Studies of the effect of stratospheric ozone depletion on tropospheric oxidising capacity over the period 1979-2010 using the UKCA Chemistry-Climate model

Paul Griffiths, James Keeble, Matthew Shin,
Alex Archibald, John Pyle

How did the oxidising capacity of the atmosphere change?

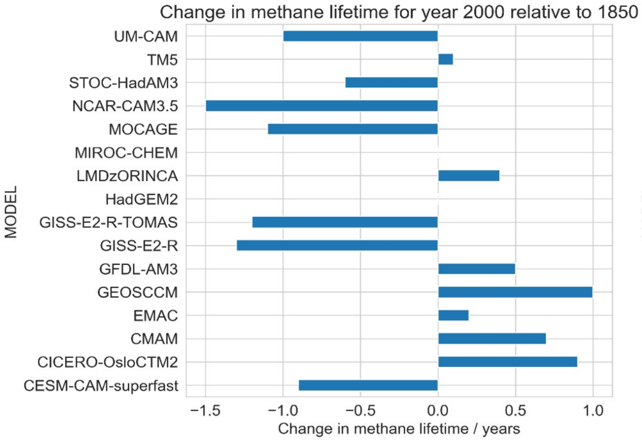
What was driving these changes?

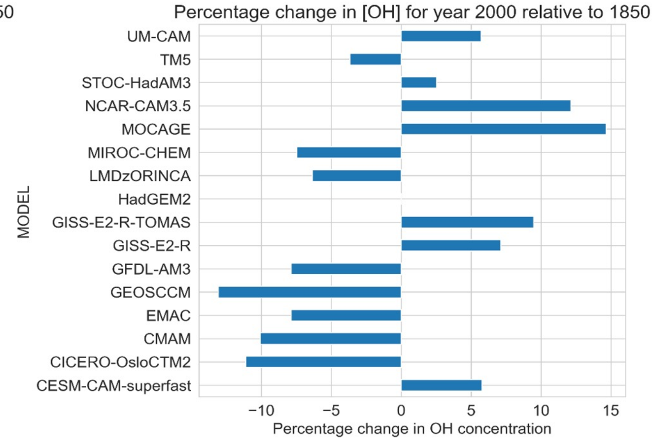
- Main oxidants - OH, NO_3, Cl, O_3 and H_2O_2 – under chemical control
- OH produced from O_3 via photolysis in near UV region
  - important for $SO_2 \rightarrow H_2SO_4$ oxidation, aerosol nucleation, CH_4 oxidation
- Ozone precursors - NO_x and VOCs - emissions changing. What is impact?
- Decreasing stratospheric O_3 burden from CFCs
  - decreases tropospheric ozone via reduced Strat-Trop Transport. What is impact?
- Episodic events affect OH and O_3 – how do these affect OH IAV, CH_4 trends?

OH trends and inter-annual variability - recent historical and also CMIP5

Author	Pub year	Period analysed	OH Trend/IAV	Comment
Prinn et al	1995	1978-1994	0.0 ± 0.2 % yr-1	Observation
Krol et al	1998	1978-19983	0.46 ± 0.6 % yr-1	drivers: O3S, CO, H2O, NOx
Karlsdottir and Isaksen	2000	1980-1996	0.43% yr	drivers: CO, NOx, VOC
Prinn et al	2001	1978-2000	-0.64 ± 0.60 % yr	Obs
Dentener et al	2003	1979-1993	0.24 ± 0.06 % yr	H2O inc
Wang et al	2004	1988-1997	0.64 % yr	Col O3 dec
Bousquet et al	2005	1979-2000	-0.7 ± 0.2 % yr-1	Inversion
Dalsoren and Isaksen	2006	1990-2001	0.08% yr	CO, NOX, NMVOC
Montzka	2011	1998-2007	IAV is 2.3 ± 1.5 %	MCF

John et al (2012)

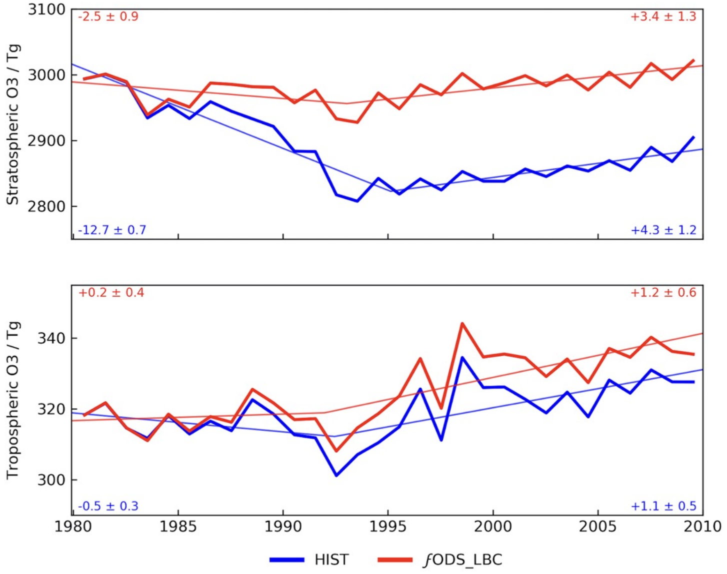


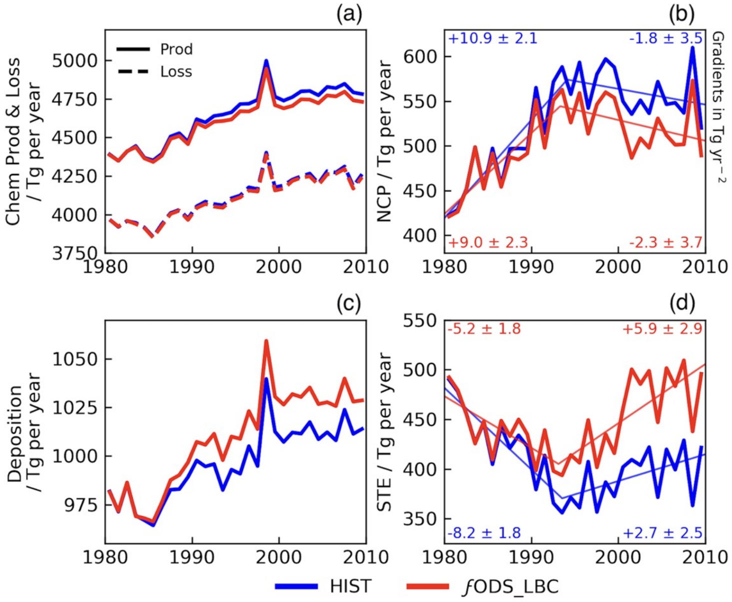


Naik et al. (2013)

What controls tropospheric ozone? Attribution studies 1979-2010

- Two experiments - HIST 1979-2009 with historical emissions (MACCity), meteorology (ERA-Interim)
- fODS_LBC - as for HIST but with ODS (LBC) held constant at 1979. Qu: What is effect of ODS on TropO3?

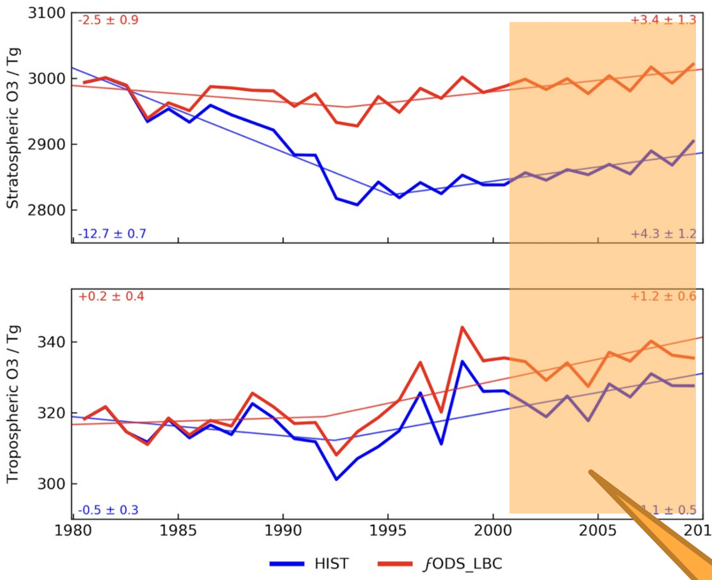




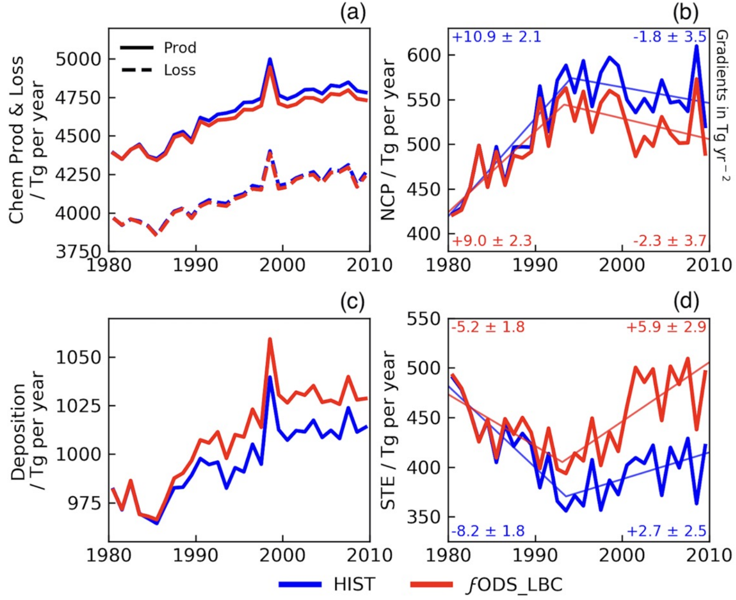
- Looking at
  - Ozone burden - decline and then recovery.
  - Ozone budget - chemical production - increases over period - chemical loss - ditto - deposition at surface - follows burden - and STE - declines and then begins to recover.

What controls tropospheric ozone? Attribution studies 1979-2010

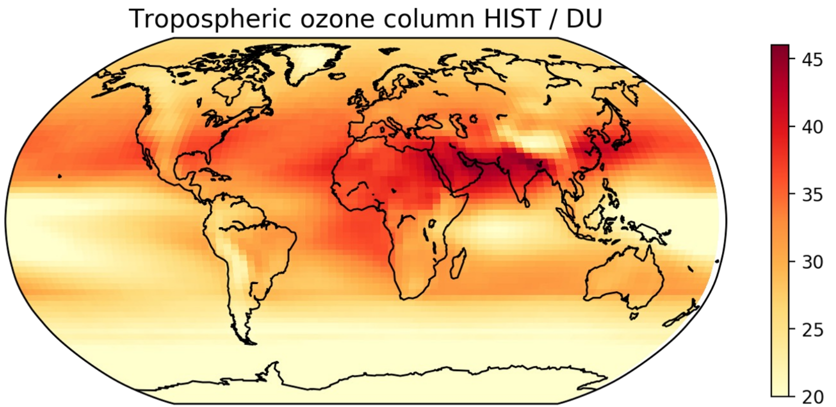
- Two experiments - HIST 1979-2009 with historical emissions (MACCity), meteorology (ERA-Interim)
- fODS_LBC - as for HIST but with ODS (LBC) held constant at 1979. Qu: What is effect of ODS on TropO3?

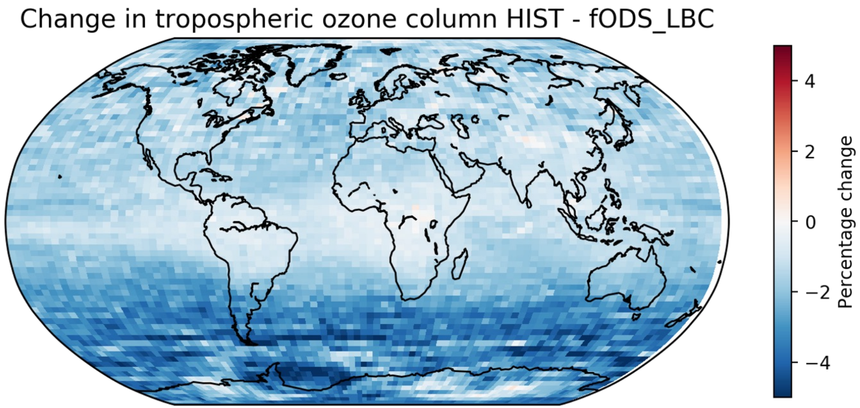


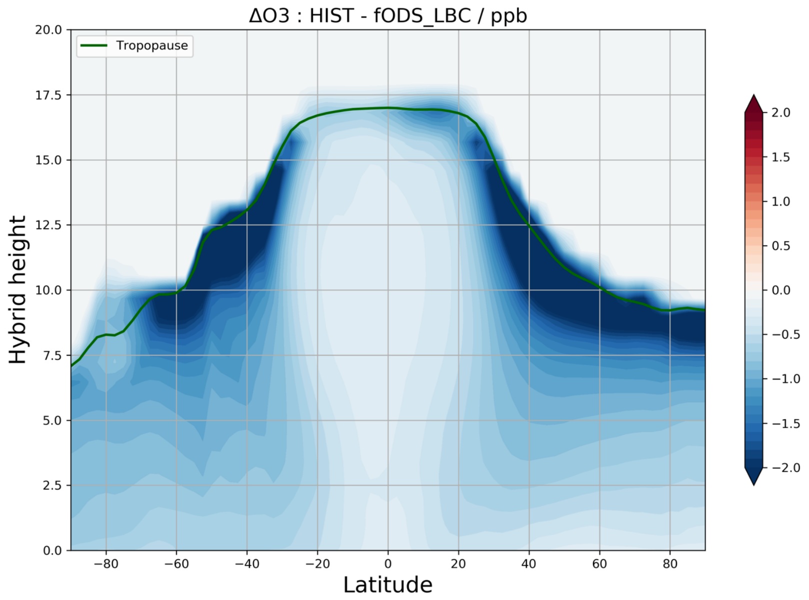
Focus of this paper



Where does O3 change? NB annual mean quantities







Small change in burden of 5 Tg in 300 Tg = 1.5%.

fODS_LBC has a higher burden, so HIST-fODS_LBC is negative

Similar changes in O3 column, noisy signal, largest in SH

Expanding this analysis - What about OH?

- How does OH concentration vary across between experiments?
- O3, the OH precursor, is lower in HIST, so what happens to OH?
- Global mean OH **higher** in HIST - change is in opposite sense to O3

$$[OH] \propto J_{O_3}\, q \frac{S_N}{S_C^{3/2}}$$

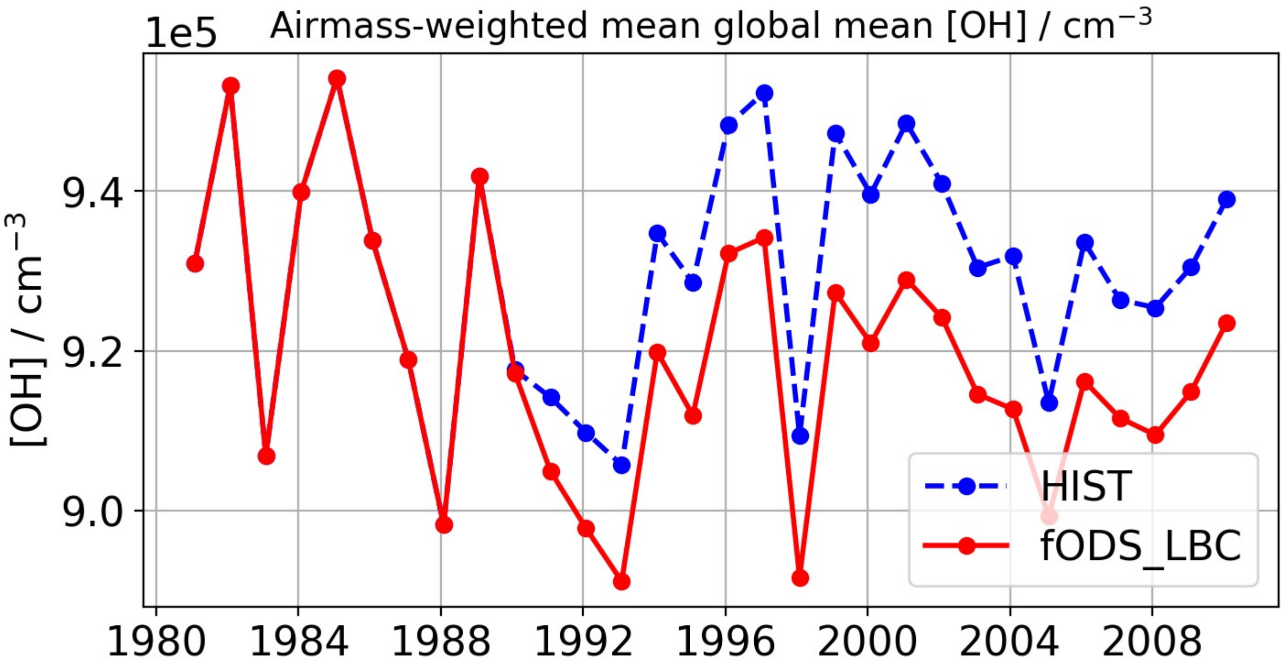
Airmass-weighted tropospheric mean

Ozone photolysis frequency (s^{-1})

Total NO_x source ($Tmol\ a^{-1}$)

Specific humidity (g/kg)

Total reactive carbon source ($Tmol\ a^{-1}$)



OH higher in HIST despite lower levels of ozone precursor

Expanding this analysis - What about OH?

- How does OH concentration vary across between experiments?
- O3, the OH precursor, is lower in HIST, so what happens to OH?
- Global mean OH **higher** in HIST - change is in opposite sense to O3

Airmass-weighted tropospheric mean

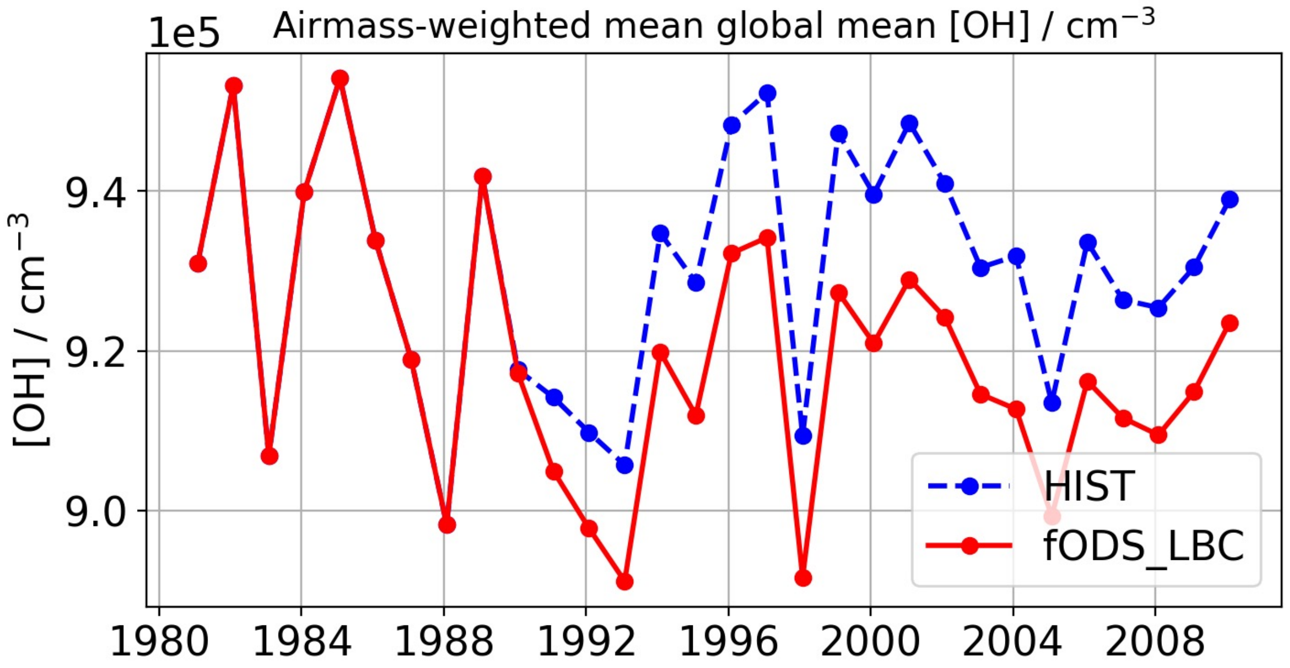
Ozone photolysis frequency (s^{-1})

Total NO_x source ($Tmol\ a^{-1}$)

$$[OH] \propto J_{O_3}\, q\, \frac{S_N}{S_C^{3/2}}$$

Sp ic humidity g/kg)

Total reactive carbon source ($Tmol\ a^{-1}$)



The loss of stratospheric ozone increases UV flux in the troposphere - increasing O3 photolysis and this is the larger effect.

Expanding this analysis - “regional” changes

$$[OH] \propto J_{O_3}\, q \frac{S_N}{S_C^{3/2}}$$

Airmass-weighted tropospheric mean

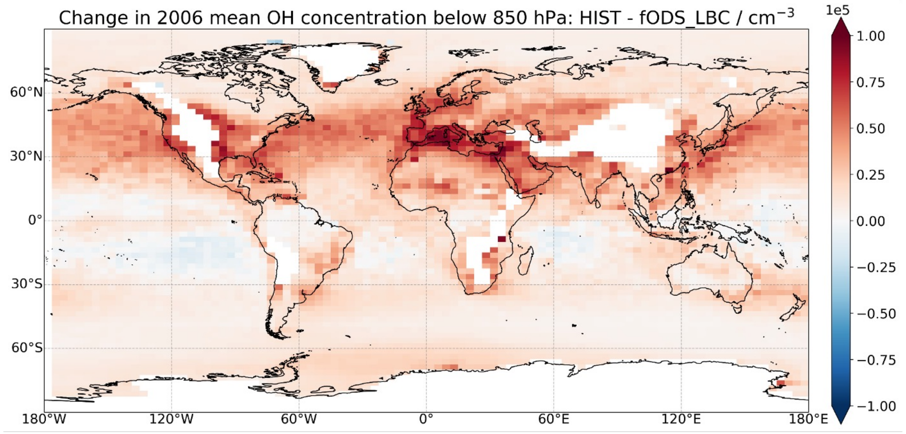
Ozone photolysis frequency (s^{-1})

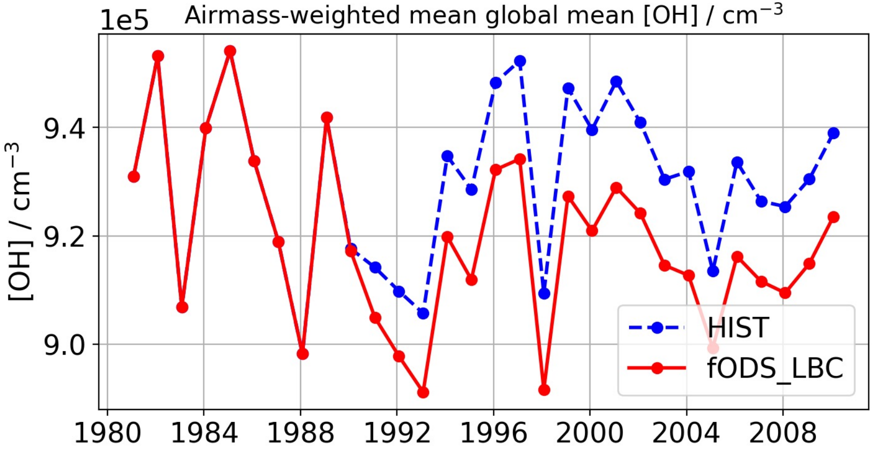
Total NO_x source ($Tmol\ a^{-1}$)

Specific humidity (g/kg)

Total reactive carbon source ($Tmol\ a^{-1}$)

- Strong local effects on OH at the surface – of the order of 3% globally

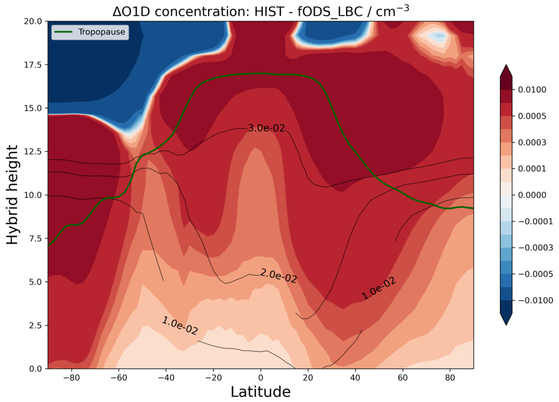


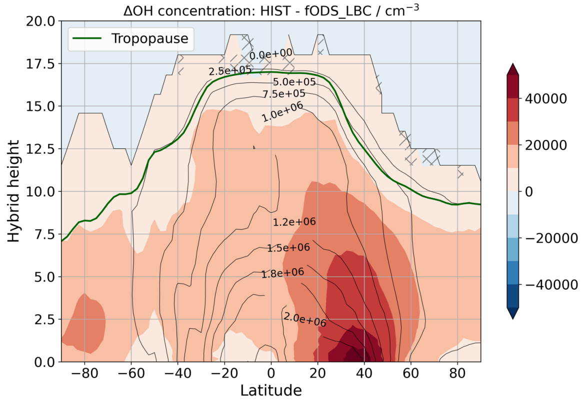


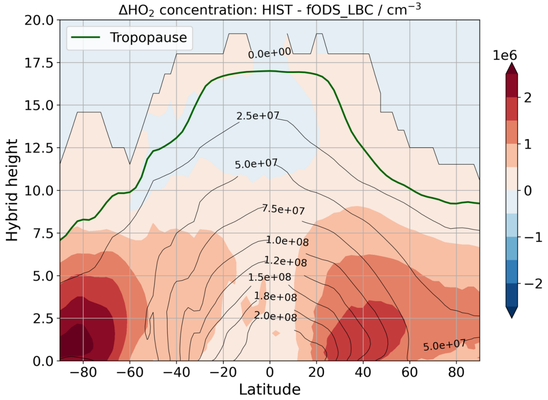
- Small increases in OH over the SH tropical ocean
  - secondary chemical effects due to OH+O3 loss reaction changing in this region

Expanding this analysis - “regional” changes

- How do HOx levels and OH precursor O1D vary across regions between the two runs?
- Plots show as HIST-fODS_LBC, showing that there was more HOx in the historical runs.







- The largest changes in O1D, OH and HO2 are **not** co-located with the largest changes in tropospheric O3.
- Other factors are at work. In this case, the loss of stratospheric ozone changes UV flux in the troposphere, leading to faster O3 photolysis to produce O1D and hence OH, and this is the larger effect.
- **HIST experiment has larger HOx levels, despite lower tropospheric ozone levels**

Regional changes 2: methane oxidation

- Principal loss of methane in the troposphere is via OH oxidation
- Rate of reaction is strongly temperature-dependent

$$[OH] \propto J_{O_3}\, q \frac{S_N}{S_C^{3/2}}$$

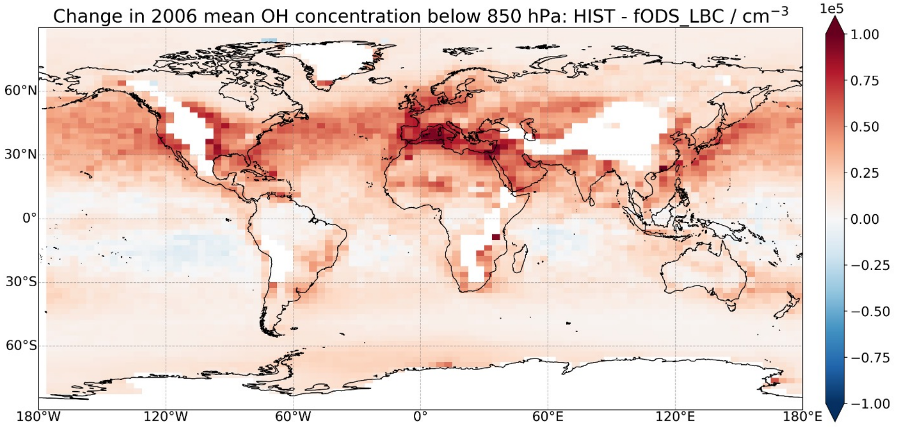
Airmass-weighted tropospheric mean

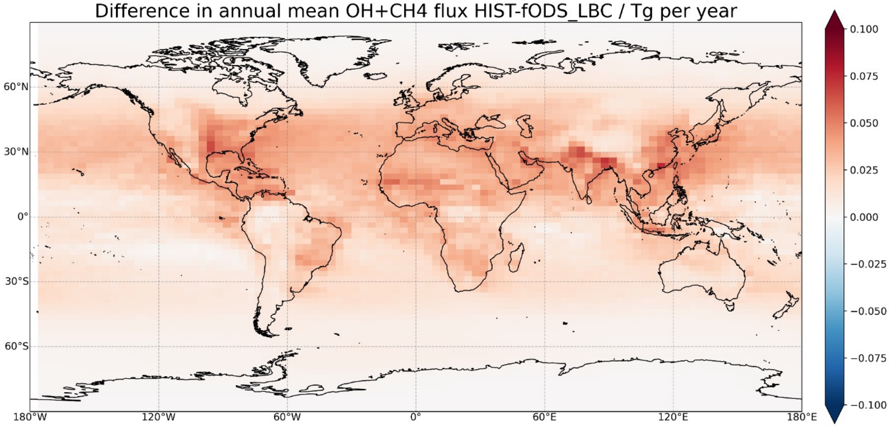
Ozone photolysis frequency (s^{-1})

Total NO_x source ($Tmol\ a^{-1}$)

Specific humidity (g/kg)

Total reactive carbon source ($Tmol\ a^{-1}$)

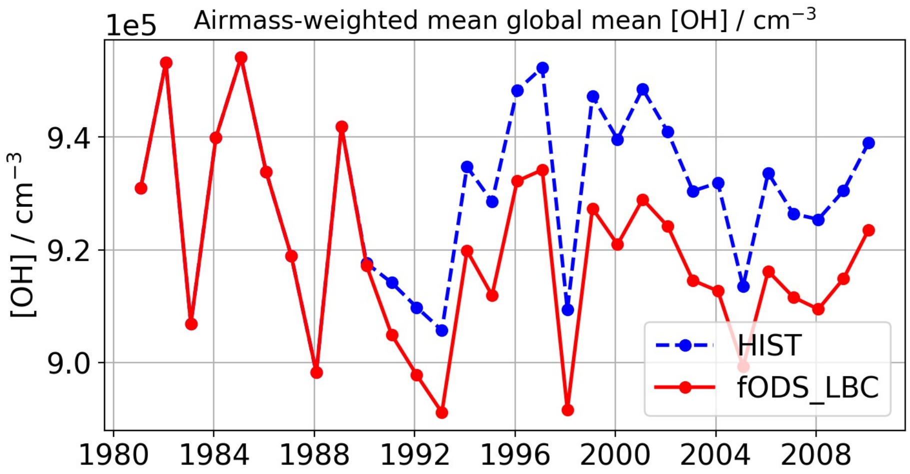


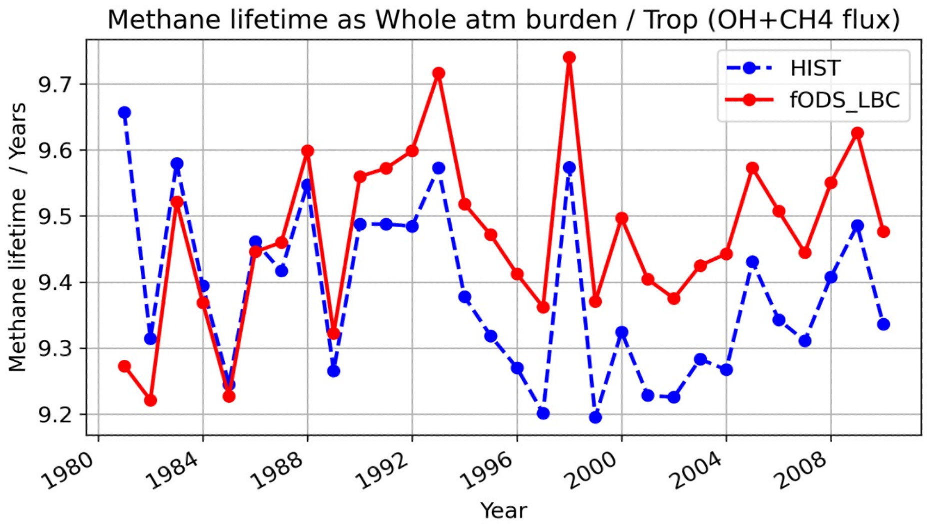


- Changes to CH4+OH loss: larger oxidation rate in the HIST experiment, due to larger OH larger
- Largest change in CH4 reactive tendency occurs in NH tropic/extratropics
- NB Small decreases in regions where OH decreases, although not as large - offset by T?
- **Montreal Protocol leads to faster CH4 oxidation by OH, shorter lifetime.**

Tropospheric methane column and methane lifetime

- How does the OH concentration vary across regions between the two runs?
- Strong local effects on OH at the surface

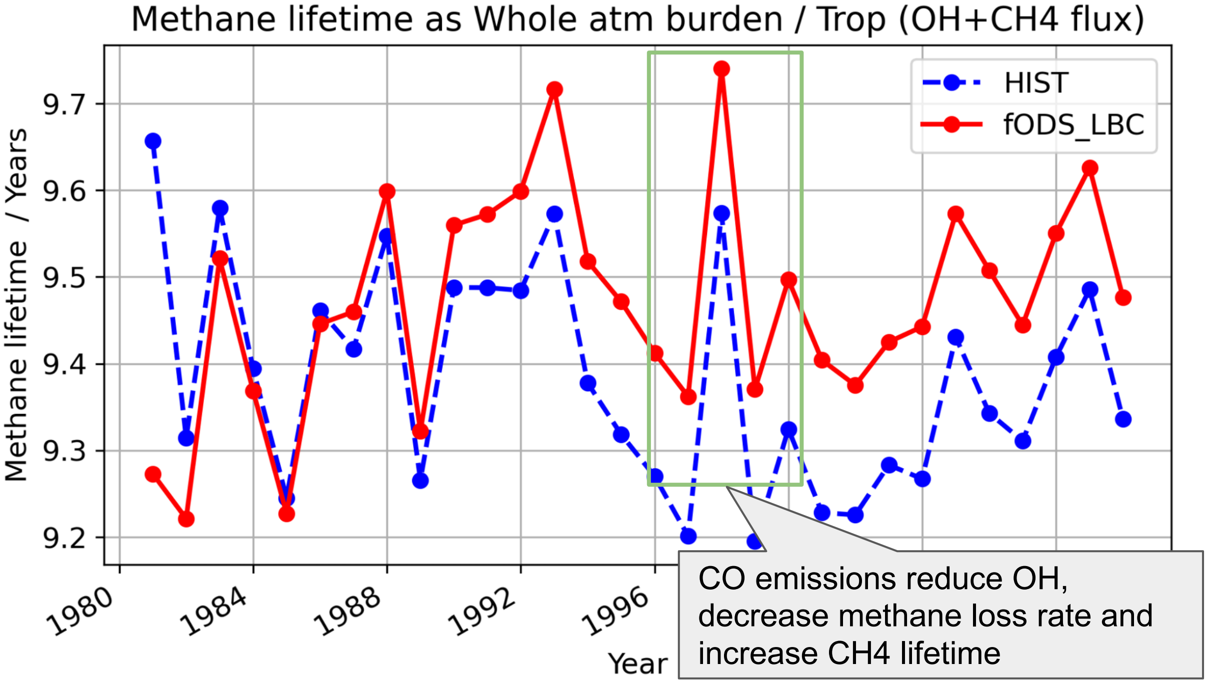


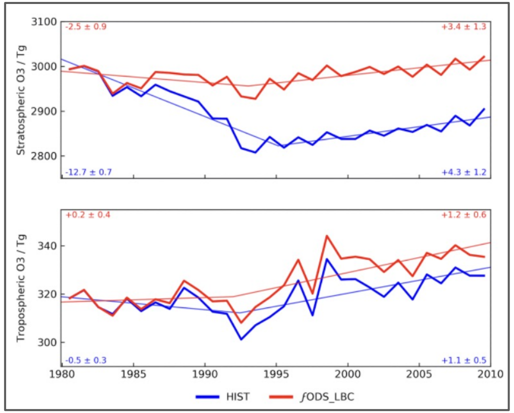


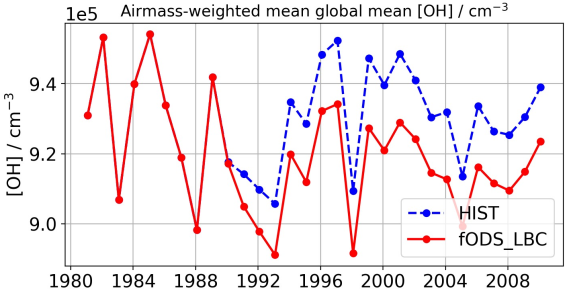
- Effect of Montreal Protocol is to reduce methane lifetime by around 2-3 months, or around 2-3%

Expanding this analysis - What about CH4? Effect of 1997 fires

- In 1997, large increase in methane lifetime, OH also lower.
- 1997 Indonesian fires included in the CO, NOx emissions.



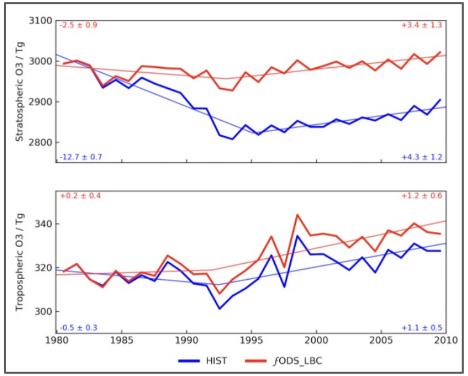




Conclusions - role of Montreal Protocol on oxidants

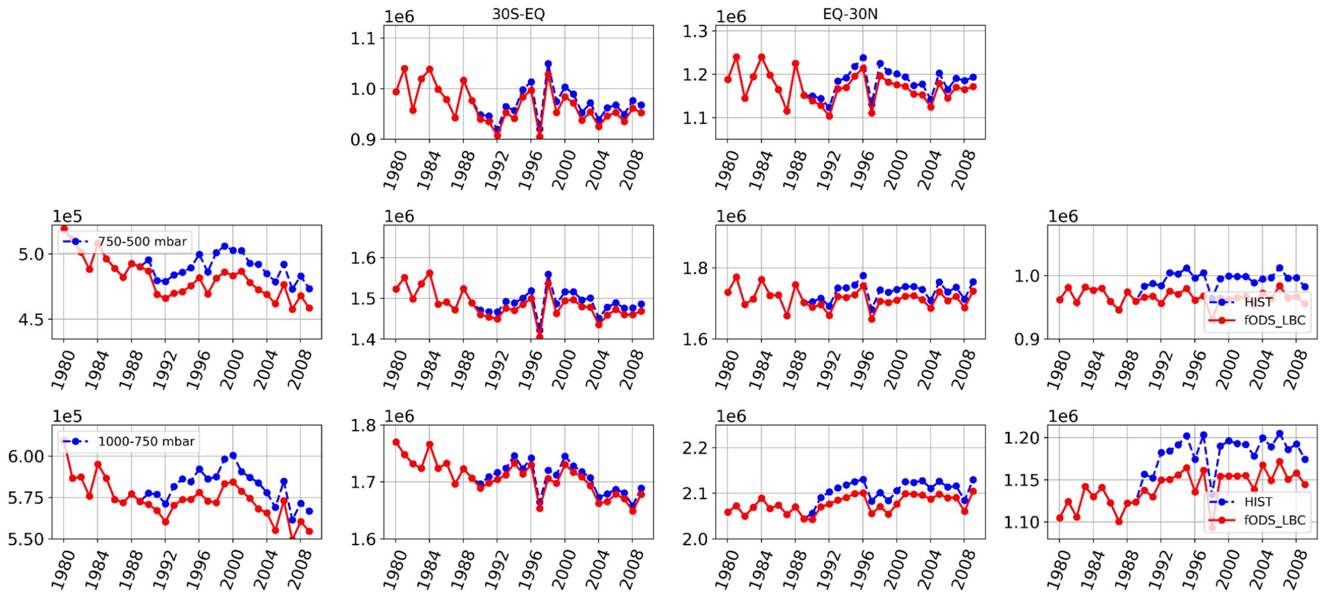
- To attribute the effects of the Montreal Protocol, consider two experiments
  - HIST: ODS and anthropogenic emissions evolve along recent historical pathway (1979-2010)
  - Counter-factual experiment fODS_LBC holding ODS levels at 1979 levels (low ODS)
  - Use nudged simulations to isolate, so far as practicable, chemical effects
- Results
  - O3: fODS has higher tropospheric ozone burden than HIST.
  - OH: HIST has higher levels of OH, despite lower levels of O3 precursor
  - OH: Changes to tropospheric photolysis rates in near UV important?
  - OH: Largest differences in NH at surface – significant role for photolysis/JO1D here?
- CH4
  - Methane lifetime in HIST shorter due to higher OH
  - Important inter-annual variation due to variability in other sinks for OH, such as CO
  - Qu: Impact of stratospheric ozone recovery on methane radiative forcing?
- Which effect is more important?
  - O3: downward transport of ozone from the stratosphere is the more important factor controlling O3
  - OH and CH4: changes to overhead ozone column affects JO1D (although sinks for OH may be important)
  - Qu: What is impact of higher HOx on ozone budget?

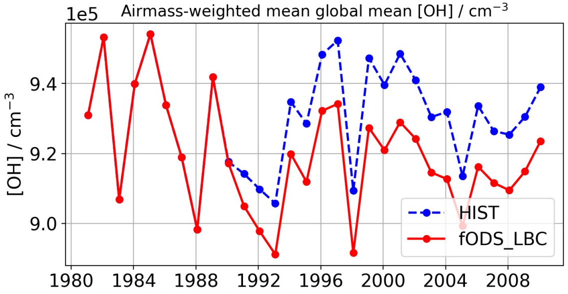
Expanding this analysis - “regional” changes

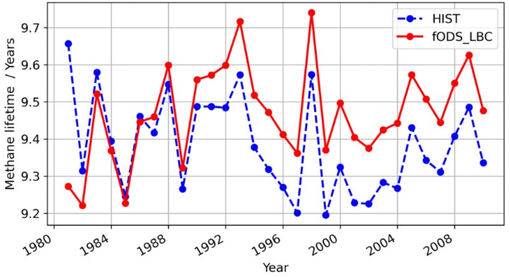


- How does OH concentration vary across regions between the two runs?
- Scale range is 25% on all figures
- Different trends in different regions!

Area-weighted annual mean OH concentration in cm-3



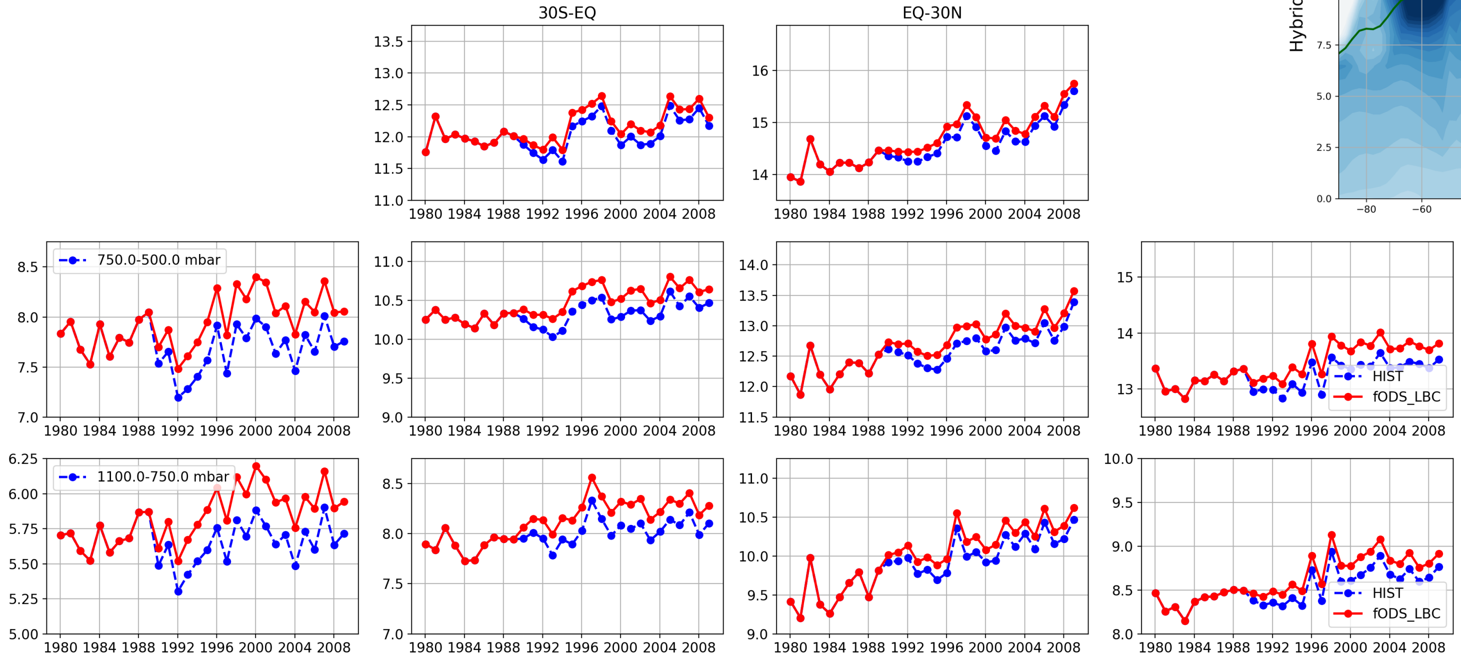


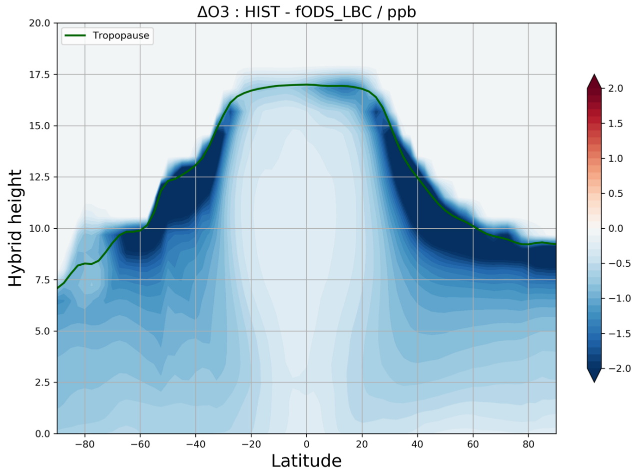


Expanding this analysis - “regional” changes

- How does O3 burden vary across regions between the two runs?
- Scale range is 25% on all figures

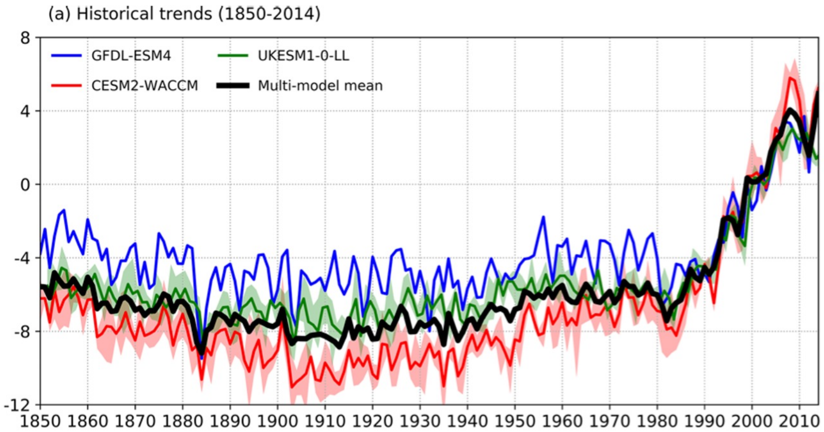
Annual mean O3 Burden per box over time

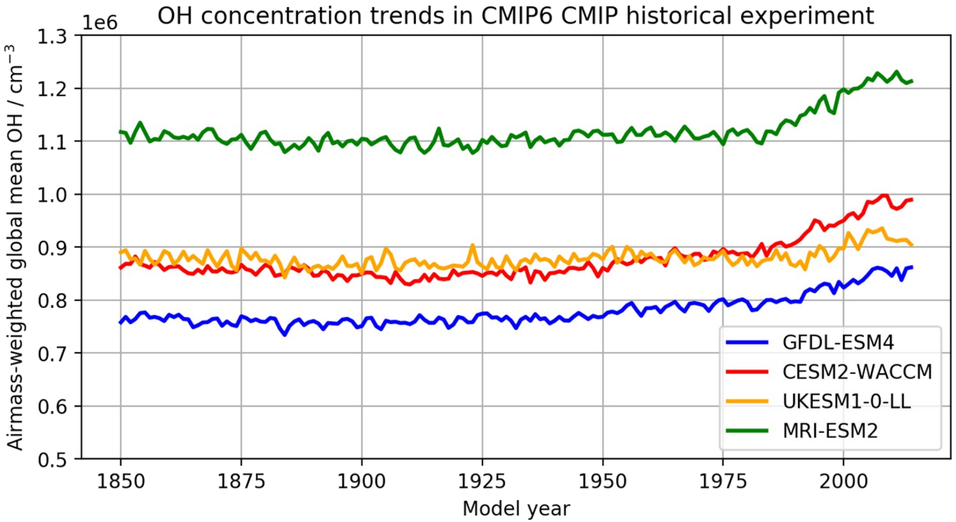




fODS_LBC has a higher burden in every region

Follow on - attributing OH drivers in CMIP6 experiments?





From Stevenson et al. 2021