

## **Response to the Referees**

### **A negative feedback between anthropogenic ozone pollution and enhanced ocean emissions of iodine**

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We are grateful to Dr. Sander and to the anonymous Referee#1 for their constructive comments and for their appreciation of our work. Also, we would like to thank the interest on our work shown by the editor. Herein we address point-by-point the different suggestions (Referee Comment- RC in bold letters, Authors Comment- AC). Besides these responses, please note that in the new version of the manuscript the reference to the work of Saiz-Lopez et al. 2014 has been updated.

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**Referee: R. Sander**

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**RC:**

**Prados-Roman et al. investigate the feedback between anthropogenic ozone and marine iodine emissions. The study is very interesting and I recommend publication in ACP after considering my suggestions as described below.**

**My only major scientific concern is the question if surface iodide will remain constant in the future. If ozone levels continue to increase, and the oxidation of surface iodide by ozone also becomes faster, will this lead to a depletion of surface iodide? As far as I can see, the model calculates iodide as a function of temperature only. How fast is surface iodide replenished? How would the results change if the concentration of surface iodide decreases in the future?**

**AC:**

We appreciate Dr. Sander's comments on our past vs. present modelling exercise. Indeed as the referee points out, predictions into the future are somehow complicated to address. Although future trends fall out of the scope of our manuscript, we understand that they are the logical progression from our work and they do deserve a whole separate study. Among changes in tropospheric ozone, there are indeed many parameters with an uncertain future trend such as the sea surface temperature (SST) or the wind speed and wind stress (IPCC) that may also affect the concentration of iodide. Further combined field and laboratory work and modelling studies would be needed to establish a future trend not only on those parameters but also on their geochemical coupling. Hopefully manuscripts like this encourage the scientific community to combine efforts towards that direction.

Regarding the model's treatment of the iodide content in sea-water, as detailed in Sect. 2.2, it is indeed computed only as a function of SST. As the ocean component of CESM is not coupled with the atmosphere model CAM (identical SST and sea-ice conditions are used for Present-Day (PD) and Pre-Industrial (PI) times), we do not compute aqueous iodide concentrations nor depletion or replenishing rates on the oceans. As detailed in the manuscript, the assumed iodide concentration in the model is always obtained by means of the SST parameterised formulations given by MacDonald et al. (2014), yielding annual average concentrations that lie within the range of the sparse measured values reported in literature (Chance et al., 2014). Projecting scenarios of aqueous iodide concentration into the future (or for the past) only by means of a SST dependent function should be done with caution, as other quantities (such as acidity, replenishing rates, etc.) could also affect its temporal evolution. But until new findings are

obtained, the parameterisations of Chance et al. (2014) and MacDonald et al. (2014) allow us to obtain a first order estimate of the impact of SST on the oceanic emissions of inorganic iodine.

**RC:**

**Minor remarks**

- **Page 21918, line 22: You write that the main sinks for ozone include “dissociation”. What is meant by this?**

**AC:**

We mean “photo-dissociation” into O<sub>2</sub> and O(<sup>1</sup>D). In the new manuscript “photo” is added.

**RC:**

- **You define ISG as “inorganic iodine source gases”. What does the “I” stand for? Why not IISG?**

**AC:**

“I” in “ISG” stands for “inorganic” in contraposition to “organic” iodine source gases mentioned earlier on in the section and follows the nomenclature of Prados-Roman et al., 2014 (acpd-14-22217-2014). Since the manuscript focuses only on iodine substances we consider adding “I” to “ISG” unnecessary.

**RC:**

- **Methods section: I think it would be good to mention CESM here as well.**

**AC:**

In the new manuscript we have now explicitly indicated that CAM-Chem belongs to the CESM framework (Sect. 2).

**RC:**

- **Page 21920, line 16: What is a “24 h annual average”? Are you averaging over a day or over a year?**

**AC:**

Our results are averaged over the 24 h of each day during the whole year. In fact the “24 h” prefix is useful when comparing annual averages obtained for only daytime, night-time or overall output. As these types of comparisons are not presented in this work, we have decided to remove “24 h” (Sect. 2.1) to avoid confusion.

**RC:**

- **Eqn. (2): Add square brackets to iodide in the last term.**

**AC:**

Added in the new manuscript.

**RC:**

- **At several places in the text, you use the term “ozone loss” even though you refer to a scenario with increased ozone concentrations. This is confusing. I think it would be better to use the expression “ozone destruction rate” in these cases.**

**AC:**

Thank you for noticing the misleading phrasing. We have included the term “rate” in the title of Sect. 3.2 as well as in Page 21925 line 22.

**RC:**

- **Page 21926, line 1: Change “bugfet” to “budget”.**

AC:  
Corrected.

**RC:**

- **The section 3.4 “Geochemical feedback mechanism” does not describe anything new. Rather, it summarizes the text from the previous sections. I suggest to move this text into the conclusions.**

AC:

We appreciate Dr. Sander’s opinion. Nevertheless the establishment of the feedback mechanism between the anthropogenic increase of tropospheric ozone and the enhanced emission of ISG from the oceans is in fact one of the main results of our study. Therefore we consider the mechanism itself deserves a separate section as appears in the manuscript.

**RC:**

- **In the acknowledgements, you mention that data supporting this article can be requested from the corresponding author. I think it would be much better if these data are included in the electronic supplement of the paper. I often had problems getting data for older papers because the authors could not be reached anymore. Putting the data into the supplement, however, they will be permanently archived together with the main article.**

AC: For a global modeling exercise like this, we think it would be unmanageable to include tables with 3-D data from all variables across the global domain. Therefore, we maintain that specific data can be provided to the interested reader upon request.

**RC:**

- **Fig. 1: Is this plot for a specific longitude or averaged?**

AC:

It refers to an average in longitude (i.e., zonal average). In the new manuscript this is now mentioned in the caption of the figure.

**RC:**

- **Fig. 6: I think that a multicolored pie-chart with a 3D effect is an overkill for presenting just 5 numbers. In my opinion, a small table would have been sufficient.**

AC:

We appreciate Dr. Sander’s opinion. If we were only indicating numbers, we would agree with him. However we are not only providing numbers but also indicating the relevance of each ozone depleting family. We consider a pie-chart the best way of remarking the fact that IO<sub>x</sub> is actually the 2<sup>nd</sup> strongest ozone depleting family. Thus we’d rather keep the pie-chart instead of using a plain table where only numbers could be read without being in context to each other.

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### **Anonymous Referee #1**

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**RC:**

**Prados-Roman et al. present an interesting progression of the topic on inorganic iodine emissions driven by the reaction between iodide and ozone at the sea surface. They attractively illustrate that sea-surface reactions between ozone and iodide may have resulted in substantial changes in the destruction of tropospheric ozone since pre-**

**industrial times and that inorganic iodine flux to the atmosphere has also altered considerably. This modeling exercise is concisely and clearly presented and the important points are generally well argued. My main concern with the paper is the limited acknowledgement of the levels of uncertainty inherent in the model and interpretation of it's output.**

AC:

We are grateful to Referee #1 for his/her comments. We proceed to address the reviewer concerns point-by-point.

RC:

**Specific points:**

**1. The manuscript would benefit from a more comprehensive assessment of the uncertainty in their interpretation in several areas, moreover, this uncertainty should be expressed in the values presented for increased ISG emissions, increased rates of ozone loss and the overall impact on radiative forcing. MacDonald et al. 2014 carried out some sensitivity analyses of their model parameterizations and a similar assessment of the robustness of the results of this model is needed.**

AC:

Although the model and the input parameters used are based on the state-of-the-art knowledge of the different compounds and processes involved in the ocean-atmosphere system, as the referee points out the modelling exercise we present- as any other modelling exercise- is linked to uncertainties. Note however that, although the magnitude of the changes in the tropospheric ozone budget or in the fluxes of ISG might be affected by those uncertainties, the establishment of the geochemical feedback describe in our study mechanism (i.e., the increase in tropospheric ozone since PI has yielded an increase emission of ISG from the oceans and this an acceleration of the ozone loss rate) is not. This paper intends to provide a hypothesis about a geochemical feedback that stills needs to be experimentally confirmed and its uncertainties further constrained by observations. Once this is said, we understand the referee's concerns regarding the degree of uncertainties and approximations assumed for the oceanic emissions of inorganic iodine. But as mentioned above, the parameterisation of the ISG fluxes based on the experimental work presented by Carpenter et al. (2014) and MacDonald et al. (2014) is, to our knowledge, the best proxy and therefore that is the one we have used in our work. Thus, we believe that the feedback mechanism and main implications presented in this work are fairly reliable. This is inherent for many other chemical, oceanic and meteorological components of chemistry-climate models which sometimes include very simplified expressions to represent extremely complex processes. Anyhow, it is worth implementing mathematical expressions that, even when approximated or simplified, allow us to represent a process "on-line" by means of other variables which are strongly constrained and coupled. This is the case for the implementation of the parameterised expression of the ISG flux (Eqs. (1)-(4)), which should be taken as a first order approximation to the real process in the atmosphere. In this way, shifting from a previous CAM-Chem setup imposing an additional ISG from a boundary condition file to this new version with an "on-line" estimation of the iodine sources, constitutes a step forward improving the knowledge upon possible geochemical-feedbacks required to understand the past-present-future evolution of the Earth-atmosphere system.

**Amongst this uncertainty are:**

**1.1 The relationship between iodide and sea-surface temperature used in Equation 4. While the recent papers by Chance et al. 2014 and Macdonald et al. 2014 found temperature to provide the best predictions of iodide concentration on a global scale, temperature explained at best, only 50 % of the variability in observed iodide. The authors acknowledge this to some extent (P21921, L 17+). It would be**

**useful to understand how variability of this magnitude would alter model predictions of ISG emission, etc and the authors' conclusions.**

AC:

As demonstrated by Chance et al. (2014) and MacDonald et al. (2014) and as stated also by the referee, SST is the best proxy for the parameterisation of the iodide concentration. Indeed, in the work MacDonald et al. (2014) the authors attribute a 50% uncertainty to the parameterization of sea surface iodide based on SST and, as the authors explained in the discussion part of their study “this parameterisation suffers from the scarce measurements reported in the literature and the lack of seasonal or long term studies”. Nevertheless, as we mentioned in Sect. 2.2 and also in the caption of Fig. 1, our modelled iodide concentrations agree with the measurements summarised in the more recent work of Chance et al. (2014) not only in values but also reproducing the variability of those measurements (see, for instance, our Fig. 1 and the measurements on open ocean shown in Fig. 3 of Chance et al. (2014)). Hence we feel confident on the ISG flux levels and on their geographical distribution reproduced in our work.

**1.2. The level of understanding of the reaction kinetics between O<sub>3</sub> and I- and emission of I<sub>2</sub> and HOI is based on a limited number of laboratory experiments, very few of which have been carried out at anything like in situ concentrations or in ‘real’ seawater. It is very ambitious to extrapolate these findings to the global scale and at the very least some acknowledgement of this uncertainty should be made in the conclusions.**

AC:

As mentioned above, we believe it is worth to implement “on-line” formulations for the ISG fluxes in CAM-Chem even when only approximated parameterised expressions for the process are known. The only validation we can perform with these types of global models is to assess if the ISG fluxes obtained lie within the range of values reported in the literature. Indeed, the global modelled emissions of HOI/I<sub>2</sub> in the current version of the model account for ~1.9 Tg (I) yr<sup>-1</sup>. This value is somewhat larger than the one ~1.2 Tg (I) yr<sup>-1</sup> used in Saiz-Lopez et al. (2012b) and within the range of values used by several authors to reconcile IO measurements in the MBL at coastal sites (i.e., in the range of  $(10 - 70) \times 10^7$  (I) cm<sup>-2</sup> s<sup>-1</sup>; see Mahajan et al. (2010), Großmann et al. (2013) and references therein). A deeper verification of the parameterised formulation is out of the scope of this work, which focuses on the proposal of a potentially important climate-feedback of the ozone-dependent strength of inorganic iodine sources from the oceans.

**1.3. MacDonald et al. 2014, acknowledged the high sensitivity of their model output to windspeed. How does uncertainty in the wind speed fields used in the present study impact the results? For instance, at low wind speeds (<0.3 m s<sup>-1</sup>) ISG emissions may be substantially overestimated.**

AC:

Indeed, MacDonald et al. (2014) established a wind speed threshold of 3 m s<sup>-1</sup> for the validity of the parameterisation of ISG fluxes as defined by Eqs. (1)-(4), which overestimates the ISG fluxes for wind speed < 3m s<sup>-1</sup>. MacDonald et al. mentioned “a factor of two at a wind speed of 0.5 m s<sup>-1</sup>”. That sort of limitation is hence intrinsic to our work since we used their ISG flux parameterisation. Nevertheless, globally speaking, the wind speed over the oceans tends to be higher than the mentioned threshold. Only in some areas of the Equator the wind speed is consistently close to the threshold value. Note that, as shown in the figure below, only in the small region of the Halmahera Sea (offshore West Papua Province) the mean wind speed is fact below 3 m s<sup>-1</sup> (never below 1 m s<sup>-1</sup> in average). Hence, in general, we can assume that the ISG flux

parameterisation based on wind speed used in our study is globally valid. As mentioned above, this is also confirmed when comparing our results to field campaign measurements (Chance et al., 2014). Noteworthy is also the fact that the major changes in tropospheric ozone, ISG fluxes and  $I_y$  over time (Fig. 3b, Fig. 4 and Fig. 5c; respectively) are not particularly located over regions of low wind speed.

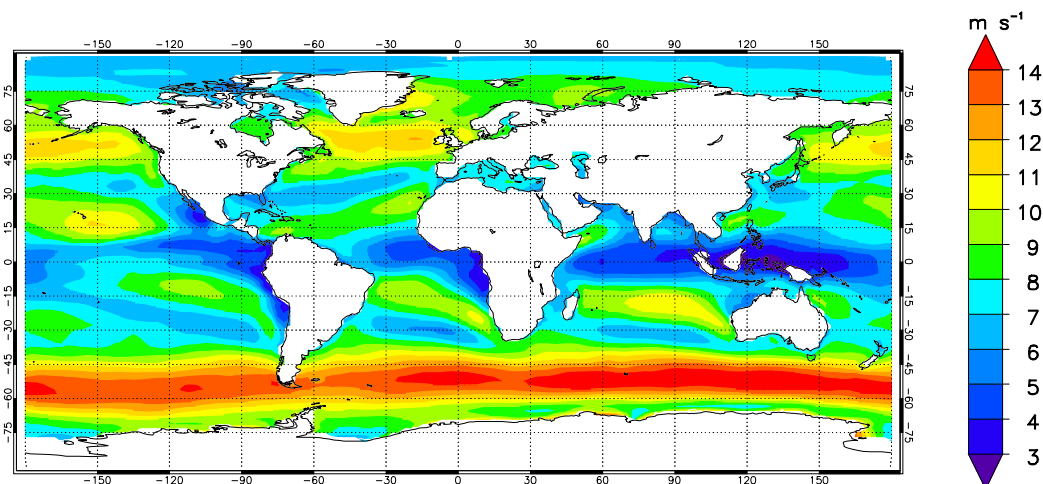


Figure 1: Modelled annual mean wind speed ( $\text{m s}^{-1}$ )

RC:

**2. In presenting the % change of the ISG fluxes since pre-industrial times (Figure 4), in the  $I_y$  budget (Figure 5) or percentage acceleration of the ozone chemical loss (Figure 7) the equation  $100 \times (\text{PD}-\text{PI})/\text{PD}$  is used. It would be more logical in my view to use  $100 \times (\text{PD}-\text{PI})/\text{PI}$  to express this percentage change when referring to change since the pre-industrial situation.**

AC:

We understand the referee and, in fact, this issue is a matter of chosen reference. We would rather keep the Present-time as the reference time in these studies since most of the community is more familiar with the current tropospheric ozone levels. Also it is worth noting that, as the  $\text{O}_3$  vmr in PI times were smaller than those for the PD, the percentage change when using PD in the denominator are smaller than those obtained if we would have used PI as the reference time.

RC:

**3. L8, I would suggest altering ‘laboratory studies have established the oceanic gaseous emission of. . .’ to ‘laboratory studies have demonstrated the potential for. . .’ ; or something along those lines.**

AC:

The referred sentence in the introduction now reads as “laboratory studies have demonstrated the potential of the ocean to emit...”

RC:

**4. P21922, L17. This point is not entirely fair. This single factor might lower the estimates of ISG fluxes but the overall results comprise many other levels of uncertainty that could shift the balance between under or overestimation.**

AC:

Indeed what we understand as a lower limit are the reproduced ISG fluxes. This has now made clearer in the new manuscript (end of Sect. 2.2) with “Hence the ISG fluxes modelled in this study should be regarded as lower limits”.

**RC:**

**5. P21925, L3.3 I suggest altering the title to ‘Iodine-mediated change in ozone radiative forcing. ...’**

**AC:**

The title of the Subsection is changed as suggested.

**RC:**

**6. P21926, L25+. As stated above, a comprehensive explanation of the model uncertainties is needed in order to demonstrate how robust these conclusions are.**

**AC:**

As mentioned above and also in the manuscript (Sec. 3.4), although the uncertainties in, e.g., the parameterisation of ISG fluxes (which appear to be rather small based on Chance et al., 2014) or in the change of SST over time (very uncertain based on IPCC), may propagate into the magnitude and geographical distribution of the changes in ISG flux, I<sub>y</sub> and ozone loss rate shown in our work; the establishment of the proposed feedback mechanism is not linked to those uncertainties since it is a result of the human activities increasing the background ozone (as demonstrated in IPCC) and the experimentally proved emission of ISG as a result of the deposition of tropospheric ozone in the ocean (Garland et al. 1980). See also comments above.

**RC:**

**7. P21926, L25+. The sentence beginning ‘Note that. ...’ could usefully be rephrased.**

**AC:**

The phrase is change to “Despite possible model uncertainties (e.g. in the parameterisation of ISG flux, dependence of ozone deposition on ocean biogeochemistry or possible changes in climatological parameters since PI times), note that...”