University of BRISTOL

OZONE BUDGETS (WITH LESSONS FROM CMIP6)

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CMIP6 and AerChemMIP data providers

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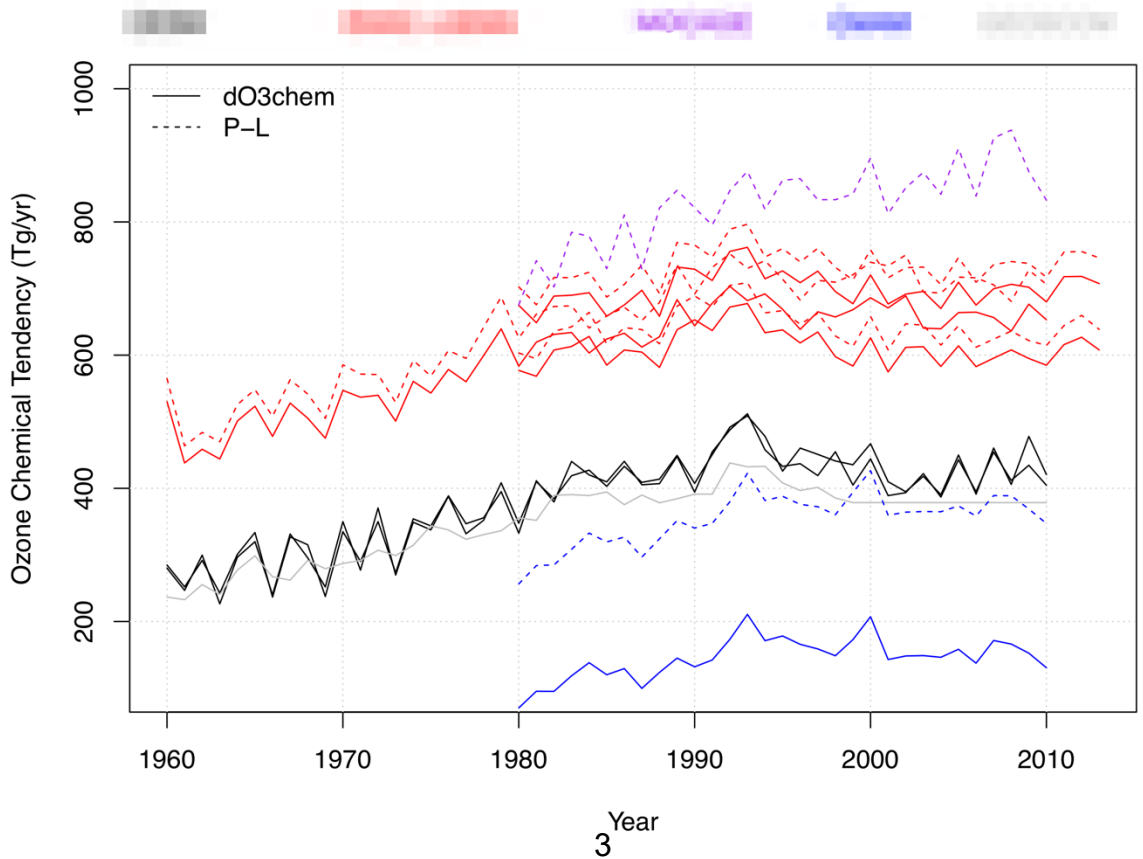
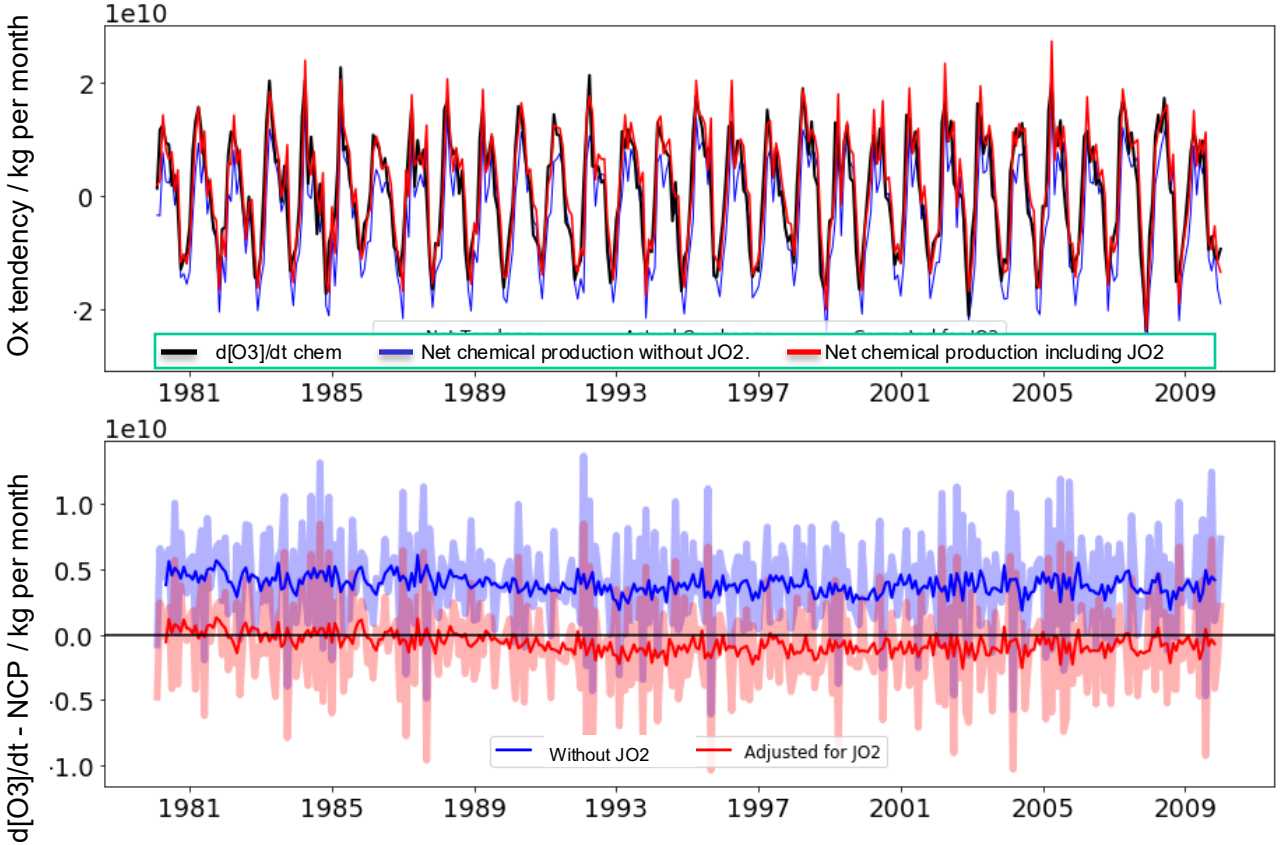
Tropospheric ozone budgets

- O3 approach: dO3/dt = O3P – O3L
- Ox approach: Ox = O1D + O + O3 + NO2 + 2NO3 + 3N2O5 + HNO3 + HNO4 + PANs+…
- Oy approach (Bates and Jacob, I have slides available if required)
- Spin budget approach (Edwards and Evans, targeting different impacts in VOCs)
- Ox budgets diagnostics mostly implemented
  - Role of the stratosphere, a.k.a. does my budget close?
  - Do and ‘do nots’ from CMIP6
  - CMIP6 attribution experiments targeting the role of methane
  - Impact of new diagnostics? dO3chem, OH budget, CO budget

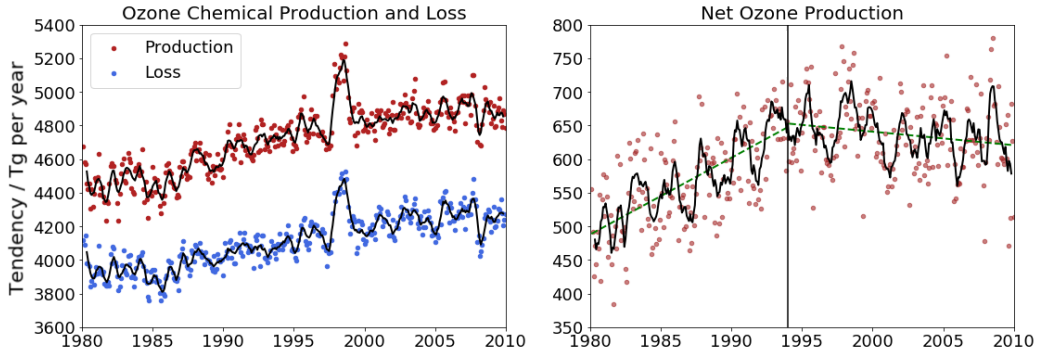
P-L in CCMI models - don’t always agree!

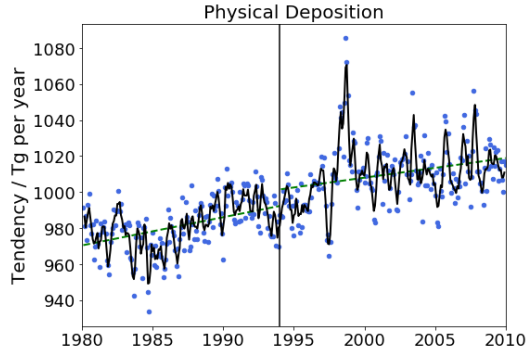


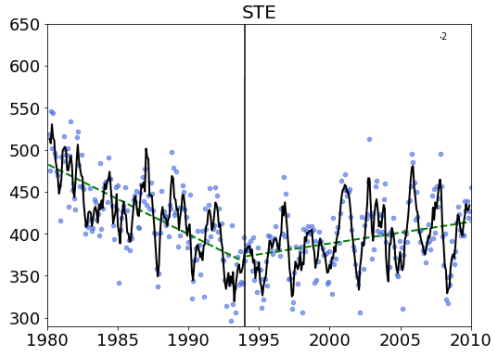
Closing the ozone budget is possible



Chemical and physical terms over the period 1979-2010







- Use transient experiments to diagnose budget terms
  - Downward transport from the stratosphere (PV+380K surface)
  - Deposition at the surface
  - In-situ chemical production and loss
- Budget comprises large and opposing terms and ozone is buffered, O3P and O3L also changing.
- Significant interannual variability

Good agreement: CESM/CAM4 vs UKCA variants

	CAM4-chem REFC1SD*	UKCA REFC1SD	UKESM-1 PI	UKESM-1 PD
Chemical O_3 production	**4701**	**4712**	**3702**	**4937**
HO_2 + NO	3032	3208	2427	3276
CH_3O_2 + NO	1102	1056	682	1022
Others	561	420	520	636
Chemical O_3 destruction	**4118**	**4200**	**3356**	**4197**
$O^1D + H_2O$	2218	2205	1719	2117
$HO_2 + O_3$	1203	1150	999	1344
$OH + O_3$	582.2	517	473	580
Others	114.6	111	164	154
NET Chemical Prod	**583**	**512**	**346**	**740**

CAM4-chem data from Tilmes et al., 2016, doi:10.5194/gmd-9-1853-2016

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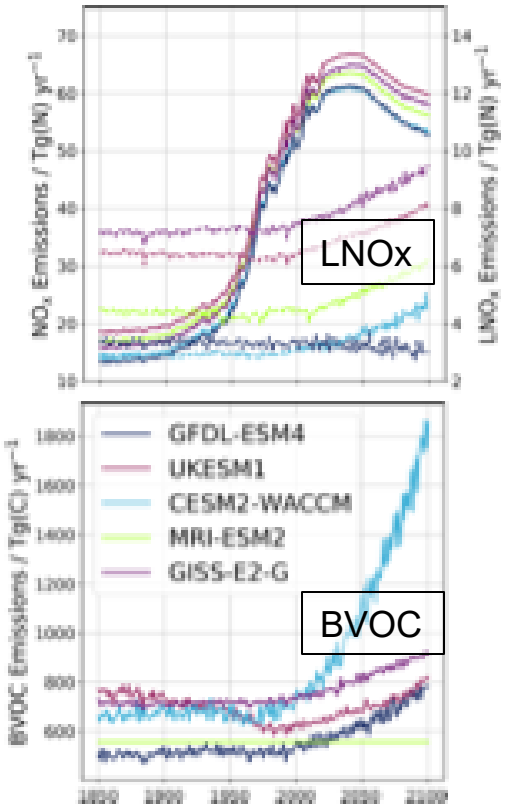
CMIP6 – ‘History repeats itself first as tragedy then as farce’

Ozone budget approaches available in CMIP6

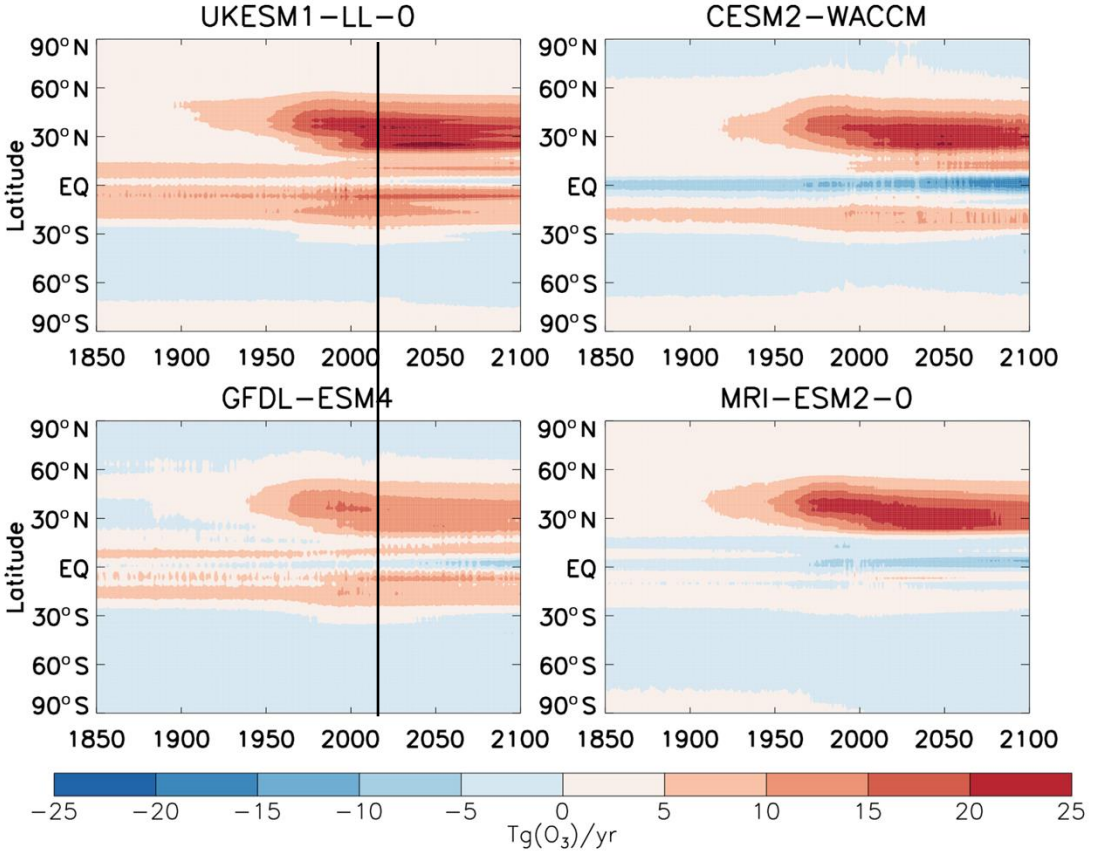
- CMIP6 models targeted Ox budget (so discount Ox interconversion reactions such NO2+hv, O+O2+M, NO+O3) via prescribed CMORized diagnostics, defined as
  - **O3PROD** = ONLY provide the sum of all the HO2/RO2 + NO reactions (as k*[HO2]*[NO])
  - **O3LOSS** = ONLY provide the sum of the following reactions: (i) O(1D)+H2O; (ii) O3+HO2; (iii) O3+OH; (iv) O3+alkenes (isoprene, ethene,...)
  - **DRYO3** = dry deposition includes gravitational settling, impact scavenging, and turbulent deposition, a.k.a. tendency_of_atmosphere_mass_content_of_ozone_due_to_dry_deposition
  - **O3STE** = Ozone **tracer** intended to map out strat-trop exchange (STE) of ozone.
- WMO tropopause diagnostics available
- TROPOZ – tropospheric ozone column calculated online
- AERmon – model output on native model grid and monthly resolution
- O3HR available for a much smaller set of models

Diversity in ozone budgets

Online (ESM) inputs – LNOx and BVOC



Column-integrated net chemical tropospheric ozone production



Defining the troposphere

Tropospheric column ozone

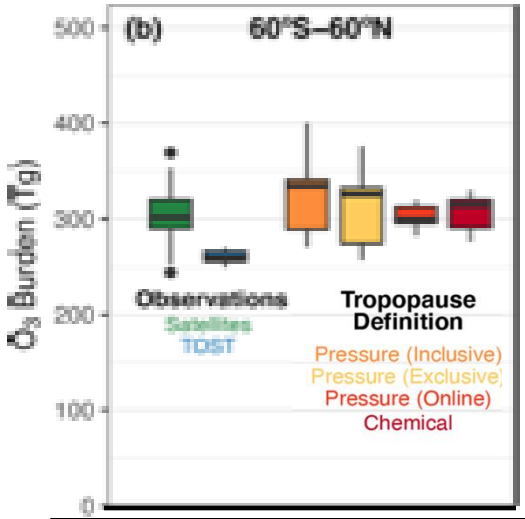
To determine **tropospheric column ozone (TCO)** values, either for the full or partial tropospheric column, two different approaches are proposed:

From the TOAR-2 community

- making use of *fixed pressure levels*:
  - from ground to 150 hPa in the tropics (within 15° of the equator)
  - from ground to 200 hPa in the subtropics (15°-30°)
  - from ground to 300 hPa in the midlatitudes (30°-60°)
  - from ground to 400 hPa in the polar regions (> 60°)
- from ground to the *tropopause*, with the tropopause being the first thermal tropopause (WMO definition*, listed below), determined from the profile data from ERA-Interim or MERRA-2 reanalyses (e.g. *Hoffmann and Spang* (2022), see also above).

Here again, we welcome sensitivity studies between both approaches for e.g. assessing tropospheric ozone trends.

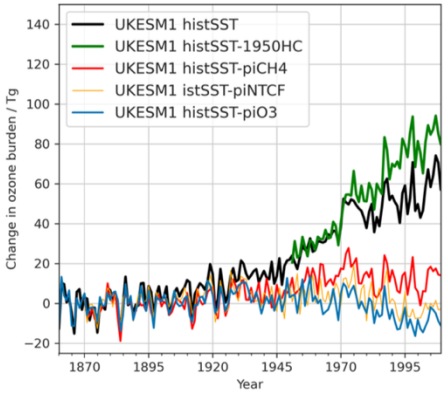
For **comparing tropospheric ozone profiles** between different techniques, we recommended applying the averaging kernels (AKs), e.g. satellite, Umkehr, or FTIR AKs, to smooth the observed ozonesonde, lidar, and reanalysis ozone profiles.

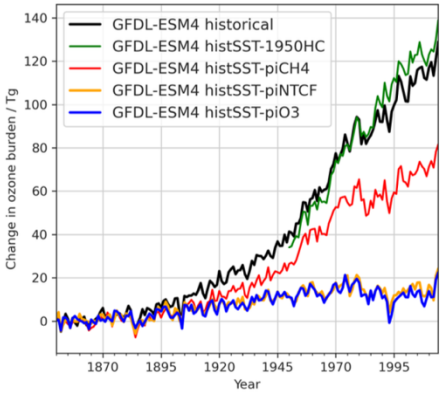


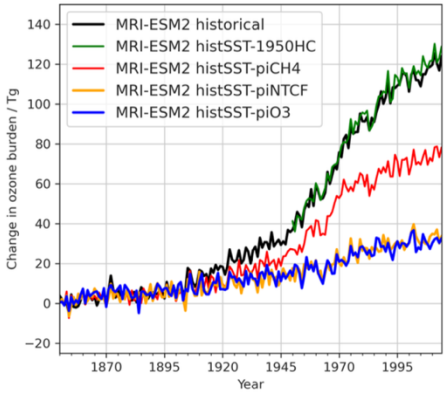
CMIP6 analysis -1997 to 2014 mean

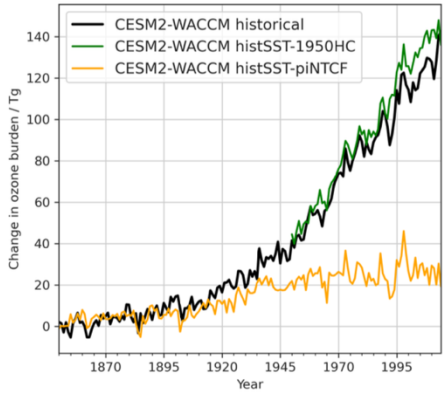
"The inter-model spread in tropospheric burdens is much higher when calculated with the pressure tropopause than the chemical tropopause (red). This is because there is large inter-model variability in the tropopause pressure…TCO calculated using the monthly mean chemical tropopause ends up being most similar in mean and variability to the online TCO diagnostic in the three models"

Ozone burdens in CMIP6 attribution (sensitivity) experiments



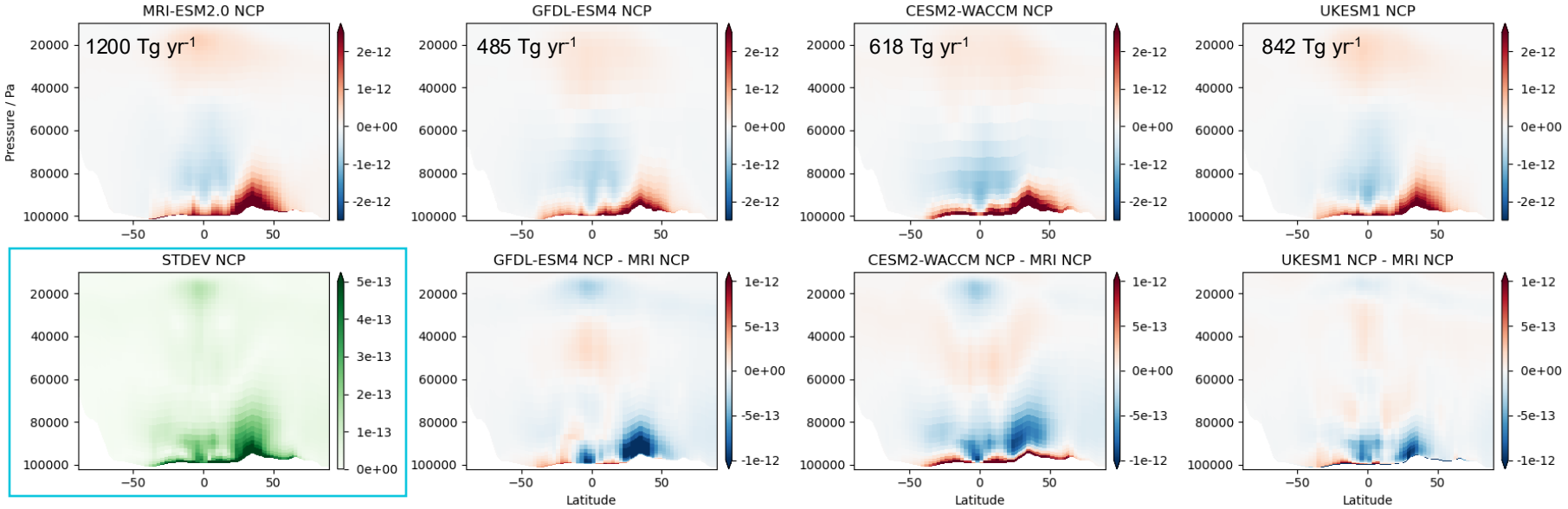






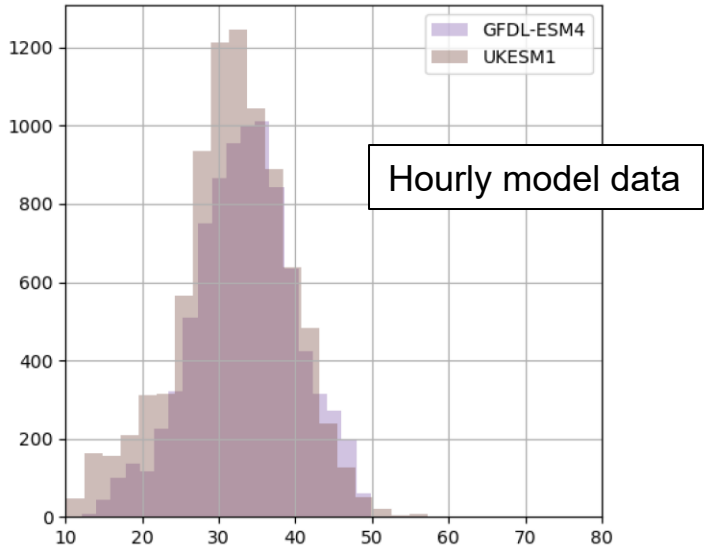
- AerChemMIP provided historical sensitivity transient experiments
- One forcing or emission held constant at 1850 (PI) levels
- Not all models provided every experiment
- Clear differences in sensitivity to CH4 and ODS

Ozone budgets in CMIP6 historical experiments

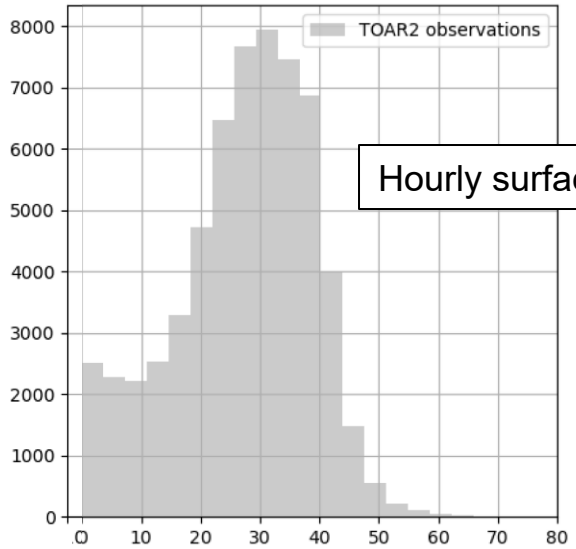


- Showing zonal mean 2010-2014 (end of experiment) O3PROD-O3LOSS = NCP O3
- Historical ‘best-guess’ emissions CEDS for 2014
- Significant diversity in NCP between models, NH BL/FT region of greatest diversity

Value of high temporal resolution output – UK surface O3



Hourly model data



Hourly surface obs

- sfo3 is the AERhr domain: only a few models archived these outputs (1850-2015 2D global hourly output =112 Gb 😭 😭 😭)
- Distribution of hourly surface ozone over the UK domain (matching coarse grid to surface stations). Signs that the models don't capture the wintertime ozone 'titration' episodes?

Proposed experiments

- **Perturbation experiments** with chemical transport models (CTMs) based on the GAINS LRTAP scenarios for the target year 2040
- **Transient Future Scenario experiments** with chemistry climate models (CCMs) using the GAINS LRTAP scenarios from 2010 to 2050
  - Provide a direct assessment of the GAINS LRTAP scenarios
  - Act as a check on the output of the ensemble emulator produced from the Perturbation experiments
  - Allow quantification of the effects of climate change on long-range transport of air pollution
- **Transient Historical experiments** from 2003 to 2020 using a historical global mosaic emission inventory.
  - Provide an assessment of the models' ability to simulate observed trends and interannual variability
  - Comprehensive deposition fields from these runs
  - Provide a baseline simulation for additional experiments in the related HTAP3-Fires exercise

Applying to HTAP analyses

- **Consistent perturbation experiments –** huge plus in attributing differences and providing consistent comparisons, but LNOx and BVOC important
- **Budgets**
  - consistent budget definitions really helpful
  - dO3chem is really essential since O3PROD and O3LOSS don't close budgets to better than +/-10%
- CO and OH budgets helpful, particularly O1D+H2O.
- Reservoir species not considered yet, but maybe useful for chain length calculations?
- Residuals in budgets should be treated with care – it's not always the STE
- Selected period for high time resolution output attractive – again need consistency
- Meaningful intercomparison needs all models to output the same diagnostics – one model dropping out can mean that the whole model is discounted to keep things consistent.

AerChemMIP diagnostics e.g. UKESM1 AERmon

ATM Props	Tracers	Aerosol chem	Deposition	Emissions	Chemical loss	Aerosol	Ozone budget	Aerosol optic	Radiation	Photochem	Clouds
airmass	c2h6	cheaqpso4	drybc	emibc	lossch4	mmraerh2o	o3loss	od440aer	rlutaf	jno2	lwp
bldep	c3h8	chegpso4	drydust	emibvoc	lossco	mmrbc	o3prod	od550aer	rlutcsaf	photo1d	cod
pfull	ch3coch3		dryo3	emico		mmrdust		od550dust	rsutaf		cdnc
phalf	ch4		dryoa	emidms		mmroa		od550lt1aer	rsutcsaf		reffclwtop
ps	co		dryso2	emidust		mmrso4		od870aer	tntrl		
ptp	dms		dryso4	emiisop		mmrss		abs550aer	tntrs		
ua	hcho		dryss	emilnox							
va	hcl		wetdust	eminox							
wa	hno3		wetso2	emioa							
zg	isop		wetso4	emiso2							
ztp	n2o			emiso4							
	no			emiss							
	no2			emivoc							
	o3										
	oh										
	pan										
	so2										
	Toz (2D)										
	Tropoz (2D)										

A man on the limit...

S2. Adjustments to the ACCMIP archive

In multi-model inter-comparison studies, native model diagnostics must be converted into standardized fields with common units for analysis, and are therefore susceptible to definitional and unit-conversion errors. For example, *eminox* is meant to include all anthropogenic and natural NO_x sources in units of kg N m^{-2} s^{-1}; however, many models archived only anthropogenic NO_x and/or in units of kg NO m^{-2} s^{-1}. We have evaluated each archived variable against reasonable physical limits and the self-reported values in the supplemental materials of the ACCMIP overview paper (3). Assumptions made to adjust the archived values to match the requested units and variable fields or disclude fields from our analysis are outlined below.

CESM-CAM-superfast. Ozone photolysis frequencies (*photo1d*) were not archived for this model. Instead, we derive them from the production rate of OH from ozone photolysis (*prodohjo3*),

$$J_{O(^1D)} = P(\mathrm{OH}) \cdot \frac{3.3 \times 10^{-11} \exp\left(\frac{55}{T}\right) [O_2] + 2.15 \times 10^{-11} \exp\left(\frac{110}{T}\right) [N_2]}{2\left(1.63 \times 10^{-10} \exp\left(\frac{60}{T}\right)\right) [H_2O][O_3]},$$

where $P(\mathrm{OH})$ is *prodohjo3* converted to molecules cm^{-3} s^{-1}, T is the local absolute temperature in K, $[N_2]$, $[O_2]$ and $[H_2O]$ are respectively the number densities of oxygen, nitrogen and water vapor in molecules cm^{-3} determined using archived temperature, pressure and mixing ratios, and the rate constants are taken from the JPL 2011 recommendations (4).

In order to match the emissions reported by Lamarque et al. (3): we consider *eminox* to be actually archived as kg NO m^{-2} s^{-1} and without lightning NO_x or a constant 2.8 Tg N yr^{-1} of other natural sources, and for *emivoc* to be actually archived as kg isoprene m^{-2} s^{-1}.

CICERO-OsloCTM2. In order to match the emissions reported by Lamarque et al. (3), we consider all archived emissions to not include any natural sources. In this study, we add the constant natural emission fluxes reported for these simulations by Skeie et al. (5): 5 Tg N yr^{-1} of lightning NO_x and 8 Tg N yr^{-1} of other natural NO_x, 180 Tg yr^{-1} of biogenic CO, and 397 Tg C yr^{-1} of biogenic NMVOCs.

CMAM. Emissions of NMVOCs are zero in this model. The chemical loss of CO for several years of the RCP 8.5 scenario is many orders of magnitude too high, and these years are discluded from this analysis.

EMAC. In order to match the emissions reported by Lamarque et al. (3): *eminox* is considered to be actually archived as kg NO m^{-2} s^{-1}, and *emivoc* is scaled by the mass ratio of C to total mass of NMVOC assumed by the model (161/210) (6). RCP 8.5 is not included in this analysis due to non-physical archived model air masses.

GEOSCCM. All variables used in this study are correctly archived.

GFDL-AM3. Archived *eminox* did not include lightning NO_x, which we add in this analysis.

GISS-E2-R. All variables used in this study are correctly archived.

GISS-E2-TOMAS. In order to match the emissions reported by Lamarque et al. (3),*emivoc* is multiplied by the molar mass ratio of isoprene in grams (68).

HadGEM2. In order to match the emissions reported by Lamarque et al. (3), *eminox* is considered to be actually archived as kg NO_2 m^{-2} s^{-1} and without lightning NO_x. One year of RCP 8.5 is not included in this analysis due to error in model level height precluding airmass calculation.

LMDzORINCA. Historical emissions of CO or NMVOC were not archived, so decadal mean *emico* and *emivoc* are prescribed from the values reported in Lamarque et al. (3) in this scenario.

MIROC-CHEM. In order to match the emissions reported by Lamarque et al. (3), *eminox* is considered to be actually archived as kg NO_2 m^{-2} s^{-1} and without lightning NO_x. Lightning emissions were not archived, so decadal mean *emilnox* is prescribed from the values reported in Lamarque et al. (3).

MOCAGE. In order to match the emissions reported by Lamarque et al. (3), *eminox* is considered to be actually archived as g N m^{-2} s^{-1}, and *emico* and *emivoc* are considered to be actually archived as g C m^{-2} s^{-1}. Lightning emissions in 1983 and 2003 of the historical scenario and 2032 of the RCP 8.5 scenario are unrealistic, and not included in this analysis.

NCAR-CAM3.5. In order to match the emissions reported by Lamarque et al. (3), *eminox* is considered to be actually archived without lightning NO_x. The *emivoc* field was not archived, so decadal mean values reported by Lamarque et al. (3) are used instead. The chemical loss rates of CO (*lossco*) and methane (*lossch4*) were treated as if they were archived as molecules cm^{-3} s^{-1}, and *lossch4* was scaled by an additional factor of 0.01 for all scenarios except RCP 6.0.

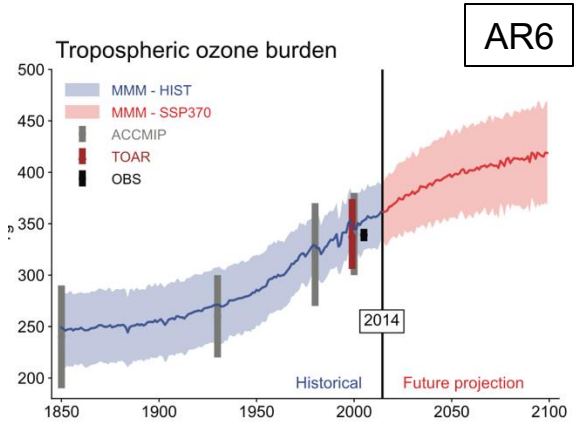
STOC-HadAM3. All variables used in this study are correctly archived.

UM-CAM. All variables used in this study are correctly archived.

Benefits of HTAP from a chemistry-climate perspective

- **ACCENT (Stephenson) -> AR5 (Young) -> AR6 (AerChemMIP)**
- **26 models -> 13 models -> 5 models by AR6 deadline**
- AerChemMIP focused on SSP3-7.0, with a lowNTCF and a low NTCFlowCH4 variants.
- Increased diversity in model treatment would be a great thing.

EXPT ID	hist-1950HC	hist-piNTCF	histSST	histSST-1950HC	histSST-piCH4	histSST-piNTCF	piClim-CH4	piClim-HC	piClim-NTCF	piClim-control
TIER	1	1	1	1	1	1	1	1	1	1
MODELS	6	11	12	6	8	11	9	6	11	22
Members	19	27	13	6	8	12	10	6	12	32
EXPT ID	**hist-piAer**	**histSST-piAer**	**histSST-piN2O**	**histSST-piO3**	**piClim-2xdust**	**piClim-2xSS**	**piClim-BC**	**piClim-N2O**	**piClim-O3**	**piClim-aer**
TIER	2	2	2	2	2	2	2	2	2	2
MODELS	10	8	4	4	9	9	11	6	6	19
Members	24	9	4	4	10	10	12	7	6	25
EXPT ID	**piClim-2xDMS**	**piClim-2xNOx**	**piClim-2xVOC**	**piClim-2xfire**	**piClim-NH3**	**piClim-NOx**	**piClim-OC**	**piClim-SO2**	**piClim-VOC**	
TIER	3	3	3	3	3	3	3	3	3	
MODELS	6	4	6	6	2	6	10	11	6	
Members	7	4	7	6	2	6	12	13	6	
EXPT ID	**ssp370-lowNTCF**	**ssp370SST**	**ssp370SST-lowNTCF**	**ssp370SST-lowAer**	**ssp370SST-BC**	**ssp370SST-lowO3**	**ssp370SST-lowCH4**	**ssp370-ssp126Lu**	**ssp370SST-lowNTCFCH4**	
TIER	1	1	1	2	2	2	2	2	2	
MODELS	13	11	8	6	6	3	4	5	6	
Members	40	11	8	6	6	3	4	5	6	
EXPT ID	**ssp370pdSST**		**ssp370-lowNTCFCH4**							
TIER	2+		1+							
MODELS	7		6							
Members	7		12							



From Griffiths, Wilcox, Allen et al., ACPD 2024

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Bates and Jacob (2020) propose an expanded definition

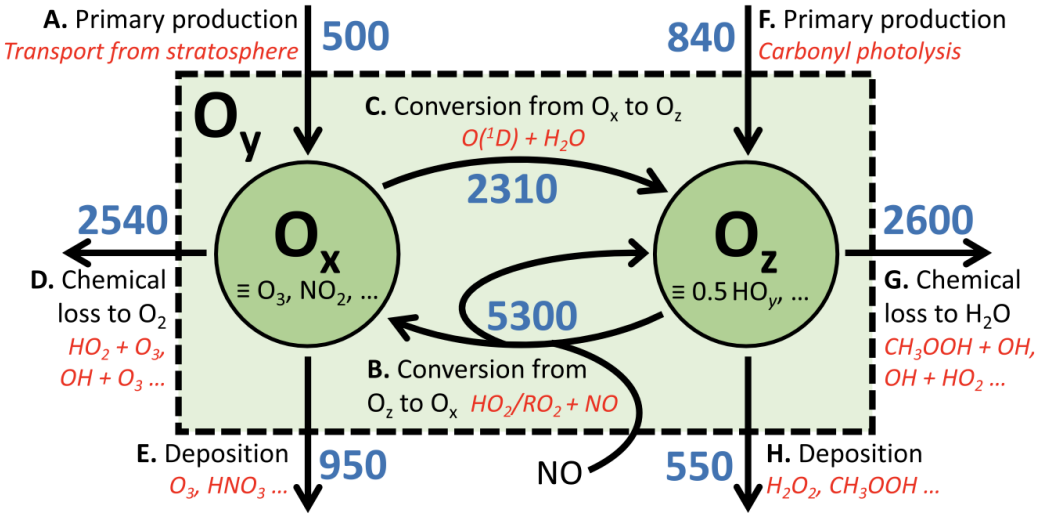
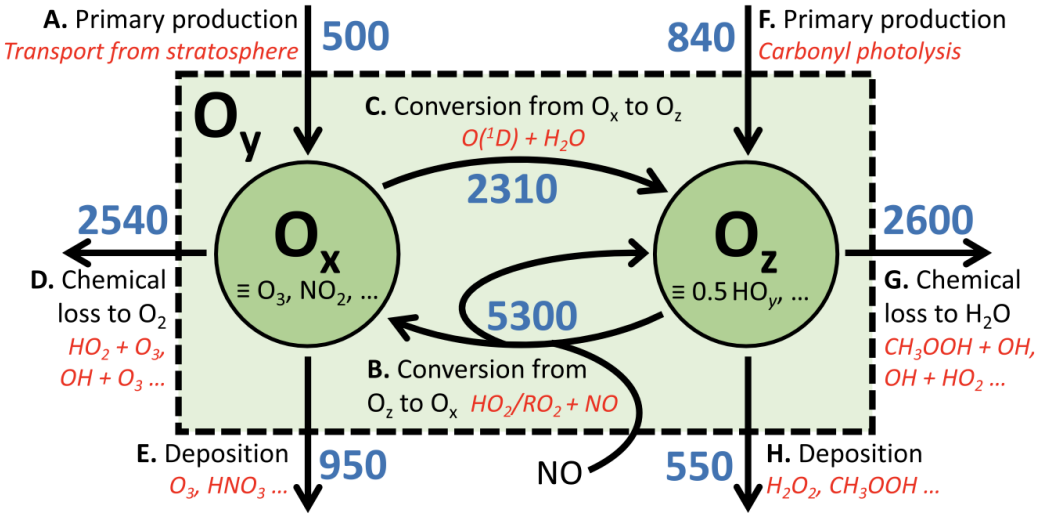


Figure from Bates and Jacob [10.1029/2019GL084486](https://doi.org/10.1029/2019GL084486)

- O*x* =O3+O3P+O1D+NO2+2NO3 +3N2O5+HNO3+HNO4+PAN+RONO2+ CR+XO+XNO2+2XNO3+∑*n*X2O*n*+2OXO
- O*z* =0.5×(H+OH+HO2+RO2+HNO2 +HNO3+HNO4+PANs+RONO2+X +XO+XNO2+XNO3+OXO)+H2O2+ROO H+X2+HOX+X2O*n*, a reservoir
- O*z* = Ox+Oy

Applying Oy budget to UKESM-UKCA CCMI-2022



- Ox → Oz: (O3+alkene)+(O1D+H2O) etc
- Oz → Ox: (RO2+NO)
- Oz production: RCHO+hv, RR'CO+hv
- Oz chemical loss: HO2+OH → H2O+O2
- Oz dep: HOBr, HOCl etc
- Oy dep: O3 dry deposition
- STE

Figure from Bates and Jacob 10.1029/2019GL084486

Applying Oy budget to UKESM-UKCA CCMI-2022

Process	UKCA	Bates&Jacob
Ox→Oz	2730	2310
Oz→Ox	5600	5300
Oz_PROD	445	500
Oz CHEM LOSS	2390	2540
Oz_LOSS_DEP	640	550
Oz PRIMARY PROD	750	840
Ox LOSS DEP	1050	950

- Ox → Oz: (O3+alkene)+(O1D+H2O) etc
- Oz → Ox: (RO2+NO)
- Oz production: RCHO+hv, RR'CO+hv
- Oz chemical loss: HO2+OH → H2O+O2
- Oz dep: HOBr, HOCl wet/dry dep
- Ox dep: O3 dry deposition

Data from Bates and Jacob 10.1029/2019GL084486

Comparing Ox and Oy budgets

Process	Ox	Oy
Chemical Prod	5740	5570+60+750 =6380
Chemical Loss	5120	2390+2830 = 5220
In-situ prod	620	1160
Deposition	1050	1690
Lifetime	23 days	72 days

- Oz chemical production from aldehydes/ketones, Ox from RO2+NO ('amplification'), OH+RCO2H etc
- Oz loss as O2 formation and H2O formation channels
- Oz dep: HOBr, HOCl wet/dry dep
- Ox dep: O3 dry deposition
- Lifetime calculations modified

Data from Bates and Jacob 10.1029/2019GL084486