

Impact of Marine Inorganic Chlorine Emissions on the Tropospheric Oxidizing Capacity

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Introduction

NIWA has been measuring isotopes of methane since 1989 at its Baring Head site. An assessment of the isotopic composition of methane strongly suggests that processes other than oxidation by the hydroxyl radical (OH) substantially contribute to the removal of methane. A prime candidate for this is oxidation by atomic chlorine (Cl). The reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ proceeds 6-8% more slowly with $^{13}\text{CH}_4$ than with $^{12}\text{CH}_4$ (Saueressig et al., 1995). The observed isotopic composition can then be well reproduced in a model assuming a mean Cl concentration in the marine planetary boundary layer of 1800 ± 900 atoms/cm³. (Allen et al., 2007).

Here we use a global whole-atmosphere chemistry-climate model to assess how such a concentration of Cl in the marine boundary would impact the methane lifetime, tropospheric ozone, and other VOCs also involved in ozone chemistry,

The Model

We use the UKCA chemistry-climate model, part of the Met Office Unified Model (MetUM) in a version similar to HadGEM3-A r2.0.

Resolution: 3.75°x2.5°, 60 levels to 84 km

Sea surface: prescribed, HadISST

Chemistry: HO_x-NO_x-VOC-Cl_y-Br_y,

Chemistry is a merger between the stratospheric UKCA chemistry (Morgenstern et al., 2009), tropospheric chemistry following Zeng et al. (2008), and some additional processes for tropospheric halogen chemistry. In particular, washout and dry deposition of inorganic halogen and reactions of the type $\text{Cl} + \text{VOC} \rightarrow \text{HCl}$ are included. Stratospheric halogen loadings, greenhouse gases and surface emissions of NO_x and VOCs are representative of year-2000 conditions.

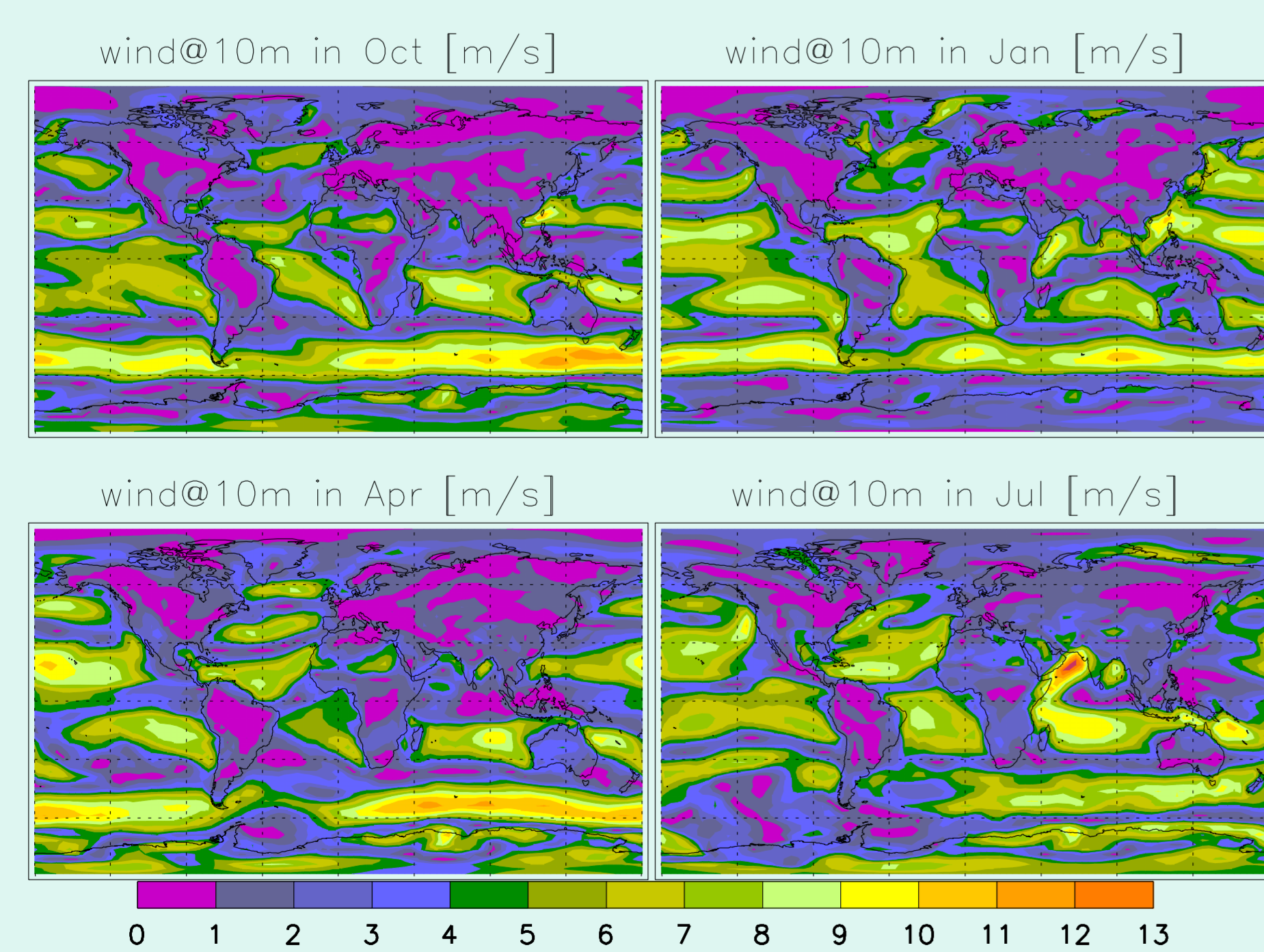
The Simulations

REF: Reference simulations, no surface emissions of inorganic halogens.

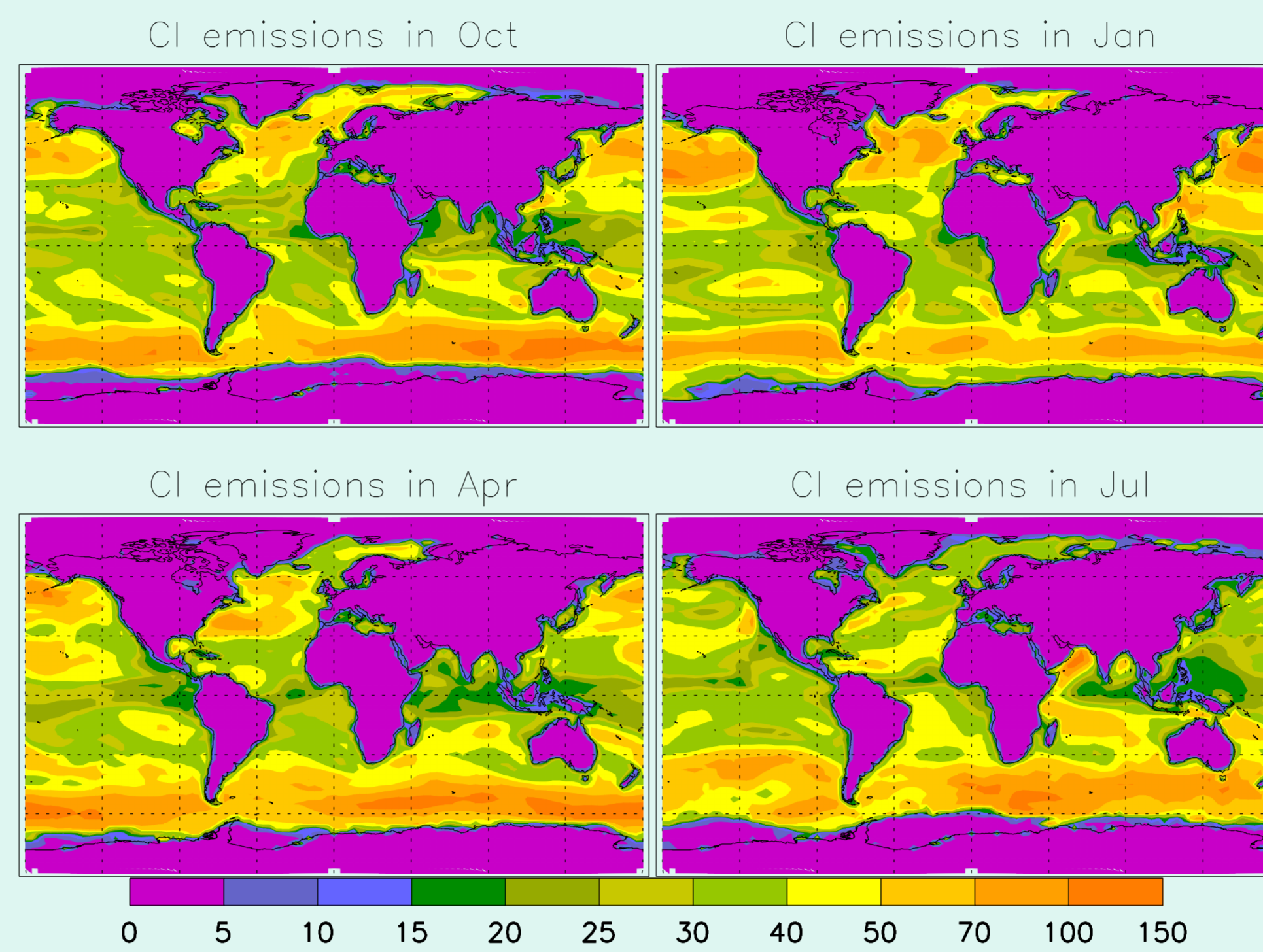
HAL: Same as REF, but with emissions of Cl₂O₂ from the ocean surface. Emissions are a function of the 10 m wind speed, following Smith et al. (1993). Emissions are scaled such that roughly 5% of methane is lost to this additional chlorine, as found by Allen et al. (2007).

Results

Surface wind



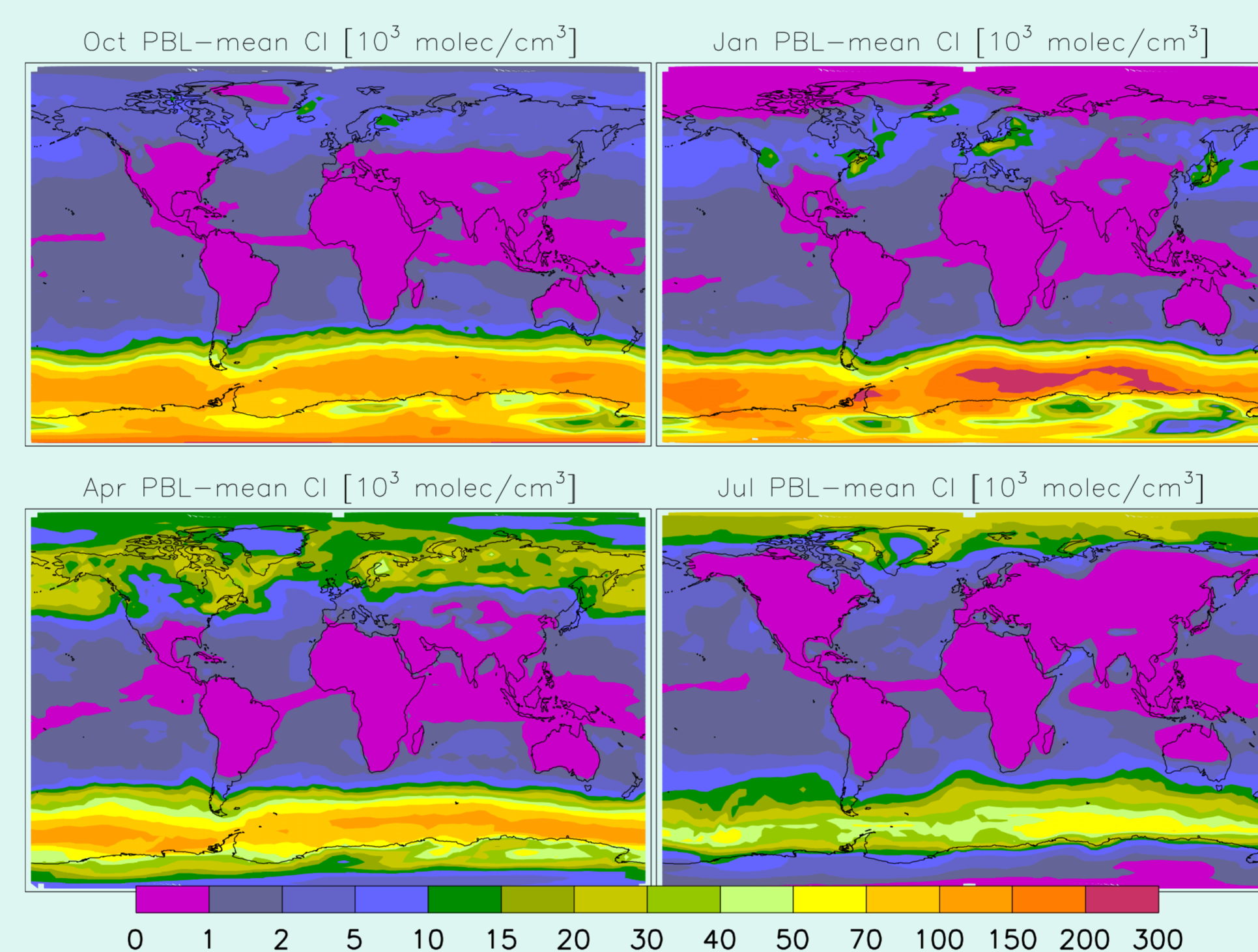
Monthly-mean 10m wind speed (m/s) in HAL, in October, January, April, and July.



Monthly-mean surface emissions of chlorine (mg(Cl) m⁻² s⁻¹) in HAL, due to release from aerosol.

Production of inorganic chlorine occurs at the storm tracks of both hemispheres, particularly over the Southern Ocean.

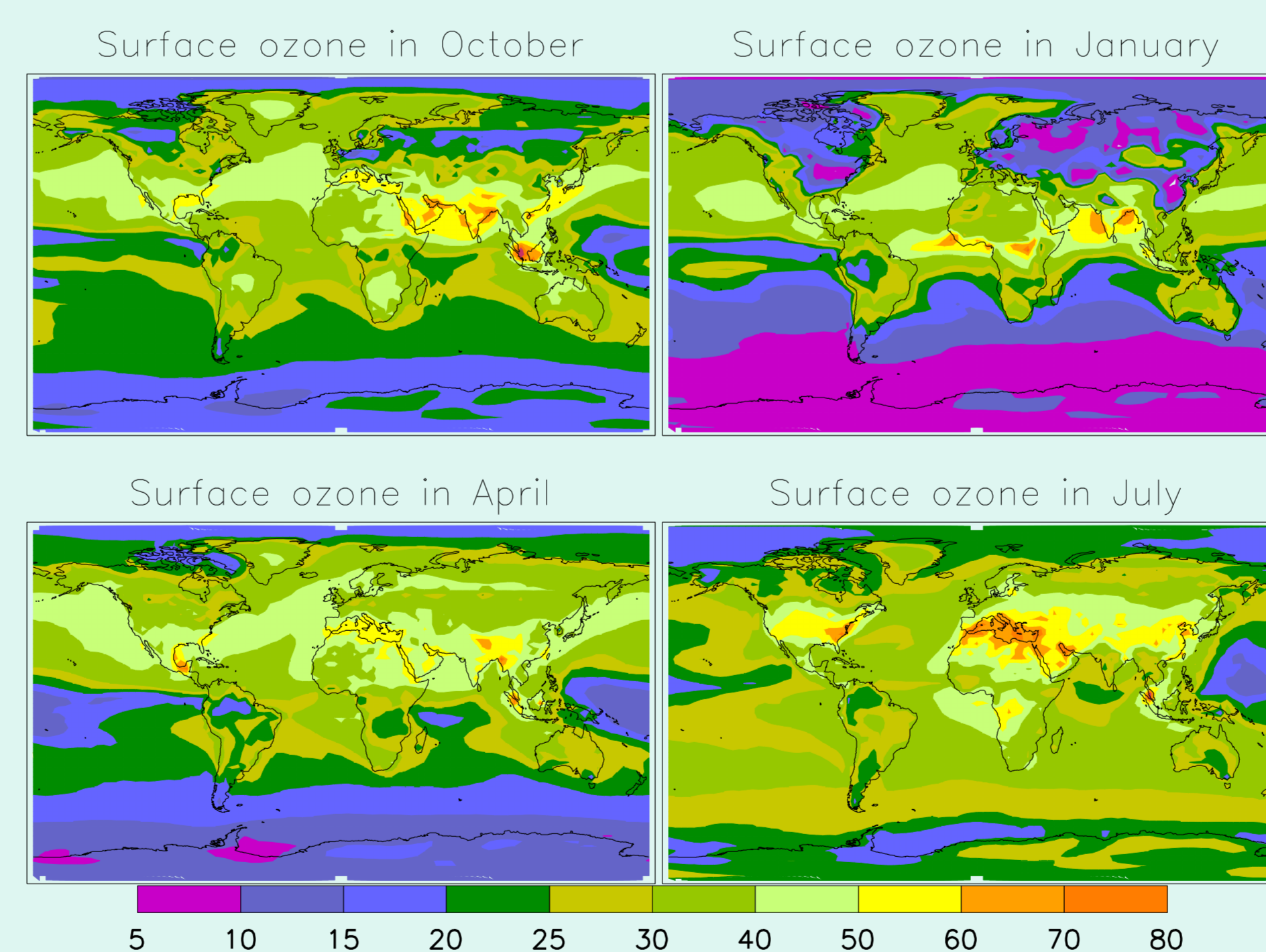
Surface atomic chlorine



Monthly-mean Cl concentration (10^6 molecules cm⁻³) in the planetary boundary layer, averaged over the depth of the PBL, for October, January, April, and July, for HAL.

The model suggests that the atomic chlorine would be dominated by a pronounced maximum over the Southern Ocean. Much less chlorine is modelled for northern high latitudes.

Surface ozone

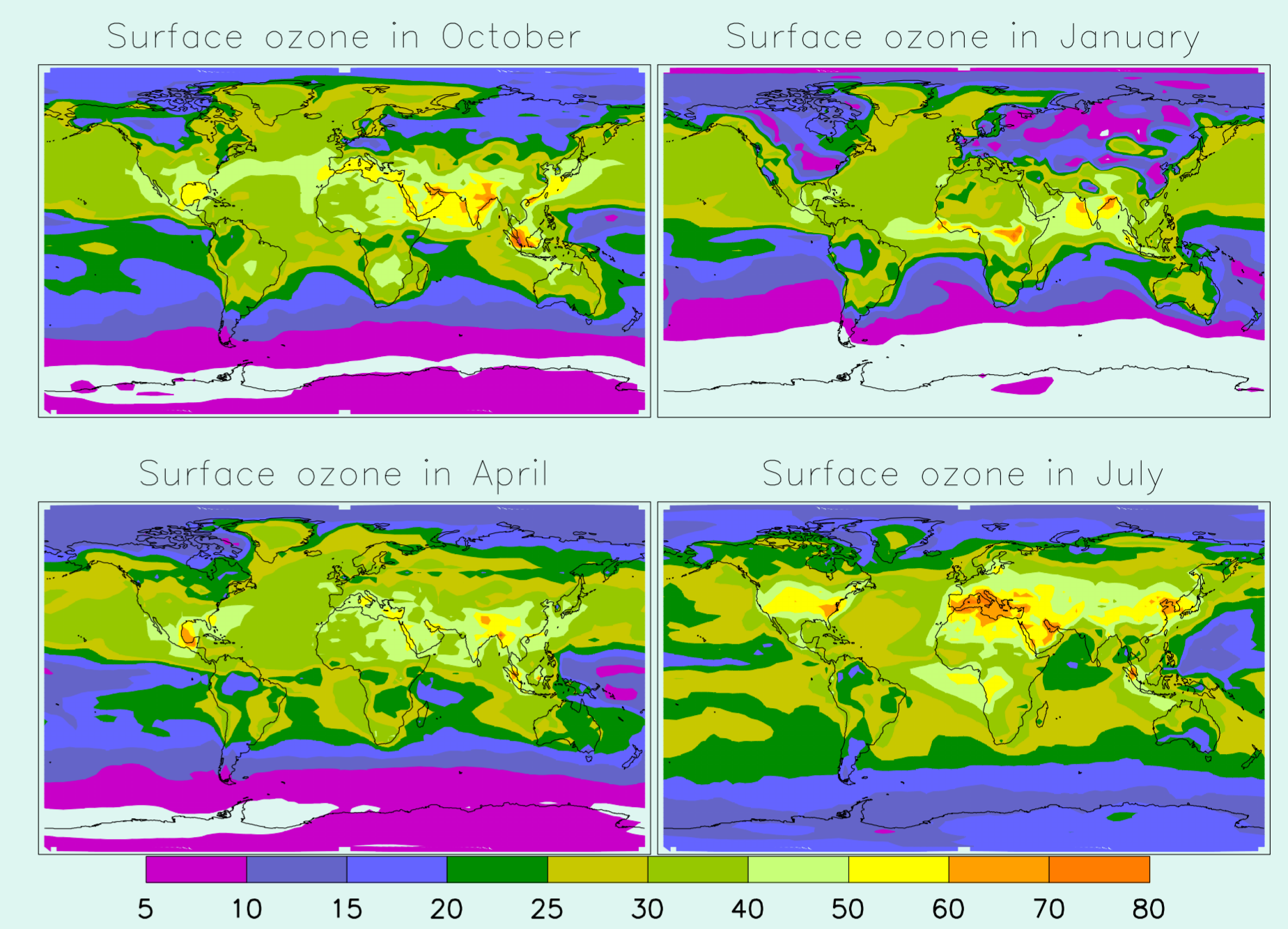


Monthly-mean surface ozone (ppbv) in REF, in October, January, April, and July.

The model produces low ozone during summer at southern middle and high latitudes.

References

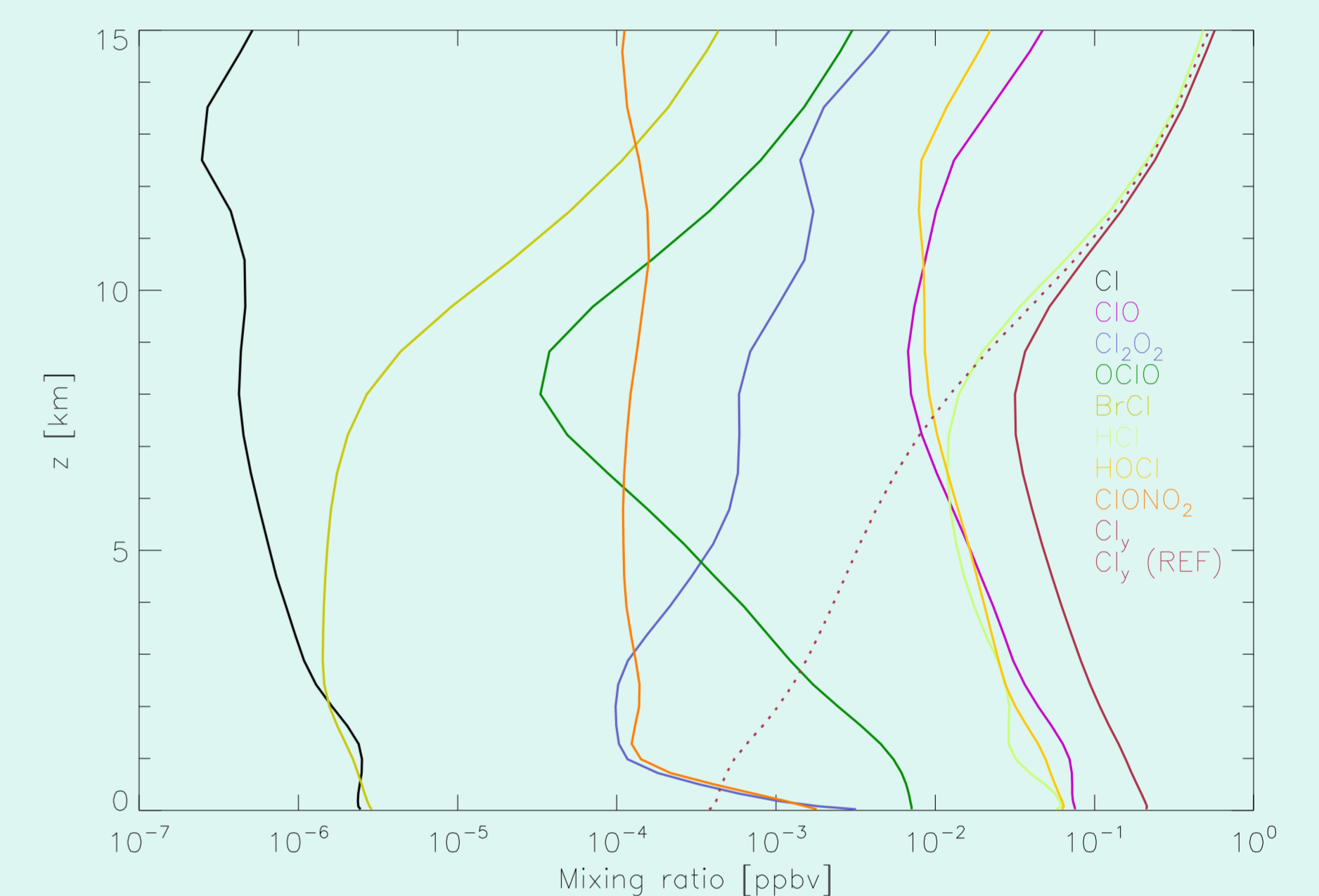
- Allen, W., et al., *J. Geophys. Res.*, 112, D04306, 2007.
Morgenstern, O., et al., *Geophys. Model Dev.*, 2, 1, 43-57, 2009.
Saueressig, G., et al., *Geophys. Res. Lett.*, 22, 10, 1225-1228, 1995.
Smith, M. H., et al., *Quart. J. Royal Meteorol Soc.*, 119, 809-824, 1993.
Zeng, G., et al., *Atmos. Chem. Phys.*, 8, 2, 369-387, 2008.



Monthly-mean surface ozone (ppbv) in HAL.

The additional chlorine substantially reduces surface ozone, particularly over the Southern Ocean.

Distribution of Cl across inorganic compounds



Annual-zonal-mean inorganic chlorine species in HAL, averaged over 45-60°S. Cl_y: Total inorganic chlorine in (solid) HAL and (dotted) REF.

Cl release from seasalt aerosol increases near-surface total Cl by 2-3 orders of magnitude, versus REF.

Impact on VOCs

	HAL	REF
CH ₄ lifetime	10.8 years	10.7 years
Loss to CH ₄ + Cl	6.3%	1%
C ₂ H ₆ lifetime	1.5 months	2.4 months
Loss to C ₂ H ₆ + Cl	19.9%	5.7%
C ₃ H ₈ lifetime	0.3 months	0.5 months
Loss to C ₃ H ₈ + Cl	7.9%	1..9%

Summary and outlook

We have added a representation for the release of inorganic chlorine from the sea surface to a global whole-atmosphere CCM. The emissions are scaled such that Cl in the PBL is similar to literature estimates. The additional Cl substantially affects tropospheric ozone, particularly over the Southern Ocean, and higher alkanes in the Northern Hemisphere. The reduction of surface ozone is probably exaggerated due to weak stratosphere-troposphere exchange. The additional Cl does not affect the CH₄ lifetime because of reduced OH.

The results need to be firmed up against observations of chlorine compounds over the Southern Ocean. Furthermore, emissions of chlorine from first-year sea ice may be important but have not been modelled here,