

## ***Interactive comment on “Halogen chemistry reduces tropospheric O<sub>3</sub> radiative forcing” by T. Sherwen et al.***

**T. Sherwen et al.**

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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 %.

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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

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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 O<sub>3</sub> (RFTO<sub>3</sub>) 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

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composition”, inline 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 NO<sub>x</sub> 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. .

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- 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” colourbar, 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 I10 from -> associated with decreases in

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Updated.

P1 I22 delete comma

Updated.

P3 I19 What about anthropogenic CO emissions? Biogenic VOC? Soil NO<sub>x</sub>? Lightning NO<sub>x</sub>?

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

P3 I20 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 wild-fires) 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 I20 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 I29 : : :to be zero in the pre-industrial.

Updated.

P3 I30 delete no

Updated.

P4 I6 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 I7 An increased stratospheric influx of Br isn't strictly an 'emissions' increase.

Updated to use the word source.

P4 I10 Same point as above, not all 'emissions'.

Updated.

P4 I15 15.2 days

Updated.

P4 I16 shorten

Updated.

P4 I16 4.5 days

Updated.

P4 I20 in -> is

Updated.

P4 I23 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 I27 Strictly, Table 2 shows Ox budgets (at least that's what the caption says). I think define Ox ( $O_3 + NO_2$ ), and include the extra minor terms in Table 2 ( $NO_2$  deposition,  $NO_2$  burden,  $NO_2+OH$  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 statement on why an ox budget is being

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used. Ox budget is present in a way consistent with companions paper on halogen's impacts in the present day.

P5 I3 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 O<sub>3</sub> deposition velocity over (sea) water? This may mean that the O<sub>3</sub> 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 and statement that we do not think that this effects the conclusions of the paper.

P5 I10 tern -> turn

Updated.

P5 I13 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 O<sub>3</sub> 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.

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

P5 I24 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 I25 in -> is

Updated.

P6 I7 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.

The 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 concen-

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tration?). 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<sup>-1</sup>.

Updated.

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Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-688, 2016.

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