Response to the Referees

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 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. Attached to this document we also include the new version of the manuscript with changes marked in red.

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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_2 and $O(^1D)$. 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, nigh-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_x is actually the 2nd 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. pesent 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 O3 and I- and emission of I2 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_2 in the current version of the model account for ~1.9 Tg (I) yr^{-1}. This value is somewhat larger than the one ~1.2 Tg (I) yr^{-1} 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^{-2} s^{-1}; 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-1) ISG emissions may be substantially overestimated.

AC:
Indeed, MacDonald et al. (2014) established a wind speed threshold of 3 m s-1 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^{-1}. MacDonald et al. mentioned "a factor of two at a wind speed of 0.5 m s^{-1}". 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^{-1} (never below 1 m s^{-1} 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.
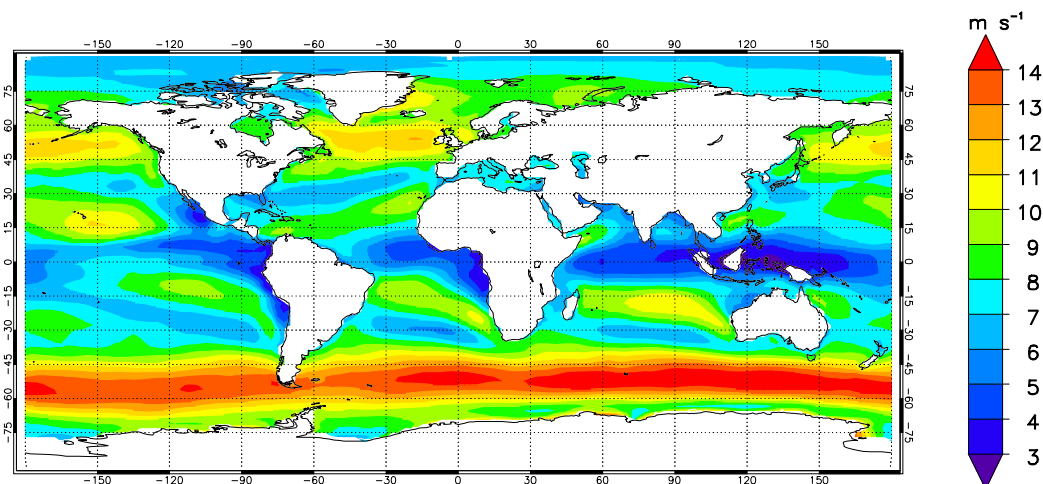

Figure 1: Modelled annual mean wind speed (m s^{-1})

RC:
2. In presenting the % change of the ISG fluxes since pre-industrial times (Figure 4), in the Iy budget (Figure 5) or percentage acceleration of the ozone chemical loss (Figure 7) the equation 100 x (PD-PI)/PD is used. It would be more logical in my view to use 100 x (PD-PI)/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 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, 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). 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…"

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 W m^{-2} (0.2- 0.6 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 (Braseur 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., 2103; Grossman et al., 2103; Lawler et al., 2014). Very

19 recently, laboratory studies have demonstrated the potential of the ocean to emit inorganic

20 hypoiodous acid (HOI) and, to a lesser extent molecular iodine (I_2), following the reaction of

21 ozone with iodide at the sea surface (Carpenter et al., 2013; MacDonald et al., 2014). The

22 oceanic emission of inorganic iodine source gases (ISG; i.e., HOI, I_2) has been experimentally

23 shown to depend on the deposition of tropospheric ozone to the oceans, wind speed and sea

24 surface temperature (SST) (Garland et al., 1980; Carpenter et al., 2013; MacDonald et al.,

25 2014).

26 Given that anthropogenic activities have led to an increase of 20-55% in tropospheric ozone

27 since 1850 (Myhre et al., 2013) and that the current halogen-mediated tropospheric ozone

28 loss in the tropical regions accounts for -0.1 W m^{-2} of the radiative flux at the tropical

29 tropopause (i.e., ~1/3 of the total tropospheric O_3 RF, Saiz-Lopez et al., 2012b), this study

30 aims at (i) assessing how the anthropogenic increase in tropospheric ozone have affected the

31 abiotic oceanic emission of ISG, and (ii) describing a geochemical feedback mechanism

32 between ozone and iodine that mitigates the positive radiative forcing of tropospheric ozone

2

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

5

6   2   Methods

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

13   2.1   Model setup

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

23   2.2   Ocean iodine emissions

24   The global emission inventory of CAM-Chem was updated by the inclusion of a state-of-the-
25   art iodine and bromine photochemical mechanism, including natural oceanic sources of VSL
26   bromo- and iodo- carbons which have previously been validated (Ordoñez et al., 2012; Saiz-
27   Lopez et al., 2012b). Particularly, the current work focuses on the emission of ISG emitted
28   from the ocean after the oxidation of aqueous iodide by O_3 deposited in the ocean (Garland et
29   al., 1980) and the resulting emission of HOI and I_2. This emission function was included in
30   CAM-Chem following the parameterisation derived by Carpenter et al. (2013):

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

2 where

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

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

5 being w the wind speed (m s^{-1}), $[O_3]$ the surface ozone mixing ratio (nmol mol^{-1}) and $[I^-_{aq}]$ the

6 concentration of aqueous iodide (mol dm^{-3}) (Carpenter et al., 2013). Based on the work of

7 MacDonald et al. (2014), the sea surface temperature (SST, K) was used as a proxy for

8 describing $[I^-_{aq}]$:

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

10 Recently, the coincident study of Chance et al. (2014) has compiled the sparse measurements

11 of sea surface iodide and has also concluded SST as the best proxy to reproduce the

12 geographical distribution of $[I^-_{aq}]$. In that work the authors estimated a slightly higher

13 correlation coefficient between measured $[I^-_{aq}]$ and SST^2 as compared to the Ln$[I^-_{aq}]$ and SST^{-}

14 ^{1} correlation considered by MacDonald et al. (2014) (Eq. (4)). Nevertheless both studies

15 concluded on the need of further investigations for a better understanding of processes linked

16 to $[I^-_{aq}]$, its global distribution and parameterisation by means of commonly available marine

17 environment parameters such as SST. The iodide concentrations modelled herein after Eq.

18 (4), with mean values of 50 nmol dm^{-3}, were in good agreement with the interquartile range of

19 28-140 nmol dm^{-3} of the measurements compiled by Chance et al. (2014). As shown in Fig. 1,

20 the modelled latitudinal distribution of $[I^-_{aq}]$ also reproduced the increasing iodide gradient

21 towards equatorial waters reported by Chance et al. (2014).

22 Following Eq. (1-3), CAM-Chem computed the ISG flux from the ocean considering the

23 modelled SST (i.e., $[I^-_{aq}]$), wind speed and surface ozone concentration for each grid-box and

24 time-step, resulting on an average iodine emission of 1.9 Tg y^{-1} from inorganic precursors

25 (95% from HOI), as compared to 0.4 Tg (I) y^{-1} yielding from organic sources. The modelled

26 geographical distribution of the ISG fluxes is shown in Fig. 2. Note that, for a given SST, the

27 $[I^-_{aq}]$ parameterisation after Eq. (4) results on lower iodide concentrations than considering the

28 abovementioned $[I^-_{aq}]$-SST^2 correlation (Chance et al., 2014). Also note that the deposition of

4

ozone to the oceans is connected to the ocean biogeochemistry (Ganzeveld et al., 2009). Thus, for instance, if the model considers the electronic affinity between iodide and ozone involved in the deposition process, the consequent emission of iodine to the atmosphere is enhanced particularly in those regions with elevated ozone pollution and high iodide concentrations. Hence the ISG fluxes modelled in this study should be regarded as lower limits.

2.3 Present-day and pre-industrial simulations

In order to assess the anthropogenic effect on the natural cycle of iodine in the MBL, two different runs were defined time-wise: present day (*PD run*) and pre-industrial time (*PI run*); representative of the emissions and resulting atmospheric chemical conditions of 2000 and 1850, respectively (Lamarque et al., 2010; Myhre et al., 2013). To avoid dynamical perturbations and to compare the chemical impacts of different states of the atmosphere, all PD and PI simulations were performed in specified dynamics mode with the same high frequency meteorological input from a previous CAM-Chem 15-years simulation for year 2000. Then, the horizontal wind components, air temperature, SST, sensible flux, latent heat flux and wind stress were read from a unique input meteorological dataset every 3-6 hrs (Lamarque et al., 2010). The chemical solver was initialized with boundary conditions representative of each of the periods modelled. In particular, O_3 initial conditions were taken from previous climatic model simulations with standard tropospheric halogen chemistry, and 2 yrs of simulations were performed in order to stabilise tropospheric iodine and ozone levels. Prescribed surface concentrations of long-lived halocarbons (CFCs, halons, CH_3Br and CH_3Cl) were also included (Lamarque et al., 2010). Even when all simulations had the same meteorology, the model was allowed to proceed with an independent inter-annual chemical evolution of all tropospheric constituents, and a direct comparison of the oxidative capacity of different types of atmospheres (PD vs. PI) could be addressed (Lamarque et al., 2012). Note that the organic iodine emissions were considered to remain unaltered in time. Thus, the selection of a setup with equivalent meteorology for both time periods allowed us to obtain a parameterised ISG flux and resulting total inorganic iodine burden (I_y = I+ IO + HOI + $IONO_2$ + HI + OIO+ INO + INO_2 + 2·I_2 + IBr + ICl + 2·I_2O_x with x = 2-4) in the marine environment dependent only on the changes in surface ozone between present and past times. Throughout this study the percentage or relative changes reported were estimated as 100 x (PD-PI)/PD.

3 Results and discussion

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

3.1 Change in ozone and atmospheric inorganic iodine since pre-industrial times

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

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

Considering all the ozone depleting families (i.e., odd oxygen, hydrogen, nitrogen, iodine, bromine, chlorine) (Brasseur and Solomon, 2005, see also Saiz-Lopez et al., 2014), we calculate that the industrialisation process has on average increased the rate of the total ozone chemical loss in the global MBL from 1.89 nmol mol^{-1} d^{-1} to 3.19 nmol mol^{-1} d^{-1}, mainly driven by changes in the abundance of odd oxygen, hydrogen and iodine. On a global annual average, 25% of that enhanced ozone loss rate results from the human-driven boosting of inorganic iodine emissions that has accelerated iodine-mediated ozone destruction from 0.54 nmol mol^{-1} d^{-1} in pre-industrial times, to 0.89 nmol mol^{-1} d^{-1} in the present-day. Figure 6

depicts the ozone loss rates by the different chemical families in the present-day scheme. As shown in Fig. 7, the ozone-driven increase in iodine emissions since PI times has resulted in a remarkable acceleration of ozone loss in the global MBL with a strong hemispheric gradient. We calculate that since 1850 the total surface O_3 loss rate has increased by 2.1 and 0.6 nmol mol^{-1} d^{-1} in NH and SH, respectively. When only the contribution of the iodine cycle is considered, hemispheric annual changes in the O_3 loss rate are 0.5 and 0.2 nmol mol^{-1} d^{-1} in NH and SH, respectively (Fig. 7). Notably, iodine was and still is the second strongest ozone depleting family in the MBL, being responsible for about 30% of the total ozone loss in that region of the atmosphere (Fig. 6). 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}.

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

3.3 Iodine-mediated change in ozone radiative forcing since pre-industrial times

Due to its long-wave absorption, present-day tropospheric ozone RF is estimated to be in the range of 0.2-0.6 W m^{-2} (Myhre et al., 2013). Investigating the effect of the ISG flux in the budget of ozone in the tropospheric column and following the methodology of Saiz-Lopez et al. (2012b), we calculate that the tropospheric ozone depletion caused by current ocean emissions of inorganic iodine reduces the warming effect of ozone in the global marine troposphere by 3-10%, up to 20% on average in the NH. Note however that these values should be regarded as lower limits. Based on the recent study of Saiz-Lopez et al. (2014), we investigated the effect that the photolysis of the higher oxides I_2O_x (x = 2, 3, or 4) formed after the reactions of IO with itself (x = 2), and with OIO (x = 3), or OIO with itself (x = 4)

(Bloss et al., 2001; Spietz et al., 2005; Gómez Martín et al., 2005 and 2007; Saiz-Lopez et al., 2008) could have on the RF of tropospheric ozone. Our results indicate that if the photolysis of I_2O_x is considered, the current negative effect of the enhanced iodine-mediated ozone loss in the marine troposphere would mitigate the warming long-wave radiative effect of tropospheric ozone by up 20% globally, and up to 40% in the NH.

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

3.4   Geochemical feedback mechanism

In this study we suggest that the human-driven increase of tropospheric ozone has led to an amplification of the natural cycle of iodine emissions that has consequently decreased the lifetime of ozone in the marine atmosphere, thus closing a negative feedback loop as conceptually illustrated in Fig. 8. The result of this geochemical feedback mechanism indicates that ocean emissions of iodine act as a natural buffer of anthropogenic ozone pollution and its associated RF in the marine troposphere. 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 the establishment of this feedback mechanism is inherent to the experimentally proven dependence of inorganic iodine emissions upon the deposition of ozone to the oceans (Garland et al., 1980; Carpenter et al., 2013; MacDonald et al., 2014).

4   Summary and conclusions

After investigating past and present interactions of iodine and ozone in the open marine environment, we conclude that the enhanced injection of iodine into the present-day atmosphere, as compared to pre-industrial times, represents a mechanism by which anthropogenic activities have increased the overall reactivity of the atmosphere and have amplified the natural cycle of iodine. The human-mediated boosting of the ISG emissions has on average increased by 25% the rate of present day ozone chemical loss in the global marine environment, with regions where this increase can be up to 70%, compared with the pre-industrial era. The subsequent negative radiative forcing induced by the enhanced iodine-

mediated ozone depletion currently mitigates up to 20-40% the effect of tropospheric ozone as a GHG in the northern hemisphere. The human-driven enhanced iodine emissions may also have two important side implications. First, it has likely led to a larger accumulation of the iodine fraction (iodate and iodide) on marine aerosols (Baker, 2004). Second, it may have increased the input of iodine, as an essential dietary element for mammals (Whitehead, 1984) that is transported from its oceanic source to the continents.

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

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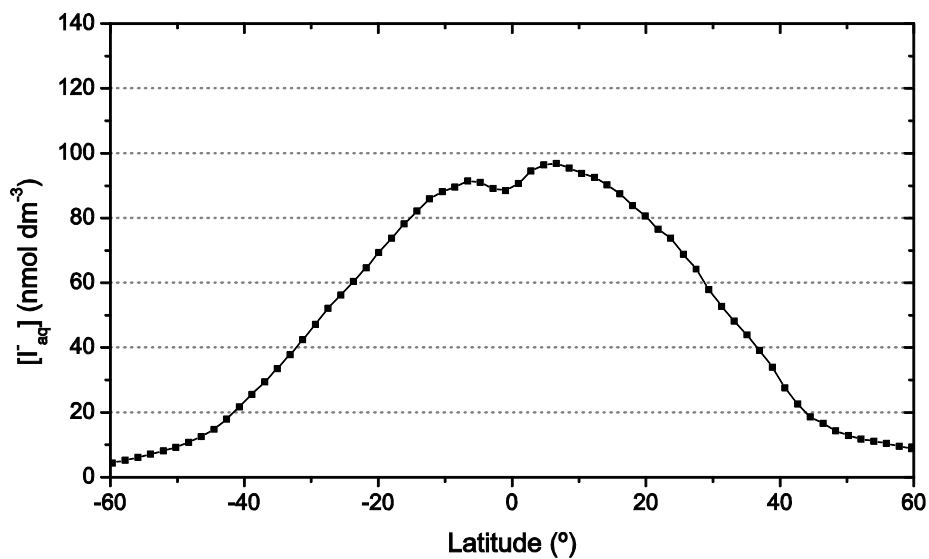
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3   Figure 1. Modelled latitudinal variation of the zonal average sea surface iodide concentration,

4     $[I^-_{aq}]$. Following Eq. (4), $[I^-_{aq}]$ is modelled with CAM-Chem using SST as a proxy. Modelled

5   iodide values fall within the range of $[I^-_{aq}]$ open ocean measurements reported by Chance et

6   al. (2014), reproducing as well the iodide gradient observed towards the equator (see also
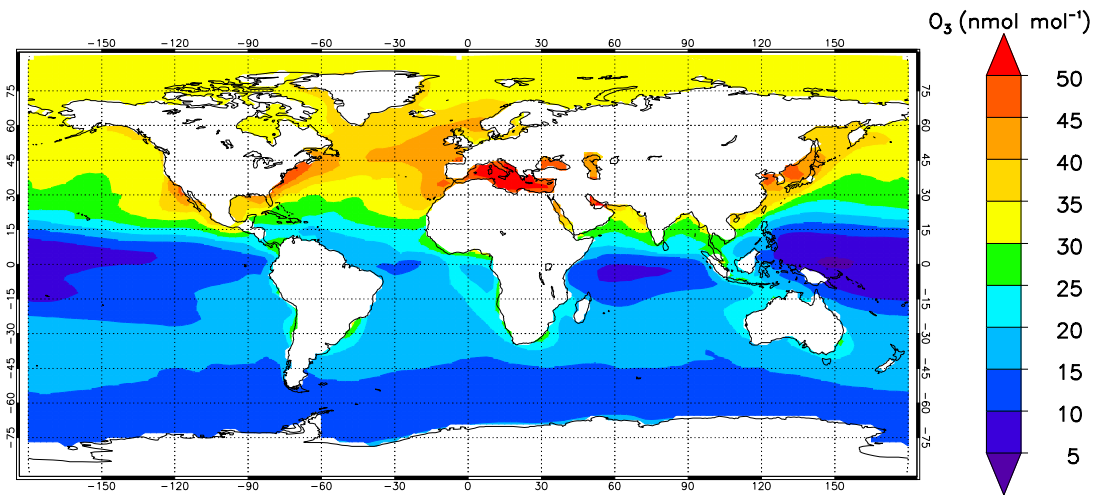
7   Ganzelved et al., 2009).

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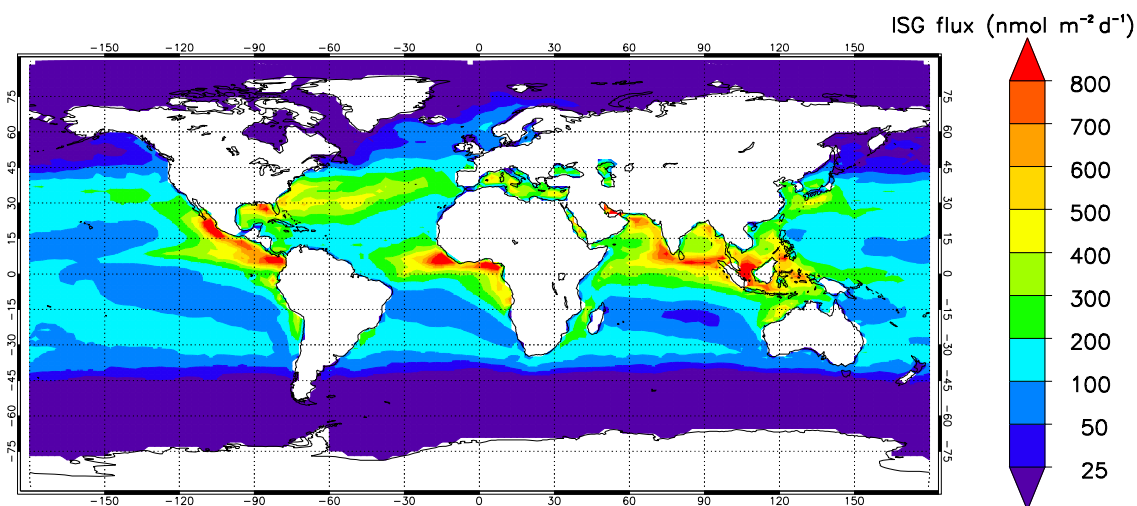
Figure 2. Modelled annual mean ocean flux of ISG. Following the laboratory work of Carpenter et al. (2013) and MacDonald et al. (2014), the parameterisation of the ISG flux given by Eq. (1-4) was newly implemented in the global chemistry-climate model CAM-Chem.

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a

2 **b**

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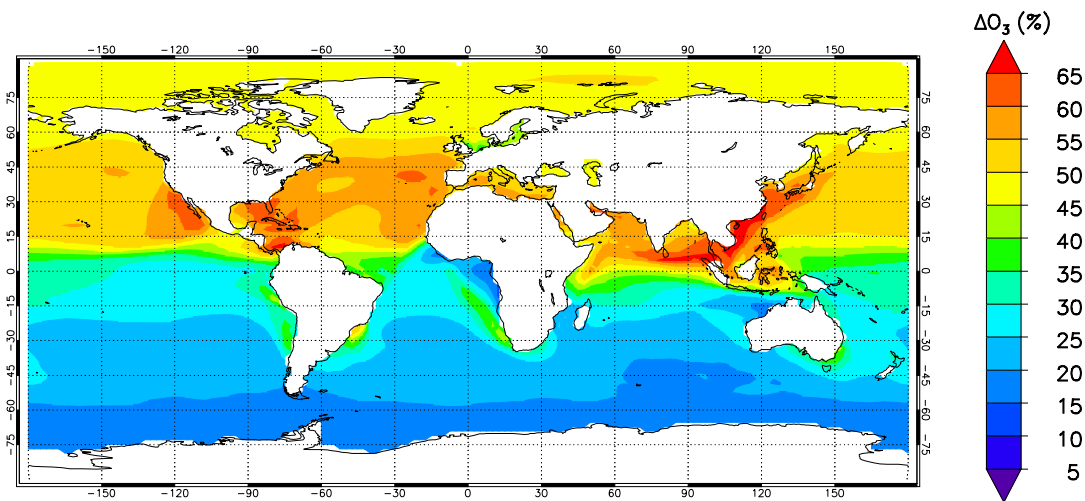
Figure 3. Modelled surface ozone in the marine environment. a. Present-day surface O_3 mixing ratio. b. Relative change of surface O_3 mixing ratio since pre-industrial times. As a result of the hemispheric gradient on the emissions of ozone precursors (Myhre et al., 2013), the increased ozone load in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

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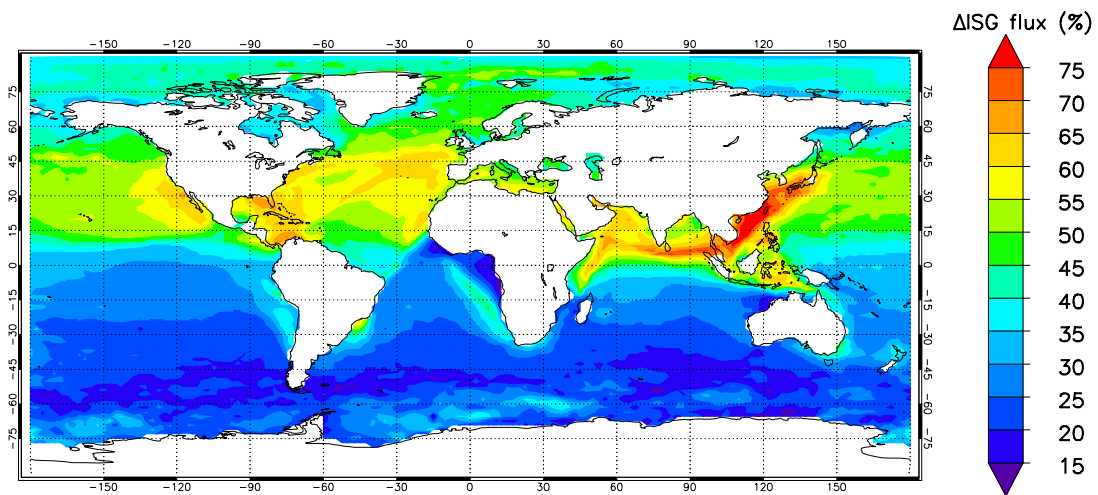
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2 Figure 4. Anthropogenic influence upon the oceanic emission of inorganic iodine. The figure

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.

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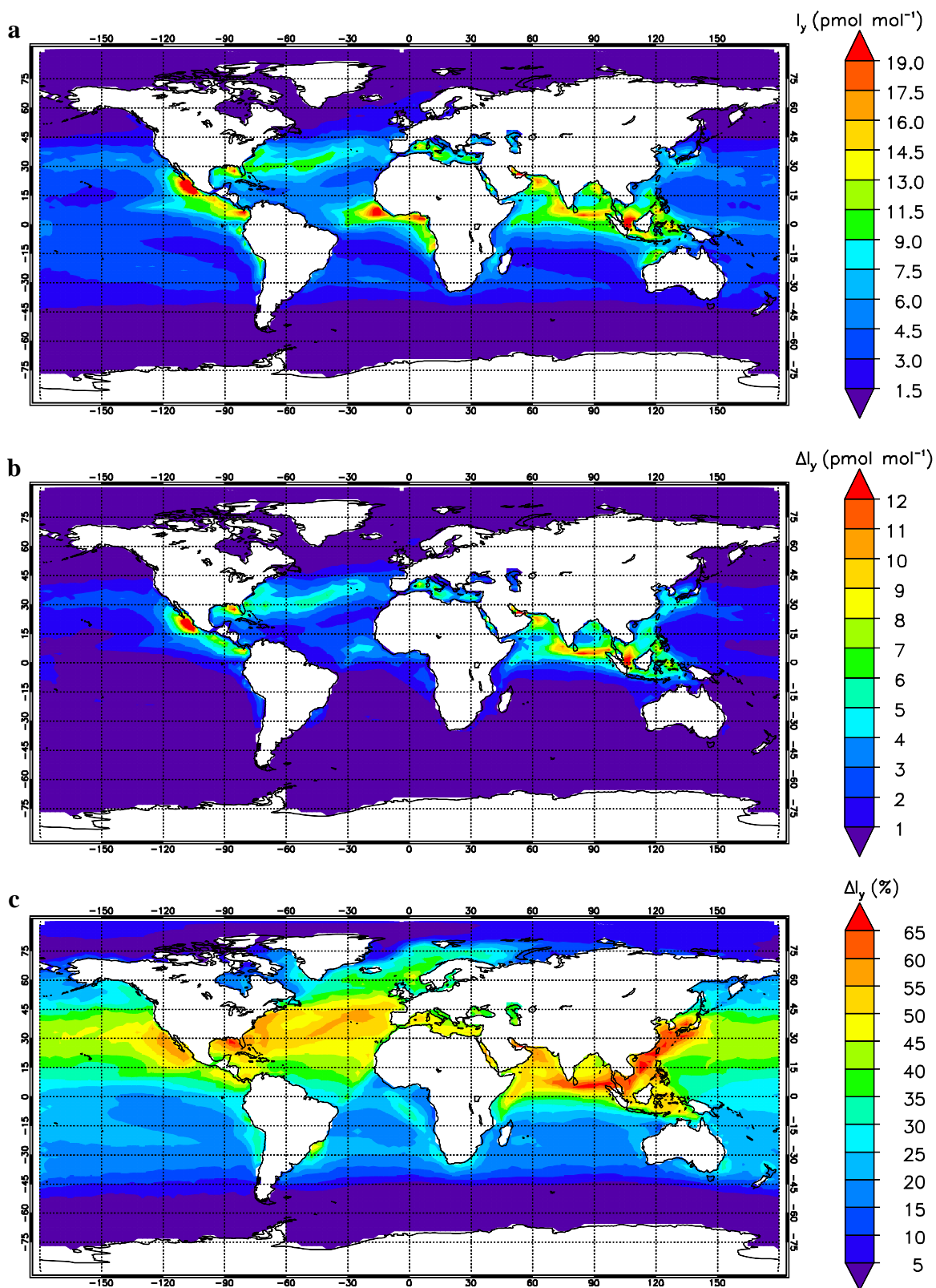
Figure 5. Geographical distribution of the budget of total gaseous inorganic iodine (I_y = I+ IO + HOI + IONO$_2$ + HI + OIO+ INO + INO$_2$ + 2·I$_2$ + IBr + ICl + 2·I$_2$O$_x$ with x = 2-4) in the

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 x (PD-PI)/PD.
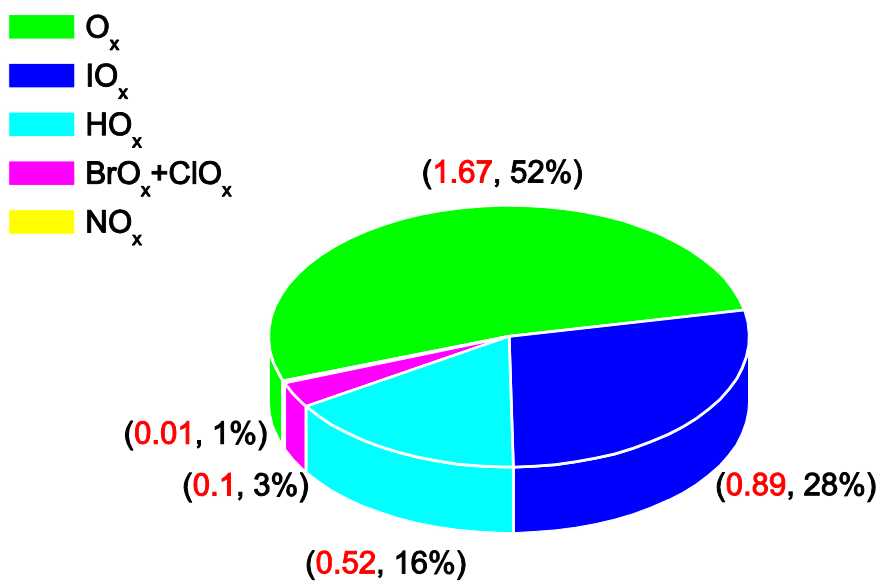
Figure 6. Calculated present-day ozone loss rates by the different chemical families in the MBL (Brasseur and Solomon 2005). The first number of each parenthesis (in red) provides the O_3 loss rate by the colour-coded family (in nmol mol^{-1} d^{-1}). The second value of each parenthesis provides the relative contribution of each depleting family to the total ozone chemical loss.
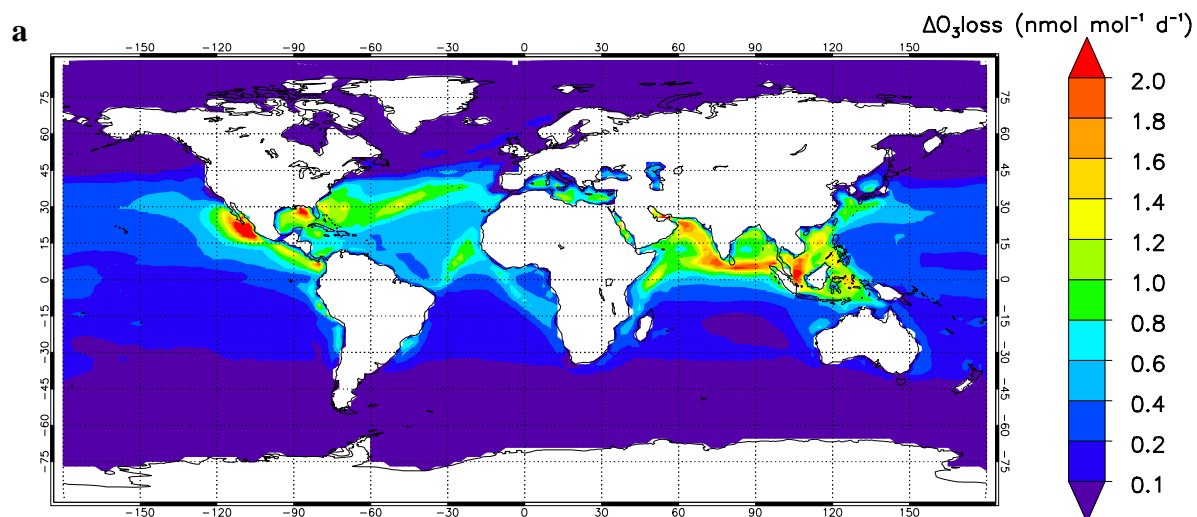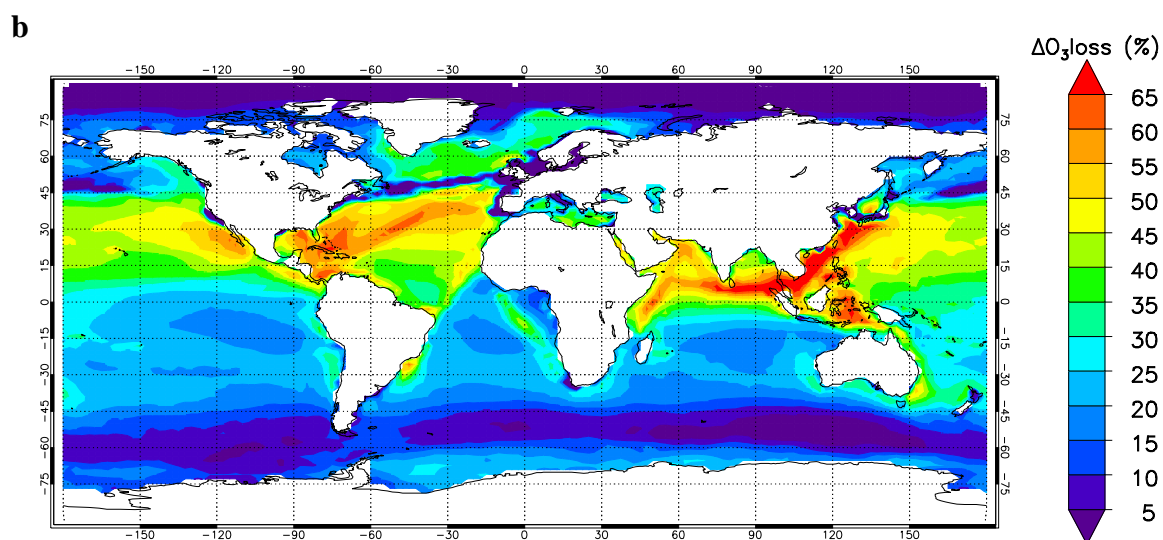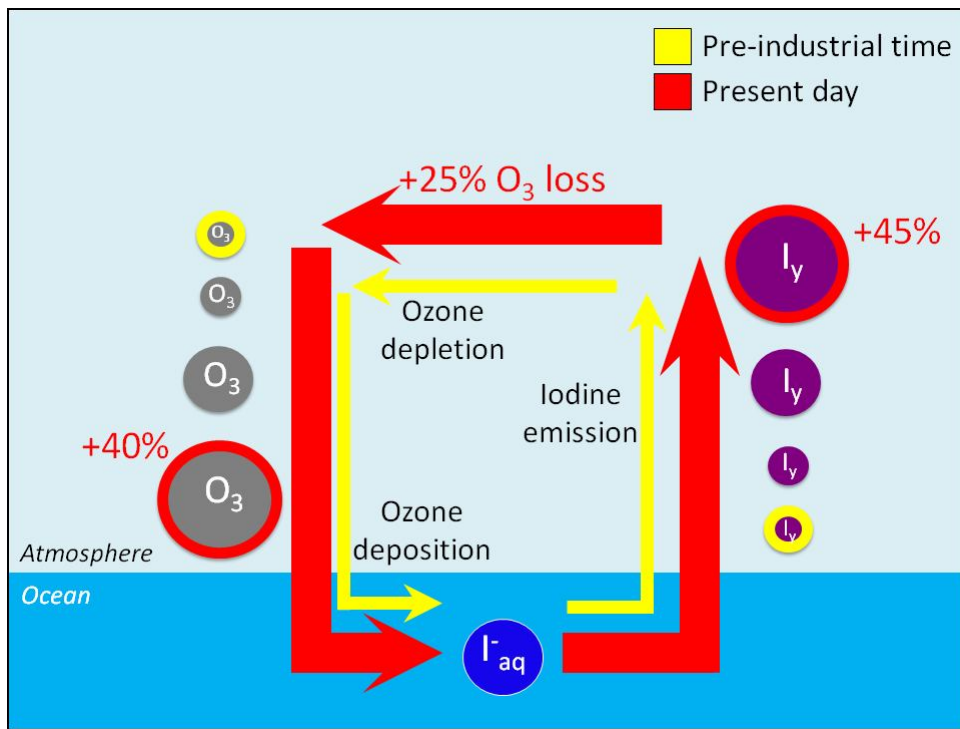
Figure 7. Geographical distribution of the annual acceleration of the ozone chemical loss rate by iodine in the MBL. a. Absolute acceleration (PD-PI); b. Percentage acceleration, i.e., 100 x (PD-PI)/PD.

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).