. The methane lifetime increases by 6.5 %, 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 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 O_3 production. Our simulation of BrO appears to be relatively consistent with those observed, however we do not include sea-salt de-bromination 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 hypothesis 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., 2016). For chlorine, bromine and iodine heterogeneous chemistry, little experimental data exists and suitable

³Abbreviated species names are defined in the GEOS-Chem manual (http://acmg.seas.harvard.edu/geos/doc/man/appendix_6.html) and here: MOH=Methanol, EOH=Ethanol, ALD2=Acetaldehyde, ISOP=Isoprene, ALK4= $\geq\text{C}_4$ alkanes, CH_3O_2 =Methylperoxy radical, A3O2= primary RO_2 from C_3H_8 , B3O2=secondary RO_2 from C_3H_8 , ATO2= RO_2 from Acetone, R4O2= RO_2 from $\geq\text{C}_4$ alkanes, RIO2= RO_2 from Acetone

⁴ Here we define families of HO_x , NO_x and SO_x as follows. HO_x : OH + HO_2 , NO_x : NO+ NO_2 , SO_x : SO_2 + SO_4 + SO_4 on sea salt.



parameterisations for the complex aerosols found in the atmosphere are unavailable (Abbatt et al., 2012; Saiz-Lopez et al., 2012b; Simpson et al., 2015).

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.

5 Appendix A: Tabulated Burden Changes on inclusion of halogens

Table 10 gives the burdens with and without halogens and the fractional change.

Appendix B: Gas phase Chemistry Scheme

Here is described the full halogen chemistry scheme as presented in previous work (Bell et al., 2002; Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016) and with updates as detailed in section 2 and Table 1. The complete gas phase photolysis, bimolecular and termolecular reactions are described in Tables 5, 6 and 7.

B1 Heterogenous reactions

The halogen multiphase chemistry mechanism is based on the iodine mechanism (“Br+I”) described in Sherwen et al. (2016) and the coupled mechanism of Schmidt et al. (2016). The heterogenous reactions in the scheme are shown in Table 8 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).

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

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, γ 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 , SO_2 , H_2SO_4 (Alexander, 2005). Sea salt aerosol with no remaining alkalinity is assumed to have pH=5. We assume no halide oxidation on alkaline sea salt aerosol.



The liquid cloud droplet surface area is modelled using cloud liquid water content from GEOS-FP (Lucchesi, 2013) and assuming effective cloud droplet radii of 10 μm 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 assuming equilibrium between gas phase HX and aerosol phase X^- .

10 B3 Reactive uptake coefficients

B3.1 HOBr + Cl⁻/Br⁻

The reactive uptake coefficient is calculated as

$$\gamma = (\Gamma^{-1} + \alpha^{-1})^{-1}, \quad (\text{B2})$$

where the mass accommodation coefficient for HOBr is $\alpha = 0.6$ and

$$15 \quad \Gamma = \frac{4H_{\text{HOBr}}RTk_{\text{HOBr}+\text{X}^-}[\text{X}^-][\text{H}^+]l_r f(l_r, r)}{c}, \quad (\text{B3})$$

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

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

with r being the radius of the aerosol. For sea salt aerosol HOBr + Cl⁻ is assumed to be limited by mass accommodation, i.e.

20 $\Gamma \gg \alpha$, due to high concentration of Cl⁻ in sea salt aerosol. The reacto-diffusive length scale is

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

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 $k_{\text{HOBr}+\text{Br}^-}$ is from Beckwith et al. (1996).

B3.2 ClNO₃ + Br⁻

25 The reactive uptake coefficient is calculated as

$$\gamma = (\Gamma^{-1} + \alpha^{-1})^{-1}, \quad (\text{B6})$$



where the mass accommodation coefficient for ClNO_3 is $\alpha = 0.108$ and

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

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 $W = 10^6 \sqrt{\text{Ms bar}^{-1}}$.

5 B3.3 $\text{O}_3 + \text{Br}^-$

The reactive uptake coefficient is calculated as

$$\gamma = \Gamma_b + \Gamma_s, \quad (\text{B8})$$

where Γ_b is the bulk reaction coefficient,

$$\Gamma_b = \frac{4H_{\text{O}_3}RTk_{\text{O}_3+\text{Br}^-}[\text{Br}^-]l_r f(r, l_r)}{c}, \quad (\text{B9})$$

- 10 with $k_{\text{O}_3+\text{Br}^-} = 6.8 \times 10^8 \exp(-4450\text{K}/T) \text{ M}^{-1}\text{s}^{-1}$. In the equation above c is the average thermal velocity of O_3 , and $f(l_r, r)$ is a reacto-diffusive correction factor,

$$f(l_r, r) = \coth\left(\frac{r}{l_r}\right) - \frac{l_r}{r}, \quad (\text{B10})$$

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

$$l_r = \sqrt{\frac{D_l}{k_{\text{O}_3+\text{Br}^-}[\text{Br}^-]}}, \quad (\text{B11})$$

- 15 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,

$$\Gamma_s = \frac{4k_s[\text{Br}^-(\text{surf})]K_{\text{LangC}}N_{\text{max}}}{c(1 + K_{\text{LangC}}[\text{O}_3(\text{g})])}, \quad (\text{B12})$$

where the surface reaction rate constant is $k_s = 10^{-16} \text{ cm}^2\text{s}^{-1}$, the equilibrium constant for O_3 is $K_{\text{LangC}} = 10^{-13} \text{ cm}^3$, 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,

20

$$[\text{Br}^-(\text{surf})] = \min(3.41 \times 10^{14} \text{ cm}^{-2}\text{M}^{-1} [\text{Br}^-], N_{\text{max}}). \quad (\text{B13})$$

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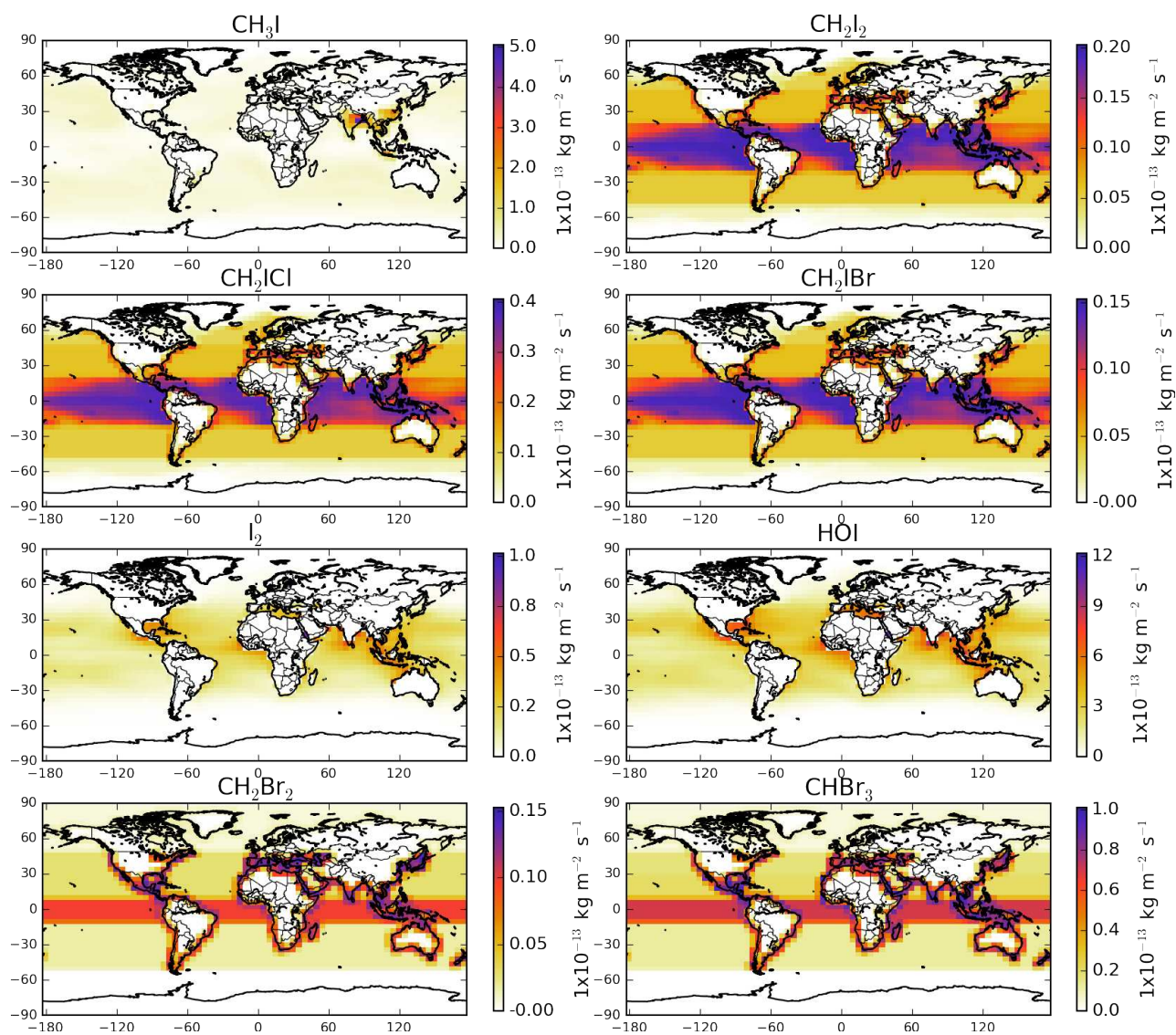


Figure 1. Average annual halogen surface emission of species and column integrated fluxes for species that have fixed surface concentrations in the model (CH_3Cl , CH_3Cl_2 , CHCl_3 , CHBr_3) or those with vertically variable sources (ClNO_2 from N_2O_5 uptake on sea-salt and IX ($\text{X}=\text{Cl},\text{Br}$) production from HOI , INO_2 , and INO_3 uptake). Values are given in $\text{kg X m}^{-2} \text{ s}^{-1}$ ($\text{X}=\text{Cl},\text{Br},\text{I}$).

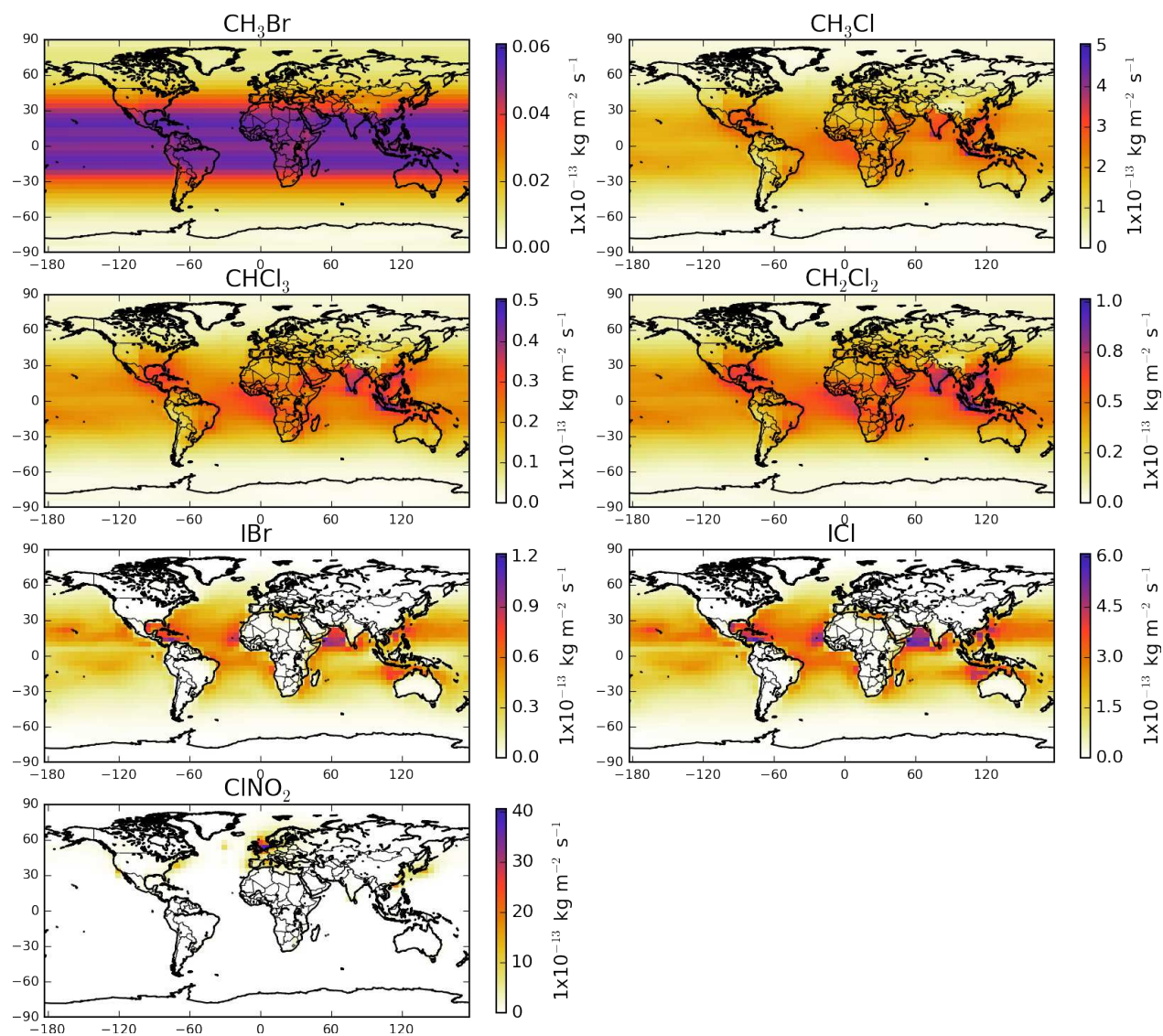


Figure 1. Continued.

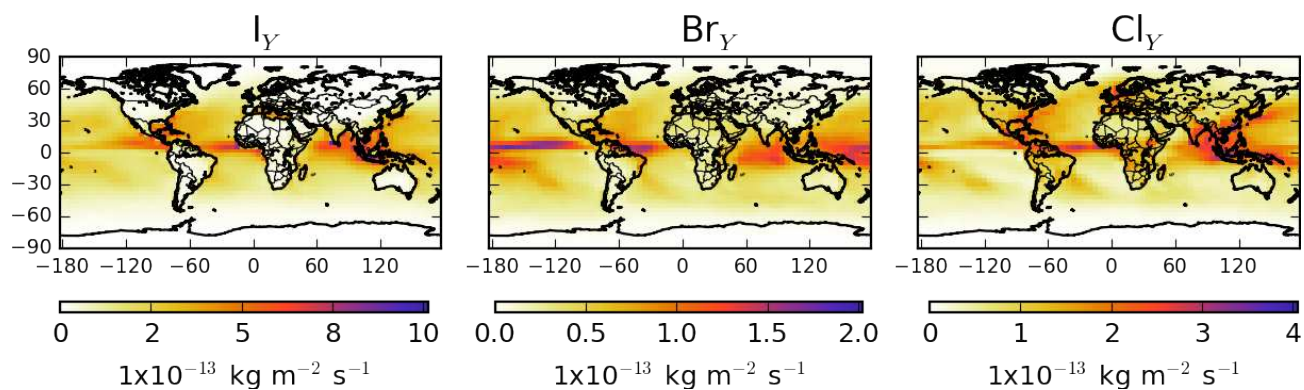


Figure 2. Annual global X_Y ($X=\text{Cl, Br, I}$) deposition (defined in Footnote 1). Values are given in terms of mass of halogen deposited ($\text{kg } X \text{ m}^{-2} \text{ s}^{-1}$, $X=\text{Cl, Br, I}$).

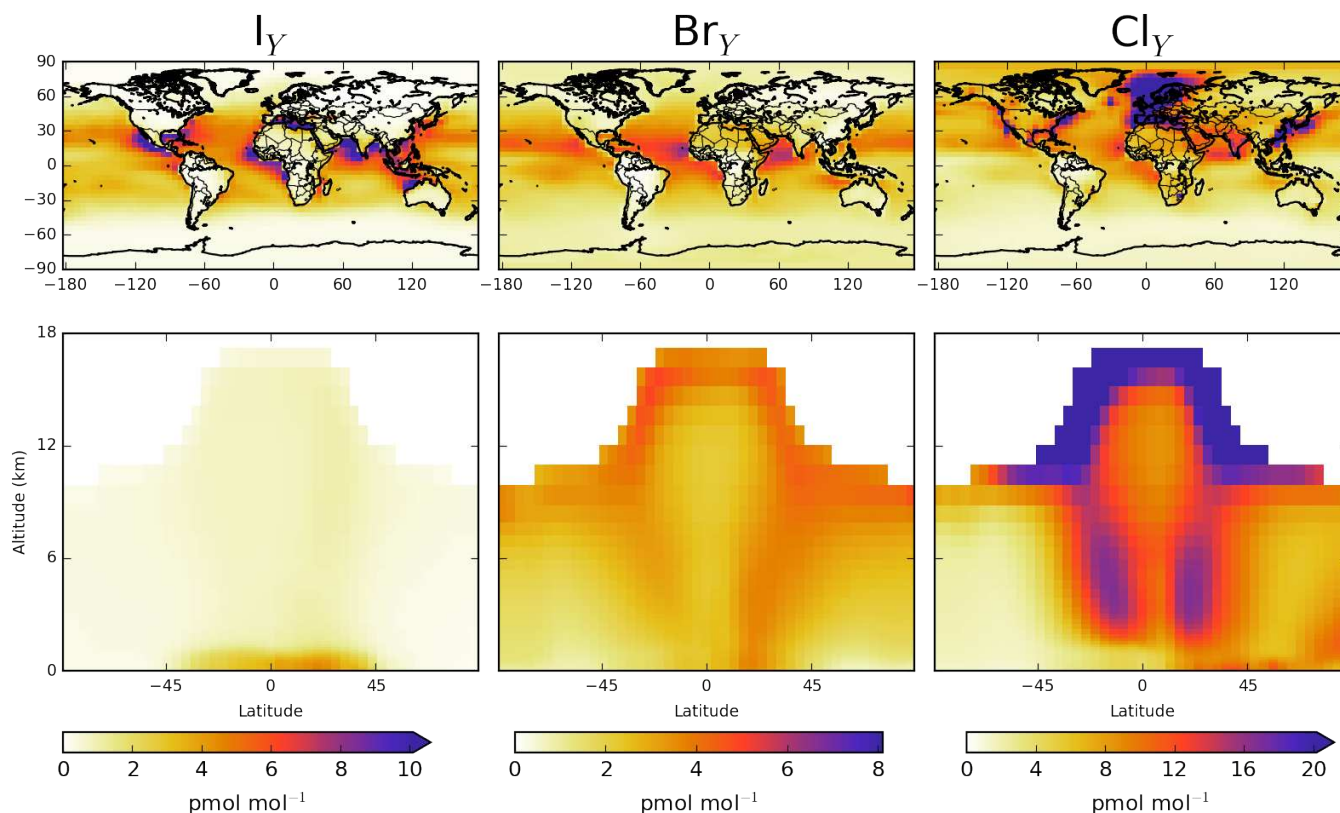


Figure 3. Tropospheric distribution of Cl_Y , Br_Y , and I_Y (defined in Footnote 1) concentrations. Upper plots show surface and lower plots show zonal values. Only boxes that are entirely tropospheric are included in this plot. The Cl_Y colourbar is capped at 20 pmol mol^{-1} , with a maximum plotted value of $118 \text{ pmol mol}^{-1}$ at the surface over the North Sea. The I_Y colorbar is capped at 10 pmol mol^{-1} , with a maximum plotted value of 17 pmol mol^{-1} at the surface over the Red Sea.

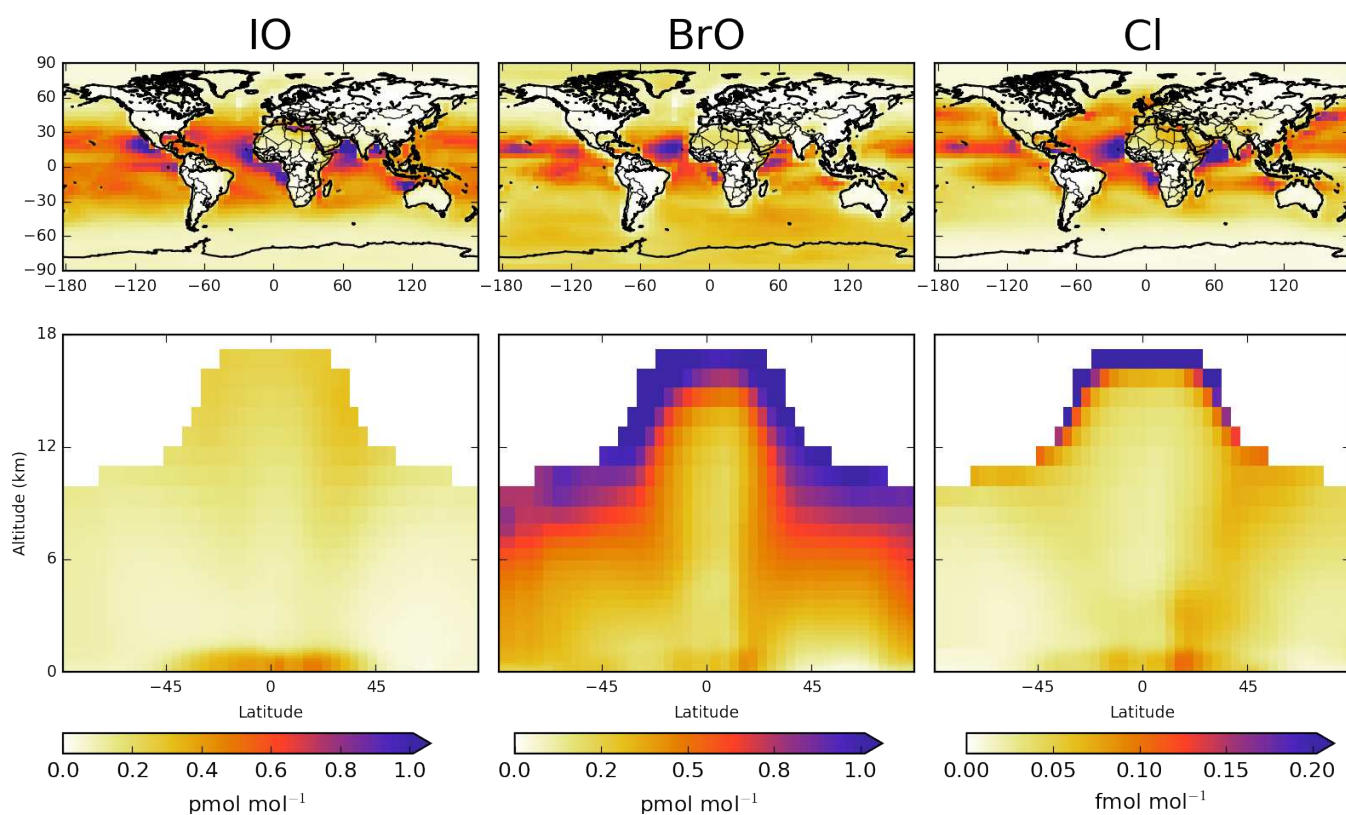


Figure 4. Tropospheric distribution of IO, BrO and Cl concentrations. Upper plots show surface and lower plots show zonal values. Only boxes that are entirely tropospheric are included in this plot.

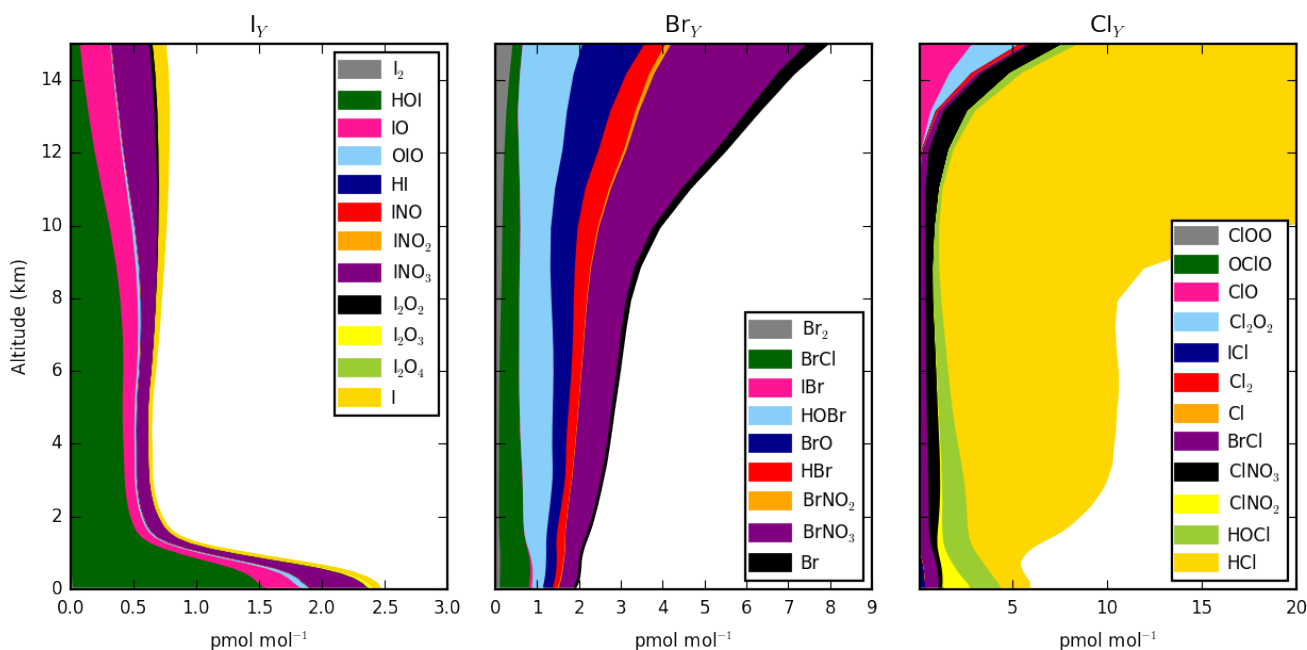


Figure 5. Modelled global average vertical X_y ($X=\text{Cl}, \text{Br}, \text{I}$) (defined in Footnote 1). Units are pmol mol^{-1} of X (where $X=\text{Cl}, \text{Br}, \text{I}$). For Cl_y the y-axis is capped at 20 pmol mol^{-1} to show speciation. A Cl_y maximum of $1062 \text{ pmol mol}^{-1}$ is found within the altitudes shown due to additional HCl contributions increasing with altitude.

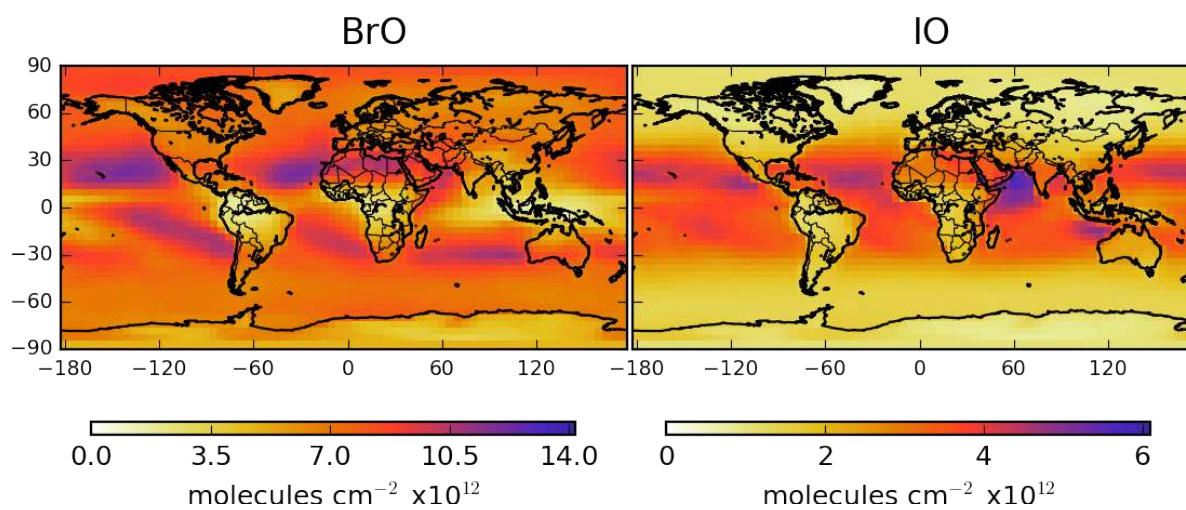


Figure 6. Annual mean integrated model tropospheric column for BrO and IO in molecules cm^{-2} .

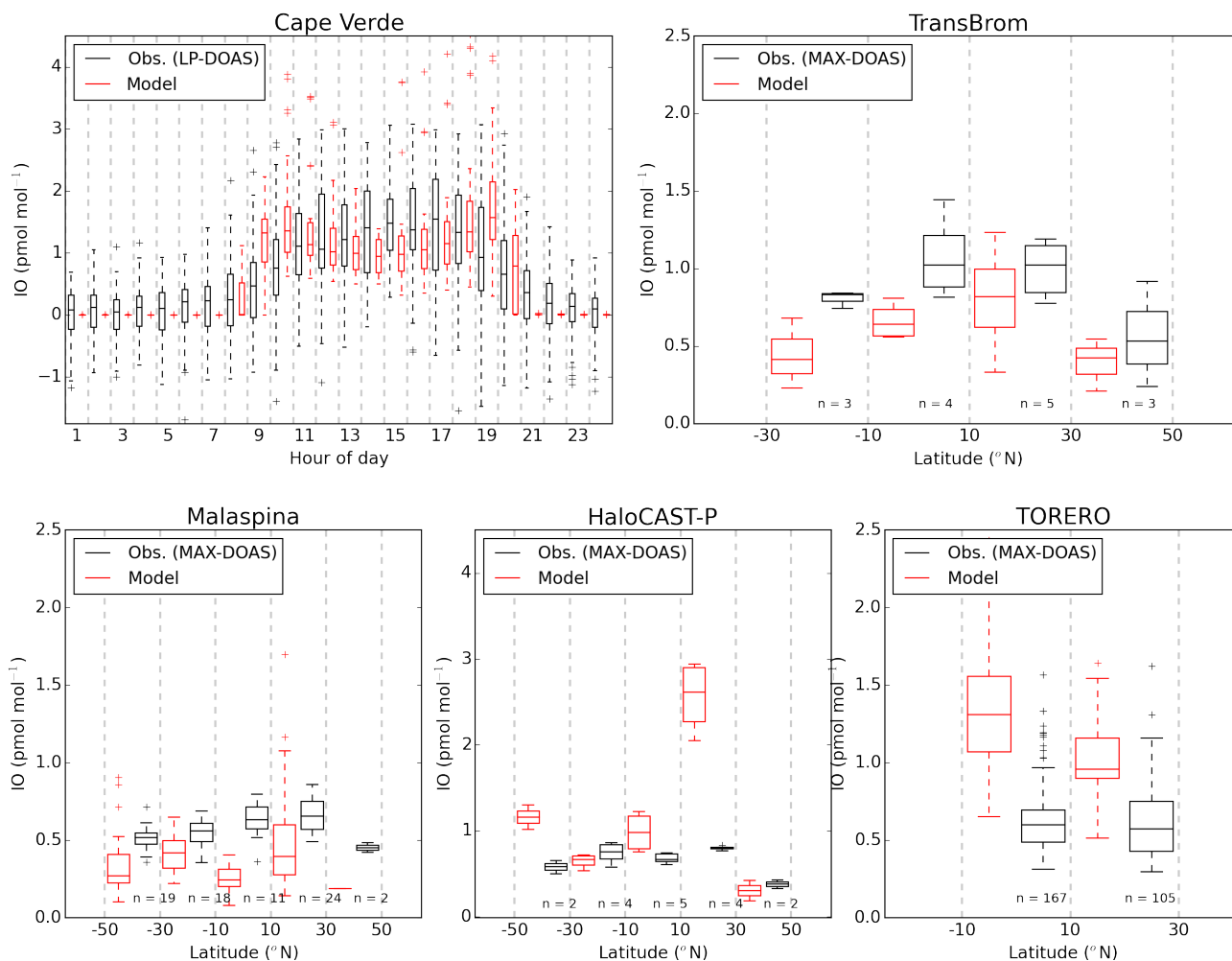


Figure 7. Iodine oxide (IO) surface observations (black) by campaign compared against the simulation with halogen chemistry (“Cl+Br+I”, red). Cape Verde measurements are shown against hour of day and others are shown as a function of latitude. Values are considered in 20° bins, with observations and modelled values at the same location and time (as described in section 2) shown side-by-side around the mid point of each bin. The extent of the bins is highlighted with grey dashed lines. Observations are from Cape Verde (Tropical Atlantic, Mahajan et al. 2010; Read et al. 2008), TransBrom (West Pacific, Großmann et al. 2013), the Malaspina circumnavigation (Prados-Roman et al., 2015b), HaloCAST-P (East Pacific, Mahajan et al. 2012), and TORERO ship (East Pacific, Volkamer et al. 2015). The number of data points within latitudinal bin are shown as “n”. The boxplot extents give the inter-quartile range, with the median shown within the box. The whiskers give the most extreme point within 1.5 times the inter-quartile range.

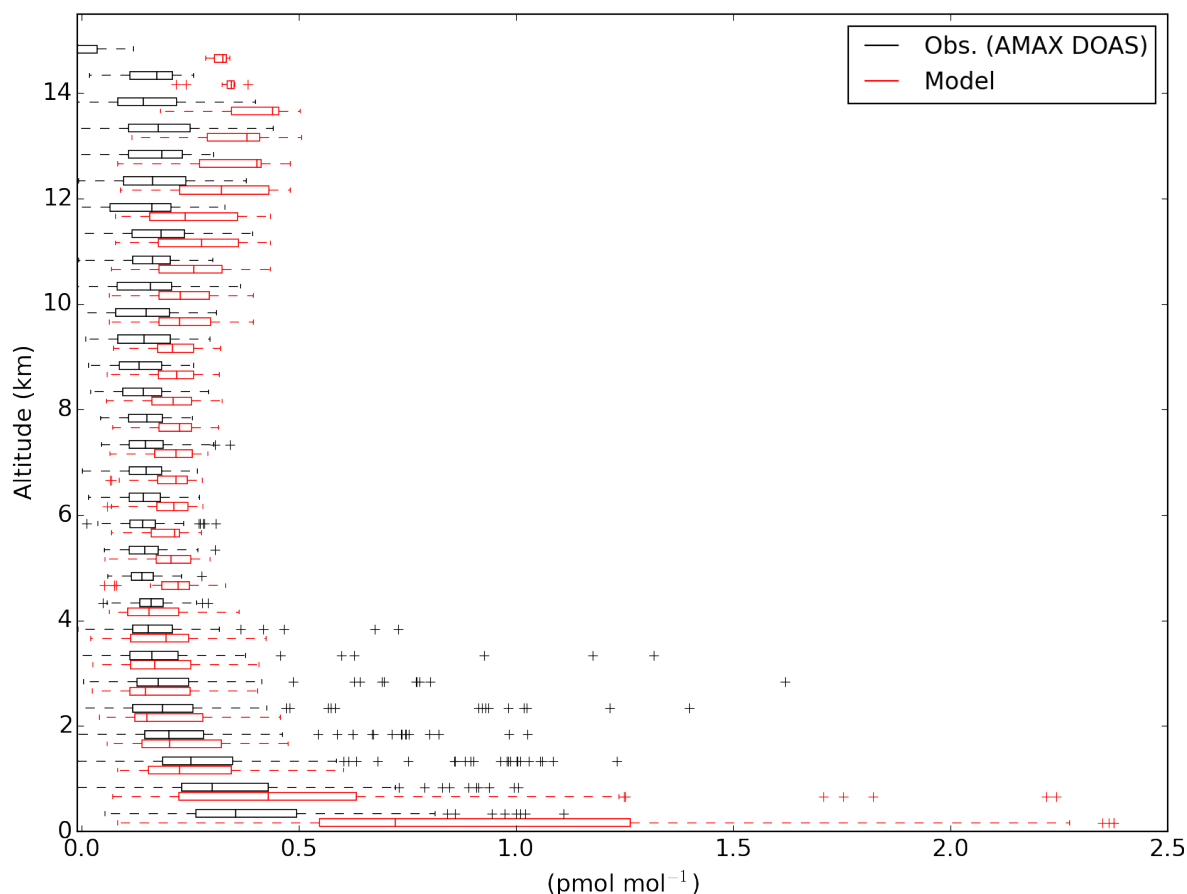


Figure 8. Vertical comparison of the model (“Cl+Br+I”) and measured iodine oxide (IO) during TORERO aircraft campaign (Volkamer et al., 2015; Wang et al., 2015). Model and observations are in red and black respectively. Values are considered in 0.5 km bins, with observations and modelled values at the same location and time (as described in section 2) shown side-by-side around the mid point 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). The boxplot extents give the inter-quartile range, with the median shown within the box. The whiskers give the most extreme point within 1.5 times the inter-quartile range.

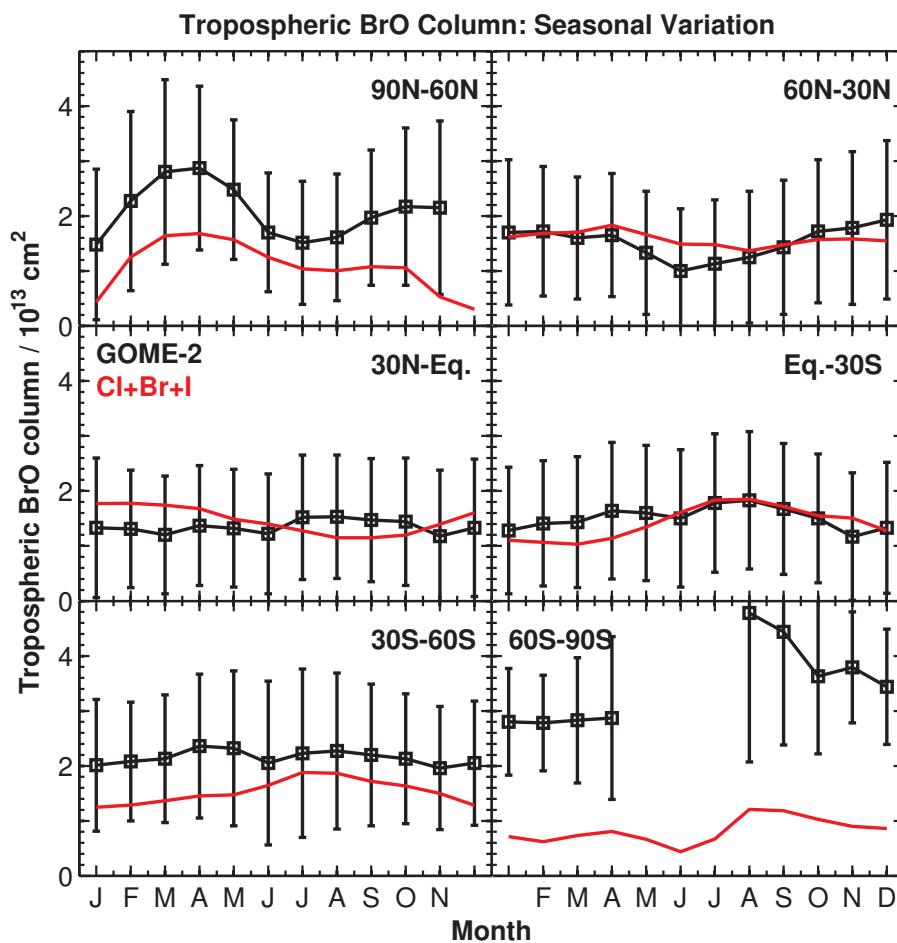


Figure 9. Seasonal variation of zonal mean tropospheric BrO columns in different latitudinal bands. 2007 observations from the GOME-2 satellite instrument (Theys et al., 2011) are compared to GEOS-Chem values at the GOME-2 local overpass time (9:00-11:00).

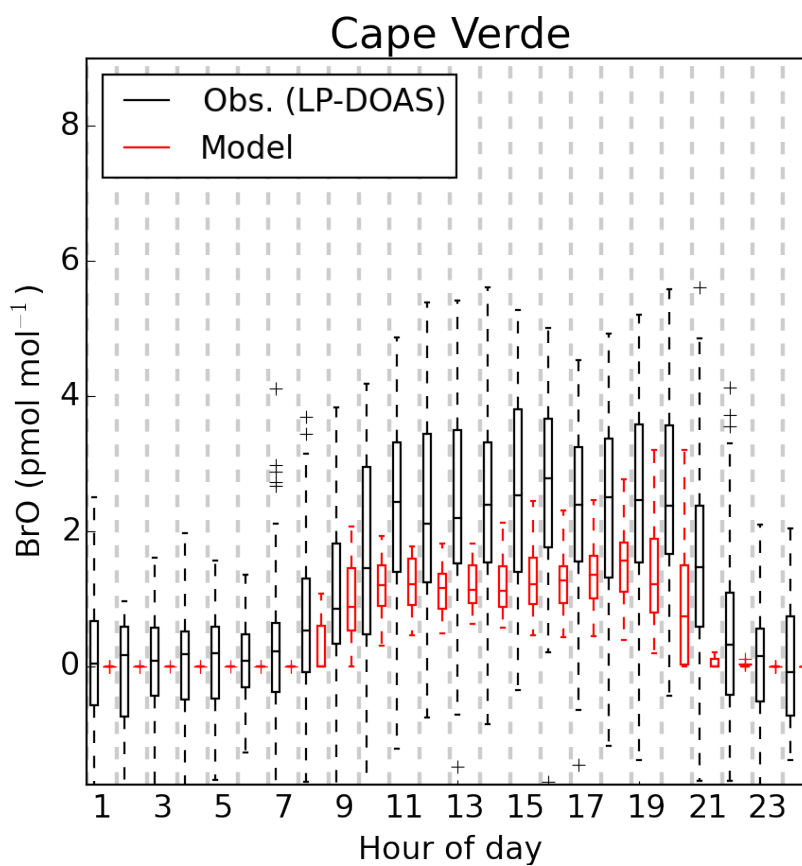


Figure 10. Bromine oxide (BrO) surface observations (black) at Cape Verde (Read et al., 2008; Mahajan et al., 2010) compared against the simulation with halogen chemistry (“Cl+Br+I”, red). Values are binned by hour of day.

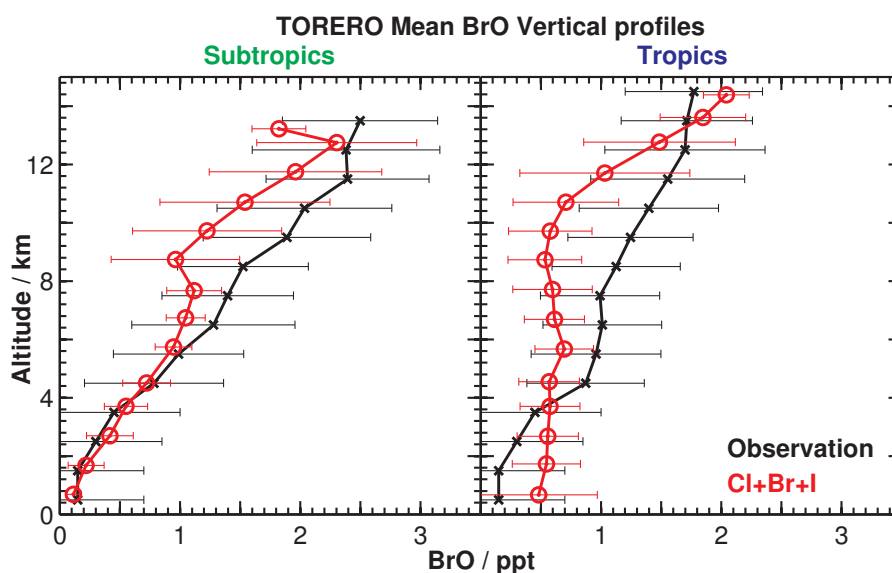


Figure 11. Vertical comparison of the model (“Cl+Br+I”) and measured iodine oxide (BrO) during TORERO aircraft campaign (Volkamer et al., 2015; Wang et al., 2015) in the Subtropics (left) and Tropics (right).. Model and observations are in red and black, respectively. Observations and modelled values at the same location and time (as described in section 2) are shown side-by-side around the mid point 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). Observations below 4 km were at or below the limit of detection, which is illustrated with a dashed green line ($\sim 0.5 \text{ pmol mol}^{-1}$).

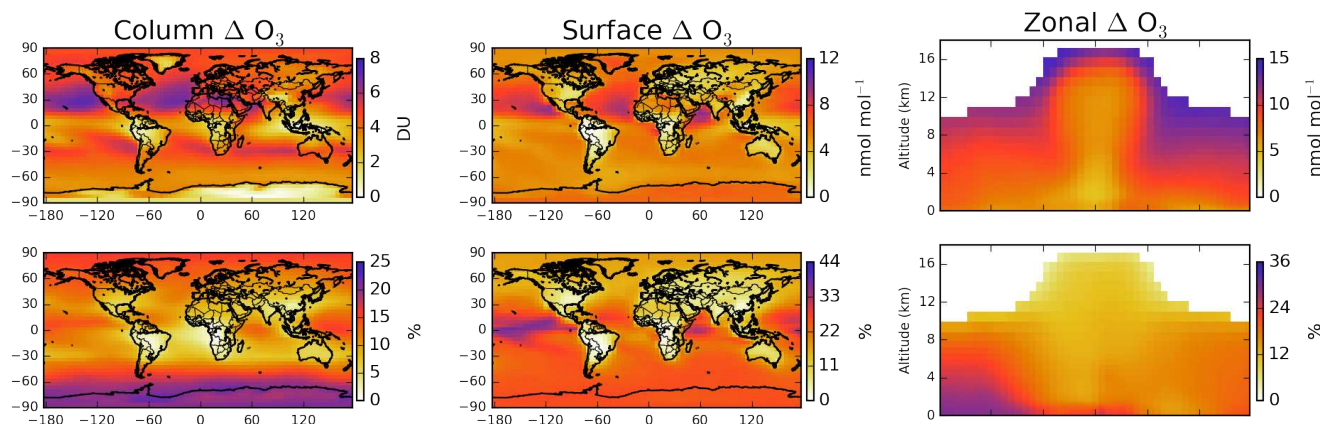


Figure 12. Change in tropospheric O₃ on inclusion of halogen chemistry. Column (left), surface (middle) and zonal (right) change are shown. Upper plots show absolute change and lower plots below give change in % terms ($(\text{“Cl+Br+I”}-\text{“NOHAL”})/\text{“NOHAL”}\times 100$).

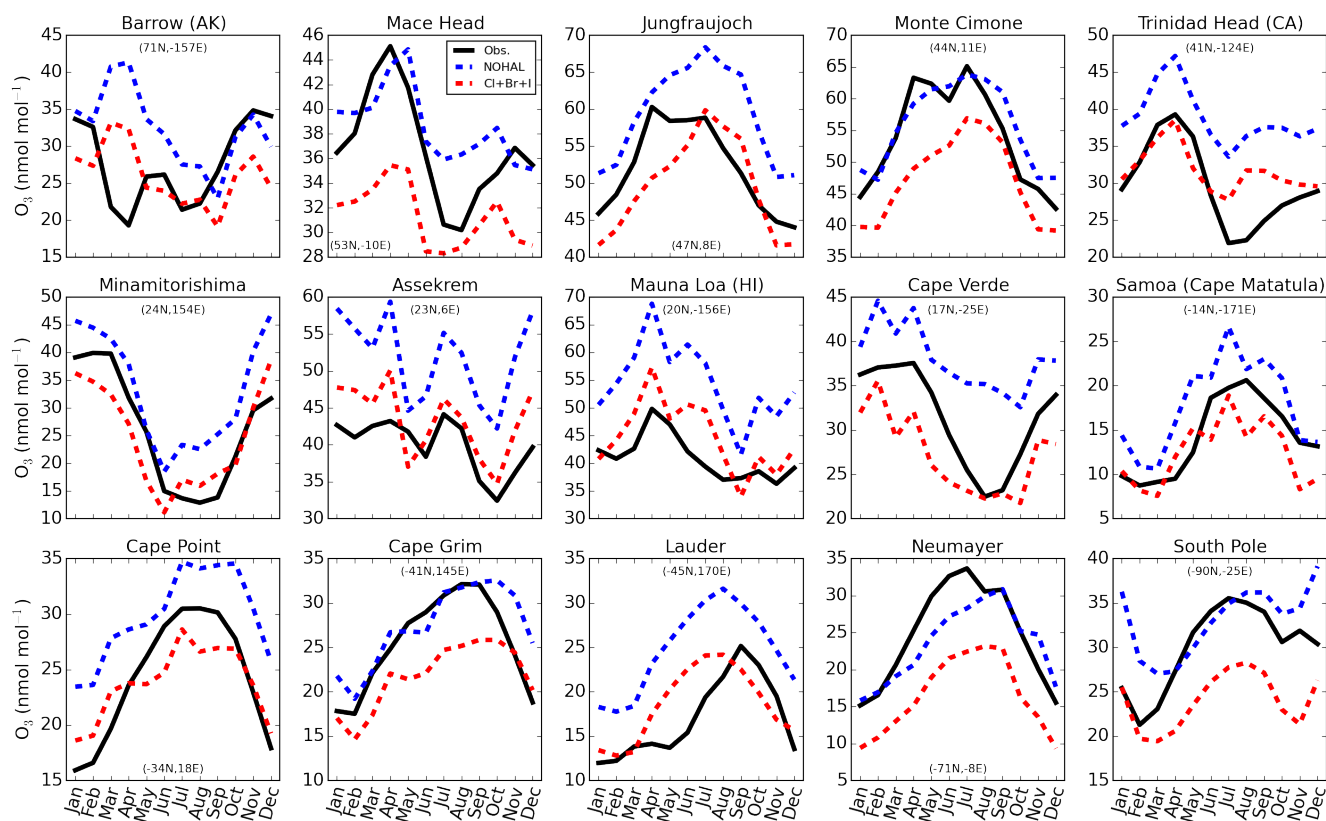


Figure 13. Seasonal cycle of near-surface O_3 at a range of Global Atmospheric Watch (GAW) sites. Observational data shown are 6 year monthly averages (2006-2012). Model data is for 2005. Data is from GAW compiled and processed as described in (Sofen et al., 2016). Blue and red lines represent simulations without halogens (“NOHAL”) with halogens (“Cl+Br+I”), respectively.

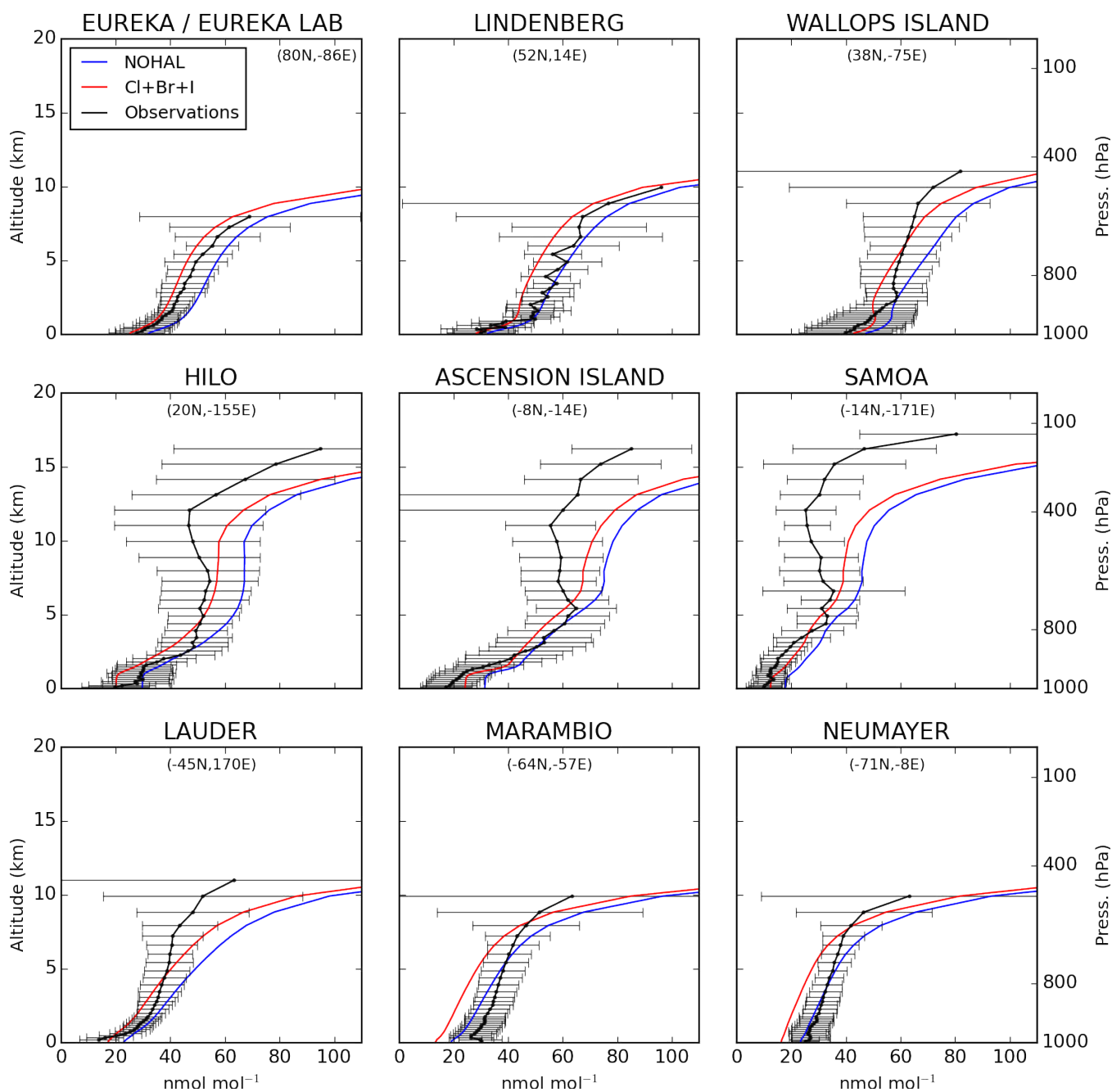


Figure 14. Comparison between annual modelled O_3 profiles and sonde data (2005). Profiles shown are the annual mean of available observations from World Ozone and Ultraviolet Radiation Data Centre (WOUDC, 2014) and model data for 2005 at given locations. Blue and red lines represent simulations without halogens (“NOHAL”) with halogens (“Cl+Br+I”), respectively. Observations (in black) show mean concentrations with upper and lower quartiles given by whiskers.

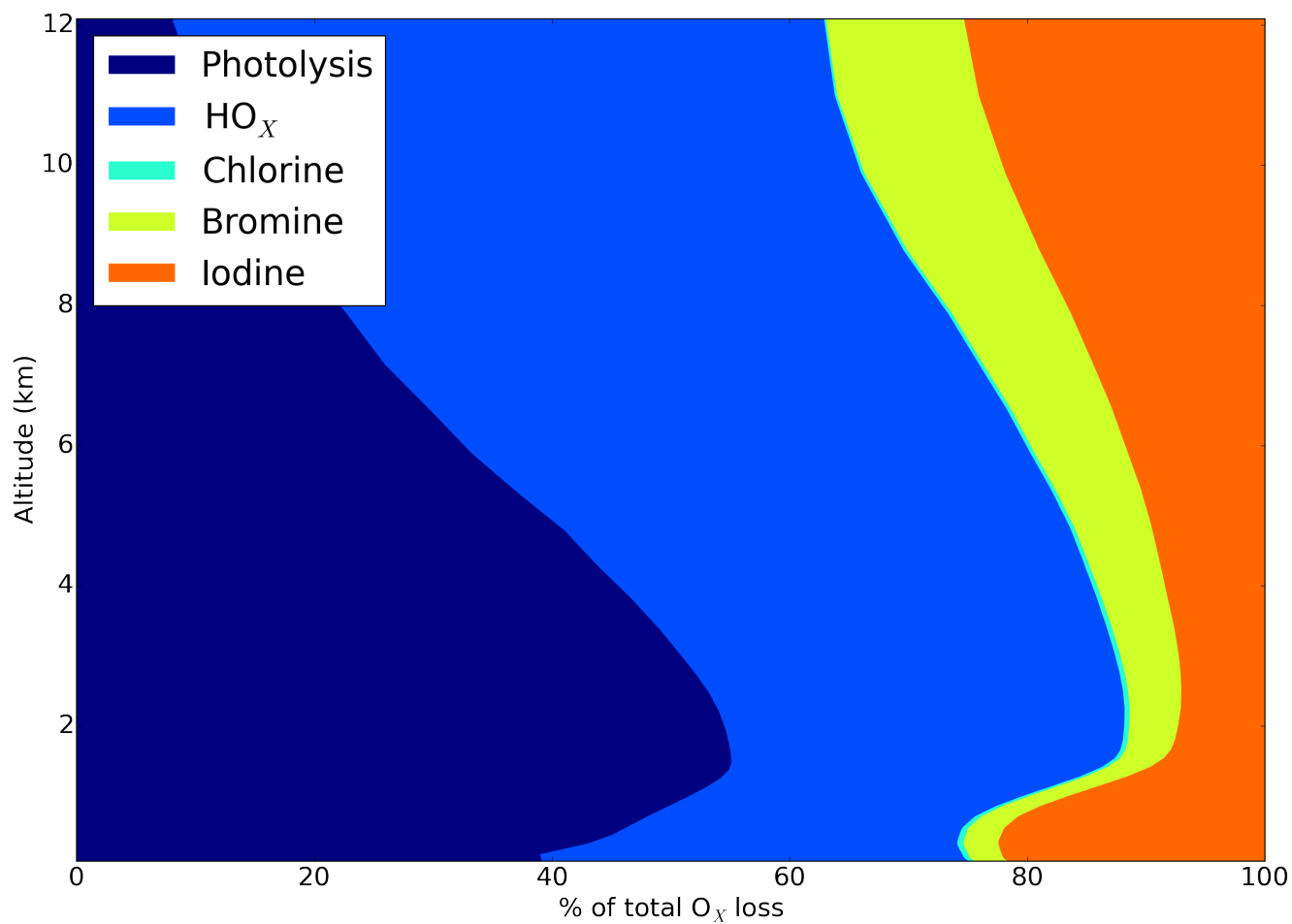


Figure 15. Global annual average tropospheric vertical odd oxygen loss (O_x) through different reaction routes (Photolysis, HO_x , IO_x , BrO_x , and ClO_x).

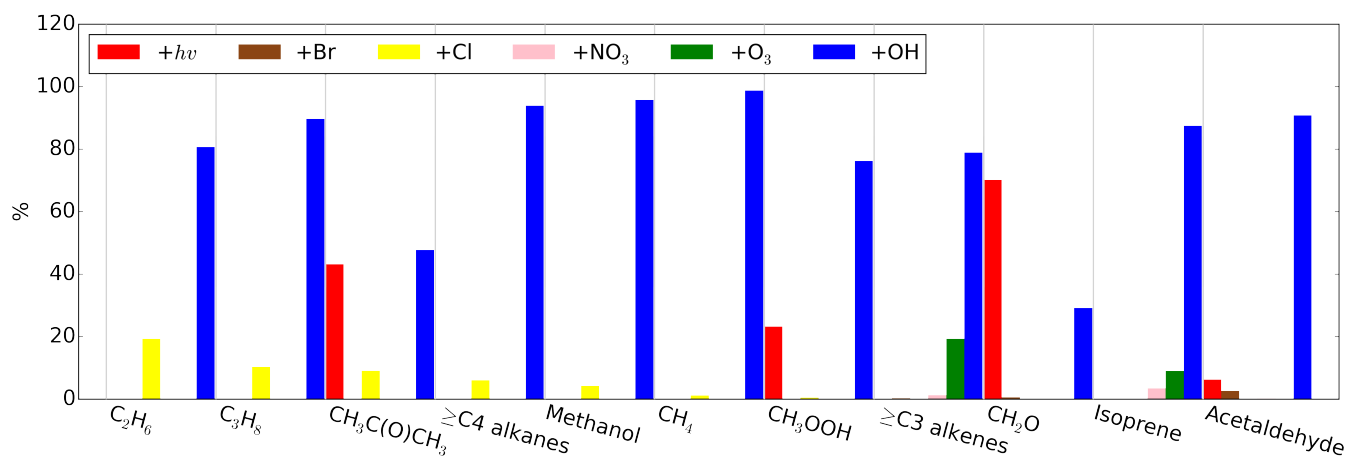


Figure 16. Global loss routes ($+h\nu$, $+Br$, $+NO_3$, $+Cl$, $+OH$) of organic compounds shown as % of total tropospheric losses.

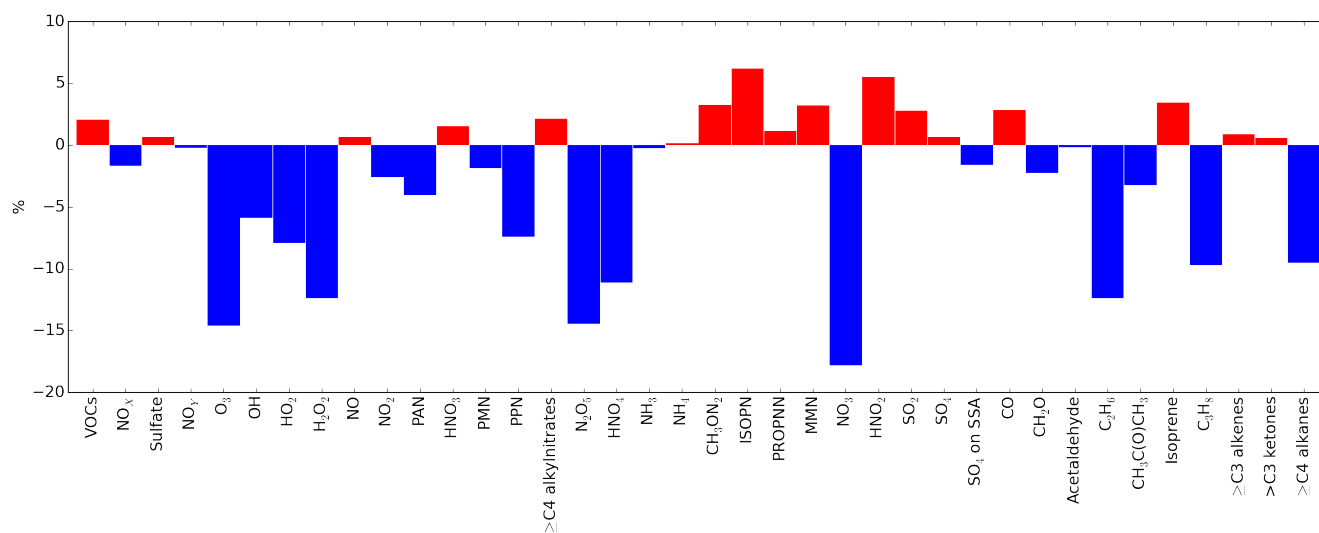


Figure 17. Changes in tropospheric burden of species and families on inclusion of halogens (“Cl+Br+I”) compared to no halogens (“NO-HAL”). Burdens are considered in elemental terms (e.g Tg S/N/C) and species masses for OH, HO₂, H₂O₂ and O₃. The family denoted by “VOCs” in this plot is defined as the sum of carbon masses of CO, formaldehyde, acetaldehyde, ethane, acetone, isoprene, propane, ≥C4 alkanes, ≥C3 alkenes, and ≥3C ketones. Abbreviations for tracers are expanded in Footnote 3

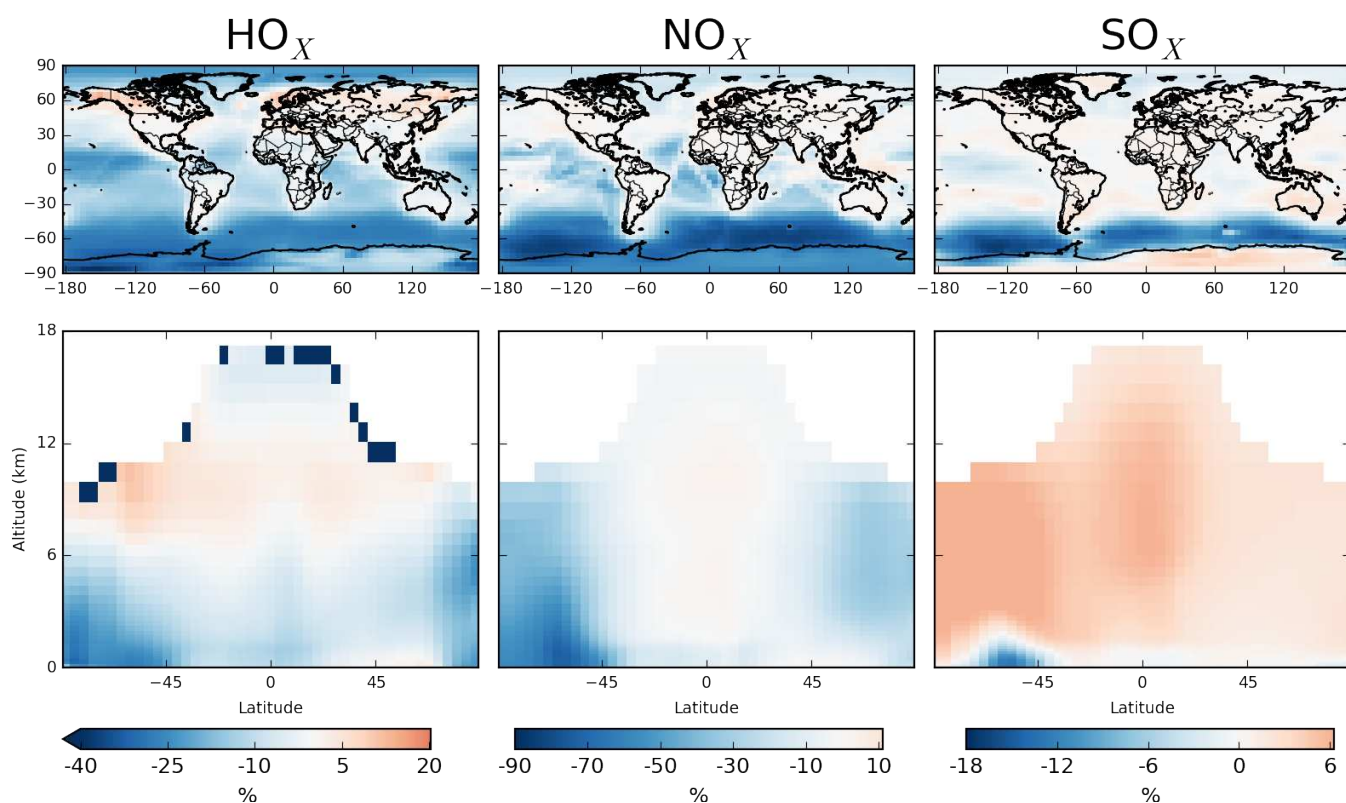


Figure 18. Global annual average surface and zonal change (%) in HO_x , NO_x and SO_x families (as defined in Footnote 4) on inclusion of halogens

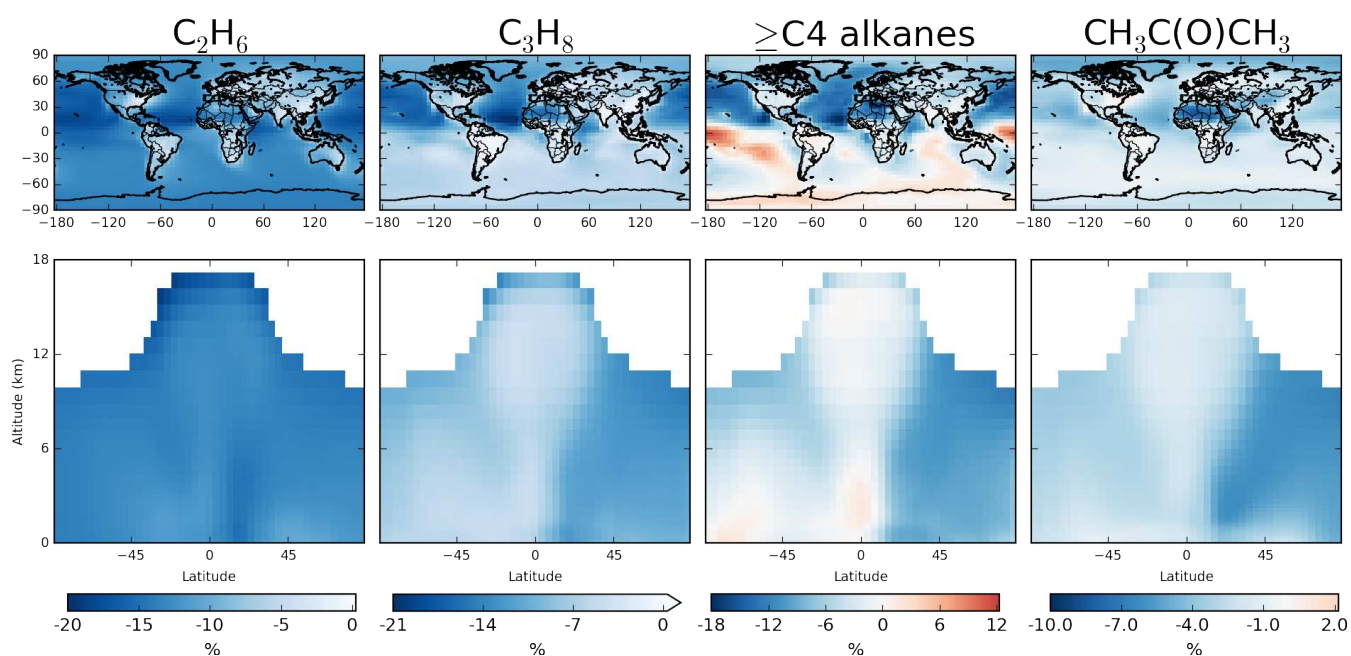


Figure 19. Global annual average surface and zonal change (%) in ethane (C_2H_6), propane (C_3H_8), $\geq C_4$ alkanes, and acetone ($CH_3C(O)CH_3$) on inclusion of halogens. For species where all average changes are negative a continuous colourbar is used (C_3H_8 and C_2H_6) and for species where both negative and positive changes are present a divergent colourbar is used ($\geq C_4$ alkanes and $CH_3C(O)CH_3$)



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., 2016). The full reaction scheme is given in the Appendix (Sections 6-9). The rate constant is calculated using a standard Arrhenius expression $Ae^{-(E_a/RT)}$

Rxn ID	Reaction	A $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	E_a/R K	Citation
M29	$\text{IO} + \text{ClO} \rightarrow \text{I} + \text{OCIO}$	2.59×10^{-12}	280	Atkinson et al. (2007)
M30	$\text{IO} + \text{ClO} \rightarrow \text{I} + \text{Cl} + \text{O}_2$	1.18×10^{-12}	280	Atkinson et al. (2007)
M31	$\text{IO} + \text{ClO} \rightarrow \text{ICl} + \text{O}_2$	9.40×10^{-13}	280	Atkinson et al. (2007)
M32	$\text{Cl} + \text{HCOOH} \rightarrow \text{HCl} + \text{CO}_2 + \text{H}_2\text{O}$	2.00×10^{-13}	-	Sander et al. (2011)
M33	$\text{Cl} + \text{CH}_3\text{O}_2 \rightarrow \text{ClO} + \text{CH}_2\text{O} + \text{HO}_2(\bullet)$	1.60×10^{-10}	-	Sander et al. (2011)
M34	$\text{Cl} + \text{CH}_3\text{OOH} \rightarrow \text{HCl} + \text{CH}_3\text{O}_2$	5.70×10^{-11}	-	Sander et al. (2011)
M35	$\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{HCl} + \text{C}_2\text{H}_5\text{O}_2$	7.20×10^{-11}	-70	Sander et al. (2011)
M36	$\text{Cl} + \text{C}_2\text{H}_5\text{O}_2 \rightarrow \text{ClO} + \text{HO}_2 + \text{ALD2}(\star)$	7.40×10^{-11}	-	Sander et al. (2011)
M37	$\text{Cl} + \text{EOH} \rightarrow \text{HCl} + \text{ALD2}(\triangleleft)$	9.60×10^{-11}	-	Sander et al. (2011)
M38	$\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{OH} \rightarrow \text{HCl} + \text{CH}_3\text{O}_2 + \text{CO}_2$	2.80×10^{-14}	-	Sander et al. (2011)
M39	$\text{Cl} + \text{C}_3\text{H}_8 \rightarrow \text{HCl} + \text{A3O2}$	7.85×10^{-11}	-80	Sander et al. (2011)
M40	$\text{Cl} + \text{C}_3\text{H}_8 \rightarrow \text{HCl} + \text{B3O2}$	6.54×10^{-11}	-	Sander et al. (2011)
M41	$\text{Cl} + \text{ACET} \rightarrow \text{HCl} + \text{ATO2}$	7.70×10^{-11}	-1000	Sander et al. (2011)
M42	$\text{Cl} + \text{ISOP} \rightarrow \text{HCl} + \text{RIO2}$	7.70×10^{-11}	500	Sander et al. (2011)
M43	$\text{Cl} + \text{MOH} \rightarrow \text{HCl} + \text{CH}_2\text{O} + \text{HO}_2$	5.50×10^{-11}	-	Sander et al. (2011)
M61	$\text{Cl} + \text{ALK4} \rightarrow \text{HCl} + \text{R4O2}$	2.05×10^{-10}	-	Atkinson et al. (2006)
M62	$\text{Br} + \text{PRPE} \rightarrow \text{HCl} + \text{PO2}$	3.60×10^{-12}	-	Atkinson et al. (2006)
M63	$\text{Cl} + \text{PRPE} \xrightarrow{M} \text{HCl} + \text{PO2} + \text{M}$	$2.80 \times 10^{-10}(\text{\$})$	-	Atkinson et al. (2006)
H1	$\text{N}_2\text{O}_5 \xrightarrow{\gamma} \text{HNO}_3 + \text{ClNO}_2(\ominus)$	-	-	(see table footnote)
H2	$\text{HOI} \xrightarrow{\gamma} 0.85\text{ICl} + 0.15\text{IBr}^*$	-	-	(see table footnote)
H3	$\text{INO}_2 \xrightarrow{\gamma} 0.85\text{ICl} + 0.15\text{IBr}^*$	-	-	(see table footnote)
H4	$\text{INO}_3 \xrightarrow{\gamma} 0.85\text{ICl} + 0.15\text{IBr}^*$	-	-	(see table footnote)
P1	$\text{ICl} \xrightarrow{h\nu} \text{I} + \text{Cl}$	-	-	Sander et al. (2011)
P2	$\text{IBr} \xrightarrow{h\nu} \text{I} + \text{Br}$	-	-	Sander et al. (2011)

Table footnote: (\bullet) Reaction from JPL, only considering the major channel (Dale and Poulet, 1996) and product of CH_3O reacts to form $\text{CH}_2\text{O} + \text{HO}_2$ ($\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$). (\star) Only first channel from JPL considered. the 2nd channel forms a criegee ($\text{HCl} + \text{C}_2\text{H}_4\text{O}_2$) and therefore cannot be represented by reduced GEOS-Chem chemistry scheme. (\triangleleft) Reaction defined by JPL and interpreted as proceeding via hydrogen abstraction, therefore the acetaldehyde product is assumed. ($\text{\$}$) $K(\infty)$ rate given in table, $K(0)$ rate = 4.00×10^{-28} with $F_c=0.6$ as shown in Table 7. (\ominus) Reaction only proceeds on sea-salt aerosol. (\ast) Reactions which were included in previous work (Sherwen et al. (2016)), but di-halogen products have been updated split between ICl and IBr (See Section 2) and only proceed on acidic sea-salt aerosol following McFiggans et al. (2000). Acidity of aerosol is calculated as described in Alexander (2005). Abbreviations for tracers are expanded in footnote 3.



Table 2. Global sources of reactive tropospheric inorganic halogens. Sources with fixed concentration in the model for Cl_Y (CH_3Cl , CH_3Cl_2 , CHCl_3) and Br_Y (CHBr_3) are shown in terms of chemical release (e.g. $+\text{Cl}$, $+\text{OH}$, $+h\nu$) and are in bold. Inclusion of chlorine and bromine organic species has been reported before in GEOS-Chem (Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016). X_2 (I_2) and HOX (HOI) are the inorganic ocean source from (Carpenter et al., 2013), XNO_2 is the source from the uptake of N_2O_5 on sea-salt (ClNO_2).

Sources	I_Y (Tg I yr^{-1})	Br_Y (Tg Br yr^{-1})	Cl_Y (Tg Cl yr^{-1})
CH_3X	0.26	0.06	2.19
CH_2X_2	0.33	0.09	0.59
CHX_3	-	0.41	0.26
HOX	2.02	-	-
X_2	0.14	-	-
IX	-	0.31(*)	0.78(*)
XNO_2	-	-	0.66
stratosphere	0.00	0.06	0.43
total source(*)	2.75	0.92	4.90

(*) Note: Acid catalysed sea-salt IX ($\text{X}=\text{Cl}$, Br) flux only stated for Cl_Y and Br_Y as it does not represent a net I_Y source.

Table 3. Comparison between modelled and observed ClNO_2 . Concentrations are shown as the maximum and average of the daily maximum value for the observational and equivalent model time period. Sites marked as (**) are considered continental sites. The model value are taken for the nearest time-step and location within the analysis year (2005).

Location	Lat.	Lon.	Obs.		"Cl+Br+I"		Reference
			Max	Mean	Max	Mean	
<i>Coastal</i>							
Pasadena, CA (2010)	34.2	-118.2	3.46	1.48	0.44	0.20	Mielke et al. (2013)
Southern China (2012)	22.2	114.3	2.00	0.31	0.61	0.18	Tham et al. (2014)
Los Angeles, California (2010)	34.1	-118.2	1.83	0.50	0.44	0.20	Riedel et al. (2012)
Houston, Texas (2006)	30.4	-95.4	1.15	0.80	0.19	0.04	Osthoff et al. (2008)
London, UK (2012)	51.5	-0.2	0.73	0.23	0.51	0.17	Bannan et al. (2015)
Texas (2013)	30.4	-95.4	0.14	0.08	0.19	0.04	Faxon et al. (2015)
<i>Continental</i>							
Hessen, Germany (2011)	50.2	8.5	0.85	0.20	0.16	0.02	Phillips et al. (2012)
Boulder, Colorado (2009)	40.0	-105.3	0.44	0.14	0.00	0.00	Thornton et al. (2010); Riedel et al. (2013)
Calgary, CAN (2010)	51.1	-114.1	0.24	0.22	0.02	0.01	Mielke et al. (2011)



Table 4. Comparison between global tropospheric O_X 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 O_3 loss equally between the two routes. Values are rounded to the nearest integer value.

	"Cl+Br+I"	"NOHAL"	ACCENT
O_3 burden (Tg)	355	416	340 ± 40
O_X chemical sources (Tg yr ⁻¹)			
NO + HO ₂	3526	3607	-
NO + CH ₃ O ₂	1327	1316	-
NO + RO ₂	524	508	-
Total chemical O_X sources (PO _X)	5376	5431	5110 ± 606
O_X chemical sinks (Tg yr ⁻¹)			
$O_3 + H_2O \xrightarrow{h\nu} 2OH + O_2$	2102	2489	-
$O_3 + HO_2 \rightarrow OH + O_2$	1136	1432	-
$O_3 + OH \rightarrow HO_2 + O_2$	611	737	-
HOBr $\xrightarrow{h\nu}$ Br + OH	214	-	-
HOBr + HCl → BrCl	28	-	-
HOBr + HBr → Br ₂ + H ₂ O (aq. aerosol)	13	-	-
BrO + BrO → 2Br + O ₂	8	-	-
BrO + BrO → Br ₂ + O ₂	3	-	-
BrO + OH → Br + HO ₂	9	-	-
IO + BrO → Br + I + O ₂	9	-	-
ClO + BrO → Br + ClO/OCIO	2	-	-
Other bromine O_X sinks	0	-	-
Total bromine O_X sinks	284	-	-
HOI $\xrightarrow{h\nu}$ I + OH	457	-	-
OIO $\xrightarrow{h\nu}$ I + O ₂	125	-	-
IO + BrO → Br + I + O ₂	9	-	-
IO + ClO → I + Cl + O ₂ /ICl + O ₂	0	-	-
Other iodine O_X sinks	2	-	-
Total iodine O_X sinks	593	-	-
HOCl $\xrightarrow{h\nu}$ Cl + OH	15	-	-
CH ₃ O ₂ + ClO → ClOO	4	-	-
ClO + BrO → Br + ClO/OCIO	2	-	-
ClNO ₃ + HBr → BrCl	1	-	-
IO + ClO → I + Cl + O ₂ /ICl + O ₂	0	-	-
Other chlorine O_X sinks	1	-	-
Total chlorine O_X sinks	23	-	-
Other O_X sinks	184	172	-
Total chem. O_X sinks (LO _X)	4933	4829	4668 ± 727
O_3 PO _X -LO _X (Tg yr ⁻¹)	443	602	618 ± 251
O_3 Dry deposition (Tg yr ⁻¹)	832	980	1003 ± 200
O_3 Lifetime (days)	22	26	22 ± 2
O_3 STE (PO _X -LO _X -Dry dep.) (Tg yr ⁻¹)	389	378	552 ± 168



Table 5. Photolysis reactions of halogens included in scheme. Photolysis is described in Eastham et al. (2014) (ClNO₂, ClNO₃, and ClOO), Sherwen et al. (2016) (I₂, HOI, IO, OIO, INO, INO₂, INO₃, I₂O₂, I₂O₃, I₂O₄, CH₃I, CH₂I₂, CH₂ICl, CH₂IBr), and Schmidt et al. (2016) (BrCl, Cl₂, ClO, HOCl, ClNO₂, ClNO₃, ClOO, Cl₂O₂, CH₃Cl, CH₃Cl₂, and CHCl₃). As stated in Section 2, we have used the I₂O₂ cross-section for I₂O₄

ID	Reaction	Cross-section reference
J1	I ₂ $\xrightarrow{h\nu}$ 2I	Sander et al. (2011)
J2	HOI $\xrightarrow{h\nu}$ I + OH	Sander et al. (2011)
J3	IO (+O ₂) $\xrightarrow{h\nu}$ I (+ O ₃)	Sander et al. (2011)
J4	OIO $\xrightarrow{h\nu}$ I + O ₂	Sander et al. (2011)
J5	INO $\xrightarrow{h\nu}$ I + NO	Sander et al. (2011)
J6	INO ₂ $\xrightarrow{h\nu}$ I + NO ₂	Sander et al. (2011)
J7	INO ₃ $\xrightarrow{h\nu}$ I + NO ₃	Sander et al. (2011)
J8	I ₂ O ₂ $\xrightarrow{h\nu}$ I + OIO	Gómez Martín et al. (2005), Spietz et al. (2005)
J9	CH ₃ I $\xrightarrow{h\nu}$ I	Sander et al. (2011)
J10	CH ₂ I ₂ $\xrightarrow{h\nu}$ 2I	Sander et al. (2011)
J11	CH ₂ ICl $\xrightarrow{h\nu}$ I + Cl	Sander et al. (2011)
J12	CH ₂ IBr $\xrightarrow{h\nu}$ I + Br	Sander et al. (2011)
J13	I ₂ O ₄ $\xrightarrow{h\nu}$ 2OIO	see caption
J14	I ₂ O ₃ $\xrightarrow{h\nu}$ OIO + IO	Gómez Martín et al. (2005), Spietz et al. (2005)
J15	CHBr ₃ $\xrightarrow{h\nu}$ 3Br	Sander et al. (2011)
J16	Br ₂ $\xrightarrow{h\nu}$ 2Br	Sander et al. (2011)
J17	BrO (+O ₂) $\xrightarrow{h\nu}$ Br (+O ₃)	Sander et al. (2011)
J18	HOBr $\xrightarrow{h\nu}$ Br + OH	Sander et al. (2011)
J19	BrNO ₂ $\xrightarrow{h\nu}$ Br + NO ₂	Sander et al. (2011)
J20	BrNO ₃ $\xrightarrow{h\nu}$ Br + NO ₃	Sander et al. (2011)
J21	BrNO ₃ $\xrightarrow{h\nu}$ BrO + NO ₂	Sander et al. (2011)
J22	CH ₂ Br ₂ $\xrightarrow{h\nu}$ 2Br	Sander et al. (2011)
J23	BrCl $\xrightarrow{h\nu}$ Br + Cl	Sander et al. (2011)
J24	Cl ₂ $\xrightarrow{h\nu}$ 2Cl	Sander et al. (2011)
J25	ClO (+O ₂) $\xrightarrow{h\nu}$ Cl (+O ₃)	Sander et al. (2011)
J26	OCIO (+O ₂) $\xrightarrow{h\nu}$ ClO (+O ₃)	Sander et al. (2011)
J27	Cl ₂ O ₂ $\xrightarrow{h\nu}$ Cl + ClOO	Sander et al. (2011)
J28	ClNO ₂ $\xrightarrow{h\nu}$ Cl + NO ₂	Sander et al. (2011)
J29	ClNO ₃ $\xrightarrow{h\nu}$ Cl + NO ₃	Sander et al. (2011)
J30	ClNO ₃ $\xrightarrow{h\nu}$ ClO + NO ₂	Sander et al. (2011)
J31	HOCl $\xrightarrow{h\nu}$ Cl + OH	Sander et al. (2011)
J32	ClOO $\xrightarrow{h\nu}$ Cl	Sander et al. (2011)
J33	CH ₃ Cl $\xrightarrow{h\nu}$ Cl + CH ₃ O ₂ ,	Sander et al. (2011)
J34	CH ₃ Cl ₂ $\xrightarrow{h\nu}$ 2Cl	Sander et al. (2011)



Table 6. Bimolecular halogen reactions included in scheme. This includes reactions from previous updates to descriptions of halogen chemistry in GEOS-Chem (Parrella et al. (2012); Eastham et al. (2014); Schmidt et al. (2016); Sherwen et al. (2016)), and those described in Section 2. These are given in the Arrhenius form with the rate equal to $A \cdot \exp\left(\frac{-E_a}{RT}\right)$. Unknown values are represented by a dash and these set to zero 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 footnote3

Rxn ID	Reaction	A cm ³ molecules ⁻¹ s ⁻¹	-E _a /R K	Citation
M1	I + O ₃ → IO + O ₂	2.10x10 ⁻¹¹	-830	Atkinson et al. (2007)
M2	I + HO ₂ → HI + O ₂	1.50x10 ⁻¹¹	-1090	Sander et al. (2011)
M3	I ₂ + OH → HOI + I	2.10x10 ⁻¹⁰	-	Atkinson et al. (2007)
M4	HI + OH → I + H ₂ O	1.60x10 ⁻¹¹	440	Atkinson et al. (2007)
M5	HOI + OH → IO + H ₂ O	5.00x10 ⁻¹²	-	Riffault et al. (2005)
M6	IO + HO ₂ → HOI + O ₂	1.40x10 ⁻¹¹	540	Atkinson et al. (2007)
M7	IO + NO → I + NO ₂	7.15x10 ⁻¹²	300	Atkinson et al. (2007)
M8	HO + CH ₃ I → H ₂ O + I	4.30x10 ⁻¹²	-1120	Atkinson et al. (2008)
M9	INO + INO → I ₂ + 2NO	8.40x10 ⁻¹¹	-2620	Atkinson et al. (2007)
M10	INO ₂ + INO ₂ → I ₂ + 2NO ₂	4.70x10 ⁻¹²	-1670	Atkinson et al. (2007)
M11	I ₂ + NO ₃ → I + INO ₃	1.50x10 ⁻¹²	-	Atkinson et al. (2007)
M12	INO ₃ + I → I ₂ + NO ₃	9.10x10 ⁻¹¹	-146	Kaltsayannis and Plane (2008)
M13	I + BrO → IO + Br	1.20x10 ⁻¹¹	-	Sander et al. (2011)
M14	IO + Br → I + BrO	2.70x10 ⁻¹¹	-	Bedjanian et al. (1997)
M15	IO + BrO → Br + I + O ₂	3.00x10 ⁻¹²	510	Atkinson et al. (2007)
M16	IO + BrO → Br + OIO	1.20x10 ⁻¹¹	510	Atkinson et al. (2007)
M17	OIO + OIO → I ₂ O ₂	1.50x10 ⁻¹⁰	-	Gómez Martín et al. (2007)
M18	OIO + NO → NO ₂ + IO	1.10x10 ⁻¹²	542	Atkinson et al. (2007)
M19	IO + IO → I + OIO	2.16x10 ⁻¹¹	180	Atkinson et al. (2007)
M20	IO + IO → I ₂ O ₂	3.24x10 ⁻¹¹	180	Atkinson et al. (2007)
M21	IO + OIO \xrightarrow{M} I ₂ O ₃	1.50x10 ⁻¹⁰	-	Gómez Martín et al. (2007)
M22	I ₂ O ₂ \xrightarrow{M} IO + IO	1.00x10 ¹²	-9770	Ordóñez et al. (2012)
M23	I ₂ O ₂ \xrightarrow{M} OIO + I	2.50x10 ¹⁴	-9770	Ordóñez et al. (2012)
M24	I ₂ O ₄ \xrightarrow{M} 2OIO	3.80x10 ⁻²	-	Kaltsayannis and Plane (2008)
M25	INO ₂ \xrightarrow{M} I + NO ₂	9.94x10 ¹⁷	-11859	(McFiggans et al., 2000)
M26	INO ₃ \xrightarrow{M} IO + NO ₂	2.10x10 ¹⁵	-13670	Kaltsayannis and Plane (2008)
M27	IO + ClO → I + ClO	2.59x10 ⁻¹²	280	Atkinson et al. (2007)
M28	IO + ClO → I + Cl + O ₂	1.18x10 ⁻¹²	280	Atkinson et al. (2007)
M29	IO + ClO → ICl + O ₂	9.40x10 ⁻¹³	280	Atkinson et al. (2007)
M30	Cl + HCOOH → HCl + CO ₂ + H ₂ O	2.00x10 ⁻¹³	-	Sander et al. (2011)
M31	Cl + CH ₃ O ₂ → ClO + CH ₂ O + HO ₂ (*)	1.60x10 ⁻¹⁰	-	Sander et al. (2011)
M32	Cl + CH ₃ OOH → HCl + CH ₃ O ₂	5.70x10 ⁻¹¹	-	Sander et al. (2011)
M33	Cl + C ₂ H ₆ → HCl + C ₂ H ₅ O ₂	7.20x10 ⁻¹¹	-70	Sander et al. (2011)
M34	Cl + C ₂ H ₅ O ₂ → ClO + HO ₂ + ALD2 (*)	7.40x10 ⁻¹¹	-	Sander et al. (2011)
M35	Cl + EOH → HCl + ALD2 (<)	9.60x10 ⁻¹¹	-	Sander et al. (2011)
M36	Cl + CH ₃ C(O)OH → HCl + CH ₃ O ₂ + CO ₂	2.80x10 ⁻¹⁴	-	Sander et al. (2011)
M37	Cl + C ₃ H ₈ → HCl + A3O2	7.85x10 ⁻¹¹	-80	Sander et al. (2011)
M38	Cl + C ₃ H ₈ → HCl + B3O2	6.54x10 ⁻¹¹	-	Sander et al. (2011)
M39	Cl + ACET → HCl + ATO2	7.70x10 ⁻¹¹	-1000	Sander et al. (2011)
M40	Cl + ISOP → HCl + RIO2	7.70x10 ⁻¹¹	500	Sander et al. (2011)
M41	Cl + MOH → HCl + CH ₂ O + HO ₂	5.50x10 ⁻¹¹	-	Sander et al. (2011)
M42	CHBr ₃ + OH → 3Br + CO	1.35x10 ⁻¹²	-600	Sander et al. (2011)
M43	CH ₂ Br ₂ + OH → 2Br + CO	2.00x10 ⁻¹²	-840	Sander et al. (2011)
M44	CH ₃ Br + OH → 3Br + CO	2.35x10 ⁻¹²	-1300	Sander et al. (2011)
M45	Br + O ₃ → BrO + O ₂	1.60x10 ⁻¹¹	-780	Sander et al. (2011)
M46	Br + CH ₂ O → HO ₂ + CO	1.70x10 ⁻¹¹	-800	Sander et al. (2011)
M47	Br + HO ₂ → HBr + O ₂	4.80x10 ⁻¹²	-310	Sander et al. (2011)
M48	Br + CH ₃ CHO → CH ₃ CO ₃	1.30x10 ⁻¹¹	-360	Atkinson et al. (2007)
M49	Br + (CH ₃) ₂ CO → CH ₃ C(O)CH ₂ OO	1.66x10 ⁻¹⁰	-7000	King et al. (1970)
M50	Br + C ₂ H ₆ → C ₂ H ₅ OO	2.36x10 ⁻¹⁰	-6411	Seakins et al. (1992)
M51	Br + C ₃ H ₈ → C ₃ H ₇ OO	8.77x10 ⁻¹¹	-4330	Seakins et al. (1992)
M52	Br + BrNO ₃ → Br ₂ + NO ₃	4.90x10 ⁻¹¹	0	Orlando and Tyndall (1996)
M53	Br + NO ₃ → BrO + NO ₂	1.60x10 ⁻¹¹	0	Sander et al. (2011)
M54	HBr + OH → Br + H ₂ O	5.50x10 ⁻¹²	200	Sander et al. (2011)
M55	BrO + NO → Br + NO ₂	8.80x10 ⁻¹²	260	Sander et al. (2011)
M56	BrO + OH → Br + HO ₂	1.70x10 ⁻¹¹	250	Sander et al. (2011)
M57	BrO + BrO → 2Br + O ₂	2.40x10 ⁻¹²	40	Sander et al. (2011)
M58	BrO + BrO → Br ₂ + O ₂	2.80x10 ⁻¹⁴	860	Sander et al. (2011)
M59	BrO + HO ₂ → HOBr + O ₂	4.50x10 ⁻¹²	460	Sander et al. (2011)
M60	Br ₂ + OH → HOBr + Br	2.10x10 ⁻¹¹	240	Sander et al. (2011)
M61	Cl + ALK4 → HCl + R4O2	2.05x10 ⁻¹⁰	-	Atkinson et al. (2006)
M62	Cl + PRPE → HCl + PO ₂	3.60x10 ⁻¹²	-	Atkinson et al. (2006)



Table 7. Termolecular halogen reactions included in the scheme. This includes reactions from previous updates to halogen chemistry in GEOS-Chem (Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016), and those detailed in section 2. The lower pressure limit rate (k_0) is given by: $A_0 \cdot (\frac{300}{T})^x$. The high pressure limit is given by k_∞ . Fc characterises the fall off curve of the reaction as described by Atkinson et al. (2007).

Rxn ID	Reaction	A_0 $\text{cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$	x	k_∞ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	Fc	Citation
T1	$\text{I} + \text{NO} \xrightarrow{M} \text{INO}$	1.80×10^{-32}	1	1.70×10^{-11}	0.6	Atkinson et al. (2007)
T2	$\text{I} + \text{NO}_2 \xrightarrow{M} \text{INO}_2$	3.00×10^{-31}	1	6.60×10^{-11}	0.63	Atkinson et al. (2007)
T3	$\text{IO} + \text{NO}_2 \xrightarrow{M} \text{INO}_3$	7.70×10^{-31}	5	1.60×10^{-11}	0.4	Atkinson et al. (2007)
T4	$\text{Br} + \text{NO}_2 \xrightarrow{M} \text{BrNO}_2$	4.20×10^{-31}	2.4	2.70×10^{-11}	0.6	Sander et al. (2011)
T5	$\text{BrO} + \text{NO}_2 \xrightarrow{M} \text{BrNO}_3$	5.20×10^{-31}	3.2	6.90×10^{-12}	0.6	Sander et al. (2011)
T5	$\text{BrO} + \text{NO}_2 \xrightarrow{M} \text{BrNO}_3$	5.20×10^{-31}	3.2	6.90×10^{-12}	0.6	Sander et al. (2011)
T6	$\text{Cl} + \text{ALK4} \xrightarrow{M} \text{HCl} + \text{R4O2}$	4.00×10^{-28}	0	2.80×10^{-10}	0.6	Atkinson et al. (2006)
T7	$\text{Cl} + \text{O}_2 \xrightarrow{M} \text{ClOO}$	2.20×10^{-33}	0	$1.80 \times 10^{-10} (*)$	0.6	Sander et al. (2011)
T8	$\text{Cl}_2\text{O}_2 \xrightarrow{M} 2\text{ClO}$	9.30×10^{-6}	2	$1.74 \times 10^{15} (*)$	0.6	Sander et al. (2011)
T9	$\text{ClO} + \text{ClO} \xrightarrow{M} \text{Cl}_2\text{O}_2$	1.60×10^{-21}	2	$3.00 \times 10^{-12} (*)$	0.6	Sander et al. (2011)
T10	$\text{ClO} + \text{NO}_2 \xrightarrow{M} \text{ClNO}_3$	1.80×10^{-31}	1.9	$1.50 \times 10^{-11} (*)$	0.6	Sander et al. (2011)
T11	$\text{ClOO} \xrightarrow{M} \text{Cl} + \text{O}_2$	3.30×10^{-9}	0	$2.73 \times 10^{14} (*)$	0.6	Sander et al. (2011)

Table footnote: (*) $k_\infty(\text{T})$ for reactions T7-T11 have a form of $k_\infty(\text{T}) = k_\infty(\frac{T}{300})^{-m}$, where $m = 3.1, 4.5, 4.5, 3.4$ and 3.1 respectively. Abbreviations for tracers are expanded in footnote 3.



Table 8. Halogen multiphase reactions and reactive uptake coefficients (γ)

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



Table 9. 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 (1×10^{20} M atm⁻¹). The INO₂ Henry's law constant is assumed equal to that of BrNO₃, from Sander (2015), by analogy. For I₂O_x ($x = 2, 3, 4$) a Henry's law constant of infinity is assumed by analogy with INO₃. (*) Effective Henry's law of HX is calculated for acid conditions through $K_H^*(T) = K_H(T) \times (1 + \frac{K_a}{[H^+]})$.

Species	Henry's Law Constant (H) at 298K M atm ⁻¹	Reference	$\frac{d(\ln H)}{d(1/T)}$ K	Reference
HOBr	6.1x10 ³	Frenzel et al. (1998)	6.01x10 ³	McGrath and Rowland (1994)
HBr(*)	7.1x10 ¹³	Frenzel et al. (1998)	1.02x10 ⁴	Schweitzer et al. (2000)
BrNO ₂	0.3	Frenzel et al. (1998)	-	-
BrNO ₃	∞	Sander (2015)	-	-
Br ₂	0.76	Dean (1992)	3.72x10 ³	Dean (1992)
HOCl	6.5x10 ³	Sander (2015)	5.9x10 ³	Sander (2015)
HCl(*)	7.1x10 ¹⁵	Sander (2015)	5.9x10 ³	Sander (2015)
ClNO ₃	∞	Sander (2015)	-	-
BrCl	0.97	Sander (2015)	-	-
ICl	1.11x10 ²	Sander (2015)	2.11x10 ³	Sander et al. (2006)
IBr	2.43x10 ¹	Sander (2015)	4.92x10 ³	Sander et al. (2006)
HOI	1.53x10 ⁴	Sander (2015)	8.37x10 ³	Sander et al. (2006)
HI (*)	7.43x10 ¹³	Sander (2015)	3.19x10 ³	Sander et al. (2006)
INO ₃	∞	Vogt et al. (1999)	3.98x10 ⁴	Kaltsoyannis and Plane (2008)
I ₂ O ₂	∞	see caption text	1.89x10 ⁴	Kaltsoyannis and Plane (2008)
I ₂	2.63	Sander (2015)	7.51x10 ³	Sander et al. (2006)
INO ₂	0.3	see caption text	7.24x10 ³	Sander et al. (2006)
I ₂ O ₃	∞	see caption text	7.70x10 ³	Kaltsoyannis and Plane (2008)
I ₂ O ₄	∞	see caption text	1.34x10 ⁴	Kaltsoyannis and Plane (2008)



Table 10. 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, HO₂, H₂O₂ and O₃ Families are defined in footnote 3

	“NOHAL”	“Cl+Br+I”	% Δ
NO ₃	1.23	1.23	-17.8
O ₃	415843.25	355123.69	-14.6
N ₂ O ₅	9.38	8.02	-14.5
H ₂ O ₂	3229.09	2828.80	-12.4
C ₂ H ₆	3258.84	2855.31	-12.4
HNO ₄	19.84	17.63	-11.1
C ₃ H ₈	609.76	550.68	-9.7
≥C4 alkanes	488.35	441.96	-9.5
HO ₂	27.55	25.37	-7.9
PPN	15.82	14.65	-7.4
PAN	202.89	194.70	-4.0
CH ₃ C(O)CH ₃	7533.51	7289.92	-3.2
OH	0.28	0.27	-2.9
NO ₂	123.53	120.35	-2.6
CH ₂ O	389.55	380.88	-2.2
PMN	0.68	0.67	-1.8
NO _x	171.01	168.15	-1.7
SO ₄ on SSA	1.97	1.94	-1.6
NH ₃	126.61	126.28	-0.3
NO _y	1374.56	1371.59	-0.2
Acetaldehyde	184.93	184.59	-0.2
NH ₄	270.93	271.43	0.2
>C3 ketones	186.99	188.11	0.6
SO _x	398.98	401.59	0.7
SO ₄	397.01	399.65	0.7
NO	47.48	47.80	0.7
≥C3 alkenes	97.93	98.79	0.9
PROPNN	7.46	7.55	1.1
HNO ₃	463.49	470.69	1.6
VOCs	148193.29	151283.71	2.1
≥C4 alkylnitrates	64.60	65.99	2.2
SO ₂	286.11	294.17	2.8
CO	134654.88	138477.76	2.8
MMN	3.15	3.26	3.2
CH ₃ NO ₂	13.80	14.25	3.3
Isoprene	788.55	815.73	3.4
HNO ₂	2.76	2.92	5.5
ISOPN	0.65	0.69	6.2

Abbreviations for tracers are expanded in footnote 3.