Role of iodine recycling on sea-salt aerosols in the global marine boundary layer

Qinyi Li[1], Yee Jun Tham[2,3], Rafael P. Fernandez[4,5], Xu-Cheng He[3], Carlos A. Cuevas[1], and Alfonso Saiz-Lopez[1,*]

[1] Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, CSIC, Madrid 28006, Spain;

[2] School of Marine Sciences, Sun Yat-Sen University, Zhuhai 519082, China;

[3] Institute for Atmospheric and Earth System Research / Physics, Faculty of Science, University of Helsinki, Helsinki 00014, Finland.

[4] Institute for Interdisciplinary Science, National Research Council (ICB-CONICET), Mendoza, 5501, Argentina

[5] School of Natural Sciences, National University of Cuyo (FCEN-UNCuyo), Mendoza, 5501, Argentina

[*] Corresponding author: Alfonso Saiz-Lopez (a.saiz@csic.es)

Published on Li et al., GRL, 2022, 10.1029/2021GL097567.

CONTENTS

Tropospheric reactive iodine

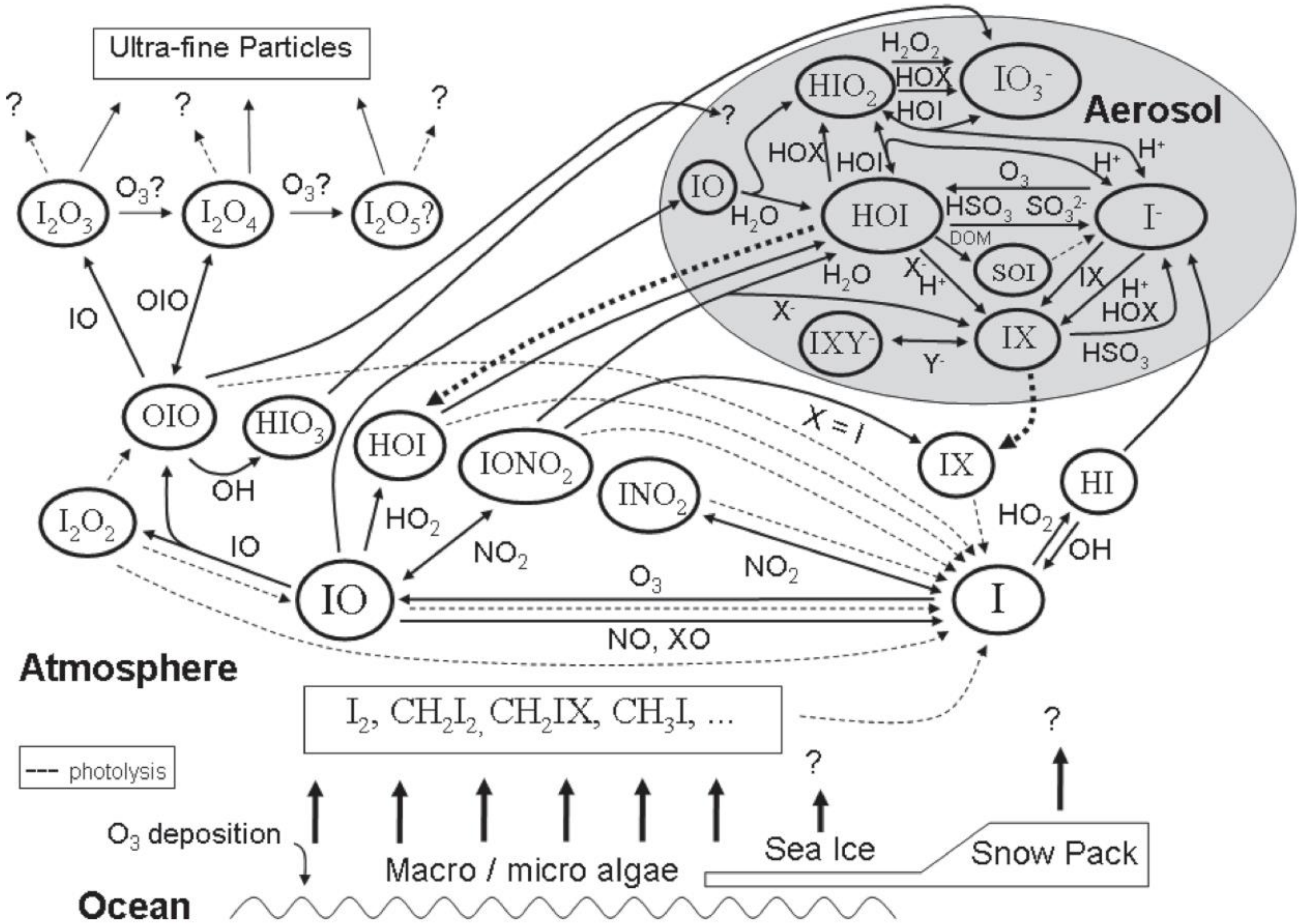
CAM-Chem simulation design

CAM-Chem simulation results in marine boundary layer

- ✓ **iodine distribution**
- ✓ **iodine speciation**
- ✓ **iodine recycling impacts on halogen atoms**
- ✓ **iodine recycling impacts on atmospheric oxidants**

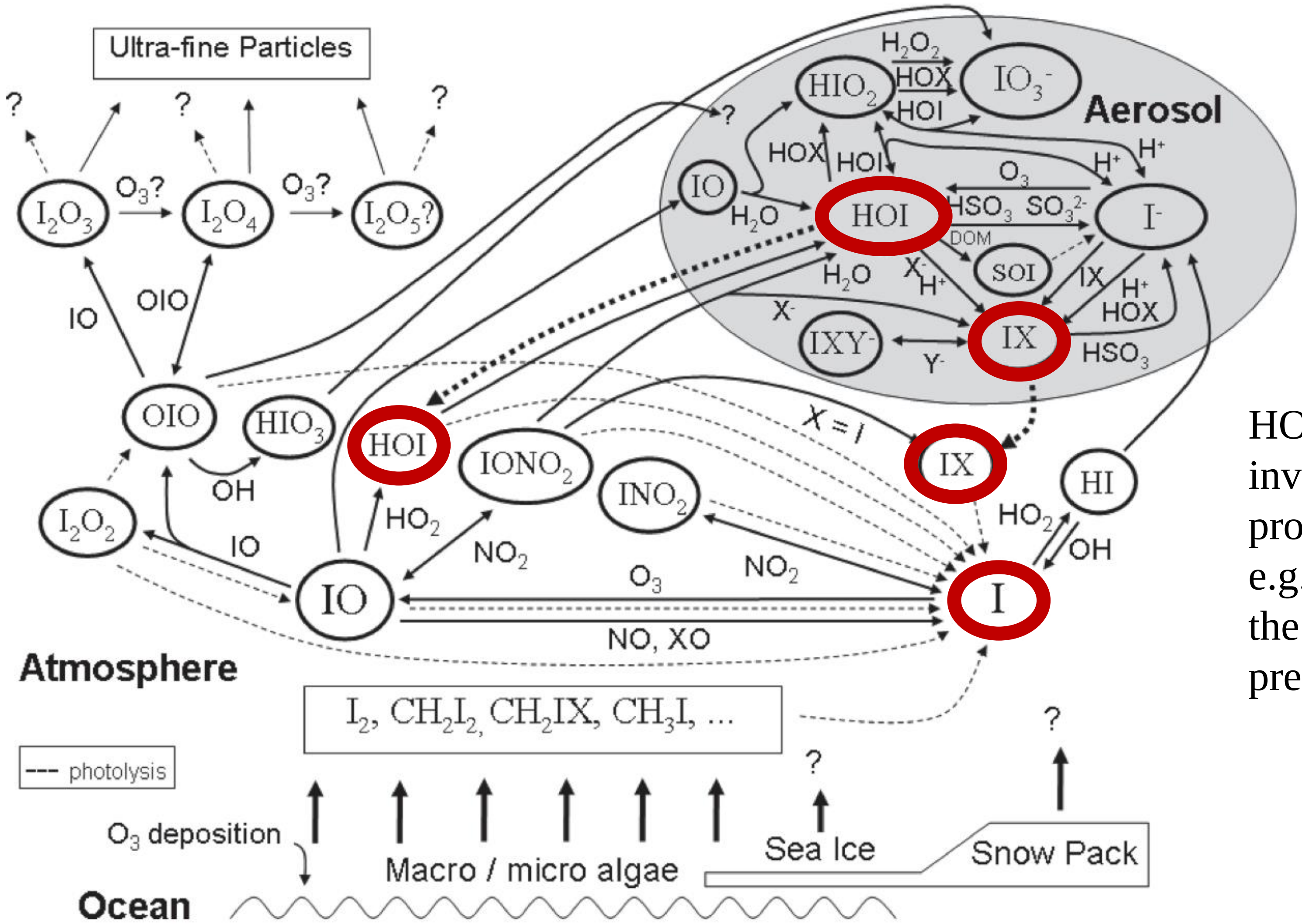
Summary

Tropospheric iodine chemistry



Iodine species have significant impacts on tropospheric chemistry and oxidation capacity.
(Saiz-Lopez et al., 2012)

Tropospheric iodine chemistry



HOI is a critical species and involved in many heterogeneous processes:
e.g., uptake on aerosols, activating the release of IBr and ICl, precursors of all halogen atoms.

$$HOI \xrightarrow{SSA} 0.5IBr + 0.5ICl$$

Tropospheric iodine chemistry

Theoretical proposal (Vogt et al., *Nature*, 1996)

Published: 26 September 1996

A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer

Rainer Vogt, Paul J. Crutzen & Rolf Sander

Nature **383**, 327–330 (1996) | Cite this article

Field evidence at one coastal site, but much faster (≥0.3) (Tham et al., *PNAS*, 2021)

RESEARCH ARTICLE | EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

Direct field evidence of autocatalytic iodine release from atmospheric aerosol

Yee Jun Tham, Xu-Cheng He, Qinyi Li, Carlos A. Cuevas, Jiali Shen, Joni Kalliokoski, Chao Yan, Siddharth Iyer, Tuuli Lehmusjärvi, Sehyun Jang, Roseline C. Thakur, Lisa Beck, Deniz Kemppainen, Miska Olin, Nina Sarnela, Jyri Mikkilä, Jani Hakala, Marjan Marbouti, Lei Yao, Haiyan Li, Wei Huang, Yonghong Wang, Daniela Wimmer, Qiaozhi Zha, Juhani Virkanen, T. Gerard Spain, Simon O'Doherty, Tuija Jokinen, Federico Bianchi, Tuukka Petäjä, Douglas R. Worsnop, Roy L. Mauldin III, Jurgita Ovadnevaite, Darius Ceburnis, Norbert M. Maier, Markku Kulmala, Colin O'Dowd, Miikka Dal Maso, Alfonso Saiz-Lopez, and Mikko Sipilä -36 Authors Info & Affiliations

Edited by Mark Thiemens, University of California San Diego, La Jolla, CA, and approved December 10, 2020 (received for review May 18, 2020)

January 21, 2021 | 118 (4) e2009951118 | https://doi.org/10.1073/pnas.2009951118

Adopted in models with assumed efficiency, 0.01 to 0.06 (e.g., Saiz-Lopez et al., *ACP*, 2014)

Atmos. Chem. Phys., 14, 13119–13143, 2014
https://doi.org/10.5194/acp-14-13119-2014

Article | Peer review | Metrics | Related articles

Research article — 10 Dec 2014

Iodine chemistry in the troposphere and its effect on ozone

A. Saiz-Lopez[1], R. P. Fernandez[*,1], C. Ordóñez[2], D. E. Kinnison[3], J. C. Gómez Martín[1,**], J.-F. Lamarque[3], and S. Tilmes[3]

[1]Atmospheric Chemistry and Climate Group, Institute of Physical Chemistry Rocasolano, CSIC, Madrid 28006, Spain
[2]Met Office, EX1 3PB, Exeter, UK
[3]Atmospheric Chemistry Division, NCAR, Boulder, CO 80301, USA
[*]now at: National Research Council (CONICET), FCEN-UNCuyo, UTN-FRM, Mendoza 5501, Argentina
[**]now at: School of Chemistry, University of Leeds, LS2 9JT, Leeds, UK

Global significance? Impacts on oxidation capacity?

Requires global model simulation.
(present work; Li et al., *GRL*, 2022)

Geophysical Research Letters

Research Letter | Open Access

Role of Iodine Recycling on Sea-Salt Aerosols in the Global Marine Boundary Layer

Qinyi Li, Yee Jun Tham, Rafael P. Fernandez, Xu-Cheng He, Carlos A. Cuevas, Alfonso Saiz-Lopez

First published: 07 March 2022 | https://doi.org/10.1029/2021GL097567

CONTENTS

Tropospheric reactive iodine

CAM-Chem simulation design

CAM-Chem simulation results in marine boundary layer

- ✓ **iodine distribution**
- ✓ **iodine speciation**
- ✓ **iodine recycling impacts on halogen atoms**
- ✓ **iodine recycling impacts on atmospheric oxidants**

Summary

CAM-Chem simulation design

1. Specified dynamic simulation.
2. Simulation period: Jan 2017 to Dec 2018 with the first 12 months as spin-up.
3. Grid resolution: ~1°.
4. From the surface to the stratosphere: 56 layers.
5. Time step: 30 min.
6. Initial condition: a previous CAM-Chem simulation (Veres et al., 2020).
7. Input meteorological condition: GEOS-5.
8. Marine boundary layer: results of the lowest seven layers (>900 hPa).

Table S1. CAM-Chem simulation design

Case	HOI uptake coefficient	IBr yield	ICl yield
Base	0.06	0.0	0.0
Conventional	0.06	0.5	0.5
Updated	0.3	0.5	0.5
Upper-limit	0.9	0.5	0.5

$$HOI \xrightarrow{SSA} 0.5IBr + 0.5ICl$$

CONTENTS

Tropospheric reactive iodine

CAM-Chem simulation design

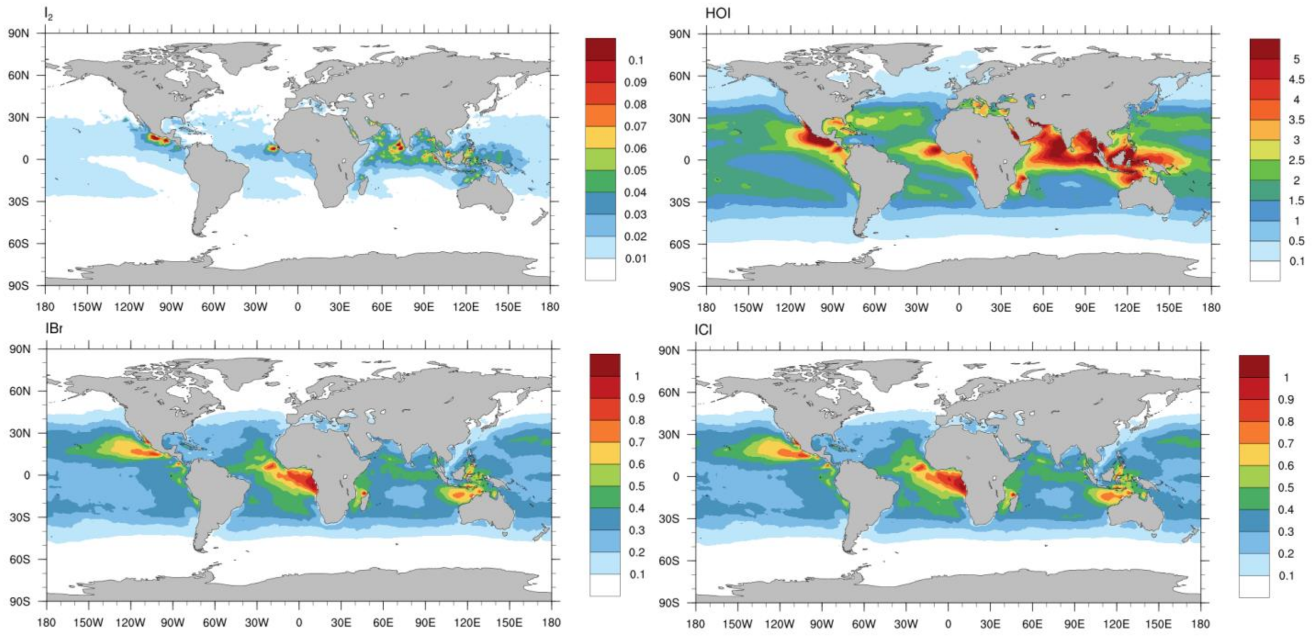
CAM-Chem simulation results in marine boundary layer

- ✓ iodine distribution
- ✓ iodine speciation
- ✓ iodine recycling impacts on halogen atoms
- ✓ iodine recycling impacts on atmospheric oxidants

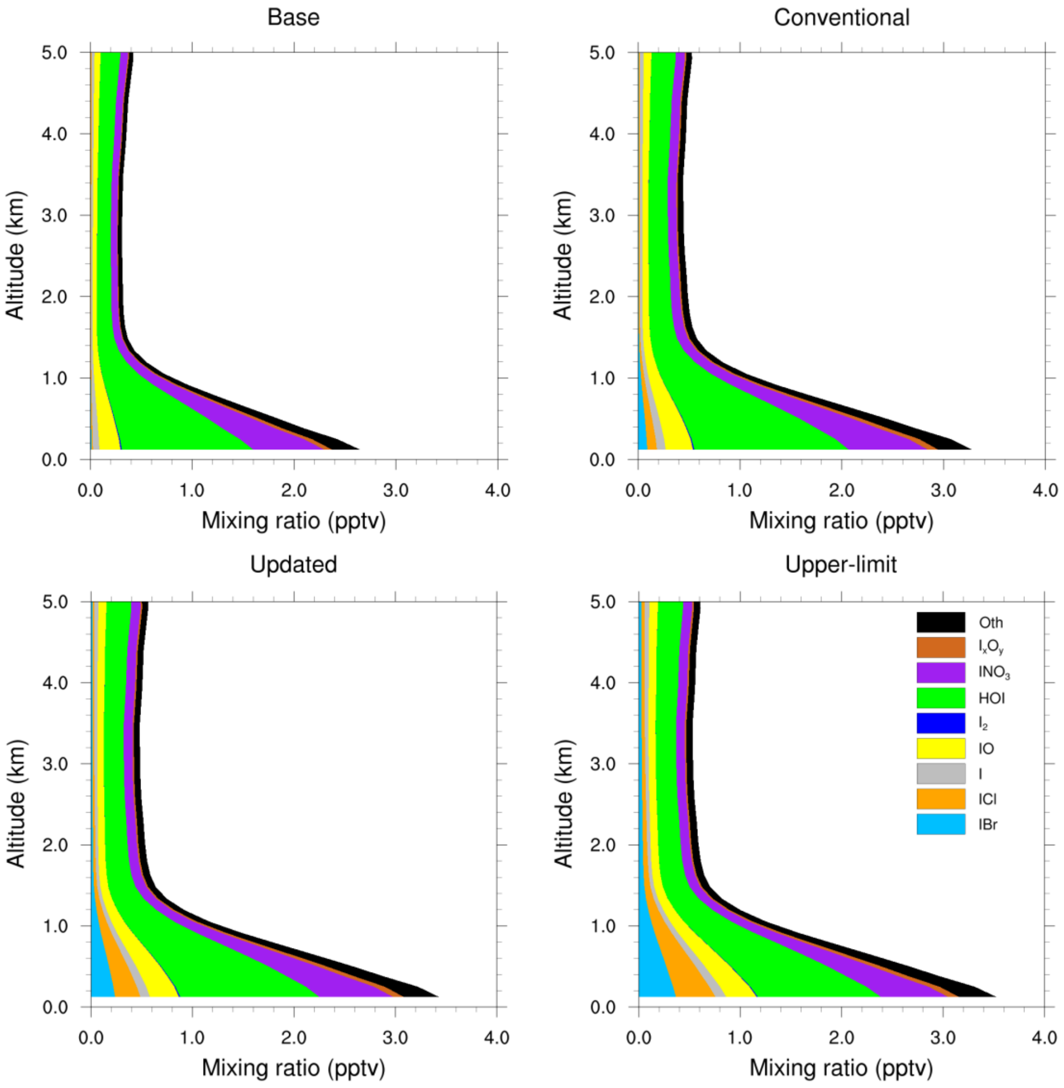
Summary

CAM-Chem simulation results in marine boundary layer

Iodine distribution

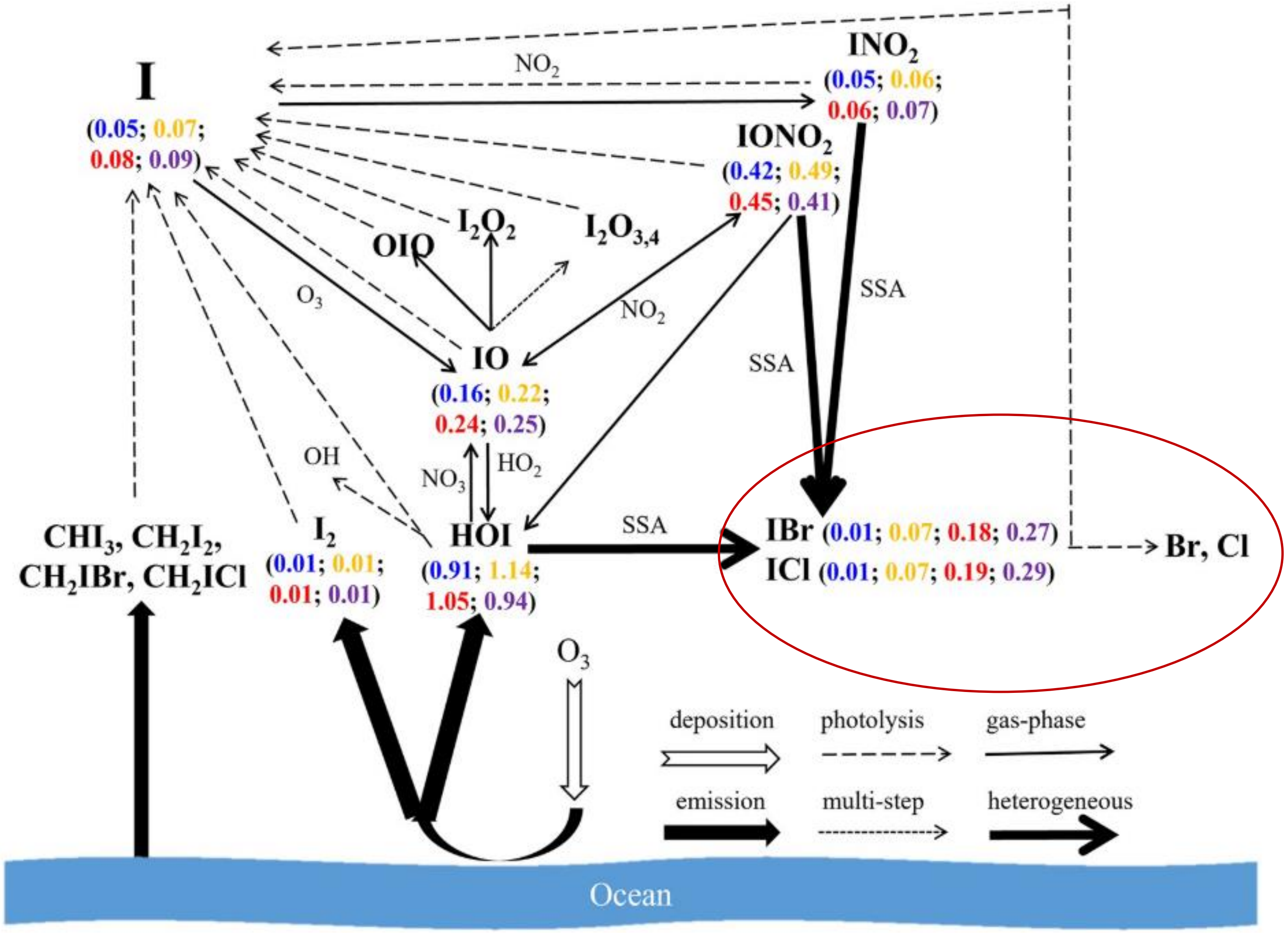


Spatial distribution of annual average I_2, HOI, IBr, and ICl mixing ratios (pptv) in MBL in the Updated case.



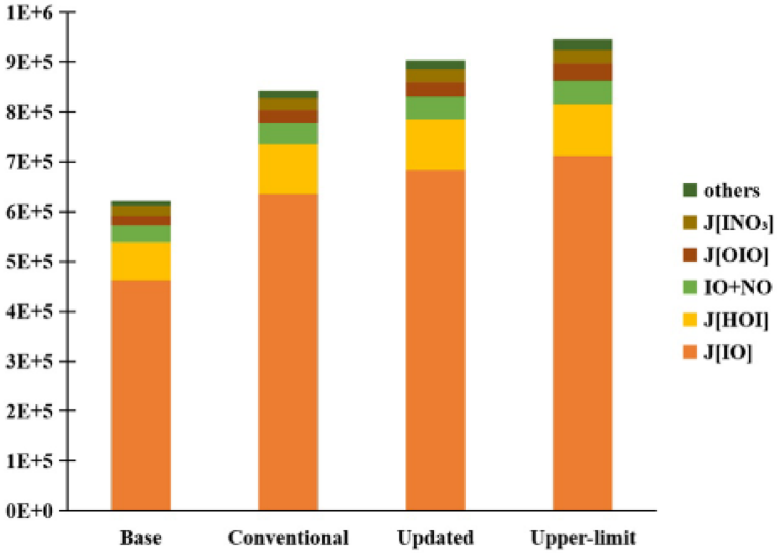
Vertical distribution of inorganic iodine species over the global ocean in the Base, Conventional, Updated, and Upper-limit scenarios. ”Oth” is the sum of other inorganic iodine species (OIO, HI, INO, and INO_2).

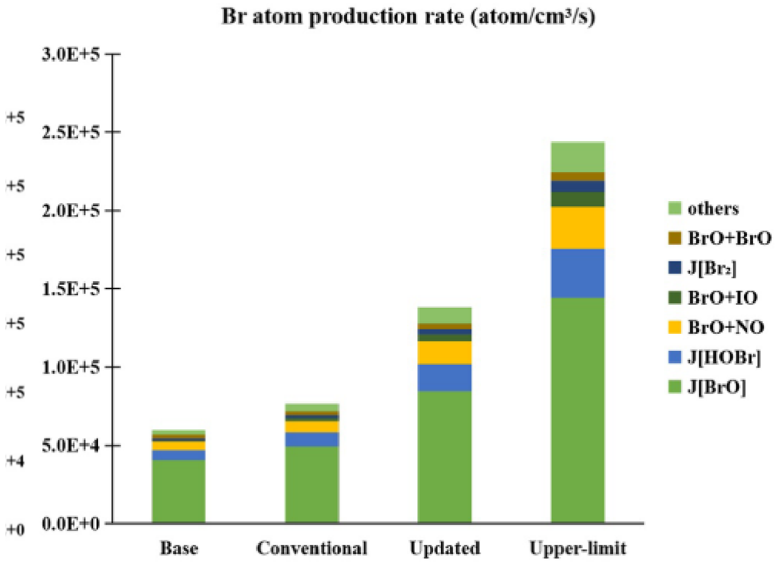
Iodine speciation

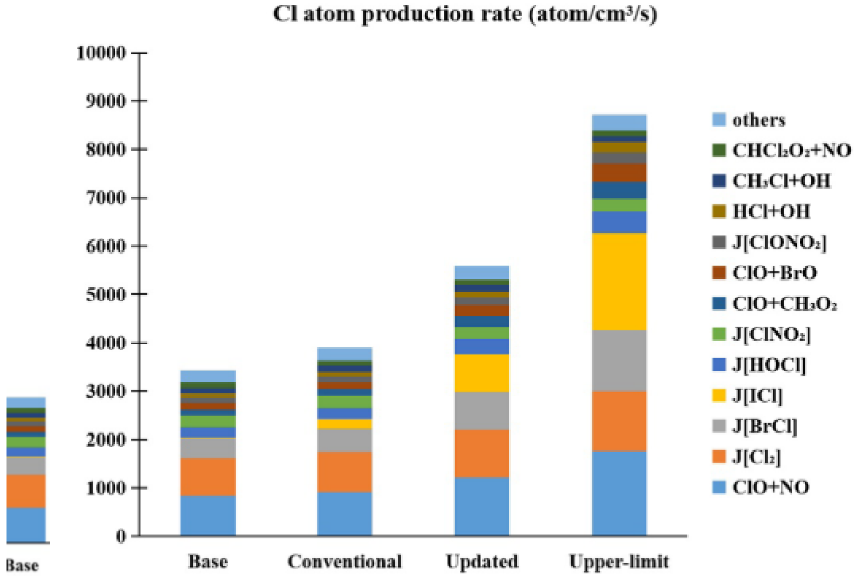


Simplified iodine chemistry in the MBL and the simulated mixing ratios (pptv) of the key iodine species in the Base (in blue font), Conventional (yellow), Updated (red), and Upper-limit (purple) cases.

Iodine recycling impacts on halogen atoms

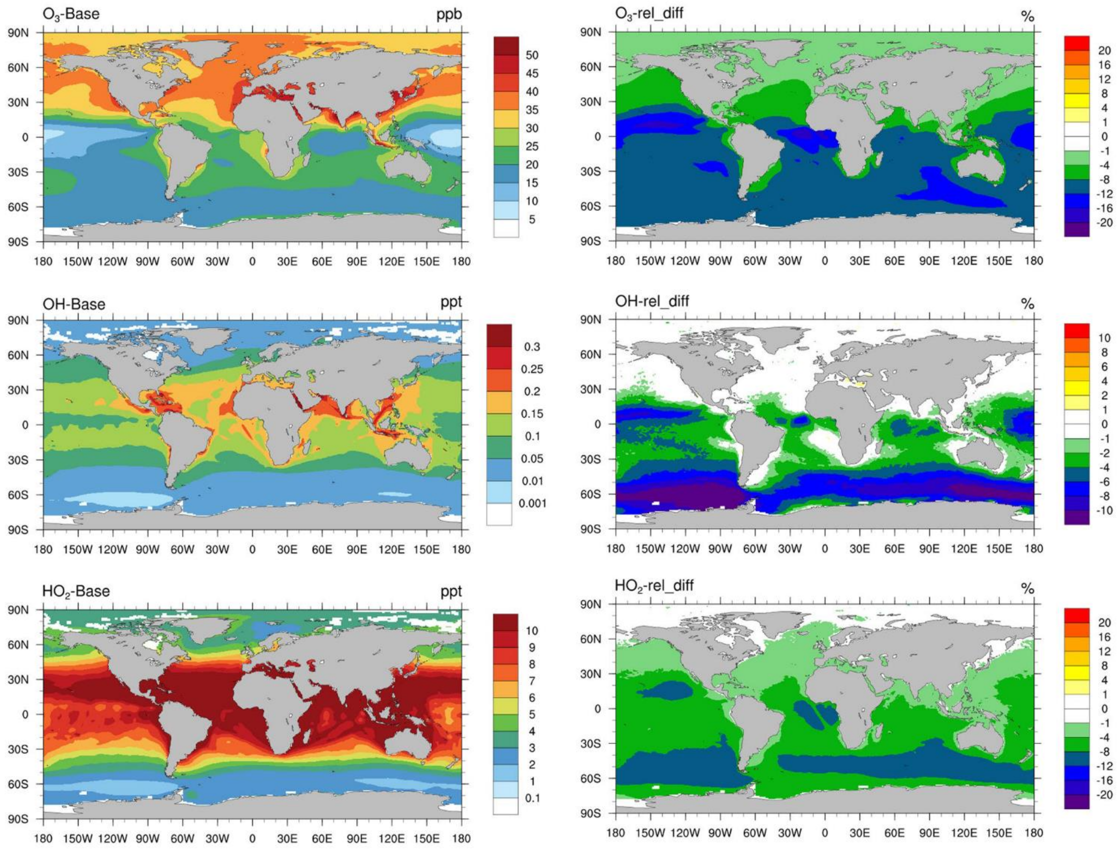






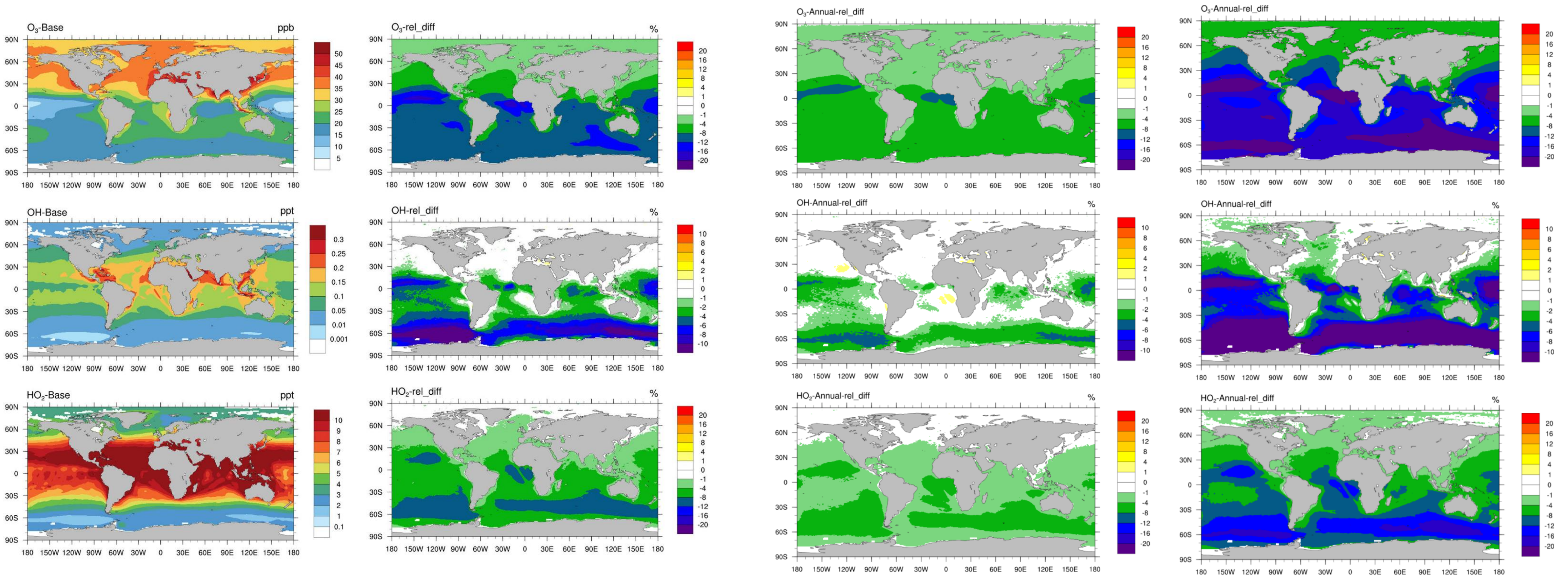
Production rate of halogen atoms (I, Br, and Cl) and the contribution of various channels in the MBL in Base, Conventional, Updated, and Upper-limit cases.

Iodine recycling impacts on atmospheric oxidants



Simulated distribution of the annual average of O_3 (ppbv; diurnal average), OH (pptv; sunlit time average), and HO_2 (pptv; sunlit time average) in the Base case in the MBL (left) and the relative change (%) between the Base and Updated cases (right).

Iodine recycling impacts on atmospheric oxidants



Simulated annual average of relative change (%) in O_3 (diurnal average), OH (sunlit time average), and HO_2 (sunlit time average) in the MBL between Base and Conventional cases (left) and between Base and Upper-limit case (right).

CONTENTS

Tropospheric reactive iodine

CAM-Chem simulation design

CAM-Chem simulation results in marine boundary layer

- ✓ **iodine distribution**
- ✓ **iodine speciation**
- ✓ **iodine recycling impacts on halogen atoms**
- ✓ **iodine recycling impacts on atmospheric oxidants**

Summary

Summary

- In the present work, we use a global chemistry-climate model, CAM-Chem to evaluate the potential role of HOI heterogeneous processing in the global MBL. Our numerical experiments show large enhancement effects of the iodine heterogeneous recycling process on the abundance of iodine species and the production rates of bromine and chlorine atoms in the MBL. Such a significant increase in halogen abundance and production leads to a noticeable reduction in the oxidation capacity particularly in the remote oceanic area, e.g., the Southern Ocean, central Pacific, etc.

- The effects of HOI uptake are very sensitive to the uptake coefficient and larger uptake coefficients (compared to the value used in current models) result in stronger impacts on oxidants, highlighting that the current models underestimate the effect of HOI heterogeneous process on global atmospheric oxidizing capacity. Further direct observations of HOI and other relevant species and parameters are necessary to constrain the efficiency of iodine heterogeneous recycling. Laboratory experiments are also required to identify and quantify the controlling factors of the HOI process and their corresponding efficiency of the different possible production channels (i.e., IBr, ICl, Cl_2, Br_2, and I_2). Simulation studies with various temporal and spatial scales are needed to further comprehend the effect of the iodine heterogeneous recycling process.

Thanks for your attention.