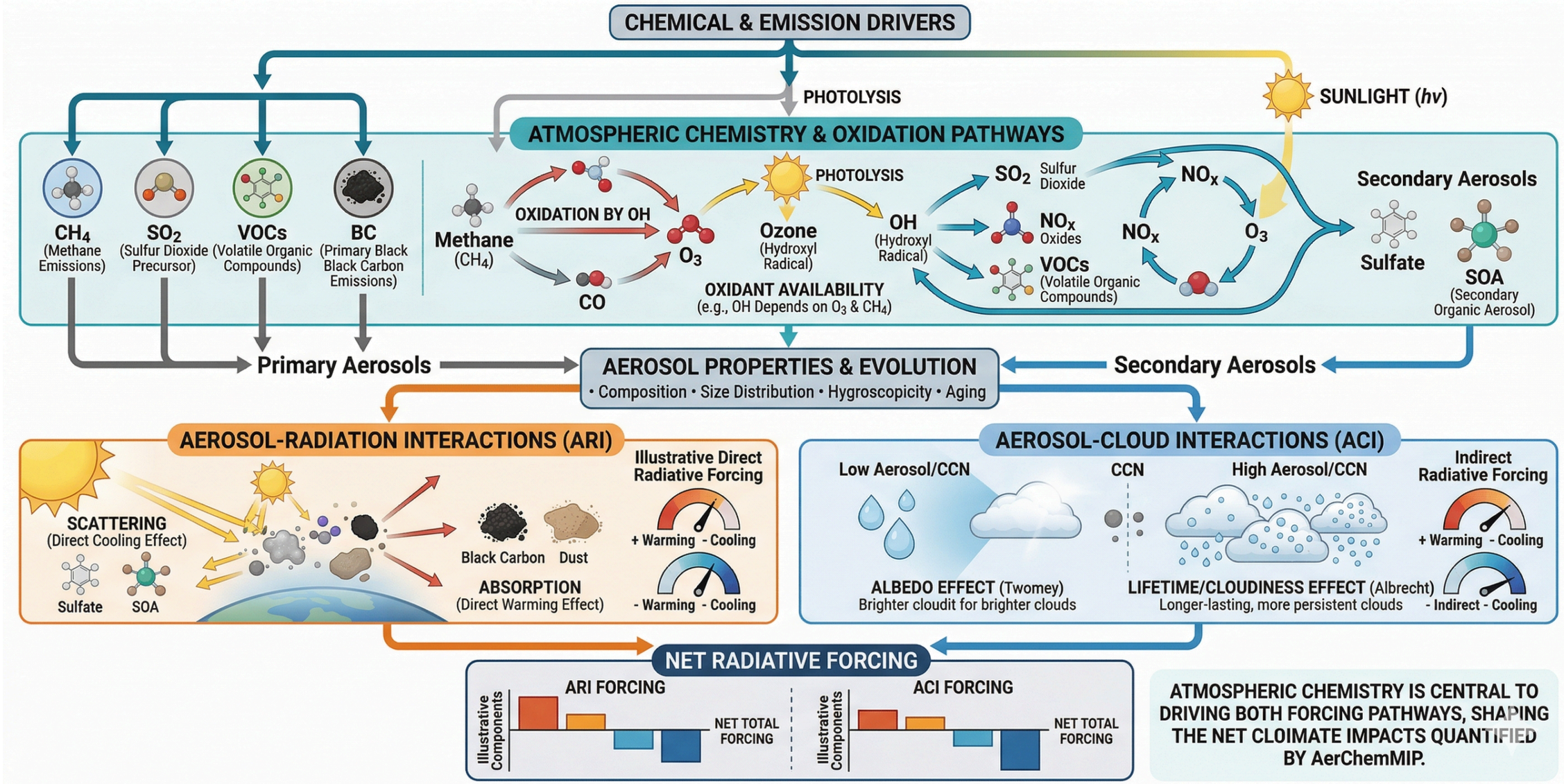


Chemistry-climate studies of short-lived climate forcing agents

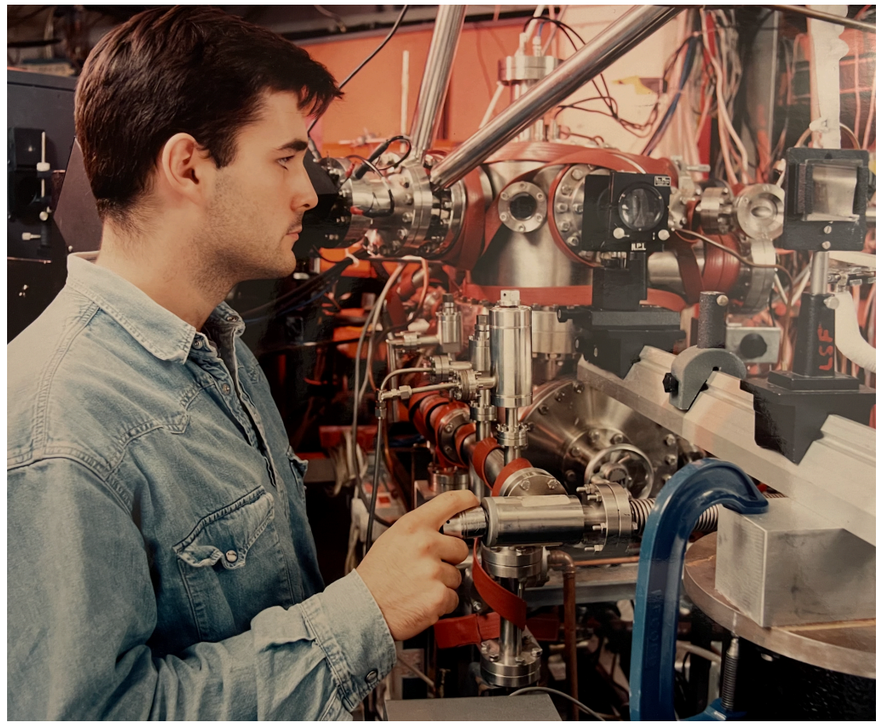
Paul Griffiths, School of Chemistry, University of Bristol

Introduction: The Chemical Engine of Climate Change

- **Beyond Direct Forcing:** Short-Lived Climate Forcers (SLCFs) act as the chemical engine of the climate system, exerting powerful indirect forcing.
- **The Atmospheric Detergent:** The Hydroxyl radical (OH) and tropospheric ozone (O3) regulate the atmosphere's oxidative capacity.
- **The Aerosol Link:** Small chemical shifts in this oxidative capacity dictate how trace gases are processed and how secondary aerosols are formed.
- **The Grand Challenge:** Bridging gas-phase chemistry and aerosol microphysics in Earth System Models (e.g., UKESM1) to capture fully-coupled climate forcing.

Hello. My name is Paul Griffiths

- Undergrad in chemistry; PhD in chemical physics. Post-doc in molecular dynamics/atom-molecule scattering.
- 2000-2009 Aerosol scientist, NCAS, Cambridge University.
- 2009-2012 Cloud modelling.
- 2012-2016 Atmospheric chemistry modelling, Cambridge.
- 2016 NCAS, Long-Term Climate Change Directorate.
- 2020 CMIP6 Contributing Author.
- 2021 Co-chair RMS Atmospheric Chemistry group.
- Since 2025 Lecturer, University of Bristol.
- **Interests:** modelling tropospheric composition, impacts of climate change, model development and assessment.
- **Recent work:** impact of ozone recovery on tropospheric oxidizing capacity; role of methane in climate change; data-driven science (tropospheric oxidants); role of atmospheric chemistry in radiative forcing.





PNAS

The Copenhagen Accord for limiting global warming: Criteria, constraints, and available avenues

Veerabhadran Ramanathan[1] and Yangyang Xu
The Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093

Edited by William C. Clark, Harvard University, Cambridge, MA, and approved March 26, 2010 (received for review February 22, 2010)

At last, all the major emitters of greenhouse gases (GHGs) have agreed under the Copenhagen Accord that global average temperature increase should be kept below 2 °C. This study develops the criteria for limiting the warming below 2 °C, identifies the constraints imposed on policy makers, and explores available mitigation avenues. One important criterion is that the radiant energy added by human activities should not exceed 2.5 (range: 1.7–4) watts per square meter (Wm^{-2}) of the Earth's surface. The blanket of man-made GHGs has already added 3 (range: 2.6–3.5) Wm^{-2}. Even if GHG emissions peak in 2015, the radiant energy barrier will be exceeded by 100%, requiring simultaneous pursuit of three avenues: (*i*) reduce the rate of thickening of the blanket by stabilizing CO_2 concentration below 441 ppm during this century (a massive decarbonization of the energy sector is necessary to accomplish this Herculean task), (*ii*) ensure that air pollution laws that reduce the masking effect of cooling aerosols be made radiant energy-neutral by reductions in black carbon and ozone, and (*iii*) thin the blanket by reducing emissions of short-lived GHGs. Methane and hydrofluorocarbons emerge as the prime targets. These actions, even if we are restricted to available technologies for avenues *ii* and *iii*, can reduce the probability of exceeding the 2 °C barrier before 2050 to less than 10%, and before 2100 to less than 50%. With such actions, the four decades we have until 2050 should be exploited to develop and scale-up revolutionary technologies to restrict the warming to less than 1.5 °C.

Ramanathan and Xu, PNAS, 2010

Short-lived climate forcers

- SLCFs can be classified as **direct** or **indirect**, with direct SLCFs exerting climate effects through their radiative forcing and indirect SLCFs being precursors of direct climate forcers.
- Direct SLCFs include methane (CH4), ozone (O3), short-lived halogenated compounds, and aerosols.
- Indirect SLCFs include nitrogen oxides (NOx), carbon monoxide (CO), nonmethane volatile organic compounds (NMVOCs), sulphur dioxide (SO2) and ammonia (NH3).
- The radiative forcing effects of most SLCFs are
  - **largest at regional scales**
  - **predominantly occur in the first two decades** after their emissions or formation.
- However, changes in their emissions can also induce long-term climate effects, for instance by altering some biogeochemical cycles.



AerChemMIP: attribution by species

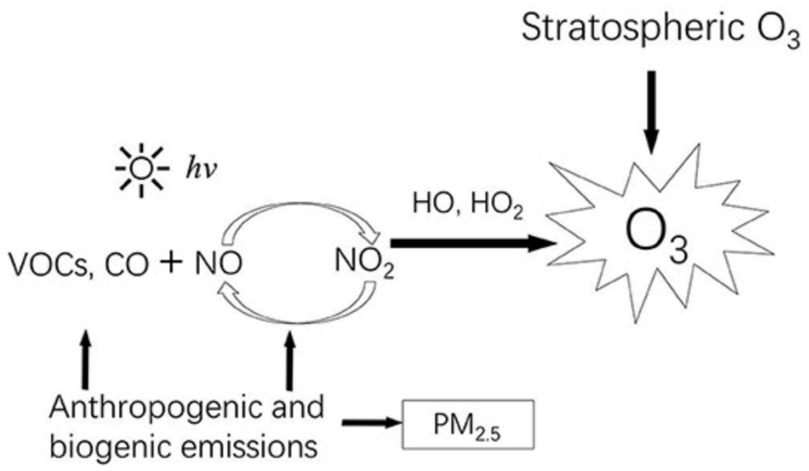
- AerChemMIP is the CMIP6 aerosol and chemistry model intercomparison project
- Uses **prescribed SSTs** (histSST) to isolate atmospheric chemistry effects from ocean feedbacks
- Each experiment fixes one SLCF species group at **1850 pre-industrial levels** while all others evolve historically
- Comparing a run to histSST isolates the **contribution of that species** to historical forcing
- Enables attribution of ERF, ozone change, and oxidant shifts to individual emitted species

Collins et al., Geosci. Model Dev., 2017

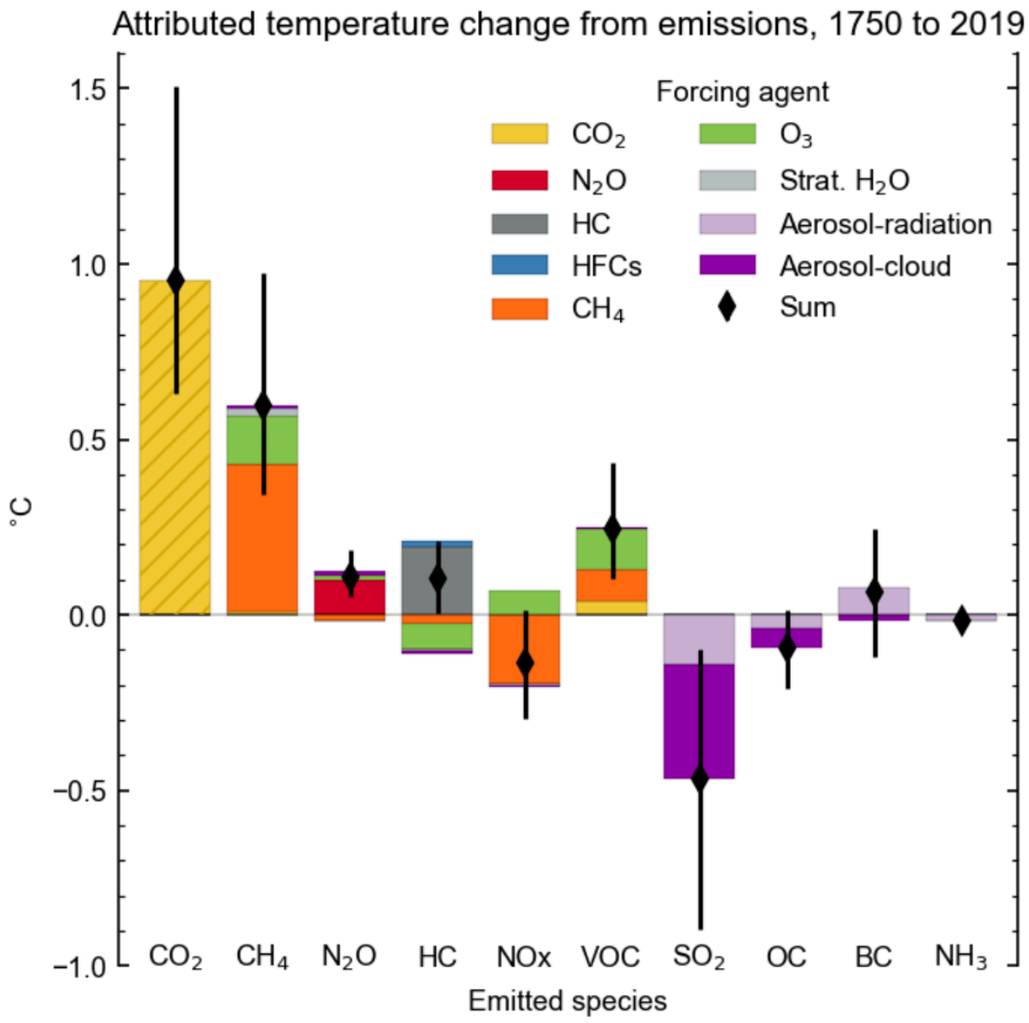
Experiment	CH4	N2O	Aerosol precursors	O3 precursors	ODS
histSST	Hist	Hist	Hist	Hist	Hist
histSST-piCH4	**1850**	Hist	Hist	Hist	Hist
histSST-piO3	Hist	Hist	Hist	**1850**	Hist
histSST-piAer	Hist	Hist	**1850**	Hist	Hist
histSST-piNTCF	**1850**	Hist	**1850**	**1850**	Hist

Ozone in the troposphere

- Ozone is interesting to a chemist because it's not emitted directly, but is formed in the atmosphere via atmospheric chemistry processes
- Also need to include dynamical transport of ozone into the stratosphere (STE)
- Ozone precursors are from anthropogenic and biogenic sources: both hydrocarbons and NOx
- Sunlight/humidity/temperature are all important to ozone formation
- **Ozone deposition at the surface** to vegetation - connection to land cover

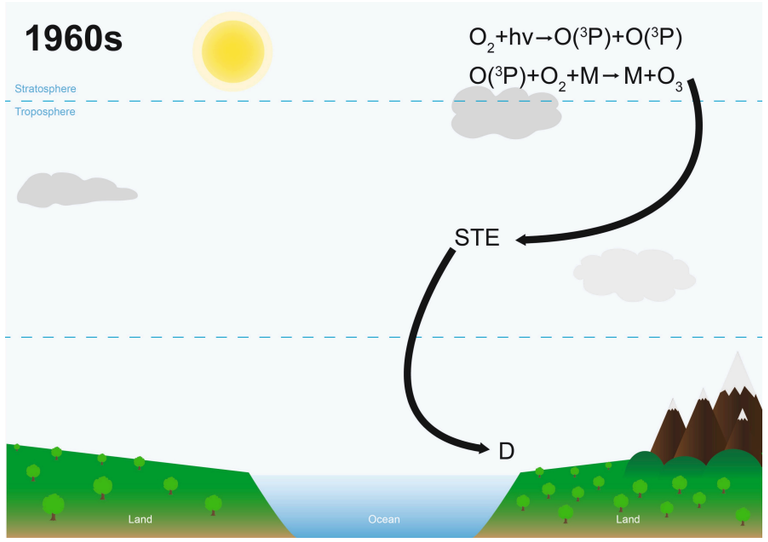


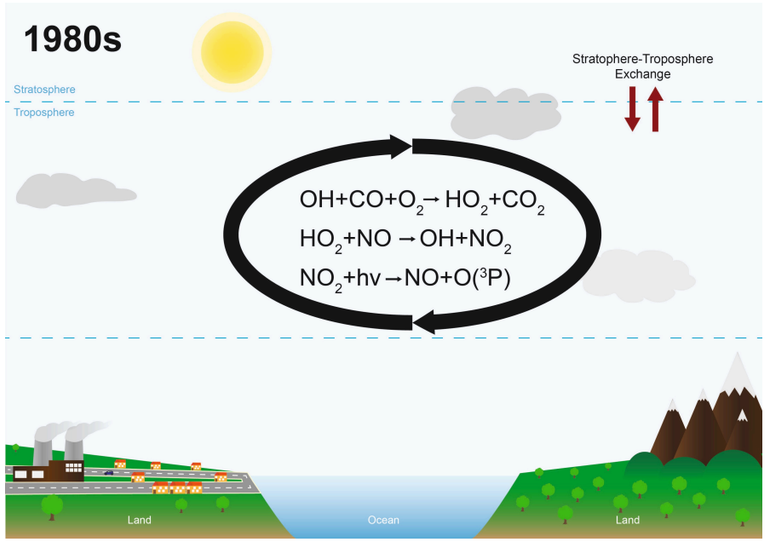
IPCC AR6: ozone as a short-lived climate forcer



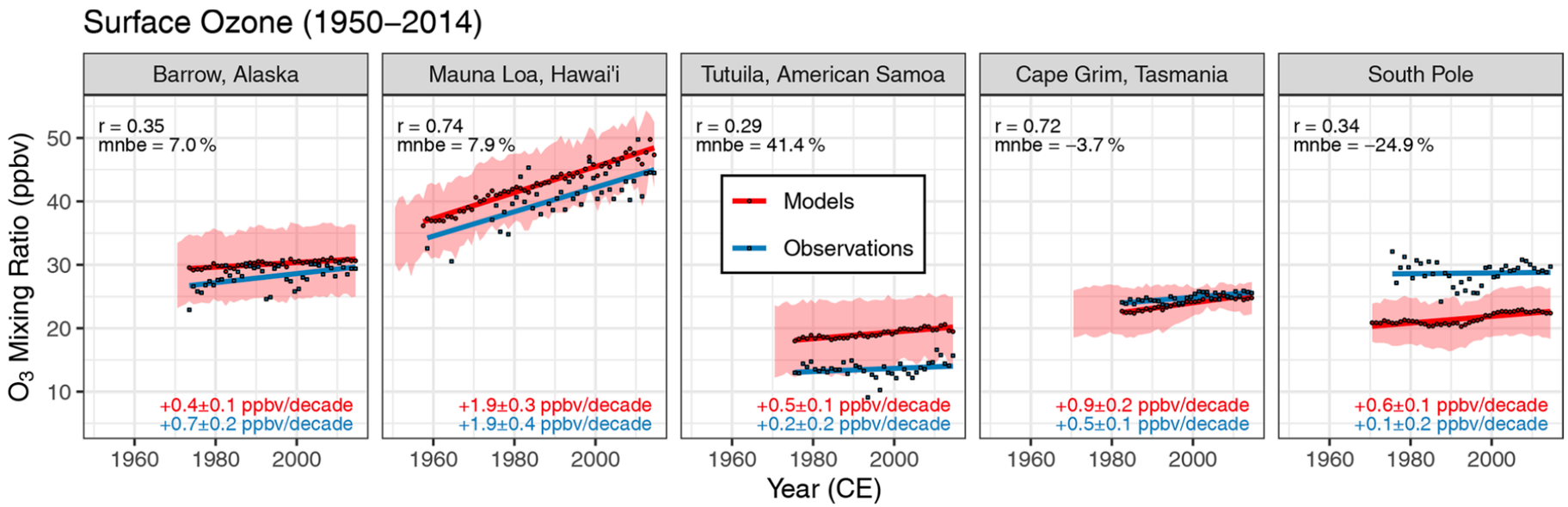
- CMIP6 produced an attribution of temperature change by species
- Also breaks down anthropogenic emissions by impact
- Positive forcing (warming) and negative forcing (cooling) are found
- Some large error bars!

Ozone in CCMs: developing complexity



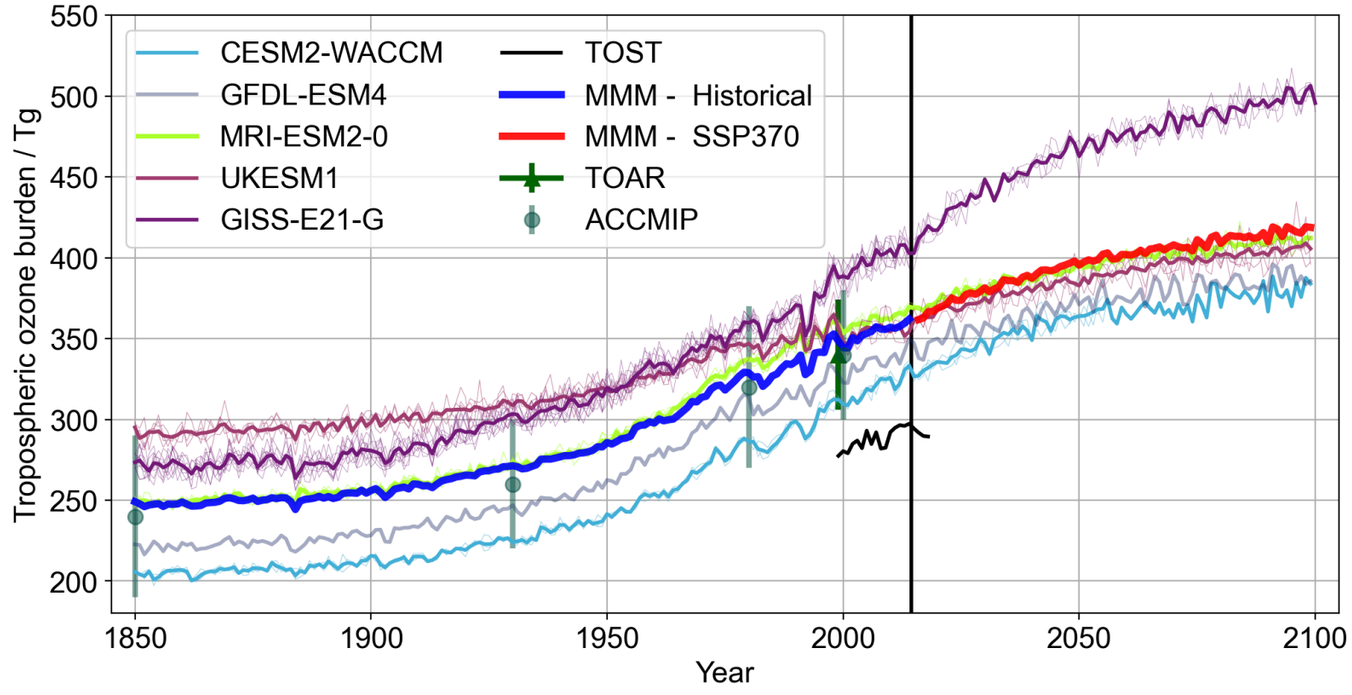


How does tropospheric ozone evolve in CMIP6? Comparison with obs



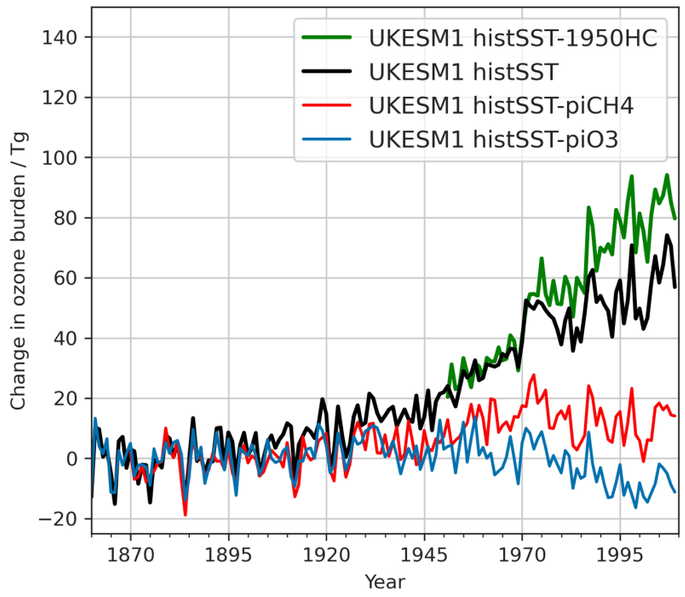
- CMIP6 featured coupled atmosphere-ocean models with online, whole-atmosphere chemistry
- **Good agreement between models and observations for the remote sites studied here**
- Also found nice agreement between in-situ ozone sonde measurements
- Assessment using EO products more of a challenge - tropopause definition?
- Consistent model biases in simulating the seasonality of free-tropospheric ozone in equatorial America, Japan and northern high latitudes and near-surface ozone over northern and north-eastern Europe

How does tropospheric ozone evolve in CMIP6?

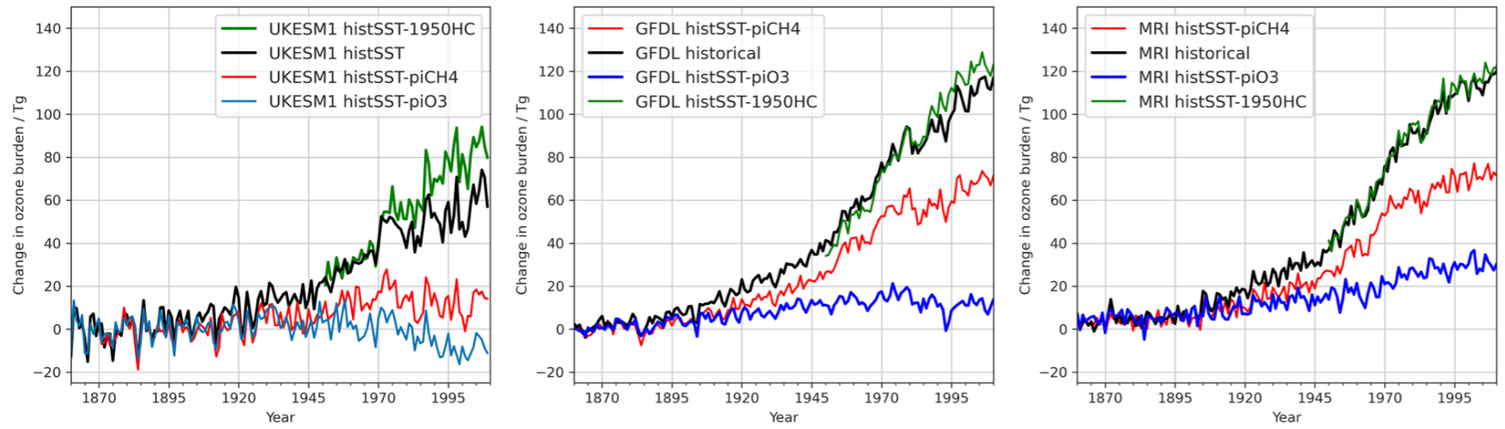


- CMIP Historical and ScenarioMIP SSP3-70 experiments, for which suitable diagnostic output was available
- Picture has changed little since CMIP5/CCMI, MM range is also similar
- Ozone burden increased by about 40% from 1850 levels of 240 Tg (MMM) with steepest rate of increase around 1960
- In SSP3-70, the rate of growth of the burden declines further, as NOx emissions start to fall along this pathway after 2050

Methane is important to tropospheric ozone - AerChemMIP



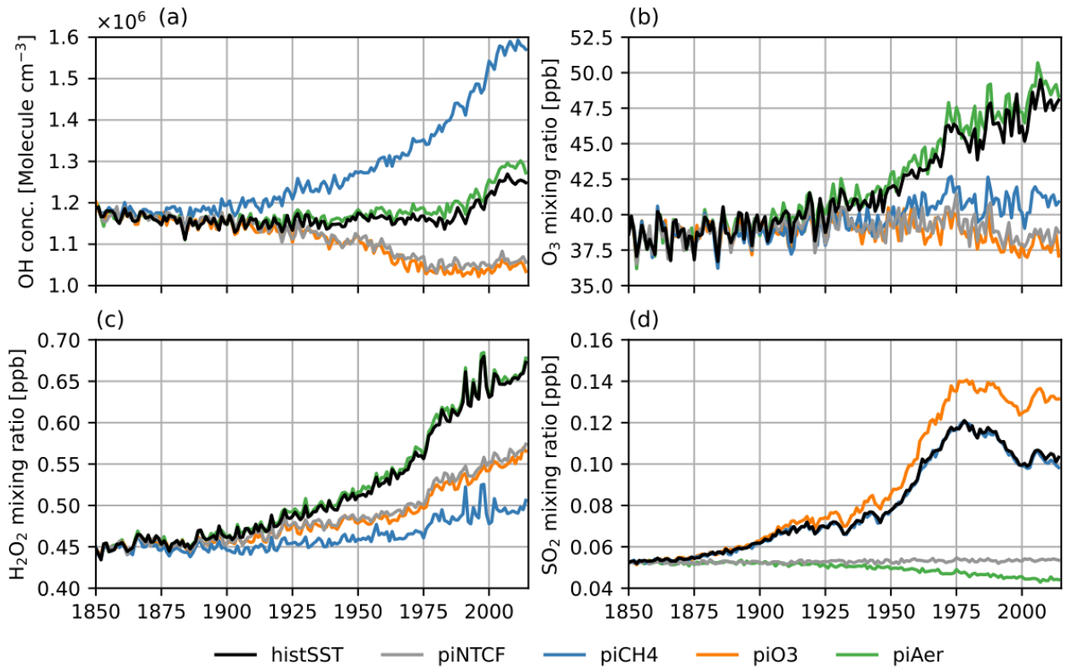
Experiment_ID	CH4	N2O	AERPRE	O3PRE	CFC/HCFC
histSST	Hist	Hist	Hist	Hist	Hist
histSST-piAer	Hist	Hist	1850	Hist	Hist
histSST-piO3	Hist	Hist	Hist	1850	Hist
histSST-piCH4	1850	Hist	Hist	Hist	Hist



Effect of historical methane and ODS emissions on tropospheric ozone burden across UKESM1, GFDL, and MRI models

The other side of SLCFs: gas-phase species impact aerosol and climate

- Sulfate aerosol forms via oxidation of SO2 by **OH** (gas phase) and **H2O2, O3** (aqueous phase)
- Gas-phase oxidation (SO2 + OH) nucleates **new particles**
- Aqueous-phase oxidation grows **existing particles** without creating new ones
- Historical CH4 and O3 precursor emissions have changed the oxidant mix -- what does this do to aerosol?



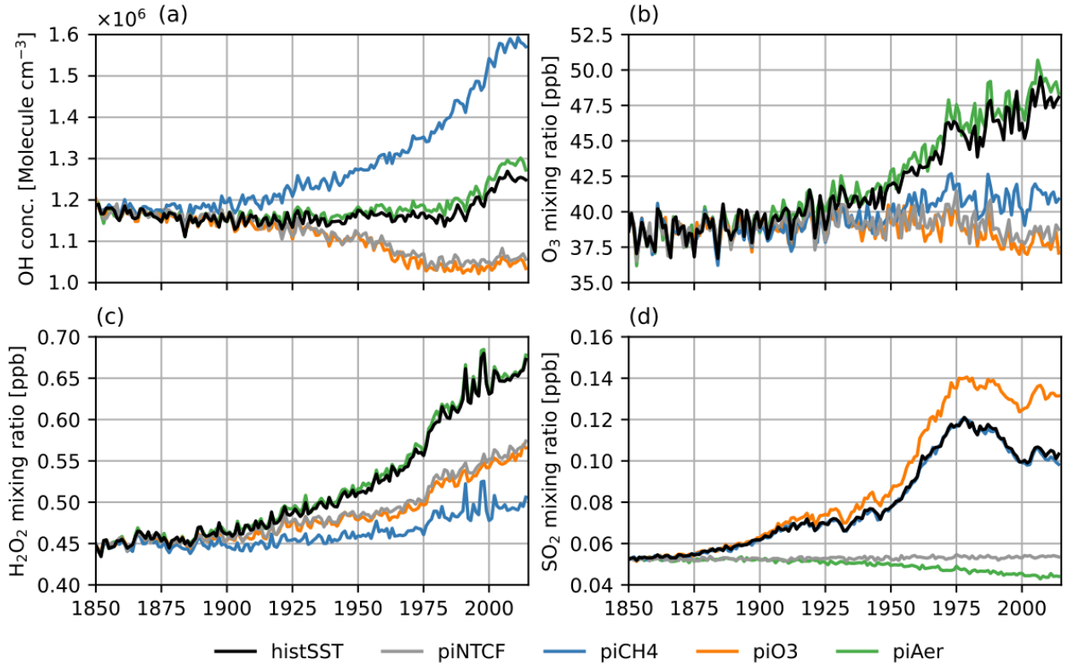
Griffiths, PhD thesis Ch. 3; uses UKESM1 AerChemMIP histSST experiments 1850-2014

Historical OH: CH4 suppresses OH; O3 precursors enhance it

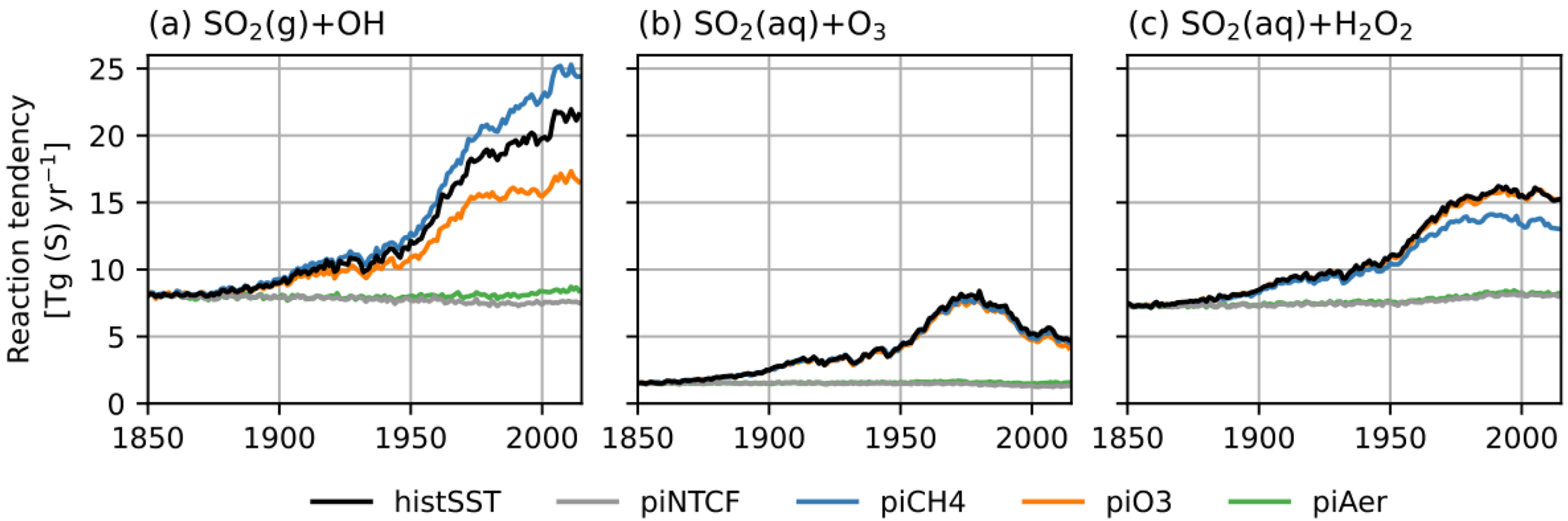
WHAT HAPPENS TO ATMOSPHERIC OXIDISING CAPACITY

- **Historical CH4 rise depletes OH by 28%** relative to a fixed-CH4 world (piCH4)
- **O3 precursor emissions (NOx, CO) increase OH by 15%** via its production from O3 photolysis producing O(1D) + H2O
- These opposing forces appear to roughly cancel, keeping OH stable until ~1980
- CH4 also boosts **H2O2** (via HO2); O3 precursors boost O3

Both OH and H2O2 matter for aqueous-phase SO2 oxidation



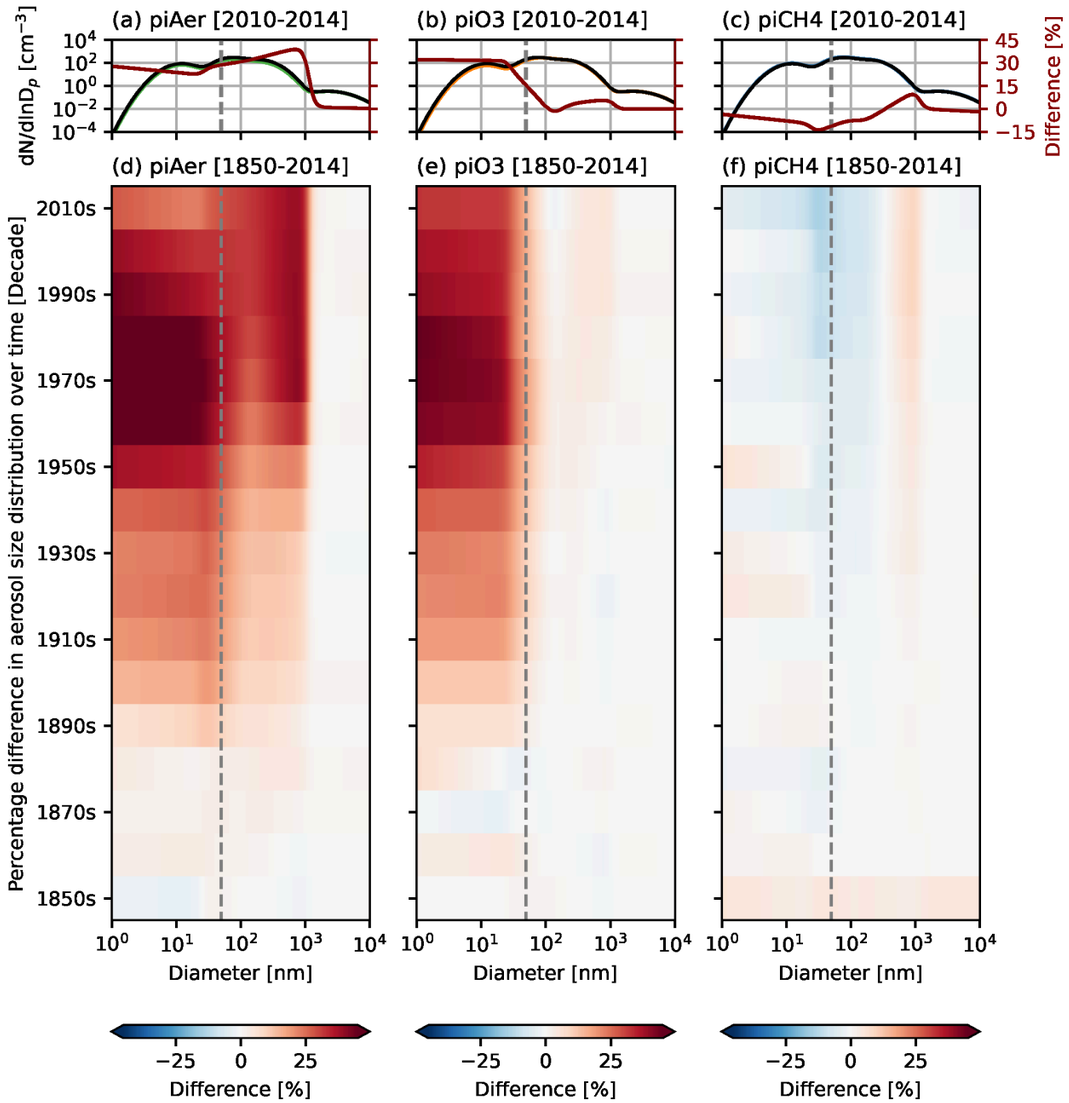
SO2 oxidation shifts between gas and aqueous pathways



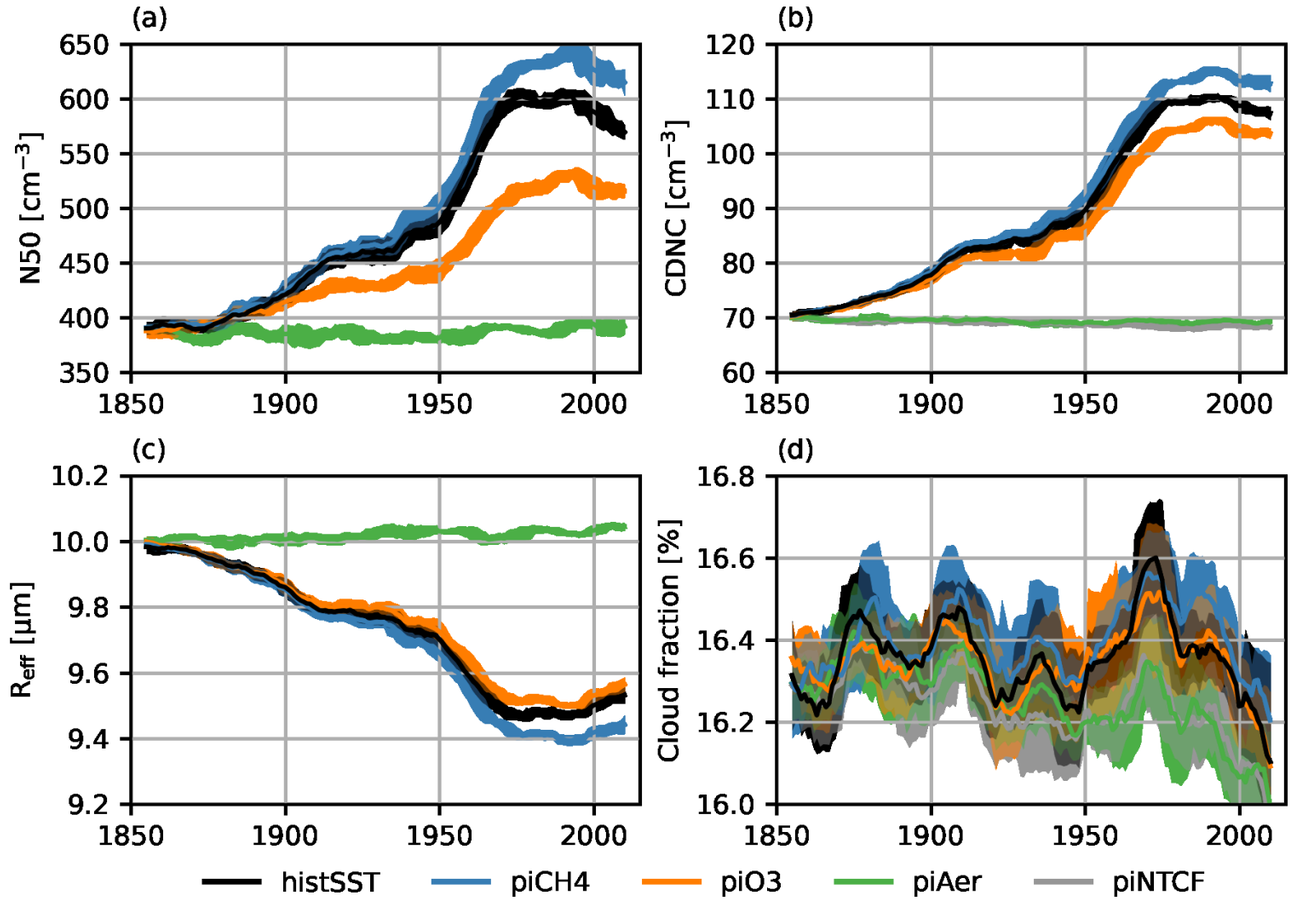
- Global SO2 oxidation tendencies 1850-2014.
- O3 precursors enhance SO2+OH by ~5 Tg(S)/yr
- CH4 suppresses it by ~4 Tg(S)/yr but increases SO2+H2O2 by 2.5 Tg(S)/yr

The consequence: aerosol size distribution shifts

- O3 precursors increase SO2+OH, nucleating **more small particles** (diameter < 50 nm)
- CH4 suppresses SO2+OH but boosts aqueous-phase oxidation, which **grows existing particles** rather than making new ones
- Result: CH4 produces **fewer but larger** aerosol particles
- The N50 population (CCN-relevant, > 50 nm) drops by **8-10%** due to historical CH4

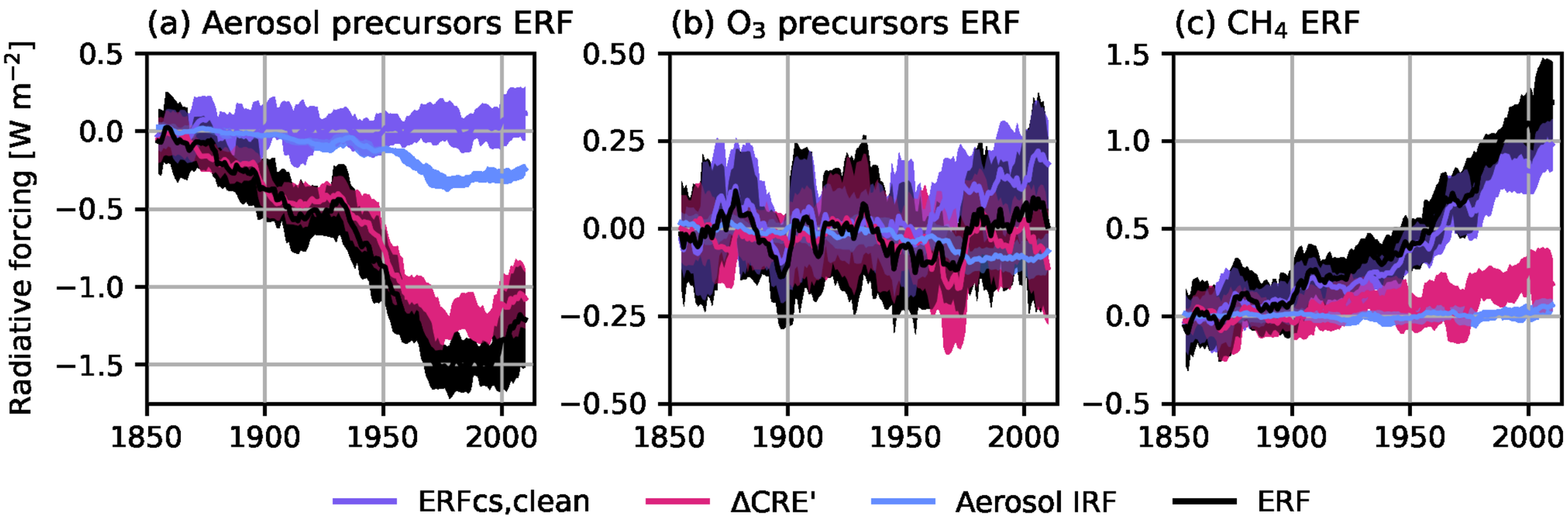


Cloud properties respond to the oxidant-driven aerosol shift



- N50, CDNC, Reff, and cloud fraction 1850-2014.
- CH4 reduces CDNC by ~5% and increases droplet radius
- O3 precursors add ~4% to CDNC

ERF decomposition: CH4 warms through clouds, O3 precursors cool through aerosol



- CH4 contributes a **positive cloud radiative effect** of 0.21 +/- 0.15 W/m2 (2000-2014) on top of its direct GHG forcing
- This is an indirect warming from fewer CCN, less reflective clouds
- O3 precursors increase aerosol IRF by **-0.08 +/- 0.05 W/m2**, which is 44% of the total aerosol direct effect
- Aerosol ERF depends on the oxidant state of the atmosphere -- it is not just about SO2 emissions

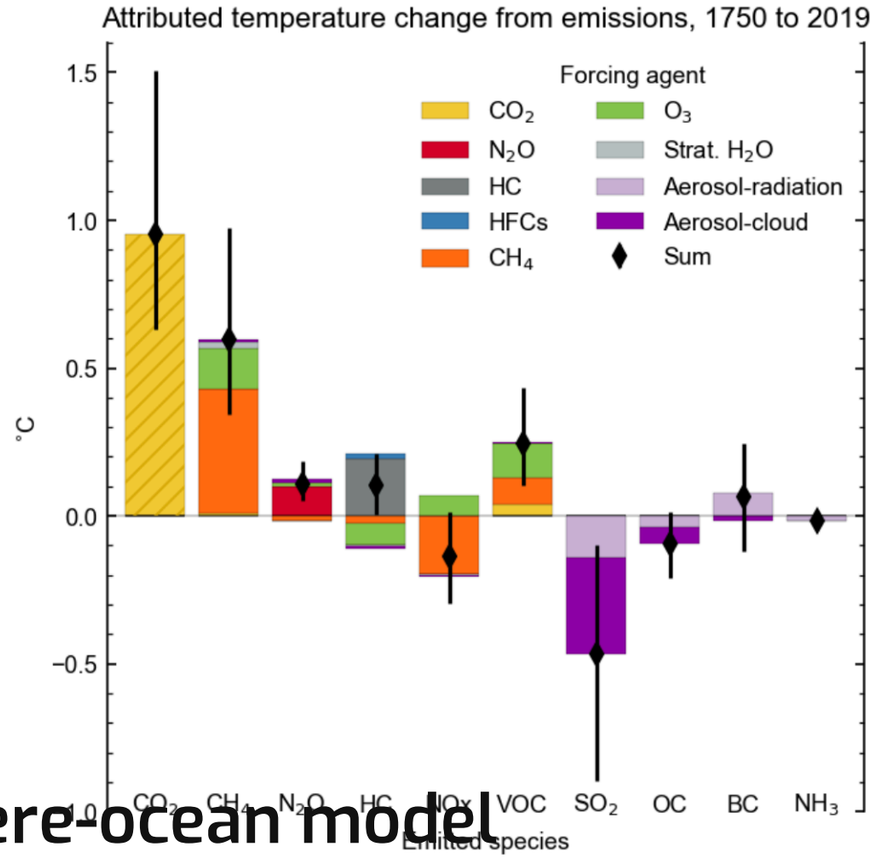
Key message: oxidants are the connective tissue

- Gas-phase chemistry (CH4, NOx, CO) controls the **oxidant budget** that in turn controls aerosol formation
- CH4 warming is amplified beyond its direct GHG effect: fewer CCN, less reflective clouds
- O3 precursors provide an additional cooling via enhanced aerosol nucleation
- Implication: ERF calculations that ignore oxidant coupling **misattribute forcing** between species
- This matters for policy: cutting CH4 delivers a **double benefit** (less GHG warming + restored aerosol cooling)

The role of methane and oxidants in climate

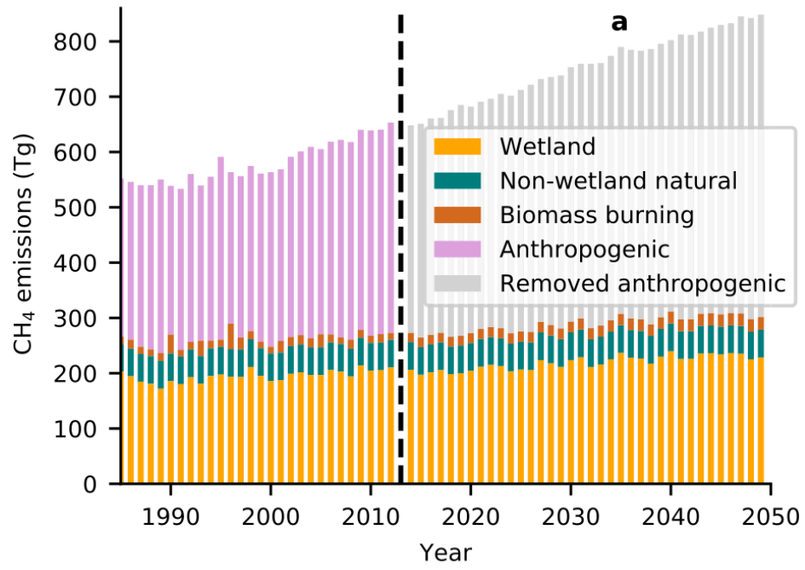
- CMIP6 attributed the radiative forcing and temperature change to various chemical species.

- **Methane provides the second largest anthropogenic climate driver.**
- It's a greenhouse gas, but is also an **ozone precursor** and has a role in **cloud radiative properties** (UKESM1).
- Modelling these gases and aerosols is a challenge. Lifetimes variable: CH4 ~10 years, ozone ~30 days, aerosol ~weeks, NOx ~days.
- Heterogeneous sources and sinks



Methane emissions in a fully coupled atmosphere-ocean model

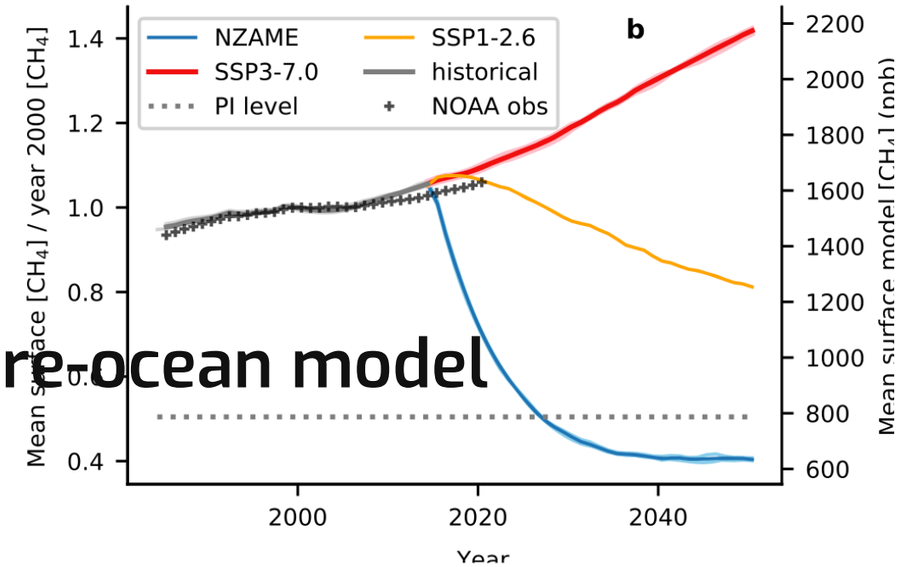
- Switch between SSP370, SSP126 and **Net-Zero Anthropogenic Emissions**
- To answer : What are the risks of methane emissions?
- And: What are the benefits of constraining future methane emissions?
- Anthropogenic emissions represent a rising sector of emissions

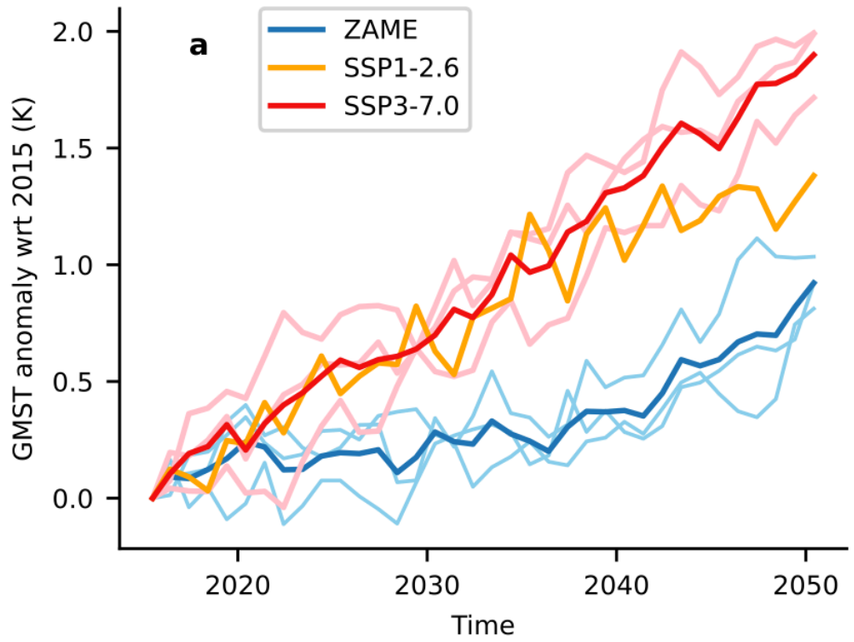


- Zeroing out anthropogenic emissions reduces CH4 emissions from >800 Tg per year down to ~300 Tg per year

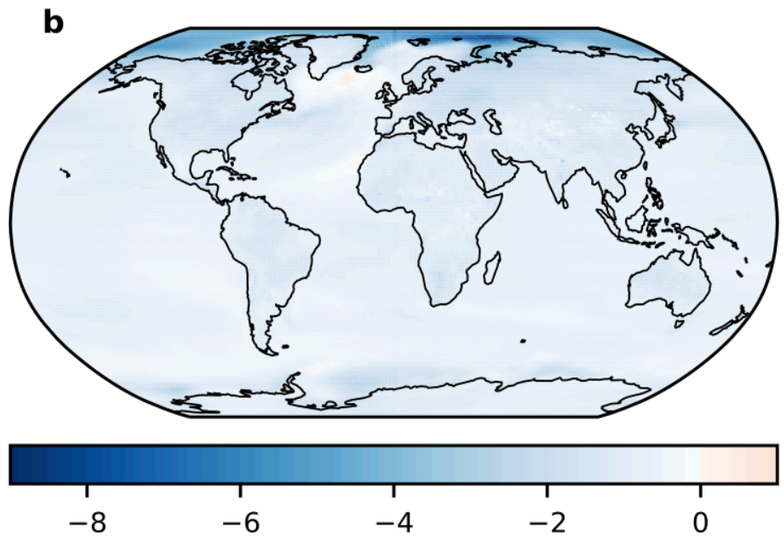
Methane emissions in a fully coupled atmosphere-ocean model

EXPERIMENT DESIGN

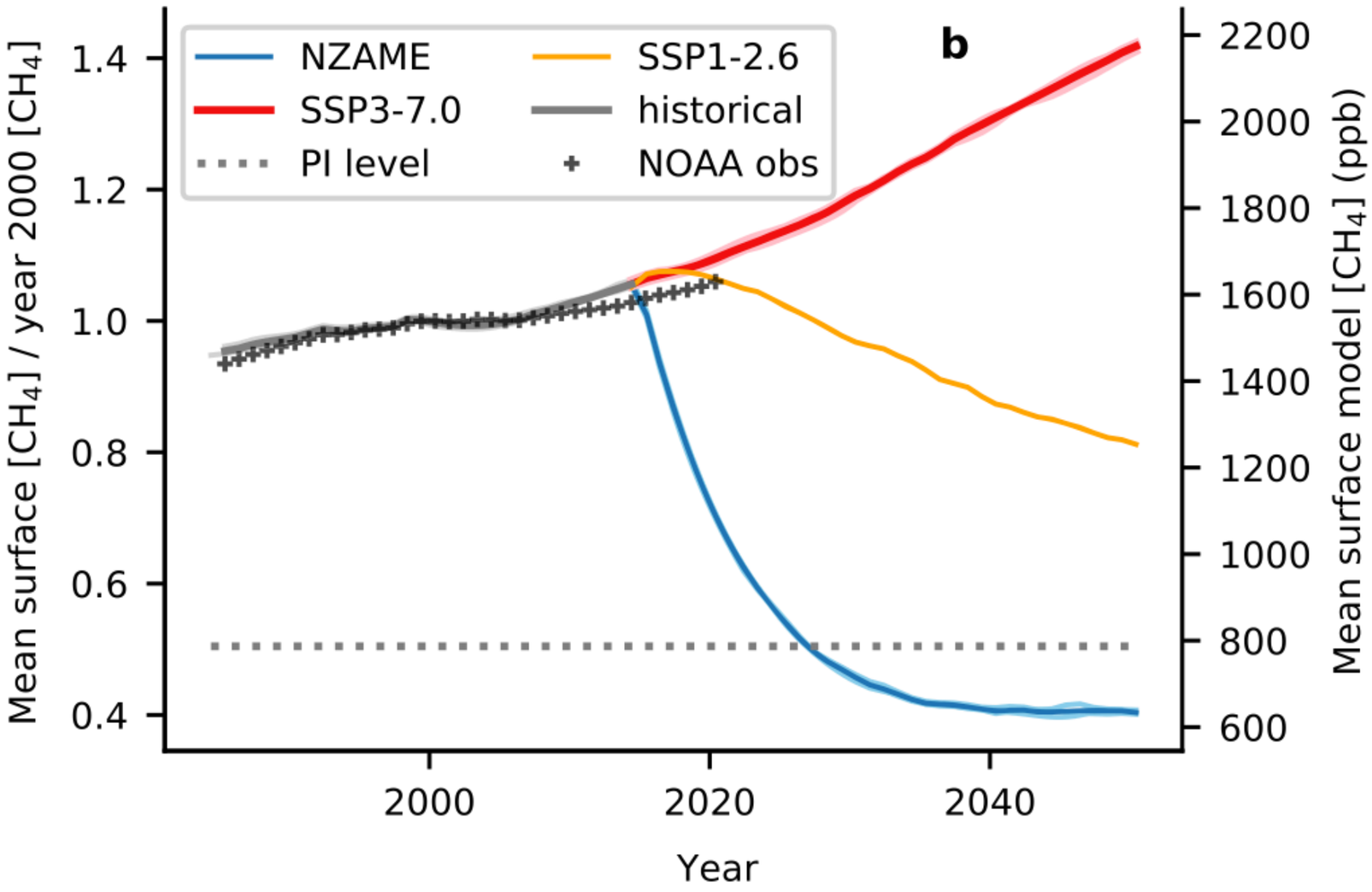


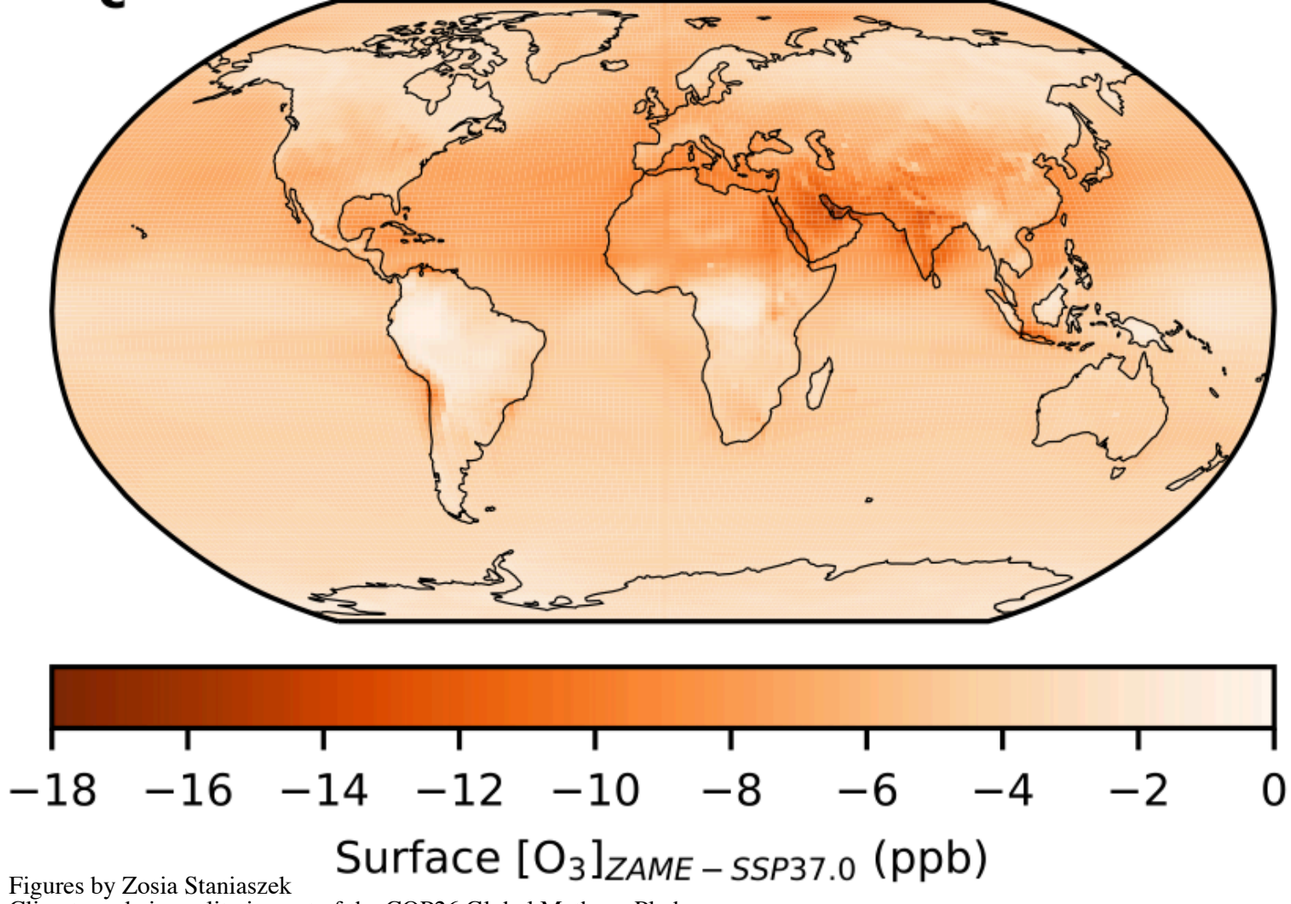


- Switch between SSP370, SSP126 and **Net-Zero Anthropogenic Emissions**
- To answer : What are the risks of methane emissions?
- And: What are the benefits of constraining future methane emissions?
- GMST is reduced compared to SSP370 by 0.5 degrees C globally
- Some strong regional impacts, e.g. Arctic warming is reduced and may even cool



- Comparison with SSP3-7.0 (regional rivalry) and SSP1-2.6 (sustainability) as a counterfactual
- Methane is a GHG, but is also an precursor to ozone
- Lower methane emissions -> less ozone at the surface (a co-benefit!)
- NZAME scenario results in lower ozone levels
- Weighting the ozone field by human exposure shows ~10% decline in ozone at surface
- Projected decrease in AQ-related mortality of the order of 500k per year

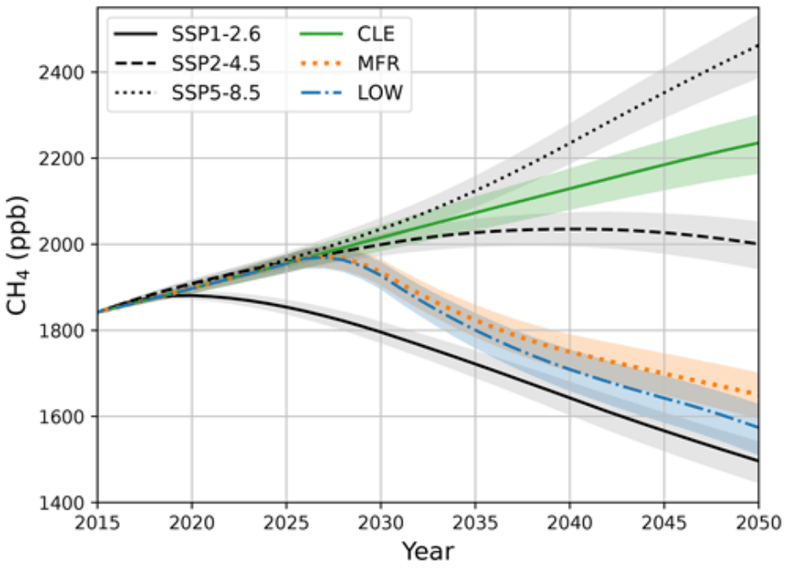

b
NZAME
SSP1-2.6
SSP3-7.0
historical
PI level
NOAA obs
Mean surface [CH4] / year 2000 [CH4]
Mean surface model [CH4] (ppb)
1.4
1.2
1.0
0.8
0.6
0.4
2200
2000
1800
1600
1400
1200
1000
800
600
2000
2020
2040
Year



Figures by Zosia Staniaszek

Climate and air quality impact of the COP26 Global Methane Pledge

- The GMP proposes a 30% reduction in methane emissions from 2020 levels be achieved by 2030.
- What would be the co-benefit? Impact on O3?
- Using our methane-emissions driven chemistry-climate model to look at the radiative forcing changes, focusing on methane and air quality interactions.
- Data coming SOON !


SSP1-2.6
SSP2-4.5
SSP5-8.5
CLE
MFR
LOW
2400
2200
2000
1800
1600
1400
CH_4 (ppb)
2015
2020
2025
2030
2035
2040
2045
2050
Year

COP30: World is falling behind on crucial methane emissions cuts, new report warns



Takeaways

- Future methane emissions affect air quality and climate. SSP370 strong response.
- Methane chemical feedbacks affect methane lifetime and hence GWP

Acknowledgements

- Methane: Zosia Staniaszek (now at CICERO, Oslo), Alex Archibald, Cambridge University; Fiona O'Connor, Gerd Folberth, Nic Gedney, UK Met Office

Conclusions: Chemistry as the Connective Tissue

- The Connective Tissue: Atmospheric chemistry is the vital link between anthropogenic emissions and radiative forcing.
- The Oxidant-Aerosol Connection: Historical shifts in O3 precursors and CH4 have fundamentally modified the atmosphere's oxidative capacity.
- Controlling the Mask: This oxidative capacity directly controls the "cooling mask" of aerosol-cloud interactions.
- Amplifiers & Interventions: SLCFs act as rapid climate amplifiers. Interventions like the Global Methane Pledge offer powerful, yet chemically complex, levers for near-term climate action.

Acknowledgements

- Methane: Zosia Staniaszek (now at CICERO, Oslo), Alex Archibald, Cambridge University; Fiona O'Connor, Gerd Folberth, Nic Gedney, UK Met Office