Linking Peroxy Radical Chemistry to Global Climate

Common Representatives Intermediates Chemical Mechanism in the United Kingdom Chemistry and Aerosols model

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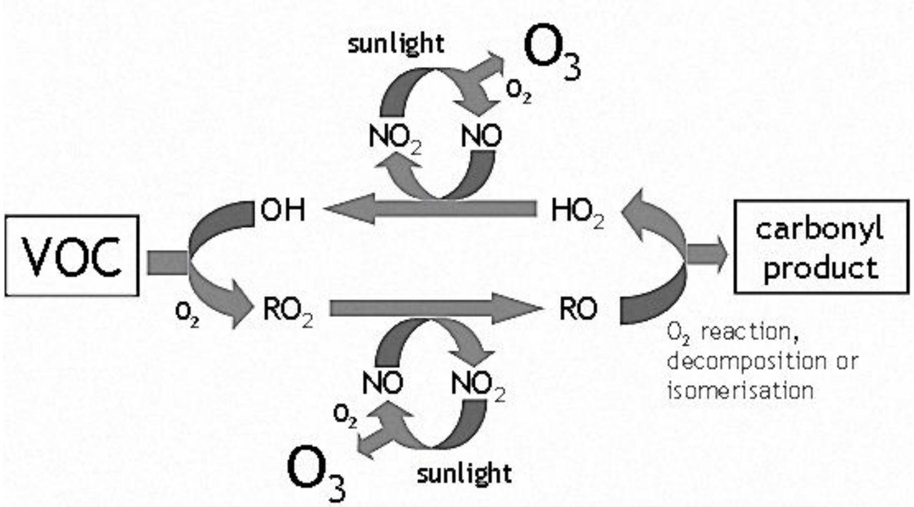
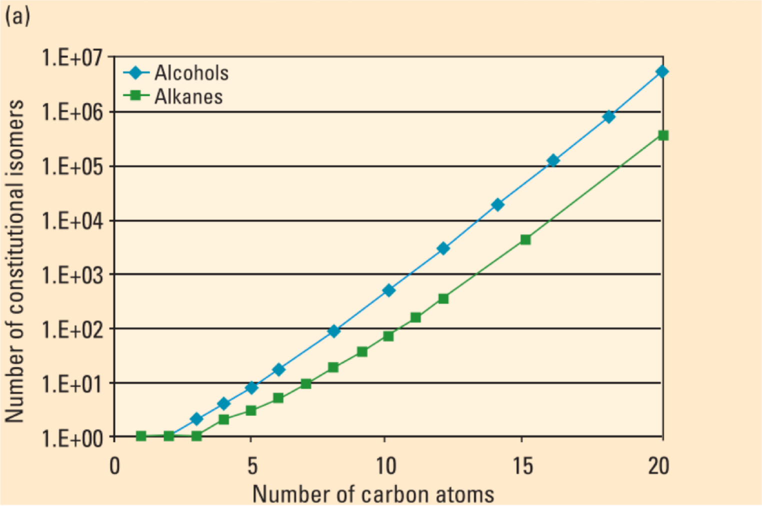
Tropospheric Volatile Organic Compound Chemistry

- VOC and NOx photochemistry drives Ozone formation (and other processes) in troposphere.
- Many 1000's of VOCs identified in the atmosphere.
- Near-explicit schemes too complex e.g. Master Chemical Mechanism, MCMv3.1: 4361 species, 12,775 reactions.
- Need to parameterise tropospheric chemistry in 3D models. But how can we be confident the necessary simplifications preserve key processes?





Goldstein et al., 2007

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INTRODUCTION

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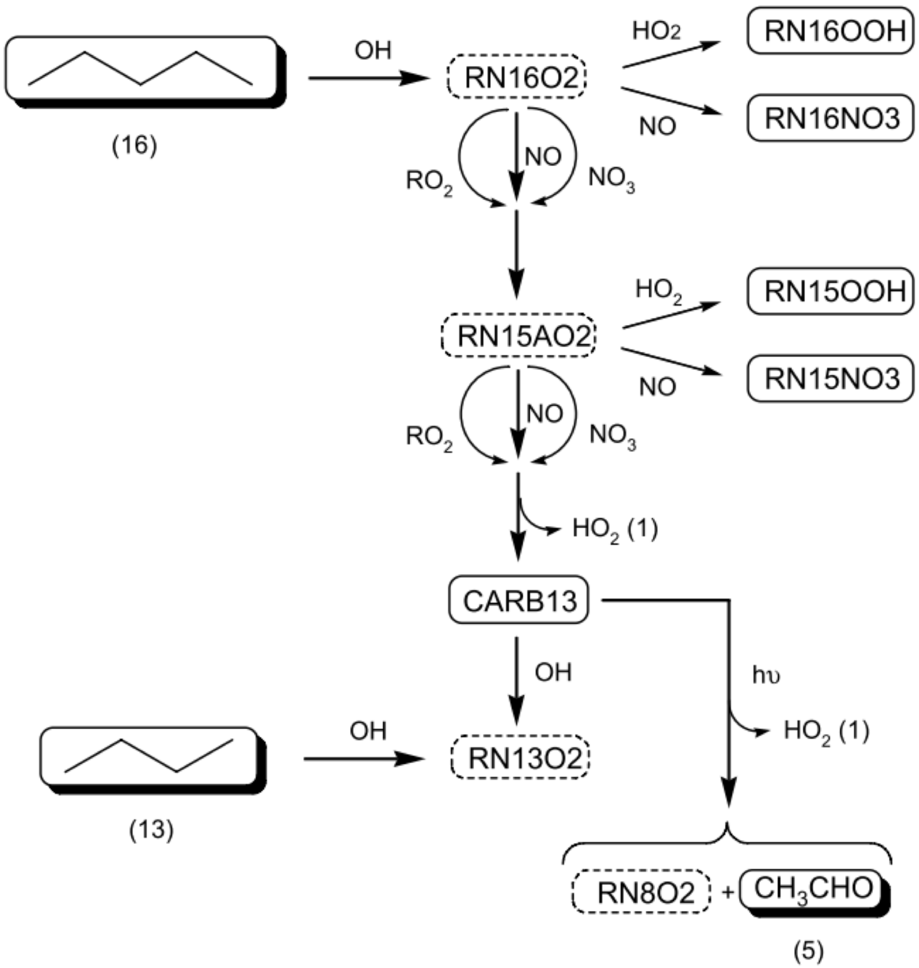
Common Representatives Intermediates Mechanism



- "Intermediate complexity" scheme, conserving ozone forming potential from MCM v3.1.
- Oxidation products lumped based on 'CRI index': number of C-C and C-H bonds in each molecule.
  - CRIv2 = 434 species, 1183 reactions; (Jenkin et al., 2008).
- Further reductions in complexity achieved by lumping emitted VOCs (Watson et al., 2008):
  - CRIv2-R5 = 196 species, 555 reactions.

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Implementation in United Kingdom Chemistry and Aerosols Model

- UKCA model – part of the UK Met Office Unified Model.
  - Chemistry of Stratosphere-troposphere (CheST) 87 species, 305 reactions.
  - CRI scheme Extended with Stratospheric & aerosol chemistry: CRIv2R5 + stratospheric chemistry (CRI-Strat): 233 species (181 transported), 724 reactions (See extra slides for details).
- Every peroxy radical undergoes pseudo-unimolecular reactions scaled by the summed concentration of all RO2 species (Jenkin et al., 1997)
  - Builds efficient framework for parameterising complex RO2+RO2 chemistry with little extra cost (see later half of presentation).

Approximately 80% more computationally expensive to run.

Real advantage in allowing traceability of key processes (e.g. ozone formation, radical chemistry) to “best” understanding.

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Experimental Setup

- Comparing StratTrop and CRIv2-R5+Stratosphere (CRI-Strat) simulations, both with GLOMAP aerosol at UM vn10.9.
- N96 (1.875° x 1.25°) 85 vertical levels.
- Nudged meteorology, 2009-2019.
- 2014 CEDS emissions, as used for CMIP6. All NMVOC emission classes mapped in CRI-Strat vs StratTrop:
  - **70.5 vs 27.9 GgC/yr anthropogenic.**
  - **40.6 vs 23.9 GgC/yr biomass burning.**
  - **900.6 vs 710.6 GgC/yr biogenic.**
- CRI-Strat simulation also run with StratTrop emissions to test sensitivity to input NMVOCs

More details: Archer-Nicholls et al., GMD, *in prep*

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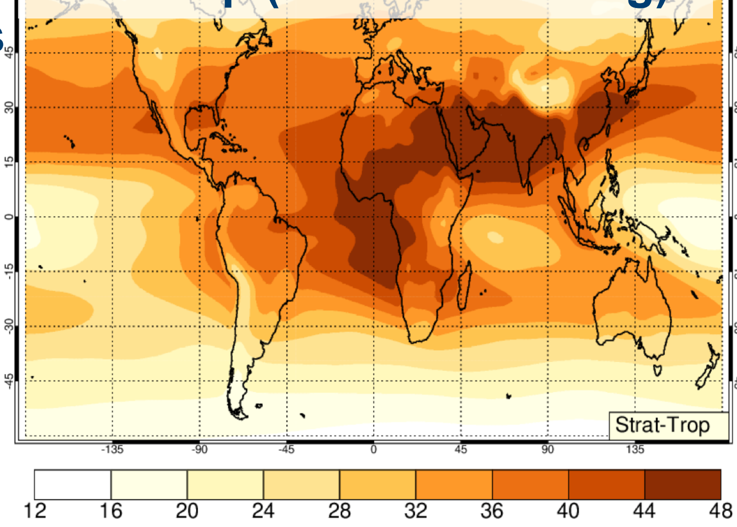
Tropospheric Ozone Column (DU)

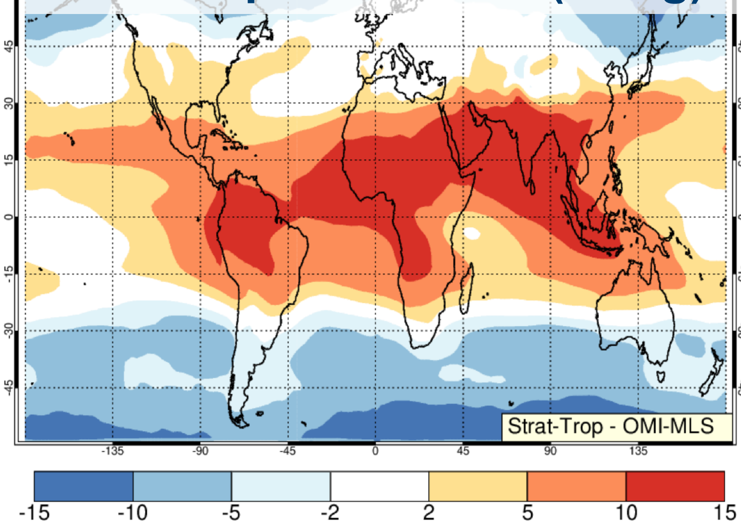
Difference to OMI-MLS Satellite

Both mechanisms show similar biases to satellite observations
- Too high at equator, too low at high latitudes.

StratTrop (Burden = 306 Tg)

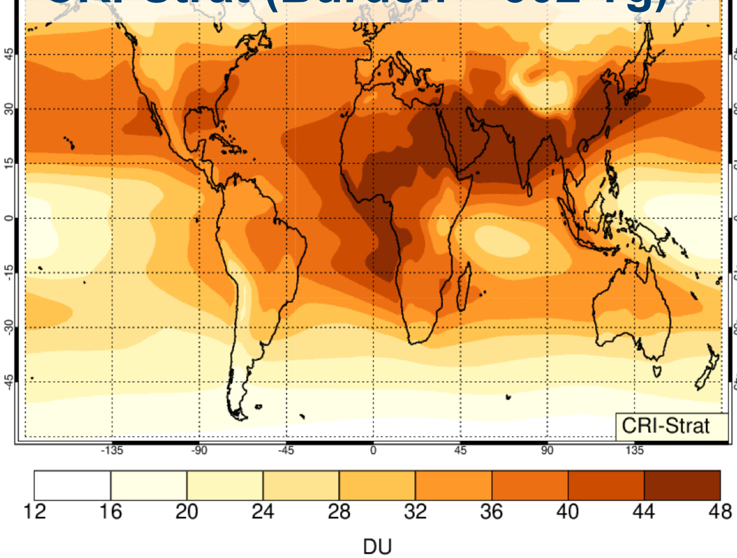


StratTrop – OMI-MLS (16 Tg)

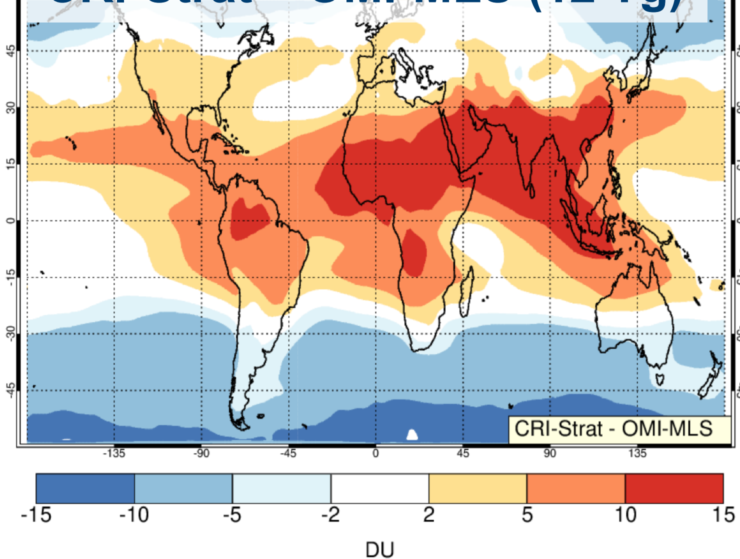


Similar tropospheric burden hides significant vertical differences

CRI-Strat (Burden = 302 Tg)



CRI-Strat – OMI-MLS (12 Tg)



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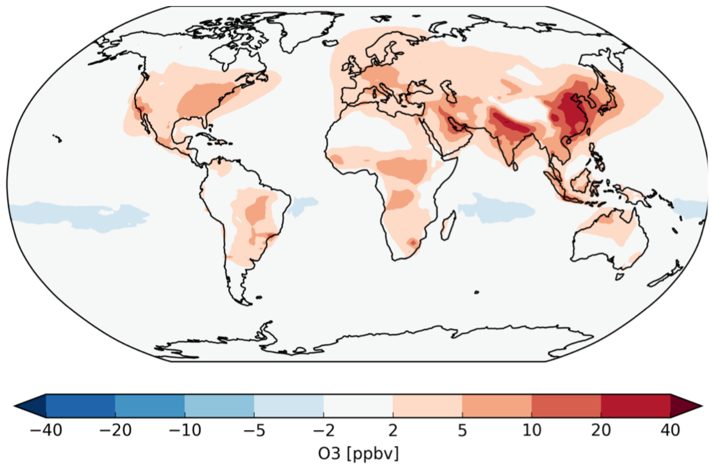
Difference in Ozone, lowest 1km of atmosphere; CRI-Strat – StratTrop

Much higher surface ozone, particularly in polluted regions

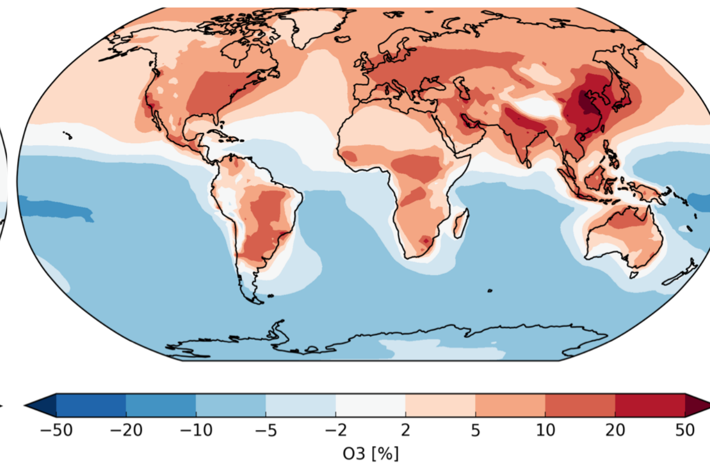
Driven by higher production rate

May need aerosol effects on oxidants [e.g. Li et al., PNAS, 2018] and/or higher resolution to accurately simulate urban O_3

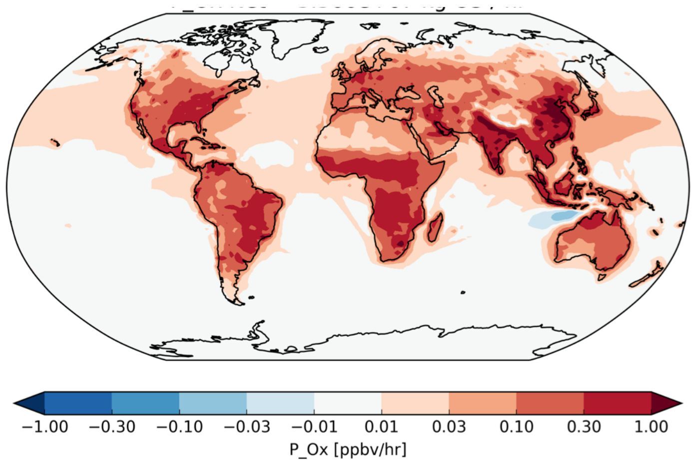
Absolute Difference in Ozone



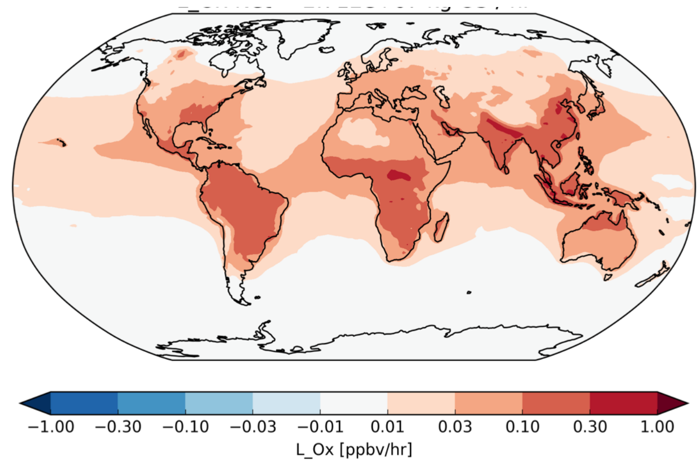
Relative Difference in Ozone



Difference in Ox Production



Difference in Ox Loss



$[Ox] = [O_3] + [O] + [NO_2] + 2[NO_3] + 3[N_2O_5] + [HNO_3] + [HNO_4] + PANs$

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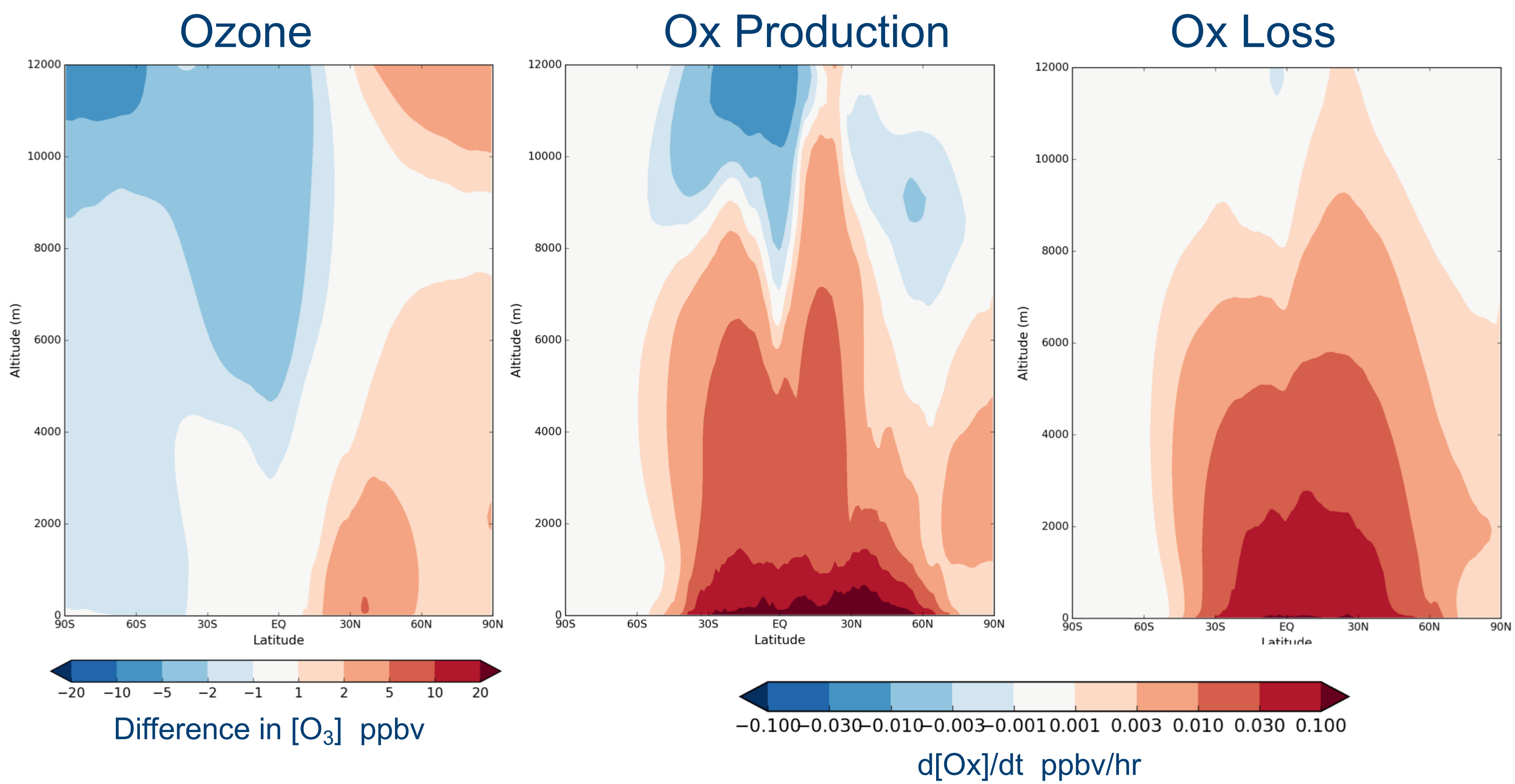
Difference in Ozone, Production of Ox and Loss of Ox CRI-Strat - Strattrop



Ox Production AND loss terms larger in CRI-Strat!

More Ox is produced in polluted regions, but also has shorter lifetime

Difference in Ox loss driven by higher O1D+H2O rate coefficient in CRI

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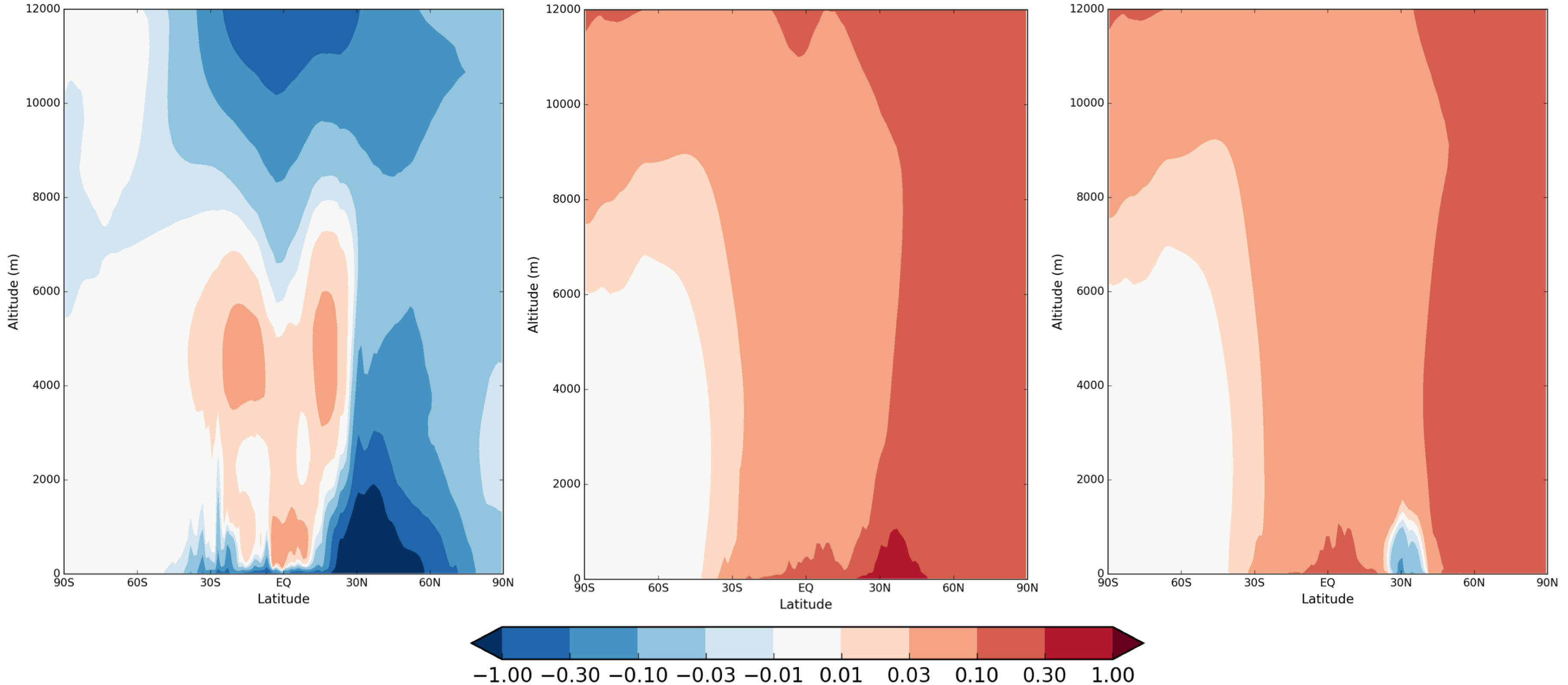
Difference in Oxidised Nitrogen; CRI-Strat – StratTrop

NOx = NO+NO2

NOz = $NO_3 + 2N_2O_5 +$
HNO_3 + PAN + RNO_3 +…

NOy = NOx + NOz



ppb

- Reactive nitrogen more efficiently stored in reservoir species in CRI, where it can be transported

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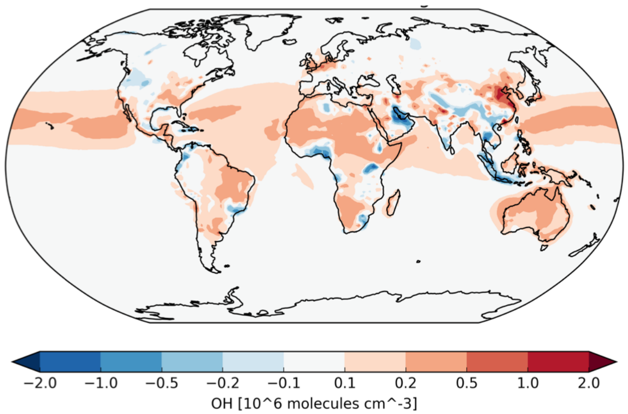
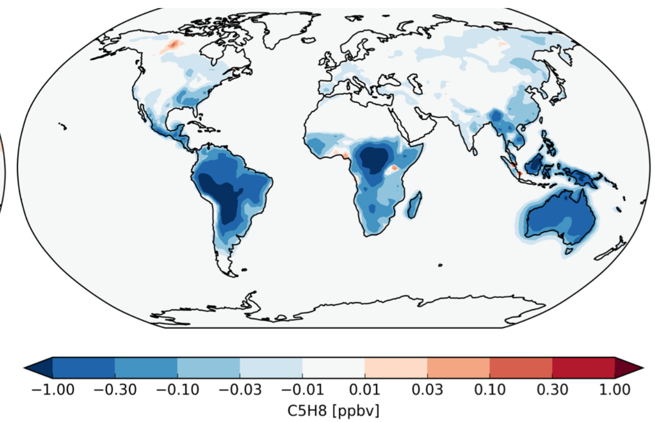
Changes to Oxidants/radicals; CRI-Strat - StratTrop

Greater HOx production and recycling in CRI

Absolute Difference in OH



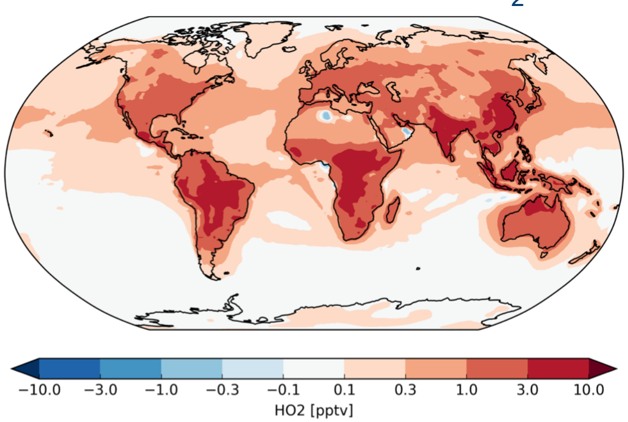
Absolute Difference in Isoprene



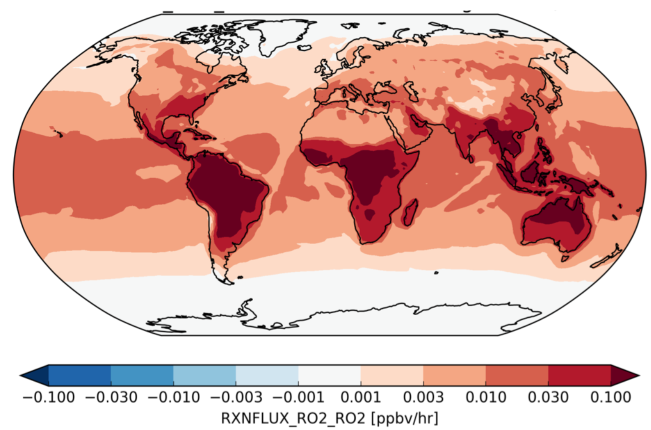
Greater loss of isoprene due to changes in oxidants

Higher HO2 – may need aerosol losses

Absolute Difference in HO_2



Difference in RO2+RO2 flux



Faster oxidation and more explicit peroxy radical chemistry: greater flux through RO2+RO2 reactions

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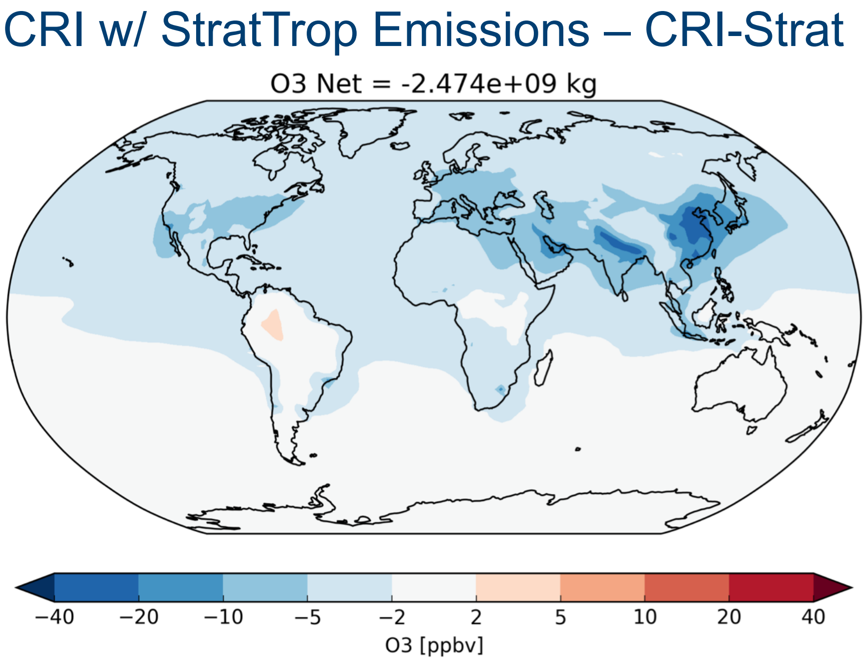
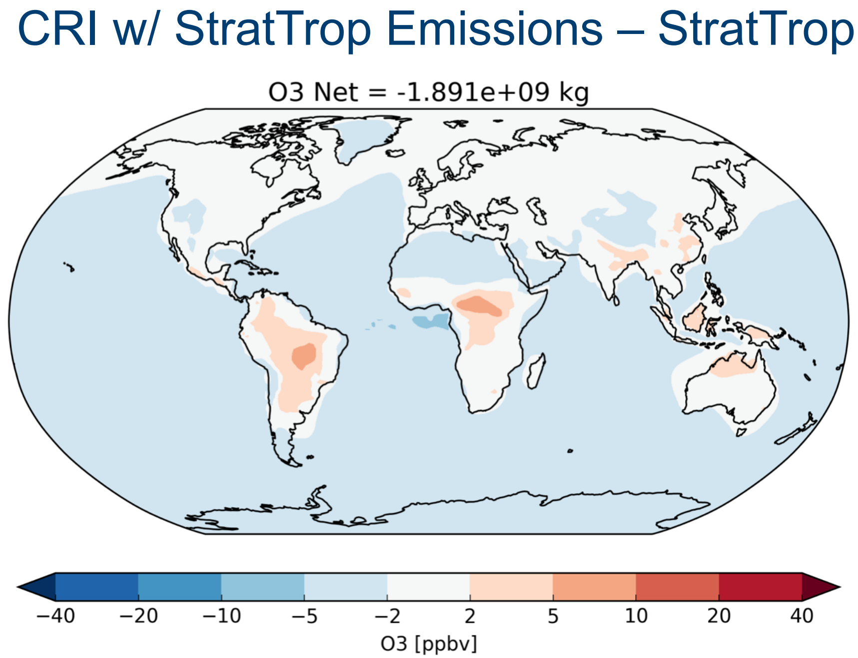
Sensitivity to NMVOC emissions





- CRI runs using StratTrop emissions – big difference in ozone. Shows
- Remaining differences between CRI and StratTrop: more ozone production due to more realistic multigenerational isoprene chemistry. Lower overall burden due to shorter O3 lifetime (O1D+H2O)
- Strong sensitivity to amount and speciation of NMVOC emissions

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Summary – CRI-Strat

- CRI-Strat has similar biases in tropospheric ozone column to StratTrop – likely due to deficiencies in other shared aspects of model (e.g. transport, resolution)

- Large differences in surface ozone – greater production *and* loss

- Higher production driven by more NMVOCs undergoing multigenerational chemistry and storing of NOx in reservoir species, allowing reactive nitrogen to be transported

- Ox loss driven by higher O1D+H2O reaction rate (see extra slides)

- High sensitivity to amount and speciation of NMVOC emissions – important to get these right in emission inventories

- CRI is a useful framework with explicit chemistry – to evaluate simpler mechanisms and build on to simulate climate impacts of novel chemistry

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Next Steps: CRIv2.2 and HOMs

CRI v2.2 (Jenkin et al., 2019, *Atmos Env*)

Update to rate coefficients and adds to isoprene scheme to include isomerisation reactions and HOx recycling. Incorporation into UKCA in progress:

+12 species, +~110 reactions

CRI-HOM (Weber et al., 2020, *ACP*, in review)

Adds HOMs (highly oxygenated organic molecules - Bianchi et al., 2019 and refs therein) to CRI v2.2. Currently only in box model.

Key processes:

- Autoxidation of a-pinene peroxy radicals from OH and O3-initiated oxidation
- Formation of multiple generations of RO2
- Formation of C10, C15 and C20 accretion products (dimers)
- Isoprene-derived suppression of dimers (McFiggans et al., 2019)

+11 species, +64 reactions

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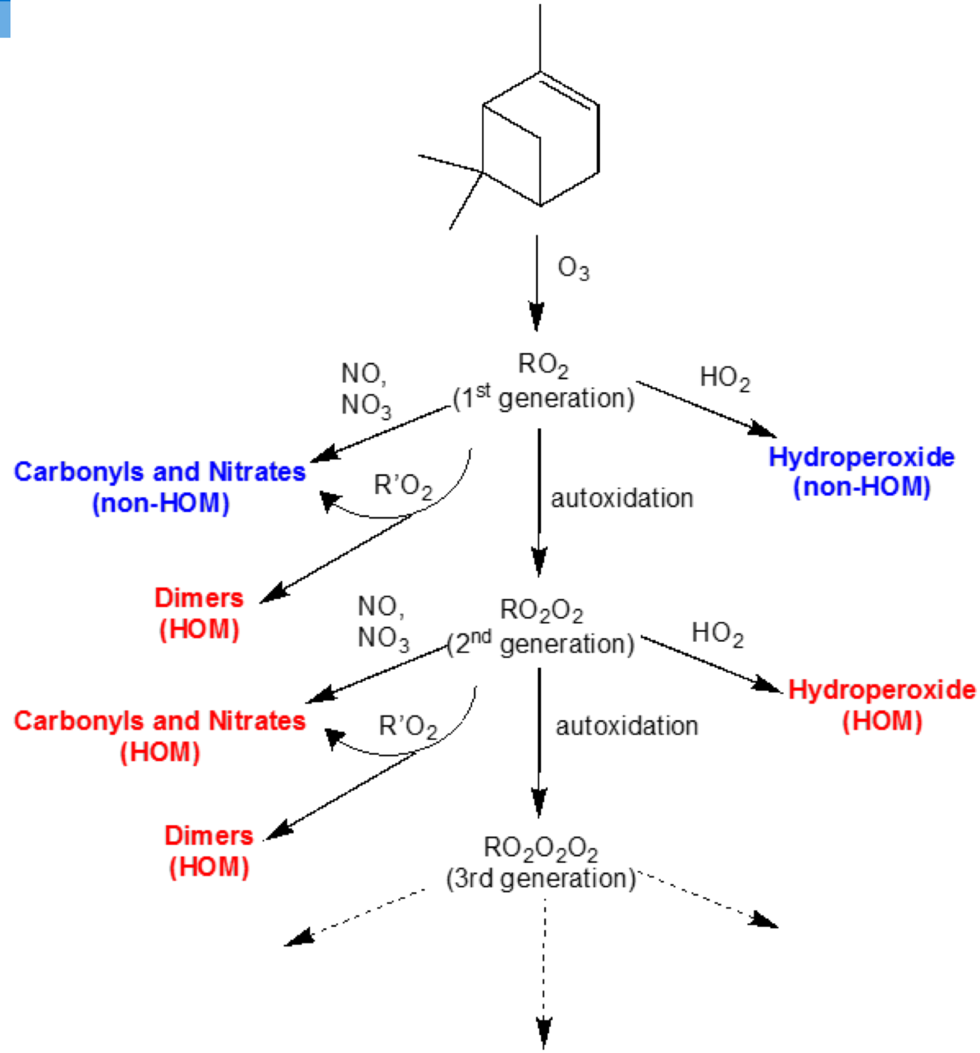
CRI-HOM: Building the Mechanism

- Alpha pinene ozonolysis and OH oxidation pathway adjusted to include autoxidation
  and dimerisation (C20 and C15 species).
- RO2 lumped into “generations” based on number of autoxidation steps.
- RO2 pool split into “big” (C8-10), “medium” (C4-7) and “small” (<C4) size pools.
  - Allows production of 20 carbon and 15 carbon dimers.
- First semi-explicit HOM mechanism suitable for GCM.



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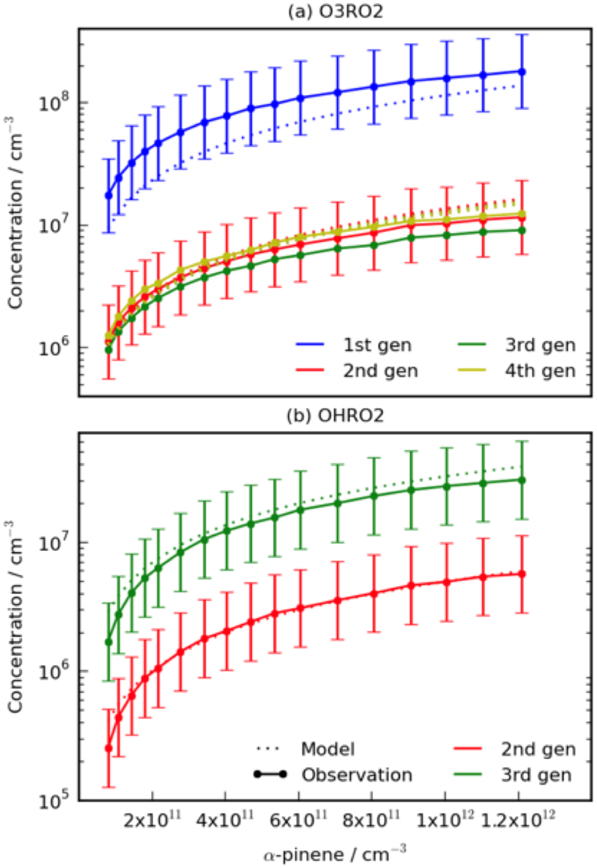
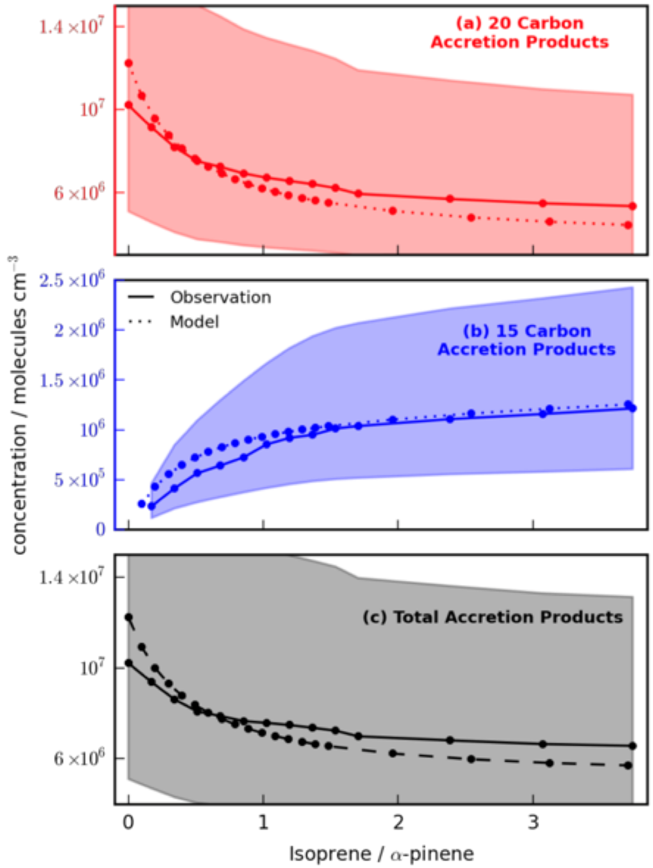
CRI-HOM: Optimisation

Parameters fitted against flow cell data (Berndt et al., 2018) and isoprene suppression of HOMs captured.



Autoxidation coefficients optimised to
to reproduce peroxy radical data.

Accretion products (dimers) decrease with increasing isoprene – recreates behavior observed by McFiggans et al., Nature (2019).



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Summary and Conclusions

- Comprehensive CRIv2-R5+Stratosphere mechanism added to UKCA: 233 species (181 transported) and 724 reactions.
    - Runs ~1.8x slower than StratTrop (87 species, 305 reactions).
    - Ready to use in release version UM from version 11.5, email me about emissions.

See: **https://code.metoffice.gov.uk/trac/um/wiki/ticket/4231**

- Early analysis highlights key differences between CRI-Strat and StratTrop:
    - Tropospheric Ozone chemistry is "hotter": greater production and loss.
    - Lower tropospheric NOx, more NOz => increased production of PANs, organic nitrates and other NOx reservoirs.
    - High sensitivity to NMVOC emissions
- Current developments:
    - Updated mechanism with CRIV2.2 (ongoing in UKCA)
    - Have developed new CRI-HOM mechanism to simulate latest understanding in HOM formation from autooxidation and RO2+RO2 accretion products
- Next – test CRIv2.2 in 3D model, incorporate CRI-HOM, link with aerosols scheme => Semi-explicit representation of HOM chemistry in coupled climate model!

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EXTRA SLIDES

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CRI vs StratTrop chemistry - details

	StratTrop + GLOMAP Aero	CRIv2-R5	CRI-Strat	CRI-Strat + GLOMAP Aero
No. Species	87	198	219	233
No. Tracers	83	146	167	181
Non transported prognostics	4	52	52	52
No. RO2 species	9 (transported)	47 (non-transported)	47	47
No. Emissions	23	27	27	38
No. photol reactions	60	100	124	126
No. Thermal reactions (bimol+termol+het)	245	446	577	598
No. wetdep species	34	74	80	83
No. drydep species	41	124	128	131

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CRI vs StratTrop chemistry - details

Key Extensions:

- Alkanes & alkenes up to C4, Aromatics (benzene, toluene & o-xylene).
- Detailed isoprene and alpha/beta-pinene chemistry.
- Peroxy radical chemistry (47 RO2 species in CRI vs 9 in StratTrop).
- Organic nitrates from RO2+NO → RONO2 for all relevant species.
- Peroxy radical chemistry -> all RO2 species react with RO2 ”pool” calculated as sum of all peroxy radicals at each iteration of solver
- 38 vs 23 emitted species, all available NMVOC emission classes mapped.

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NMVOC Emissions: Anth+BBurn+Biog

Raw emissions	Emission Mass (TgC/year)	CRIv2-R5	StratTrop
VOC01: Alcohols	0.4 + 3.5 + 48.5 3 + 0.1 + 9.5	MeOH EtOH	MeOH (via NVOC)
VOC02: Ethane VOC07: Ethene VOC09: Ethyne	5.3 + 2.8 + 1.0 4.9 + 4.1 + 25.8 3.1 + 1.1	C2H6 C2H4 C2H2	C2H6
VOC03: Propane VOC08: Propene	5.5 + 0.6 + 1.0 3.0 + 3.5 + 14	C3H8 C3H6	C3H8
VOC04–6: Butanes and higher alkanes	4.8 + 0.4 + 0.1	C4H10	N/A
VOC10: Isoprene	0.6 + 588	C5H8	C5H8
VOC11: Monoterpenes	1.2 + 94.7	67% -> APINENE 33% -> BPINENE	Monoterp (unreactive)
VOC12: Other alkenes and alkynes	6.5 + 0.8 + 2.6	TBUT2ENE (t-butene)	N/A
VOC13: Benzene VOC14: Toluene VOC15-17: Xylenes + other aromatics	6.1 + 2.0 7.0 + 3.9 + 86.5 11.9 + 0.2	BENZENE TOLUENE OXYLENE	N/A
VOC21: Formaldehyde	1.0 + 2.1 + 1.8	HCHO	HCHO
VOC22: Other aldehydes	0.5 + 3.4 + 10.0 0.6 + 0.8 + 2.0	MeCHO EtCHO	MeCHO
VOC23: Ketones	1.5 + 1.1 + 22.9 1.0 + 0.9 + 0.5	Me2CO MEK	Me2CO
VOC24: Acids	0.5 + 1.4 4.4 + 7.1 + 1.9	HCOOH MeCO2H	N/A
Total (TgC/year):	70.5 + 40.6 + 900.6		27.9 + 23.9 + 710.6

But how much does it all cost?...

Average Wallclock times per month at N96e ($1.875^\circ \times 1.25^\circ$ L85) after 200 months on 432 cores

Chemistry	Mean wall-clock time per month ± SE	Speed-up
StratTrop	4194 ± 6s ~ 1h 10m	+80%
CRI-Strat	7540 ± 7s ~ 2h 5m	-44%

- 1.8 x as expensive, … but with >> double the chemical complexity.

Not cheap, but long integration (decades-centuries) simulations are definitely feasible!

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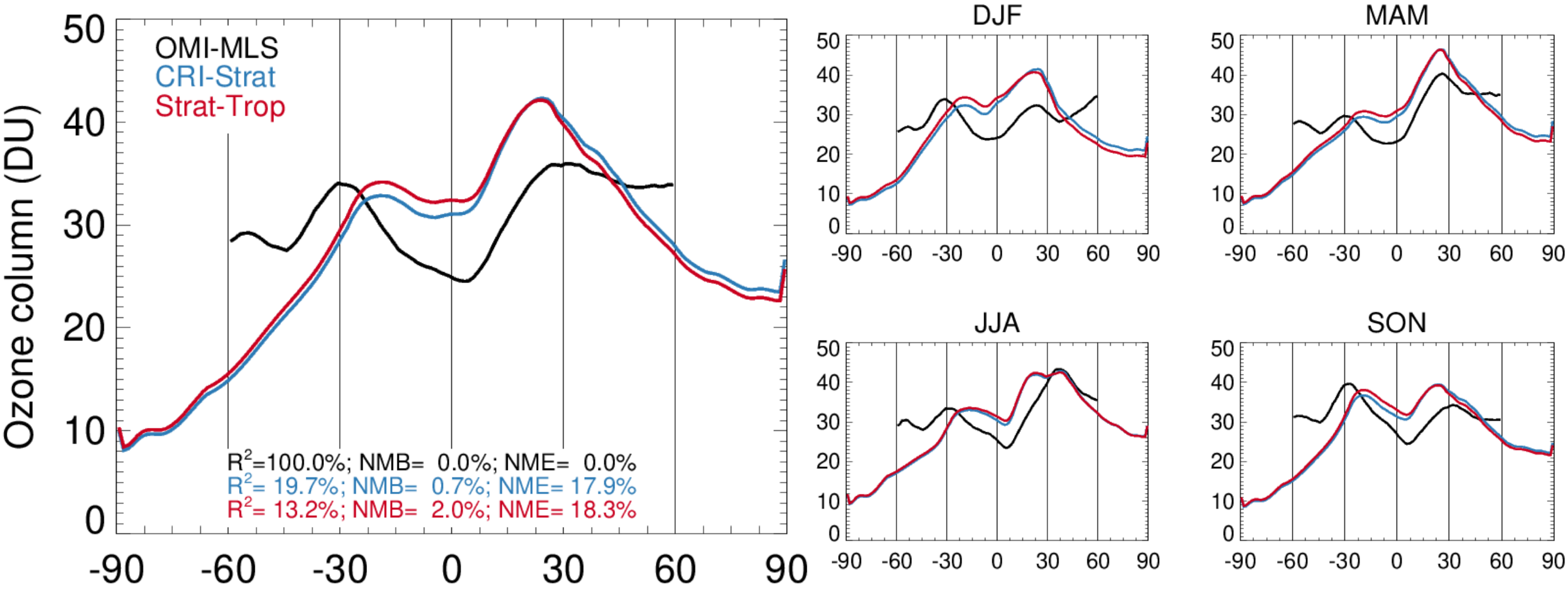
Seasonal & Zonal comparison Model vs OMI-MLS variation



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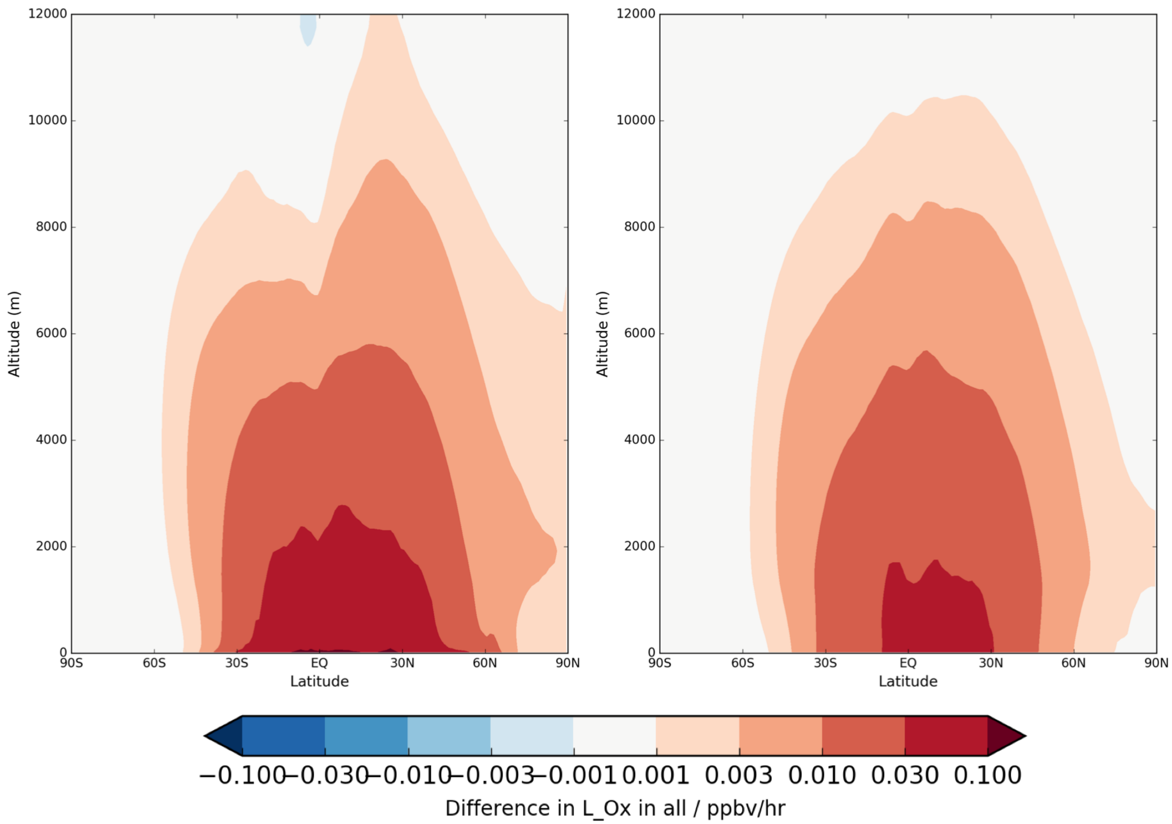
Loss of Ox due to O1D+H2O; CRI-Strat - StratTrop

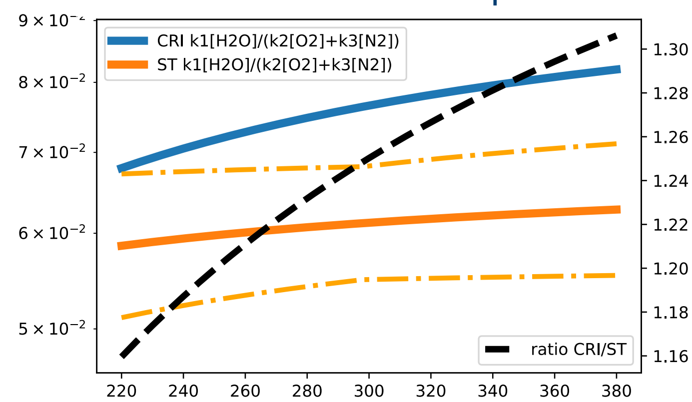
Difference in Ox Loss

Difference in O¹D+H2O Flux

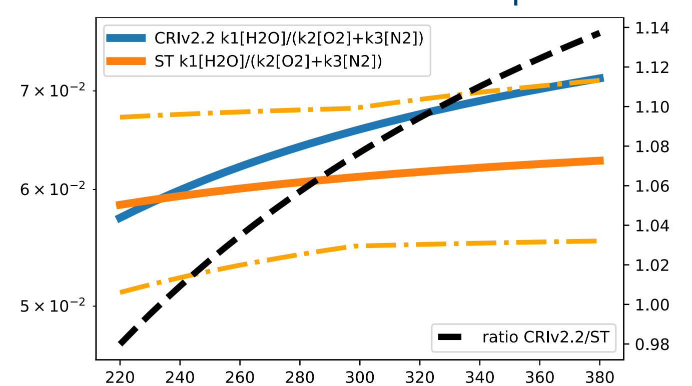


Ratio Flux (O¹D+H2O)/(O¹D+M)

CRIv2 & StratTrop



CRIv2.2 & StratTrop



Increased Ox loss in CRIv2 almost entirely driven by faster O1D + H2O flux

CRIv2.2 has updated rate much closer to StratTrop

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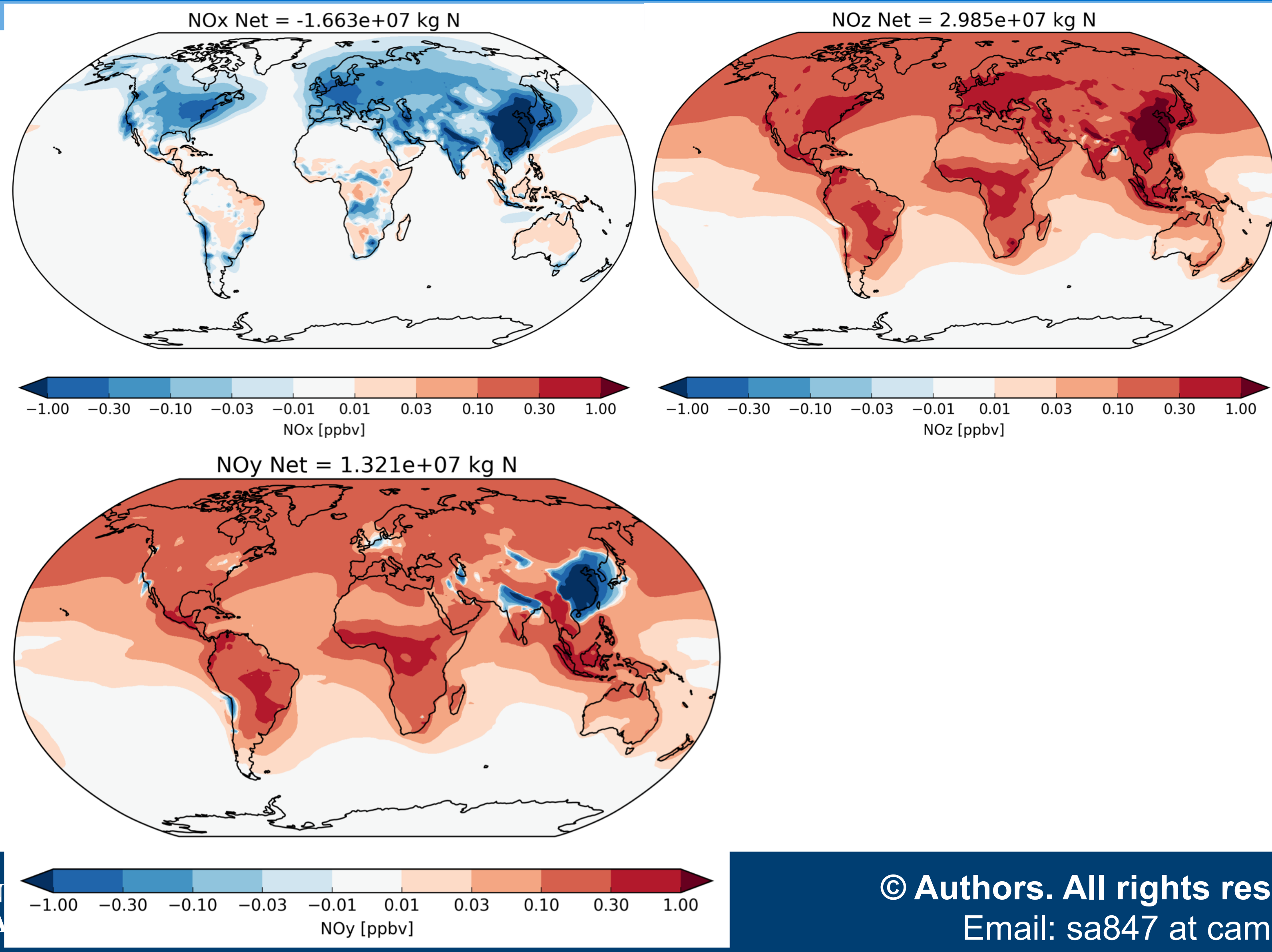
Boundary Layer NOy, CRI-Strat - StratTrop



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