We thank anonymous reviewers #1, #2 and #3 for their positive reviews and constructive comments on our paper. We have updated the manuscript following these comments and addressed all points raised. We feel that the reviewers have improved our manuscript and are grateful for their time and contributions.

Two errors in the code have been identified following submission to ACPD (The calculation of cloud surface area and a typographic error in the representation of a bromine + VOC reaction). The conclusions of the paper are unaffected, but the magnitude of the impacts of halogen chemistry has increased slightly. For instance, the modelled decrease in the radiative forcing of tropospheric ozone on inclusions of halogens is now 25% instead of 18 %.

We now discuss individual comments below.

Reviewer #1

General comments:

During the last decade, increasing measurements of concentration and reactivity of halogenated compounds have been made. They have shown that the role of these compounds in the destruction of tropospheric ozone is more important than previously thought. The present paper of Sherwen et al. aims to quantify the radiative forcing of tropospheric ozone by considering, in addition to the chemical "classical" pathways of ozone production and loss, those involving halogenated compounds. This paper is based on a huge and consistent job done to implement the chemistry of halogenated in the GEOS-Chem model as already detailed in Sherwen et al. 2016 a and b. In the present work, the determination of the current and pre-industrial ozone concentration fields is conducted using a 3D model of chemistry transport GEOS-Chem. Whereas it is central for this study, the computation of the radiative forcing seems relatively simple (using a linear relationship between ozone column and radiative forcing) and is just mentioned in one sentence in the "involvement" part and not detailed in the methodological part. The methodological limits are not raised nor discussed. The authors, considering the ozone destruction due to halogenated compounds found an increase in tropospheric ozone since preindustrial lower than the one obtained when this chemistry is neglected. Consequently forcing of tropospheric ozone is significantly reduced, by about 20%.

The question investigated in the paper is pertinent regarding the field of study. However, several points in the methodology limit the scope of the results. Some key choices are not at all discussed. Furthermore various "shortcuts" in the rhetoric, especially in the introduction shows a misunderstanding of the purpose for which models were originally developed. The discourse justifying this work needs to be reorganized. Finally, the article has no conclusion; appearing incomplete and looking, at this stage, like an extract of publication. If the uncertainties in the current understanding of halogenated chemistry mechanisms are well discussed, it lacks a critical discussion of the other assumptions used in the modelling chain (pre-industrial emissions, calculation of radiative forcing: : :) and a discussion of the magnitude of the results found compared with the range of radiative forcing values given in the IPCC report. In conclusion, the results presented in this study are insufficiently documented and discussed in a critical way to be published in the state. Some items previously mentioned are detailed below.

We thank reviewer #2 for their comments and respond below.

Specific comments:

- The introduction states: "the fact that the models that are used to calculate radiative forcing of tropospheric O3 (RFTO3) do not contain this [halogen] 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". This point is exaggerated because
(1) the tropospheric composition is not limited to ozone;
(2) The models contain the main sources and sinks of tropospheric ozone (as also shown by your results in Table 2) so they are able to reproduce the main feature of ozone distribution as shown by
comparisons with the observation-based climatology. It does not mean that they do not need improvement like done in the present paper, but such shortcuts undermine the justification;
(3) The aim of such models is to implement the state of the art of the chemistry when it is well understood. The models do not and will probably never describe all the atmospheric chemical pathways, but they are useful tools if only considered like that. It is thus unfair to argue that models developed in the 90's were wrong to neglect processes which have been maturely understood recently.

We agree with the reviewer that we may have been overly harsh in our statements here. We have softened our language in this section.

(1) The sentence in the introduction has been updated to say "ozone and possibly composition", in line with the companion paper reporting impacts on present-day composition.
(2) A sentence has been added to highlight the chemical transport model's skill against the observational comparison when halogens are not included.
(3) This study highlights a likely decrease in tropospheric ozone change and does not overtly aim to criticise existing models that were developed prior to current understanding of halogens.

- The radiative forcing is calculated by applying a linear relationship between ozone column and radiative Forcing. This is surprising knowing the vertical gradient of RF sensitivity to ozone. It needs to be discussed.

A more detailed discussion has been added of the linear relationship and the vertical gradient of sensitivity.

- The IPCC radiative forcing or ACCMIP ozone column changes should be given with their range of uncertainty. Hence, the radiative forcing found by these authors is within the range indicated by IPCC.

This has been added to the manuscript.

- Much of the uncertainty in the ozone RF comes from the poor knowledge of natural sources (in particular for preindustrial times), we do not know the assumptions considered in this work for these preindustrial emissions. The biogenic emissions, including the crucial soil NOx are not given. The justification for considering that biomass burning is 10% of the current one has to be explained because many recent studies consider rather a 30-50% reduction (van der Werf et al. Climate of the Past 2013, Lamarque et al. ACP 2010) and even, for some of them, higher emissions than the present ones, as in the 'high fire' hypothesis of Murray et al. ACP 2013.

A table showing emissions employed in present-day and preindustrial has been added to the appendix. The uncertainties involved in pre-industrial modelling have now been highlighted notably in biomass burning. .

- Too much significant numbers in the RF given in the introduction

We have reduced the number of significant figures used.

- The figures are sometimes difficult to read/interpret due to the color palette (1, 2, 4 and 6).

The colour palette used is from a list of suggested replacements for the "jet"/"rainbow" colour bar, which has not been used here due to a growing awareness of its limitations for those with colour blindness and its propensity to give false artefacts in representation of data.

Reviewer #2

General Comments:

This modelling study nicely illustrates that including tropospheric halogen chemistry has important consequences for ozone changes since pre-industrial, and likely means that the radiative forcing from tropospheric ozone is smaller than previously thought. The scientific approach is broadly sound, although a few caveats and extra discussion points should be added (see specific comments below). In particular: whether some representation of halogen losses may have been included (inadvertently) previously in the ozone deposition to sea-water term (and whether there is a danger of double counting if this is not adjusted for); and the approximation of calculating O3 RF from a column change. These potentially add some extra uncertainties, but don't change the fundamental conclusions reached here. Somewhat unbelievably, the authors fail to include a Conclusions section. I think such a section must be added for completeness. If these revisions are included, then this paper should be acceptable for ACP.

We thank reviewer #2 for their comments and respond below.

Specific Comments:

P1 l10 from -> associated with decreases in

Updated.

P1 l22 delete comma

Updated.

P3 l19 What about anthropogenic CO emissions? Biogenic VOC? Soil NOx? Lightning NOx?

A table has been added (Table 4) to summarise emissions present in runs for clarity.

P3 l20 Reducing biomass burning emissions to 10% of their present-day values may

be what Wang and Jacob did in 1998. However, more recent studies (e.g. Knorr et al., 2016; doi:10.5194/bg-13-267-2016) suggest that biomass burning (at least wildfires) in pre-industrial times may well have been higher than present day values (less fire suppression; more vegetation). I am not suggesting you redesign and rerun your experiments, but mention any implications of uncertainty in the evolution of fire emissions.

This manuscript has been updated to acknowledge this uncertainty.

P3 l20 If you insist on using the (I believe more 'correct') way of expressing trace gas mixing ratios (i.e. pmol/mol, etc.), do get the prefixes correct. I think that pre-industrial methane was 700 ppb, or 700 nmol/mol.

Updated.

P3 l29 : : :to be zero in the pre-industrial.

Updated.

P3 l30 delete no

Updated.

P4 l6 Do you really mean Br emissions increase 'due to increased iodine driven seasalt cycling'? Or do you mean I (or halogen) emissions increase?

The statement is correct and the sentence has been updated for clarity.

P4 l7 An increased stratospheric influx of Br isn't strictly an 'emissions' increase.

Updated to use the word source.

P4 l10 Same point as above, not all 'emissions'.

Updated.

P4 l15 15.2 days

Updated.

P4 l16 shorten

Updated.

P4 l16 4.5 days

Updated.

P4 l20 in -> is

Updated.

P4 l23 Fig. 2 doesn't show the change in O3 since pre-industrial – I'm not sure the figure reference is helpful.

Figure 2 does show annual average O3 surface concentrations in the preindustrial (A) and the % increase from this value to present day (B).

P4 l27 Strictly, Table 2 shows Ox budgets (at least that's what the caption says). I think define Ox (O3 + NO2), and include the extra minor terms in Table 2 (NO2 deposition, NO2 burden, NO2+OH sink(?)), or at least clarify the (subtle) differences between an O3 budget and an Ox budget.

A definition of Ox budget has been added and a statement on why an Ox budget is being used. The Ox budget is presented in a way consistent with our companion paper on halogen's impacts in the present day.

P5 l3 that -> than

Updated.

Much of the ozone difference due to halogens over the oceans is near the surface (I think – you don't actually show a vertical profile of the ozone change). I wonder if some models previously inadvertently 'accounted' for this within the O3 deposition velocity over (sea) water? This may mean that the O3 deposition velocity over water needs reducing when halogens are included, or you risk the models double-counting this effect. It is obviously better to include it explicitly as a halogen chemistry process, but clearly we don't want to double count it. Is this possibility worth discussing?

This point - that processes might have inadvertently been considered - has been added to the conclusions, with a statement that we do not think that this effects the conclusions of the paper.

P5 l10 tern -> turn

Updated.

P5 l13 NB, using a column ozone change to calculate radiative forcing adds the approximation that you assume the vertical profile of the ozone change is the same as that in the original full calculation. If most/all of the ozone change is originating at lower levels, the real radiative forcing will be less, as the RF depends upon the temperature of the layer of the atmosphere where the ozone changes, as ozone changes in colder layers generate a larger RF. (This is why ozone changes in the very cold tropical upper troposphere generate the largest RFs.) As your O3 changes are mainly near the surface (?), this suggests that this approximate way of calculating the RF will return a higher value than if the full radiative calculations were performed. I think this should at least be mentioned.

Added a discussion of this uncertainty and added statement about location of changes in the column.

P5 l24 Related to the above point, I think the O3 RF from the stratospheric flux changes are likely underestimated, and those originating nearer the surface over-estimated, simply by using the O3 column approach.

Added a sentence to acknowledge this.

P5 l25 in -> is

Updated.

P6 l7 radiative forcing
A Conclusions section should be added. Isn't a Conclusions section almost mandatory for a scientific paper? You certainly have some, so include one! This seems a rather inexplicable omission.

A Conclusions section header has been updated.

P12 Figure 1A. The caption states this is a flux, but the units are labelled as pmol/mol. A flux must have units of mol or kg per unit time.

Updated.

P13 Figure 3. The vertical axes need units (km?)

Updated.

P14 Figure 4 caption. Zonal mean. Increase -> increased. The last 2 sentences have 5 "due to" s!

Updated.

P15 Figure 5 Units of ozone should be nmol/mol?

Updated.

P18 Table 2. How is the troposphere defined? (i.e., by PV, T-gradient, or O3 concentration?).
As mentioned earlier, clarify if you mean O3 or Ox.

The definition used for the troposphere has been added to the "model description" section. A table showing a definition of Ox has been added and the sentences clarified.

Reviewer #3

The authors present a calculation of the radiative forcing due to tropospheric ozone, using the GEOS-Chem model run with and without halogens and for present-day and pre-industrial conditions. The model runs show that halogen chemistry is more prevalent in the present-day, thus the ozone radiative forcing is significantly less when halogens are included. The paper is quite straightforward, is clearly written, with findings and conclusions quantitatively detailed. I really have no criticisms or suggestions to offer, the paper is suitable and essentially ready for publication in ACP in my opinion.

We thank reviewer #3 for their positive comments and respond below.

There are typos here and there that should be dealt with – e.g., pre-industrial methane (page 3, line 20) should be 700 nmol mol^-1.

Updated.

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~~ preindustrial 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 likely more active in the ~~present-day~~ present day than in the ~~pre-industrial~~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 ~~pre-industrial~~ preindustrial to present-day increases in the tropospheric O_3 burden of 113 Tg without halogens but only ~~95~~ 90 Tg with, leading to a reduction in RF_{TO3} from ~~0.432 to 0.366~~ 0.43 to 0.35 Wm^{-2}. We attribute $\sim$~~40~~50% of this reduction to increased bromine flux from the stratosphere, $\sim$35% to the ocean-atmosphere iodine feedback ~~, $\sim$30% to increased anthropogenic halogens in the troposphere~~ and $\sim$~~30~~15% to increased ~~bromine flux from the stratosphere~~tropospheric sources of anthropogenic halogens. This reduction of ~~RF_{TO3} (0.066~~ tropospheric O_3 radiative forcing due halogens (0.087 Wm^{-2}) is greater than that from ~~stratospheric ozone~~ the radiative forcing of stratospheric O_3 ($\sim$0.05 Wm^{-2}). Estimates of RF_{TO3} that fail to consider halogen chemistry are likely overestimates ($\sim$~~20~~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 ~~(Parrella et al., 2012; Saiz-Lopez et al., 2012a, 20 The fact that the models that~~ (Read et al., 2008; Volkamer et al., 2015; Wang et al., 2015). Models that are used to calculate radiative forcing of tropospheric O_3 (RF_{TO3}) 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) ~~raises questions over their ability to reproduce tropospheric composition as more and more~~ 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., concerns grow~~.

Tropospheric O_3 is a climate gas and a potent air pollutant. Understanding the change in its concentration from the "natural" ~~pre-industrial~~ preindustrial (∼1750) atmosphere to the ~~present-day,~~ 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~~ 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 ~~pre-industrial and the present-day~~ 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)~~, which concluded that pre-industrial~~. This concluded that preindustrial tropospheric O_3 burdens were 98 Tg lower than the ~~present-day~~ present day and estimated a RF_{TO3} of ~~0.410~~ 0.41 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, ~~the emphasis for tropospheric chemistry has been on improving the representation of organic chemistry with~~ 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). ~~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~~ 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

5 shown previously ~~(Eastham et al., 2014; Schmidt et al., 2016; Sherwen et al., 2016a, b)~~(Bell et al., 2002; Eastham et al., 2014; Parrella et al. 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~~ 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.

10 ## 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

15 previous work (Abbatt et al., 2012; Braban et al., 2007; Ammann et al., 2013; Sherwen et al., 2016a). Short lived organo-halogens (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

20 ($HOI/INO_2/INO_3 \xrightarrow{sea-salt} IX$, 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.,

25 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~~ preindustrial 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~~

30 nmol mol^{-1} (Wang and Jacob, 1998). A summary of changes to base emissions from present day are given in Table 4 and described in detail on the GEOS-Chem website (www.geos-chem.org). Uncertainties in pre-industrial 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, however 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. Emission of iodocarbons are unchanged between the ~~pre-industrial and the present-day~~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~~ present day to 5 pmol mol^{-1} to match ice core records (Saltzman et al., 2004). ~~Pre-industrial emissions~~ 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 ~~pre-industrial and the present-day~~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 ~~pre-industrial~~ preindustrial 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 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 ~~pre-industrial~~ preindustrial to present

Table 1 shows our estimate of halogen emissions for the ~~pre-industrial and the present-day~~preindustrial and the present day. Iodine, bromine and chlorine ~~emissions~~ sources increase by 50 %, ~~25 % and 40 %~~ 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 ~~emissions~~ sources lead to increased concentrations of halogens in the ~~present-day~~ present day compared to the ~~pre-industrial~~ preindustrial with global burdens of reactive inorganic halogen species increasing by ~~19, 42 and 18~~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 ~~2.9~~3.0 days in the ~~pre-industrial~~ preindustrial to 2.3 days in the ~~present-day~~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 ~~13.4~~16.4 days in the ~~pre-industrial to 15.2 in the present-day~~preindustrial to 18.2 days in the present day. This is predominantly due to the increase in Br_y ~~flux~~ source from the stratosphere which is a region of low depositional loss. Inorganic chlorine lifetimes ~~shortens from 5.3~~ shorten from 6.1 days in

4

the ~~pre-industrial to 4.5 in the present-day~~ 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.

The inclusion of halogens reduces the concentration of O_3 in both the ~~present-day and the pre-industrial~~ present day and the preindustrial simulations. The O_3 simulated in the ~~present-day~~ present day (see Fig. 12 in Sherwen et al. 2016b) appears to be more consistent with observations when halogen chemistry ~~in~~ 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 ~~pre-industrial~~ preindustrial locations (Marenco et al., 1994; Pavelin et al., 1999; Volz and Kley, 1988) and the model. ~~Globally~~ Both with and without halogen chemistry the model simulates significantly lower O_3 concentrations in the pre-industrial but the addition of halogens reduces globally averaged surface O_3 concentrations ~~are reduced by 9.2~~ by 8.8 nmol mol^{-1} (~~37%) in the pre-industrial on inclusion of halogens~~ 39%) (Fig. 2), making the model more consistent with observations. This reduction is largest over the oceans. Confidence in the ~~pre-industrial~~ 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 ~~61~~ 77 Tg in the ~~present-day and 43~~ present day and 54 Tg in the ~~pre-industrial~~ preindustrial (Table 3).

~~The~~ 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 pre-industrial~~ present day and the preindustrial the halogens are responsible for around 20 % of the O_3 destruction, with iodine dominating (~~66 %: 32 %: 3~~ 57 %: 49 %: 4 % I:Br:Cl for the ~~present-day and 69 %: 28 %: 2~~ present day and 61 %: 36 %: 4 % I:Br:Cl for the ~~pre-industrial~~preindustrial). Although chlorine concentrations have increased almost as much as iodine between the ~~pre-industrial~~ preindustrial and the present, it plays little role in determining O_3 loss ~~(Schmidt et al., 2016; Sherwen et al., 2016a, b)~~(Schmidt et al., 2016; Sherwen et al., 2016a, b). Tropospheric O_3 lifetimes drop from 26 days to 22 days in the ~~present-day~~ present day with the inclusion of halogens and from 28 days to ~~25~~ 24 days in the ~~pre-industrial~~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 ~~159~~ 194 Tg yr^{-1} in the ~~present-day and only 119~~ present day and 145 Tg yr^{-1} in the ~~pre-industrial~~preindustrial. In our ~~pre-industrial~~ 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 that~~ present day than 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.~~ preindustrial.

3   Implications

Figure 6 shows the change in tropospheric O_3 column between the ~~pre-industrial and the present-day~~preindustrial 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 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 concentration increase the most over the oceans leading to increases in oceanic inorganic iodine emissions, 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 unit O_3 column within a range of models (Stevenson et al., 2013; Fry et al., 2012; Gauss and they calculate values of NRF of in the range 36 - 42 mW m^{-2} DU^{-1}. Here we use the the most recent value Stevenson et al. (2013) calcu NRF (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 inter-comparison (Stevenson et al., 2013) and within the range reported by IPCC (+0.40 ($\pm$0.2) Wm^{-2}, Myhre et al. 2013). Our simulations with halogens though give a significantly lower radiative forcing of 0.345 Wm^{-2}. Thus, the increases in halogen chemistry associated with human activity are acting to dampen the anthropogenic radiative forcing of O_3 by 0.087 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 Wm^{-2} 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$_{TO3}$ 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 preindustrial 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 0.374 Wm^{-2}. In addition to that change, using a present-day stratosphere for the preindustrial gives a RF$_{TO3}$ of 0.389 Wm^{-2}. Although the system is non-linear we thus attribute $\sim$50 % to the increase in the flux of inorganic halogens from the stratosphere, $\sim$35 % of the halogen-driven reduction in O_3 radiative forcing to the ocean-atmosphere O_3-iodine feedback and $\sim$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, chlorine and between the different emission ~~types~~ 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 ~~(Sherwen et al., 2016b)~~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 ~~18~~ 25 % found here to ~~23 %.~~ 34 %. There is also a question as to whether models have some aspects of this 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, however 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~~ 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 $\sim$~~20~~25% too large.

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

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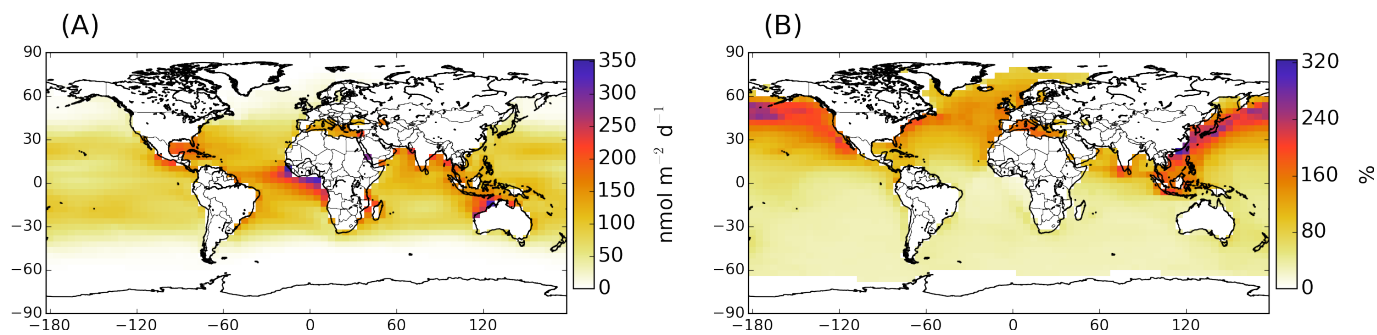**Figure 1.** Inorganic emission flux (HOI, I$_2$) in the ~~pre-industrial~~ preindustrial (A) and % change from the ~~pre-industrial~~ preindustrial to ~~present-day~~ present day ((PD-PI)/PI*100) (B).
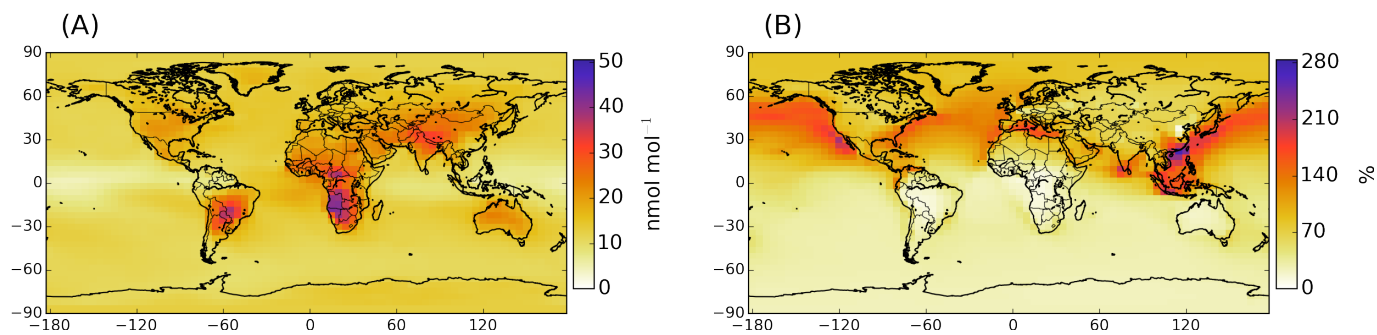
Figure 2. (A) O$_3$ surface concentration in the ~~pre-industrial~~ preindustrial and (B) % change from the ~~pre-industrial~~ preindustrial to ~~present-day~~ present day ((PD-PI)/PI*100).

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

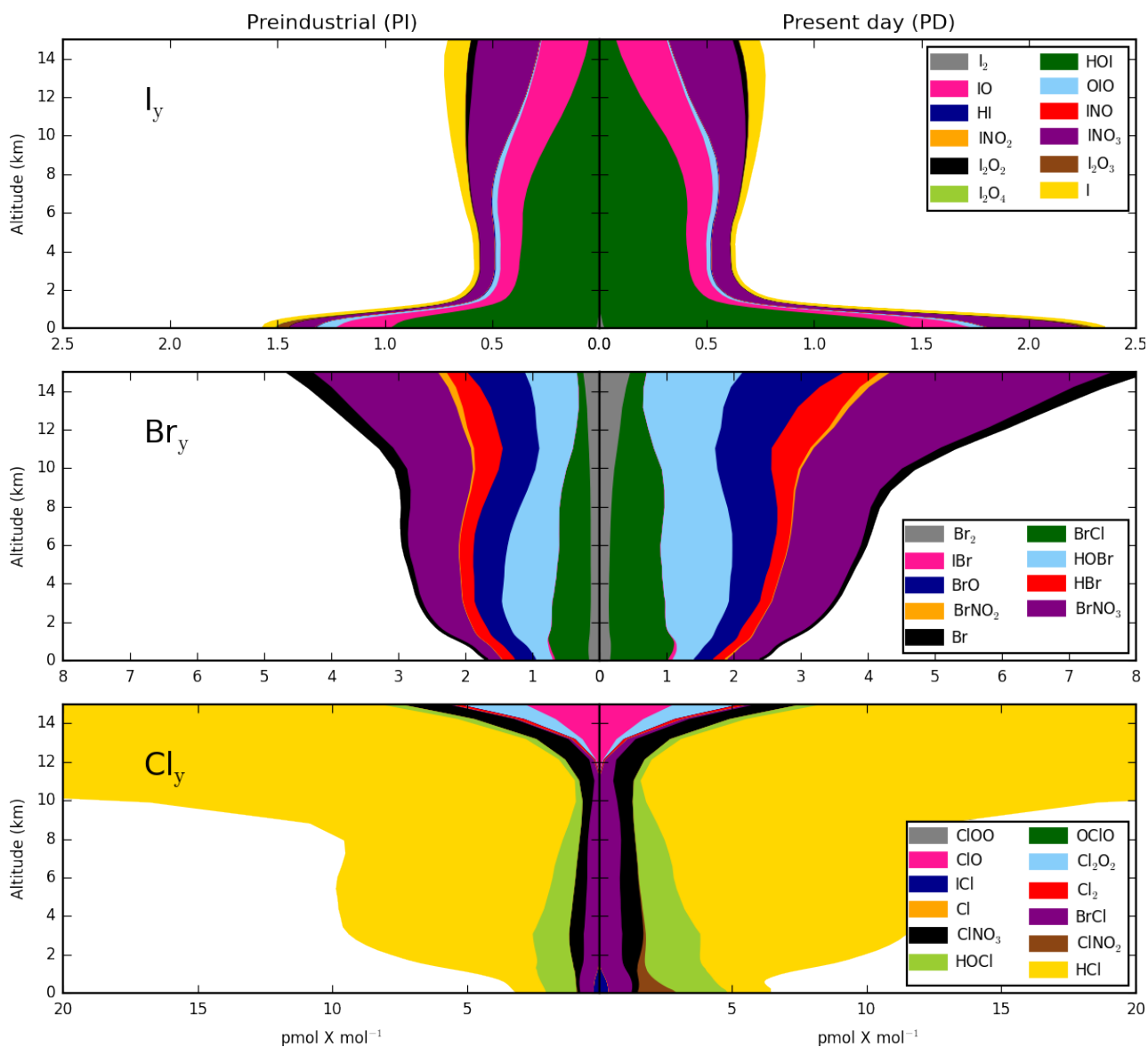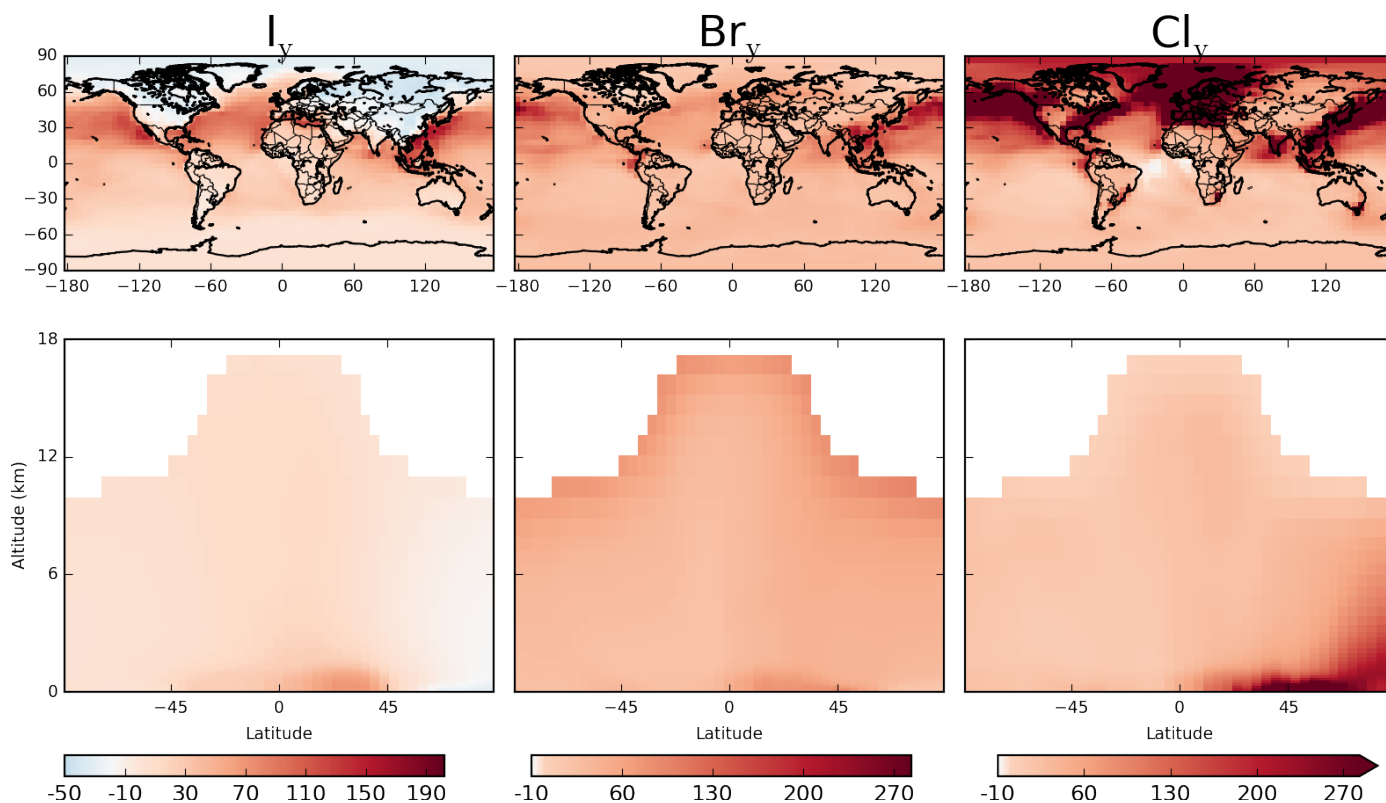**Figure 4.** Percentage change from ~~pre-industrial~~ preindustrial to ~~present-day~~ present day in tropospheric distribution of I_y, Cl_y, and Br_y ((PD-PI)/PI*100). Upper plots show surface and lower plots show zonal values. Reductions in I_y concentration over land are due to a shortening of the I_y lifetime due to enhanced $IONO_2$ hydrolysis due to increase NO_x emissions in the ~~present-day~~present day. Increases in surface Cl_y are due to increased release of $ClNO_2$ ~~due~~ attributable to higher N_2O_5 concentrations in ~~present-day~~present day
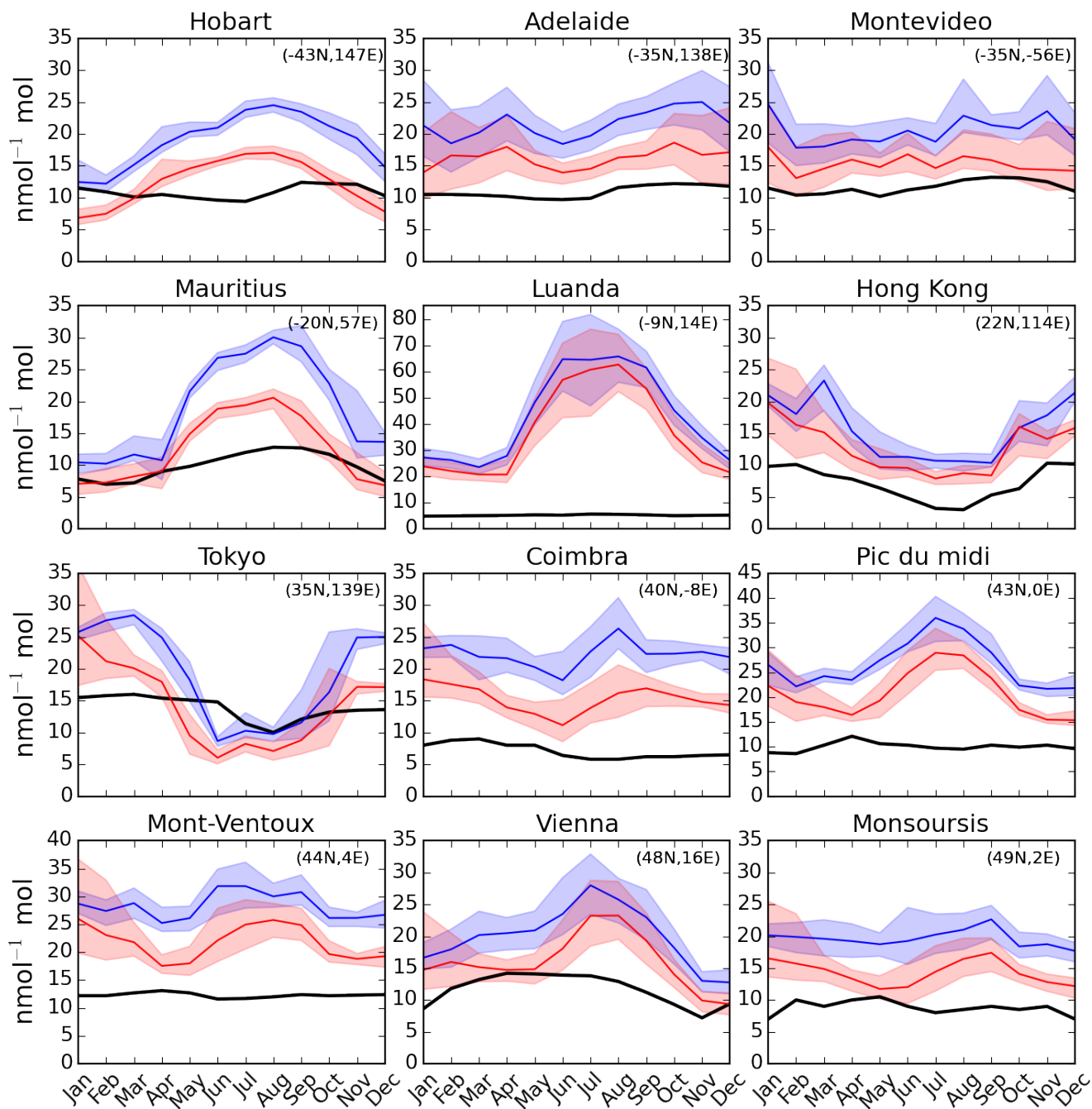
Figure 5. Comparison between observed and modelled ~~pre-industrial~~ preindustrial monthly mean O_3. Observations are shown in black, ~~pre-industrial~~ preindustrial model simulation with halogens in red and without halogens in blue. The shaded areas for the model simulation shows the 1st and 3rd quartiles 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~~ preindustrial and ~~present-day~~ present day without and with halogens. Left and centre panels show the difference in annually averaged column O_3 (DU) between ~~pre-industrial~~ preindustrial and the ~~present-day~~ present day without (left) and with halogens (centre). Right panel shows the difference.

Table 1. Emission of halogen source gases for the ~~pre-industrial~~ preindustrial (PI) and ~~present-day~~ present day (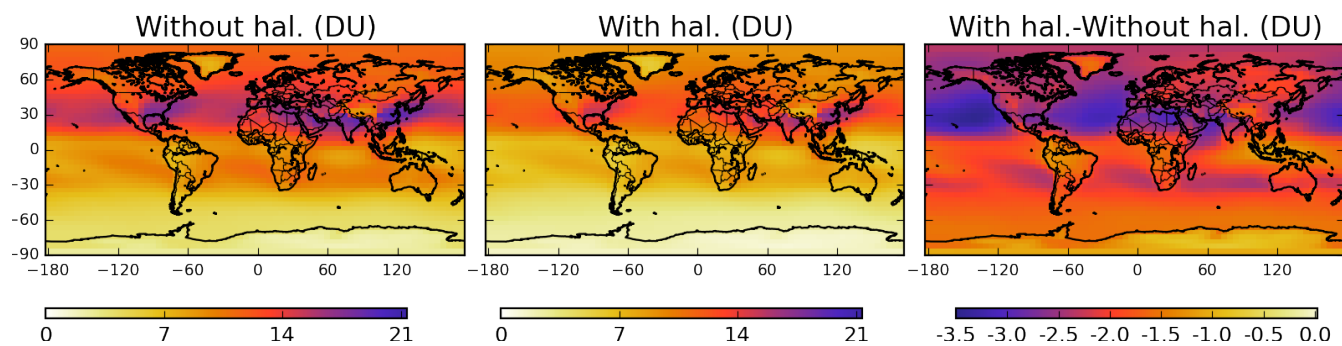PD). Long lived sources which have fixed concentrations in the model for Cl (CH_3Cl, CH_2Cl_2, $CHCl_3$) and Br ($CHBr_3$) are shown in terms of chemical release (e.g. reaction with +OH, +$h\nu$, +Cl) and are in in bold. I_2 and HOI are the inorganic ocean source from O_3 reacting with oceanic iodide (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.

Sources	I PI	(Tg I yr^{-1}) PD	Br PI	(Tg Br yr^{-1}) PD	Cl PI	(Tg Cl yr^{-1}) PD
CH_3X	0.26	0.26	**0.04**	**0.06**	**2.28**	**~~2.19~~2.10**
CH_2X_2	0.33	0.33	0.09	0.09	**0.11**	**~~0.59~~0.57**
CHX_3	-	-	0.41	0.41	**0.21**	**~~0.26~~0.25**
HOI	~~1.17~~1.09	~~2.02~~1.97	-	-	-	-
I_2	0.08	0.14	-	-	-	-
IX	-	-	0.19	~~0.31~~0.30	0.46	~~0.78~~0.73
$ClNO_2$	-	-	-	-	0.02	~~0.66~~0.65
Stratosphere	0.00	0.00	~~0.02~~0.00	0.06	0.44	0.43
Total source	~~1.84~~1.76	~~2.75~~2.70	0.74	~~0.92~~0.91	3.52	4.9

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)

Table 3. Global tropospheric O_x (defined in Table 2) budgets for ~~pre-industrial~~ preindustrial and ~~present-day~~ 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~~ Preindustrial	~~Pre-industrial~~ Preindustrial	~~present-day~~ Present day	~~present-day~~ Present day
	With halogens	Without	With halogens	Without
O_3 burden (Tg)	~~260~~ 249	303	~~355~~ 339	416
O_x chemical sources (Tg yr^{-1})				
NO + HO$_2$	~~2,256~~ 2218	~~2,357~~ 2357	~~3,526~~ 3436	~~3,607~~ 3607
NO + CH$_3$O$_2$	~~662~~ 652	668	~~1,327~~ 1288	~~1,316~~ 1316
NO + RO$_2$	~~423~~ 388	375	~~524~~ 525	508
Total chemical O_x sources (PO$_x$)	~~3,341~~ 3341	~~3,401~~ 3401	~~5,376~~ 5249	~~5,431~~ 5431
O_x chemical sinks (Tg yr^{-1})				
O$_3$ + H$_2$O $\xrightarrow{h\nu}$ 2OH + O$_2$	~~1,421~~ 1350	~~1,711~~ 1711	~~2,102~~ 1997	~~2,489~~ 2489
O$_3$ + HO$_2$ $\rightarrow$ OH + O$_2$	~~641~~ 600	822	~~1,136~~ 1061	~~1,432~~ 1432
O$_3$ + OH $\rightarrow$ HO$_2$ + O$_2$	~~497~~ 459	601	~~611~~ 562	737
HOBr $\xrightarrow{h\nu}$ Br + OH	~~139~~ 188	-	~~214~~ 285	-
HOBr + HCl $\rightarrow$ BrCl	~~13~~ 27	-	~~28~~ 54	-
HOBr + HBr $\rightarrow$ Br$_2$ + H$_2$O (aq. aerosol)	~~7~~ 12	-	~~13~~ 22	-
BrO + BrO $\rightarrow$ 2Br + O$_2$	~~4~~ 8	-	~~8~~ 13	-
BrO + BrO $\rightarrow$ Br$_2$ + O$_2$	~~1~~ 3	-	~~3~~ 4	-
BrO + OH $\rightarrow$ Br + HO$_2$	~~8~~ 11	-	~~9~~ 12	-
IO + BrO $\rightarrow$ Br + I + O$_2$	~~7~~ 9	-	~~9~~ 11	-
ClO + BrO $\rightarrow$ Br + ClOO/OClO	~~1~~ 3	-	~~2~~ 4	-
Other bromine O_x sinks	0	-	0	-
Total bromine O_x sinks	~~180~~ 261	-	~~284~~ 405	-
HOI $\xrightarrow{h\nu}$ I + OH	~~336~~ 322	-	~~457~~ 438	-
OIO $\xrightarrow{h\nu}$ I + O$_2$	~~99~~ 112	-	~~125~~ 140	-
IO + BrO $\rightarrow$ Br + I + O$_2$	~~7~~ 9	-	~~9~~ 11	-
IO + ClO $\rightarrow$ I + Cl + O$_2$/ ICl + O$_2$	~~0~~ 1	-	~~0~~ 1	-
Other iodine O_x sinks	1	-	2	-
Total iodine O_x sinks	443	-	~~593~~ 591	-
HOCl $\xrightarrow{h\nu}$ Cl + OH	~~10~~ 18	-	~~15~~ 27	-
CH$_3$O$_2$ + ClO $\rightarrow$ ClOO	~~3~~ 4	-	~~4~~ 6	-
ClO + BrO $\rightarrow$ Br + ClOO/OClO	~~1~~ 3	-	~~2~~ 4	-
ClNO$_3$ + HBr $\rightarrow$ BrCl	0	-	~~1~~ 2	-
IO + ClO $\rightarrow$ I + Cl + O$_2$/ ICl + O$_2$	~~0~~ 1	-	~~0~~ 1	-
Other chlorine O_x sinks	1	-	1	-
Total chlorine O_x sinks	~~15~~ 28	-	~~23~~ 40	-
Other O_x sinks	101	151	184	172
Total chem. O_x sinks (LO$_x$)	~~3299~~ 3259	3240	~~4933~~ 4841	4829
O_3 PO$_x$-LO$_x$ (Tg yr^{-1})	~~42~~ 16	161	~~443~~ 408	602
O_3 Dry deposition (Tg yr^{-1})	~~545~~ 520	659	~~832~~ 799	980
O_3 Lifetime (days)	~~25~~ 24	28	22	26
O_3 STE (PO$_x$-LO$_x$-Dry dep.) (Tg yr^{-1})	503	498	~~389~~ 391	378

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, aersols	(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 fertilizer emissions
Global ship NO_x	NO	(Wang et al., 2008)	✓	✗

Table footnote: VOCs=Volatile organic carbon, see reference for details.