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Halogen chemistry reduces tropospheric O_3 radiative forcing

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Abstract. Tropospheric ozone (O_3) is a global warming gas, but the lack of a firm observational record since the preindustrial period means that estimates of its radiative forcing (RF_{TO_3}) rely on model calculations. Recent observational evidence shows that halogens are pervasive in the troposphere and need to be represented in chemistry-transport models for an accurate simulation of present-day O_3. Using the GEOS-Chem model we show that tropospheric halogen chemistry is likely more active in the present day than in the preindustrial. This is due to increased oceanic iodine emissions driven by increased surface O_3, higher anthropogenic emissions of bromo-carbons, and an increased flux of bromine from the stratosphere. We calculate preindustrial to present-day increases in the tropospheric O_3 burden of 113 Tg without halogens but only 90 Tg with, leading to a reduction in RF_{TO_3} from 0.43 to 0.35 Wm^{-2}. We attribute ∼ 50 % of this reduction to increased bromine flux from the stratosphere, ∼ 35 % to the ocean–atmosphere iodine feedback, and ∼ 15 % to increased tropospheric sources of anthropogenic halogens. This reduction of tropospheric O_3 radiative forcing due to halogens (0.087 Wm^{-2}) is greater than that from the radiative forcing of stratospheric O_3 (∼ 0.05 Wm^{-2}). Estimates of RF_{TO_3} that fail to consider halogen chemistry are likely overestimates (∼ 25 %).

1 Introduction

The prevailing paradigm has been for tropospheric halogen chemistry not to be considered important for estimating the climate change due to increasing tropospheric ozone (O_3) concentrations. However, recent observational studies have shown that halogens play an important and pervasive role in the chemistry of the present-day troposphere (Read et al., 2008; Volkamer et al., 2015; Wang et al., 2015). Models that were used to calculate radiative forcing of tropospheric O_3 (RF_{TO_3}) in the past do not contain this halogen chemistry (Hauglustaine et al., 1994; Levy et al., 1997; Myhre et al., 2013; Young et al., 2013), raising concerns that they may have a systematic bias in their simulation of past, present, and future tropospheric O_3 and more widely the composition of the troposphere. As increased observations of tropospheric halogens are made (Dix et al., 2013; Gómez Martín et al., 2013; Mahajan et al., 2010, 2012; Prados-Roman et al., 2015; Read et al., 2008; Volkamer et al., 2015; Wang et al., 2015) and models are used to understand them (Parrella et al., 2012; Saiz-Lopez et al., 2012a, 2014; Schmidt et al., 2016; Sherwen et al., 2016a, b), these concerns grow.

Tropospheric O_3 is a climate gas and a potent air pollutant. Understanding the change in its concentration from the "natural" preindustrial (∼ 1750) atmosphere to the present day is important in defining those roles and informing policy decisions. Global tropospheric O_3 concentrations are thought to have increased substantially in this period (Lamarque et al., 2010; Myhre et al., 2013), but the observational record for this change is highly uncertain. Unlike carbon dioxide and methane, O_3 does not remain trapped in ice so modern analytical techniques cannot be applied to old air. Past observations suggest much lower concentrations of O_3 than are presently measured (Volz and Kley, 1988; Marenco et al., 1994; Pavelin et al., 1999). However, there are only a small number of past observations, and significant uncertainties exist in the methods used and their representativeness. Because of concerns over the validity of these observations, our

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assessment of the change in O_3 concentrations is predominantly based on computer simulations (Hauglustaine et al., 1994; Levy et al., 1997; Myhre et al., 2013; Young et al., 2013). Estimates of the emissions in the preindustrial and the present day (Lamarque et al., 2010), together with an understanding of the chemistry, transport, and physics of the atmosphere, underpin these simulations. An assessment of the change in O_3 concentrations between the preindustrial and the present day and a calculation of the associated radiative forcing was undertaken as part of the ACCMIP project (Lamarque et al., 2013; Stevenson et al., 2013; Young et al., 2013; Voulgarakis et al., 2013). This concluded that preindustrial tropospheric O_3 burdens were 98 Tg lower than the present day and estimated a $\mathrm{RF_{TO_3}}$ of $0.41\,\mathrm{W m^{-2}}$.

These model calculations are only as good as the emissions used to drive them and their representation of physical and chemical processes. These uncertainties are probably largest for the emissions, especially for the biomass burning source (Fry et al., 2012; Knorr et al., 2016; Murray et al., 2014; van der Werf et al., 2013). Over the last decades, improvements have been made in the organic tropospheric chemistry included in these models with a particular emphasis on the role of biogenic compounds such as isoprene and monoterpenes (Glasius and Goldstein, 2016).

The tropospheric impact of halogens in polar regions during springtime has been known for some time (Barrie et al., 1988; Jacob et al., 1992), but their significance for the global troposphere has only been evident in the last decade (Read et al., 2008; Saiz-Lopez et al., 2012a; Prados-Roman et al., 2015; Wang et al., 2015). Reviews of the appropriate processes are given elsewhere (Simpson et al., 2015). Sources of halogens include natural and anthropogenic organic halogen precursor gases (Montzka et al., 2011), heterogeneous chemistry on sea salt (McFiggans et al., 2000; Braban et al., 2007; Roberts et al., 2009; Bertram and Thornton, 2009), and chemistry involving atmospheric O_3 and iodide in the ocean surface (Carpenter et al., 2013; MacDonald et al., 2014). Once emitted into the atmosphere there is rapid photochemical processing of these compounds (Simpson et al., 2015). Catalytic cycles similar to those occurring in the stratosphere can lead to O_3 destruction (von Glasow et al., 2004; Simpson et al., 2015), changes to $\mathrm{HO_x}$ and $\mathrm{NO_x}$ cycling (Chameides and Davis, 1980; Long et al., 2014), and impacts on the distribution and deposition of mercury (Holmes et al., 2010; Parrella et al., 2012; Schmidt et al., 2016).

Here, we investigate the impact of tropospheric halogen chemistry on the change in O_3 concentrations between the preindustrial and the present day using the GEOS-Chem model of tropospheric chemistry and transport (Bey et al., 2001), which has been extended to provide a description of the chemistry of chlorine, bromine, and iodine (see Sect. 2 and Sherwen et al., 2016b). Comparisons between the model and present-day observations of halogen compounds have been shown previously (Bell et al., 2002; Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016a, b). The model provides a good simulation of present-day bromine and iodine compounds but appears (given the limited observational record) to underestimate tropospheric chlorine sources (Sherwen et al., 2016b). We run simulations with preindustrial and present-day emissions, with and without halogen chemistry. From these we evaluate the changes in the tropospheric O_3 and hence radiative forcing.

2 Model description

We use the GEOS-Chem model of chemistry and transport (http://www.geos-chem.org, Bey et al., 2001), which includes O_x, $\mathrm{HO_x}$, $\mathrm{NO_x}$, and VOC chemistry. The model is an enhancement of this with a representation of halogen chemistry (Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016a) described elsewhere (Sherwen et al., 2016b), with gas-phase chemistry based on JPL/IUPAC recommendations (Sander et al., 2011; Atkinson et al., 2006, 2007, 2008) and heterogeneous chemistry from previous work (Abbatt et al., 2012; Braban et al., 2007; Ammann et al., 2013; Sherwen et al., 2016a). Short-lived organohalogens (CH_3I, CH_2I_2, CH_2ICl, CH_2IBr, $CHBr_3$, CH_2Br_2) are emitted into the model surface level and then transported (Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016a), whereas longer-lived species (CH_3Br, CH_3Cl, $CHCl_3$, CH_2Cl_2) are given fixed boundary layer concentrations (Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016). Chlorine and bromine from sea salt can be released into the gas phase through heterogeneous chemistry involving iodine ($\mathrm{HOI/INO_2/INO_3} \xrightarrow{\text{seasalt}} \mathrm{IX}$, $\mathrm{X = Cl}$, Br) and N_2O_5 ($N_2O_5 \xrightarrow{\text{seasalt}} \mathrm{ClNO_2} + \mathrm{HNO_3}$, for Cl) as described in Sherwen et al. (2016b). HOI and I_2 are emitted from the ocean surface dependent on the O_3 concentration in the model's lowest level and the calculated iodide concentration in the ocean (Carpenter et al., 2013; MacDonald et al., 2014). The combined impact of this chemistry for the present day has been summarised previously (Sherwen et al., 2016b) and the model has been evaluated against a range of halogenated compounds (Eastham et al., 2014; Parrella et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016a, b).

The model is run for 2 years (2004 and 2005), discarding the first year as a "spin-up" period and using the second year (2005) for analysis. We run with and without halogen chemistry.

To simulate the preindustrial troposphere, anthropogenic $\mathrm{NO_x}$, VOC, and SO_2 emissions are removed, biomass burning emissions are reduced to 10 % of their present-day values, and the methane concentration is reduced to $700\,\mathrm{nmol\,mol^{-1}}$ (Wang and Jacob, 1998). A summary of changes to base emissions from present day are given in Table 4 and the base emissions described in detail on the GEOS-Chem website (www.geos-chem.org). Uncertain-

Table 1. Emission of halogen source gases for the preindustrial (PI) and present day (PD). Long-lived sources which have fixed concentrations in the model for Cl (CH_3Cl, CH_2Cl_2, $CHCl_3$) and Br ($CHBr_3$) are shown in terms of chemical release (e.g. reaction with +OH, $+h\nu$, +Cl) and are in bold. I_2 and HOI are the inorganic ocean source from O_3 reacting with oceanic iodide (Carpenter et al., 2013), IX is from the uptake of iodine gases onto sea salt to release IBr or ICl, and $ClNO_2$ is the source from the uptake of N_2O_5 on sea salt.

	I	($Tg\,I\,yr^{-1}$)	Br	($Tg\,Br\,yr^{-1}$)	Cl	($Tg\,Cl\,yr^{-1}$)
Sources	PI	PD	PI	PD	PI	PD
CH_3X	0.26	0.26	**0.04**	**0.06**	**2.28**	**2.10**
CH_2X_2	0.33	0.33	0.09	0.09	**0.11**	**0.57**
CHX_3	–	–	0.41	0.41	**0.21**	**0.25**
HOI	1.09	1.97	–	–	–	–
I_2	0.08	0.14	–	–	–	–
IX	–	–	0.19	0.30	0.46	0.73
$ClNO_2$	–	–	–	–	0.02	0.65
Stratosphere	0.00	0.00	0.00	0.06	0.44	0.43
Total source	1.76	2.70	0.74	0.91	3.52	4.9

ties in preindustrial emissions are large, especially for the biomass burning. We make a very large reduction here (90 %). Other estimates give smaller changes (20 %, Lamarque et al., 2010). Using a smaller change will likely reduce the overall tropospheric O_3 radiative forcing that we calculate, but our objective here is not primarily to calculate the tropospheric O_3 radiative forcing but to investigate the change that halogen chemistry makes to this value. Emissions of iodocarbons are unchanged between the preindustrial and the present day. For bromocarbons we follow a previous methodology (Parrella et al., 2012) of not changing $CHBr_3$ and CH_2Br_2 from their present-day values, but reducing the CH_3Br concentration assumed from 6–9 $pmol\,mol^{-1}$ in the present day to 5 $pmol\,mol^{-1}$ to match ice core records (Saltzman et al., 2004). Preindustrial concentrations of CH_3Cl, $CHCl_3$, and CH_2Cl_2 are scaled from their present-day values using the estimated natural contributions to their sources (92.5, 75, and 10 %, respectively; Montzka et al., 2011; Reimann et al., 2014).

We do not explicitly treat the chemistry of the stratosphere. The model uses the same linearised stratospheric chemistry (Murray et al., 2012) in the preindustrial and the present day except we set the concentration of anthropogenic halogen species (CFCs, halons, etc.) to be zero. We scale the concentration of stratospheric Br_y in the preindustrial by 0.56 to reflect the anthropogenically driven increase in bromine (Liang et al., 2010; Montzka et al., 2011). We make no similar changes to Cl_y as chlorine's impact on tropospheric O_3 in this model has previously been shown to be insignificantly small (Sherwen et al., 2016b). The tropopause is defined here as the altitude where the lapse rate of temperature falls below 2 $K\,km^{-1}$.

2.1 Results and discussion

2.1.1 Changes from preindustrial to present

Table 1 shows our estimate of halogen emissions for the preindustrial and the present day. Iodine, bromine, and chlorine sources increase by 50, 28, and 41 % over this period. The enhanced iodine emission is due to the increases in the surface ocean inorganic (HOI, I_2) source (Fig. 1) driven by anthropogenically enhanced surface O_3 (Fig. 2). Bromine emissions increase mainly because of increased anthropogenic precursor emissions but also due to increased iodine-driven sea-salt cycling of bromine (Sherwen et al., 2016b) and an increased stratospheric flux. Chlorine emissions increase due to enhanced NO_x concentration leading to more heterogeneous uptake of N_2O_5 on sea-salt liberating $ClNO_2$, together with increased anthropogenic emissions of chlorinated halocarbons and faster iodine-driven sea-salt release of ICl.

These increased sources lead to increased concentrations of halogens in the present day compared to the preindustrial with global burdens of reactive inorganic halogen species increasing by 18, 39, and 20 % for I_y, Br_y, and Cl_y, respectively (shown vertically in Fig. 3 and spatially in Fig. 4). Iodine concentrations increase less than emissions do due to a shortening of its lifetime from 3.0 days in the preindustrial to 2.3 days in the present day. This is mainly due to higher NO_x concentrations, which enhance iodine nitrate hydrolysis (Ammann et al., 2013; Schmidt et al., 2016). Bromine lifetimes lengthen from 16.4 days in the preindustrial to 18.2 days in the present day. This is predominantly due to the increase in Br_y source from the stratosphere, which is a region of low depositional loss. Inorganic chlorine lifetimes shorten from 6.1 days in the preindustrial to 5.2 in the present day due to the increase in methane concentrations which push Cl_y into HCl, which is then readily deposited.

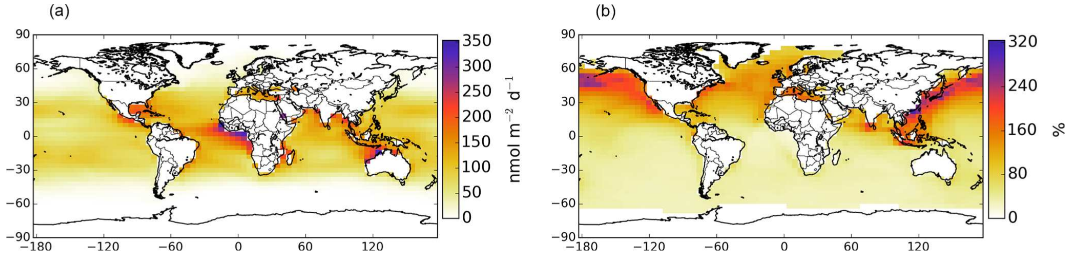

Figure 1. Inorganic emission flux (HOI, I_2) in the preindustrial **(a)** and percent change from the preindustrial to present day ($(\mathrm{PD}-\mathrm{PI})/\mathrm{PI} \cdot 100$) **(b)**.

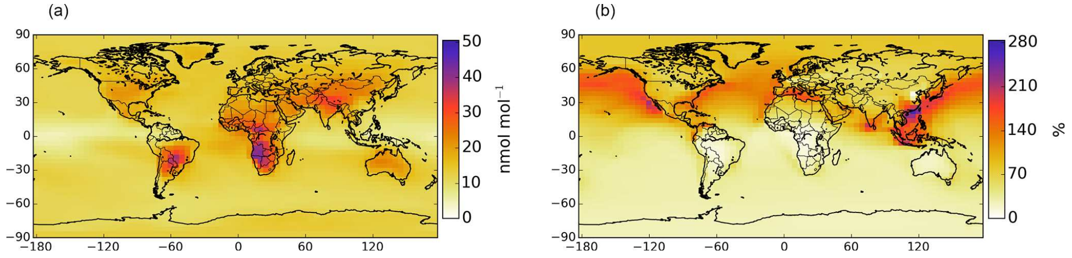

Figure 2. **(a)** O_3 surface concentration in the preindustrial and **(b)** percent change from the preindustrial to present day ($(\mathrm{PD}-\mathrm{PI})/\mathrm{PI} \cdot 100$).

The inclusion of halogens reduces the concentration of O_3 in both the present-day and the preindustrial simulations. The O_3 simulated in the present day (see Fig. 12 in Sherwen et al., 2016b) appears to be more consistent with observations when halogen chemistry is included than without (other than for the Southern Ocean) and captures the observed diurnal cycle (Sherwen et al., 2016a). Figure 5 shows a comparison between the limited number of O_3 observations for preindustrial locations (Marenco et al., 1994; Pavelin et al., 1999; Volz and Kley, 1988) and the model. Both with and without halogen chemistry the model simulates significantly lower O_3 concentrations in the preindustrial but the addition of halogens reduces globally averaged surface O_3 concentrations by 8.8 nmol mol^{-1} (39 %) (Fig. 2), making the model more consistent with observations. This reduction is largest over the oceans. Confidence in the preindustrial observation datasets is, however, low (Marenco et al., 1994; Mickley et al., 2001; Pavelin et al., 1999) and so interpreting the model overestimate is difficult. Globally, halogens reduce the tropospheric O_3 burden by 77 Tg in the present day and 54 Tg in the preindustrial (Table 3).

We consider halogens impacts on O_3 through changes to the family of odd oxygen species (O_x, defined in Table 2) to account for their rapid interchange. The O_x budgets for the four simulations are shown in Table 3. In both the present day and the preindustrial the halogens are responsible for around 20 % of the O_3 destruction, with iodine dominating (57 % : 49 % : 4 % I : Br : Cl for the present day and 61 % : 36 % : 4 % I : Br : Cl for the preindustrial). Although chlorine concentrations have increased almost as much as iodine between the preindustrial and the present, it plays little role in determining O_3 loss (Schmidt et al., 2016; Sherwen et al., 2016a, b). Tropospheric O_3 lifetimes drop from 26 to 22 days in the present day with the inclusion of halogens and from 28 to 24 days in the preindustrial.

Tropospheric chemistry is a highly coupled system with significant interplay between the NO_x, HO_x, and RO_x systems (Monks et al., 2015). Changes in the individual production and loss terms are relatively small, but halogens reduce net O_3 production by 194 Tg yr^{-1} in the present day and 145 Tg yr^{-1} in the preindustrial. In our preindustrial simulation with halogens, the troposphere is close to being a net chemical sink for O_3. Thus the impact of halogen chemistry on the overall O_3 burden of the troposphere is more important for the present day than it was in the preindustrial.

3 Implications

Figure 6 shows the change in tropospheric O_3 column between the preindustrial and the present day, with and without halogens. Consistent with previous work, the largest increases occur in the northern midlatitudes notably over eastern North America and Asia (Lamarque et al., 2005). Halogens reduce the column change by an average of 2.0 DU. The largest halogen-driven reductions (up to 3.5 DU) are seen over the northern Pacific and Atlantic oceans. This is where surface O_3 concentrations increase the most over the oceans, leading to increases in oceanic inorganic iodine emissions and in turn giving more active O_3 destruction by iodine chemistry.

Various studies have calculated a normalised radiative forcing (NRF), which is the radiative forcing response to per

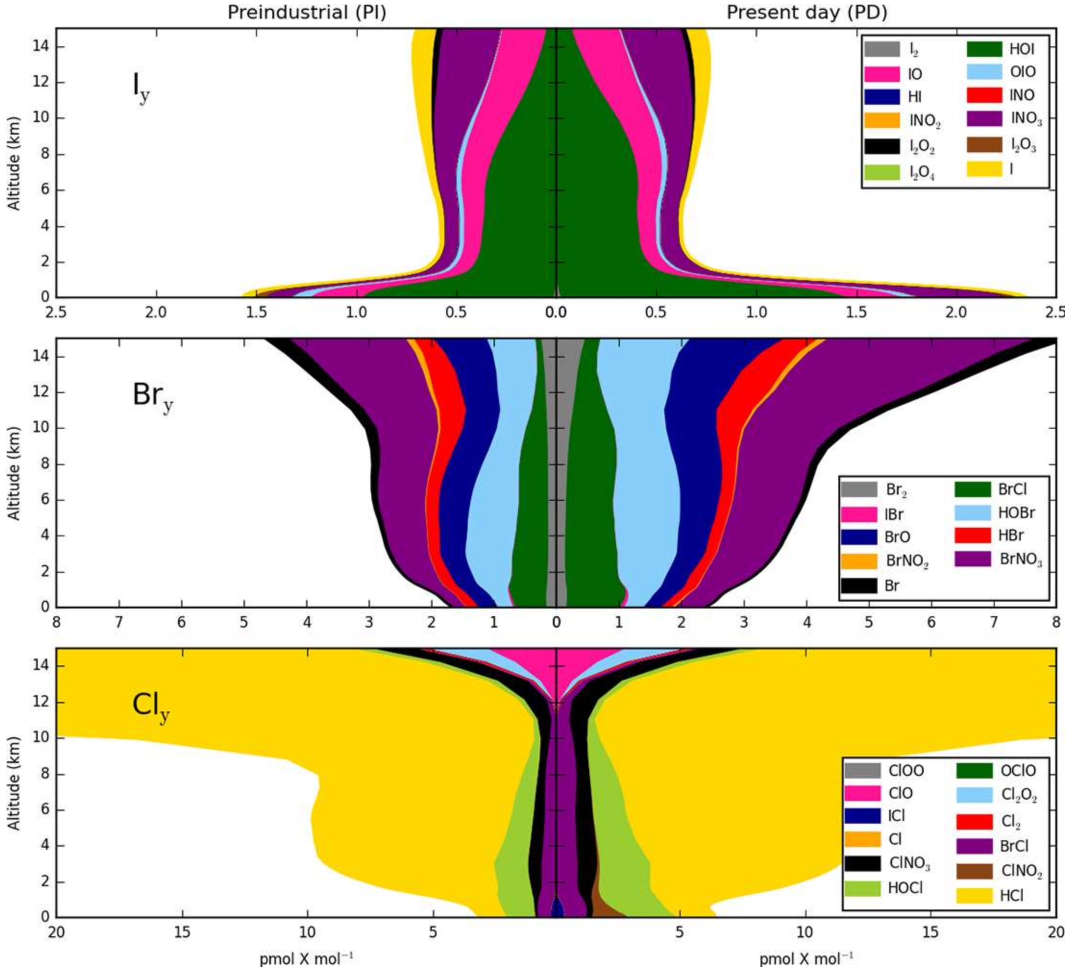

Figure 3. Global mean vertical distribution of iodine, bromine, and chlorine inorganic gases (X_y, X = Cl, Br, I) for the preindustrial (left) and present day (right) in terms of mixing ratios of halogen. Increased halogen concentrations in the present day are predominantly at the surface for iodine but are throughout the column for bromine and chlorine.

Table 2. Odd oxygen (O_x) family definition used here.

Abbreviation	Detail
O_x	$O_3 + NO_2 + 2NO_3 + PAN + PMN + PPN + HNO_4 + 3N_2O_5 + HNO_3 + MPN + XO + HOX + XNO_2 + 2XNO_3 + 2OIO + 2I_2O_2 + 3I_2O_3 + 4I_2O_4 + 2Cl_2O_2 + 2OClO$ (where X = Cl, Br, I)

unit O_3 column within a range of models (Stevenson et al., 2013; Fry et al., 2012; Gauss et al., 2003), and they calculate values of NRF in the range of 36–42 mW m^{-2} DU^{-1}. Here we use the most recent NRF value calculated by Stevenson et al. (2013) (42 mW m^{-2} DU^{-1}) and used by the IPCC (Myhre et al., 2013) to consider the implications of tropospheric halogens on O_3. We acknowledge that this approach does not allow consideration of sensitivities to vertical or latitudinal changes in O_3, and this offers an uncertainty on our calculation, as discussed further elsewhere (e.g. Myhre et al., 2013). Furthermore, as greatest percentage changes in O_3 burden on inclusions of halogens are seen closest to the surface (Sherwen et al., 2016b), this could possibly lead to overestimating changes in radiative forcing due to increased sensitivity seen in colder and higher altitudes (Myhre et al., 2013).

For our simulations without halogens we calculate a tropospheric O_3 radiative forcing of 0.432 Wm^{-2}, close to the 0.410 Wm^{-2} found from the ACCMIP intercomparison (Stevenson et al., 2013) and within the range reported by IPCC (+0.40 (±0.2) Wm^{-2}; Myhre et al., 2013). Our simulations with halogens, however, give a significantly lower radiative forcing of 0.345 Wm^{-2}. Thus, the increases in halogen chemistry associated with human activity are act-

Table 3. Global tropospheric O_x (defined in Table 2) budgets for preindustrial and present day, with and without halogens. For the $X'O + X''O$ halogen crossover reactions where $X' \neq X''$ we split the O_x loss equally between the two routes. Values are rounded to the nearest integer value.

	Preindustrial	Preindustrial	Present day	Present day
	With halogens	Without	With halogens	Without
O_3 burden (Tg)	249	303	339	416
O_x chemical sources (Tg yr^{-1})				
$NO + HO_2$	2218	2357	3436	3607
$NO + CH_3O_2$	652	668	1288	1316
$NO + RO_2$	388	375	525	508
Total chemical O_x sources (PO_x)	3341	3401	5249	5431
O_x chemical sinks (Tg yr^{-1})				
$O_3 + H_2O \xrightarrow{h\nu} 2OH + O_2$	1350	1711	1997	2489
$O_3 + HO_2 \rightarrow OH + O_2$	600	822	1061	1432
$O_3 + OH \rightarrow HO_2 + O_2$	459	601	562	737
$HOBr \xrightarrow{h\nu} Br + OH$	188	–	285	–
$HOBr + HCl \rightarrow BrCl$	27	–	54	–
$HOBr + HBr \rightarrow Br_2 + H_2O$ (aq. aerosol)	12	–	22	–
$BrO + BrO \rightarrow 2Br + O_2$	8	–	13	–
$BrO + BrO \rightarrow Br_2 + O_2$	3	–	4	–
$BrO + OH \rightarrow Br + HO_2$	11	–	12	–
$IO + BrO \rightarrow Br + I + O_2$	9	–	11	–
$ClO + BrO \rightarrow Br + ClOO/OClO$	3	–	4	–
Other bromine O_x sinks	0	–	0	–
Total bromine O_x sinks	261	–	405	–
$HOI \xrightarrow{h\nu} I + OH$	322	–	438	–
$OIO \xrightarrow{h\nu} I + O_2$	112	–	140	–
$IO + BrO \rightarrow Br + I + O_2$	9	–	11	–
$IO + ClO \rightarrow I + Cl + O_2/ ICl + O_2$	1	–	1	–
Other iodine O_x sinks	1	–	2	–
Total iodine O_x sinks	443	–	591	–
$HOCl \xrightarrow{h\nu} Cl + OH$	18	–	27	–
$CH_3O_2 + ClO \rightarrow ClOO$	4	–	6	–
$ClO + BrO \rightarrow Br + ClOO/OClO$	3	–	4	–
$ClNO_3 + HBr \rightarrow BrCl$	0	–	2	–
$IO + ClO \rightarrow I + Cl + O_2/ICl + O_2$	1	–	1	–
Other chlorine O_x sinks	1	–	1	–
Total chlorine O_x sinks	28	–	40	–
Other O_x sinks	101	151	184	172
Total chemical O_x sinks (LO_x)	3259	3240	4841	4829
O_3 PO_x-LO_x (Tg yr^{-1})	16	161	408	602
O_3 Dry deposition (Tg yr^{-1})	520	659	799	980
O_3 Lifetime (days)	24	28	22	26
O_3 STE (PO_x-LO_x-Dry dep.) (Tg yr^{-1})	503	498	391	378

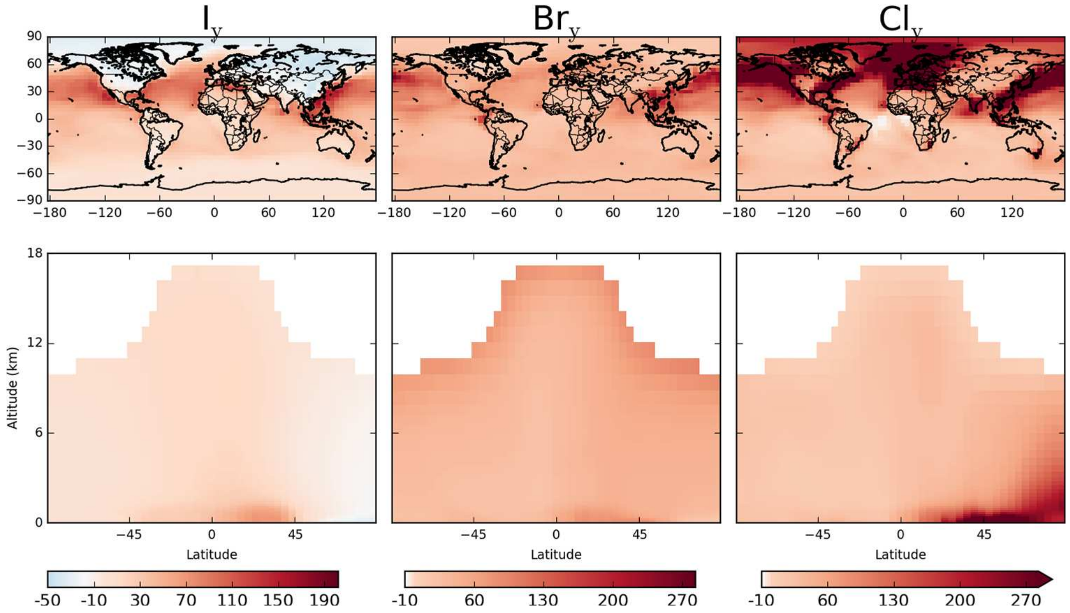

Figure 4. Percentage change from preindustrial to present day in tropospheric distribution of I_y, Cl_y, and Br_y ($(PD-PI)/PI \cdot 100$). Upper plots show surface and lower plots show zonal values. Reductions in I_y concentration over land are due to a shortening of the I_y lifetime due to enhanced $IONO_2$ hydrolysis due to increase NO_x emissions in the present day. Increases in surface Cl_y are due to increased release of $ClNO_2$ attributable to higher N_2O_5 concentrations in present day.

Table 4. Summary of base emissions changed between for present day and preindustrial. Full documentation of emissions implemented in the model (version 10) is documented on the GEOS-Chem website (www.geos-chem.org).

General descriptor	Species	Reference	Included?	
			Present day	Preindustrial
GEIA – global anthropogenic	NH_3	Benkovitz et al. (1996)	✓	×
EDGAR – global anthropogenic	NO, CO, SO_2, SO_4, NH_3	JRC/NEAA (2011)	✓	×
Global anthropogenic	C_2H_6	Xiao et al. (2008)	✓	×
EMEP – European anthropogenic	NO, CO, SO_2, SO_4, NH_3, VOCs	Vestreng et al. (2009)	✓	×
BRAVO – Mexican anthropogenic	NO, CO, SO_2, SO_4	Kuhns et al. (2003)	✓	×
CAC – Canadian anthropogenic	NO, CO, SO_2, SO_4	Environment Canada (2013)	✓	×
GFED – global biomass burning	NO, CO, NH_3, SO_2, SO_4, VOCs, Organic and black carbon aerosols	van der Werf et al. (2010)	✓	Scaled to 10 % of present day
RETRO – global anthropogenic	VOCs	Benkovitz et al. (1996)	✓	×
NEI – USA anthropogenic	NO, NO_2, VOCs	EPA (2015)	✓	×
BOND – global carbon aerosol	Organic and black carbon aerosols	Bond et al. (2007)	✓	Anthropogenic removed and biomass burning scaled to 10 %
AEIC – global aircraft	NO, NO_2, VOCs, aerosols	Stettler et al. (2011)	✓	×
MIX – Asian anthropogenic	NO, NO_2, CO, SO_2, SO_4, NH_3, VOCs	Li et al. (2015)	✓	×
Global soil NO_x	NO	Hudman et al. (2012)	✓	No fertiliser emissions
Global ship NO_x	NO	Wang et al. (2008)	✓	×

VOC is volatile organic carbon; see reference for details.

ing to dampen the anthropogenic radiative forcing of O_3 by $0.087\,Wm^{-2}$. Given that none of the models which participated in the last IPCC assessment incorporate tropospheric halogen chemistry, it would appear that they may overestimate tropospheric O_3 radiative forcing by $\sim 25\,\%$. Our estimate for the reduction in tropospheric O_3 radiative forcing due to halogens is larger than the $-0.05\,Wm^{-2}$ (-0.15 to $+0.05\,Wm^{-2}$) estimate of the radiative forcing of stratospheric O_3, which is predominantly due to halogens (Myhre et al., 2013).

This halogen-induced reduction in the RF_{TO_3} is due to a combination of the increased oceanic iodine source from the increased O_3, the increase in tropospheric organohalogens, and the increase in stratospheric halogen flux between the preindustrial and the present day. Removing the oceanic inorganic iodine source from the model but keeping the increase

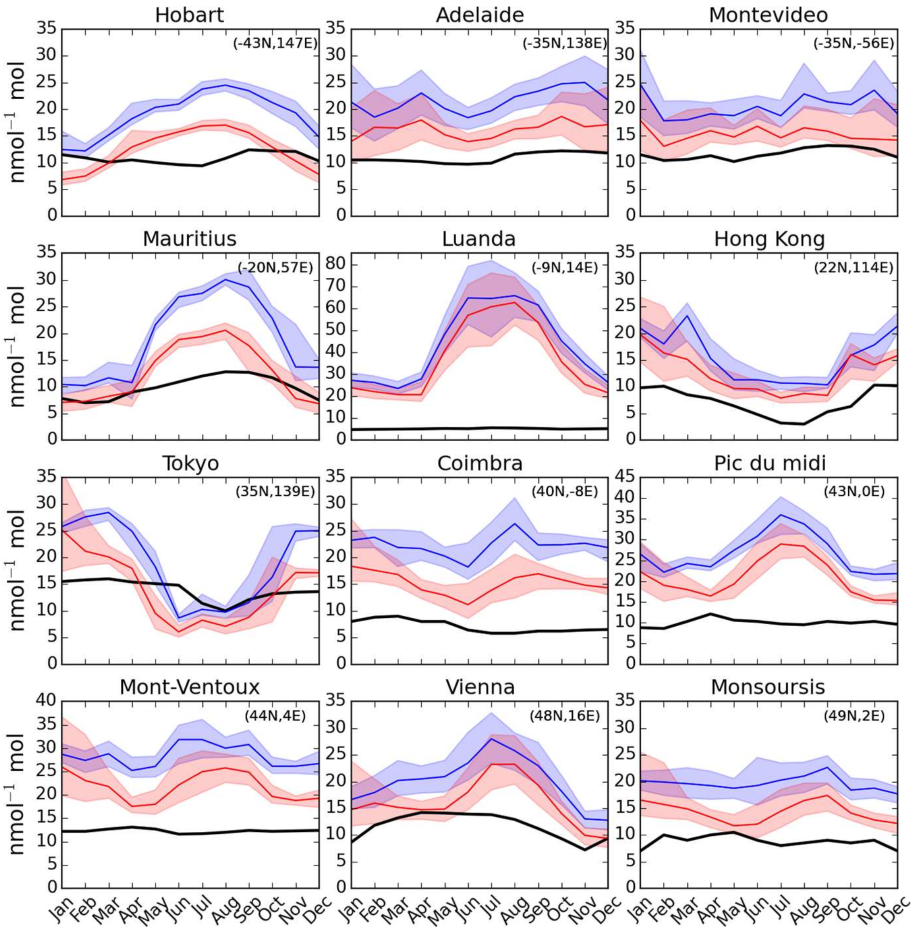

Figure 5. Comparison between observed and modelled preindustrial monthly mean O_3. Observations are shown in black; preindustrial model simulation with halogens are in red and without halogens are in blue. The shaded areas for the model simulation shows the first and third quartiles in the hourly values. The O_3 data are reproduced (Mickley et al., 2001) from previously reported observations: Mont Ventoux, Hong Kong, Tokyo, Adelaide, Coimbra, Hobart, Luanda, Mauritius, Vienna, and Montevideo (Marenco et al., 1994); Pic du Midi (Pavelin et al., 1999); Montsouris (Volz and Kley, 1988).

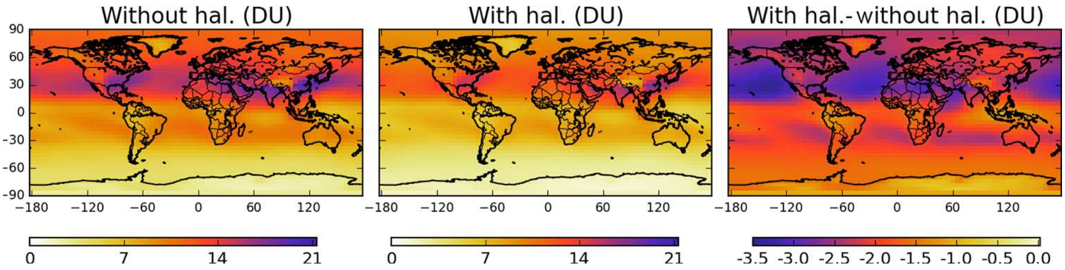

Figure 6. Increases in tropospheric O_3 column between the preindustrial and present day without and with halogens. Left and centre panels show the difference in annually averaged column O_3 (DU) between preindustrial and the present day without (left) and with halogens (centre). Right panel shows the difference.

in tropospheric halocarbons and stratospheric halogen flux gives a RF_{TO_3} of 0.374 Wm^{-2}. In addition to that change, using a present-day stratosphere for the preindustrial gives a RF_{TO_3} of 0.389 Wm^{-2}. Although the system is non-linear we thus attribute ∼ 50 % to the increase in the flux of inorganic halogens from the stratosphere, ∼ 35 % of the halogen-driven reduction in O_3 radiative forcing to the ocean–atmosphere O_3–iodine feedback, and ∼ 15 % to the increase in the tropospheric halocarbons.

4 Conclusions

There are significant uncertainties in the chemistry of tropospheric halogens. Although the basic gas-phase chemistry of Cl and Br is well known there are larger uncertainties to the chemistry of I (Saiz-Lopez et al., 2012b). The largest uncertainties though likely lie in our understanding of the heterogeneous processing of halogens (Abbatt et al., 2012; Saiz-Lopez et al., 2012b; Sherwen et al., 2016a; Simpson et al., 2015), which affords a coupling between iodine, bromine, and chlorine and between the different emission species and sea salt. Relatively small changes to parameters here can make substantial changes to the O_3 radiative forcing. For example, the partitioning between ICl and IBr emissions following uptake of condensable iodine compounds to sea-salt aerosol is not well known. Changing the ICl to IBr ratio from 0.85 : 0.15 (as used here and in Sherwen et al., 2016b) to a the IBr yield (0.5 : 0.5), as used in other studies (McFiggans et al., 2000; Saiz-Lopez et al., 2014), increases the reduction in the O_3 radiative from the 25 % found here to 34 %. There is also a question as to whether models have some aspects of this halogen chemistry "tuned" into them through enhanced O_3 deposition to the ocean surface, or other mechanisms for the present day. This needs to be explored through a more detailed understanding of the deposition of O_3 to the ocean, but it seems unlikely that the parameterisation would slow the loss of O_3 in the preindustrial in the manner described here and so have the same impact on radiative forcing.

Uncertainties in the role of halogens in determining tropospheric O_3 radiative forcing may be reduced by more observations of halogen compounds in the present day (in the atmosphere and oceans) and by reducing uncertainties in the kinetics of the gas- and aerosol-phase chemistry. However, it would appear that model estimates of O_3 radiative forcing that do not consider tropospheric halogen chemistry are likely ~ 25 % too large.

5 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)

Competing interests. The authors declare that they have no conflict of interest.

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