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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, however the lack of a firm observational record since the pre-industrial period means that estimates of its radiative forcing (RF_{TO3}) 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 more active in the present-day than in the pre-industrial. 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 pre-industrial to present-day increases in the tropospheric O_3 burden of 113 Tg without halogens but only 95 Tg with, leading to a reduction in RF_{TO3} from 0.432 to 0.366 Wm^{-2}. We attribute ∼40% of this reduction to the ocean-atmosphere iodine feedback, ∼30% to increased anthropogenic halogens in the troposphere and ∼30% to increased bromine flux from the stratosphere. This reduction of RF_{TO3} (0.066 Wm^{-2}) is greater than that from stratospheric ozone (∼0.05 Wm^{-2}). Estimates of RF_{TO3} that fail to consider halogen chemistry are likely overestimates (∼20%).

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 studies have shown that halogens play an important and pervasive role in the chemistry of the present-day troposphere (Parrella et al., 2012; Saiz-Lopez et al., 2012a, 2014; Schmidt et al., 2016; Sherwen et al., 2016a, b). The fact that the models that are used to calculate radiative forcing of tropospheric O_3 (RF_{TO3}) do not contain this chemistry (Hauglustaine et al., 1994; Levy et al., 1997; Myhre et al., 2013; Young et al., 2013) raises questions over their ability to reproduce tropospheric composition as more and more 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).

Tropospheric O_3 is a climate gas and a potent air pollutant. Understanding the change in its concentration from the "natural" pre-industrial (∼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), however, 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 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 pre-industrial 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 concentrations between the pre-industrial 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), which concluded that pre-industrial tropospheric O_3 burdens were 98 Tg lower than the present-day and estimated a RF_{TO3} of 0.410 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. Over the last decades, the emphasis for tropospheric chemistry has been on improving the representation of organic chemistry with particular emphasis on the role of biogenic compounds such as isoprene and monoterpenes (Glasius and Goldstein, 2016). This has contrasted with the stratosphere where the emphasis has been on halogen (predominantly Br and Cl) chemistry (Morgenstern et al., 2010).

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 HO_x and 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 pre-industrial 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 (Eastham et al., 2014; 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 pre-industrial 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 (www.geos-chem.org, Bey et al. 2001), which includes O_x, HO_x, NO_x, and VOC chemistry. The model is an enhancement of this with a representation of halogen chemistry (Eastham et al., 2014; 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 ($HOI/INO_2/INO_3 \xrightarrow{sea-salt}$ IX, X=Cl, Br) and N_2O_5 ($N_2O_5 \xrightarrow{sea-salt} ClNO_2 + HNO_3$, 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 iodide concentration of 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 two 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 pre-industrial troposphere, anthropogenic 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 pmol mol^{-1} (Wang and Jacob, 1998). Emission of iodocarbons are unchanged between the pre-industrial 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). Pre-industrial emissions 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 pre-industrial 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 pre-industrial by 0.56 to reflect the anthropogenically driven increase in bromine (Liang et al., 2010; Montzka et al., 2011). We make no similar no changes to Cl_y as chlorine's impact on tropospheric O_3 has previously been shown to be insignificantly small (Sherwen et al., 2016b).

2.1 Results and Discussion

2.1.1 Changes from pre-industrial to present

Table 1 shows our estimate of halogen emissions for the pre-industrial and the present-day. Iodine, bromine and chlorine emissions increase by 50 %, 25 % and 40 %. 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 (Sherwen et al., 2016b) and an increased stratospheric flux. Chlorine emissions increase due to enhanced $\mathrm{NO_x}$ 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 emissions lead to increased concentrations of halogens in the present-day compared to the pre-industrial with global burdens of reactive inorganic halogen species increasing by 19, 42 and 18 % for $\mathrm{I_y}$, $\mathrm{Br_y}$, and $\mathrm{Cl_y}$, 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 2.9 days in the pre-industrial to 2.3 days in the present-day. This is mainly due to higher $\mathrm{NO_x}$ concentrations which enhance iodine nitrate hydrolysis (Ammann et al., 2013; Schmidt et al., 2016). Bromine lifetimes lengthen from 13.4 days in the pre-industrial to 15.2 in the present-day. This is predominantly due to the increase in $\mathrm{Br_y}$ flux from the stratosphere which is a region of low depositional loss. Inorganic chlorine lifetimes shortens from 5.3 days in the pre-industrial to 4.5 in the present-day due to the increase in methane concentrations which push $\mathrm{Cl_y}$ into HCl, which is then readily deposited.

The inclusion of halogens reduces the concentration of O_3 in both the present-day and the pre-industrial 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 in 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 pre-industrial locations (Marenco et al., 1994; Pavelin et al., 1999; Volz and Kley, 1988) and the model. Globally surface O_3 concentrations are reduced by 9.2 nmol $\mathrm{mol^{-1}}$ (37%) in the pre-industrial on inclusion of halogens (Fig. 2), making the model more consistent with observations. This reduction is largest over the oceans. Confidence in the pre-industrial 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 61 Tg in the present-day and 43 Tg in the pre-industrial (Table 2).

The O_3 budgets for the four simulations are shown in Table 2. In both the present-day and the pre-industrial the halogens are responsible for around 20 % of the O_3 destruction, with iodine dominating (66 %: 32 %: 3 % I:Br:Cl for the present-day and 69 %: 28 %: 2 % I:Br:Cl for the pre-industrial). Although chlorine concentrations have increased almost as much as iodine between the pre-industrial 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 days to 22 days in the present-day with the inclusion of halogens and from 28 days to 25 days in the pre-industrial.

Tropospheric chemistry is a highly coupled system with significant interplay between the $\mathrm{NO_x}$, $\mathrm{HO_x}$ and $\mathrm{RO_x}$ systems (Monks et al., 2015). Changes in the individual production and loss terms are relatively small but halogens reduce net O_3

production by 159 Tg yr^{-1} in the present-day and only 119 Tg yr^{-1} in the pre-industrial. In our pre-industrial 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 that it was in the pre-industrial. This is mainly due to the higher O_3 concentrations in the present-day leading to higher oceanic iodine emissions.

3 Implications

Figure 6 shows the change in tropospheric O_3 column between the pre-industrial and the present-day, with and without halogens. Consistent with previous work, the largest increases occur in the northern mid-latitudes notably over eastern North America and Asia (Lamarque et al., 2005). Halogens reduce the column change by an average of 1.6 DU. The largest halogen-driven reductions (up to 3 DU) are seen over the northern Pacific and Atlantic oceans. This is where surface O_3 concentration increase the most over the oceans leading to increases in oceanic inorganic iodine emissions, in tern giving more active O_3 destruction by iodine chemistry.

We calculate the radiative forcing caused by these changes based on previous work (Myhre et al., 2013) using a linear relationship between radiative forcing and O_3 column change (0.042 Wm^{-2} DU^{-1}). For our simulations without halogens we calculate a tropospheric ozone radiative forcing of 0.432 Wm^{-2}, close to the 0.410 Wm^{-2} found from the ACCMIP inter-comparison (Stevenson et al., 2013). Our simulations with halogens though give a radiative forcing of 0.366 Wm^{-2}. Thus, the increases in halogen chemistry associated with human activity are acting to dampen the anthropogenic radiative forcing of O_3 by 0.066 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 over-estimate tropospheric O_3 radiative forcing by $\sim$20 %. Our estimate for the reduction in tropospheric O_3 radiative forcing due to halogens is larger than the -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$_{TO3}$ is due to a combination of the increased oceanic iodine source from the increased O_3, the increase in tropospheric organo-halogens, and the increase in stratospheric halogen flux between the pre-industrial and the present-day. Removing the oceanic inorganic iodine source from the model but keeping the increase in tropospheric halocarbons and stratospheric halogen flux, gives a RF$_{TO3}$ of 0.391 Wm^{-2}. In addition to that change, using a present-day stratosphere for the preindustrial gives a RF$_{TO3}$ of 0.411 Wm^{-2}. Although the system in non-linear we thus attribute $\sim$40 % of the halogen-driven reduction in O_3 radiative forcing to the ocean-atmosphere O_3-iodine feedback, $\sim$30 % to the increase in the tropospheric halocarbons and $\sim$30 % to the increase in the flux of inorganic halogens from the stratosphere.

4 Disscussion

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, chlorine and between the different emission types 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 (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 18 % found here to 23 %.

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 ∼20% too large.

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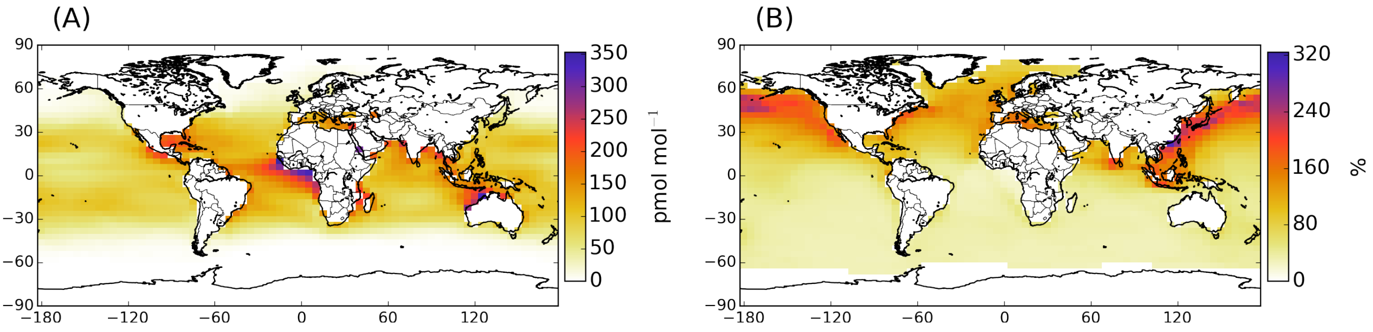

Figure 1. Inorganic emission flux (HOI, I_2) in the pre-industrial (A) and % change from the pre-industrial to present-day ((PD-PI)/PI*100) (B).

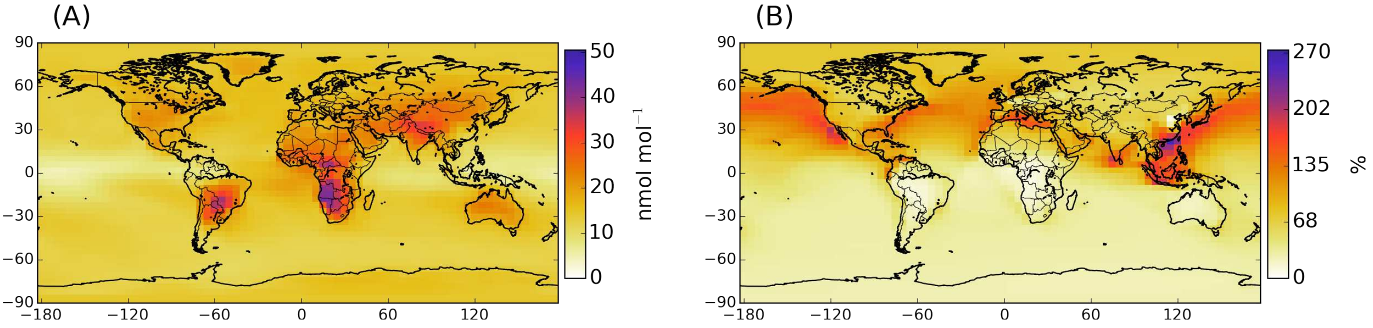

Figure 2. (A) O_3 surface concentration in the pre-industrial and (B) % change from the pre-industrial to present-day (PD-PI)/PI*100).

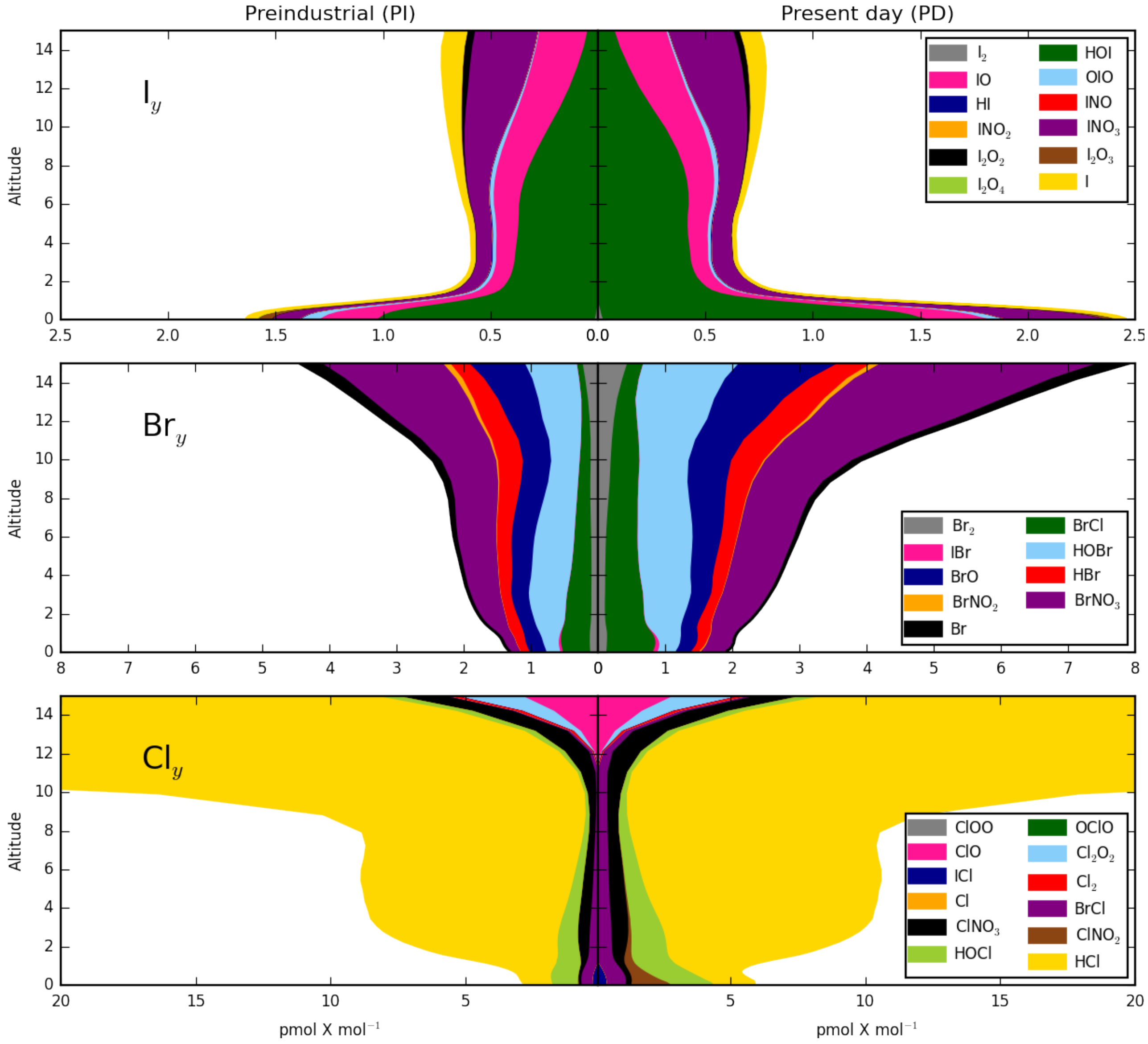

Figure 3. Global mean vertical distribution of iodine, bromine and chlorine inorganic gases (X_y, X=Cl, Br, I) for the pre-industrial (left) and present-day (right) in terms of mixing ratios of halogen. Increased halogen concentrations in the present-day are predominantly at the surface for iodine, but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

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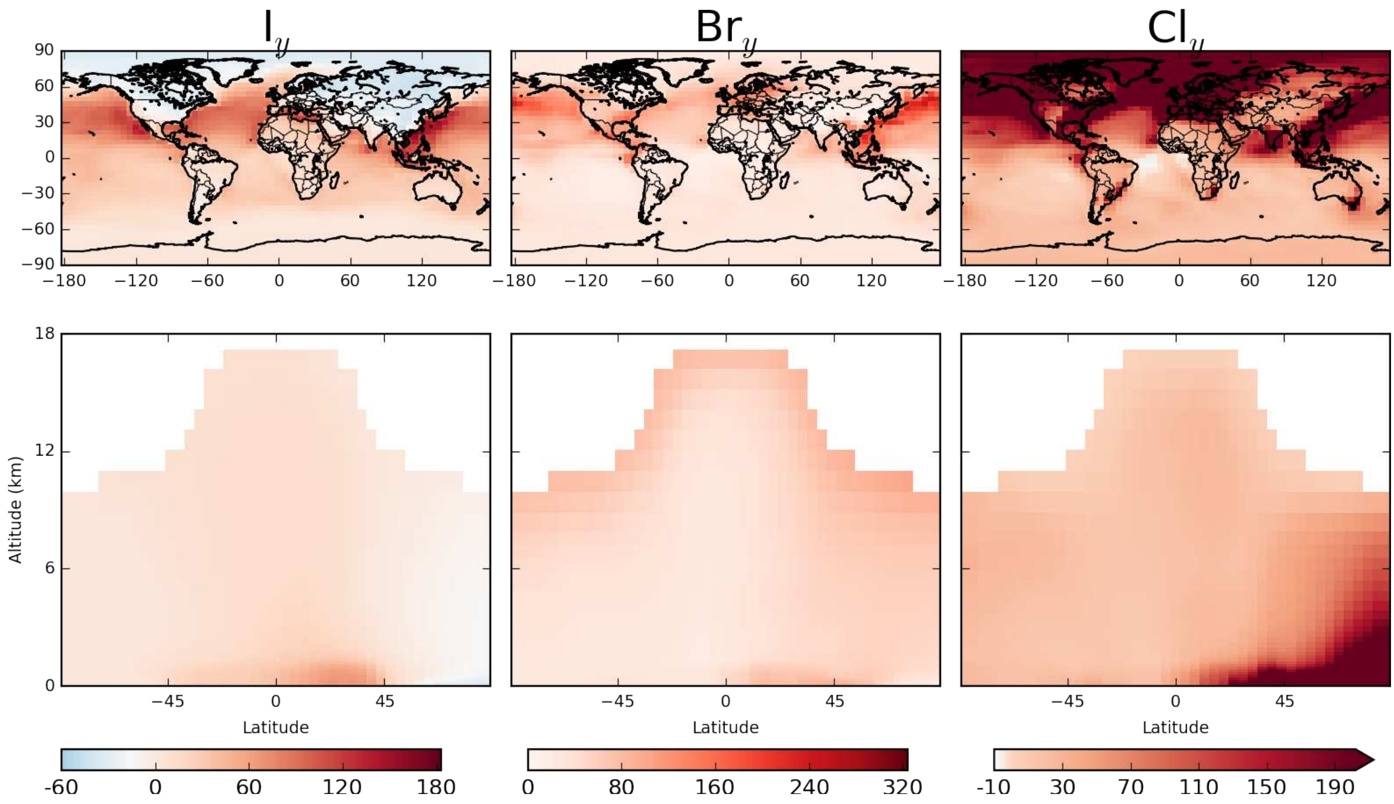

Figure 4. Percentage change from pre-industrial to present-day in tropospheric distribution of I_y, Cl_y, and Br_y ((PD-PI)/PI*100). Upper plots show surface and lower plots show zonal values. Reductions in I_y concentration over land are due to a shortening of the I_y lifetime due to enhanced $IONO_2$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

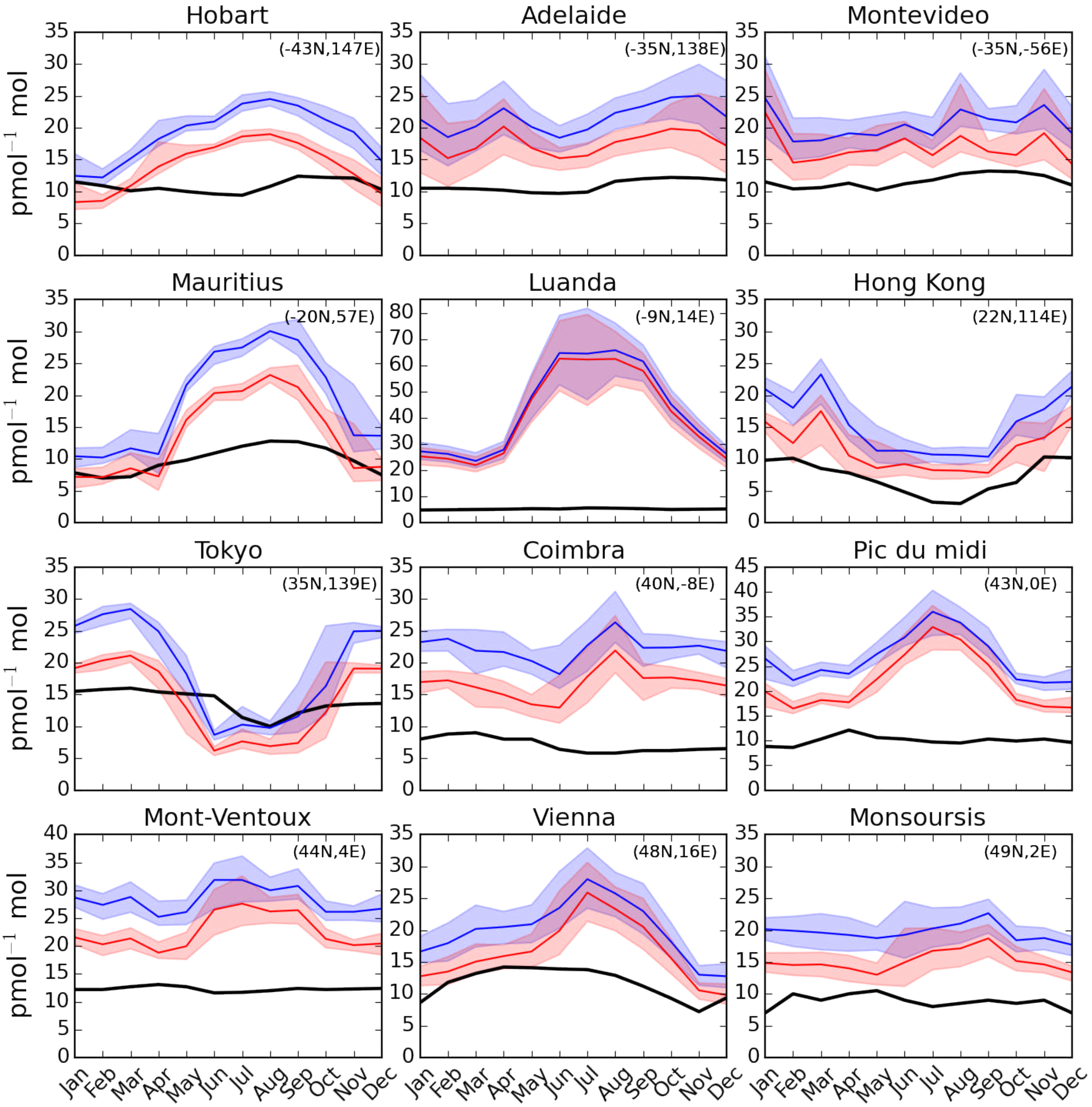

Figure 5. Comparison between observed and modelled pre-industrial monthly mean O_3. Observations are shown in black, pre-industrial model simulation with halogens in red and without halogens in blue. The shaded areas for the model simulation shows the 1^{st} and 3^{rd} quartiles in the hourly values. The O_3 data is 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).

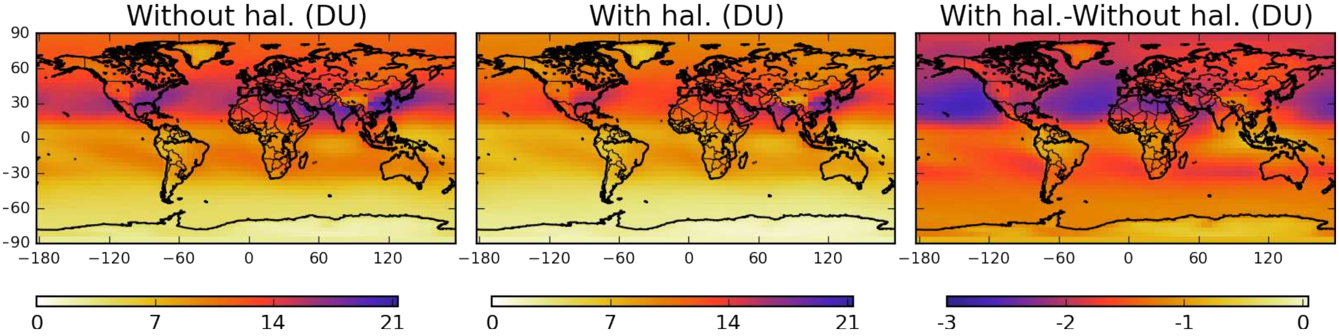

Figure 6. Increases in tropospheric O_3 column between the pre-industrial and present-day without and with halogens. Left and centre panels show the difference in annually averaged column O_3 (DU) between pre-industrial and the present-day without (left) and with halogens (centre). Right panel shows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

Table 1. Emission of halogen source gases for the pre-industrial (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 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, $ClNO_2$ 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**	**2.19**
CH_2X_2	0.33	0.33	0.09	0.09	**0.11**	**0.59**
CHX_3	-	-	0.41	0.41	**0.21**	**0.26**
HOI	1.17	2.02	-	-	-	-
I_2	0.08	0.14	-	-	-	-
IX	-	-	0.19	0.31	0.46	0.78
$ClNO_2$	-	-	-	-	0.02	0.66
Stratosphere	0.00	0.00	0.02	0.06	0.44	0.43
Total source	1.84	2.75	0.74	0.92	3.52	4.9

Table 2. Global tropospheric O_x budgets for pre-industrial 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.

	Pre-industrial	Pre-industrial	present-day	present-day
	With halogens	Without	With halogens	Without
O_3 burden (Tg)	260	303	355	416
O_x chemical sources (Tg yr^{-1})				
$NO + HO_2$	2,256	2,357	3,526	3,607
$NO + CH_3O_2$	662	668	1,327	1,316
$NO + RO_2$	423	375	524	508
Total chemical O_x sources (PO_x)	3,341	3,401	5,376	5,431
O_x chemical sinks (Tg yr^{-1})				
$O_3 + H_2O \xrightarrow{h\nu} 2OH + O_2$	1,421	1,711	2,102	2,489
$O_3 + HO_2 \rightarrow OH + O_2$	641	822	1,136	1,432
$O_3 + OH \rightarrow HO_2 + O_2$	497	601	611	737
$HOBr \xrightarrow{h\nu} Br + OH$	139	-	214	-
$HOBr + HCl \rightarrow BrCl$	13	-	28	-
$HOBr + HBr \rightarrow Br_2 + H_2O$ (aq. aerosol)	7	-	13	-
$BrO + BrO \rightarrow 2Br + O_2$	4	-	8	-
$BrO + BrO \rightarrow Br_2 + O_2$	1	-	3	-
$BrO + OH \rightarrow Br + HO_2$	8	-	9	-
$IO + BrO \rightarrow Br + I + O_2$	7	-	9	-
$ClO + BrO \rightarrow Br + ClOO/OClO$	1	-	2	-
Other bromine O_x sinks	0	-	0	-
Total bromine O_x sinks	180	-	284	-
$HOI \xrightarrow{h\nu} I + OH$	336	-	457	-
$OIO \xrightarrow{h\nu} I + O_2$	99	-	125	-
$IO + BrO \rightarrow Br + I + O_2$	7	-	9	-
$IO + ClO \rightarrow I + Cl + O_2/ ICl + O_2$	0	-	0	-
Other iodine O_x sinks	1	-	2	-
Total iodine O_x sinks	443	-	593	-
$HOCl \xrightarrow{h\nu} Cl + OH$	10	-	15	-
$CH_3O_2 + ClO \rightarrow ClOO$	3	-	4	-
$ClO + BrO \rightarrow Br + ClOO/OClO$	1	-	2	-
$ClNO_3 + HBr \rightarrow BrCl$	0	-	1	-
$IO + ClO \rightarrow I + Cl + O_2/ ICl + O_2$	0	-	0	-
Other chlorine O_x sinks	1	-	1	-
Total chlorine O_x sinks	15	-	23	-
Other O_x sinks	101	151	184	172
Total chem. O_x sinks (LO_x)	3299	3240	4933	4829
O_3 PO_x-LO_x (Tg yr^{-1})	42	161	443	602
O_3 Dry deposition (Tg yr^{-1})	545	659	832	980
O_3 Lifetime (days)	25	28	22	26
O_3 STE (PO_x-LO_x-Dry dep.) (Tg yr^{-1})	503	498	389	378