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Potential Effect of Halogens on Atmospheric Oxidation and Air Quality in China

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C O N T E N T S

Background

Degraded air quality has become one of the dominant worldwide causes of mortality, with 3.3 million premature deaths each year in the world and 1.3 million in China. (Lelieveld et al., 2015)

Emission

- Anthropogenic source
- Natural source (land)
- Natural source(ocean)

Oxidation process (less reported)

- OH
- HO_2
- O_3
- NO_3
- Cl

Meteorology

- Wind
- Turbulence
- Radiation
- Temperature
- Humidity

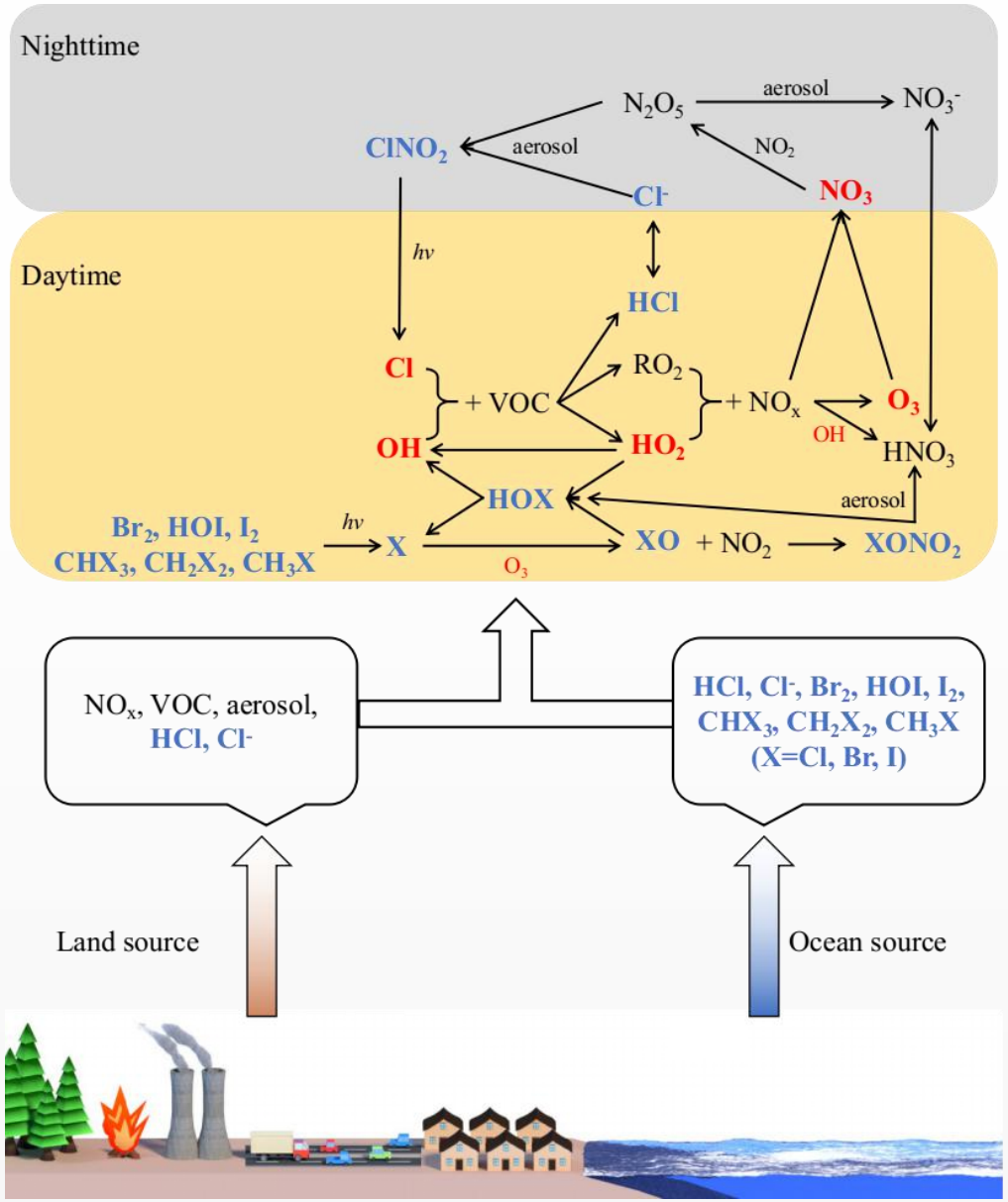
Motivation

Air pollution in China

- Reduced emission of primary air pollutants (Zheng et al., 2018).
- Increased level of ambient secondary air pollutants (Li K et al., 2019).
- **Raised attention of oxidation capacity.**

Potential significant effects of halogens

- Large control of reactive halogens (Cl, Br, and I) on oxidants in marine boundary layer (Saiz-Lopez & von Glasow, 2012).
- Noticeable emission of halogens in mainland China and along the coast.
- **No report of overall halogen impact on oxidation capacity and air quality in China.**



Method

WRF-Chem model

- Grell et al., 2005.
- Badia et al. (2019) implemented comprehensive reactive halogen sources and chemistry.
- Heterogeneous production of HONO on aerosol and ground surface was also implemented in this work following Zhang et al. (2017).

Data

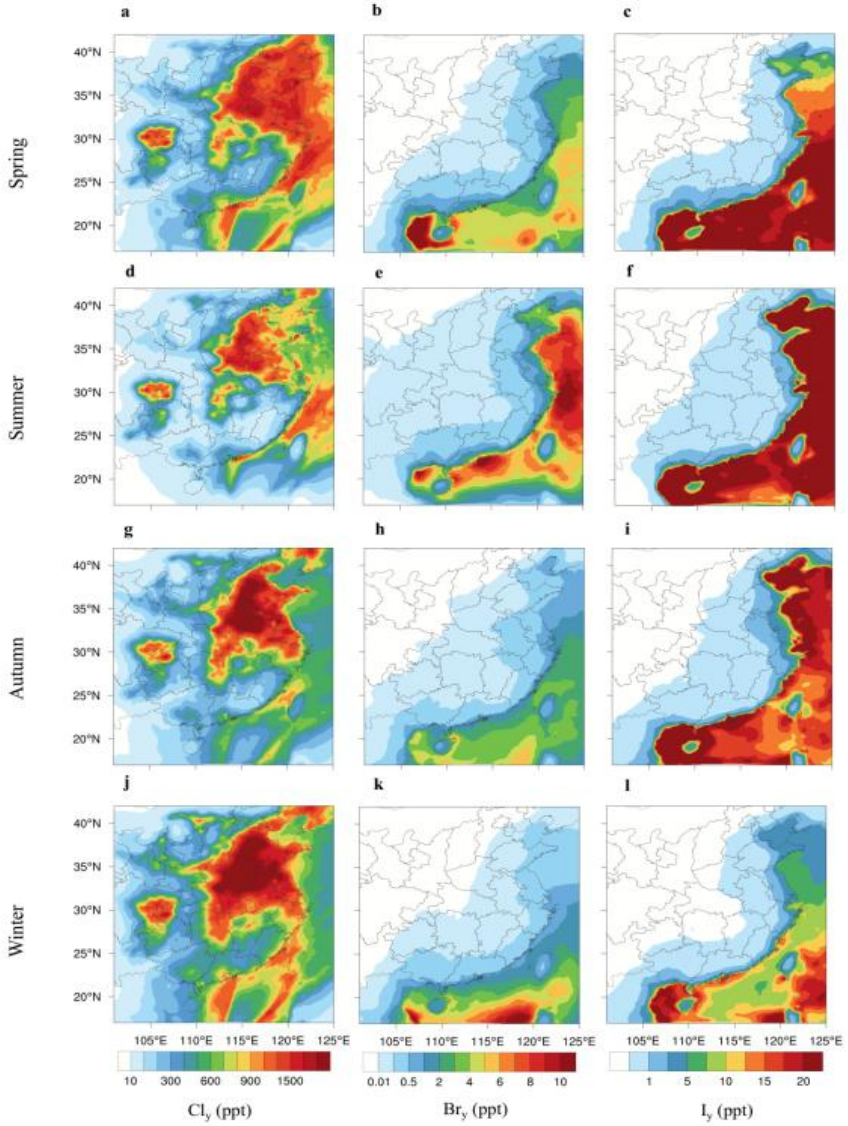
- Emission: routine air pollutants (MEIC, meicmodel.org), anthropogenic chlorine (Fu et al., 2018), oceanic halogen (Badia et al., 2019), fire emission (FINN, Wiedinmyer et al., 2011).
- Air pollutant data: O_3 (MEE, www.mee.gov.cn/hjzl/dqhj/qgkqzlssfb).
- Meteorological data: NCEP datasets, including ds083.2, ds351.0, and ds461.0.

Simulation setup

- Simulations were conducted for each month in 2018 with a spin up of ten days.
- Five scenarios were designed. Only BASE and HAL are presented here. Changes in atmospheric compositions between BASE and HAL represent the impact of the overall halogen sources and chemistry.

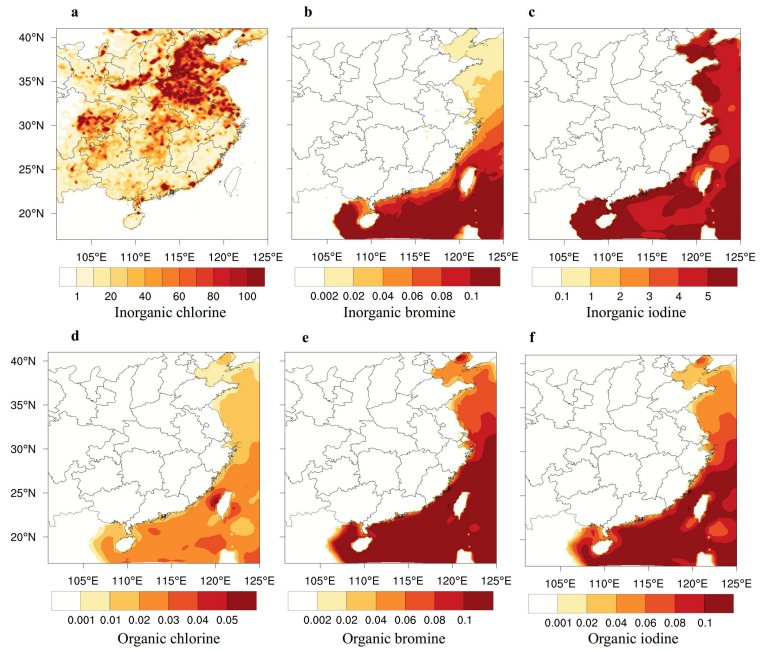
Cases	Anthropogenic chlorine emission	Oceanic halogen emission	Chlorine chemistry	Bromine chemistry	Iodine chemistry
BASE	**No**	**No**	**No**	**No**	**No**
HAL	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**
OCN	No	Yes	Yes	Yes	Yes
CHL	Yes	Yes	Yes	No	No
CHL+BRM	Yes	Yes	Yes	Yes	No

Simulated halogens



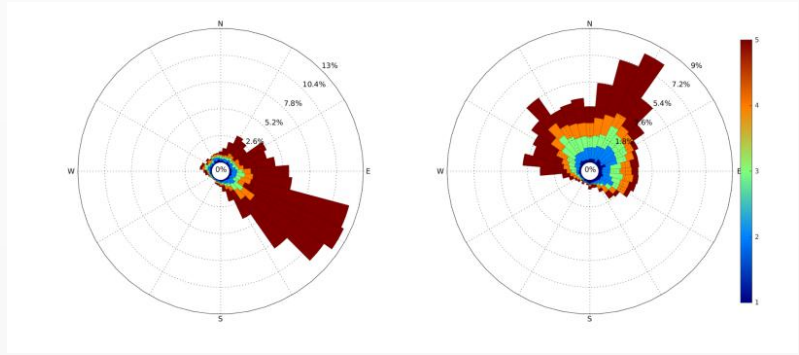
Seasonal averages of daily-maximum of Cl_y, Br_y, and I_y (pptv) at the surface in the HAL scenario.

Emissions



Annual average emissions (multiplied by 10^{13}) of Cl, Br, and I species (kg m^{-2} s^{-1}).

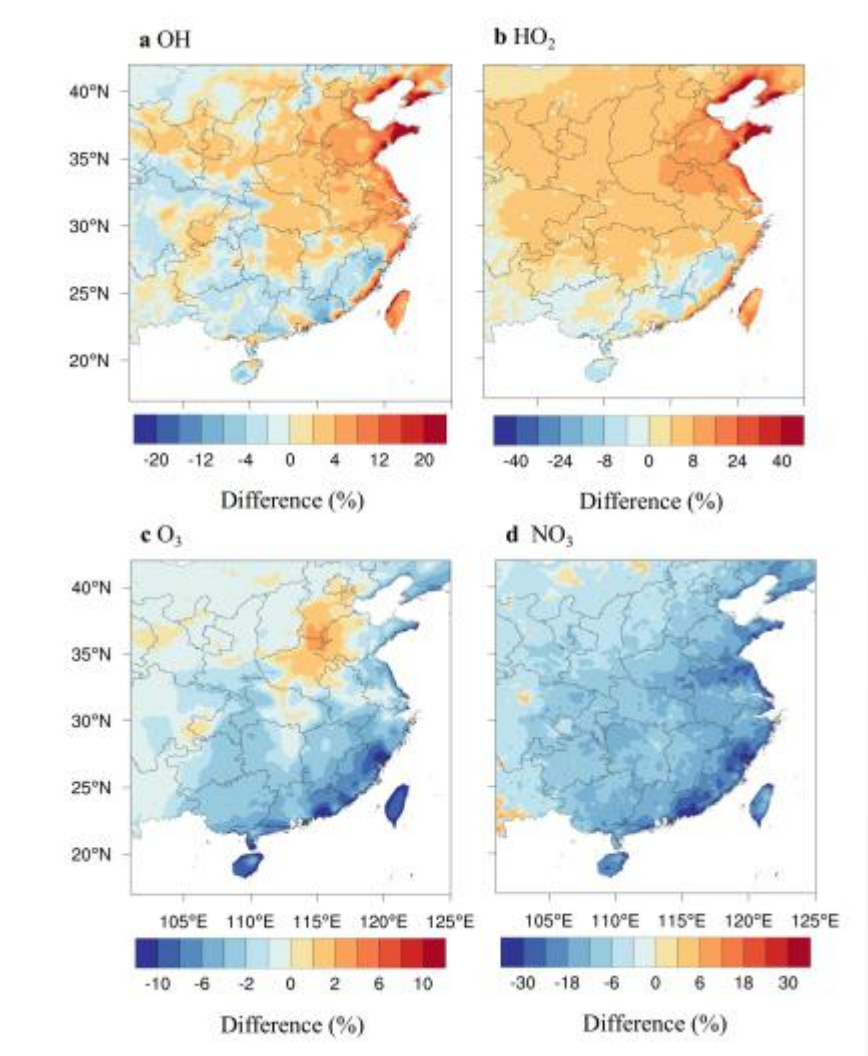
Meteorology



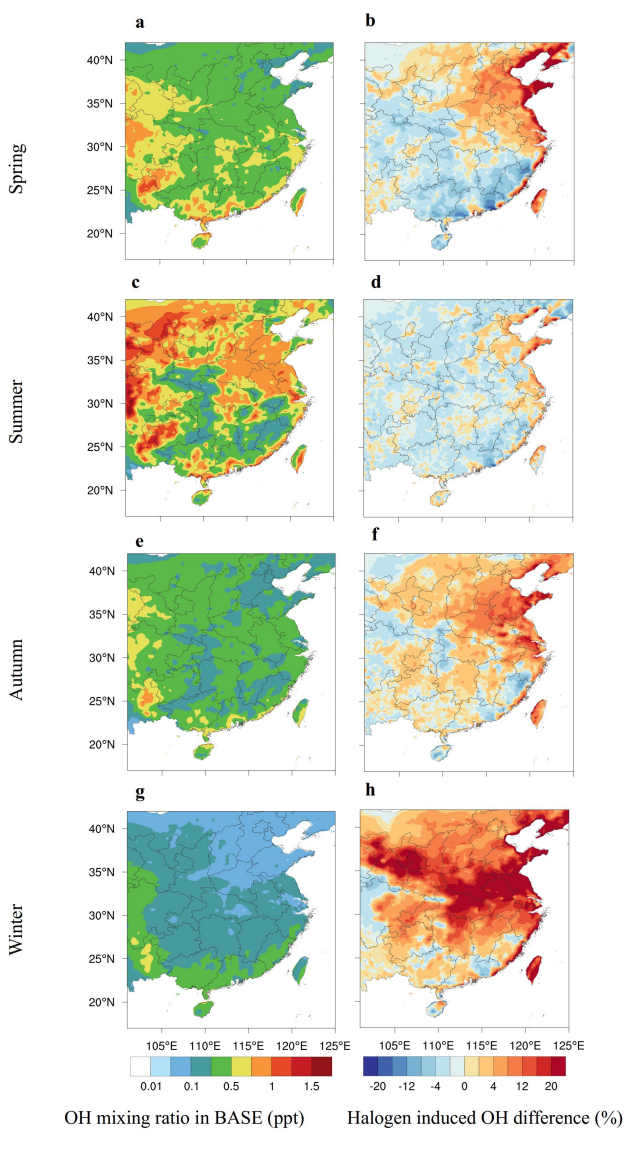
Wind rose in summer

Wind rose in winter

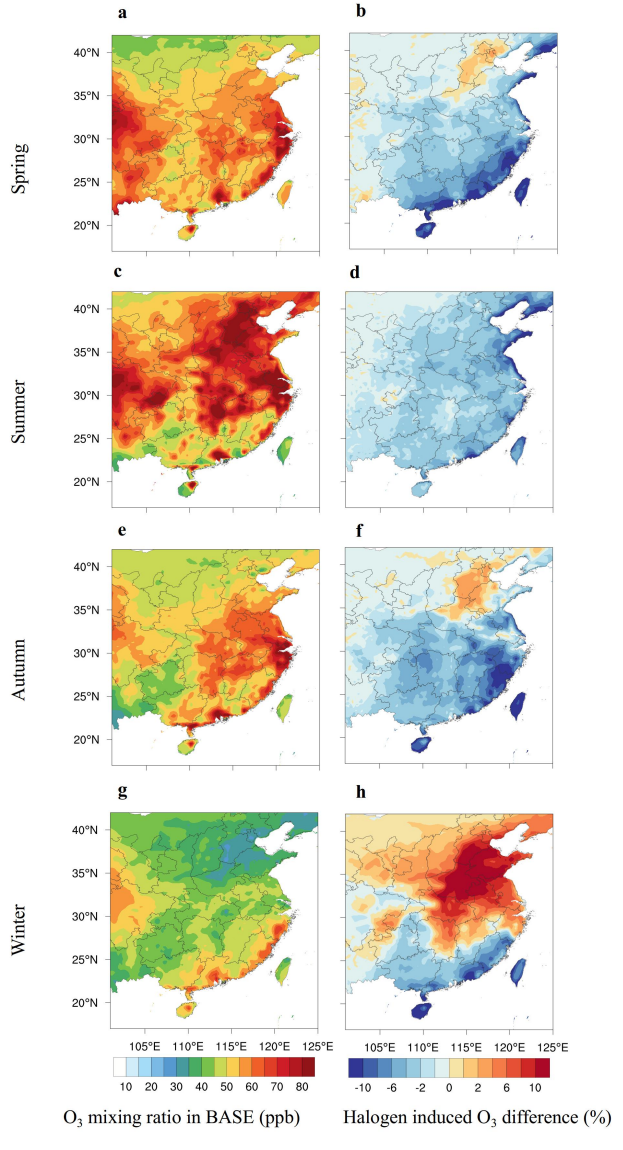
Halogen impact on oxidants



Annual average impact of halogen chemistry on the level of atmospheric oxidants (OH, HO_2, O_3, and NO_3) at the surface in China.



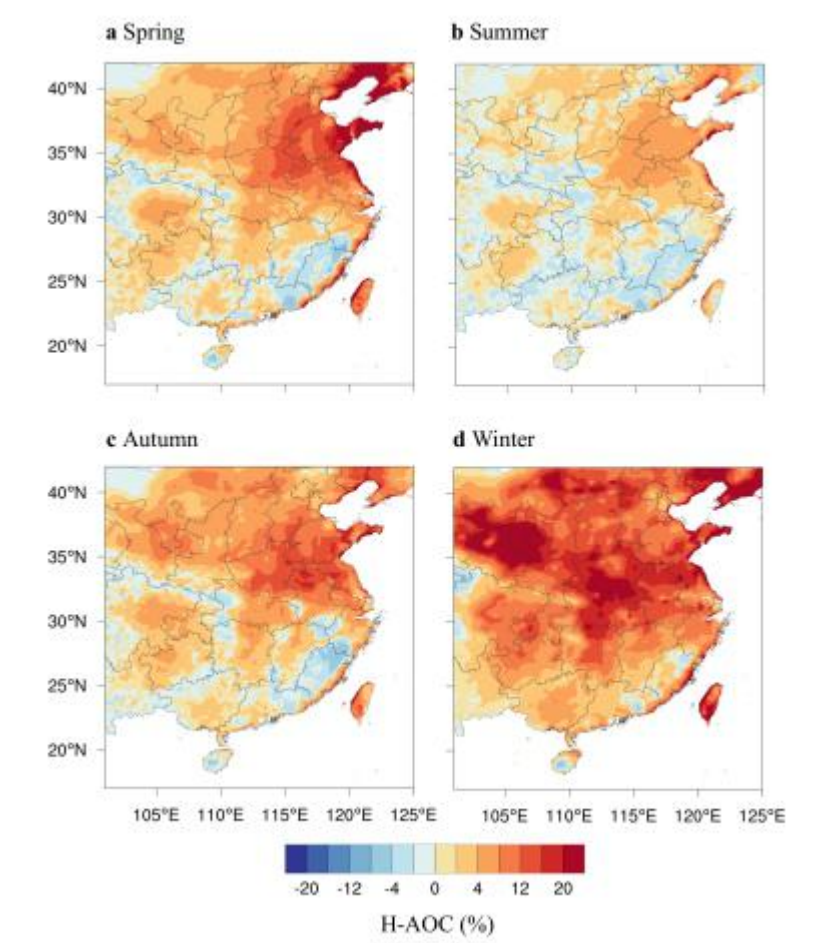
Seasonal average for OH



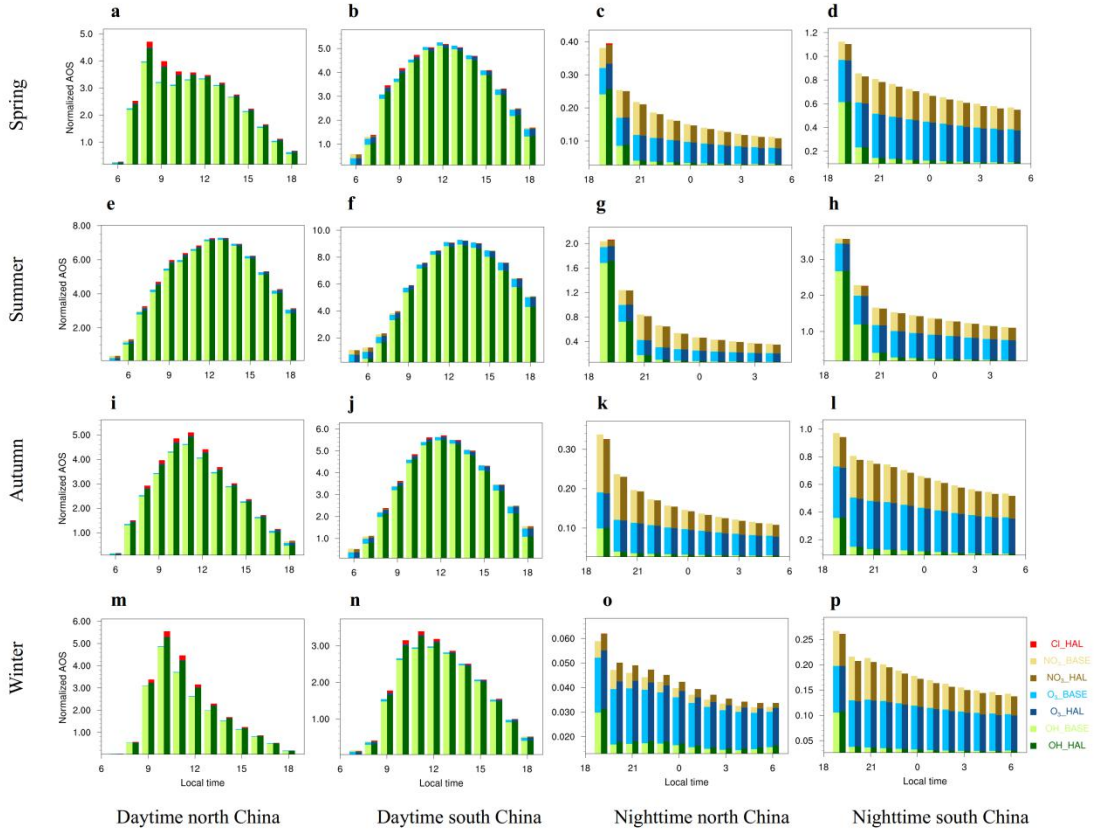
Seasonal average for O_3

Halogen impact on Atmospheric Oxidation Capacity (HAOC)

AOC is a unified metric combining all oxidants, OH, O_3, NO_3, and Cl, their reactants, and rates of reactions (Calculation is attached at the end of this file). HAOC is the halogen impact on AOC.

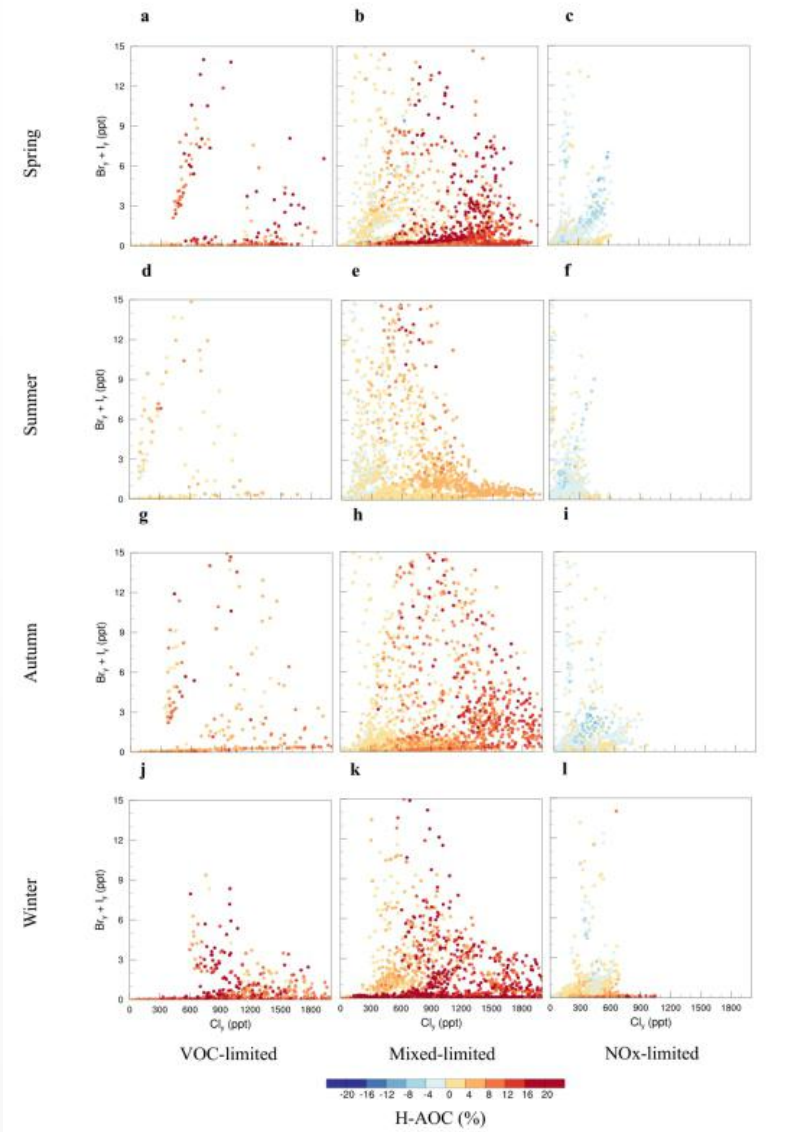


HAOC at the surface in China.



Daytime and nighttime hourly variations of AOC at the surface in north and south China in four seasons. AOC is normalised by dividing the annual average AOC in China, 2.2×10^7 # cm^{-3} s^{-1}.

Connection of HAOC and O_3 formation regime



Dependence of HAOC on the levels of halogen species under different O_3 formation regimes in four seasons.

- HAOC is closely related to the O_3 formation chemical regime.
  - In VOC-limited regions, HAOC shows an increase pattern in all seasons;
  - In mixed-limited regions, HAOC is significantly increased when Cl_y is over 600 pptv (typical value over polluted China) or when Br_y+I_y levels are negligible, and is near zero or decreased when Cl_y is lower than 600 pptv;
  - In NO_x-limited regions, HAOC is generally decreased except in winter, when the levels of bromine and iodine species are negligible in mainland China.
  - A dynamic strategy is required to curb the enhancement effect of halogens on AOC under various O_3 regimes.

Conclusion and implication

❖ Highlights:

- First assessment of halogen impact on atmospheric oxidation and air quality over China.
- Halogens result in enhanced oxidation throughout the year in polluted regions in China.
- Large spatio-temporal heterogeneity of the halogen-mediated effect on oxidation capacity, which can be explained by the Asian monsoon, the location and intensity of halogen sources, and the ozone formation regime.

❖ Implication:

- Halogens potentially contributes to close the gap between the observation and simulation of atmospheric oxidation in China.
- Current study implies a gap in our understanding of air pollution in China and a potential bias in policy design.
- Halogens affect China's air pollution exports to other parts of the world.
- A similar large influence is also expected in other regions with similar air quality issues and halogen emissions from anthropogenic and oceanic sources.
- The emission of halogens is expected to increase as a result of the projected natural phenomena (Iglesias-Suarez et al., 2020) and anthropogenic activity (Fang et al., 2019; Young et al., 2013) which warrants further investigation of the influence of halogen compounds on future atmospheric oxidation.

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Computation support

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Model support

- ✓ The development and maintenance of the WRF-Chem model are conducted by NOAA/ESRL/GSD in active collaboration with other institutes.

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Supplementary materials

$$AOC = \sum_{i=1}^{m} \left([OX_i] \times \sum_{j=1}^{n} \left(a_j \times [C_j] \times k_{i,j} \right) \right)$$

m and n denote the number of oxidants (4) and the number of reactant (VOC and CO) species (61), $[OX_i]$ is the concentration of oxidant i (# cm^{-3}), a_j is the number of carbon atoms in reactant j, $[C_j]$ is the concentration of reactant j (# cm^{-3}), and $k_{i,j}$ is the reaction rate constant of oxidant i and reactant j (cm^3 $\#^{-1}$ s^{-1}).