

## **Response to the Editor**

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

**C. Prados-Roman, C. A. Cuevas, R. P. Fernandez, D. E. Kinnison, J-F. Lamarque and A. Saiz-Lopez**

We would like to thank Prof. Laurens Ganzeveld for his work as the editor of our Manuscript. In the following we present our point-by-point answer (Authors Comment-AC) to his remarks (Editor Comment- EC, in block letters). Attached to this document we include the manuscript with tracking changes.

**EC:**

**Dear authors/co-authors,**

**Some weeks ago you submitted your revised version of the ms as well as your response to the comments provided by two reviewers. Overall, I see that the comments provided by the reviewers have been properly addressed and would like to thank both reviewers for their constructive comments.**

**There has been some delay in my decision being out of the office for some weeks but can now inform you that I am accepting your ms for publication in ACP. There are only some further suggestions from my side on some other potential modifications/typos as you can find them below and that you should consider for the final version to be published in ACP.**

**In your reply to the comments that have been provided by reviewer #1 on the uncertainties involved in some of the components involved in the feedback mechanism you address the issue on the dependence of the Iodide concentrations on SST as reported by Chance et al., 2014, and MacDonald et al., 2014. I also noticed that you included in the figure caption now the reference to the Ganzeveld 2009 study in which there was also an evaluation of the inferred and observed latitudinal gradients in oceanic Iodide concentrations and where the inferred Iodide was not based on SST as a proxy but rather using oceanic nitrate concentrations. These alternative approaches to infer Iodide are discussed in more detail by Chance et al (2014) but with respect to this discussion on uncertainties, it would be worthwhile to also shortly mention here**

**that there are these alternative approaches compared to the one you applied in your study and which result in quite comparable Iodide concentrations.**

AC:

As suggested, for the different proxies that might be used for inferring iodide concentrations now we direct the reader to the work of Chance et al. 2014 (Pag 4: “other possible proxies are also detailed in the work of Chance et al., 2014”).

EC:

**In the model set-up, you indicate that used one and the same SST climatology for your simulations. Since this SST is used to infer your Iodide concentrations, which in turn determines the ISG fluxes, differences between the pre-industrial and present-day SST would also affect this feedback mechanism where you have now only considered the role of changes in O3. I think you should also discuss the potential implications of this experiment set-up.**

AC:

As detailed in the manuscript, the parameterisation of the oceanic iodine fluxes (Eq. (1)-(4)) depends mainly on the tropospheric ozone concentration and, in second order, on SST. Indeed, as the editor mentions, we do use the same SST climatology for the present-day and pre-industrial time simulations. Based on the IPCC report, the change on SST since pre-industrial times is assumed to be small ( $\sim 1^\circ \text{C}$ ) compared to the change in tropospheric ozone. Hence the change in tropospheric ozone is the parameter directing the change in the ocean emission of iodine into the atmosphere. Once this is said and bearing in mind that SST is one proxy for the iodide concentration in the ocean (and as the editor referred above, not the only proxy), for the uncertainties derived from using a constant SST over time we kindly refer the editor to our responses to the referees. “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”. Also, as mentioned to Referee#2, “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, Iy 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).”.

EC:

**In addition, because of the link between O3 deposition (concentration x deposition velocity) and the Iodide source, I think it is worthwhile to spend one sentence on how oceanic O3 deposition is calculated in the CAM CESM modelling system (presumably using a prescribed constant oceanic uptake rate of ~0.05 cm s-1)**

AC:

Although, focusing on oceanic values, indeed the ozone dry deposition is in the range of 0.05 cm s<sup>-1</sup>, in fact in CAM-Chem that rate is not a fixed quantity but uses the Wesely approach, as mentioned in the work of Lamarque et al. (2012). In fact this study is the core reference for the details on the CAM-Chem model. This is now made clearer in Pag. 2 (“A summary of the model setup and simulations used in this study are provided below, whereas a detailed description of the model as well as the iodine chemical scheme and reaction rates is described elsewhere (Lamarque et al., 2012; Ordoñez et al., 2012; Saiz-Lopez et al. 2014).”).

EC:

**Line 18: pp2, Gómez Martín et al., 2013; Grossman et al., 2013;**

AC:

Both years are now corrected.

EC:

**I suggest to change the following sentence to:**

**Page 4, lines 27-28: Note that, for a given SST, the [I-aq] parameterisation according to MacDonald et al. (2014) results in lower iodide concentrations than considering the abovementioned [I-aq]-SST2 correlation according to Chance et al. (2014).**

AC:

Sentenced changed in the new version.

EC:

**Page 7: “Integrating the tropospheric column, the rate of iodine catalyzed ozone destruction has increased by 90 Tg y-1 since the pre-industrialisation era, yielding a total present day tropospheric ozone removal by iodine of 280 Tg y-1.”. Would it be**

**worthwhile to put these numbers further in perspective, e.g., by comparing this with a global annual ocean O<sub>3</sub> deposition flux on the order of 300 Tg y<sup>-1</sup>.**

AC:

We understand the editor's point-of-view. However we consider that adding such information referred to the ozone deposited into the oceans (information already provided in the previously referred work of Ganzeveld et al. (2009)) could not only deviate the focus of the sentence (i.e., comparing the ozone removal by iodine in present-day vs. pre-industrial times), but also confuse the reader. Thus, we would rather keep the scope of the sentence and subsection (i.e., "Change in iodine-mediated ozone loss rate since pre-industrial times"). Nevertheless we also consider relevant the magnitude of the ozone deposited into the oceans. This is now mentioned on Pag. 2 ("estimated range of 200-350 Tg O<sub>3</sub> y<sup>-1</sup>; Ganzeveld et al. (2009)").

EC:

**In the figure caption of Figure 1 there was a typo: (see also Ganzeveld et al., 2009).**

AC:

The reference is now corrected.

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

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## Abstract

Naturally emitted from the oceans, iodine compounds efficiently destroy atmospheric ozone and reduce its positive radiative forcing effects in the troposphere. Emissions of inorganic iodine have been experimentally shown to depend on the deposition to the oceans of tropospheric ozone, whose concentrations have significantly increased since 1850 as a result of human activities. A chemistry-climate model is used herein to quantify the current ocean emissions of inorganic iodine and assess the impact that the anthropogenic increase of tropospheric ozone has had on the natural cycle of iodine in the marine environment since pre-industrial times. Our results indicate that the human-driven enhancement of tropospheric ozone has doubled the oceanic inorganic iodine emissions following the reaction of ozone with iodide at the sea surface. The consequent build-up of atmospheric iodine, with maximum enhancements of up to 70% with respect to preindustrial times in continental pollution outflow regions, has in turn accelerated the ozone chemical loss over the oceans with strong spatial patterns. We suggest that this ocean-atmosphere interaction represents a negative

1 geochemical feedback loop by which current ocean emissions of iodine act as a natural buffer  
2 for ozone pollution and its radiative forcing in the global marine environment.

3

## 4 **1 Introduction**

5 Tropospheric ozone ( $O_3$ ) is a short-lived greenhouse gas (GHG) with a positive radiative  
6 forcing (RF) of  $0.4 \text{ W m}^{-2}$  ( $0.2\text{-}0.6 \text{ W m}^{-2}$ ) (Myhre et al., 2013). The main precursors of this  
7 GHG are  $NO_x$  (NO and  $NO_2$ ), hydrocarbons, CO,  $CH_4$  and stratospheric downward transport;  
8 whereas its main sinks include photodissociation, deposition and reactions with the chemical  
9 families of odd oxygen, hydrogen, nitrogen and halogens (Brasseur and Solomon 2005; Myhre  
10 et al., 2013).

11 About a decade ago iodine oxide was detected in the marine boundary layer (MBL) (Alicke et  
12 al., 1999). Since then, several studies have aimed at determining the source gases of iodine  
13 and their chemical pathways (see Saiz-Lopez et al., 2012a and references therein). While  
14 emissions of very-short lived (VSL) organic source gases ( $CH_3I$ ,  $CH_2I_2$ ,  $CH_2ICl$  and  $CH_2IBr$ )  
15 have been observed in supersaturated waters (Carpenter et al., 2012), the existence of an  
16 abiotic ocean source of iodine has been directly and indirectly inferred throughout scattered  
17 field campaigns and 1-D model works (Read et al., 2008; Jones et al., 2010; Mahajan et al.,  
18 2010 and 2012; Gómez Martín et al., [24032013](#); Grossman et al., [24032013](#); Lawler et al.,  
19 2014). Very recently, laboratory studies have demonstrated the potential of the ocean to emit  
20 inorganic hypoiodous acid (HOI) and, to a lesser extent molecular iodine ( $I_2$ ), following the  
21 reaction of ozone with iodide at the sea surface (Carpenter et al., 2013; MacDonald et al.,  
22 2014). The oceanic emission of inorganic iodine source gases (ISG; i.e., HOI,  $I_2$ ) has been  
23 experimentally shown to depend on the deposition of tropospheric ozone to the oceans  
24 ([estimated the range of 200-350 Tg  \$O\_3\$   \$y^{-1}\$ ; Ganzeveld et al. \(2009\)](#)), wind speed and sea  
25 surface temperature (SST) (Garland et al., 1980; Carpenter et al., 2013; MacDonald et al.,  
26 2014).

27 Given that anthropogenic activities have led to an increase of 20-55% in tropospheric ozone  
28 since 1850 (Myhre et al., 2013) and that the current halogen-mediated tropospheric ozone  
29 loss in the tropical regions accounts for  $-0.1 \text{ W m}^{-2}$  of the radiative flux at the tropical  
30 tropopause (i.e.,  $\sim 1/3$  of the total tropospheric  $O_3$  RF, Saiz-Lopez et al., 2012b), this study  
31 aims at (i) assessing how the anthropogenic increase in tropospheric ozone have affected the  
32 abiotic oceanic emission of ISG, and (ii) describing a geochemical feedback mechanism

1 between ozone and iodine that mitigates the positive radiative forcing of tropospheric ozone  
2 in the global marine environment. In this work Sect. 2 provides details on the setup of the  
3 chemistry-climate model employed in this study, while the results for pairs of model runs for  
4 different periods of time are discussed in Sect. 3. The summary and conclusions are presented  
5 in Sect. 4.

6

## 7 **2 Methods**

8 The chemical simulations in this study were performed with the 3-D CAM-Chem chemistry-  
9 climate model (Community Atmospheric Model with Chemistry, version 4.0) , included into  
10 the CESM framework (Community Earth System Model, version 1.1.1) (Lamarque et al.,  
11 2012). A summary of the model setup and simulations used in this study are provided below,  
12 whereas a detailed description of the [model as well as the](#) iodine chemical scheme and  
13 reaction rates is described elsewhere ([Lamarque et al., 2012](#); Ordoñez et al., 2012; Saiz-Lopez  
14 et al. 2014).

### 15 **2.1 Model setup**

16 The model setup used for all simulations considered a horizontal grid resolution of  $1.9^\circ$   
17 (latitude)  $\times$   $2.5^\circ$  (longitude) and 26 hybrid vertical levels from the surface to approximately 40  
18 km (Lamarque et al., 2012). In order to allow the stabilization of the tropospheric conditions  
19 and to perform a direct chemical comparison between simulations representative of different  
20 time periods, all simulation schemes considered identical prescribed SST and sea-ice  
21 boundary conditions representative of year 2000 (Rayner et al., 2003). Since model results are  
22 not representative of the meteorology of any specific year, annual averages are presented. In  
23 all cases, ocean and land masks were applied to the model streaming in order to compute the  
24 global absolute and relative averages presented here.

### 25 **2.2 Ocean iodine emissions**

26 The global emission inventory of CAM-Chem was updated by the inclusion of a state-of-the-  
27 art iodine and bromine photochemical mechanism, including natural oceanic sources of VSL  
28 bromo- and iodo- carbons which have previously been validated (Ordoñez et al., 2012; Saiz-  
29 Lopez et al., 2012b). Particularly, the current work focuses on the emission of ISG emitted  
30 from the ocean after the oxidation of aqueous iodide by  $O_3$  deposited in the ocean (Garland et

1 al., 1980) and the resulting emission of HOI and I<sub>2</sub>. This emission function was included in  
2 CAM-Chem following the parameterisation derived by Carpenter et al. (2013):

$$3 \quad ISG = Flux(HOI) + 2 \times Flux(I_2), \quad (1)$$

4 where

$$5 \quad Flux(HOI) = [O_3] \times \left( 4.15 \times 10^5 \times \left( \frac{\sqrt{[I^-_{aq}]}}{w} \right) - \left( \frac{20.6}{w} \right) - 23600 \times \sqrt{[I^-_{aq}]} \right) \quad (2)$$

$$6 \quad Flux(I_2) = [O_3] \times [I^-_{aq}]^{1.3} \times (1.74 \times 10^9 - (6.54 \times 10^8 \times \ln w)), \quad (3)$$

7 being  $w$  the wind speed (m s<sup>-1</sup>),  $[O_3]$  the surface ozone mixing ratio (nmol mol<sup>-1</sup>) and  $[I^-_{aq}]$  the  
8 concentration of aqueous iodide (mol dm<sup>-3</sup>) (Carpenter et al., 2013). Based on the work of  
9 MacDonald et al. (2014), the sea surface temperature (SST, K) was used as a proxy for  
10 describing  $[I^-_{aq}]$ :

$$11 \quad [I^-_{aq}] = 1.46 \times 10^6 \times \exp\left(\frac{-9134}{SST}\right). \quad (4)$$

12 Recently, the coincident study of Chance et al. (2014) has compiled the sparse measurements  
13 of sea surface iodide and has also concluded SST as the best proxy to reproduce the  
14 geographical distribution of  $[I^-_{aq}]$ . In that work the authors estimated a slightly higher  
15 correlation coefficient between measured  $[I^-_{aq}]$  and SST<sup>2</sup> as compared to the Ln $[I^-_{aq}]$  and SST<sup>-1</sup>  
16 correlation considered by MacDonald et al. (2014) (Eq. (4)). Nevertheless both studies  
17 concluded on the need of further investigations for a better understanding of processes linked  
18 to  $[I^-_{aq}]$ , its global distribution and parameterisation by means of commonly available marine  
19 environment parameters such as SST (other possible proxies are also detailed in the work of  
20 Chance et al., 2014). The iodide concentrations modelled herein after Eq. (4), with mean  
21 values of 50 nmol dm<sup>-3</sup>, were in good agreement with the interquartile range of 28-140 nmol  
22 dm<sup>-3</sup> of the measurements compiled by Chance et al. (2014). As shown in Fig. 1, the modelled  
23 latitudinal distribution of  $[I^-_{aq}]$  also reproduced the increasing iodide gradient towards  
24 equatorial waters reported by Chance et al. (2014).

25 Following Eq. (1-3), CAM-Chem computed the ISG flux from the ocean considering the  
26 modelled SST (i.e.,  $[I^-_{aq}]$ ), wind speed and surface ozone concentration for each grid-box and  
27 time-step, resulting on an average iodine emission of 1.9 Tg y<sup>-1</sup> from inorganic precursors  
28 (95% from HOI), as compared to 0.4 Tg (I) y<sup>-1</sup> yielding from organic sources. The modelled



1 geographical distribution of the ISG fluxes is shown in Fig. 2. Note that, for a given SST, the  
2  $[I_{aq}]$  parameterisation [according to MacDonald et al. \(2014\) \(i.e., after Eq. \(4\)\)](#) results ~~in~~  
3 lower iodide concentrations than considering the abovementioned  $[I_{aq}]$ -SST<sup>2</sup> correlation  
4 [according to \(Chance et al., \(2014\)\)](#). Also note that the deposition of ozone to the oceans is  
5 connected to the ocean biogeochemistry (Ganzeveld et al., 2009). Thus, for instance, if the  
6 model considers the electronic affinity between iodide and ozone involved in the deposition  
7 process, the consequent emission of iodine to the atmosphere is enhanced particularly in those  
8 regions with elevated ozone pollution and high iodide concentrations. Hence the ISG fluxes  
9 modelled in this study should be regarded as lower limits.

### 10 **2.3 Present-day and pre-industrial simulations**

11 In order to assess the anthropogenic effect on the natural cycle of iodine in the MBL, two  
12 different runs were defined time-wise: present day (*PD run*) and pre-industrial time (*PI run*);  
13 representative of the emissions and resulting atmospheric chemical conditions of 2000 and  
14 1850, respectively (Lamarque et al., 2010; Myhre et al., 2013). To avoid dynamical  
15 perturbations and to compare the chemical impacts of different states of the atmosphere, all  
16 PD and PI simulations were performed in specified dynamics mode with the same high  
17 frequency meteorological input from a previous CAM-Chem 15-years simulation for year  
18 2000. Then, the horizontal wind components, air temperature, SST, sensible flux, latent heat  
19 flux and wind stress were read from a unique input meteorological dataset every 3-6 hrs  
20 (Lamarque et al., 2010). The chemical solver was initialized with boundary conditions  
21 representative of each of the periods modelled. In particular, O<sub>3</sub> initial conditions were taken  
22 from previous climatic model simulations with standard tropospheric halogen chemistry, and  
23 2 yrs of simulations were performed in order to stabilise tropospheric iodine and ozone levels.  
24 Prescribed surface concentrations of long-lived halocarbons (CFCs, halons, CH<sub>3</sub>Br and  
25 CH<sub>3</sub>Cl) were also included (Lamarque et al., 2010). Even when all simulations had the same  
26 meteorology, the model was allowed to proceed with an independent inter-annual chemical  
27 evolution of all tropospheric constituents, and a direct comparison of the oxidative capacity of  
28 different types of atmospheres (PD vs. PI) could be addressed (Lamarque et al., 2012). Note  
29 that the organic iodine emissions were considered to remain unaltered in time. Thus, the  
30 selection of a setup with equivalent meteorology for both time periods allowed us to obtain a  
31 parameterised ISG flux and resulting total inorganic iodine burden ( $I_y = I + IO + HOI + IONO_2$   
32  $+ HI + OIO + INO + INO_2 + 2 \cdot I_2 + IBr + ICl + 2 \cdot I_2O_x$  with  $x = 2-4$ ) in the marine environment

1 dependent only on the changes in surface ozone between present and past times. Throughout  
2 this study the percentage or relative changes reported were estimated as  $100 \times (\text{PD}-\text{PI})/\text{PD}$ .

3

### 4 **3 Results and discussion**

5 Once the current ISG flux and its global pattern have been determined (Sect. 2.2), in the  
6 following we proceed to investigate their evolution since 1850 as well as the implications of  
7 such evolution.

#### 8 **3.1 Change in ozone and atmospheric inorganic iodine since pre-industrial** 9 **times**

10 Figure 3 shows the geographical distribution of the modelled present-day ozone burden in the  
11 MBL and its change since pre-industrial times (Lamarque et al. 2010). In agreement with  
12 observations (Myhre et al., 2013), our simulations indicate that anthropogenic activities since  
13 1850 have caused a mean ozone increase of 40% in MBL. As a result of the deposition and  
14 subsequent reaction of ozone with iodide in the surface ocean, our results reveal that the  
15 human-mediated increase in ozone levels has yielded a rise of the global oceanic ISG flux  
16 from  $1.04 \text{ Tg (I) y}^{-1}$  emitted in 1850, to  $1.9 \text{ Tg (I) y}^{-1}$  emitted currently. That ISG flux rise of  
17 45% (Fig. 4) has caused a similar increase in the total inorganic iodine budget of the global  
18 MBL over the last two centuries (Fig. 5). Human activities including industrial processes,  
19 energy use and agricultural activities have had a more pronounced effect in the northern  
20 hemisphere where anthropogenic emissions of ozone precursors have dramatically increased  
21 since the industrial revolution (Volz and Kley 1988; Lamarque et al., 2010; Myhre et al.,  
22 2013) (Fig. 3b). Consequently, the anthropogenic amplification of the natural oceanic  
23 emission of iodine and, therefore the  $\text{I}_y$  abundance in the MBL, also reflects a strong north  
24 (NH) to south (SH) hemispheric gradient as shown in Fig. 5.

#### 25 **3.2 Change in iodine-mediated ozone loss rate since pre-industrial times**

26 Considering all the ozone depleting families (i.e., odd oxygen, hydrogen, nitrogen, iodine,  
27 bromine, chlorine) (Brasseur and Solomon, 2005, see also Saiz-Lopez et al., 2014), we  
28 calculate that the industrialisation process has on average increased the rate of the total ozone  
29 chemical loss in the global MBL from  $1.89 \text{ nmol mol}^{-1} \text{ d}^{-1}$  to  $3.19 \text{ nmol mol}^{-1} \text{ d}^{-1}$ , mainly  
30 driven by changes in the abundance of odd oxygen, hydrogen and iodine. On a global annual

1 average, 25% of that enhanced ozone loss rate results from the human-driven boosting of  
2 inorganic iodine emissions that has accelerated iodine-mediated ozone destruction from 0.54  
3  $\text{nmol mol}^{-1} \text{d}^{-1}$  in pre-industrial times, to  $0.89 \text{ nmol mol}^{-1} \text{d}^{-1}$  in the present-day. Figure 6  
4 depicts the ozone loss rates by the different chemical families in the present-day scheme. As  
5 shown in Fig. 7, the ozone-driven increase in iodine emissions since PI times has resulted in a  
6 remarkable acceleration of ozone loss in the global MBL with a strong hemispheric gradient.  
7 We calculate that since 1850 the total surface  $\text{O}_3$  loss rate has increased by 2.1 and  $0.6 \text{ nmol}$   
8  $\text{mol}^{-1} \text{d}^{-1}$  in NH and SH, respectively. When only the contribution of the iodine cycle is  
9 considered, hemispheric annual changes in the  $\text{O}_3$  loss rate are  $0.5$  and  $0.2 \text{ nmol mol}^{-1} \text{d}^{-1}$  in  
10 NH and SH, respectively (Fig. 7). Notably, iodine was and still is the second strongest ozone  
11 depleting family in the MBL, being responsible for about 30% of the total ozone loss in that  
12 region of the atmosphere (Fig. 6). Integrating the tropospheric column, the rate of iodine-  
13 catalyzed ozone destruction has increased by  $90 \text{ Tg y}^{-1}$  since the pre-industrialisation era,  
14 yielding a total present day tropospheric ozone removal by iodine of  $280 \text{ Tg y}^{-1}$ .

15 In general, marine regions surrounding northern developed and developing countries, and  
16 areas connecting them, have undergone the strongest amplification of the natural cycle of  
17 inorganic iodine emissions as a result of the enhanced deposition of ozone to those regions of  
18 the ocean (Figs. 4-7). Remarkably, the current anthropogenic influence maximizes in highly  
19 polluted coastal regions such as the East-South China Sea, the South Bay of Bengal, the Gulf  
20 of Mexico and California's offshore waters (Fig. 3) where we calculate an increase of up to  
21 70% in atmospheric iodine since PI times (Fig. 5). In these regions of continental ozone-rich  
22 outflow the iodine-mediated ozone loss rate in recent times has accelerated by a similar factor,  
23 i.e. about 6 times more (up to  $2 \text{ nmol mol}^{-1} \text{d}^{-1}$ ) than the global average of  $0.35 \text{ nmol mol}^{-1} \text{d}^{-1}$   
24 (Figs. 6 and 7).

### 25 **3.3 Iodine-mediated change in ozone radiative forcing since pre-industrial** 26 **times**

27 Due to its long-wave absorption, present-day tropospheric ozone RF is estimated to be in the  
28 range of  $0.2\text{-}0.6 \text{ W m}^{-2}$  (Myhre et al., 2013). Investigating the effect of the ISG flux in the  
29 budget of ozone in the tropospheric column and following the methodology of Saiz-Lopez et  
30 al. (2012b), we calculate that the tropospheric ozone depletion caused by current ocean  
31 emissions of inorganic iodine reduces the warming effect of ozone in the global marine  
32 troposphere by 3-10%, up to 20% on average in the NH. Note however that these values

1 should be regarded as lower limits. Based on the recent study of Saiz-Lopez et al. (2014), we  
2 investigated the effect that the photolysis of the higher oxides  $I_2O_x$  ( $x = 2, 3, \text{ or } 4$ ) formed  
3 after the reactions of IO with itself ( $x = 2$ ), and with OIO ( $x = 3$ ), or OIO with itself ( $x = 4$ )  
4 (Bloss et al., 2001; Spietz et al., 2005; Gómez Martín et al., 2005 and 2007; Saiz-Lopez et al.,  
5 2008) could have on the RF of tropospheric ozone. Our results indicate that if the photolysis  
6 of  $I_2O_x$  is considered, the current negative effect of the enhanced iodine-mediated ozone loss  
7 in the marine troposphere would mitigate the warming long-wave radiative effect of  
8 tropospheric ozone by up to 20% globally, and up to 40% in the NH.

9 As compared to 1850, we estimate that the abovementioned 45% increase in  $I_y$  loading has  
10 yielded a significant decrease in the RF associated with tropospheric ozone, reinforcing the  
11 need of a better process-level understanding of the uncertainties in atmospheric iodine  
12 chemistry in order to assess the impact of iodine on the tropospheric ozone RF and its future  
13 trends.

#### 14 **3.4 Geochemical feedback mechanism**

15 In this study we suggest that the human-driven increase of tropospheric ozone has led to an  
16 amplification of the natural cycle of iodine emissions that has consequently decreased the  
17 lifetime of ozone in the marine atmosphere, thus closing a negative feedback loop as  
18 conceptually illustrated in Fig. 8. The result of this geochemical feedback mechanism  
19 indicates that ocean emissions of iodine act as a natural buffer of anthropogenic ozone  
20 pollution and its associated RF in the marine troposphere. Despite possible model  
21 uncertainties (e.g. in the parameterisation of ISG flux, dependence of ozone deposition on  
22 ocean biogeochemistry or possible changes in climatological parameters since PI times), note  
23 that the establishment of this feedback mechanism is inherent to the experimentally proven  
24 dependence of inorganic iodine emissions upon the deposition of ozone to the oceans  
25 (Garland et al., 1980; Carpenter et al., 2013; MacDonald et al., 2014).

#### 26 **4 Summary and conclusions**

27 After investigating past and present interactions of iodine and ozone in the open marine  
28 environment, we conclude that the enhanced injection of iodine into the present-day  
29 atmosphere, as compared to pre-industrial times, represents a mechanism by which  
30 anthropogenic activities have increased the overall reactivity of the atmosphere and have  
31 amplified the natural cycle of iodine. The human-mediated boosting of the ISG emissions has

1 on average increased by 25% the rate of present day ozone chemical loss in the global marine  
2 environment, with regions where this increase can be up to 70%, compared with the pre-  
3 industrial era. The subsequent negative radiative forcing induced by the enhanced iodine-  
4 mediated ozone depletion currently mitigates up to 20-40% the effect of tropospheric ozone  
5 as a GHG in the northern hemisphere. The human-driven enhanced iodine emissions may also  
6 have two important side implications. First, it has likely led to a larger accumulation of the  
7 iodine fraction (iodate and iodide) on marine aerosols (Baker, 2004). Second, it may have  
8 increased the input of iodine, as an essential dietary element for mammals (Whitehead, 1984)  
9 that is transported from its oceanic source to the continents.

10 The negative feedback mechanism described in this work represents a natural buffer of ozone-  
11 related pollution and its radiative forcing in the marine environment. This feedback represents  
12 a potentially important new link between climate change and tropospheric ozone since the  
13 oceanic emissions of iodine are not only linked to surface ozone, but also to SST and wind  
14 speed (both parameters with a high uncertainty regarding future trends, Rhein et al., 2013),  
15 and might also be linked to climatically driven changes in the state of the World's oceans  
16 (e.g., upwelling, acidity). All of this highlights the importance of a better understanding of  
17 background natural oceanic biogeochemical processes in currently changing environments.

## 18

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### 29

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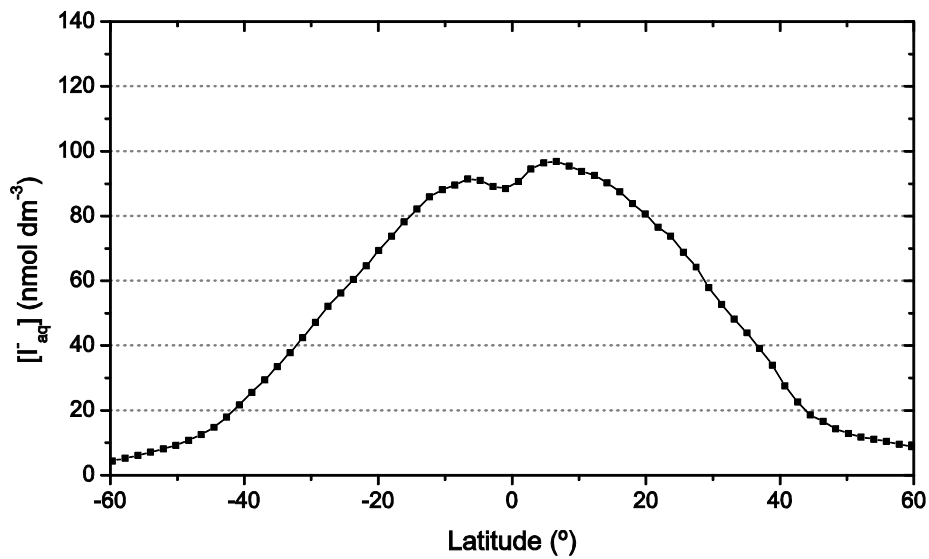
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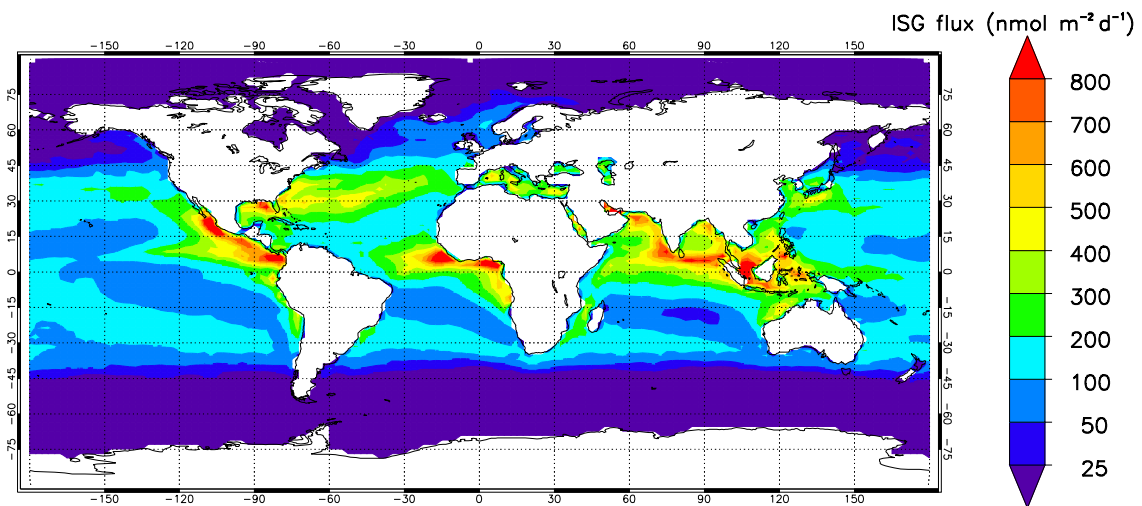
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3 Figure 1. Modelled latitudinal variation of the zonal average sea surface iodide concentration,  
4 [I<sub>aq</sub>]. Following Eq. (4), [I<sub>aq</sub>] is modelled with CAM-Chem using SST as a proxy. Modelled  
5 iodide values fall within the range of [I<sub>aq</sub>] open ocean measurements reported by Chance et  
6 al. (2014), reproducing as well the iodide gradient observed towards the equator (see also  
7 [Ganzeveld-Ganzeveld et al., 2009](#)).

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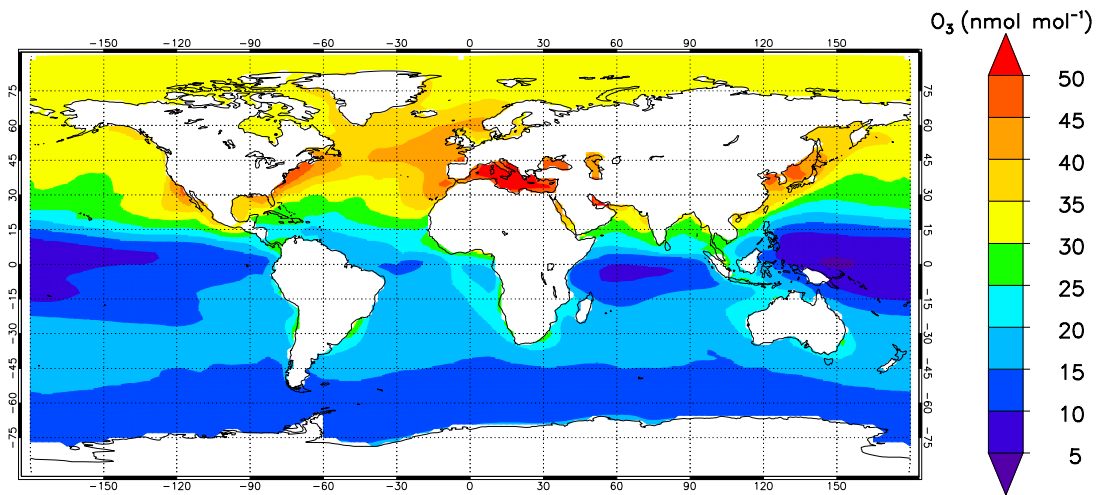
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2 Figure 2. Modelled annual mean ocean flux of ISG. Following the laboratory work of  
3 Carpenter et al. (2013) and MacDonald et al. (2014), the parameterisation of the ISG flux  
4 given by Eq. (1-4) was newly implemented in the global chemistry-climate model CAM-  
5 Chem.

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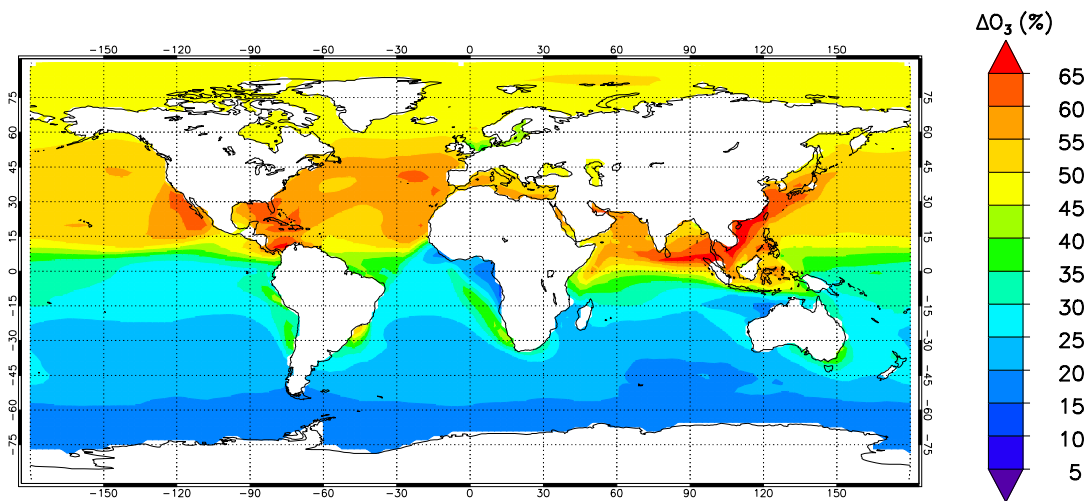
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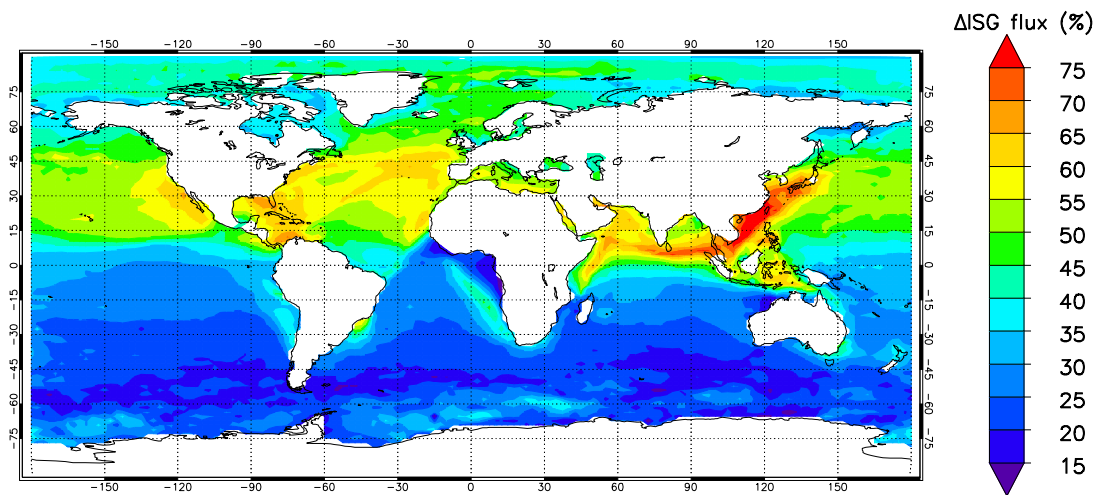
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3

4 Figure 3. Modelled surface ozone in the marine environment. a. Present-day surface  $O_3$   
5 mixing ratio. b. Relative change of surface  $O_3$  mixing ratio since pre-industrial times. As a  
6 result of the hemispheric gradient on the emissions of ozone precursors (Myhre et al., 2013),  
7 the increased ozone load in the NH has doubled that of the southern hemisphere.

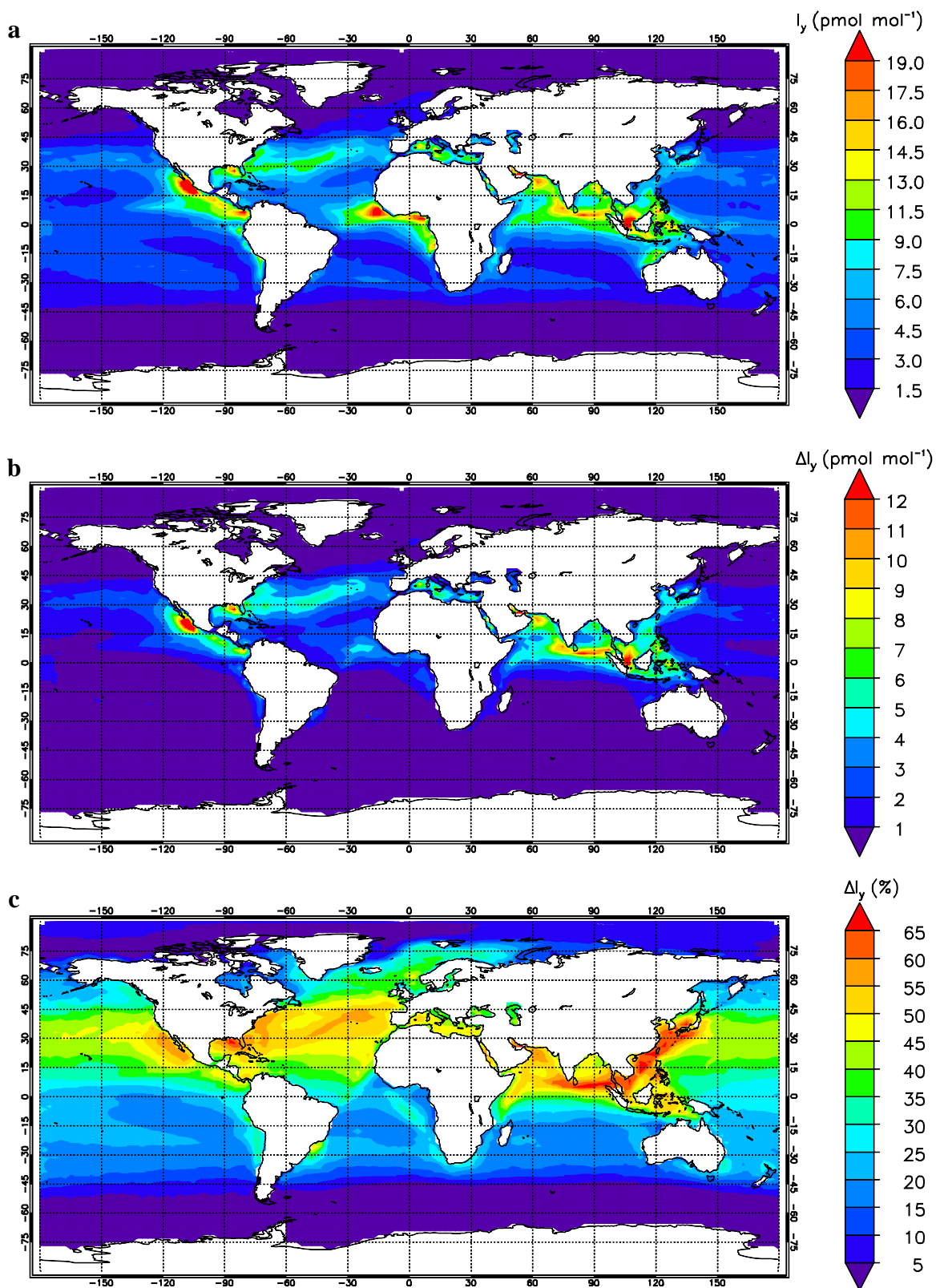
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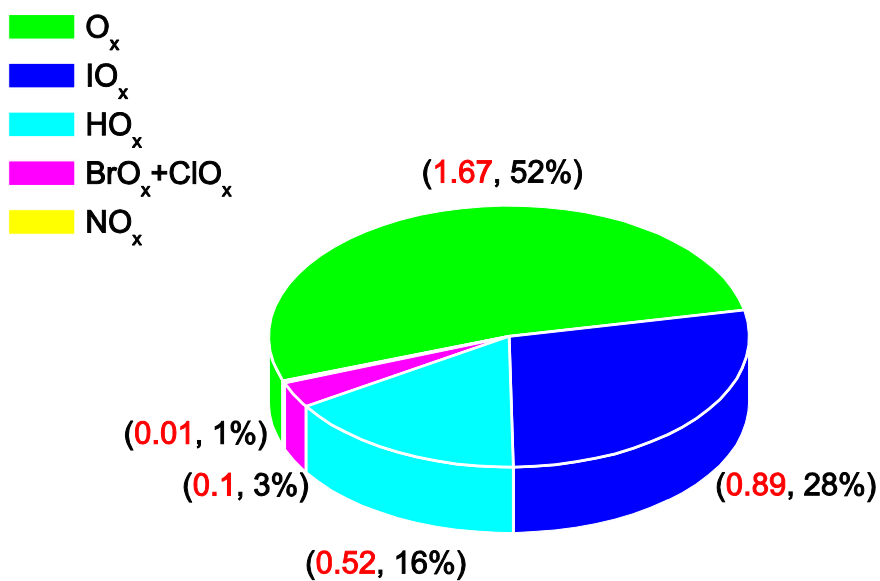
2 Figure 4. Anthropogenic influence upon the oceanic emission of inorganic iodine. The figure  
3 presents the percentage change of the ISG fluxes since pre-industrial times. The annual  
4 oceanic flux of ISG for the PD run is shown in Fig. 2.

5



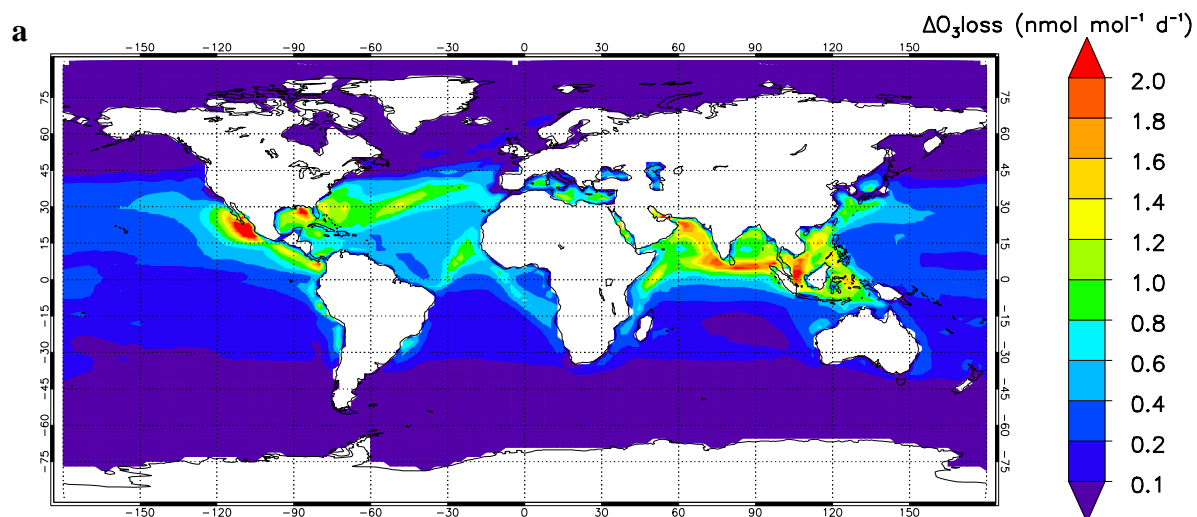
1  
 2 Figure 5. Geographical distribution of the budget of total gaseous inorganic iodine ( $I_y = I + IO$   
 3  $+ HOI + IONO_2 + HI + OIO + INO + INO_2 + 2 \cdot I_2 + IBr + ICl + 2 \cdot I_2O_x$  with  $x = 2-4$ ) in the

- 1 MBL. a. Modelled  $I_y$  mixing ratio in the PD scheme. b. Enhancement of the  $I_y$  budget since
- 2 pre-industrial times (PD-PI). c. Percentage increase of the  $I_y$  budget since industrial
- 3 revolution, i.e.,  $100 \times (\text{PD-PI})/\text{PD}$ .

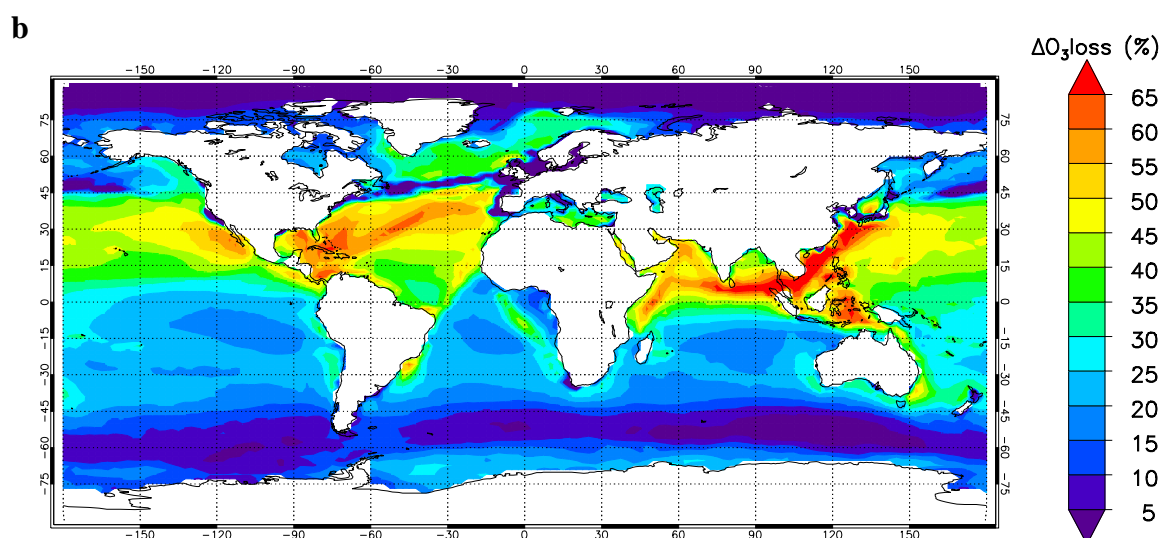


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 2 Figure 6. Calculated present-day ozone loss rates by the different chemical families in the  
 3 MBL (Brasseur and Solomon 2005). The first number of each parenthesis (in red) provides  
 4 the O<sub>3</sub> loss rate by the colour-coded family (in nmol mol<sup>-1</sup> d<sup>-1</sup>). The second value of each  
 5 parenthesis provides the relative contribution of each depleting family to the total ozone  
 6 chemical loss.





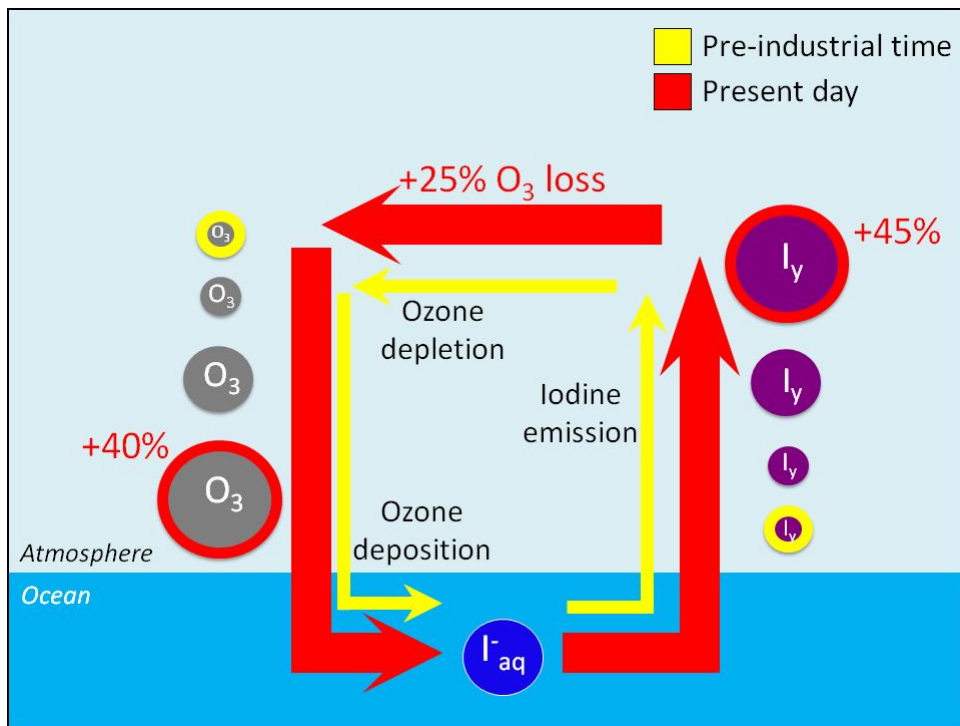
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2

3 Figure 7. Geographical distribution of the annual acceleration of the ozone chemical loss rate  
 4 by iodine in the MBL. a. Absolute acceleration (PD-PI); b. Percentage acceleration, i.e.,  $100 \times$   
 5 (PD-PI)/PD.

6



1  
 2 Figure 8. Geochemical feedback mechanism. The anthropogenic increase in tropospheric  
 3 ozone during the last two centuries (20-55%, Myhre et al., 2013) has led to an amplification  
 4 of the natural cycle of iodine emissions since pre-industrial times (PI cycle in yellow). This  
 5 has consequently decreased the lifetime of ozone in the marine atmosphere and its associated  
 6 RF, thus closing a negative feedback loop and presenting the ocean emissions of iodine as a  
 7 natural mitigating factor for anthropogenic RF in the marine environment (PD cycle in red).