Natural halogens buffer tropospheric ozone in a changing climate

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Tropospheric ozone (O_3) and halogen chemistry

Stratospheric influx

Stratosphere

Troposphere

O_3

Chemical production
(Emissions of O_3 precursors)

Chemical destruction
(10-20% reactive halogens [Cl, Br, I])[1-4]

Deposition

Pole

Equator

Pole
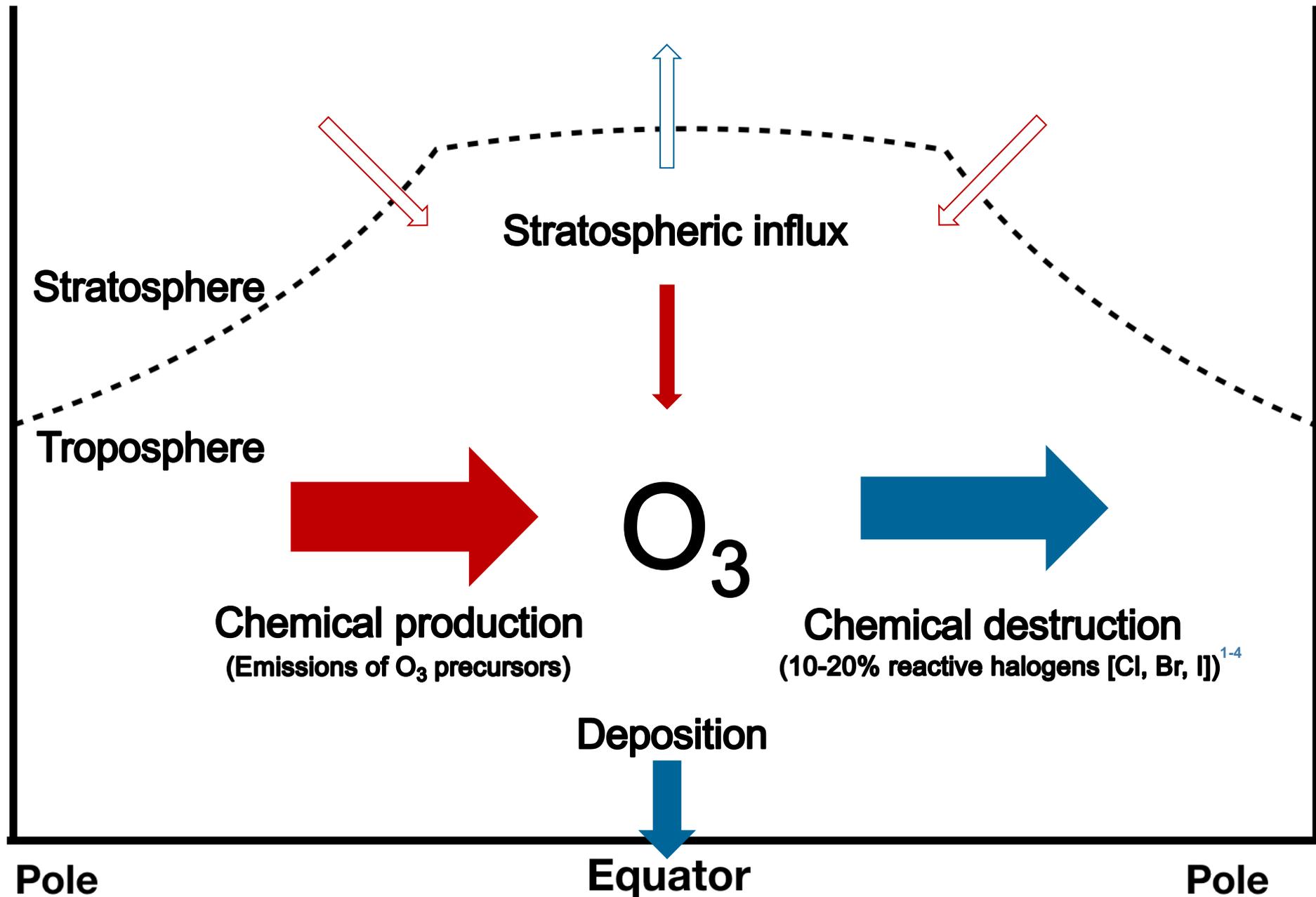
Biogenic sources: Very short-lived (VSL) halocarbons fluxes

Present-day
(10^6 molec m^{-2} s^{-1})
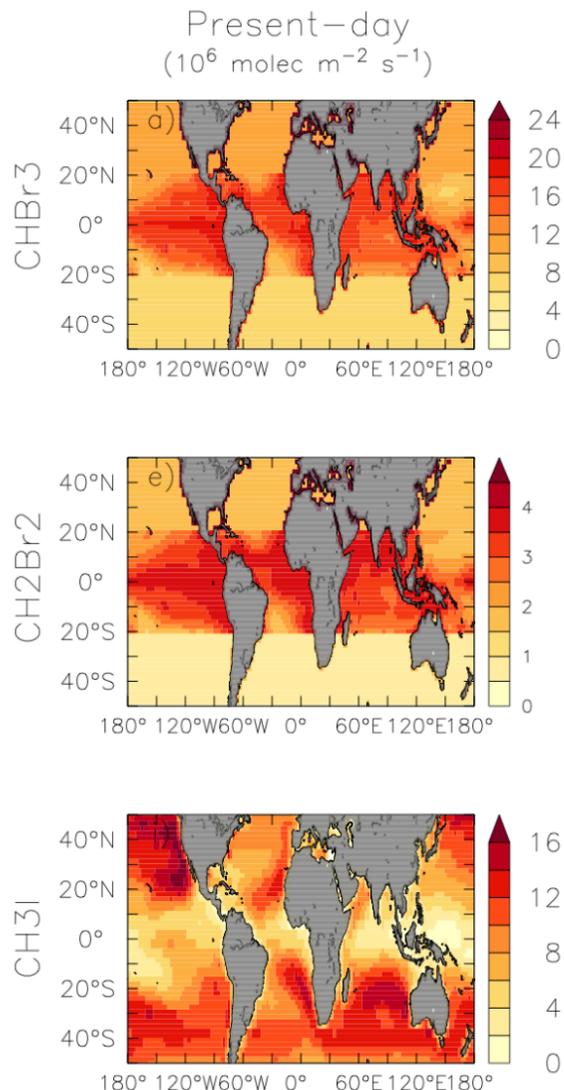
From SF. 3 | Emission inventories of natural halogens (present-day: 1990–2009; nominally yr2000).

From Table 1–8[5] | Global and annual inventories of VSL halocarbons.

References	CHBr$_3$ flux (Gg Br yr^{-1})	CH$_2$Br$_2$ flux (Gg Br yr^{-1})	CH$_3$I flux (Gg I yr^{-1})
Bell et al. (2002)			272
Yokouchi et al. (2005)	820		
Warwick et al. (2006)	560	100	
Butler et al. (2007)	800	280	550
O'Brien et al. (2009)	820		
Liang et al. (2010)	430	57	
Jones et al. (2010)			300
Young et al. (2010)			236
Ordóñez et al. (2012)[6]	506	62	270
Ziska et al. (2013)[7]	120–200	62–78	157–184

- Via the metabolism of marine organisms (phytoplankton and micro- and macroalgae), VSL halocarbons are emitted to the atmosphere.
- They are important sources of reactive halogens to the troposphere, and to a lesser extent the stratosphere (lifetimes of less than ~6 months).

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Abiotic sources: Inorganic halogens fluxes
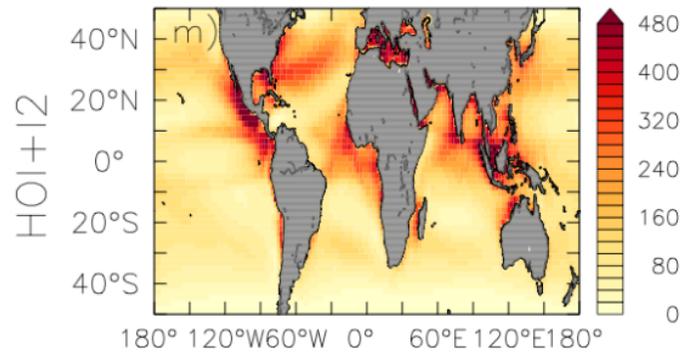
From SF. 3 | Inorganic halogens fluxes in 10^6 molec. m^{-2} s^{-1} (present-day: 1990–2009; nominally yr2000).

Modelled "present-day" global annual fluxes of inorganic halogens.

References	HOI+I$_2$ flux (Tg I yr^{-1})
Prados-Roman et al. (2015)[8]	1.90
Sherwen et al. (2016)[9]	2.11
Iglesias-Suarez et al. (2020)*	2.67

- Inorganic iodine (HOI and I$_2$) is also emitted from the ocean, which is the result of O$_3$ deposition into the ocean and subsequent oxidation of seawater iodide.

- Approximately 95% from HOI fluxes.

- Inorganic iodine can account for up to 75% of its atmospheric budget.

Present-day halogen-driven tropospheric O$_3$ loss in CAM-Chem
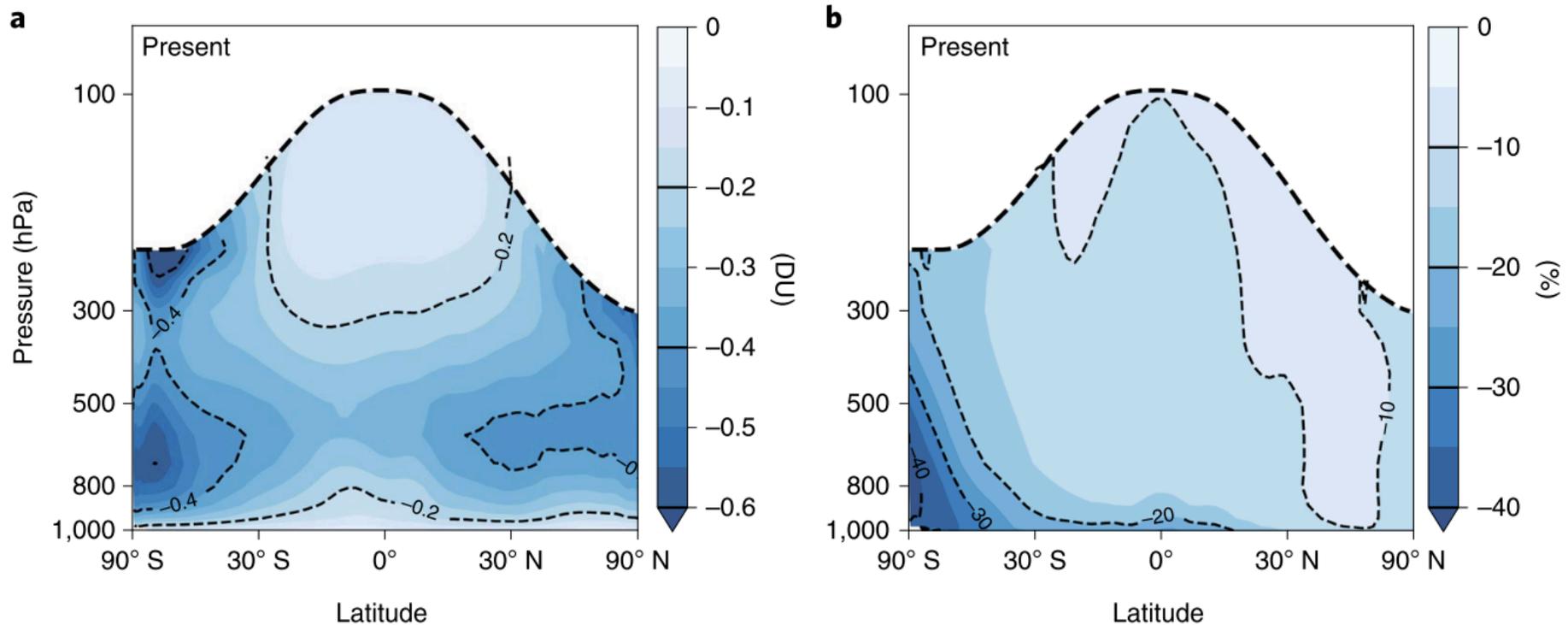
From Fig. 3 | Present-day halogen-mediated tropospheric O$_3$ loss (*cliVSL* minus *noVSL*) is shown in absolute (DU) (**a**) and relative (%) (**b**) values.

- O$_3$ loss is ~4 DU globally integrated at present, due to bromine (16%) and iodine (80%).
- Largest halogen-mediated O$_3$ loss mass are simulated in the free troposphere (65% of the total loss).
- Smallest O$_3$ losses are constrained to the tropical lower and upper troposphere (largely controlled by reactions with water vapour and odd hydrogen radicals).
- Relative O$_3$ loss, increasing from upper to lower troposphere and from north to south, responds to the O$_3$ burden distribution in the troposphere.

Scientific question and scope

- Natural fluxes of VSL halocarbons may have increased by ~7% over 1979–2013[10], whereas inorganic iodine tripled during 1950–2010[11,12].

- Warming in sea surface temperatures, can accelerate air–sea exchange up to ~30% for some halogenated VSL species[10,13] by the end of the century.

- Yet, how changes in naturally emitted halogens will affect O_3 and tropospheric chemistry and climate remains unknown.

This work explores halogen-driven tropospheric O_3 loss in a warming climate during the 21st century.

Outline

1. Natural halogen emissions and concentrations

2. Halogen-driven tropospheric O_3 loss columns

3. Zonal mean tropospheric O_3 loss due to reactive halogens
   - Stratospheric chemistry-climate feedback

4. Halogen-driven near-surface O_3 loss changes:
   - Maps
   - Time-series

5. Conclusions

Appendices:
   * Simulations
   * References

# Natural halogen emissions and tropospheric concentrations
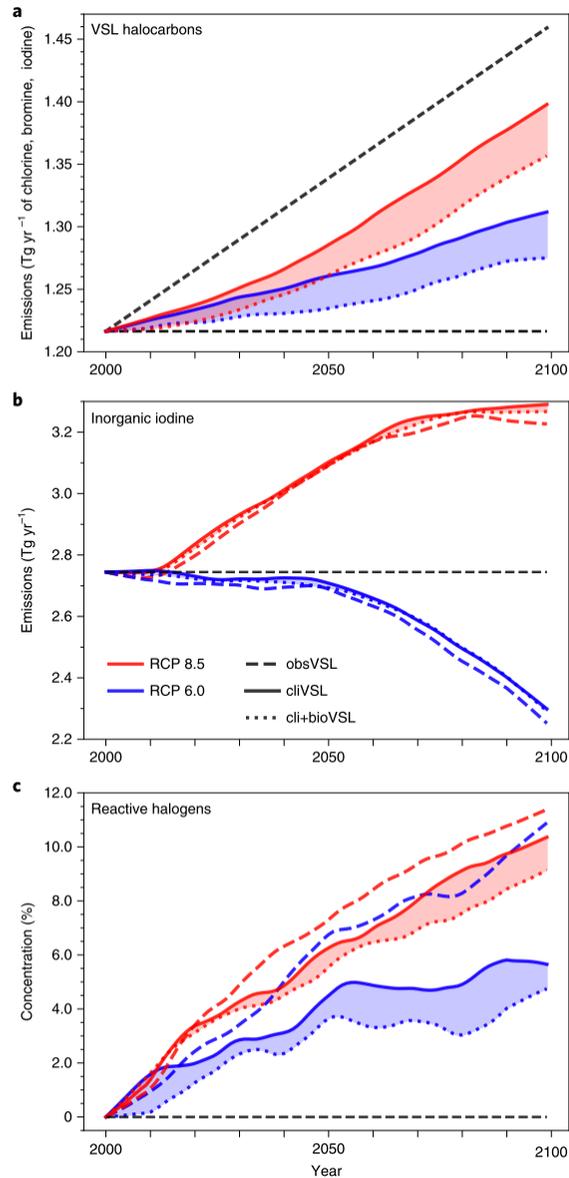
Fig. 1 | Global and annual mean changes in natural halogens emissions and tropospheric concentrations.

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VSL halocarbons

- Physical climate-induced ('cliVSL') changes in VSL emissions increase ~ 7.4% and 13.5% for the RCP 6.0 and RCP 8.5 scenarios, respectively, by the end of the century.
- Including physical and biogeochemical changes related to climate ('cli+bioVSL') results in ~ 2–3% lower emissions since mid-century compared with cliVSL, due to declining marine primary production (~4% by 2080).
- Extrapolating trends from the recent past (1979–2013) out to 2100 ('obsVSL'), results in 18.1% increase in VSL emissions compared with present.

Inorganic iodine

- Global emissions of inorganic iodine increase by ~20% following RCP 8.5, but decrease around 10% for RCP 6.0.

Tropospheric concentrations

- Reactive natural halogen concentrations increase by approximately 4–10%, depending on the precursor emission scenario and forcing.
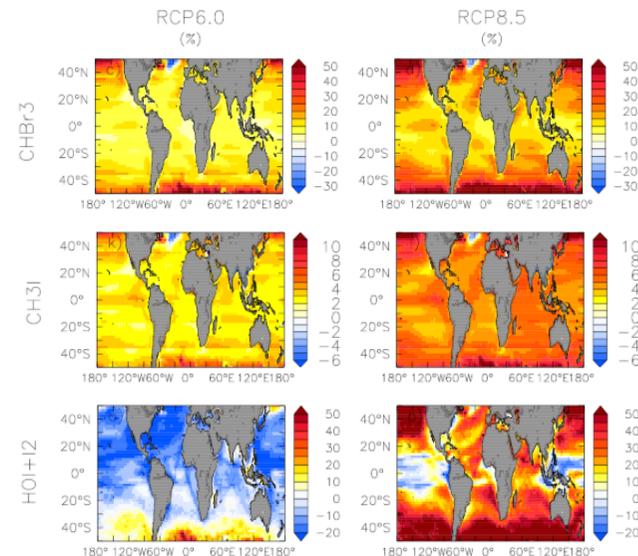
SF. 3 | Relative changes in nat. halogens emissions by the end of the 21st century are shown for 'cliVSL'.

Halogen-driven tropospheric O₃ loss columns
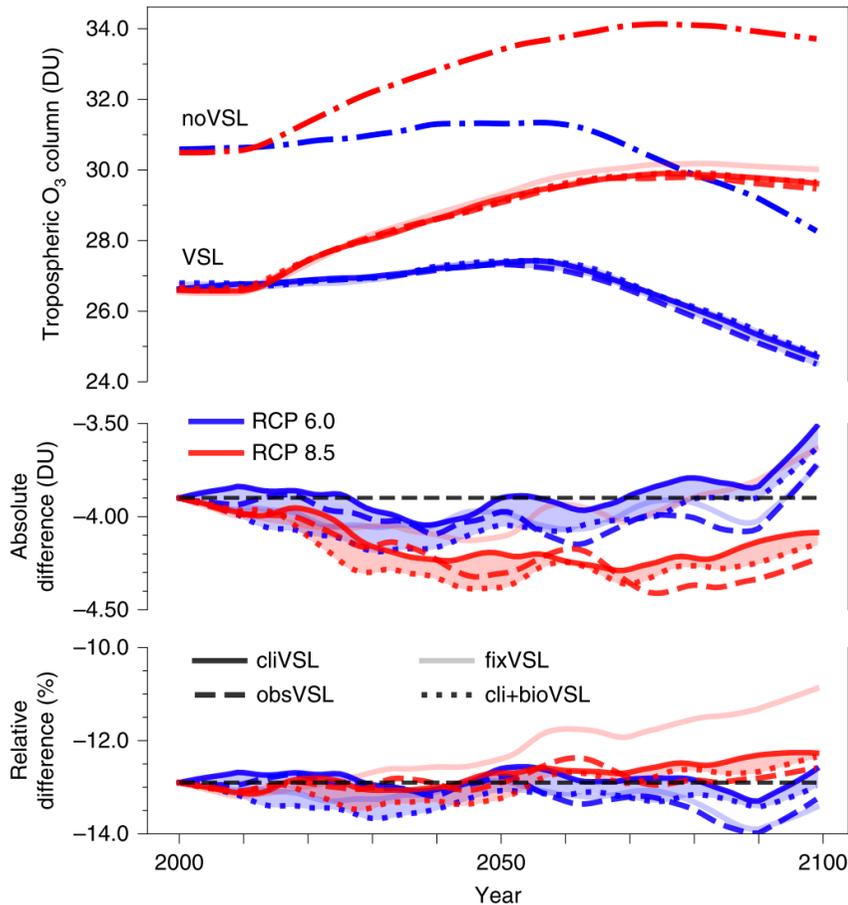
Fig. 2 | Global and annual mean tropospheric O₃ column time series from 2000 to 2100.

- The upper and middle panels clearly show halogen-driven O_3 loss is closely linked to the total amount of tropospheric O_3 and the key role of halogen chemistry acting as a natural buffer.

- Intuitively, increasing VSL halocarbon emissions would result in greater tropospheric O_3 loss. However, global halogen-driven tropospheric O_3 column loss is projected to remain nearly constant (~13%) regardless of the emissions scenario.
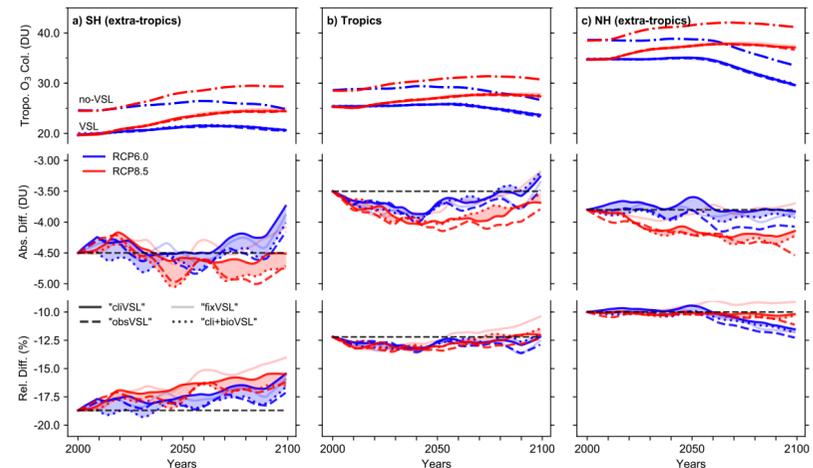
SF. 4 | Same as Fig. 2 but for regions.

Zonal mean: Tropospheric O₃ loss due to reactive halogens
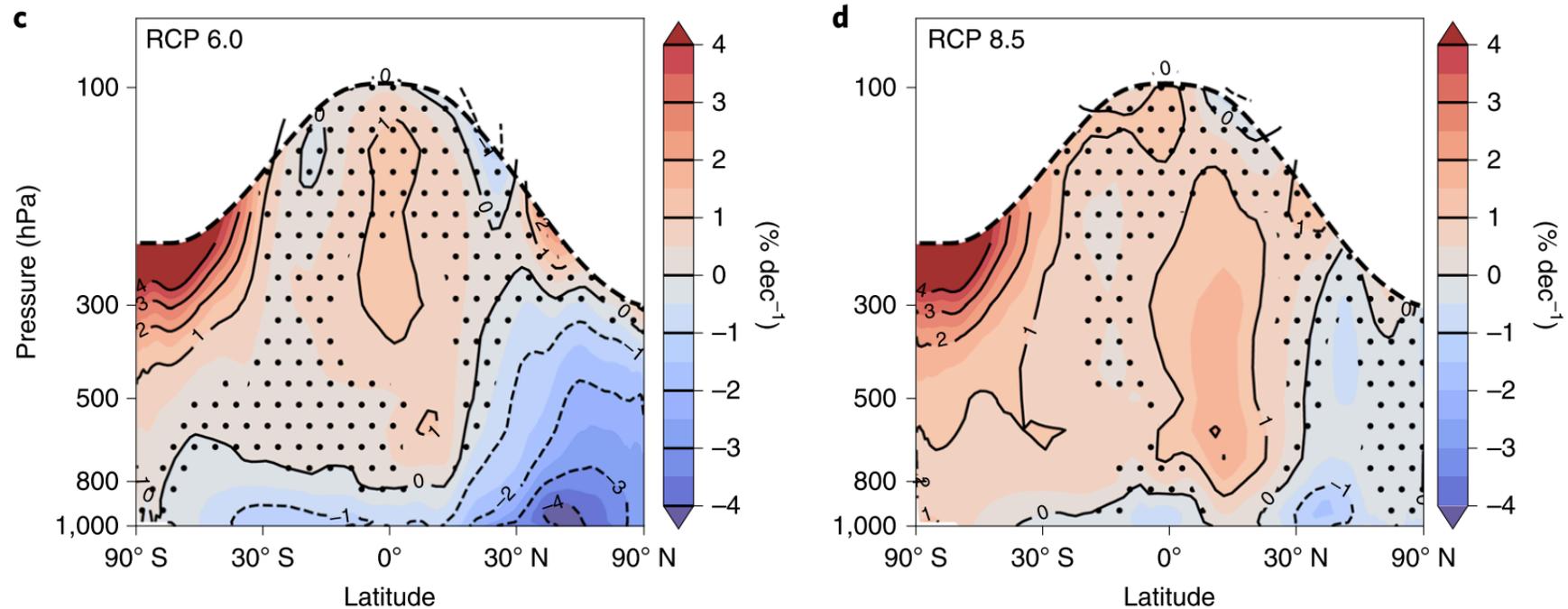
From Fig. 3 | Future trends in halogen-driven tropospheric O_3 loss (% dec^{-1}) from 2000 to 2100, relative to the present and normalized to O_3 levels, are shown for the RCP 6.0 (**c**) and RCP 8.5 (**d**) emission scenarios.

- Future changes in halogen-mediated O_3 loss are heterogeneous, with marked hemispheric and vertical gradients, and consistent for both emission scenarios.

- In the lower troposphere, halogen-driven O_3 loss is projected to be larger, particularly during the second half of the century owing to decreases in O_3 precursor emissions (e.g. greater O_3 loss trend in the more 'polluted' Northern Hemisphere).

- In the mid- and upper troposphere the relative O_3 loss weakens (i.e., particularly at high latitudes), explained by an enhanced stratospheric influx. This feature is linked to a strong chemistry–climate feedback and the expected ozone hole recovery (see next slide).

Zonal mean: Stratospheric chemistry-climate feedback
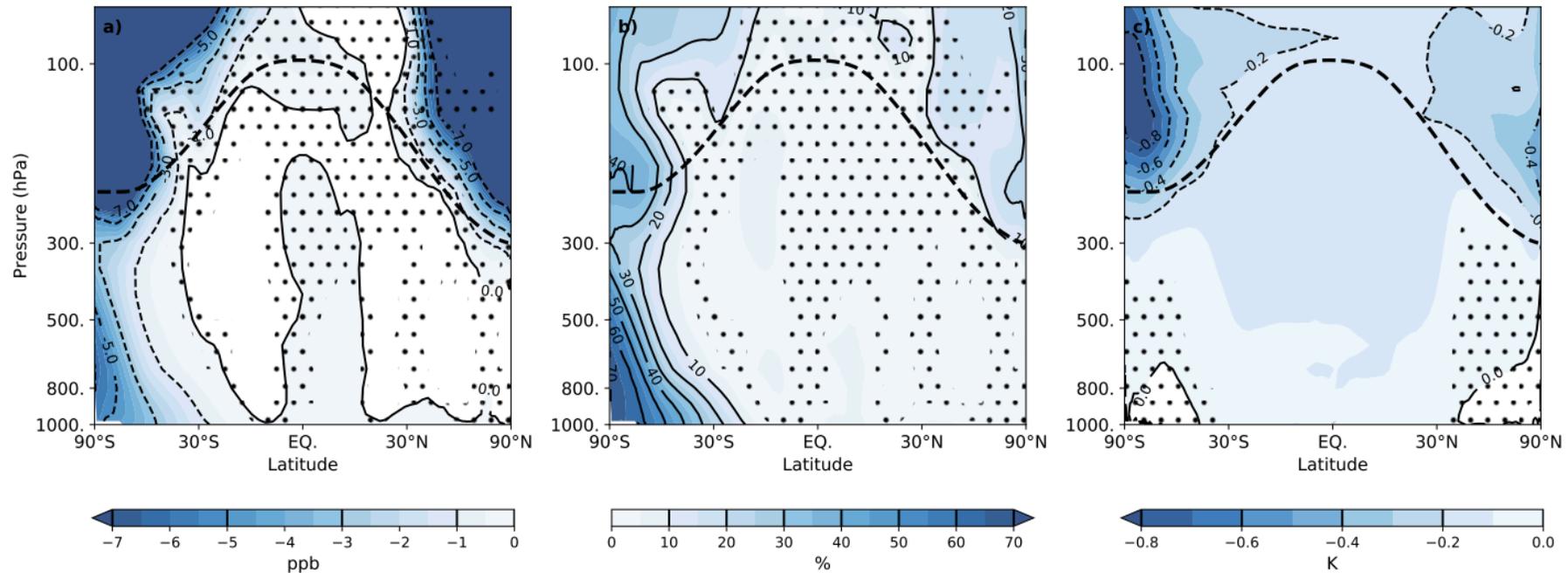
SF. 5 | Differences of tropospheric O_3 loss and temperature at present-day. Tropospheric O_3 loss due to reactive halogens (*VSL* minus *noVSL* cases) differences between fully-coupled (*cliVSL*) and specified dynamics (*SD–cliVSL*) simulations are shown in **a**) absolute (ppb), and **b**) relative (%) values. **c**) Temperature differences (K), due to reactive halogens chemistry-climate feedback (*cliVSL* minus *noVSL* cases). Hatching is for the ± 1.96 standard error greater than the 20-year (1990–2009) mean difference.

- A significant fraction of brominated VSL reaches the stratosphere (i.e. currently, 5 ± 2 ppt of atomic bromine), which enhances stratospheric ozone depletion and substantial cooling (i.e. stratospheric temperatures are largely determined by O_3 and its chemical processing).

- In the extra-tropics, this stratospheric cooling results in further O_3 loss in the lower stratosphere associated with enhanced heterogeneous activation of halogenated substances.

Halogen-driven near-surface O$_3$ loss changes: Maps

- Largest O$_3$ loss associated with reactive halogens is projected to occur over polluted continental regions rather than in remote marine environments.

- In particular, large halogen-driven O$_3$ losses are projected over the eastern United States (50–70%), Europe (20–30%) and eastern Asia (7–20%).

- Observational and modelling evidence suggests that climate-related impacts over the next century will have negative effects for O$_3$ pollution ('climate penalty').

- Should future policies on anthropogenic emissions be more relaxed (compared to the RCP scenarios), the implications of halogen chemistry for surface O$_3$ in a changing climate (opposing the climate penalty effect) will be even more important for air quality and human health.

Fig. 5 | Maps of halogen-driven near-surface O$_3$ loss change between the present (1990–2009) and the end of the century (2080–2099). **a,c,** Maps for emission scenarios RCP 6.0 (**a**) and RCP 8.5 (**c**) (*cliVSL*). Changes are normalized to O$_3$ levels. Hatchings are for changes that are not statistically significant. **b,d,** Zonal mean O$_3$ loss changes for the RCP 6.0 (**b**) and RCP 8.5 (**d**) emission scenarios, as well as the *cliVSL* (solid), *obsVSL* (dashed), *cli+bioVSL* (dotted) and *fixVSL* (solid light) simulations.

Halogen-driven near-surface O₃ loss changes: Time-series
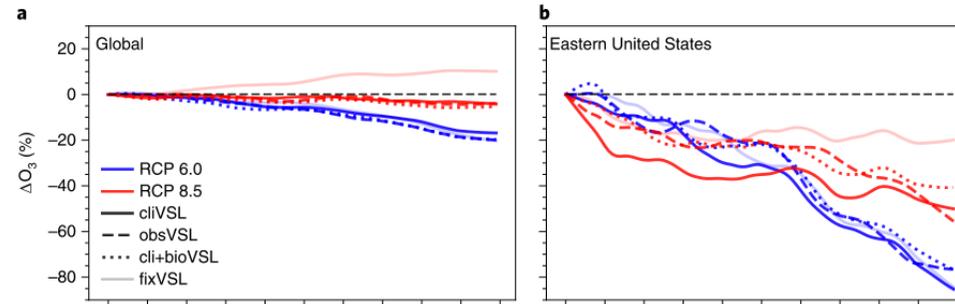
From Fig. 6 | Halogen-driven near-surface O₃ loss time series from 2000 to 2100. Relative changes with respect to the present (normalized to O₃ levels).

- The <u>impact of natural halogens on surface O₃ is driven largely by iodine catalytic cycles</u> (SF. 11b,f), especially over polluted areas that experience the largest change in future O₃ precursor emissions (i.e. Fig. 6b).

- The relative shift in surface O₃ loss chemistry is compensated by a <u>relative decrease in other key families</u> (i.e., photolysis and reaction with water vapour and direct loss via hydrogen radicals).

From SF. 11 | Same as Fig. 6 in the manuscript, but for O₃ depleting families (*cliVSL* minus *noVSL*). Globally, the contribution of each family to the total O₃ loss at present-day for the *cliVSL* case is shown in brackets.

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Conclusions

- Globally integrated, <u>halogen-driven tropospheric O_3 column loss is constant (~13%) throughout the twenty-first century</u> despite varying natural halogen emissions.

- Tropospheric O_3 loss by halogens shows a <u>marked hemispheric asymmetry</u> for both the present and the end of the century.

- <u>Largest halogen-mediated O_3 losses (up to 70%) are projected near the surface over polluted regions of the Northern Hemisphere</u> (e.g. eastern United States and Europe), with beneficial implications for air quality and mitigating O_3 pollution.

These results highlight **a key role of halogen chemistry in the troposphere, controlling a large fraction of O_3 at present, as well as determining its abundance and distribution in a warming climate**.

Simulations: fully-cloupled

Supplementary Table 1 | Summary of the CAM-Chem simulations[a].

Simulations	VSL chemistry	VSL halocarbon emissions[b]	Inorganic iodine emissions[c]
"noVSL"	No	No	No
"fixVSL"	Yes	Present-day[d]	Present-day[e]
"obsVSL"	Yes	Observed trends[f]	O_3, wind, and SST drivers
"cliVSL"	Yes	Physical drivers[g]	O_3, wind, and SST drivers
"cli+bioVSL"	Yes	Physical-biogeochemical drivers[h]	O_3, wind, and SST drivers

[a] Each simulation used in this work refers to a three ensemble member mean (removing large fraction of internal climate variability); Further details of the simulations and the chemical mechanism of natural halogens are described in the main text (see Methods) and in the Supplementary Information (see above). [b] Natural organic halogen sources include 9 halocarbons ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$, $CHBrCl_2$, CH_3I, CH_2I_2, CH_2IBr, and CH_2ICl). [c] Inorganic halogen sources include 2 inorganic iodine gases (HOI and I_2). [d] Ordoñez et al.[1] emission inventory. [e] Monthly and seasonally varying present-day (1990–2009) climatology, derived from a former simulation with an equivalent configuration (REFC2) and constant VSL halocarbons. [f] Ordoñez et al.[1] emission inventory was forced –from year 2000– following observationally derived trends (Table 2 in Ziska et al.)[15] [g] Varying VSL fluxes were driven by climate-induced changes in physical factors (i.e. SSTs and salinity). [h] Varying VSL fluxes were driven by both, physical and biogeochemical (i.e. marine net primary production) factors related to climate ("cli+bioVSL").

Simulations: specified-dynamics (SD)

Supplementary Table 2 | Summary of the specified dynamics (SD) sensitivity simulations[a].

Simulations	VSL chemistry	VSL halocarbon emissions[b]	Inorganic iodine emissions[b]
"SD−noVSL"	No	No	No
"SD−cliVSL"	Yes	Seasonal climatology[c]	Seasonal climatology[c]

[a] Each SD sensitivity simulation used in this work was driven by high frequency meteorological fields, which determine the physics (e.g. boundary layer fluxes, transport and the hydrologic cycle), and therefore neglecting chemistry-climate feedbacks. Meteorological fields were derived for present-day (nominally year 2000), and the end of the 21st century following the RCP2.6, RCP6.0 and RCP8.5 emission scenarios (nominally year 2100). [b] Natural organic and inorganic halogens sources are equivalent to the reference simulations (Supplementary Table 1). [c] Seasonally varying climatologies of organic and inorganic emissions of natural halogens were derived from the "cliVSL" case for each period (20 years) and emission scenario, except the RCP2.6 (10 years). A branch case with natural halogens was run for 15 years (2080–2095) for the latter scenario, using the initial conditions of a former RCP2.6 run, and the last 10 years were used to create the seasonal climatology of natural halogen emissions. Further details of the simulations and the chemical mechanism of natural halogens are described in the main text (see Methods) and in the Supplementary Information (see above).

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