# Interactions between natural short-lived halogens and short-lived climate forcers (ozone, methane and aerosols)

Alfonso Saiz-Lopez[1], Rafael P. Fernandez[1,2], Qinyi Li[1], Carlos A. Cuevas[1], Xiao Fu[3], Douglas E. Kinnison[4], Simone Tilmes[4], Anoop S. Mahajan[5], Juan Carlos Gómez Martín[6], Fernando Iglesias-Suarez[7], Ryan Hossaini[8], John M. C. Plane[9], Gunnar Myhre[10] and Jean-François Lamarque[11]

[1]Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, CSIC, Madrid, Spain
[2]Institute for Interdisciplinary Science (ICB), National Research Council (CONICET), FCEN-UNCuyo, Mendoza, Argentina
[3]Institute of Environment and Ecology, Tsinghua Shenzhen International Graduate School, Tsinghua University, China
[4]Atmospheric Chemistry Observations & Modeling Laboratory, National Center for Atmospheric Research, Boulder, CO, USA
[5]Centre for Climate Change Research, Indian Institute of Tropical Meteorology, Ministry of Earth Sciences, India
[6]Instituto de Astrofísica de Andalucía, CSIC, Spain
[7]Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Physik der Atmosphäre, Oberpfaffenhofen, Germany
[8]Lancaster Environment Centre, Lancaster University, Lancaster, UK
[9]School of Chemistry, University of Leeds, Leeds, UK
[10]CICERO Center for International Climate Research, Norway
[11]Climate and Global Dynamics Laboratory, National Center for Atmospheric Research, Boulder, CO, USA

# Introduction: Halogen chemistry

**Short-lived halogens**
**(τ < 6 months)**

| Source gas | Local Lifetime (WMO, 2010) | Main loss |
|---|---|---|
| $CH_2BrCl$ | 137 days | OH, hv |
| $CH_2Br_2$ | 123 days | OH, hv |
| $CHBrCl_2$ | 78 days | OH, hv |
| $CHBr_2Cl$ | 59 days | hv, OH |
| $CHBr_3$ | 24 days | hv, OH |
| $CH_3I$ | 7 days | hv, OH |
| $CH_2ICl$ | ~ 2–3 h | hv |
| $CH_2IBr$ | ~1 h | hv |
| $CH_2I_2$ | ~ 5 min | hv |
| $HOI/I_2$ | 1 min | hv |

**Oceans are the main source of Short-Lived Halogens (SLH)**

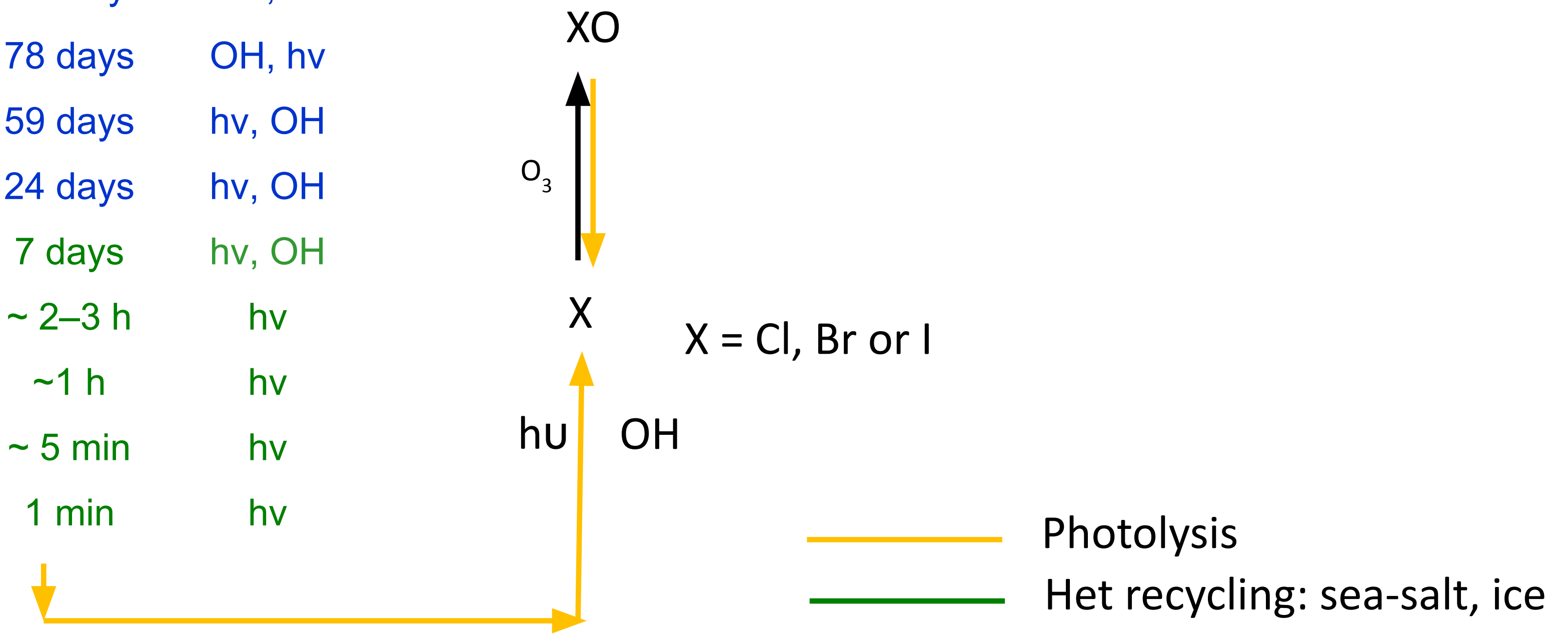
**Biologically and photochemically produced**

**Different lifetimes determine their atmospheric impact**

Saiz-Lopez and von Glasow, *Chemical Society Reviews*, 2012

## Short-lived halogens
## (τ < 6 months)

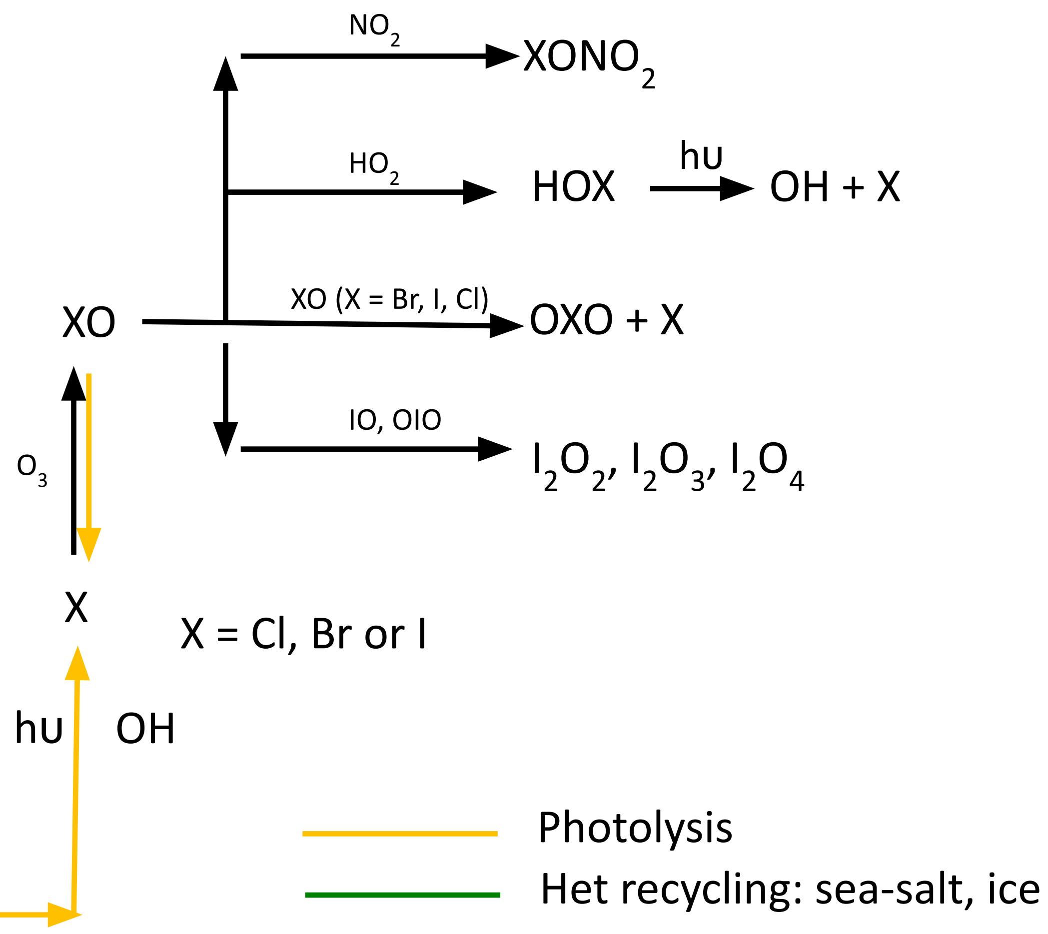
| **Source gas** | **Local Lifetime (WMO, 2010)** | **Main loss** |
|---|---|---|
| $CH_2BrCl$ | 137 days | OH, hv |
| $CH_2Br_2$ | 123 days | OH, hv |
| $CHBrCl_2$ | 78 days | OH, hv |
| $CHBr_2Cl$ | 59 days | hv, OH |
| $CHBr_3$ | 24 days | hv, OH |
| $CH_3I$ | 7 days | hv, OH |
| $CH_2ICl$ | ~ 2–3 h | hv |
| $CH_2IBr$ | ~1 h | hv |
| $CH_2I_2$ | ~ 5 min | hv |
| $HOI/I_2$ | 1 min | hv |




Saiz-Lopez and von Glasow, *Chemical Society Reviews*, 2012

## Short-lived halogens ($\tau$ < 6 months)

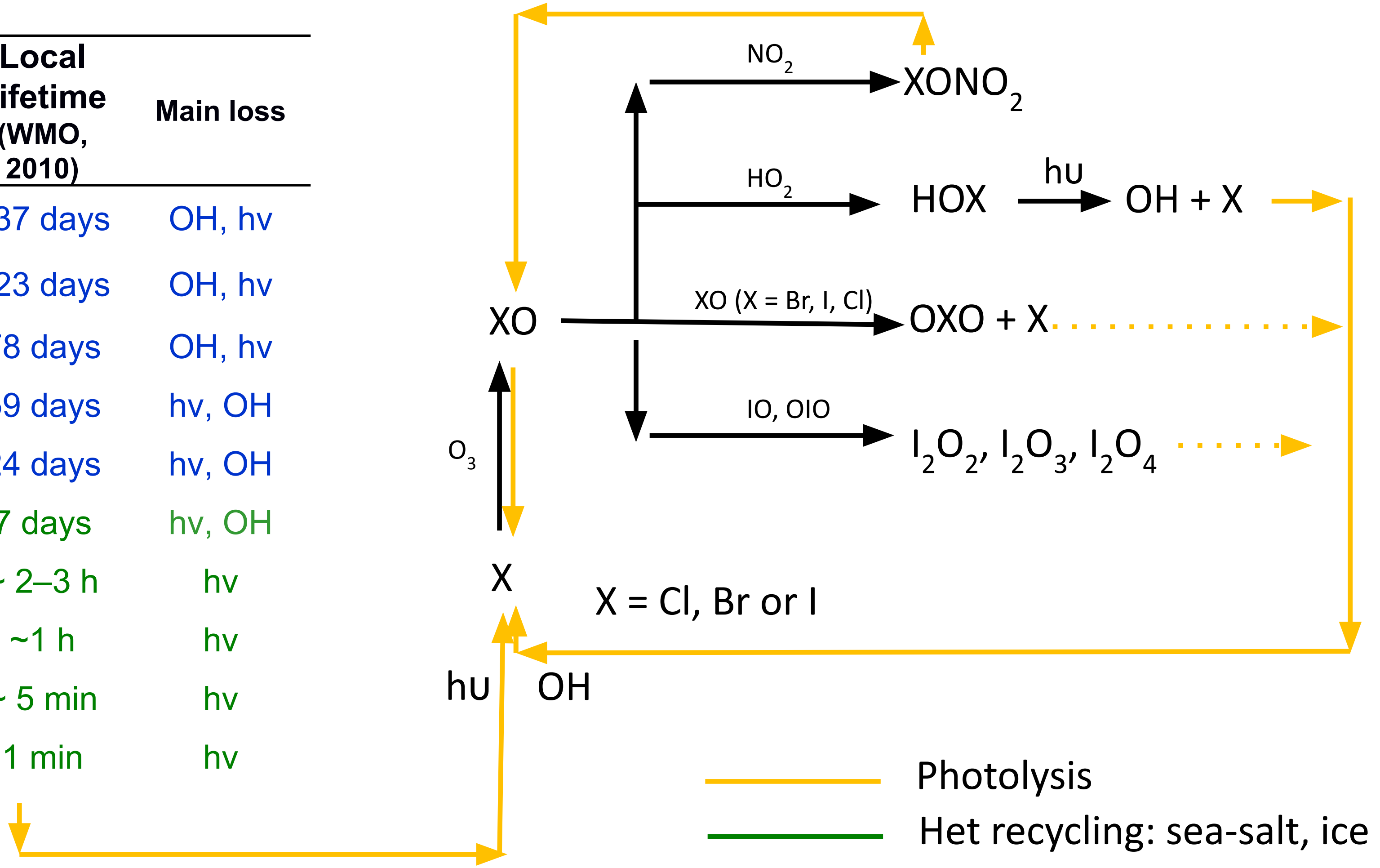
| Source gas | Local Lifetime (WMO, 2010) | Main loss |
|---|---|---|
| $CH_2BrCl$ | 137 days | OH, hv |
| $CH_2Br_2$ | 123 days | OH, hv |
| $CHBrCl_2$ | 78 days | OH, hv |
| $CHBr_2Cl$ | 59 days | hv, OH |
| $CHBr_3$ | 24 days | hv, OH |
| $CH_3I$ | 7 days | hv, OH |
| $CH_2ICl$ | ~ 2–3 h | hv |
| $CH_2IBr$ | ~1 h | hv |
| $CH_2I_2$ | ~ 5 min | hv |
| $HOI/I_2$ | 1 min | hv |




Saiz-Lopez and von Glasow, *Chemical Society Reviews*, 2012

**Short-lived halogens**
**(τ < 6 months)**

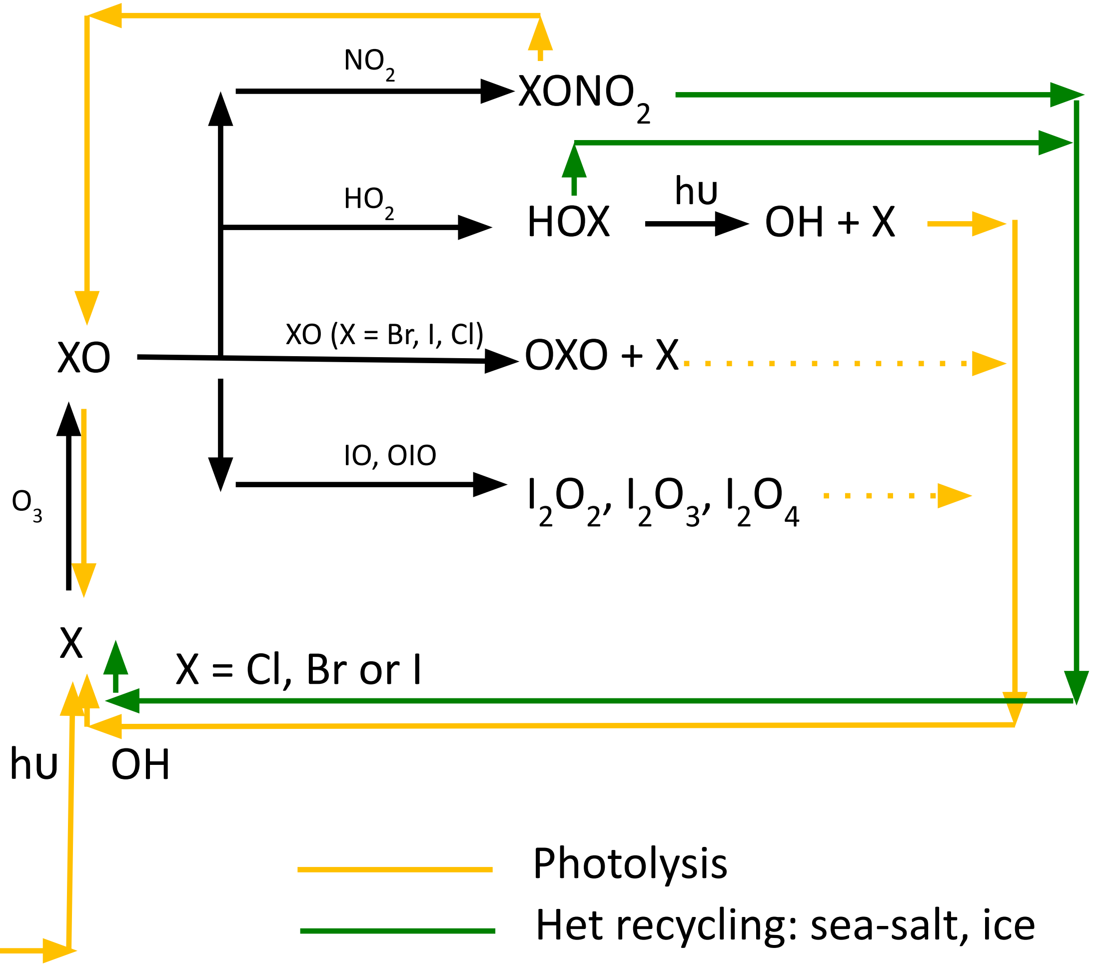
| Source gas | Local Lifetime (WMO, 2010) | Main loss |
|---|---|---|
| $CH_2BrCl$ | 137 days | OH, hv |
| $CH_2Br_2$ | 123 days | OH, hv |
| $CHBrCl_2$ | 78 days | OH, hv |
| $CHBr_2Cl$ | 59 days | hv, OH |
| $CHBr_3$ | 24 days | hv, OH |
| $CH_3I$ | 7 days | hv, OH |
| $CH_2ICl$ | ~ 2–3 h | hv |
| $CH_2IBr$ | ~1 h | hv |
| $CH_2I_2$ | ~ 5 min | hv |
| $HOI/I_2$ | 1 min | hv |




Saiz-Lopez and von Glasow, *Chemical Society Reviews*, 2012

**Short-lived halogens**
**(τ < 6 months)**

| Source gas | Local Lifetime (WMO, 2010) | Main loss |
|---|---|---|
| $CH_2BrCl$ | 137 days | OH, hv |
| $CH_2Br_2$ | 123 days | OH, hv |
| $CHBrCl_2$ | 78 days | OH, hv |
| $CHBr_2Cl$ | 59 days | hv, OH |
| $CHBr_3$ | 24 days | hv, OH |
| $CH_3I$ | 7 days | hv, OH |
| $CH_2ICl$ | ~ 2–3 h | hv |
| $CH_2IBr$ | ~1 h | hv |
| $CH_2I_2$ | ~ 5 min | hv |
| $HOI/I_2$ | 1 min | hv |



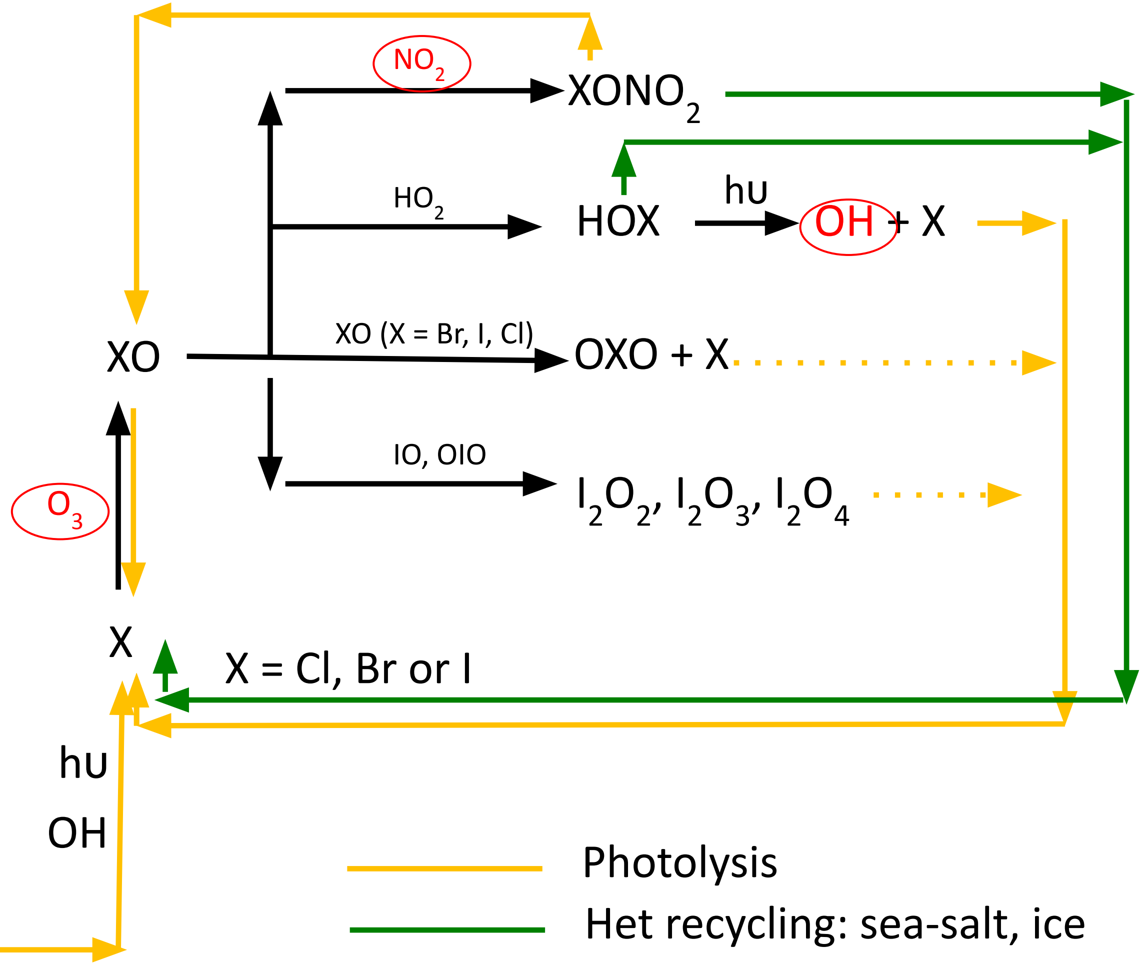

Saiz-Lopez and von Glasow, *Chemical Society Reviews*, 2012

# Introduction: Halogen chemistry

Introductory conclusion: halogen chemistry affects oxidizing capacity even at parts per trillion levels ($10^{-12}$)

**Short-lived halogens**
**(τ < 6 months)**

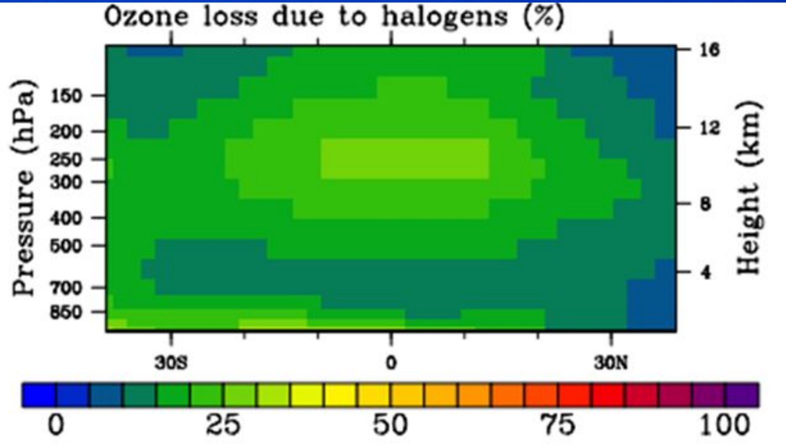
| Source gas | Local Lifetime (WMO, 2010) | Main loss |
|---|---|---|
| $CH_2BrCl$ | 137 days | OH, hv |
| $CH_2Br_2$ | 123 days | OH, hv |
| $CHBrCl_2$ | 78 days | OH, hv |
| $CHBr_2Cl$ | 59 days | hv, OH |
| $CHBr_3$ | 24 days | hv, OH |
| $CH_3I$ | 7 days | hv, OH |
| $CH_2ICl$ | ~ 2–3 h | hv |
| $CH_2IBr$ | ~1 h | hv |
| $CH_2I_2$ | ~ 5 min | hv |
| $HOI/I_2$ | 1 min | hv |




Saiz-Lopez and von Glasow, *Chemical Society Reviews*, 2012

# Impact on atmospheric composition: Ozone

Troposphere




**Natural halogens reduce global tropospheric ozone by 13-20%, particularly over oceans and polar regions**

Saiz-Lopez et al., *Science*, 2007
Read et al., *Nature*, 2008
Navarro et al, *PNAS*,2016
Benavent et al., *Nature Geoscience*, 2022

**Natural halogens (I, Br, Cl)**

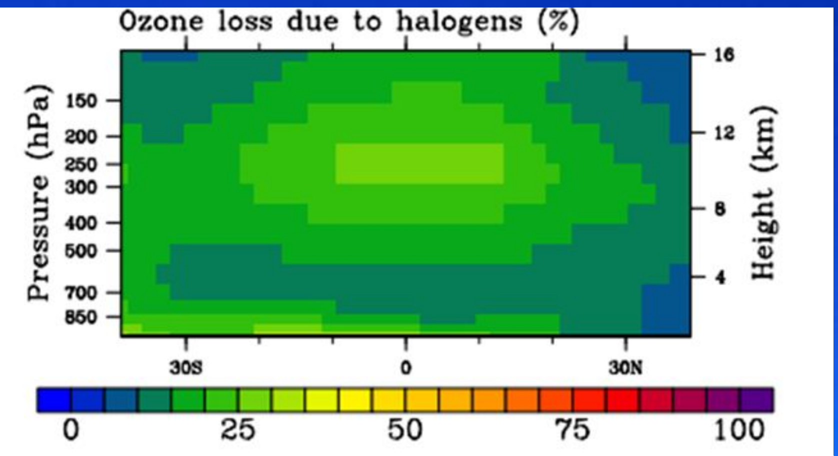
OCEAN

Biosphere

ICE

# Impact on atmospheric composition: Ozone

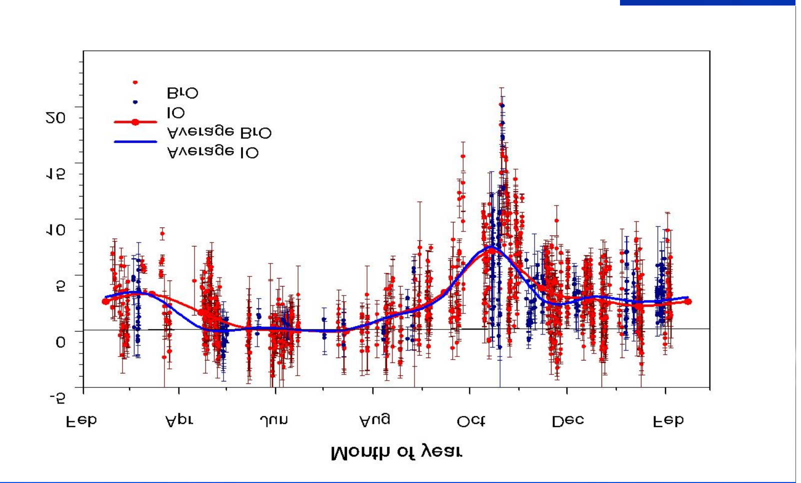
## Troposphere (CAM-Chem)

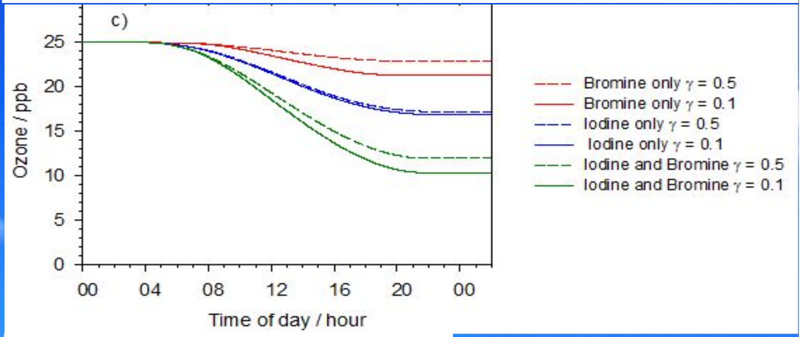



**Natural halogens reduce global tropospheric ozone by 13-20%, particularly over oceans and polar regions**

Saiz-Lopez et al., *Science*, 2007
Read et al., *Nature*, 2008
Navarro et al, *PNAS*,2016
Benavent et al., *Nature Geoscience*, 2022

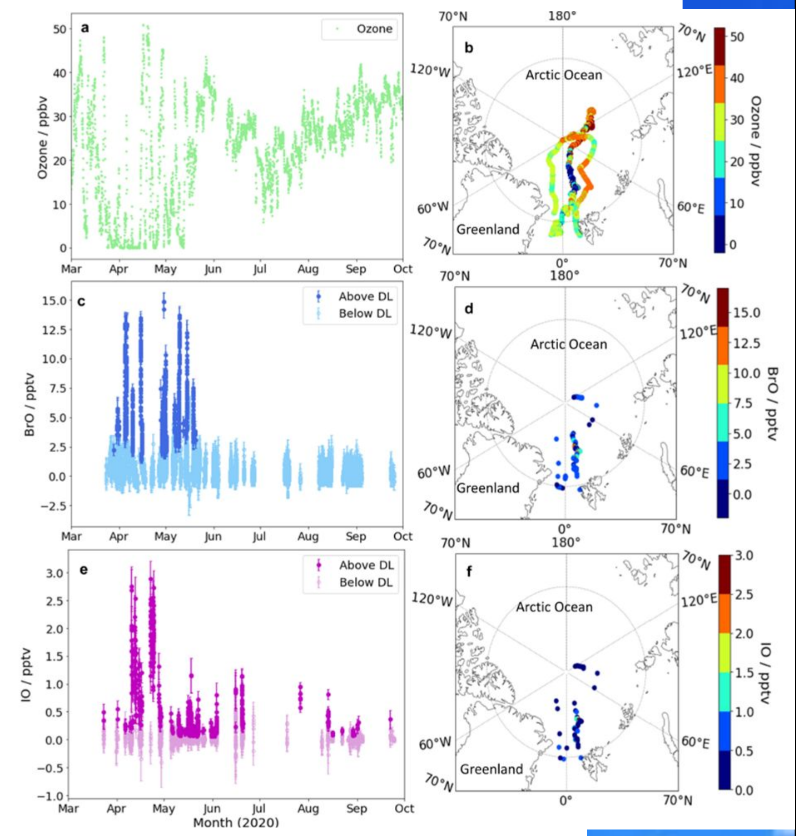
**Br+I - driven ozone depletion in the ANTARCTIC**






Saiz-Lopez et al., *Science*, 2007

**MOSAiC: Br+I - driven ozone depletion in the ARCTIC**




Benavent et al., *Nature Geoscience*, 2022

**Natural halogens (I, Br, Cl)**

Ozone depletion events: ozone is reduced to below detectable levels during polar spring.

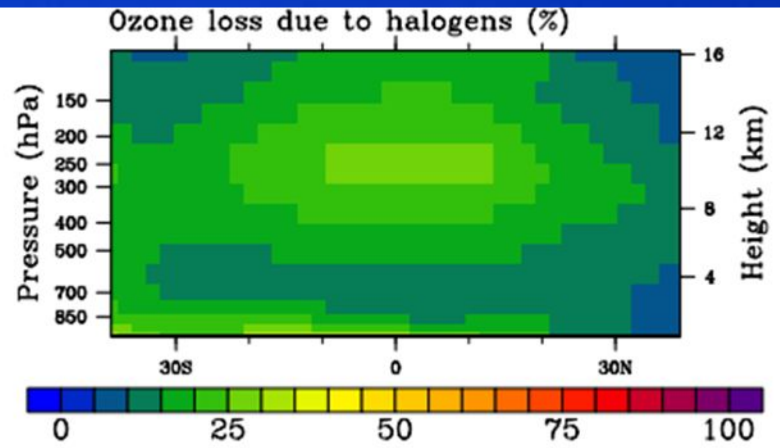
OCEAN

Biosphere

ICE

# Impact on atmospheric composition: Ozone

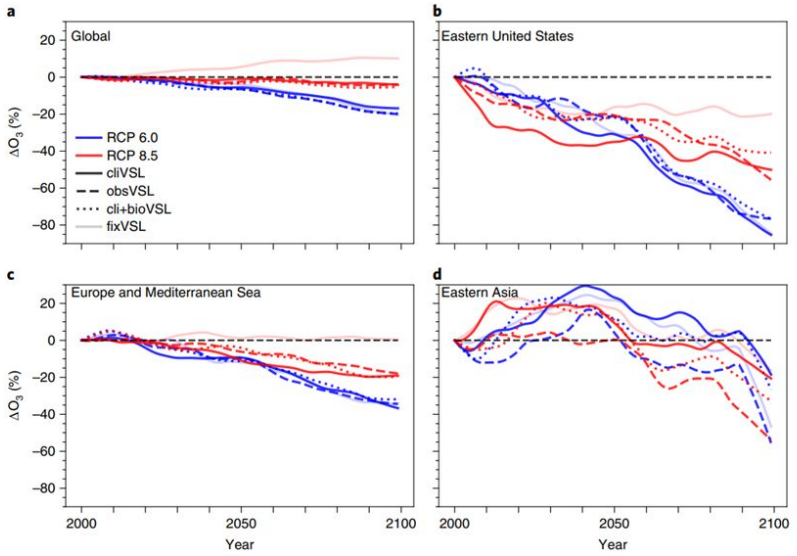
## Troposphere (CAM-Chem)




**Natural halogens reduce global tropospheric ozone by 13-20%, particularly over oceans and polar regions**

Saiz-Lopez et al., *Science*, 2007
Read et al., *Nature*, 2008
Navarro et al, *PNAS*,2016
Benavent et al., *Nature Geoscience*, 2022

**21st century**




Iglesias-Suarez et al., *Nature Climate Change*, 2020

news & views

AIR QUALITY

Natural control on ozone pollution

**Natural halogens (I, Br, Cl)**

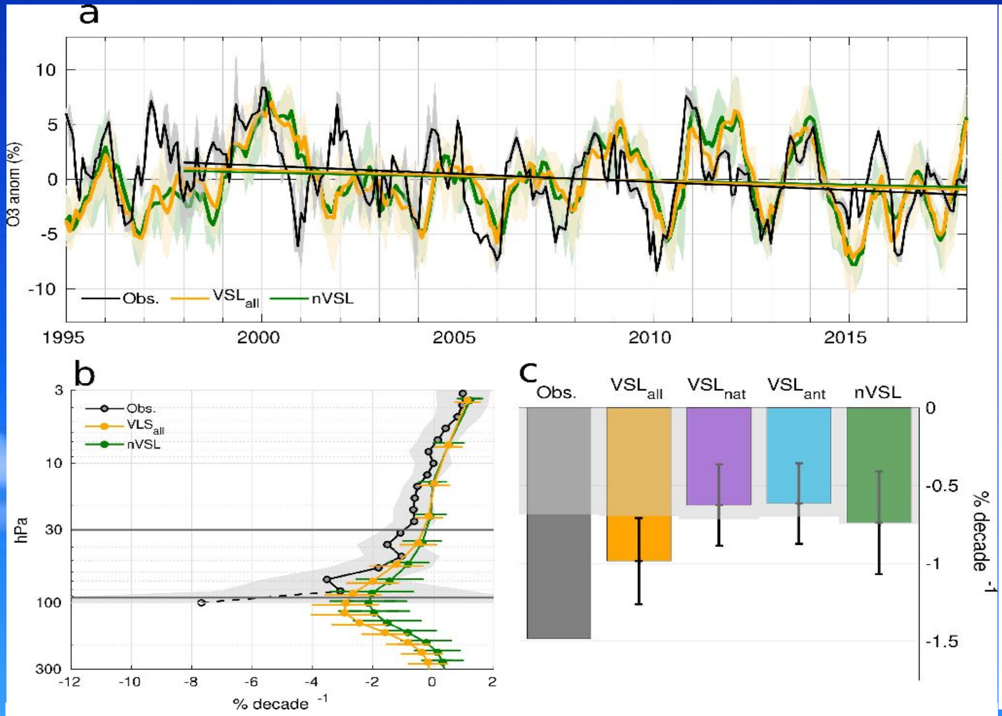
OCEAN

Biosphere

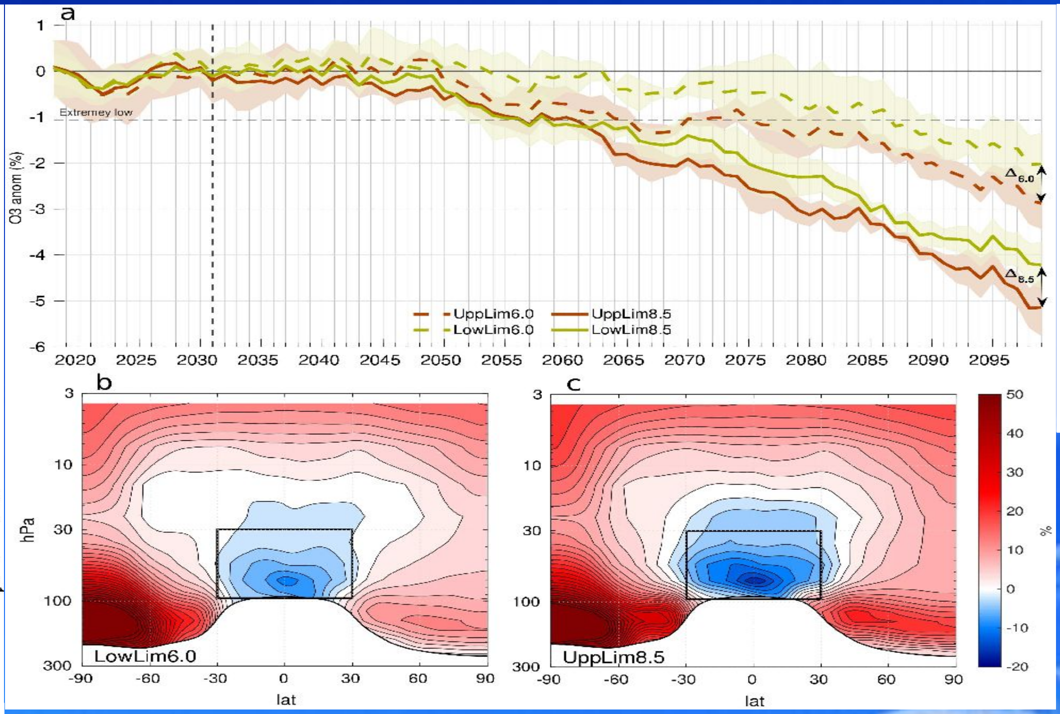
ICE

# Impact on atmospheric composition: Ozone

## Stratosphere (WACCM)




**Halogens amplify (25%) ozone depletion trends in the tropical lower stratosphere**




Villamayor et al., *Nature Climate Change*, 2023

**Conclusions:**

**i) halogens are key for the future ozone in this region**

**ii) Antropogenic short-lived chlorocarbons should be regulated in the Montreal Protocol**

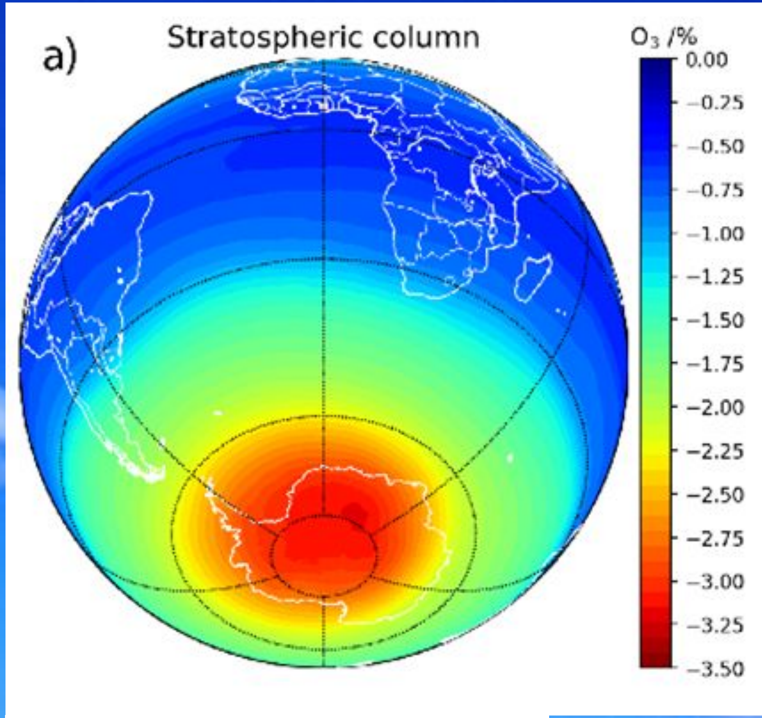
**Natural halogens (I, Br, Cl)**

OCEAN

Biosphere

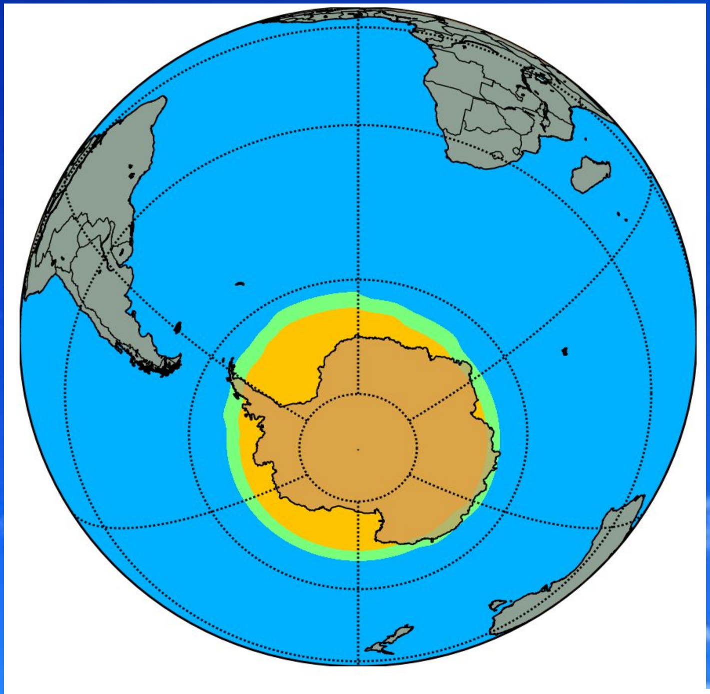
ICE

## Stratosphere (WACCM)




Cuevas et al., *PNAS*, 2022

**Natural halogens (0.7 pptv iodine and 5 pptv bromine) reduce about 10-20% ozone in the Antarctic lower stratosphere**



**Natural halogens expand the size of the ozone hole by 11% or 1.2 million $km^2$**

**Natural halogens (I, Br, Cl)**

OCEAN

Biosphere

ICE

# Impact on atmospheric composition: Methane

**Methane oxidation:**

$CH_4 + Cl \rightarrow CH_3O_2 + HCl$

$CH_4 + OH \rightarrow CH_3O_2 + H_2O$

→ **Increases loss of $CH_4$**

→ **Main loss channel of $CH_4$**

**Halogens – ozone destruction**

$X + O_3 \rightarrow XO + O_2$

$O_3 + h\nu \rightarrow O^1D + O_2$

$O^1D + H_2O \rightarrow 2\ OH$

→ **Halogens indirectly reduce OH** ↑ (Main loss channel of $CH_4$)

Net effect →

**Natural halogens increase methane´s lifetime and radiative forcing by 10%**

Li et al., *Nature Communications*, 2022

**Natural halogens (I, Br, Cl)**

OCEAN

Biosphere

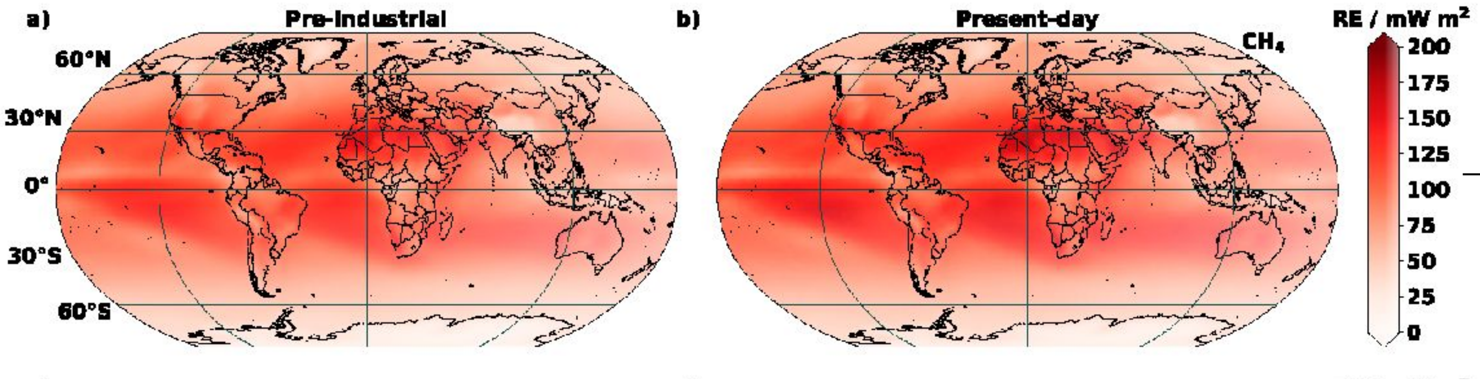
ICE

# Effect on the global radiative balance

**Short-lived halogens have an effect on the short-lived climate forcers…..so, what is the effect of natural halogens on the radiative balance?**

# Effect on the global radiative balance

Halogens in CESM

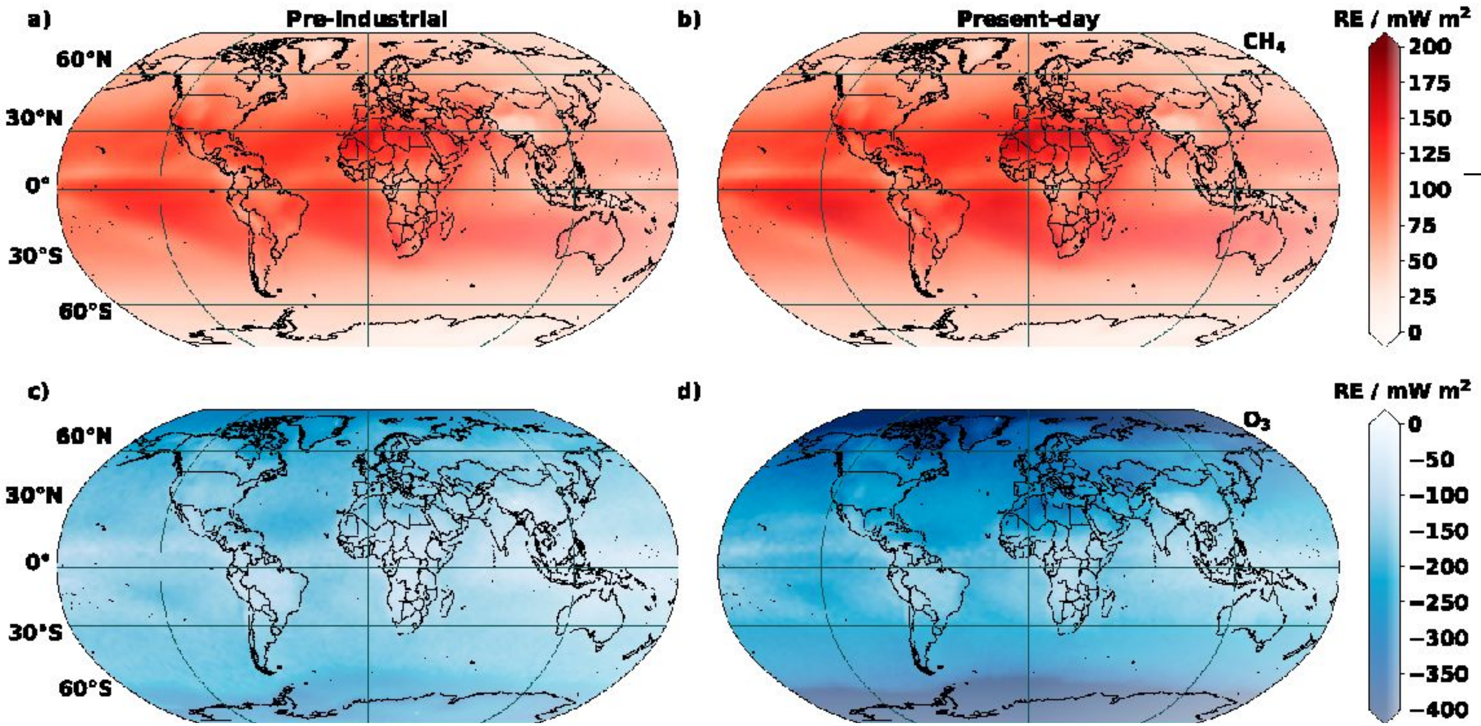



Halogens **increase** methane and its radiative effect

Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance

Halogens in CESM



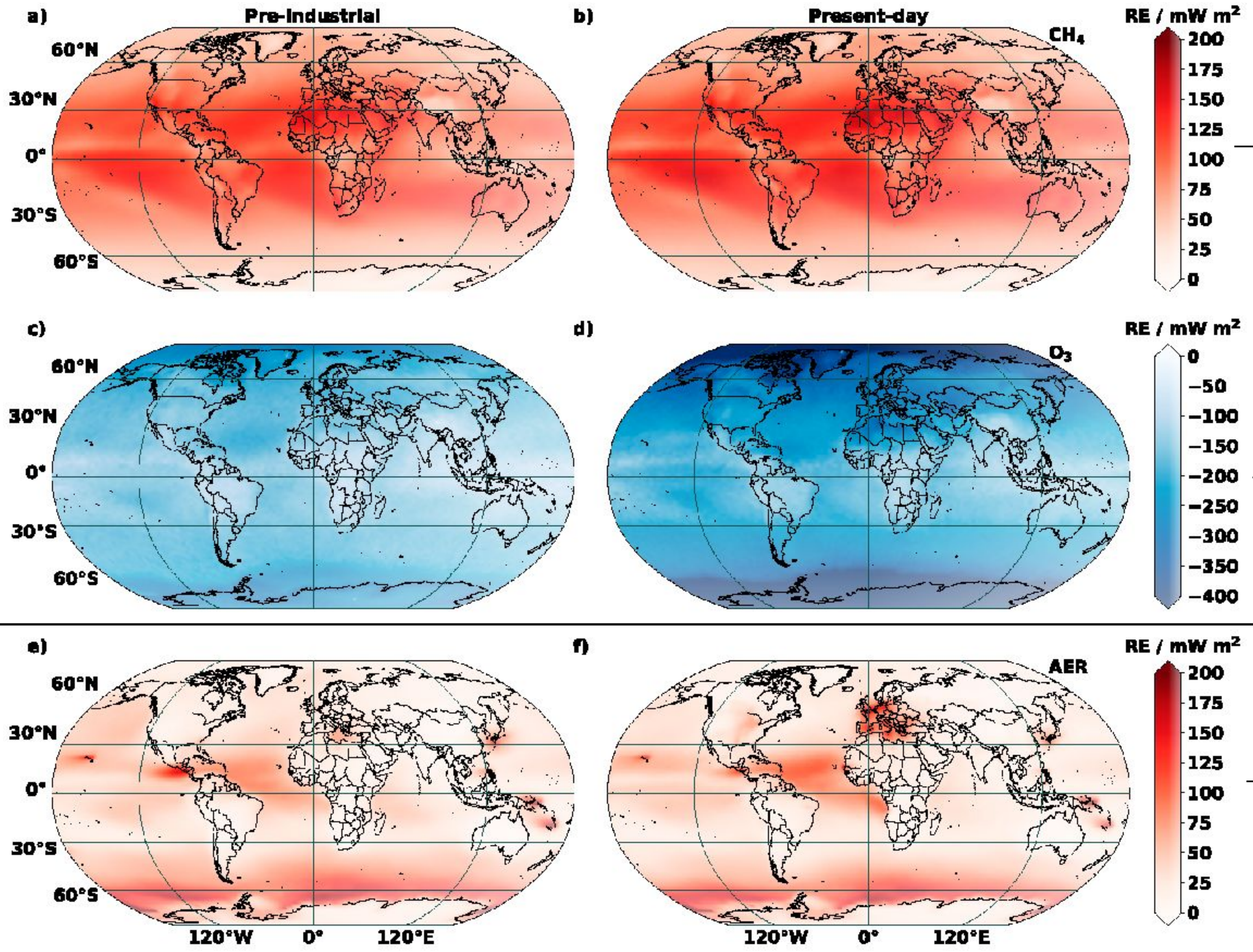

Halogens **increase** methane and its radiative effect

Halogens **reduce** ozone and its radiative effect (dominated by iodine)

Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance

Halogens in CESM



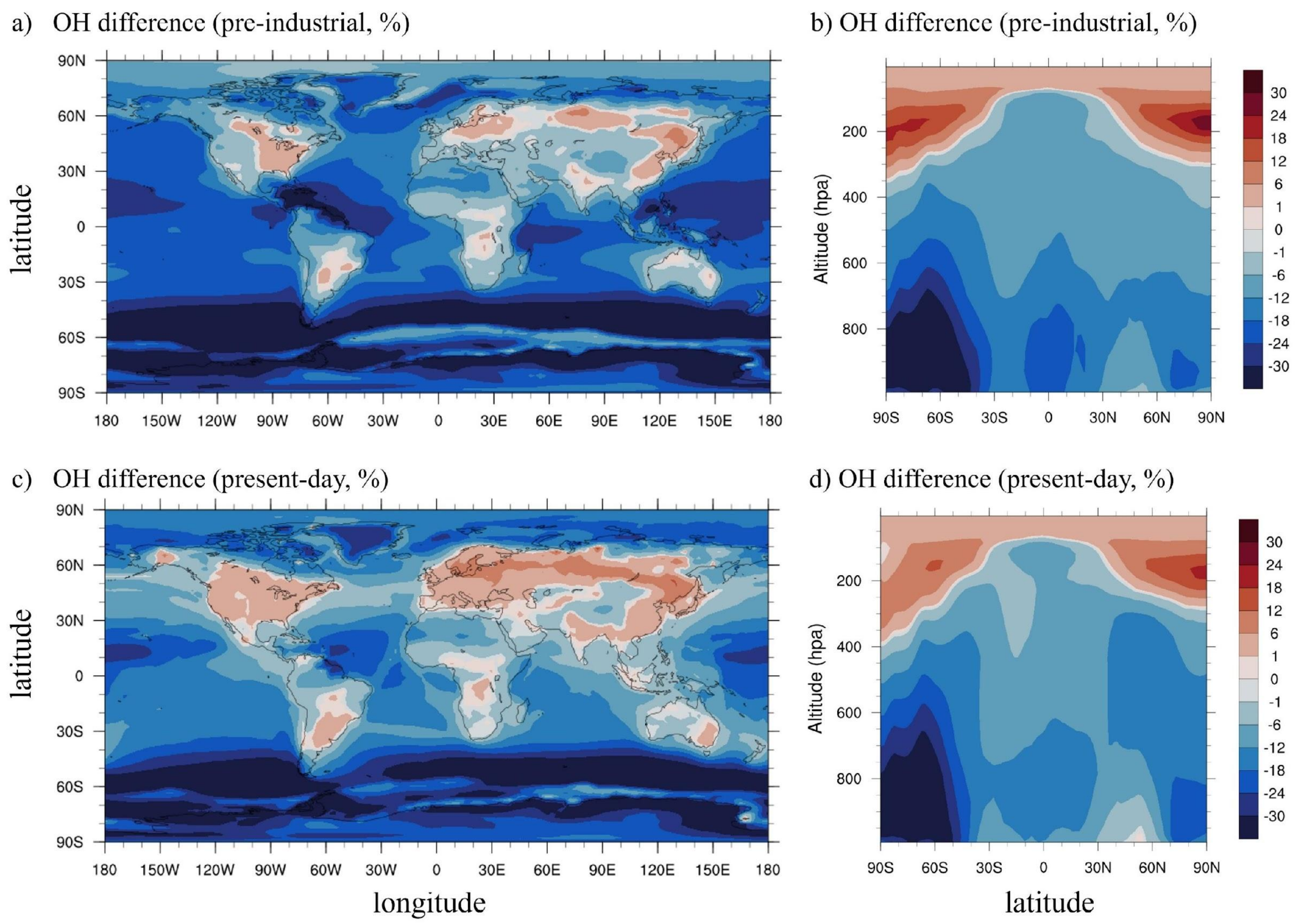

Halogens **increase** methane and its radiative effect

Halogens **reduce** ozone and its radiative effect (dominated by iodine)

Halogens **reduce** aerosols and its radiative effect

Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance: aerosols




Halogens globally **reduce** OH (ozone is the main precursor of OH) and as a consequence they reduce the OH-driven secondary aerosol formation.

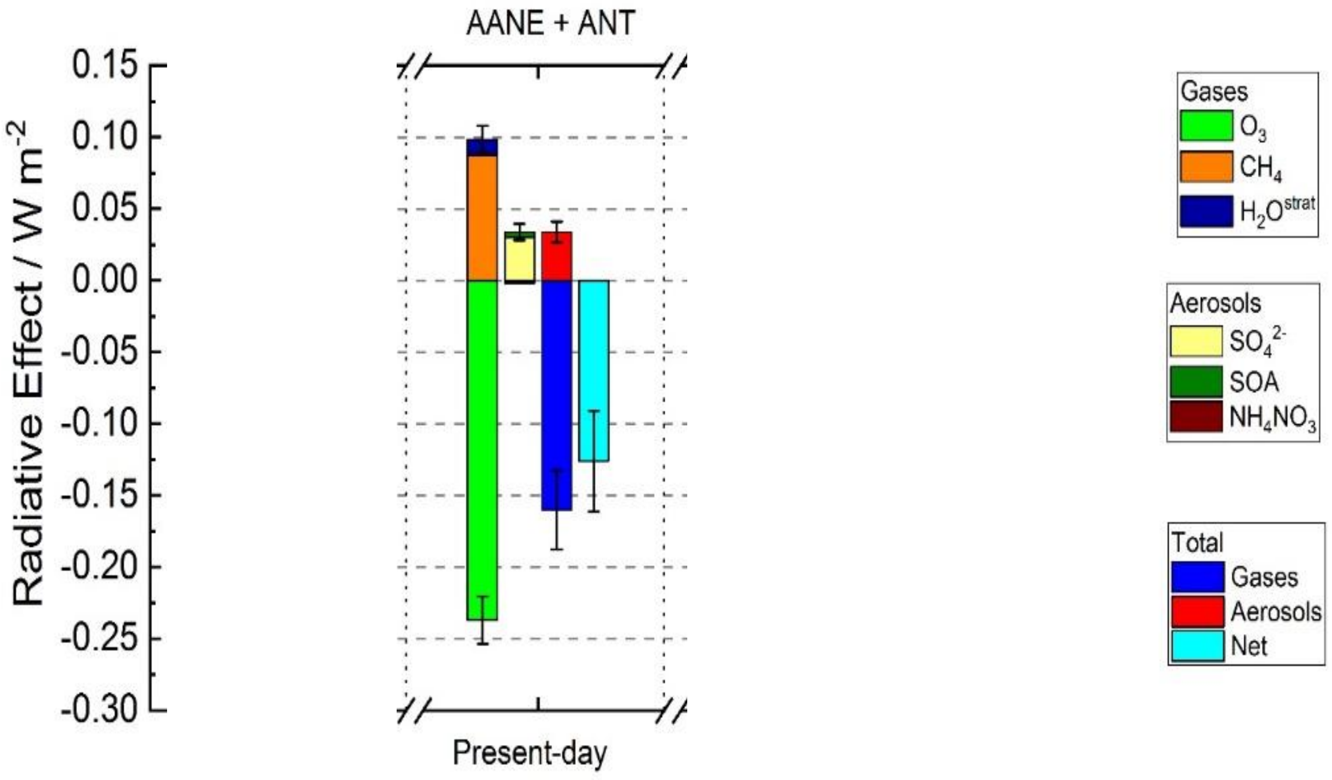
Less aerosol formation leads to less aerosol cooling. **Therefore, halogens reduce indirectly the aerosol cooling.**

Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance: net effect

Halogens in CESM

Summary of radiative effect

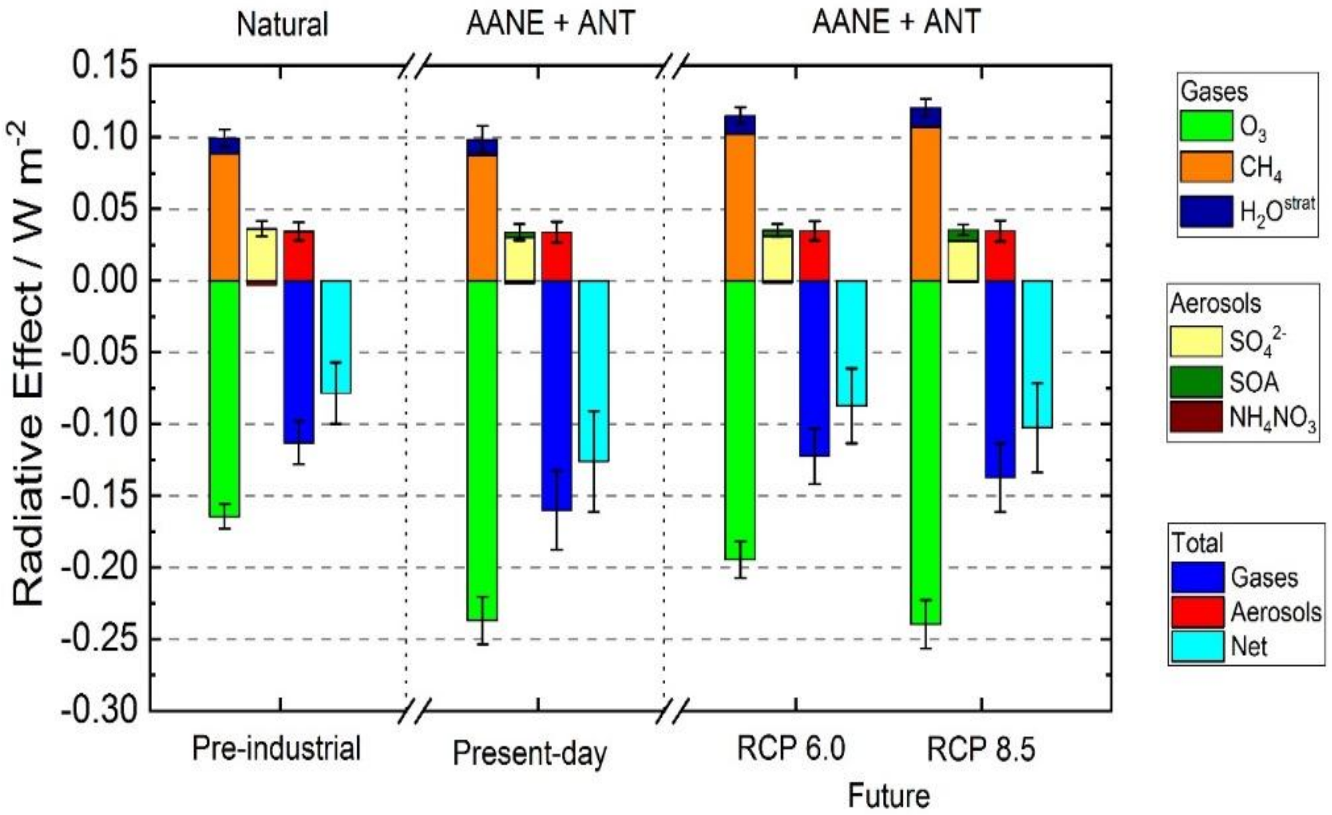



*Stratospheric water vapour is driven by chemical oxidation of methane.

Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance: net effect

Summary of radiative effect

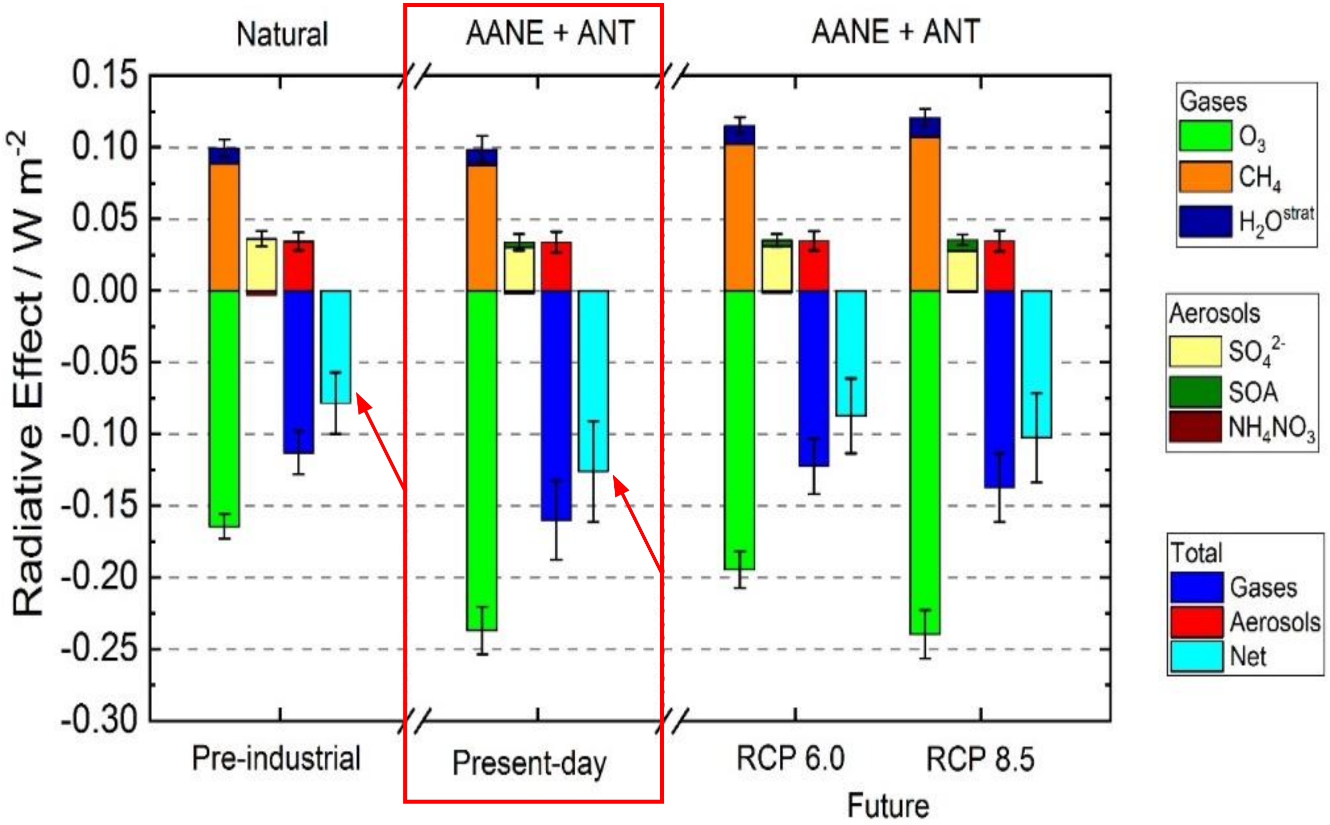



*Stratospheric water vapour is driven by chemical oxidation of methane.

Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance: net effect

Summary of radiative effect




Three categories of halogen emissions

Pre-industrial:

**Natural**: Natural emissions, strongly linked to climate (depend on SST, primary productivity, lifting of SSA by winds and sea ice extent)

Present and Future:

**AANE**: Anthropogenically-amplified natural emissions (depend on O3 deposition to oceans and atmospheric acidification)

**ANT**: Anthropogenic emissions (e.g. $CH_2Cl_2$, $CHCl_3$….

not controlled by Montreal Protocol)

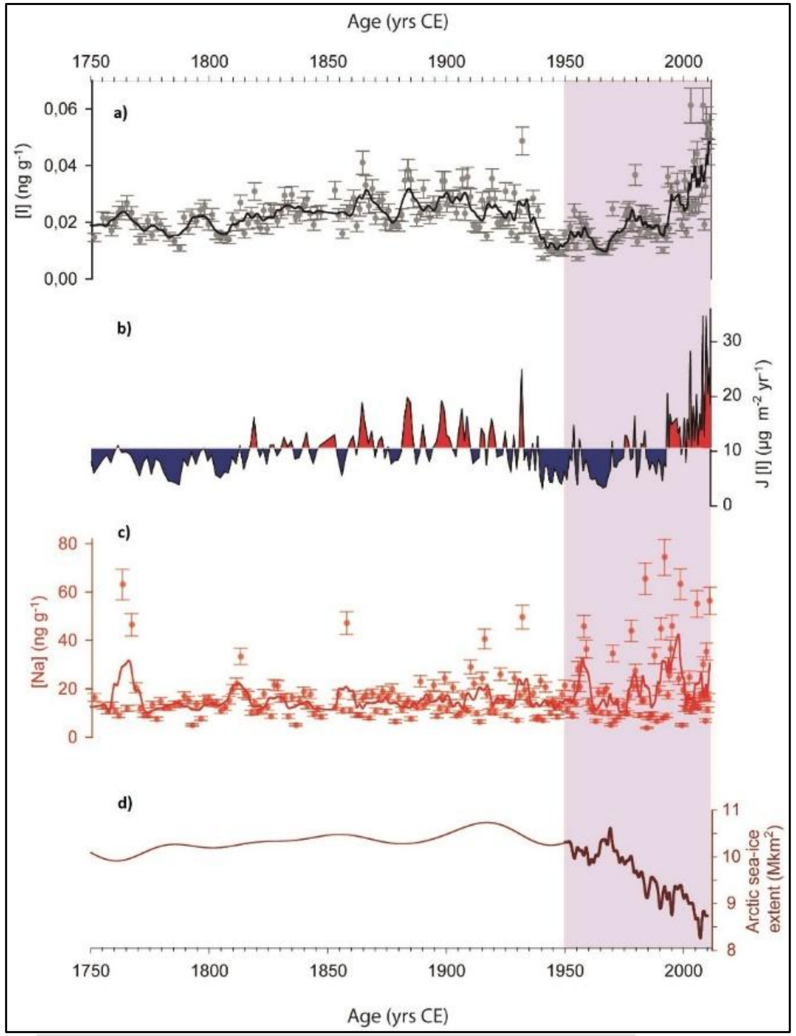
Inorganic halogen burden is larger at present wrt PI:

147-187% for chlorine
8-9% for bromine
24-29% for iodine

Saiz-Lopez et al., *Nature*, in press

# AANE: Anthropogenically-amplified natural emissions

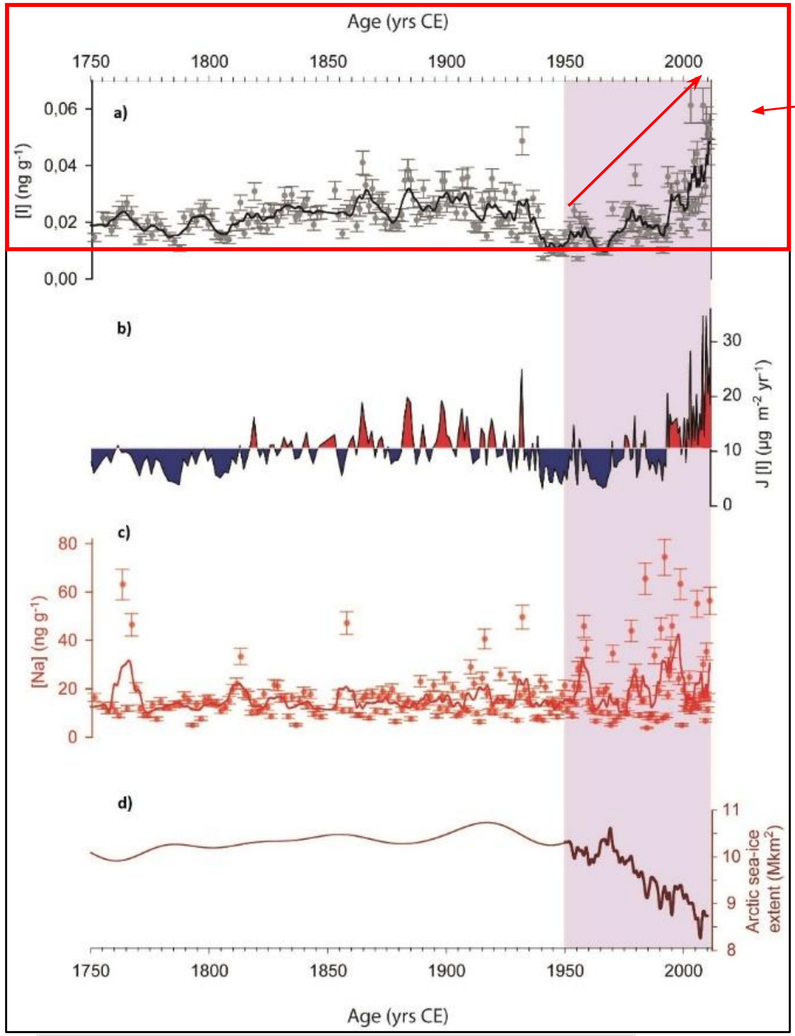
Evolution of iodine levels in the atmosphere (Ice core observations at Renland, Greenland)




Cuevas et al., *Nature Communications*, 2018

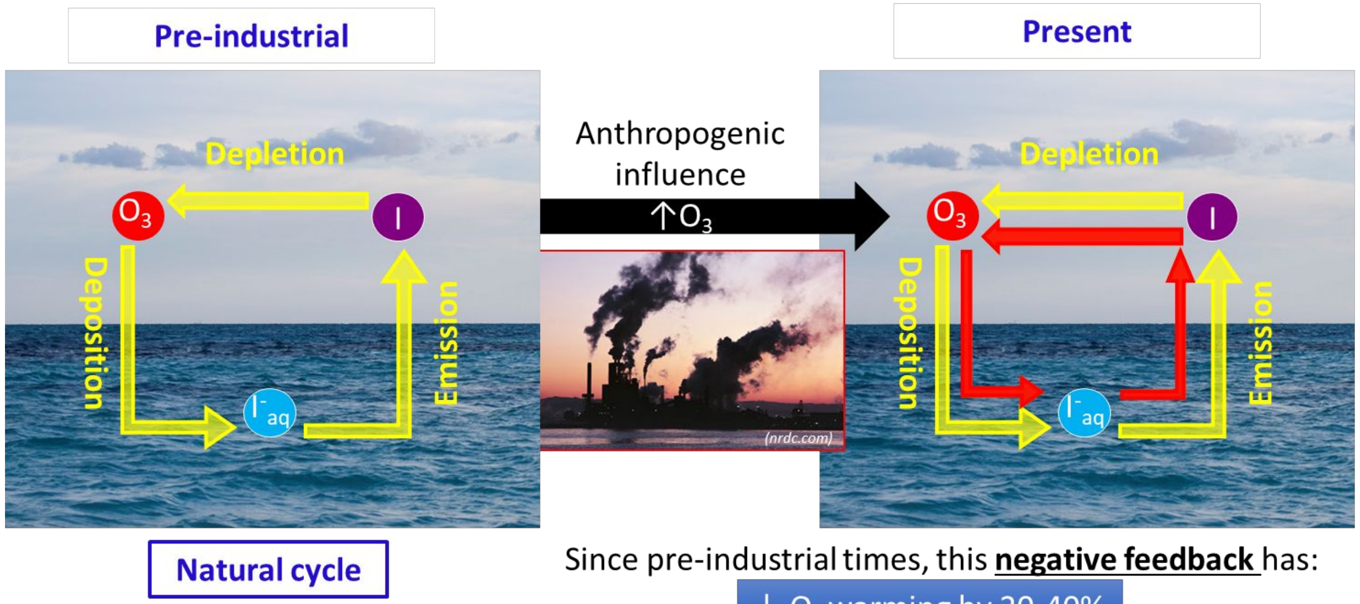
# AANE: Anthropogenically-amplified natural emissions

Evolution of iodine levels in the atmosphere




Cuevas et al., *Nature Communications*, 2018

**Ozone pollution and sea ice decrease have tripled iodine emissions since mid-XX century**



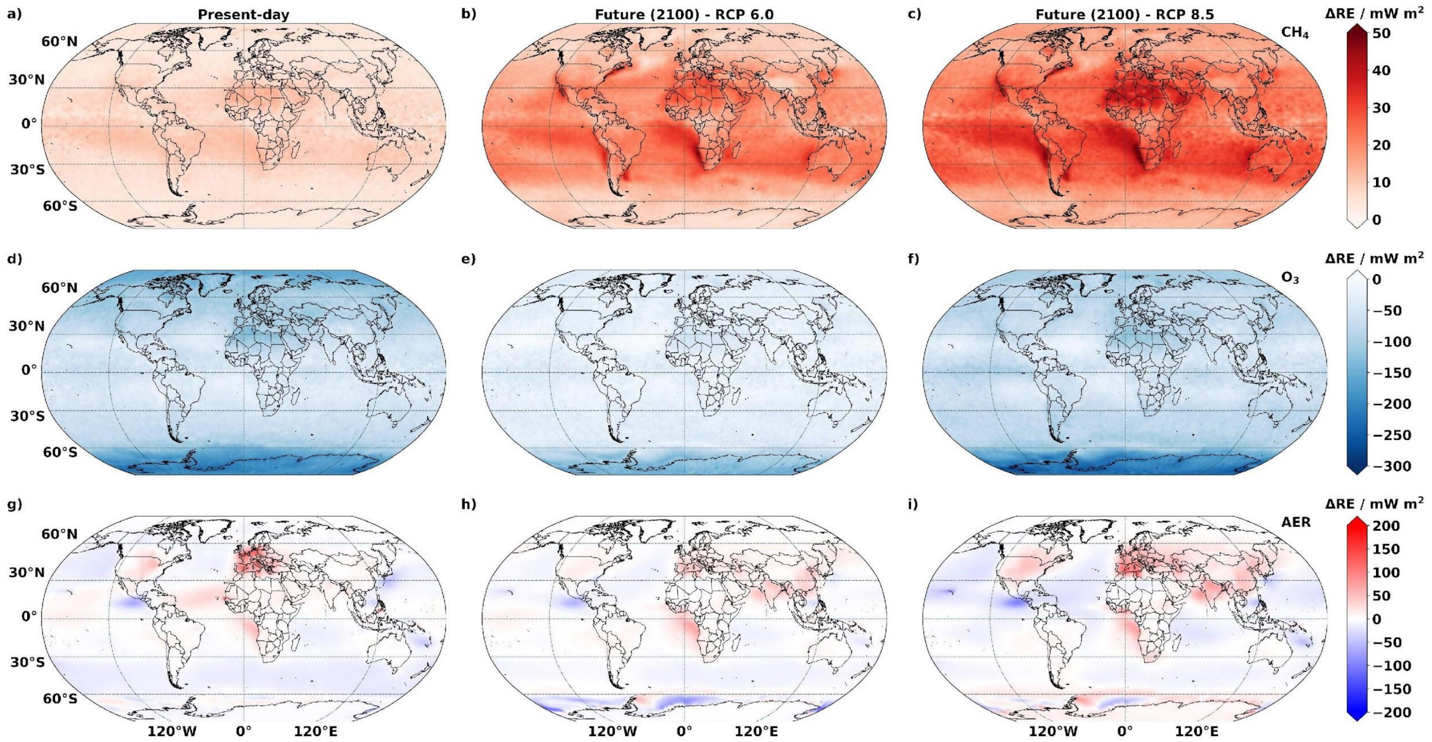

Since pre-industrial times, this **negative feedback** has:

↓ $O_3$ warming by 20-40%

Prados-Román et al., *ACP*, 2015

# Effect on the global radiative balance: change relative to pre-industrial

Spatial distribution of RE in present and future relative to PI



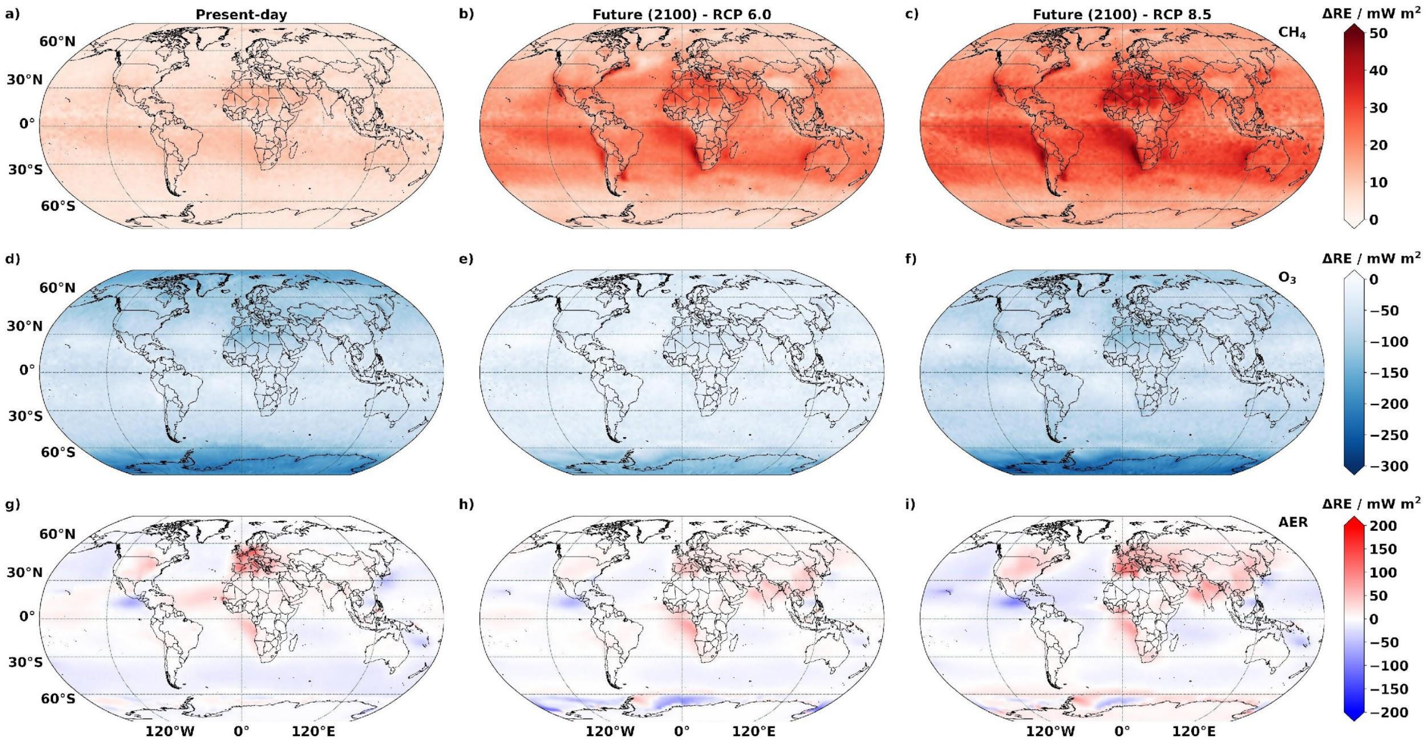

ΔRE of methane **increases** towards the future

ΔRE of ozone remains relatively constant although depending on future climate projections

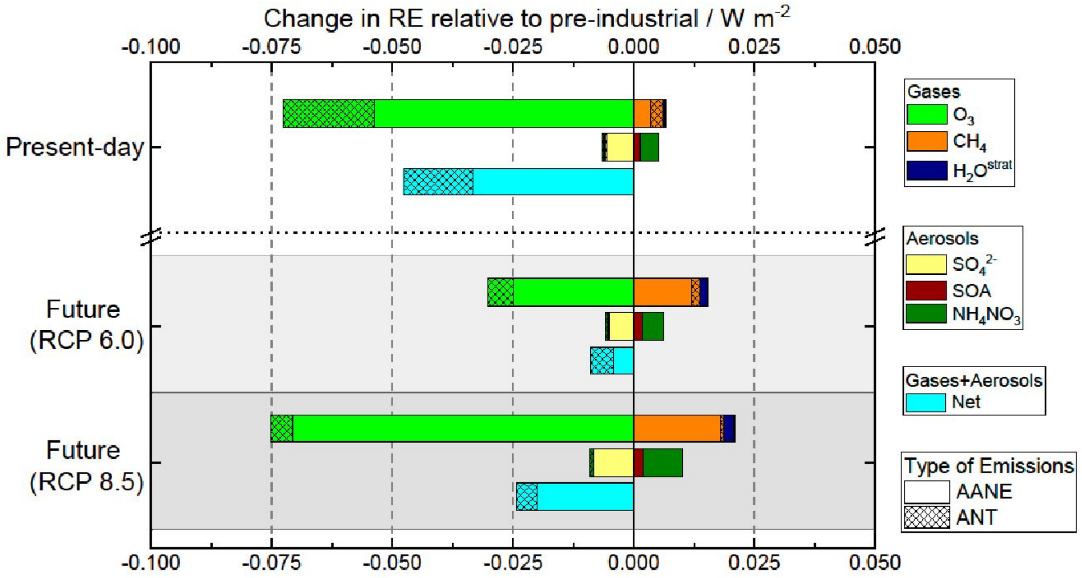
ΔRE of aerosols is highly non-linear across aerosol types (sulphate dominates the signal), time and space depending on future anthropogenic emissions.

# Effect on the global radiative balance: change relative to pre-industrial

## Spatial distribution of RE in present and future relative to PI



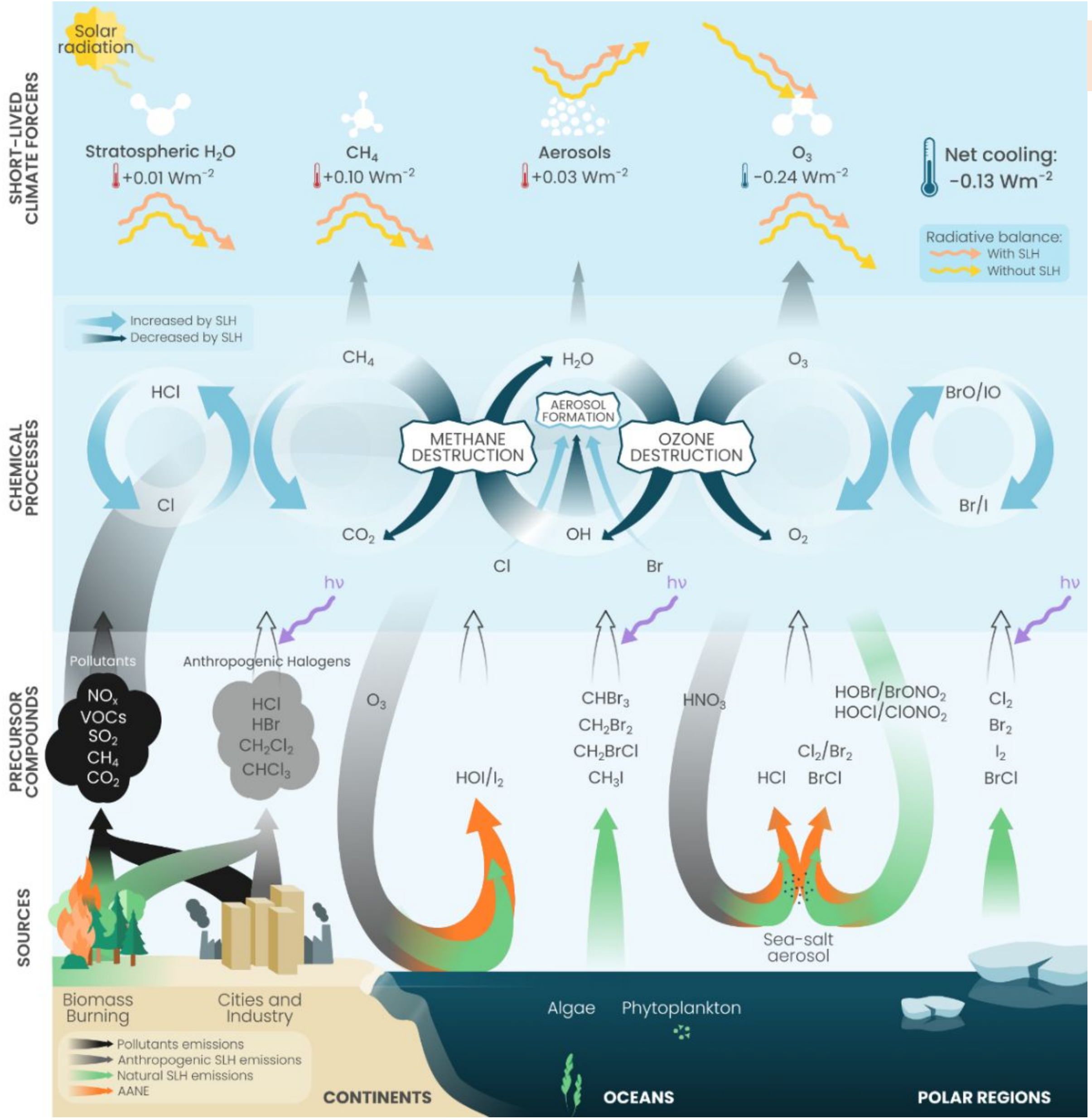

## RE in present and future relative to PI




The overall conclusion is that **net halogen-driven cooling effect has been amplified since PI due to AANE** and is expected to future change towards the future depending on climate and socioeconomic development.

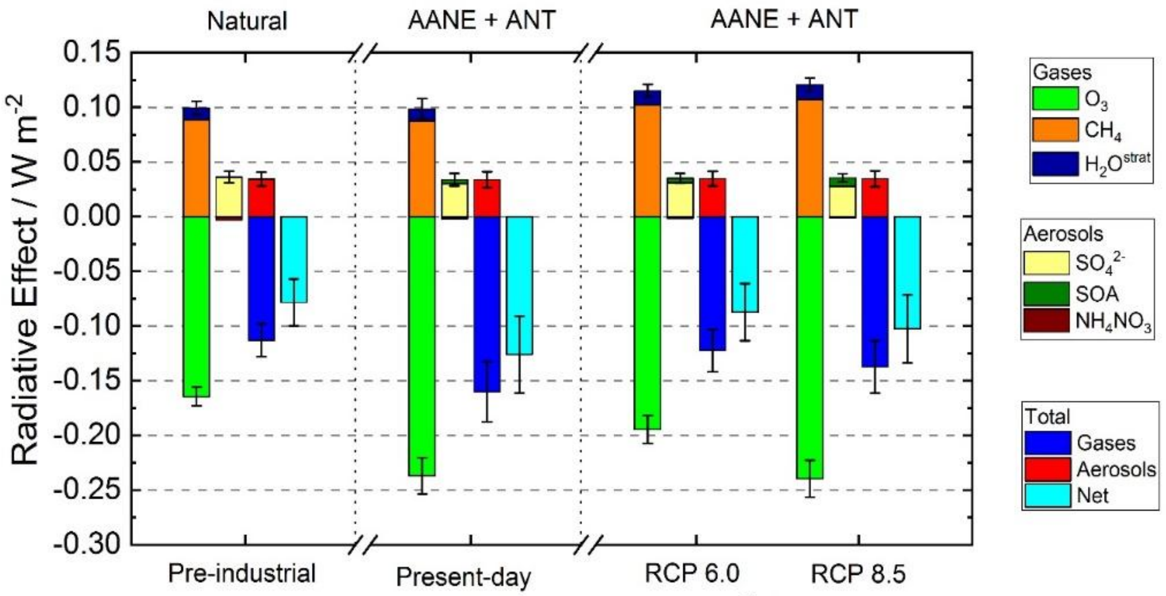
Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance: net effect




Saiz-Lopez et al., *Nature*, in press

Natural halogens exert an indirect cooling effect on climate




The changing indirect cooling effect of natural halogens across pre-industrial, present and future climates results from the complex non-linear chemical interactions between halogens and the abundance of key chemically active SLCF

This newly identified cooling mechanism is not accounted for in current climate models such as those used in CMIP or IPCC assessments.

**CESM is the only climate model with a full representation of SLH sources and chemistry.**

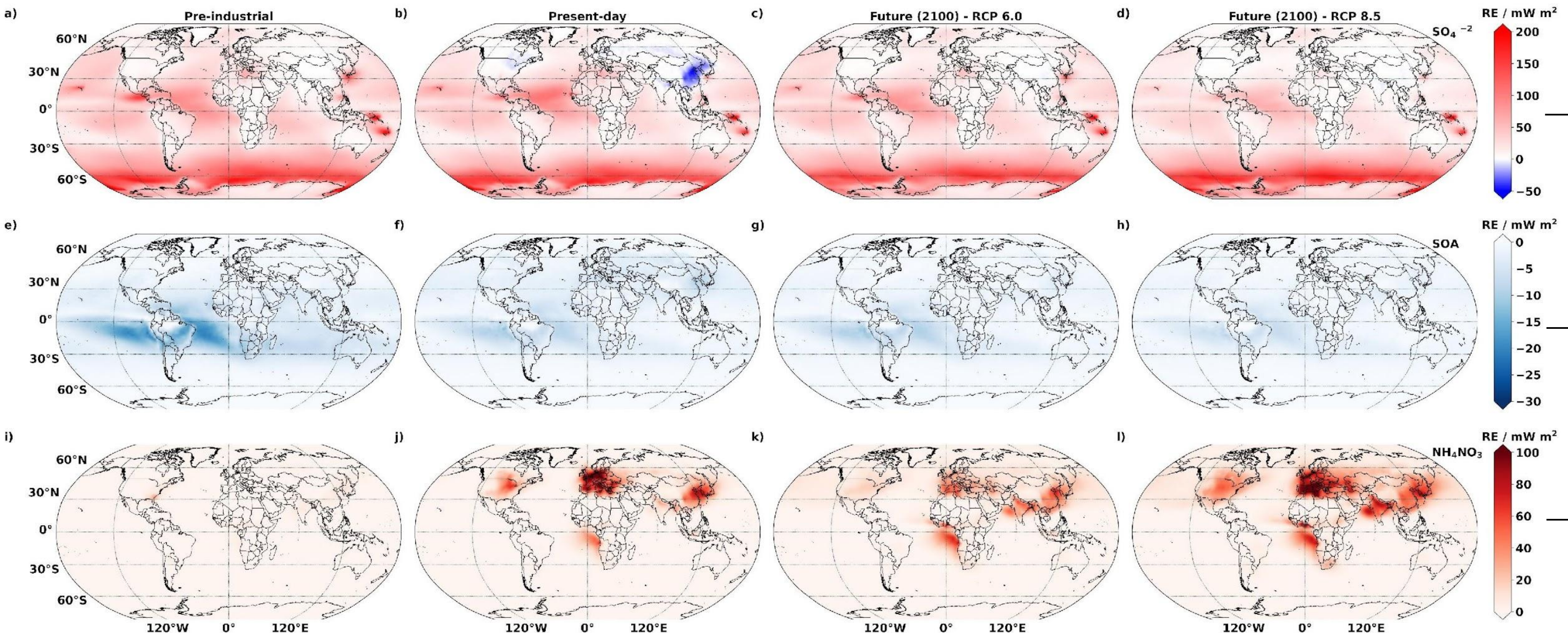
# Conclusions

- We have identified that natural halogen chemistry exert a substantial indirect cooling effect on climate that arises from highly non-linear interactions with short-lived climate forcers (ozone, methane, aerosols and stratospheric water vapour).

- Importantly, this cooling effect has increased since pre-industrial times driven by the anthropogenic amplification of natural halogen emissions.

# Effect on the global radiative balance: aerosols

The aerosol radiative effect (RE) response is highly non-linear across aerosol types, time and space.




Halogen-mediated OH reduction **leads to reduction of sulfate aerosol (e.g. reducing DMS oxidation)**

Halogen-mediated OH reduction **does not compensate for Cl-driven VOC oxidation**

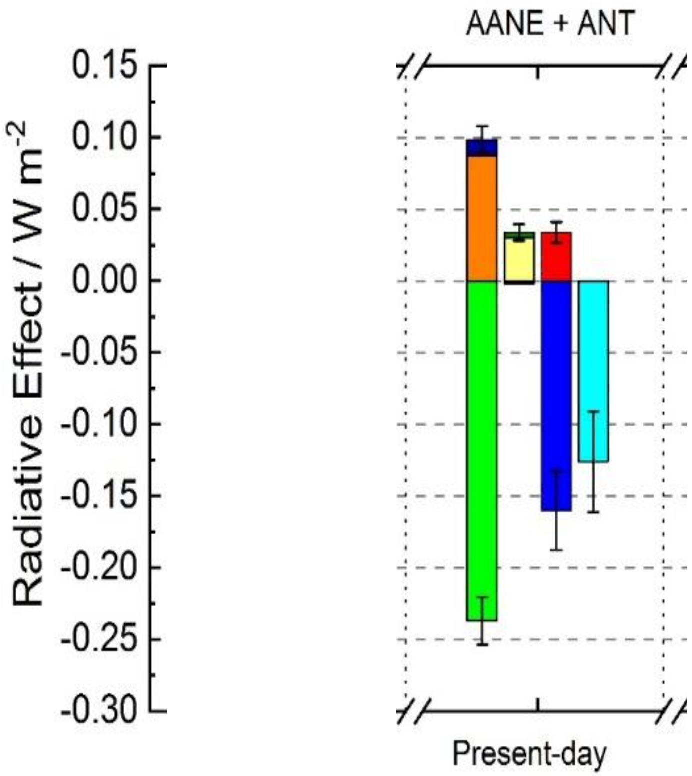
Halogen-mediated OH reduction **leads to decrease of ammonium nitrate aerosol (e.g. reducing $HNO_3$ formation)**

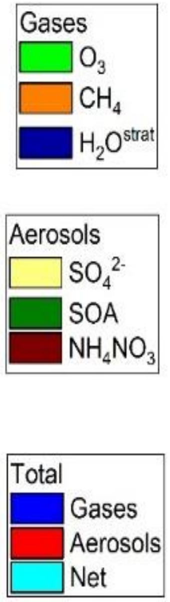
Saiz-Lopez et al., *Nature*, in press

# Effect on the global radiative balance: net effect

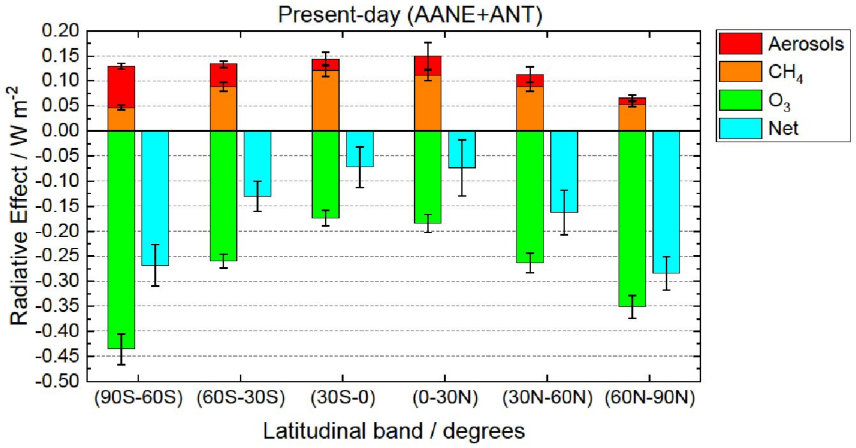
Halogens in CESM

## Summary of radiative effect




## Latitudinal variation of halogen-driven radiative effect




**Cooling effect of halogens peaks at high latitudes (up to 3 times larger than over tropics).**

*Stratospheric water vapour is driven by chemical oxidation of methane.

Saiz-Lopez et al., *Nature*, in press