Global ozone reduction driven by dust-catalyzed halogens chemistry

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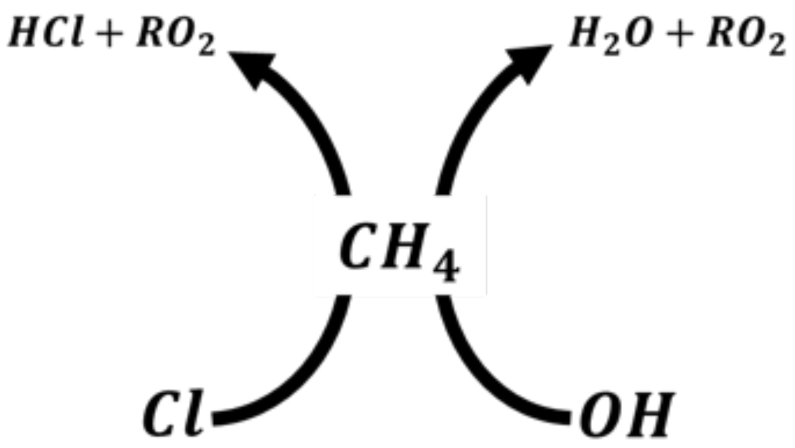
Introduction

- OH and Cl are **directly** competing on CH_4 consumption.



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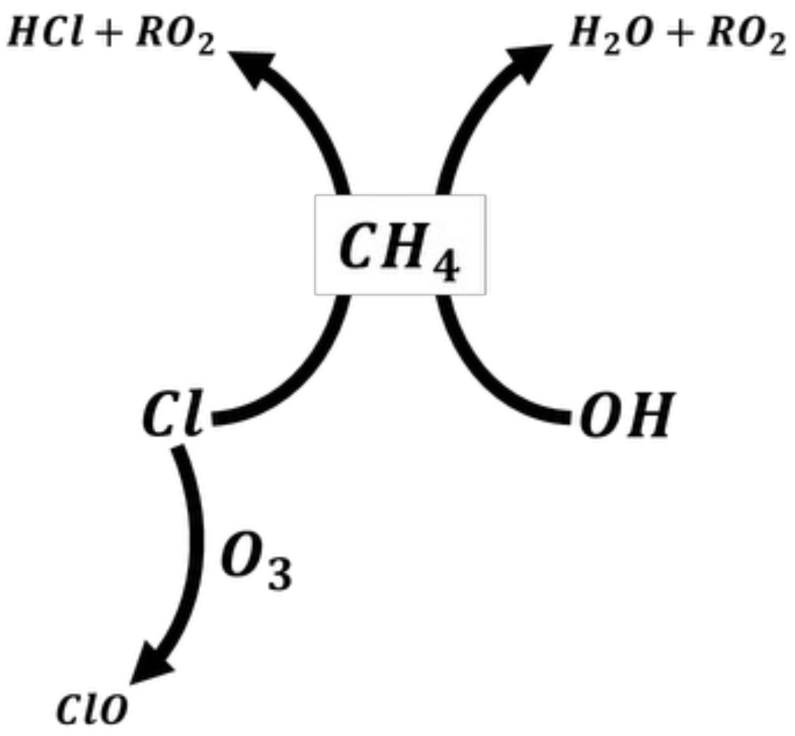

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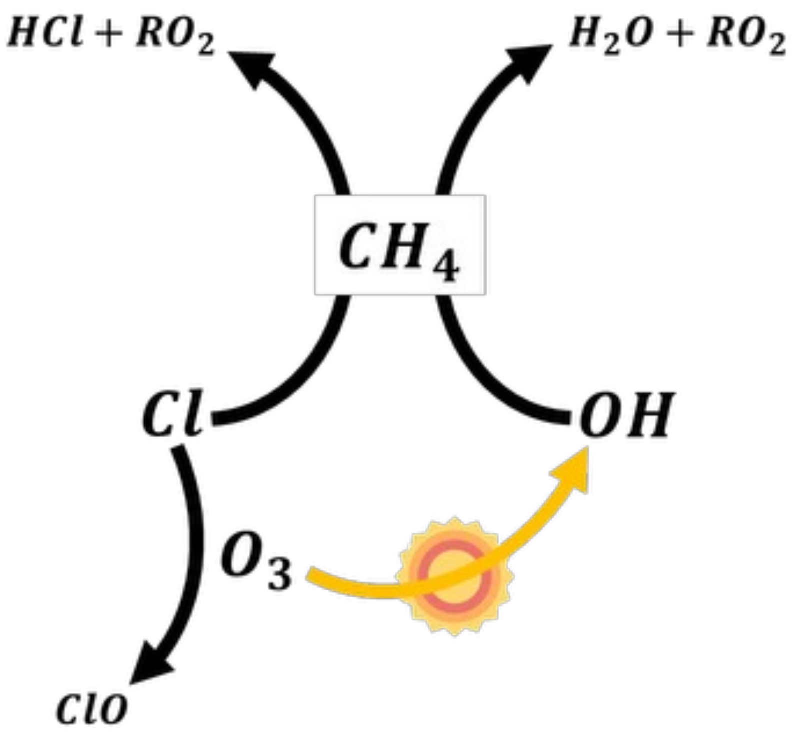


- Cl will affect OH through **indirect** reactions.

(clean environments)

$Cl + O_3 \rightarrow ClO + O_2$

$O_3 + hv \rightarrow O^1D + O_2$

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

Net: OH decrease

(polluted environments)

$Cl + VOCs \rightarrow RO_2 + HCl$

$RO_2 + NO \rightarrow NO_2 + RO$

$RO + O_2 \rightarrow HO_2 + \textit{Products}$

$HO_2 + NO \rightarrow NO_2 + OH$

$ClO + HO_2 \rightarrow HOCl$

$HOCl + hv \rightarrow Cl + OH$

Net: OH increase

One mechanism, multiple implications

Recent research demonstrated the correlation between North African mineral dust and chemical methane removal through iron salt aerosol for chlorine atom production.

Science fiction: Methane Mitigation

Could technologies that mimic dust-driven halogen activation provide a significant pathway for atmospheric methane removal?

Atmospheric consequences: The ozone (O_3) impact

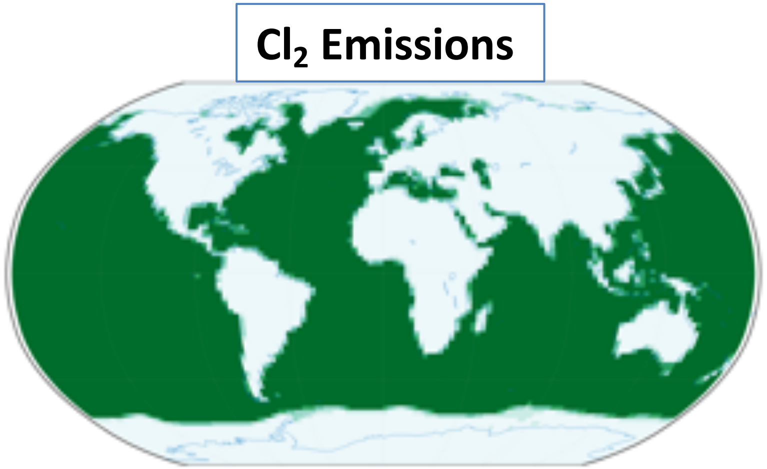
What are the "side effects" of dust to halogen activation? To what extent does dust-driven halogen activation impact the tropospheric ozone budget?

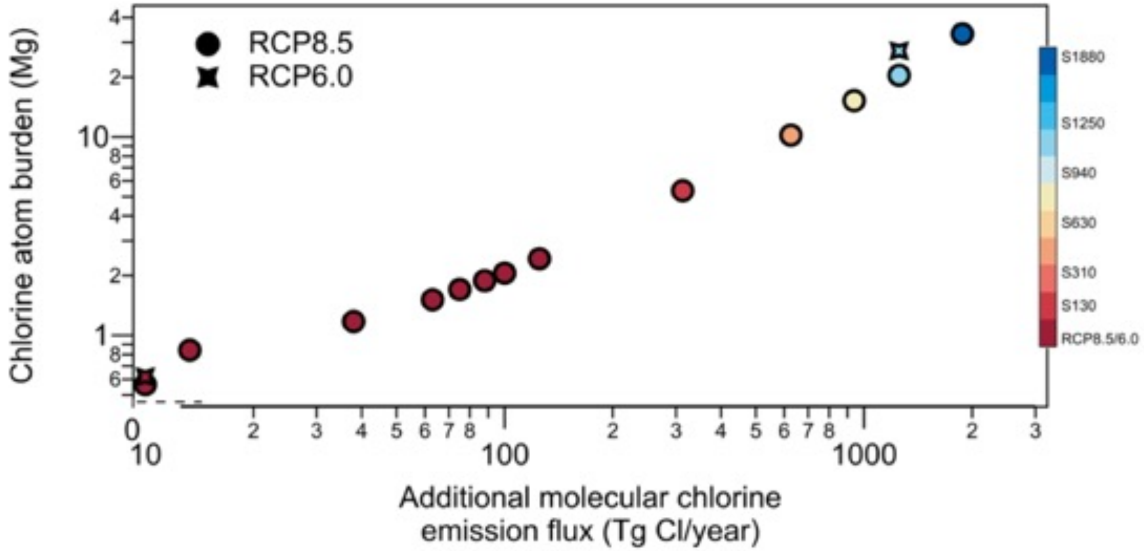
Li Q, Meidan D. *et al.* Global environmental implications of atmospheric methane removal through chlorine-mediated chemistry-climate interactions Nat Commun (2023). https://doi.org/10.1038/s41467-023-39794-7

Meidan D, Li Q. *et al.* Evaluating the potential of iron-based interventions in methane reduction and climate mitigation Environmental Research Letters (2024). http://iopscience.iop.org/article/10.1088/1748-9326/ad3d72

Science fiction: Methane Mitigation

- Model description:
  CESM1 CAM-Chem Halogen model (Li et al. 2022 & 2023), resolution 2.5º x 1.9º.
- Surface Cl_2 emissions above ocean.





Li, Q., Fernandez, R.P., Hossaini, R. *et al.* Reactive halogens increase the global methane lifetime and radiative forcing in the 21st century. *Nat Commun*. (2022). https://doi.org/10.1038/s41467-022-30456-8

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Science fiction: Methane Mitigation

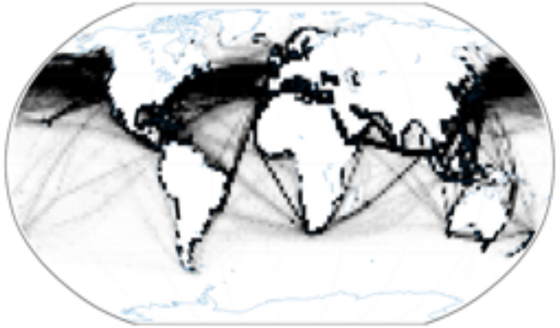
Different mitigation scenarios –

Constant Cl_2 above ocean.

Constant iron above ocean.

Iron from ships.

Point source emissions.



Calculation:

- Photoactive iron = total soluble iron * α (31.6%) (from Zhu et al. 1997)
- **Overestimation due to assumption of instant mixing of iron and sea salt aerosol!!**

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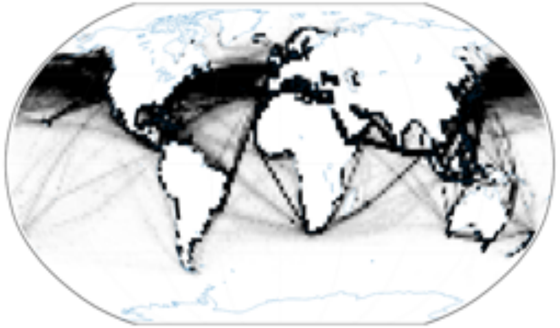
MAGICC



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Methods

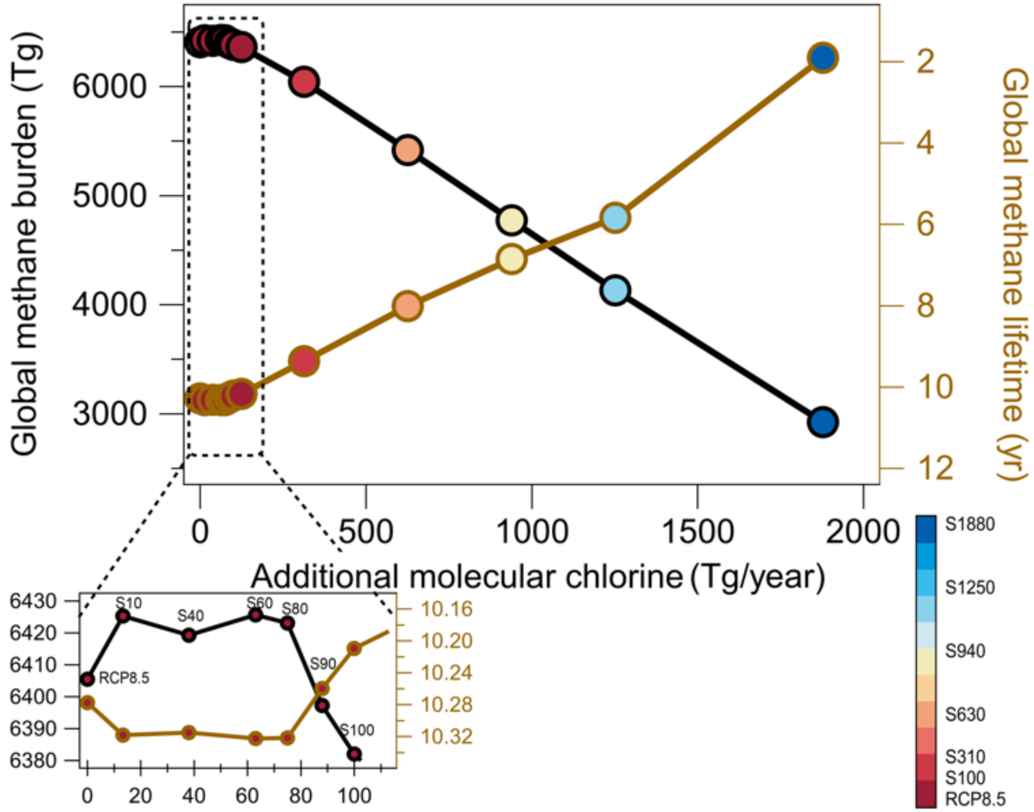
Model for the Assessment of Greenhouse Gas Induced Climate Change version 6 (MAGICC6)

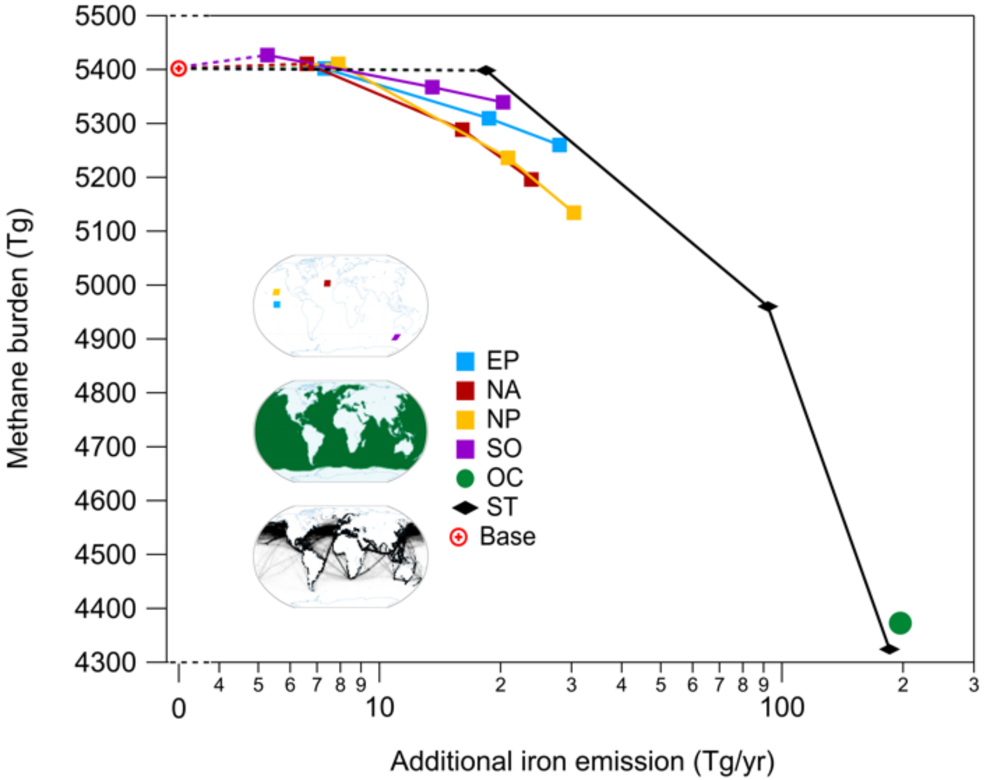
- Using the the timeseries of surface CH_4, sulfate aerosols, and O_3 computed globally, we manipulate the RCP8.5 and RCP6.0 initial concentrations given in MAGICC.
- Changing the energy-balance component of MAGICC6, we could simulate the change in surface temperature and radiative forcing between 1850 through 2050 for all future cases and scenarios.
- To account for the iron radiative forcing, as calculated in MIMI, we use the percentage radiative change of iron (between the different scenarios and the Base scenario) and increase the black carbon (BC) aerosols in MAGICC6 to match the radiative forcing from added iron aerosols.

Science fiction: Methane Mitigation

Non linear methane response –

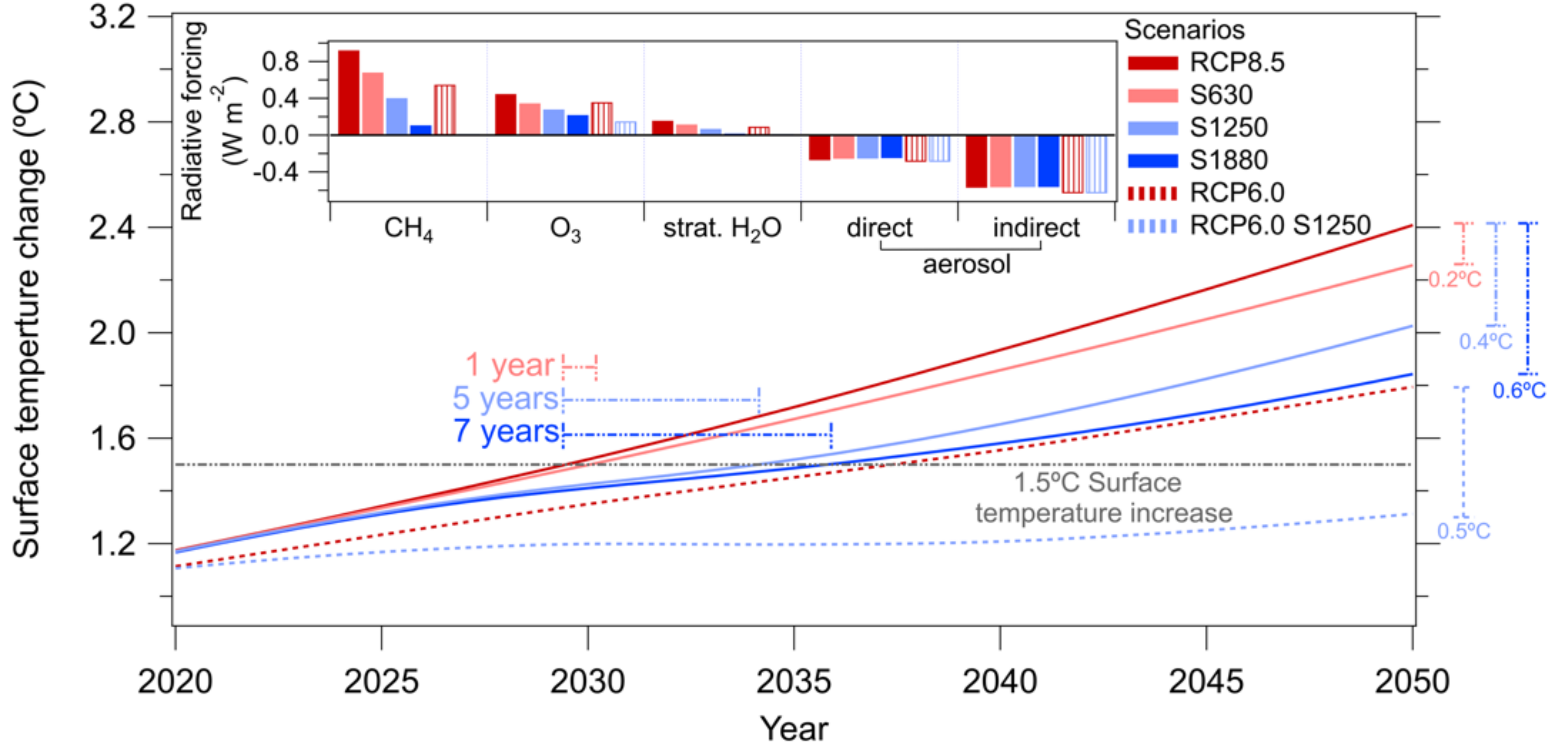
- The additional chlorine reacts with ozone, which in turn decreases the production of OH and increases methane burden.
- When sufficient Cl_2 is produced/added, the reaction with ozone no longer limits the reaction with methane, effectively lowering methane concentrations.





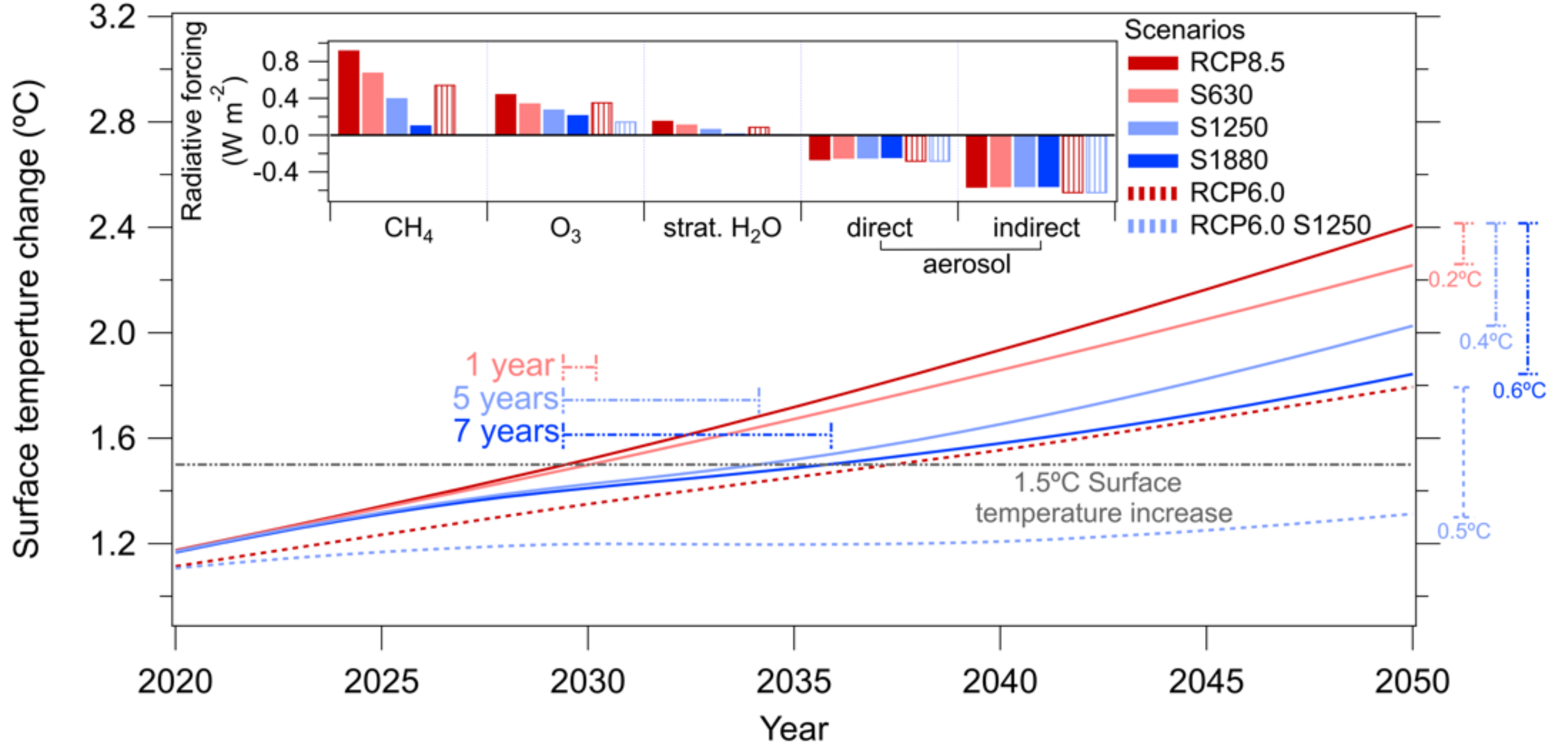
Radiative forcing and surface temperature –

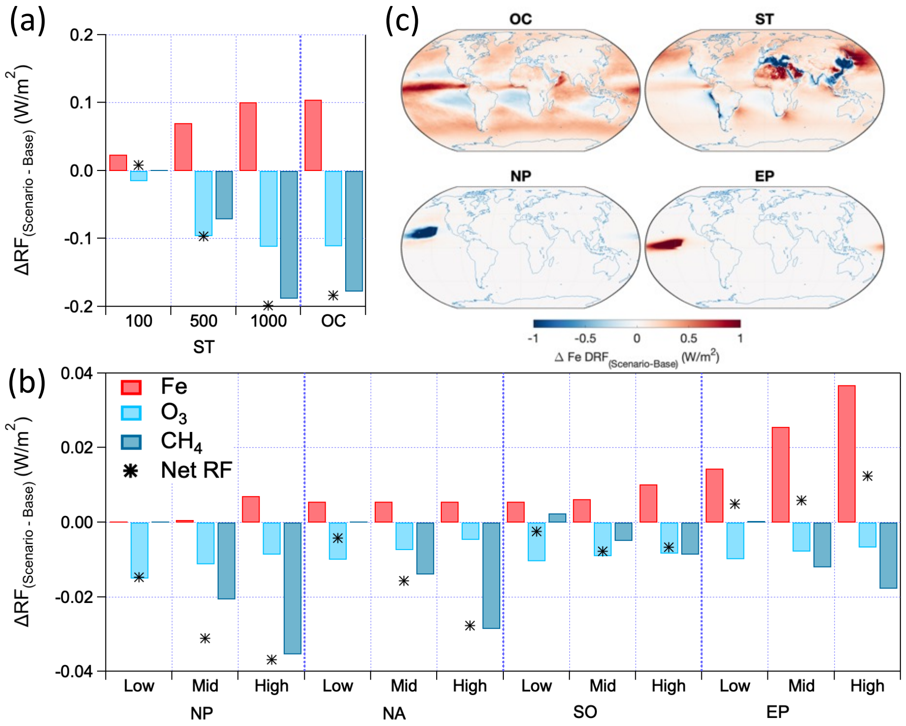
- Changes in ozone and methane concentrations reduce the radiative forcing.
- The reduction in radiative forcing from changes in ozone is of a similar magnitude as of methane.

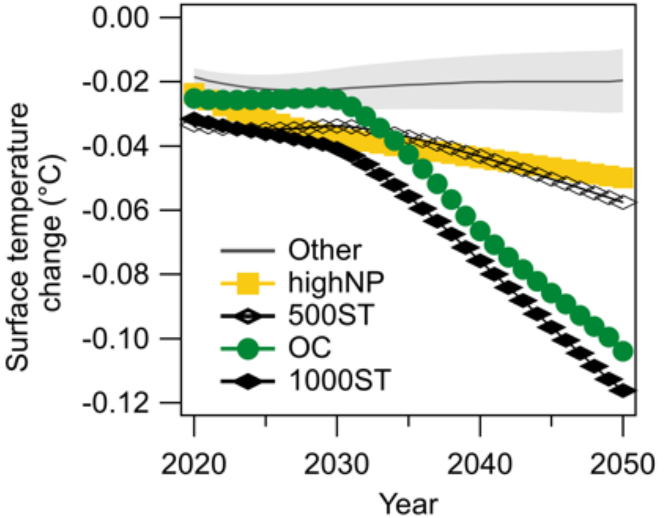


Radiative forcing and surface temperature –

- Changes in ozone and methane concentrations reduce the radiative forcing.
- The reduction in radiative forcing from changes in ozone is of a similar magnitude as of methane.
- Iron aerosols tend to warm the atmosphere, and the direct radiative effect depends on where and how much iron is added.



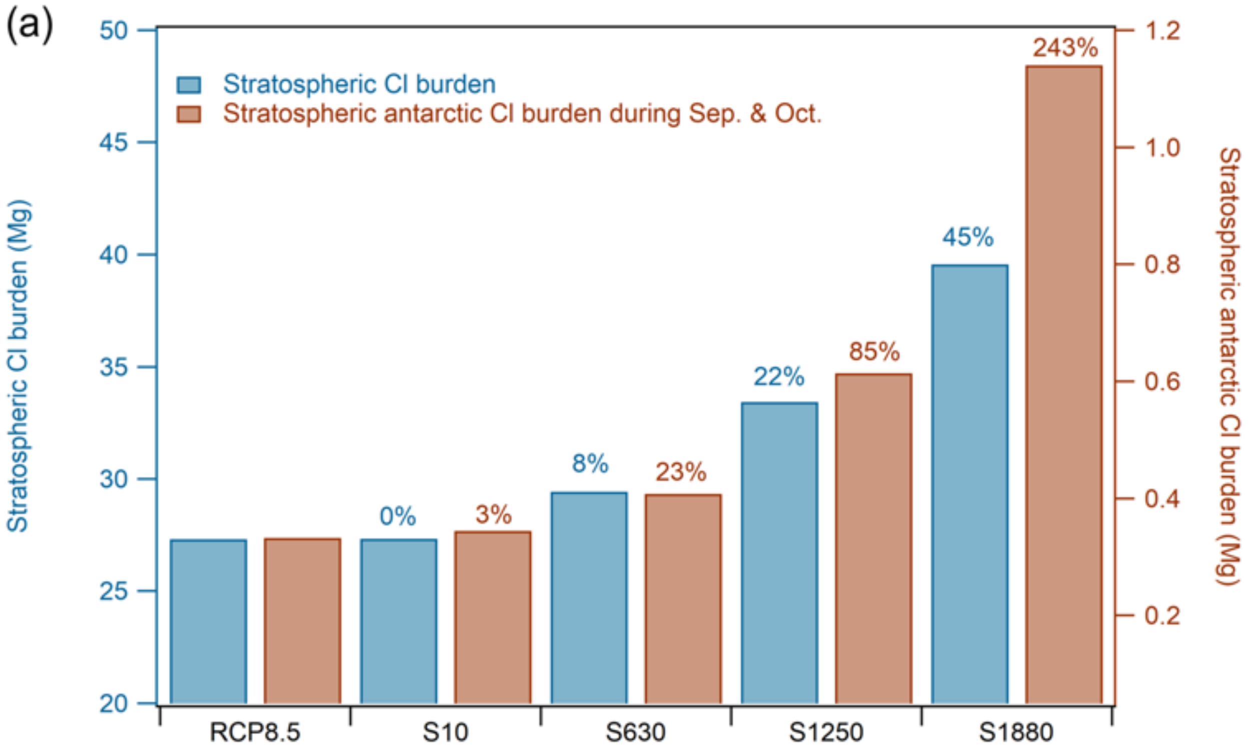


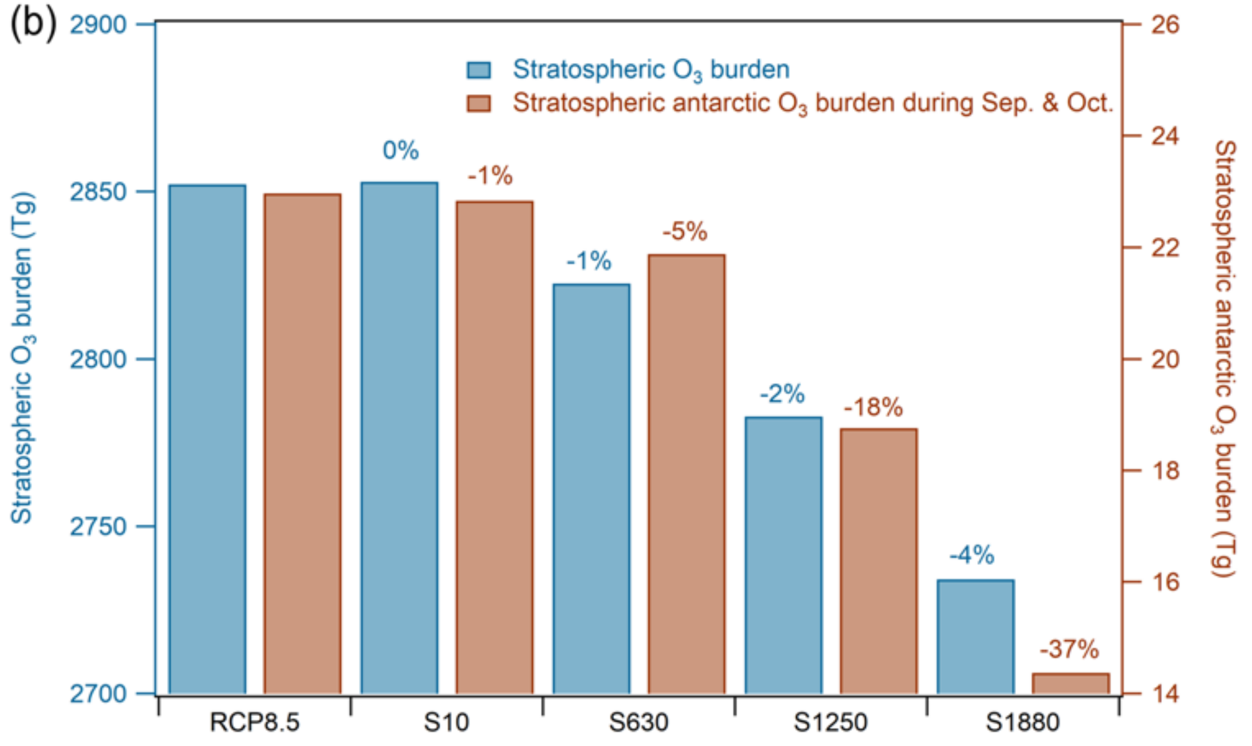


Science fiction: Methane Mitigation

Stratospheric ozone, and chlorine –

- An increase of 243% in the chlorine burden during September and October at the highest chlorine addition resulted in a 37% reduction in the Antarctic stratosphere ozone burden.

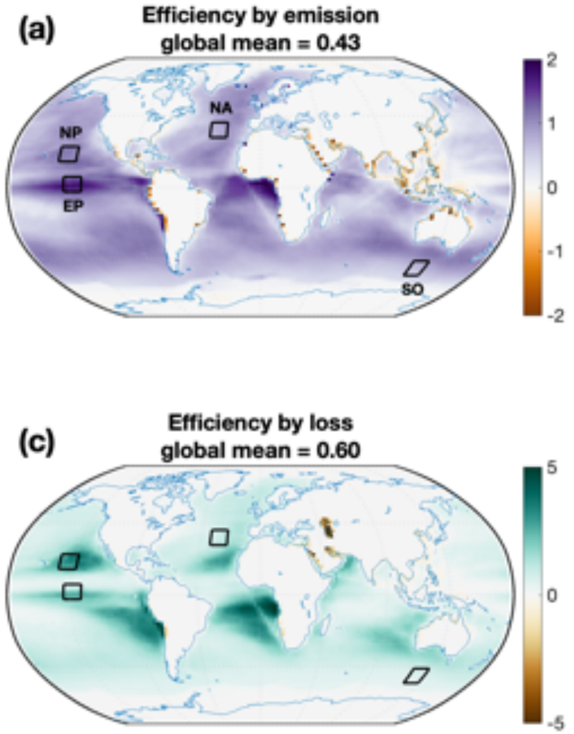


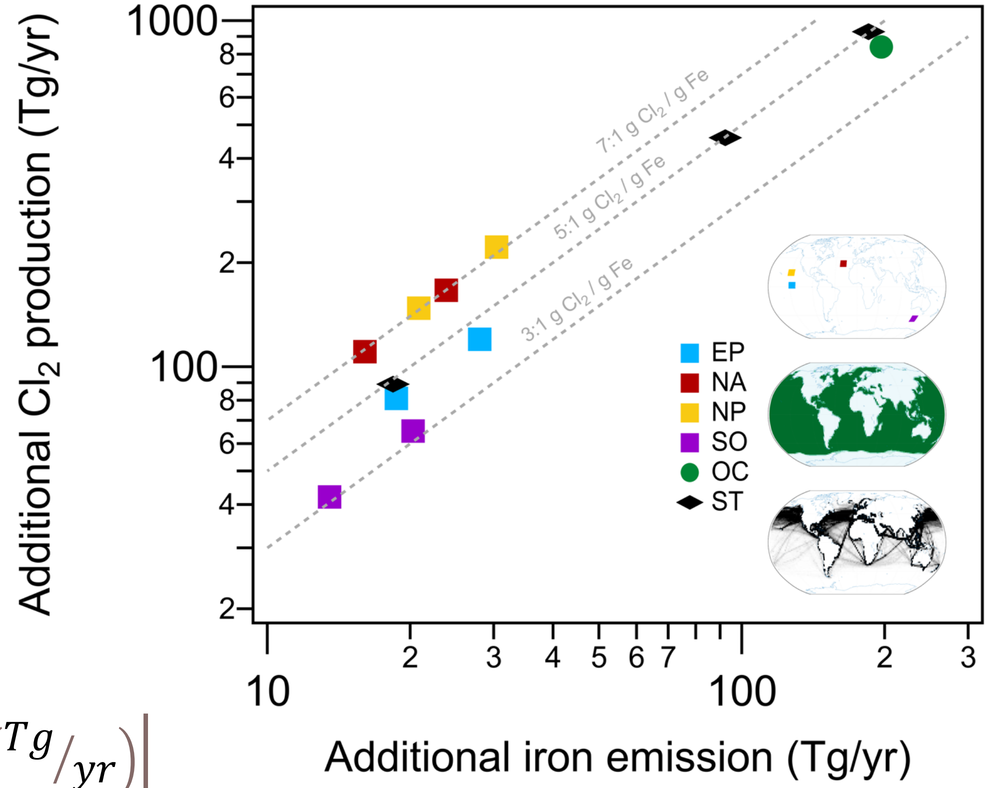


Science fiction: Methane Mitigation

Iron addition –

- Efficiency of the methane removed is better defined by the iron loss.
- Mainly, longer iron lifetimes will lead to higher chlorine production.

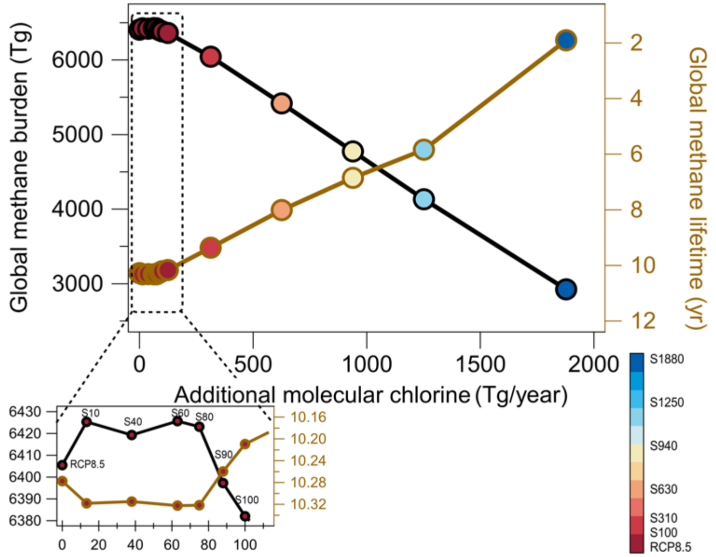


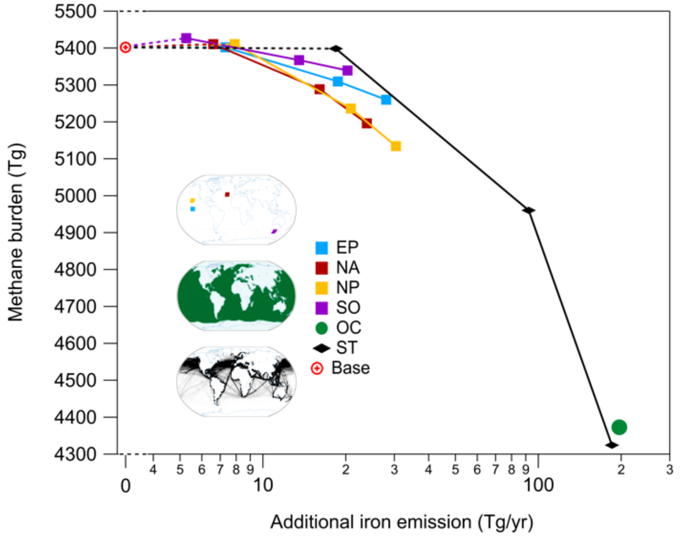


$$Spatial\ efficiency = \left.\frac{\Delta\ total\ CH_4\ loss\ \left({}^{Tg}/_{yr}\right)}{\Delta\ iron\ flux\ \left({}^{Tg}/_{yr}\right)}\right|_{lat,lon}$$

Science fiction: Methane Mitigation

- A **non linear methane response** to the addition of iron/chlorine will result in an unwanted methane burden increase.





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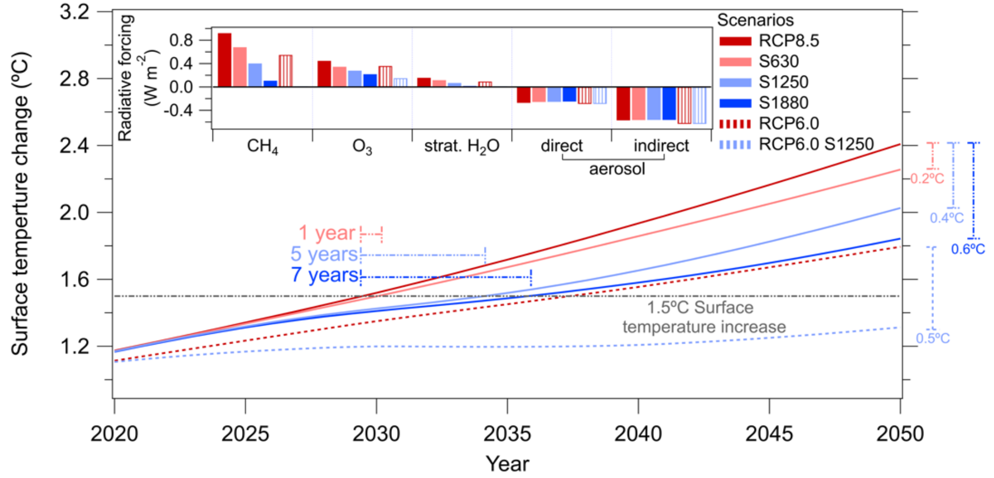
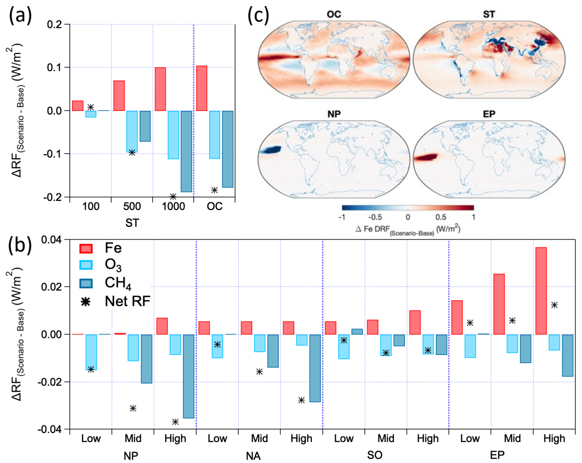
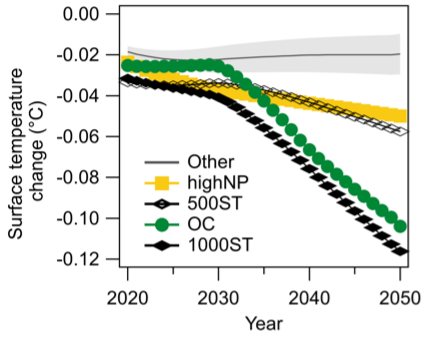
- A **non linear methane response** to the addition of iron/chlorine will result in an unwanted methane burden increase.
- The addition of iron/chlorine reduces the **radiative forcing of both ozone and methane**. Iron addition will offset some of these reductions.







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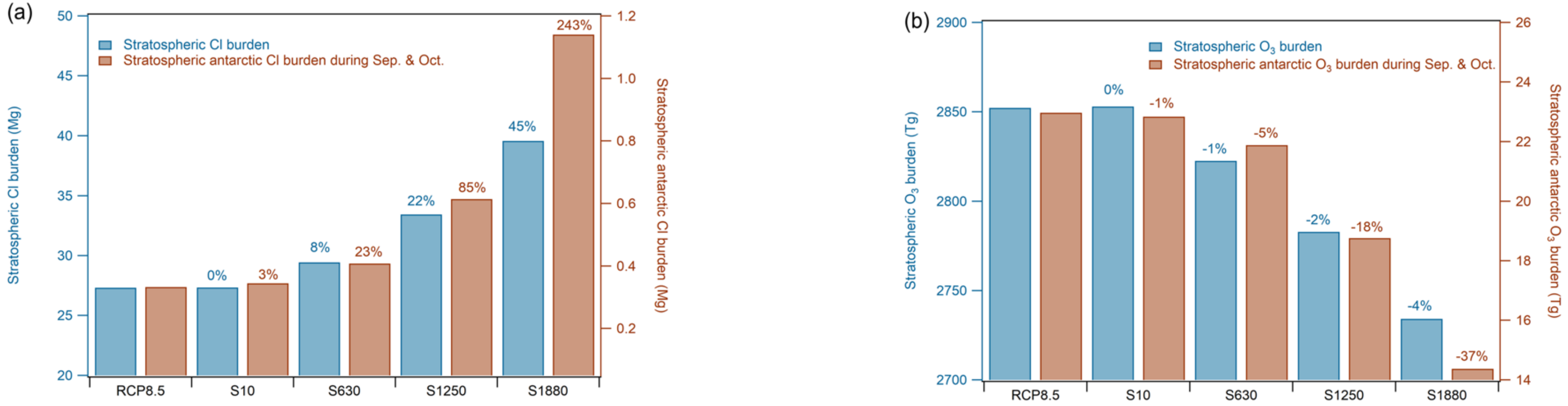

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- **Stratospheric ozone** is reduced in all our scenarios.
- A better understanding of the **positive and negative implications** of adding iron aerosols and the resulting chlorine production is **vital** to advance our understanding of effective iron- and chlorine- based strategies to mitigate atmospheric methane.

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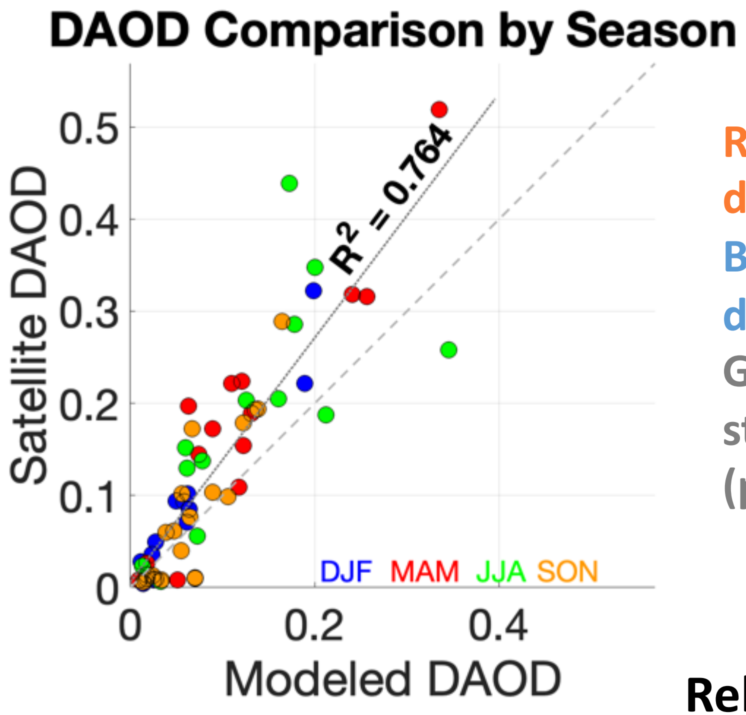
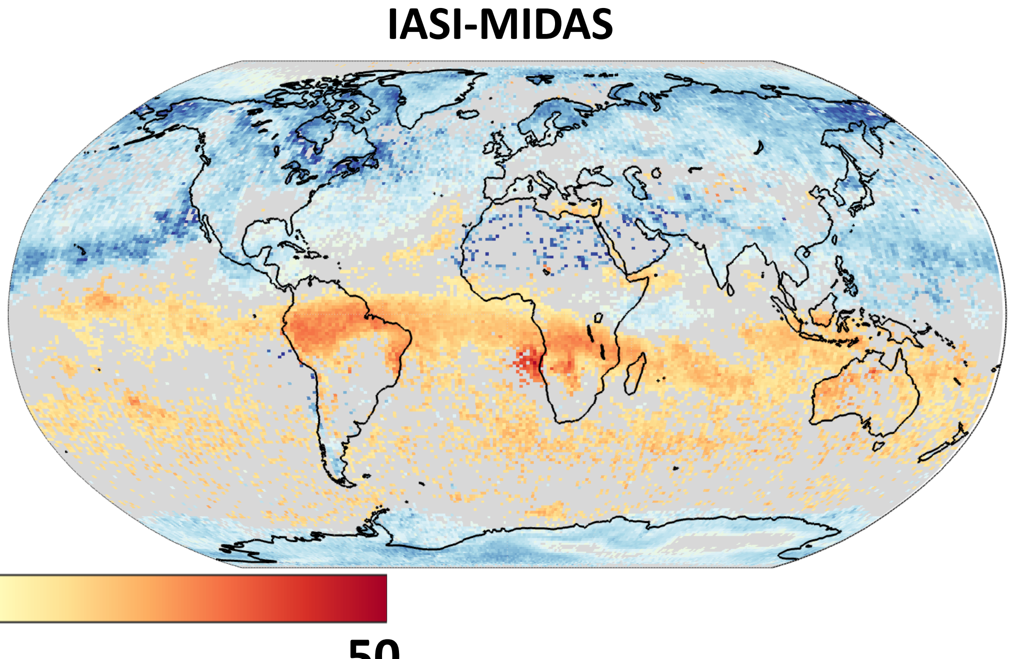
Atmospheric consequences: The ozone impact



Red: O_3 lower on high-dust days
Blue: O_3 higher on high-dust days
Grey: Missing data or statistically insignificant ($p \geq 0.05$)



Relative change in Tropospheric O_3 Column (%) due to high dust conditions

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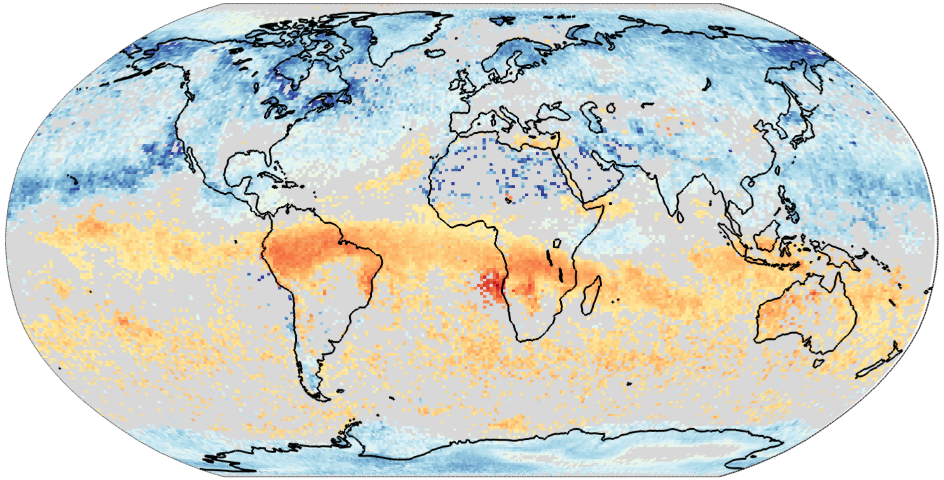
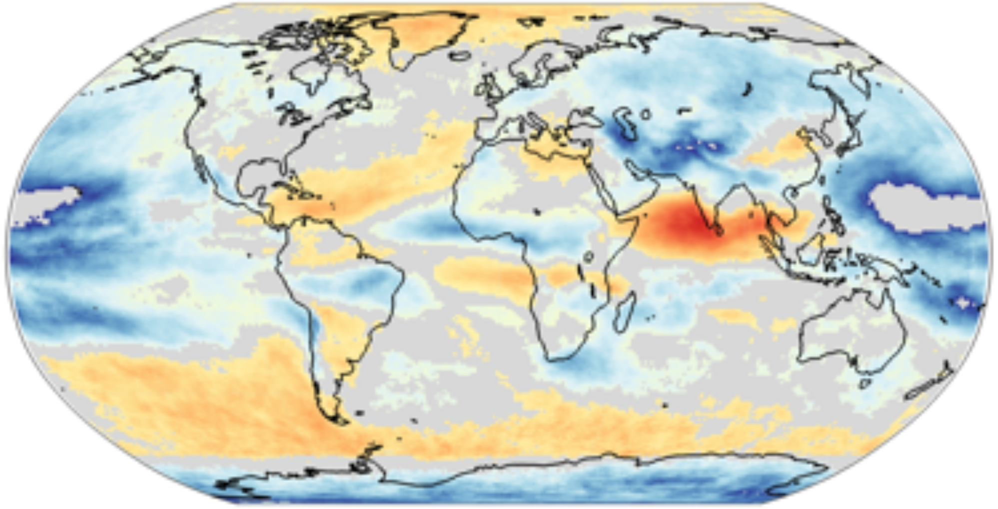
IASI-MIDAS



$dust2hal_{on}$



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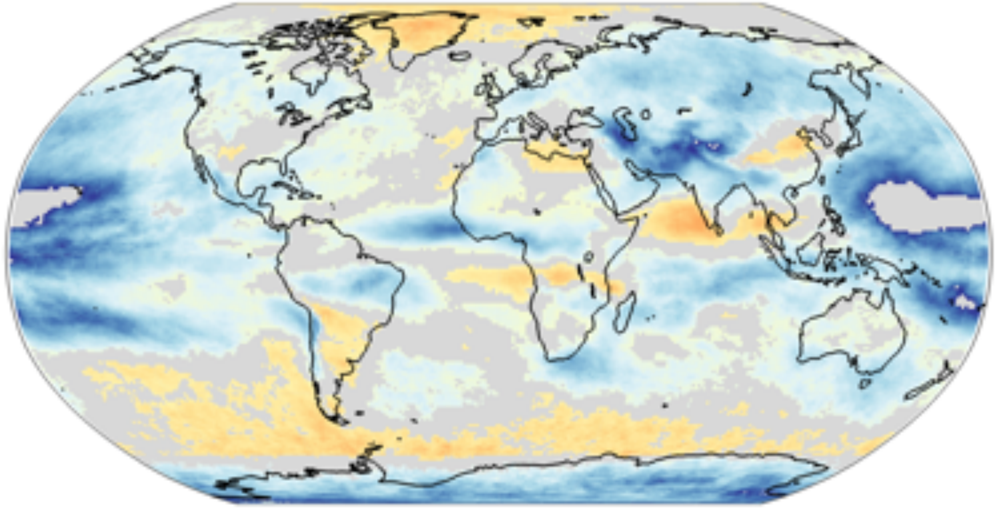

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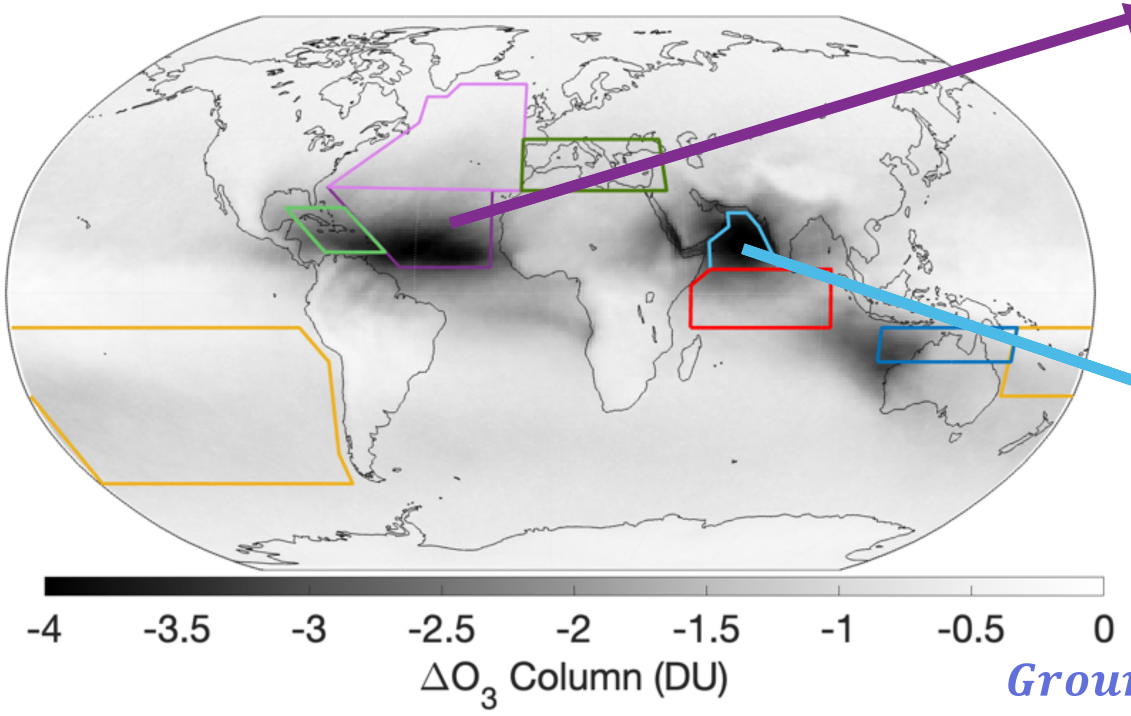
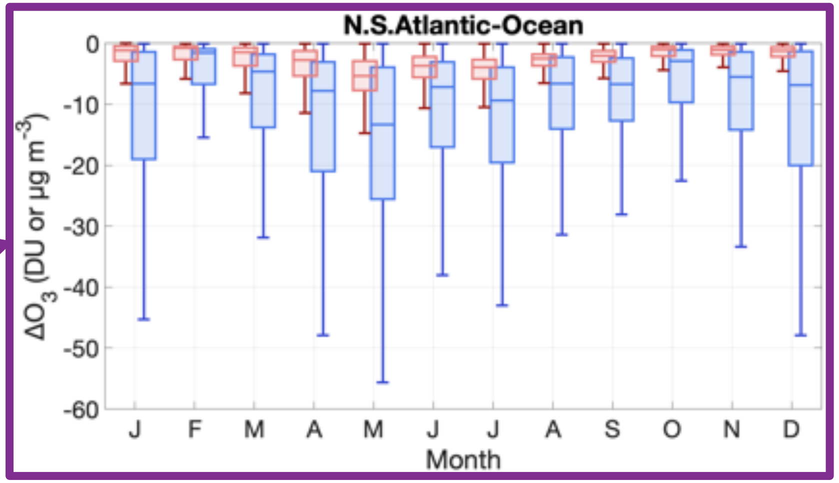
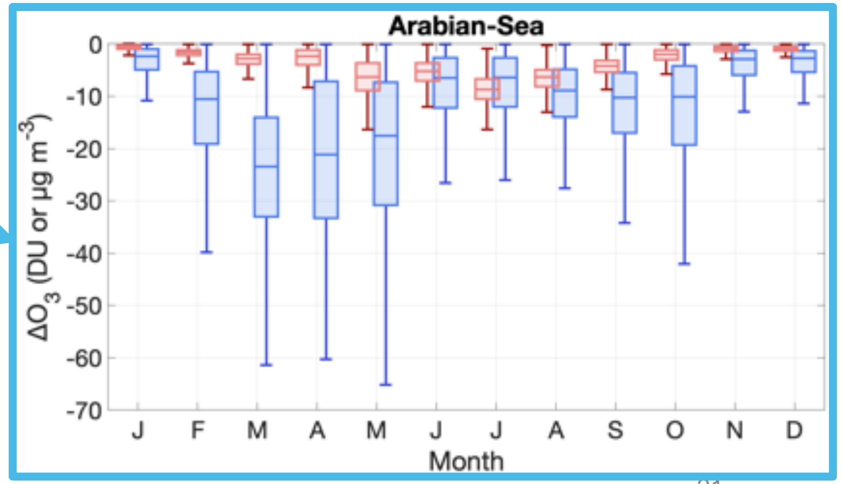
Atmospheric consequences: The ozone impact

Local ozone reduction–

- Dust-driven halogen chemistry lowers tropospheric and surface ozone, ~5% at the surface and ~3–4% in the tropospheric column.
- Boundary-layer chemistry vs. lofted plume transport drive distinct ozone responses.







$Ground-level\ (\mu g\ m^{-3})$
$Column\ (DU)$

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Key take home messages

Non-linear methane respose – methane reduction from 3 times current chlorine ≅ 16 times current combustion iron emission

Trop. ozone reduction – radiative forcing reduction due to ozone reduction similar to the direct reduction from methane

Strat. ozone reduction – Antarctic strat. ozone burden during September and October reduced by up to 37%

Surface temperature – 50-fold current chlorine will reduce surface temperature by 0.6°C in 2050. Iron additions will offset this reduction

Unresolved Questions of the MDSA Mechanism

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Unresolved Questions of the MDSA Mechanism

- Aerosol Size Efficiency
- Optimal pH
- Competition with Other Species (Sulfate, Hydroxide, Oxalate)
- HCl Recycling

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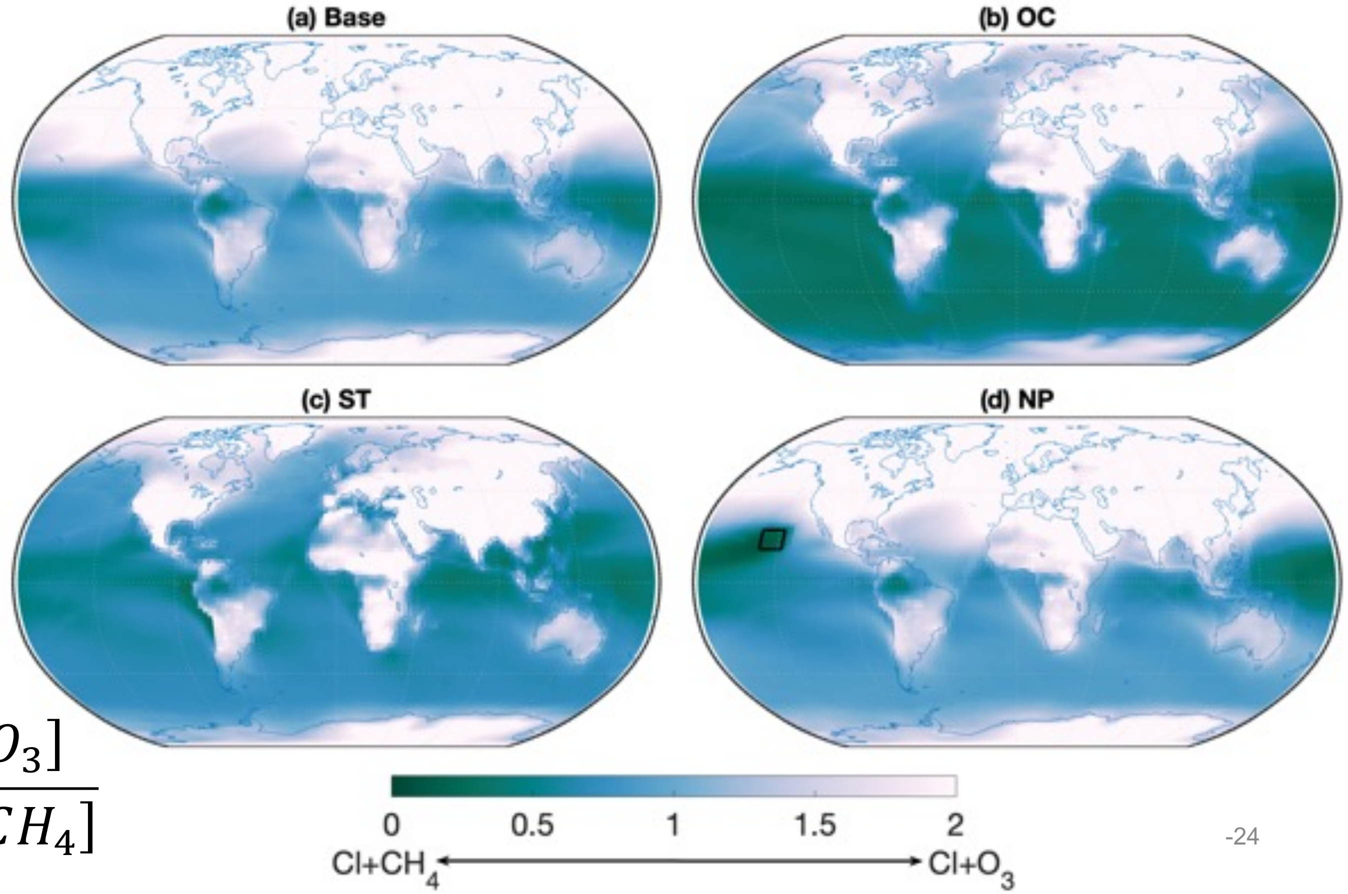
Results & discussion

Chlorine reactivity –

Green colors indicate more Cl reactivity towards methane, and white colors indicate more Cl reactivity towards ozone.

Chlorine reactivity towards ozone is higher where the ozone concentrations are higher, i.e., in the northern hemisphere.

The global averaged CRS shifts from Cl+O_3 dominated in the Base scenario to a regime where the reaction of chlorine with ozone and methane are comparable in the highest scenarios.



$$Cl + CH_4 \overset{O_2}{\rightarrow} CH_3O_2 + HCl$$

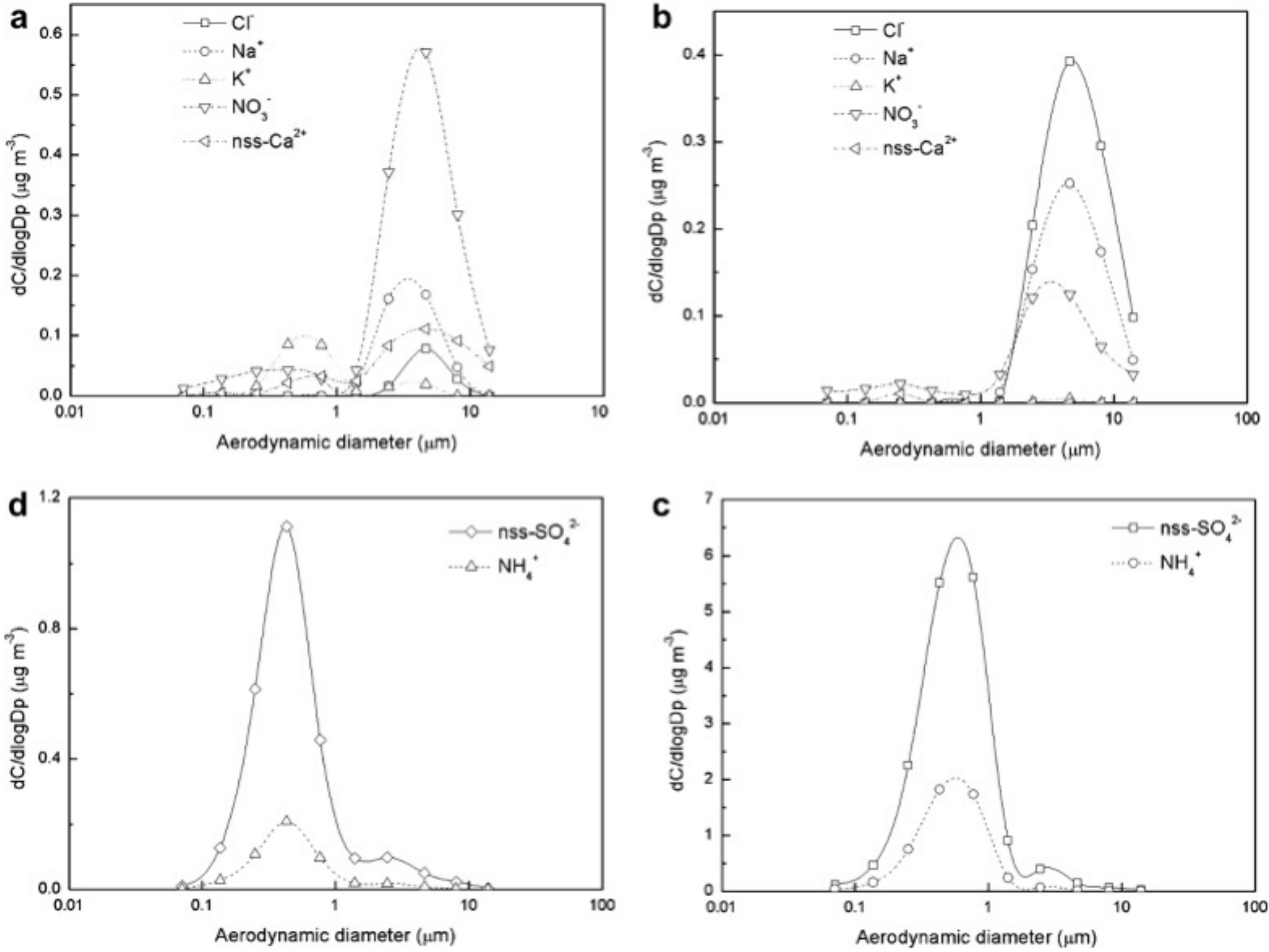
$$Cl + O_3 \rightarrow ClO + O_2$$

$$Chlorine\ Reactivity\ Sensitivity = \frac{k_{Cl+O_3} * [O_3]}{k_{Cl+CH_4} * [CH_4]}$$

-https://www.sciencedirect.com/science/article/pii/S1352231011010442

-Xiaohong Yao, Leiming Zhang: Chemical processes in sea-salt chloride depletion observed at a Canadian rural coastal site,

-Atmospheric Environment, Volume 46, 2012, DOI: 10.1016/j.atmosenv.2011.09.081.



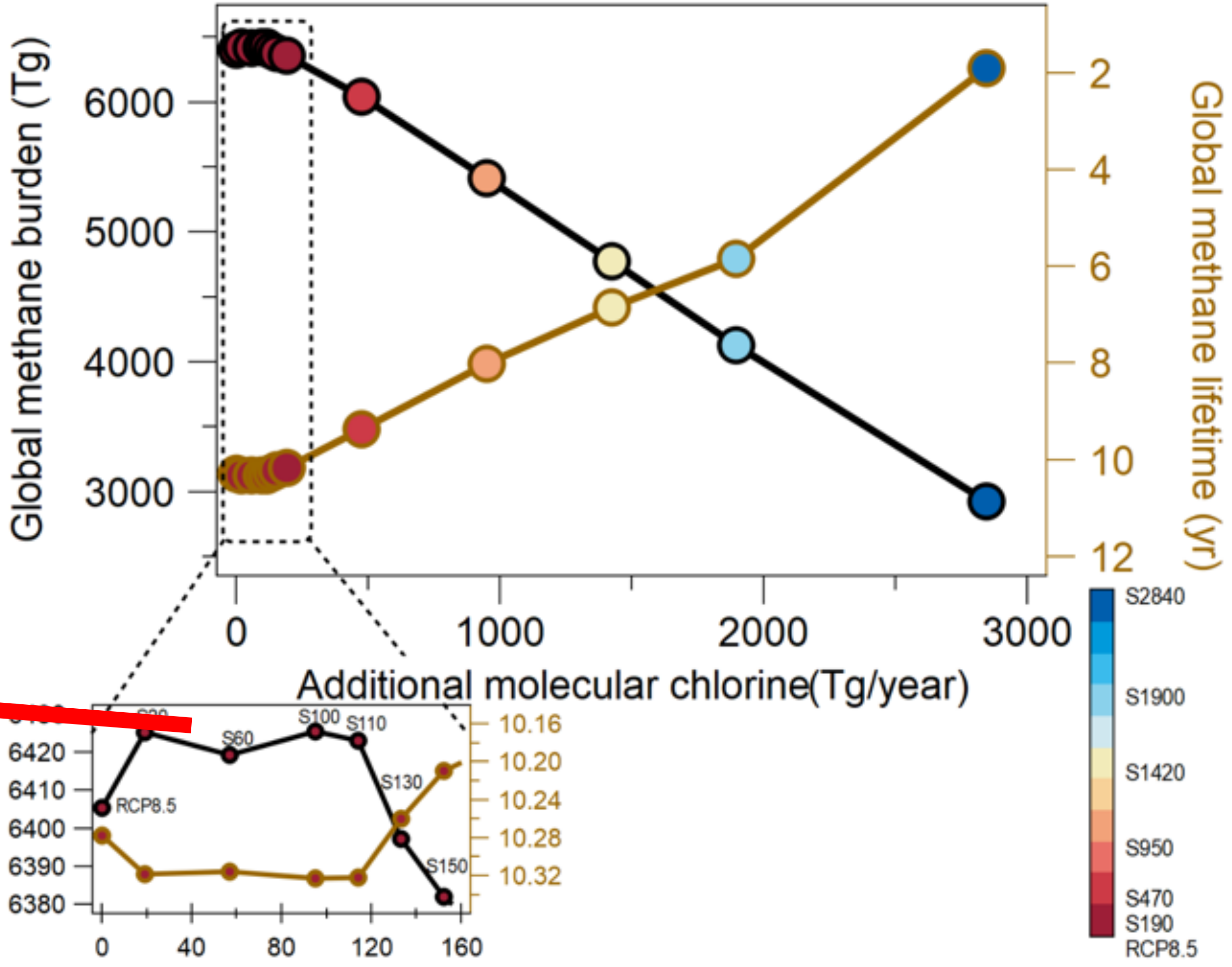
-Fig. 1. Size distributions of the averaged ionic concentrations during the two campaigns, (a) and (c): the summer campaign; (b) and (d): the fall campaign.

Methane response

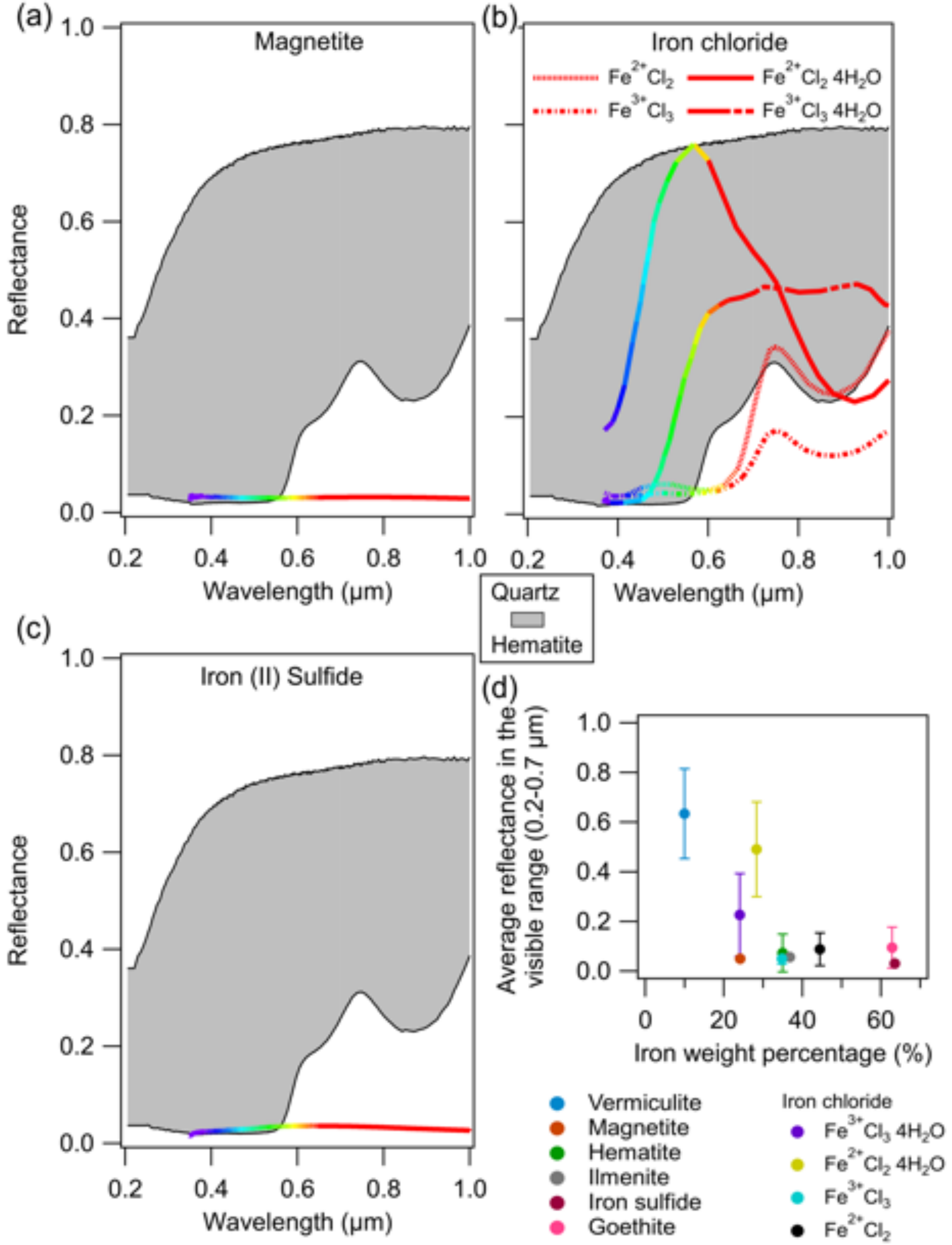
- Non-linear response below 130 Tg Cl/yr.
- Different model (GEOS-Chem) showed this increase.

	Standard	MCBlow	MCBhigh
Total, yr	8.54	8.77	9.01
Trop. OH, yr	10.15	10.55	10.95
Trop. Cl, yr	278	237	207

Table S2. Methane lifetime simulated in GEOS-Chem. The total lifetime also accounts for loss the stratosphere and soil (120 yr and 150 yr, respectively; Holmes, 2018).

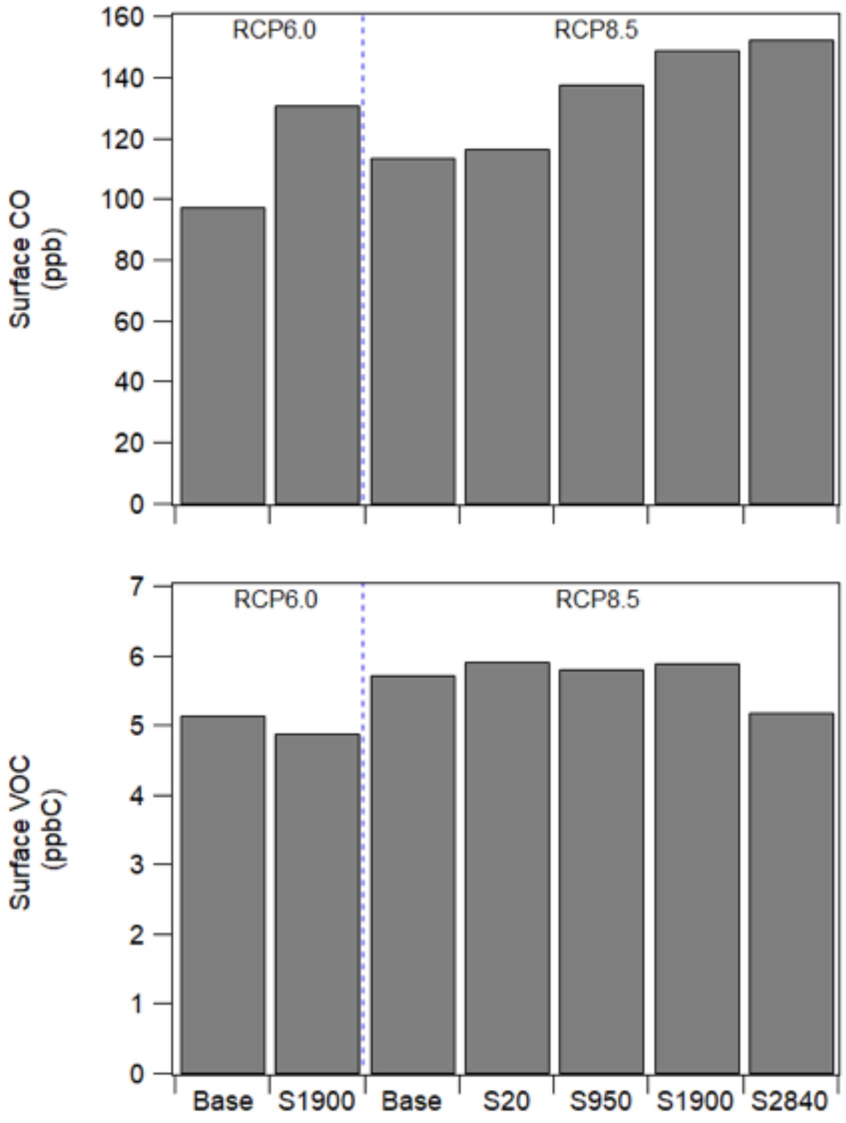


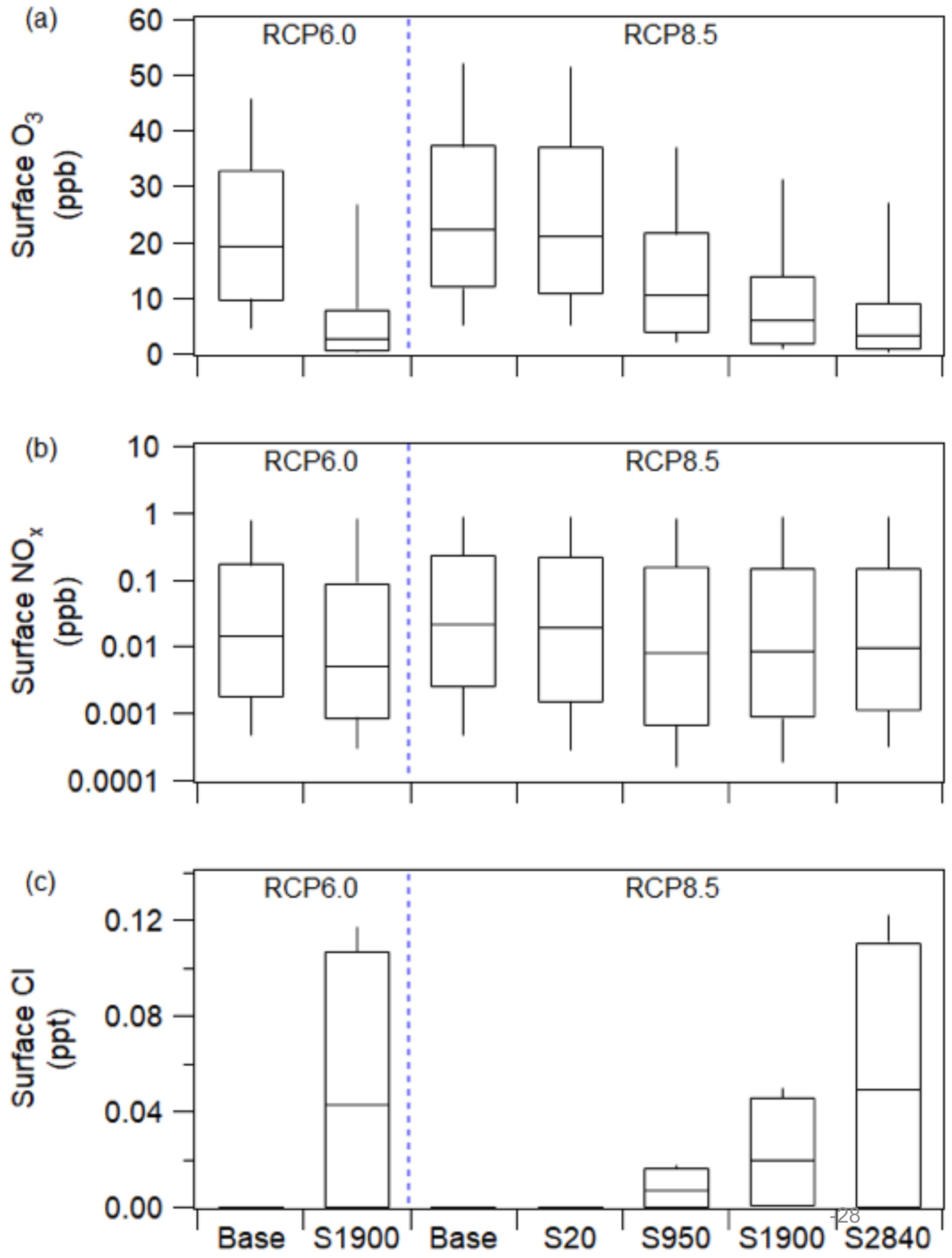
-Horowitz HM, Holmes C, Wright A, Sherwen T, Wang X, Evans M, Huang J, Jaeglé L, Chen Q, Zhai S, Alexander B. Effects of Sea Salt Aerosol Emissions for Marine Cloud Brightening on Atmospheric Chemistry: Implications for Radiative Forcing. Geophys Res Lett. doi: 10.1029/2019GL085838, 2020.



(a)
Magnetite
Reflectance
Wavelength (µm)
(b)
Iron chloride
Fe2+Cl2
Fe2+Cl2 4H2O
Fe3+Cl3
Fe3+Cl3 4H2O
Wavelength (µm)
Quartz
Hematite
(c)
Iron (II) Sulfide
Reflectance
Wavelength (µm)
(d)
Average reflectance in the visible range (0.2-0.7 µm)
Iron weight percentage (%)
Vermiculite
Magnetite
Hematite
Ilmenite
Iron sulfide
Goethite
Iron chloride
Fe3+Cl3 4H2O
Fe2+Cl2 4H2O
Fe3+Cl3
Fe2+Cl2

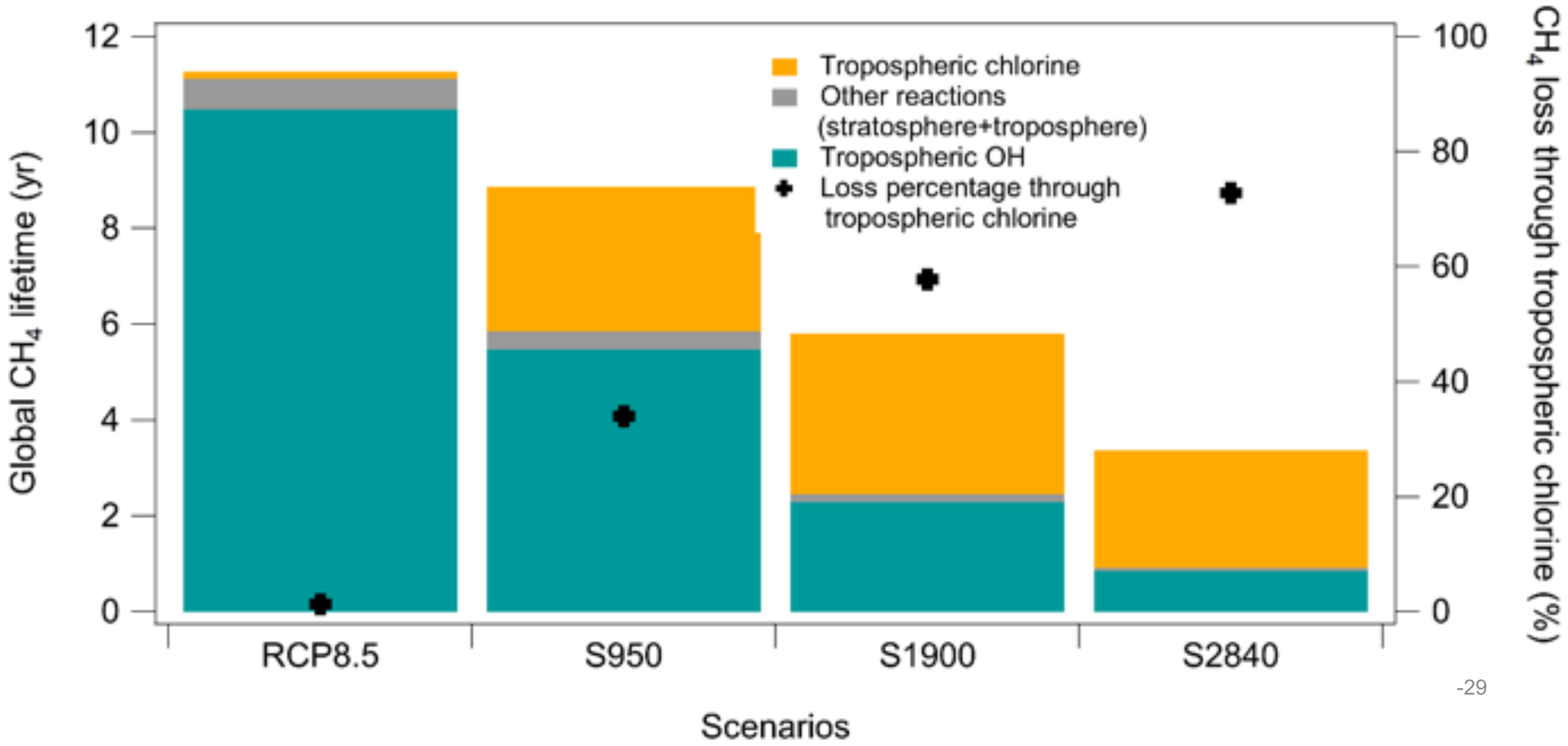
NOx, VOC and CO





Methane chemical loss

- Methane loss to chlorine increases, while loss through OH decreases.
- Methane lifetime decreases.



Cl reactivity – CH_4 or O_3