Re-defining the standard - CRI-Strat: a new framework for chemistry developments within the UKCA model

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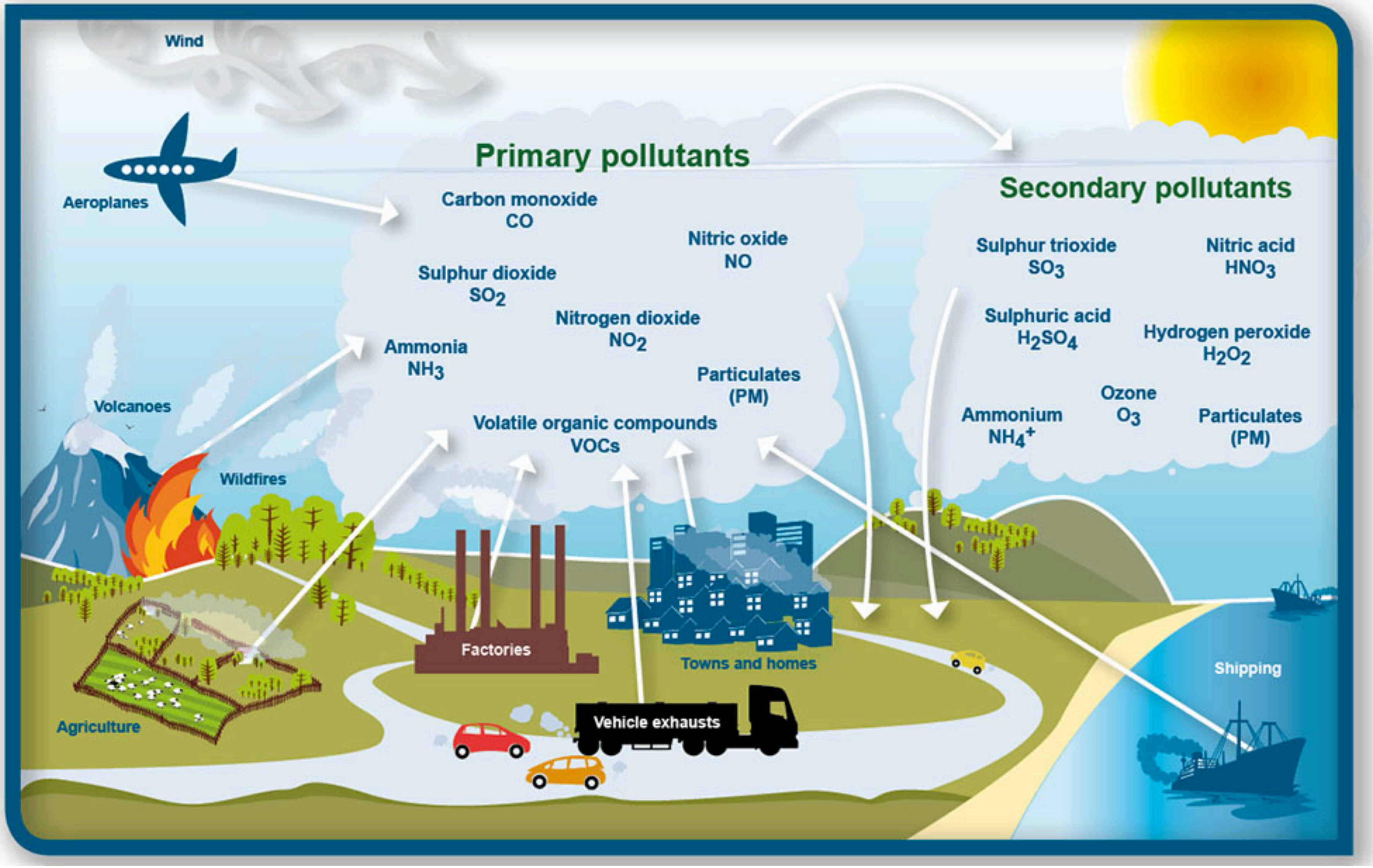
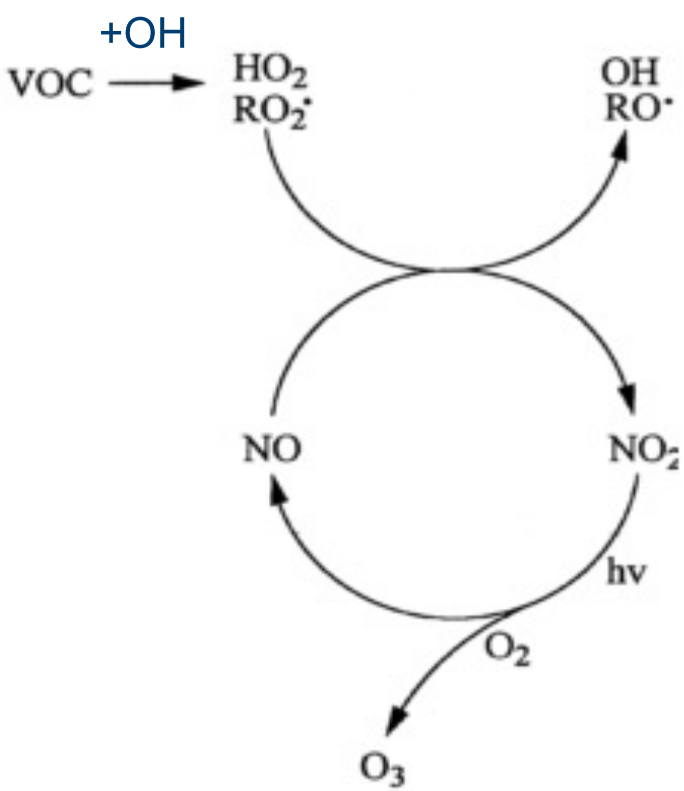
Modelling Tropospheric Chemistry



Recipe for Tropospheric Ozone

Catalytic cycle of tropospheric ozone production, Atkinson 2004



- OH radical can oxidise VOCs (and CO) to make peroxy radicals; e.g. for the simplest VOC:

$$CH_4 + OH \rightarrow CH_3^{\cdot} + H_2O$$
$$CH_3 + O_2 \rightarrow CH_3O_2$$

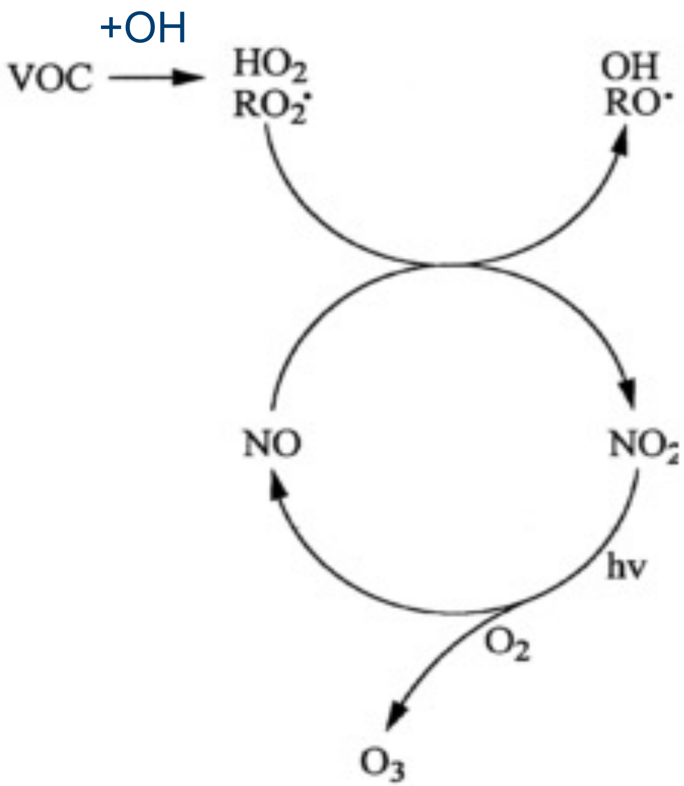
- Peroxy radicals react quickly with NO to make NO2, which photolyses to make ozone:

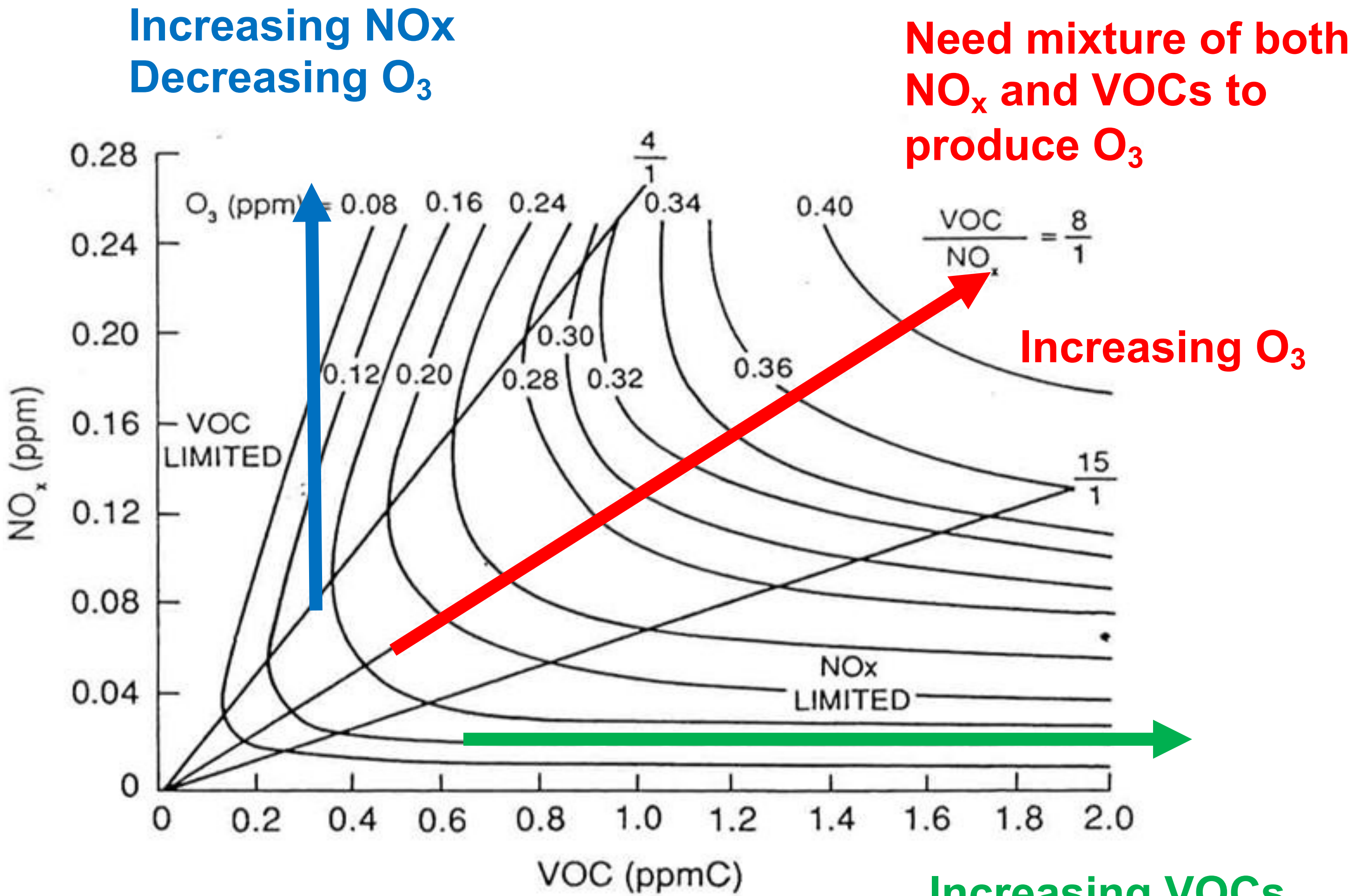
$$CH_3O_2^{\cdot} + NO \rightarrow NO_2 + CH_3O^{\cdot}$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O_2 + O + M \rightarrow O_3 + M$$

O_3 is a by-product of VOC oxidation reactions, catalysed by NO_x

Recipe for Tropospheric Ozone

Catalytic cycle of tropospheric ozone production, Atkinson 2004

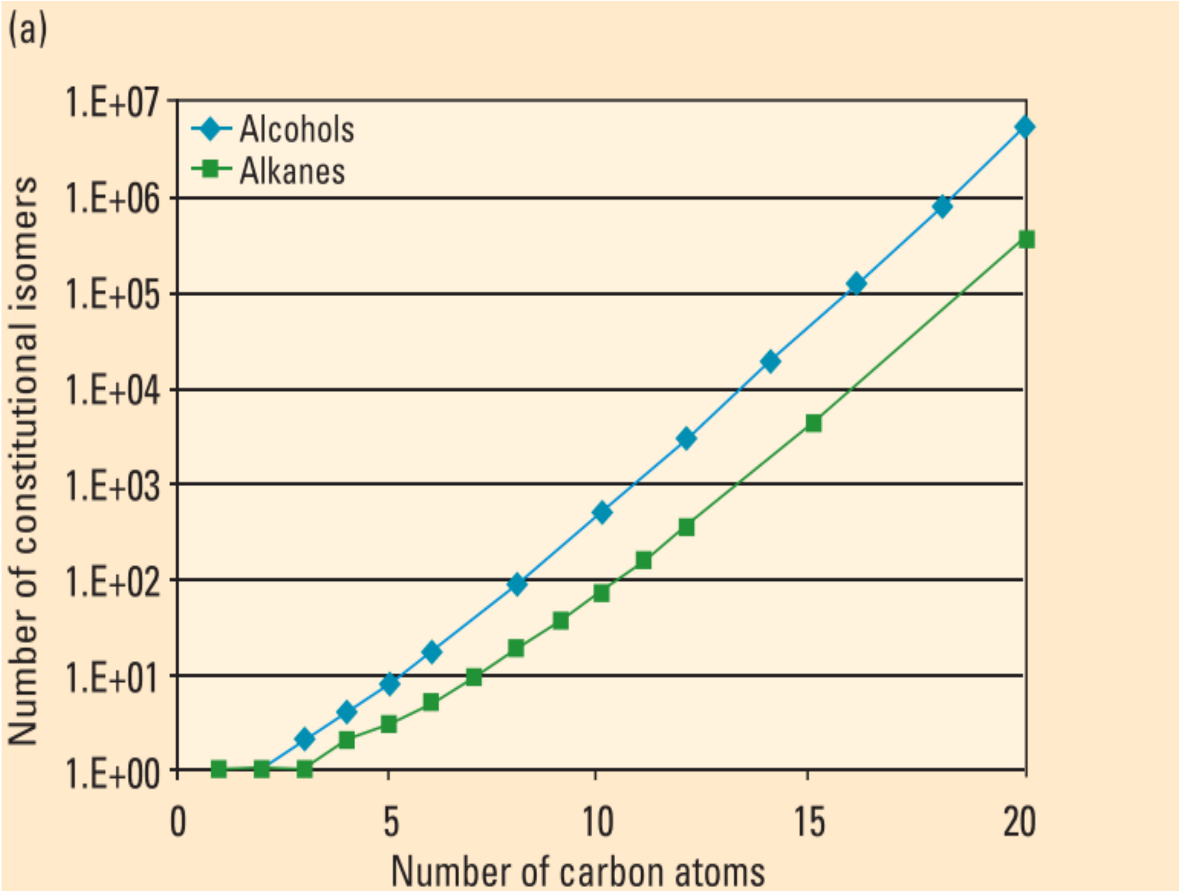




Ozone Isopleths, Dodge 1977

Problem: Deep Complexity of Volatile Organic Compound (VOC) Chemistry

- VOC and NOx photochemistry drives formation of Ozone and secondary organic aerosols.
- Very complicated - many 1000's of VOCs identified in the atmosphere.
- Need to parameterise tropospheric chemistry in 3D models. But how can we be confident the necessary simplifications preserve key processes?

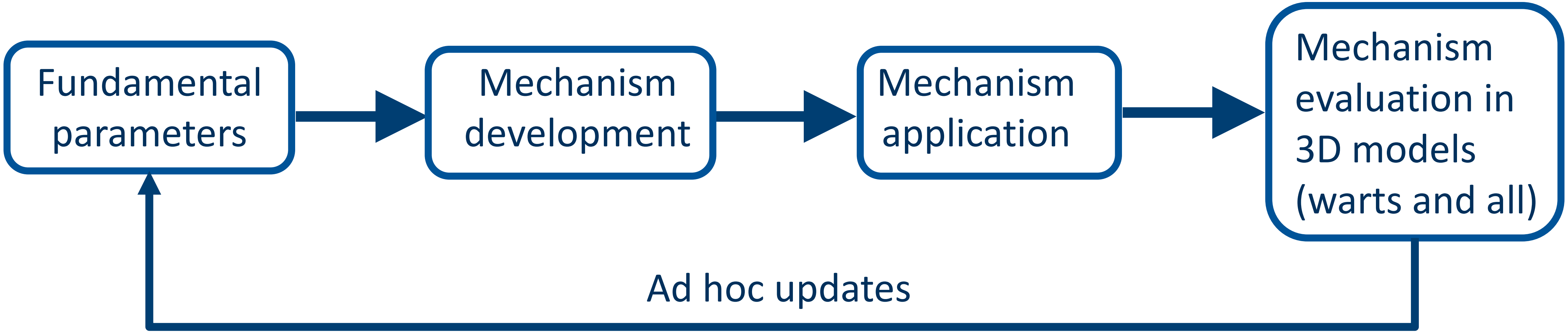


Goldstein et al., 2007

Models vs Reality

"Essentially, all models are wrong, but some are useful" George Box

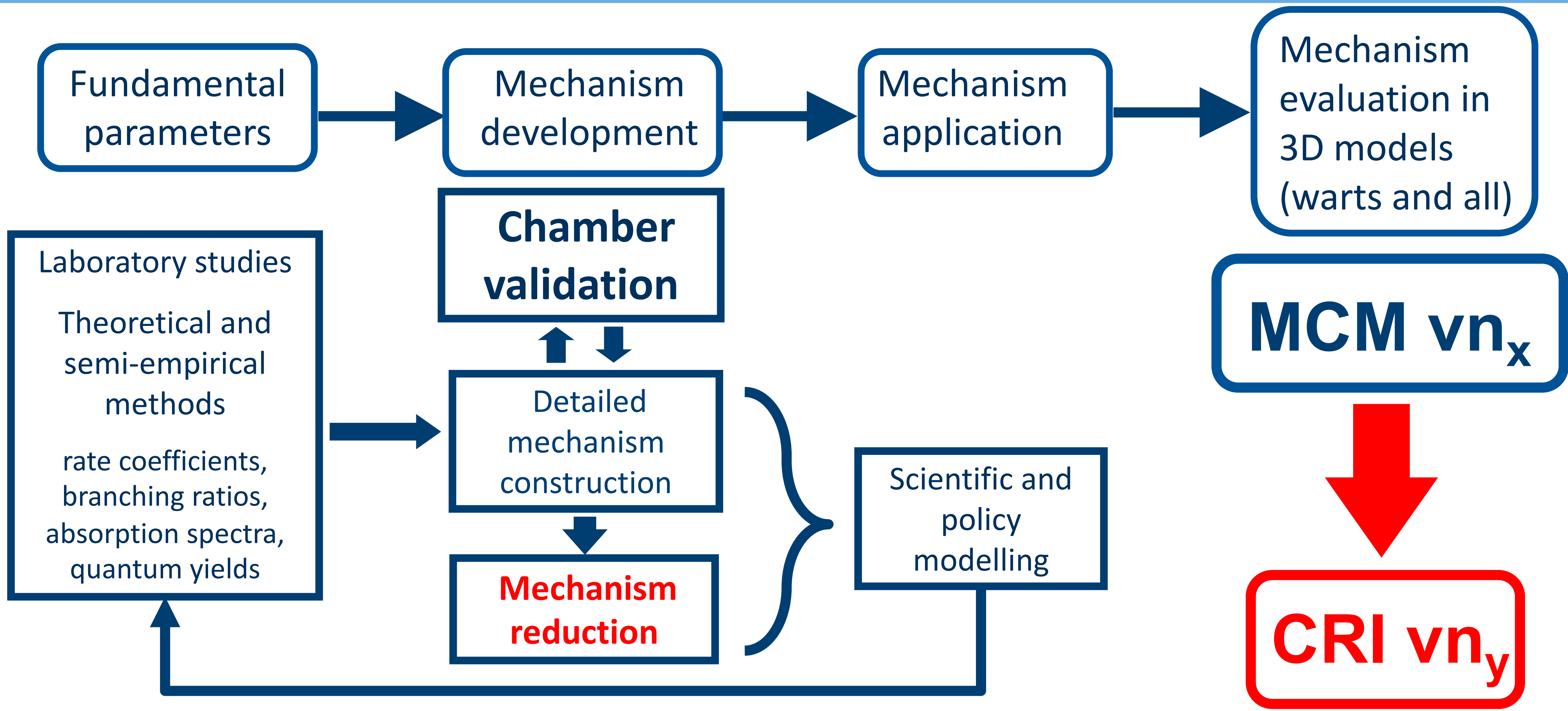
“Traditional” Chemical mechanism development (e.g. for StratTrop)



Issues

- How can we be sure the most “important” reactions are captured?
- Impossible to separate biases due to mechanism from other model errors.
- Risk of compounding errors as mechanism is expanded - different levels of complexity or sources of kinetic data for different aspects of chemistry.
- No **traceability** to explicit mechanisms.

The Common Representative Intermediates Approach



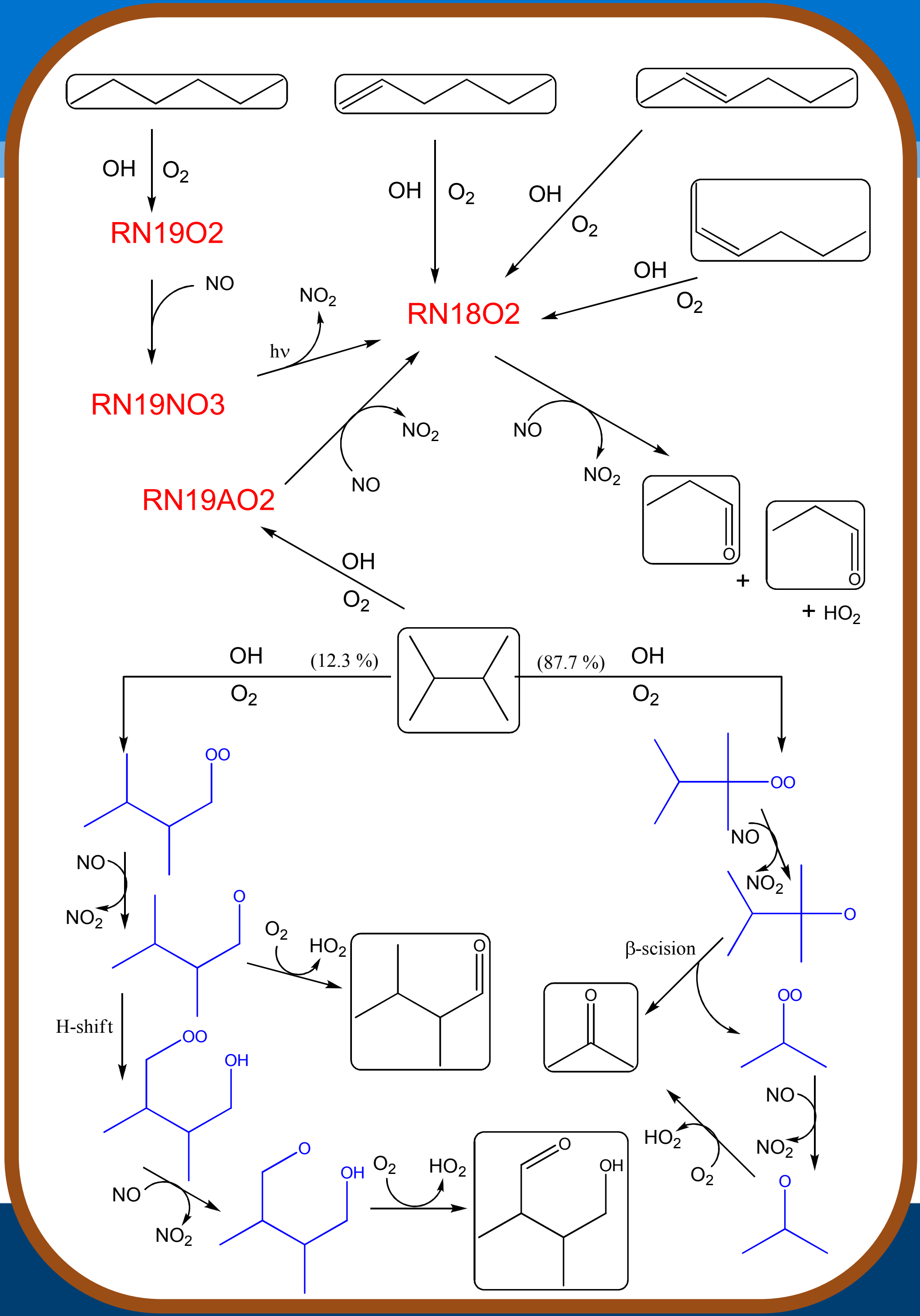
Common Representative Intermediates

Master Chemical Mechanism (MCM) chemistry highlights the complex oxidation of one C_6 alkane.

The CRI approach is one which conserves the O_3 forming potential of VOCs. Lumping the intermediate reactive products (RO_2 and their daughters).

Each version of CRI fully **traceable** to a version of the MCM

Further reductions: primary VOCs are lumped only if ozone production is conserved, as tested by rigorous evaluation against MCM.



CRI Implementation in UKCA

Common Representative Intermediates (CRIv2.1-R5) **traceable** to MCMv3.2

Extended with Stratospheric & aerosol chemistry to make CRI-Strat+GLOMAP:

- 233 species (181 transported) and 724 reactions

	StratTrop + GLOMAP-mode	CRI-v2-R5	CRI-Strat	CRI-Strat + GLOMAP-mode
No. Species	87	198	219	233
No. Tracers	83	146	167	181
No. Non transported prognostics	4	52	52	52
No. Peroxy radicals*	9	47	47	47
No. Emitted species	23	27	27	38
No. Photolysis reactions	60	100	124	128
No. Bimolecular reactions	212	451	536	554
No. Termolecular reactions	25	29	36	39
No. Heterogeneous reactions	8	0	5	8
No. Wet deposited species	34	74	80	83
No. Dry deposited species	41	124	128	131

* Peroxy radicals are transported tracers in the StratTrop mechanism,

Additional chemistry to StratTrop:

- Alkanes & alkenes up to C4
- Aromatics (benzene, toluene & o-xylene).
- Detailed BVOC chemistry.
- Organic nitrates (RO2+NO → RONO2) for all relevant species.
- Self- and cross- reactions parameterized for all 47 RO2 species.
- All available VOC emission classes mapped.

CRI Implementation in UKCA
AKA Alice and Bob on steroids

Followed step-by-step process:

- Add new species to STASHMASTER_A file (use existing species where possible), plus *m_** and *c_** values for each species
- Add bimolecular, termolecular and photolysis reactions for all new species to *ukca_chem_master* (use existing reactions where possible)
- Make emission files for species that are emitted and code to read emissions
- Add wet and dry deposition coefficients for species that are deposited
- Copied stratospheric and aerosol chemistry as needed
- Test, run, break, debug, cry, rinse, repeat…..

…UKCA training course exercises proved invaluable

STASHMASTER

```
1|    1 |   34 |  161 |CARB14 MASS MIXING RATIO AFTER TSTEP|
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000000100000000000 | 00000000000000000001 |    1 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  162 |CARB17 MASS MIXING RATIO AFTER TSTEP|
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000000100000000000 | 00000000000000000001 |    1 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  163 |CARB11A MASS MIXING RATIO AFTER TS  |
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000000100000000000 | 00000000000000000001 |    1 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  164 |CARB7 MASS MIXING RATIO AFTER TSTEP |
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000000100000000000 | 00000000000000000001 |    1 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  165 |CARB10 MASS MIXING RATIO AFTER TSTEP|
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000000100000000000 | 00000000000000000001 |    1 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  166 |CARB13 MASS MIXING RATIO AFTER TSTEP|
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000000100000000000 | 00000000000000000001 |    1 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  167 |CARB16 MASS MIXING RATIO AFTER TSTEP|
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000000100000000000 | 00000000000000000001 |    1 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
```

- Using existing tracers where possible and filling in spaces up to S34i150
- S34i151 to S34i249 all new CRI tracers

```
1|    1 |   34 |  872 |RTX2202 MASS MIXING RATIO AFTER TS  |
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000800000000000000 | 00000000000000000001 |    3 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  873 |RTX2402 MASS MIXING RATIO AFTER TS  |
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000800000000000000 | 00000000000000000001 |    3 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  874 |NRTX2802 MASS MIXING RATIO AFTER TS |
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000800000000000000 | 00000000000000000001 |    3 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
#
1|    1 |   34 |  875 |RTX2802 MASS MIXING RATIO AFTER TS  |
2|    2 |    0 |    1 |    1 |    2 |   40 |   11 |    0 |    0 |    0 |    0 |
3| 000000000000000800000000000000 | 00000000000000000001 |    3 |
4|    1 |    0 | -99  -99  -99  -99  -99  -99  -99  -99  -99  -99 |
5|    0 |    0 |    0 |   65 |    0 |    0 |    0 |    0 |    0 |
```

- S34i872 to S34i913 New Peroxy Radical Species
- Defined new RO2 type – non-transported prognostics that behave like normal chemical species within solver

CRIv2-R5 KPP file

http://cri.york.ac.uk/home.htt

Ukca_chem_master.F90

```
{190:095} HCOOH+OH=HO2 : 4.50D-13 ;
{191:096} CH3CO2H+OH=CH3O0 : 8.00D-13 ;
{192:097} CH3OO+NO=HCHO+HO2+NO2 : 0.999*ARR2( 3.00D-12, -280.0_dp, TEMP) ;
{193:098} C2H5O2+NO=CH3CHO+HO2+NO2 : 0.991*ARR2( 2.60D-12, -365.0_dp, TEMP) ;
{194:099} RN10O2+NO=C2H5CHO+HO2+NO2 : 0.980*ARR2( 2.80D-12, -360.0_dp, TEMP) ;
{195:100} IC3H7O2+NO=CH3COCH3+HO2+NO2 : 0.958*ARR2( 2.70D-12, -360.0_dp, TEMP) ;
{196:101} RN13O2+NO=CH3CHO+C2H5O2+NO2 : 2.40d-12*EXP(360.0/temp)*0.917*0.398 ;
{197:102} RN13O2+NO=CARB11A+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.917*0.602 ;
{198:103} RN16O2+NO=RN15AO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.877 ;
{199:104} RN19O2+NO=RN18AO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.788 ;
{200:105} RN13AO2+NO=RN12O2+NO2 : 2.40d-12*EXP(360.0/temp) ;
{201:106} RN16AO2+NO=RN15O2+NO2 : 2.40d-12*EXP(360.0/temp) ;
{202:107} RA13O2+NO=CARB3+UDCARB8+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.918 ;
{203:108} RA16O2+NO=CARB3+UDCARB11+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.889*0.7 ;
{204:109} RA16O2+NO=CARB6+UDCARB8+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.889*0.3 ;
{205:110} RA19AO2+NO=CARB3+UDCARB14+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.862 ;
{206:111} RA19CO2+NO=CARB9+UDCARB8+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.862 ;
{207:112} HOCH2CH2O2+NO=HCHO+HCHO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.995*0.776 ;
{208:113} HOCH2CH2O2+NO=HOCH2CHO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.995*0.224 ;
{209:114} RN9O2+NO=CH3CHO+HCHO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.979 ;
{210:115} RN12O2+NO=CH3CHO+CH3CHO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.959 ;
{211:116} RN15O2+NO=C2H5CHO+CH3CHO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.936 ;
{212:117} RN18O2+NO=C2H5CHO+C2H5CHO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.903 ;
{213:118} RN15AO2+NO=CARB13+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.975 ;
{214:119} RN18AO2+NO=CARB16+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.946 ;
{215:120} CH3CO3+NO=CH3OO+NO2 : 8.10d-12*EXP(270.0/temp) ;
{216:121} C2H5CO3+NO=C2H5O2+NO2 : 8.10d-12*EXP(270.0/temp) ;
{217:122} HOCH2CO3+NO=HO2+HCHO+NO2 : 8.10d-12*EXP(270.0/temp) ;
{218:123} RN8O2+NO=CH3CO3+HCHO+NO2 : 2.40d-12*EXP(360.0/temp) ;
{219:124} RN11O2+NO=CH3CO3+CH3CHO+NO2 : 2.40d-12*EXP(360.0/temp) ;
{220:125} RN14O2+NO=C2H5CO3+CH3CHO+NO2 : 2.40d-12*EXP(360.0/temp) ;
{221:126} RN17O2+NO=RN16AO2+NO2 : 2.40d-12*EXP(360.0/temp) ;
{222:127} RU14O2+NO=UCARB12+HO2+ NO2 : 2.40d-12*EXP(360.0/temp)*0.900*0.252 ;
{223:128} RU14O2+NO=UCARB10+HCHO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.900*0.748 ;
{224:129} RU12O2+NO=CH3CO3+HOCH2CHO+NO2 : 2.40d-12*EXP(360.0/temp)*0.7 ;
{225:130} RU12O2+NO=CARB7+CO+HO2+NO2 : 2.40d-12*EXP(360.0/temp)*0.3 ;
{226:131} RU10O2+NO=CH3CO3+HOCH2CHO+NO2 : 2.40d-12*EXP(360.0/temp)*0.5 ;
```

"cs" signifier to include in CRI-Strat scheme

```
! B143 IUPAC2007 see also asad_bimol
ratb_t1(143,'OH        ','C3H8      ','n-PrOO    ','H2O       ','          ',  &
'          ',7.60e-12,  0.00,  585.00, 0.00, 0.00, 0.00, 0.00,ti+t+st,0,0,107),&
! B143 - Different rates in CRI, and different product (equiv. to n-PrOO)
ratb_t1(143,'OH        ','C3H8      ','RN10O2    ','          ','          ',  &
'          ',2.01e-12,  0.00,  585.00, 0.00, 0.00, 0.00, 0.00,cs,0,0,107),     &
! B144 IUPAC2009
ratb_t1(144,'OH        ','C5H8      ','ISO2      ','          ','          ',  &
'          ',2.70e-11,  0.00, -390.00, 0.00, 0.00, 0.00, 0.00,ti+st,0,0,107),  &
ratb_t1(144,'OH        ','C5H8      ','HOIPO2    ','H2O       ','          ',  &
'          ',2.54e-11,  0.00, -410.00, 0.00, 0.00, 0.00, 0.00,r,0,0,107),      &
! B144 - Different rates and prods in CRI
ratb_t1(144,'OH        ','C5H8      ','RU14O2    ','          ','          ',  &
'          ',2.54e-11,  0.00, -410.00, 0.00, 0.00, 0.00, 0.00,cs,0,0,107),     &
! B145 JPL2011
ratb_t1(145,'OH        ','CH4       ','H2O       ','MeOO      ','          ',  &
'          ',2.45e-12,  0.00, 1775.00, 0.00, 0.00, 0.00, 0.00,st+r,0,0,107),   &
ratb_t1(145,'OH        ','CH4       ','H2O       ','MeOO      ','          ',  &
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"a" used to include/exclude for aerosol chemistry

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ratb_t1(317,'APINENE   ','OH        ','RTN28O2   ','          ','          ',  &
'          ',1.20e-11,  0.00, -444.00, 0.00, 0.00, 0.00, 0.00,cs,0,a,107),     &
ratb_t1(317,'APINENE   ','OH        ','RTN28O2   ','Sec_Org   ','          ',  &
'          ',1.20e-11,  0.00, -444.00, 1.00, 0.13, 0.00, 0.00,cs,a,0,107),     &
```
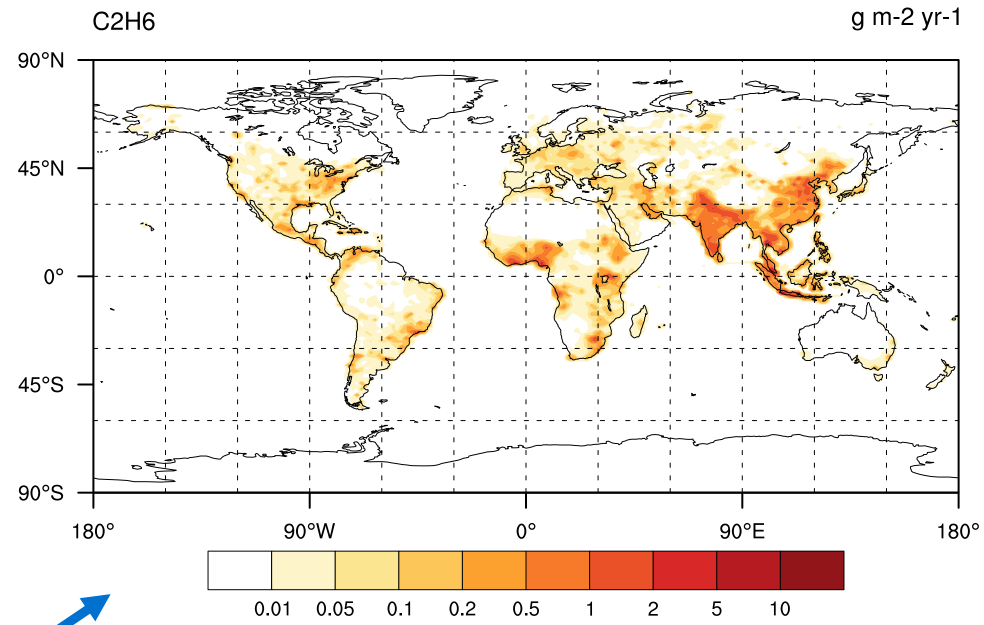

Emissions

Table 3. Mapping of raw CMIP6 NMVOC emissions to CRI-Strat and StratTrop mechanisms, with total emitted carbon mass for 2014 from Anthropogenic, biomass burning and biogenic sources.

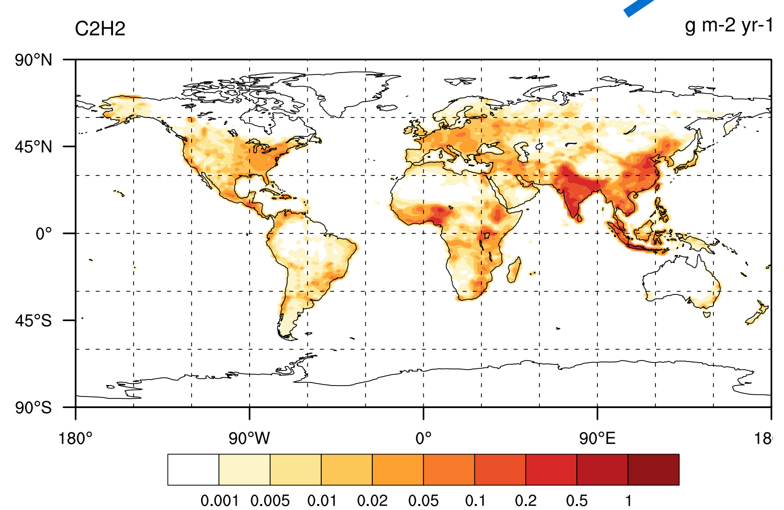
Raw emission classes	Anthropogenic $TgC\ yr^{-1}$	Biomass Burning $TgC\ yr^{-1}$	Biogenic $TgC\ yr^{-1}$	CRIv2-R5 Species	StratTrop Species
VOC1: Alcohols	0.4	3.5	48.5	MeOH	MeOH
	3.	0.1	9.5	EtOH	to MeOH
VOC2: Ethane	5.3	2.8	1.0	C2H6	C2H6
VOC7: Ethene	4.9	4.1	25.8	C2H4	to C2H6
VOC9: Ethyne	3.1	1.1	–	C2H2	to C2H6
VOC3: Propane	5.5	0.6	1.0	C3H8	C3H8
VOC8: Propene	3.0	3.5	14.	C3H6	to C3H8
VOC4-6: 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% to APINENE*	Monoterp†
				33% to BPINENE*	
VOC12: Other Alkenes and Alkyenes	6.5	0.8	2.6	TBUT2ENE	N/A
VOC13: Benzene	6.1	2.0	–	BENZENE	N/A
VOC14: Toluene	7.0	3.9	86.5	TOLUENE	N/A
VOC15-17: Xylenes and higher aromatics	3.1	1.1	–	oXYLENE	N/A
VOC21: Formaldehyde	1.0	2.1	1.8	HCHO	HCHO
VOC22: Other Aldehydes	0.5	3.4	10.0	MeCHO	MeCHO
	0.6	0.8	2.0	EtCHO	to MeCHO
VOC23: Ketones	1.5	1.1	22.9	Me2CO	Me2CO
	1.0	0.9	0.5	MEK	to Me2CO
VOC24: Acids	–	0.5	1.4	HCOOH	N/A‡
	4.4	7.1	1.9	MeCO2H	
Total CRI:	70.5	40.6	900.6		
Total StratTrop:	27.9	23.9	710.6		

C2H6 SUM = 16.7599 TG/yr

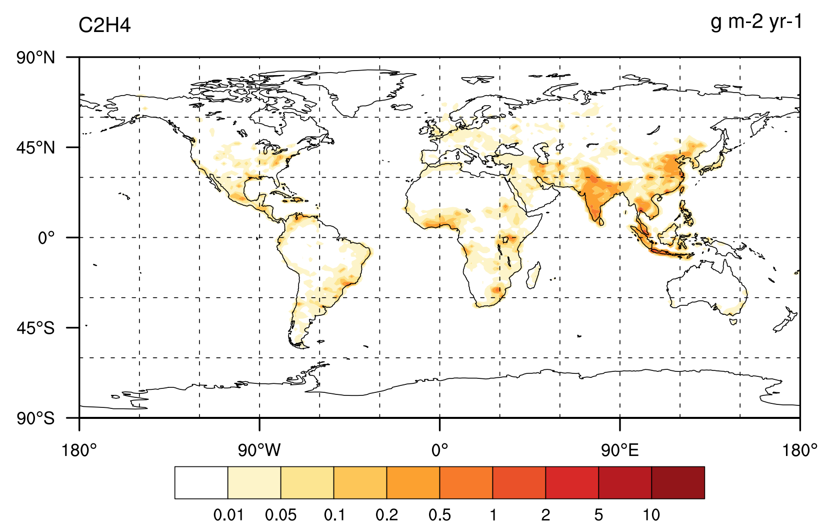


- All C2 emissions summed to ethane in StratTrop
- Separate ethyne, ethene and ethane emissions in CRI_Strat

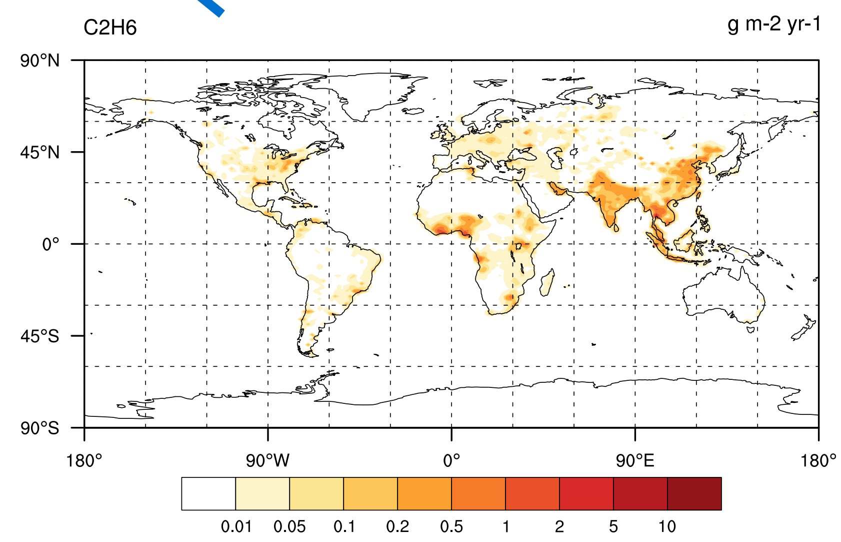
C2H2 Anthro SUM = 3.39239 TG/yr



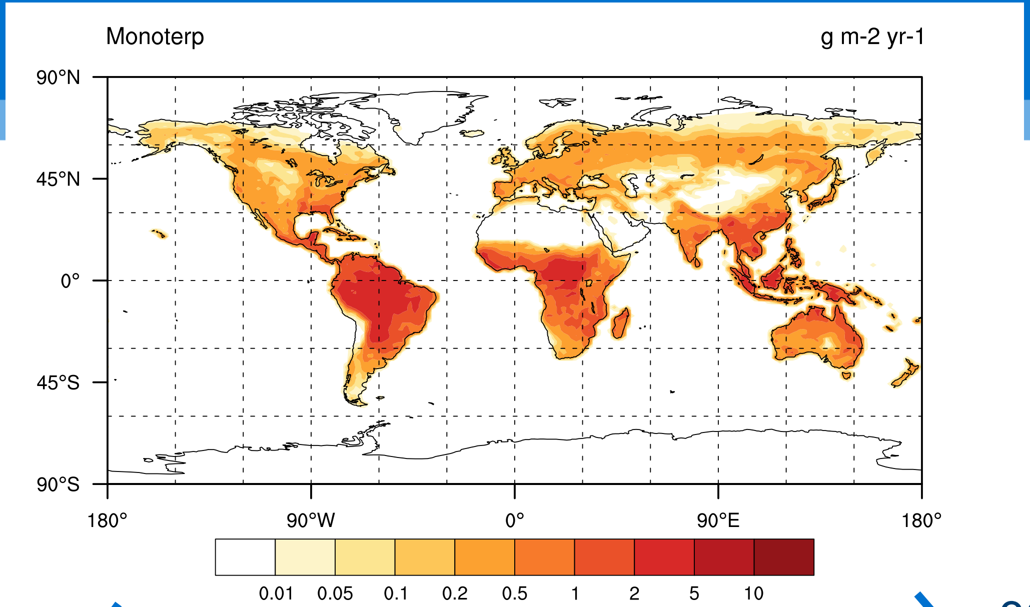
C2H4 Anthro SUM = 5.77303 TG/yr



C2H6 Anthro SUM = 6.65383 TG/yr

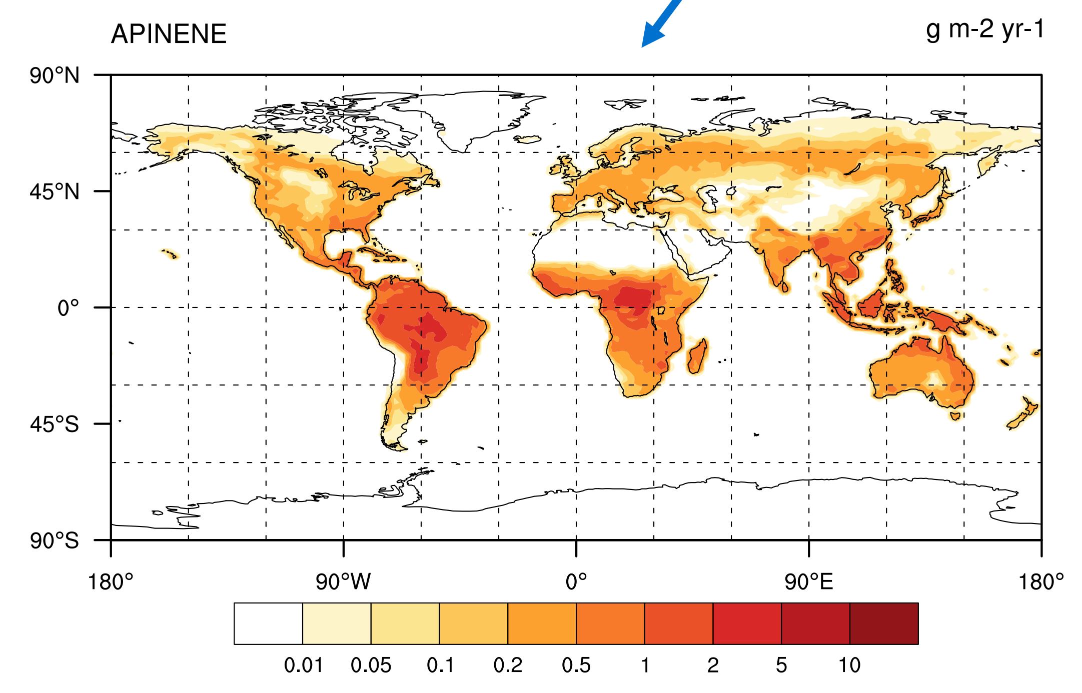


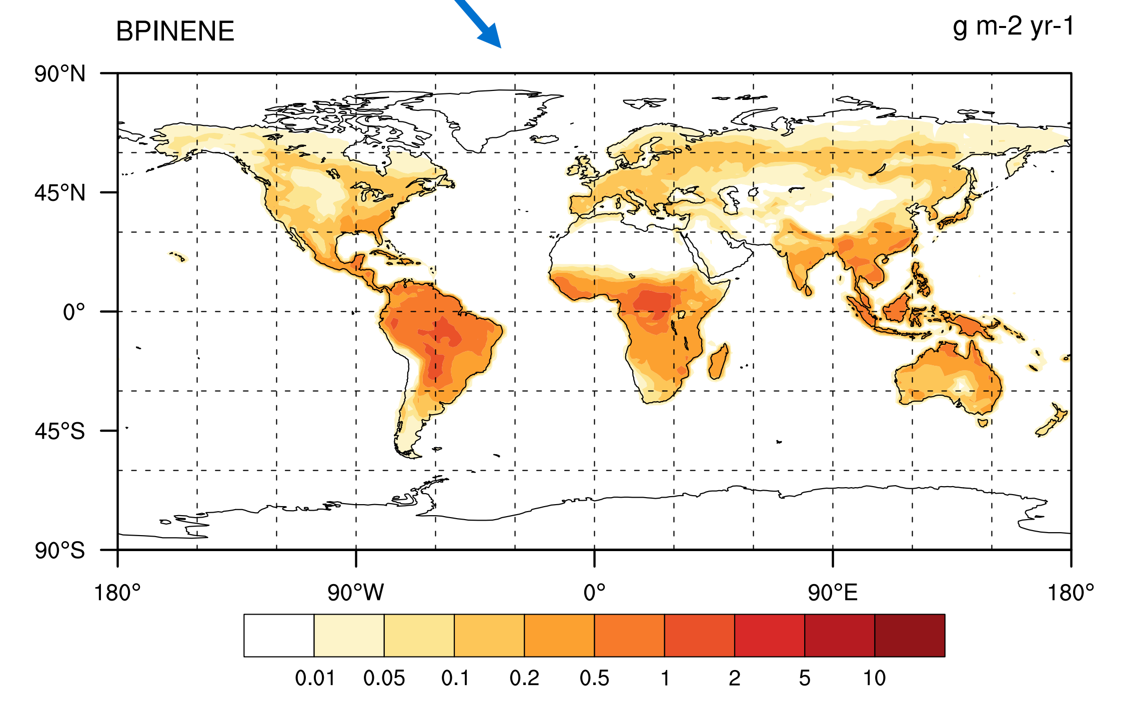
Monoterpene Emissions



67%

33%





Monoterpene Chemistry

- In StratTrop – very simple conversion of Monoterp to Sec_Org with 13% yield (usually doubled to 26%)

```
! B211
ratb_t1(211,'Monoterp  ','OH        ','Sec_Org   ','          ','          ',  &
'          ',1.20e-11,  0.00, -444.0, 0.13, 0.0, 0.0, 0.0, ti+st+ol+r,a,0,107),&
! B212
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```

- CRIv2-R5 has multigenerational alpha-pinene and beta-pinene chemistry, but no SOA production

- Added aerosol option with same yield of sec_org production

- James Weber working on further developments that will lead to more realistic description of SOA…

```
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```

RO2-permutation Chemistry

- In low-NOx high-VOC environments, peroxy radicals preferentially react with themselves (self-reactions) and other RO2 species (cross-reactions).

$$\begin{aligned} \mathrm{CH_3OO + CH_3OO} &\rightarrow \mathrm{2HO_2 + 2HCHO}; \quad \mathrm{BR_1 \times k} \\ &\rightarrow \mathrm{CH_3OH + HCHO}; \quad \mathrm{BR_2 \times k} \end{aligned}$$

- Can be efficiently replaced with "RO2-permutation" reactions, reacting with an "RO2-pool" (Jenkin et al., 1997):

$$RO2(i,j,k,t) = \sum_{i}^{N_{RO2}} RO2_i\,(i,j,k,t)$$

$$\begin{aligned} \mathrm{CH_3OO + RO_2} &\rightarrow \mathrm{HO_2 + HCHO}; \quad \mathrm{2 \times BR_1 \times k} \\ &\rightarrow \tfrac{1}{2}\mathrm{CH_3OH} + \tfrac{1}{2}\mathrm{HCHO}; \quad \mathrm{2 \times BR_2 \times k} \end{aligned}$$

- Much more comprehensive representation of RO2 chemistry with little additional cost.

N.b. RO2-permutation chemistry and removal of RO2 transport also added to StratTrop, version 11.3. See ticket #3959. Speeds up model run by ~2-3%!

But how much does it all cost?...

Average Wallclock times per month at N96e (1.875°×1.25° L85) after 200 months of integration on MONSooN2 with 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%

- Nearly twice as expensive… but with >> double the chemical complexity.

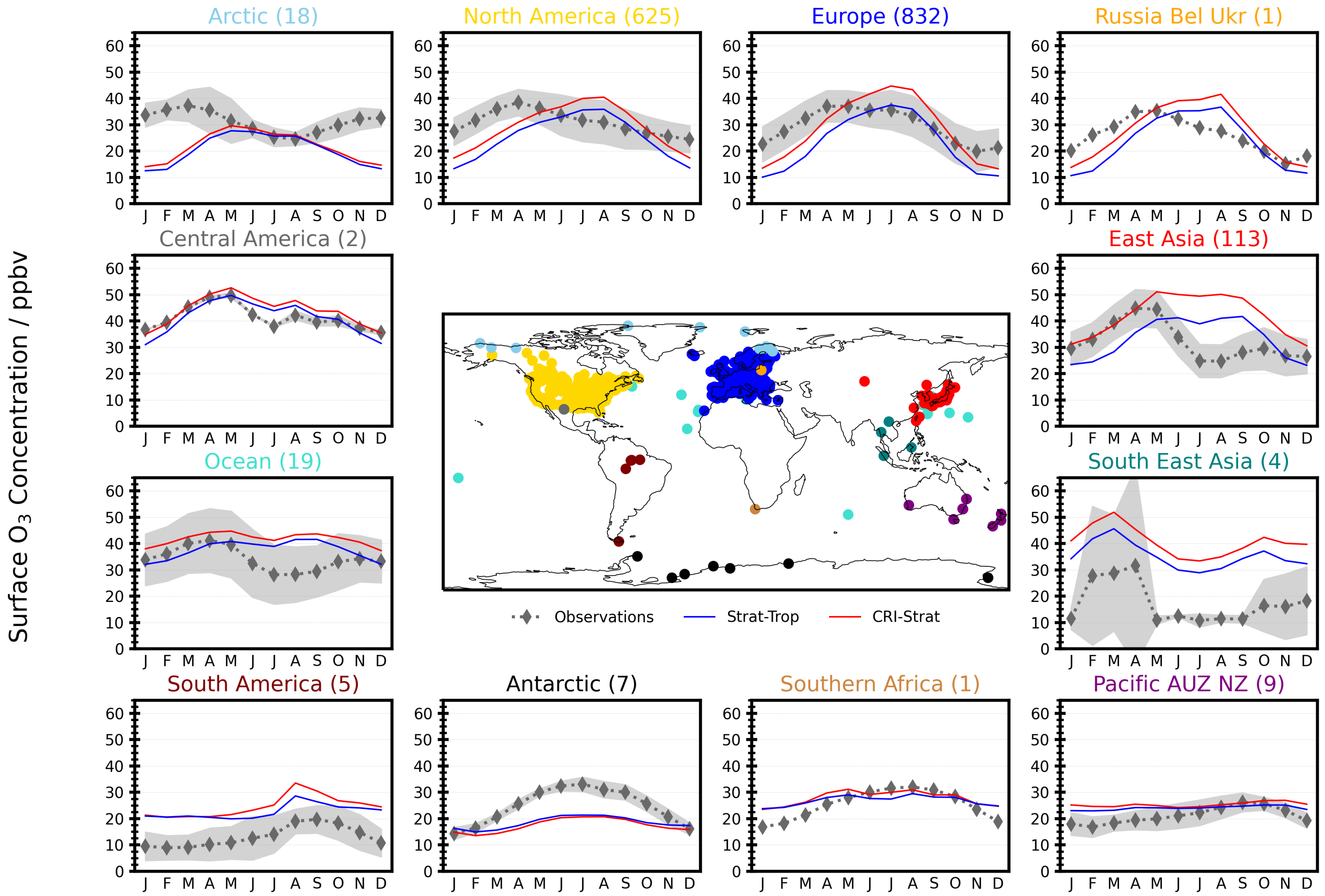
Not cheap, but long integration (decades-centuries) simulations are definitely feasible!

Experiments

- 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
  - Use additional runs to differentiate impact of chemistry vs NMVOC emissions

Scenario	Mechanism	NMVOC Emissions ($Tg\ C\ yr^{-1}$)
CRI-Strat	CRI-Strat	1012 - CRI speciation
StratTrop	StratTrop	762 - ST speciation
CRI_Emiss_ST	CRI-Strat	762 - ST speciation
CRI_Emiss_C2C3	CRI-Strat	762 - CRI speciation

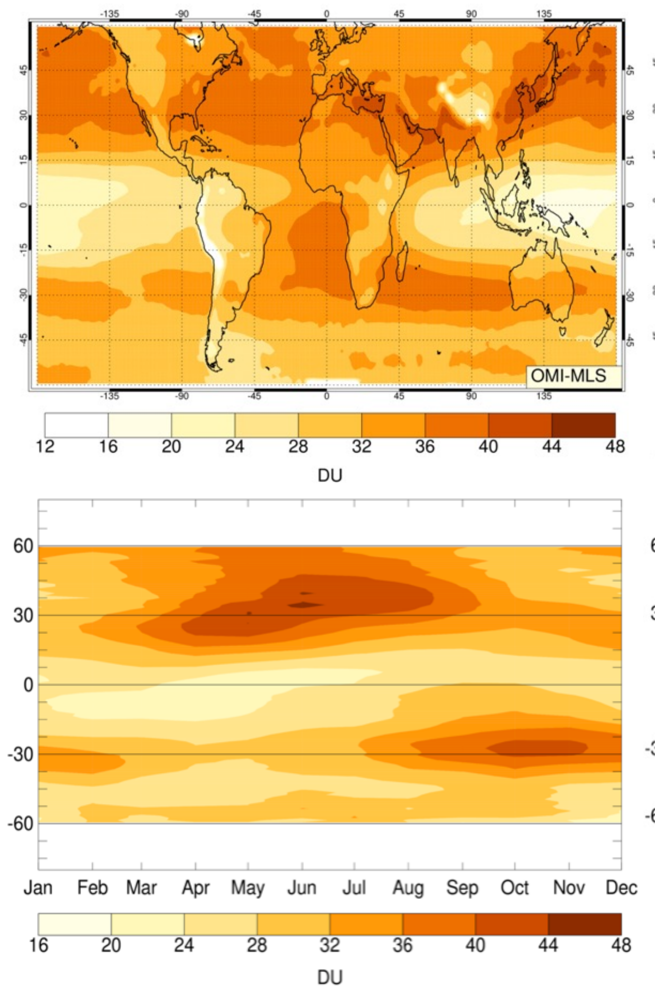
TOAR rural comparison



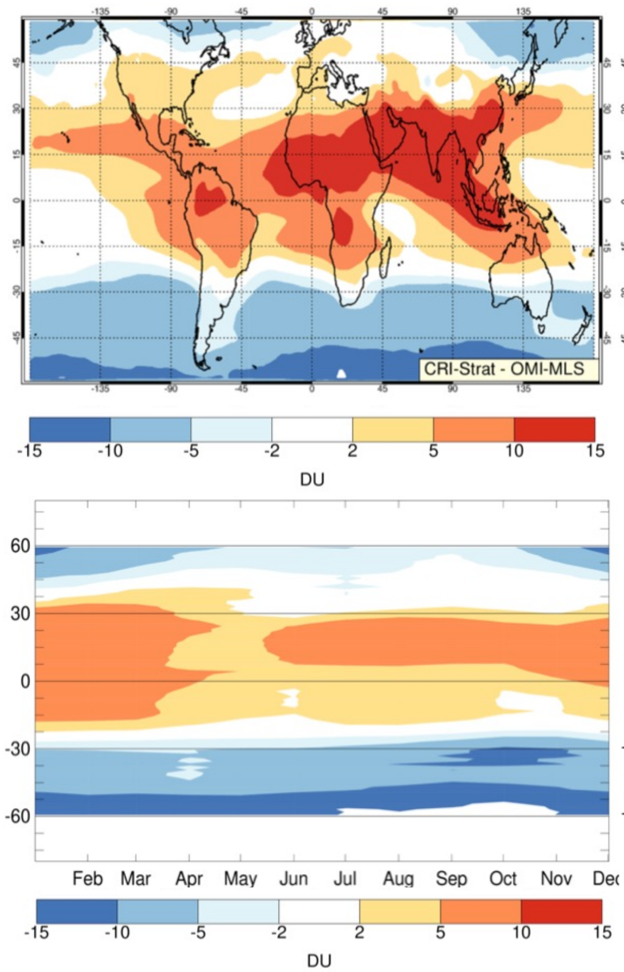
- Year-round increase in surface ozone in most regions
- Reduces winter low bias but increases summer high bias

Tropospheric ozone column vs OMI-MLS

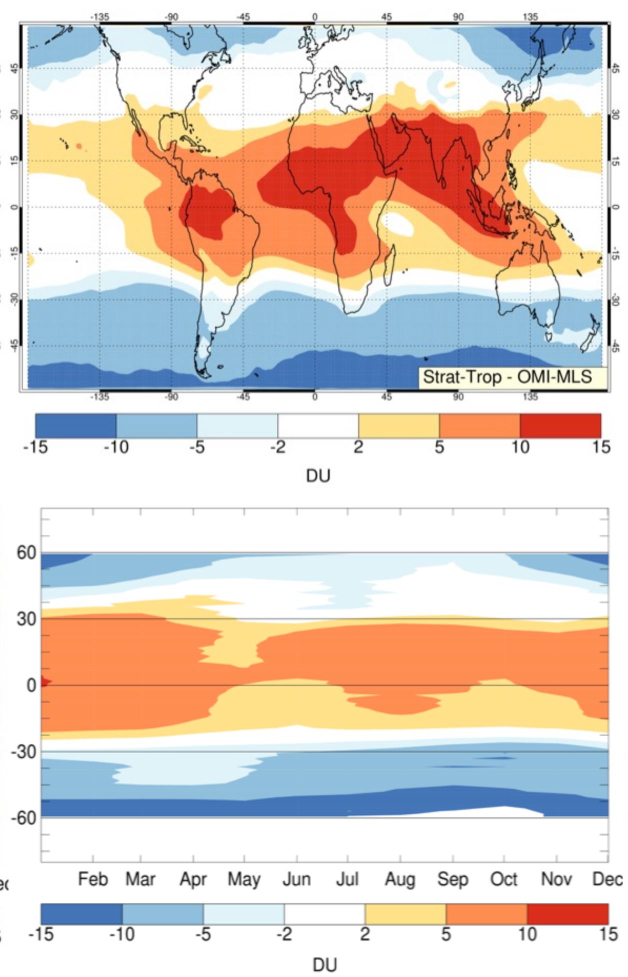
OMI-MLS
60N:60S Burden = 301 Tg



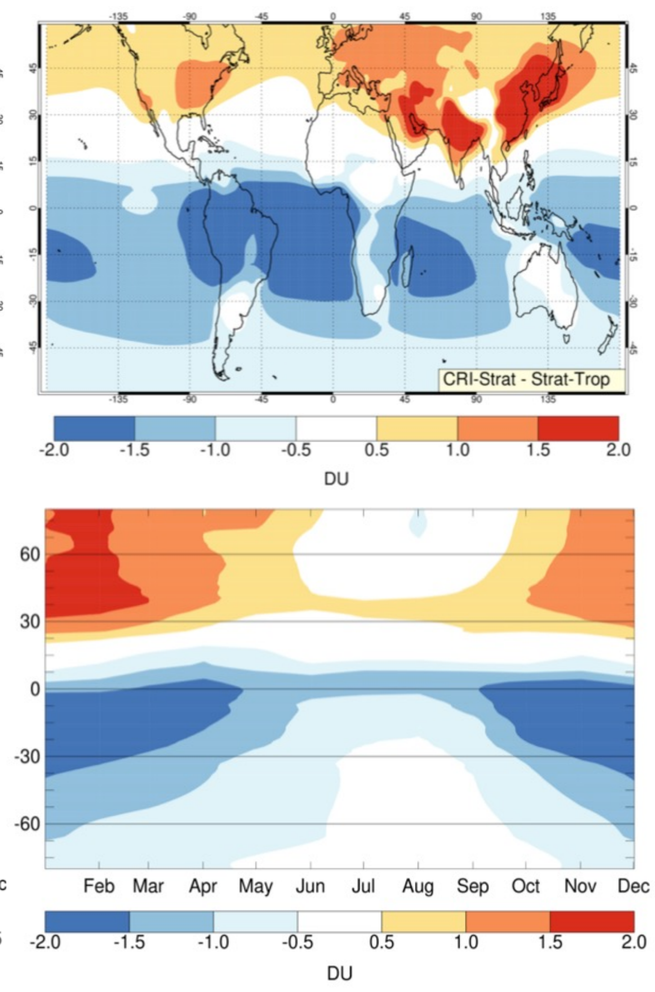
CRI-Strat – OMI-MLS
CS Burden = 303 Tg



StratTrop – OMI-MLS
ST Burden = 303 Tg



CRI-Strat - StratTrop



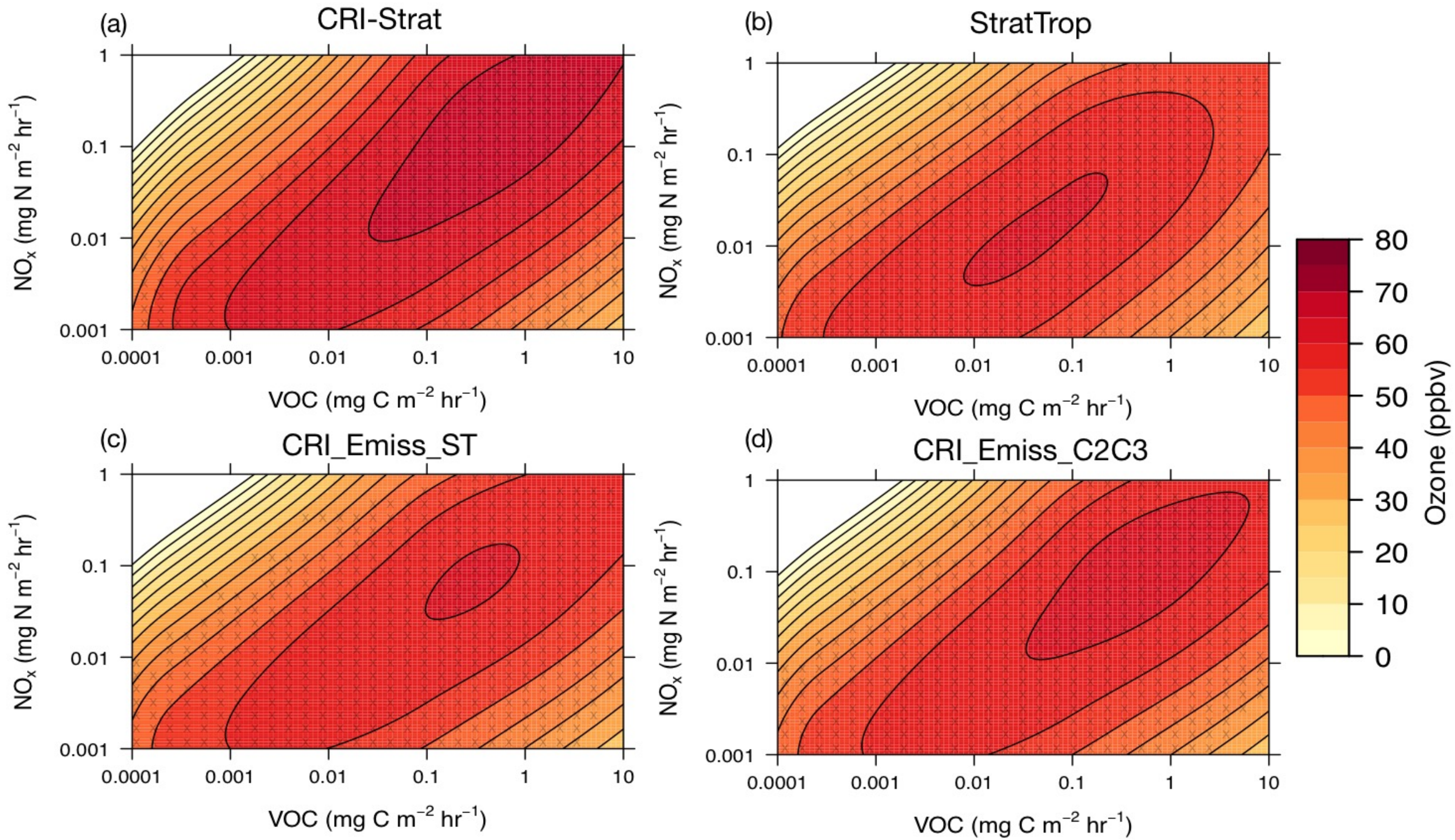
Ox production and loss

- Similar tropospheric ozone burden between CRI-Strart and ST
- But much more production and loss in CRI-Strat.
- How much of this extra production is due to additional NMVOC emissions in CRI-Strat?

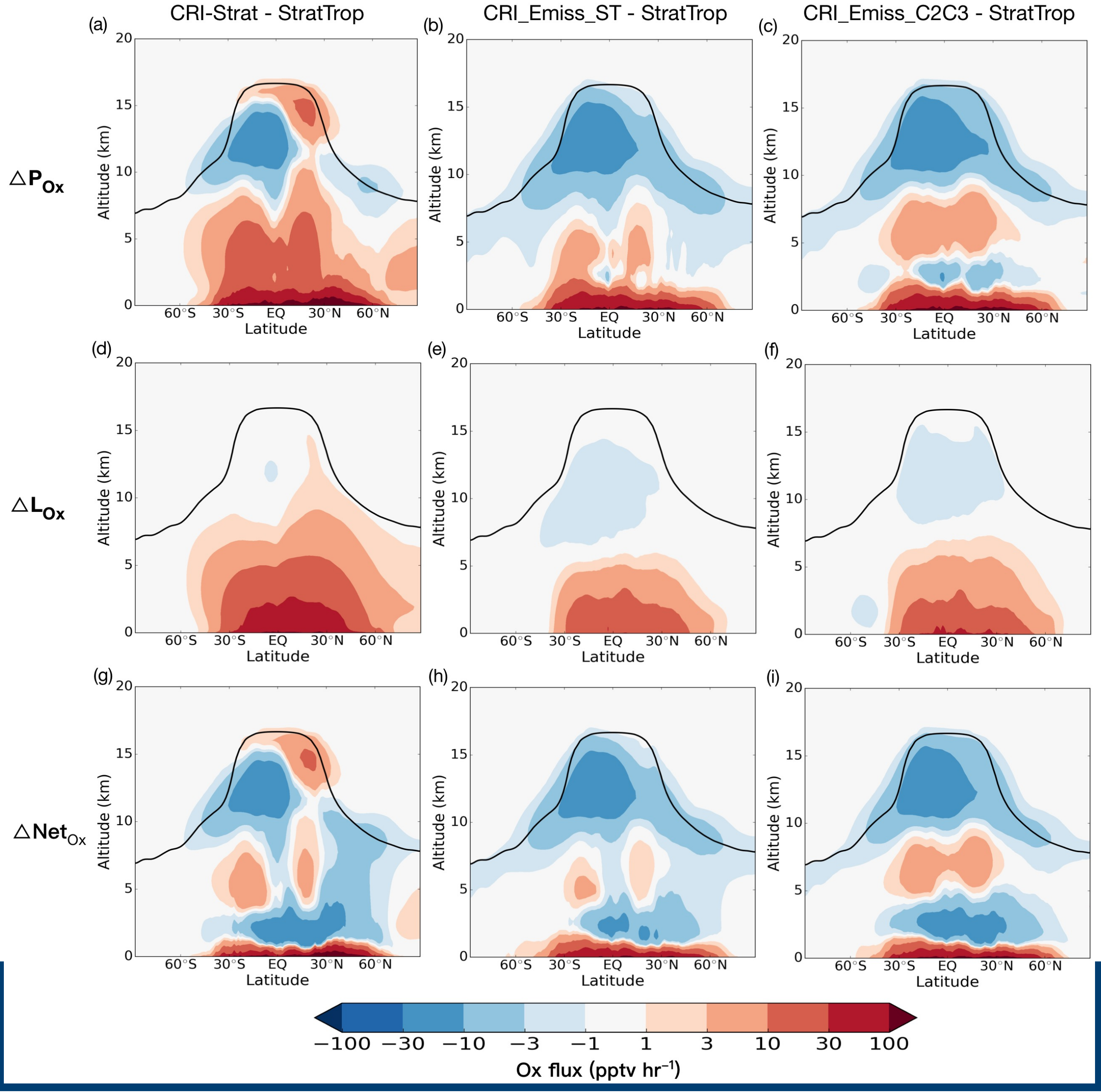
		CRI-Strat	StratTrop	CRI_STEmiss	CRI_C2-C3ExpEmiss
O_3 burden (Tg)		**331.9**	**336.8**	**308.0**	**306.8**
O_x lifetime (days)		17.3	19.8	17.5	17.4
NMVOC emissions (Tg C $year^{-1}$)		1012	762	762	762†
OPE ($mole_{O_3}\ mole^{-1}_{NOx}$)		31.4	27.2	28.7	28.9
O_x production	**Total**	**6624**	**5725**	**6057**	**6092**
(Tg O_3 $year^{-1}$)	$HO_2 + NO$	4152 (62.7%)	3853 (67.3%)	3886 (64.2%)	4001 (65.7%)
	$CH_3O_2 + NO$	1540 (23.3%)	1285 (22.5%)	1452 (24.0%)	1419 (23.3%)
	$R'O_2 + NO$	882 (13.3%)	545 (9.5%)	676 (11.2%)	629 (10.3%)
	Other	64.5 (0.7%)	41.3 (0.7%)	41.5 (0.7%)	43.2 (0.7%)
O_x chemical Loss	**Total**	**5853**	**5128**	**5355**	**5380**
(Tg O_3 $year^{-1}$)	$O(^1D) + H_2O$	3196 (45.5%)	2660 (42.9%)	3022 (47.1%)	3005 (46.6%)
	$HO_2 + O_3$	1713 (24.4%)	1596 (25.7%)	1498 (23.4%)	1513 (23.5%)
	$OH + O_3$	708 (10.1%)	714 (11.5%)	667 (10.4%)	680 (10.6%)
	O_3 + Alkene	160 (2.3%)	96.5 (1.6%)	115 (1.79%)	129 (2%)
	Other	76.3 (1.1%)	61.5 (1.0%)	53.1 (0.8%)	52.6 (0.8%)

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

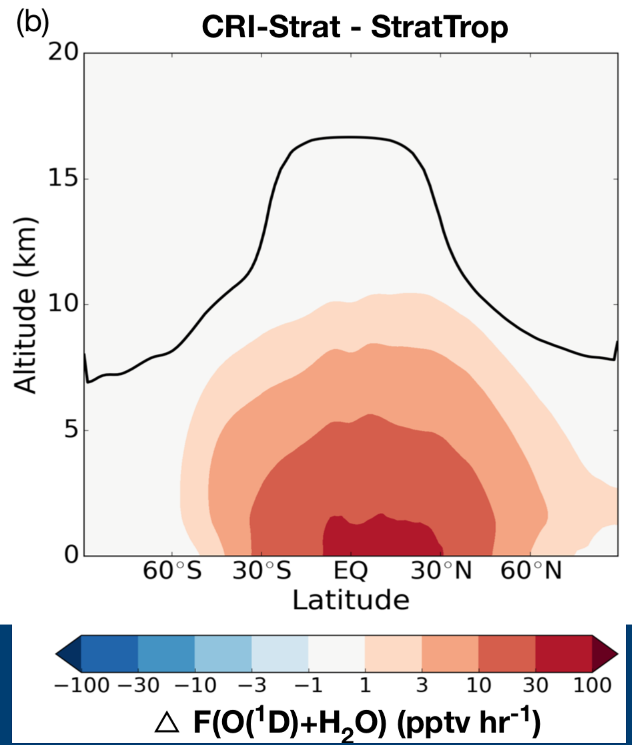
Ozone isopleths



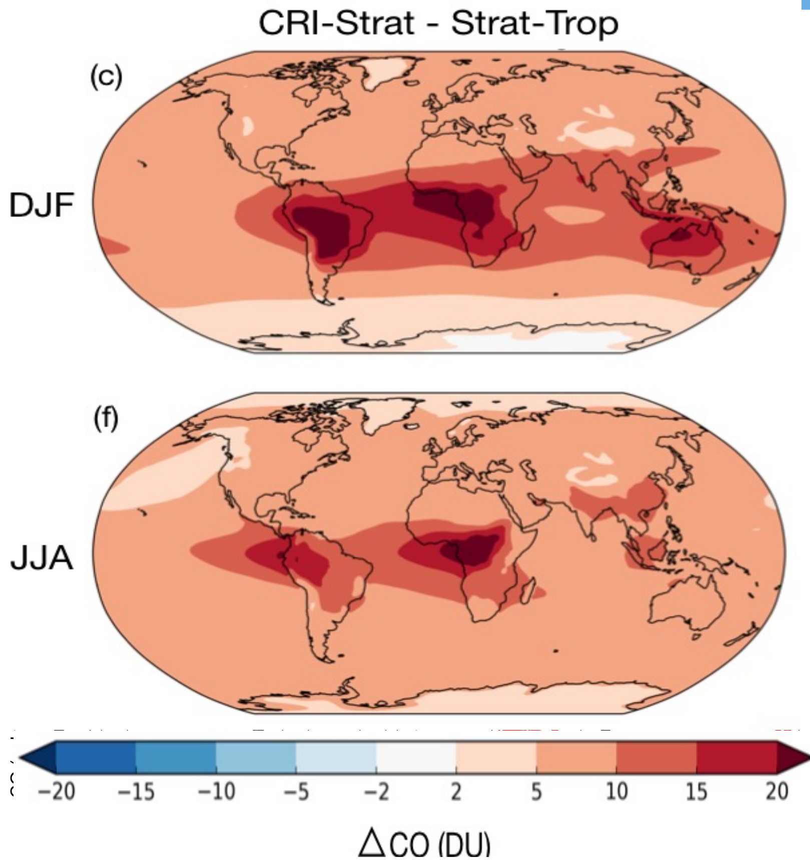
Difference in Ox Production and Loss



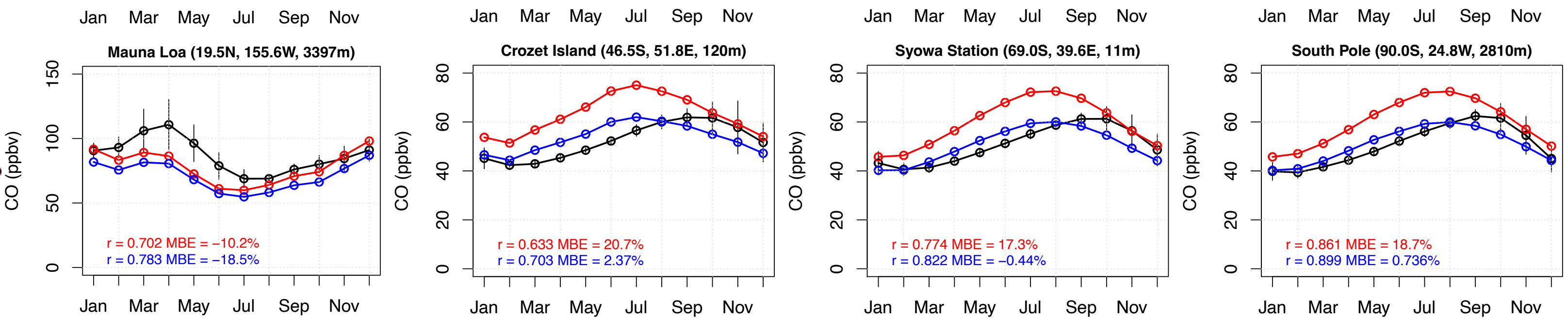
- CRI-Strat produces much more ozone downwind of emissions
- But loss is of Ox also much higher
  - Primarily due to O(1)D+H_2O – small difference in rate coefficients have large impact on ozone chemistry



Carbon Monoxide



Flux		CRI-Strat	StratTrop	CRI_Emiss_ST	CRI_Emiss_C2C3
CO burden (Tg)		354.9	300.2	317.2	315.2
CO lifetime (days)		39.1	38.6	38.1	37.2
CO production	**Total**	**3402**	**2915**	**3121**	**3171**
(Tg CO year^{-1})	Emissions	1111 (32.7%)	1111 (38.1%)	1111 (35.6%)	1111 (35%)
	HCHO + OH	580.3 (17.1%)	492 (16.9%)	551 (17.7%)	566 (17.8%)
	HCHO + $h\nu$	1293 (38%)	1076 (36.9%)	1163 (37.3%)	1177 (37.1%)
	Other Chem	125 (3.7%)	71.5 (2.5%)	101 (3.25%)	107 (3.4%)
	Other Phot	293 (8.6%)	164 (5.6%)	194 (6.23%)	211 (6.7%)
CO Loss	**Total**	**3311**	**2841**	**3041**	**3090**
(Tg CO year^{-1})	CO + OH	3157 (95.4%)	2704 (95.2%)	2900 (95.4%)	2948 (95.4%)
	CO Dry Dep	153 (4.6%)	137 (4.8%)	141 (4.7%)	142 (4.6%)



Greater CO in CRI-Strat due to secondary production, particularly from more explicit isoprene and monoterpene chemistry.

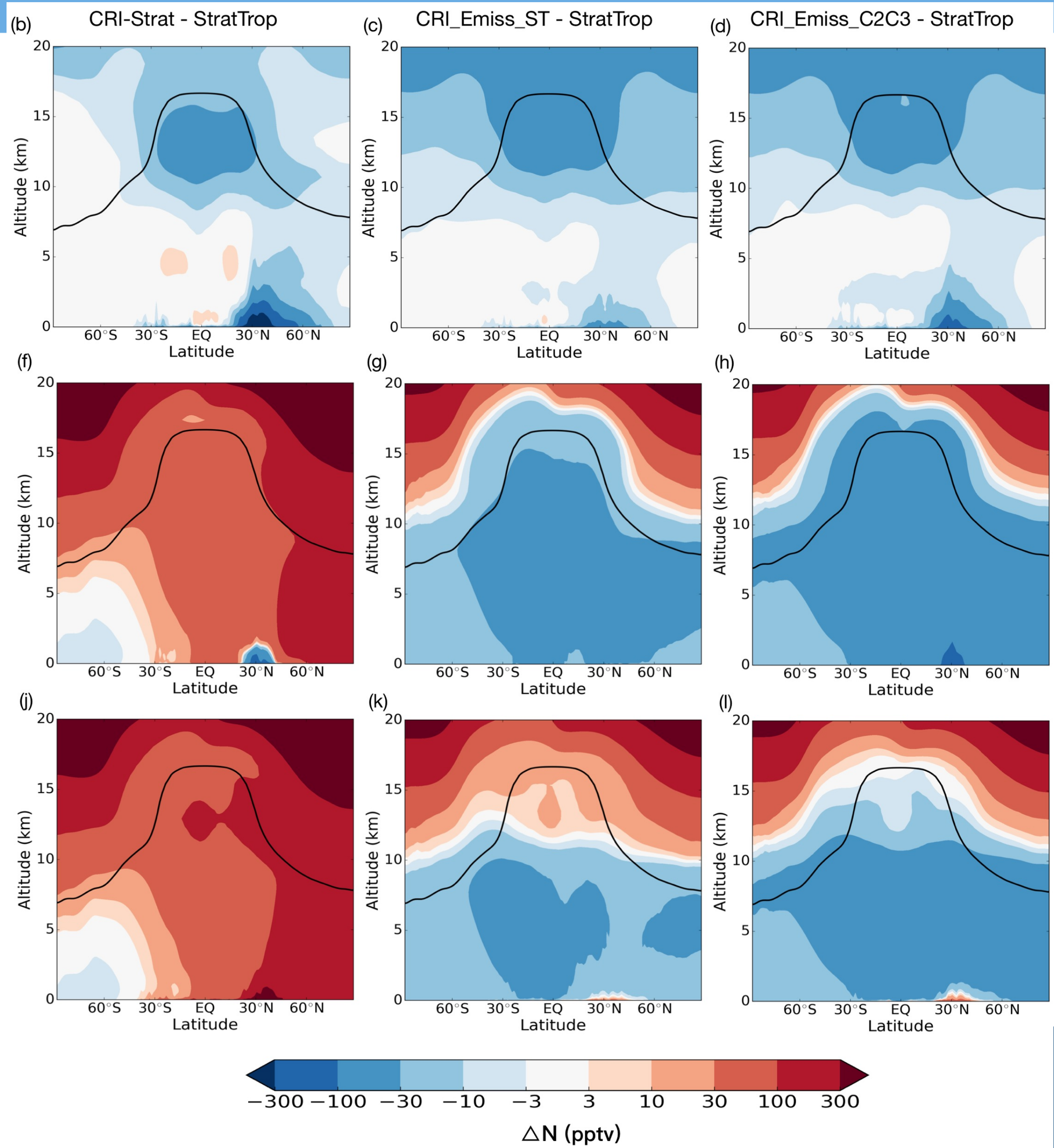
NOx, NOy and NOz

- Much less NOx in CRI-Strat
- More nitrogen stored in NOz reservoir species
- Additional NMVOCs provide more capacity to form RONO2

NOx

NOy

NOz



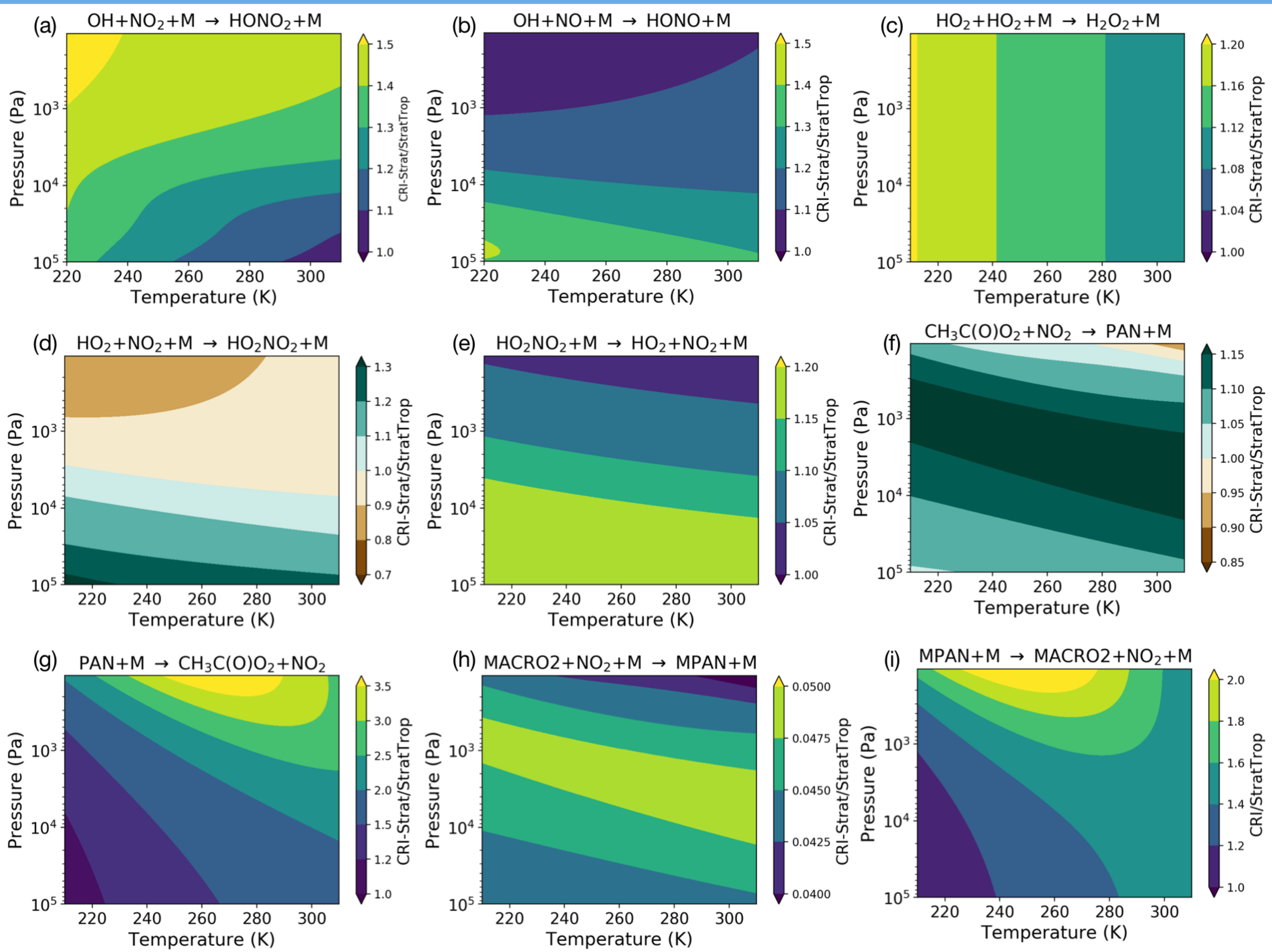
$NOx = NO + NO_2$

$NOz = NO_3 + 2 * N_2O_5 + HONO_2 + HO_2NO_2 + PAN + RONO_2 + \ldots$

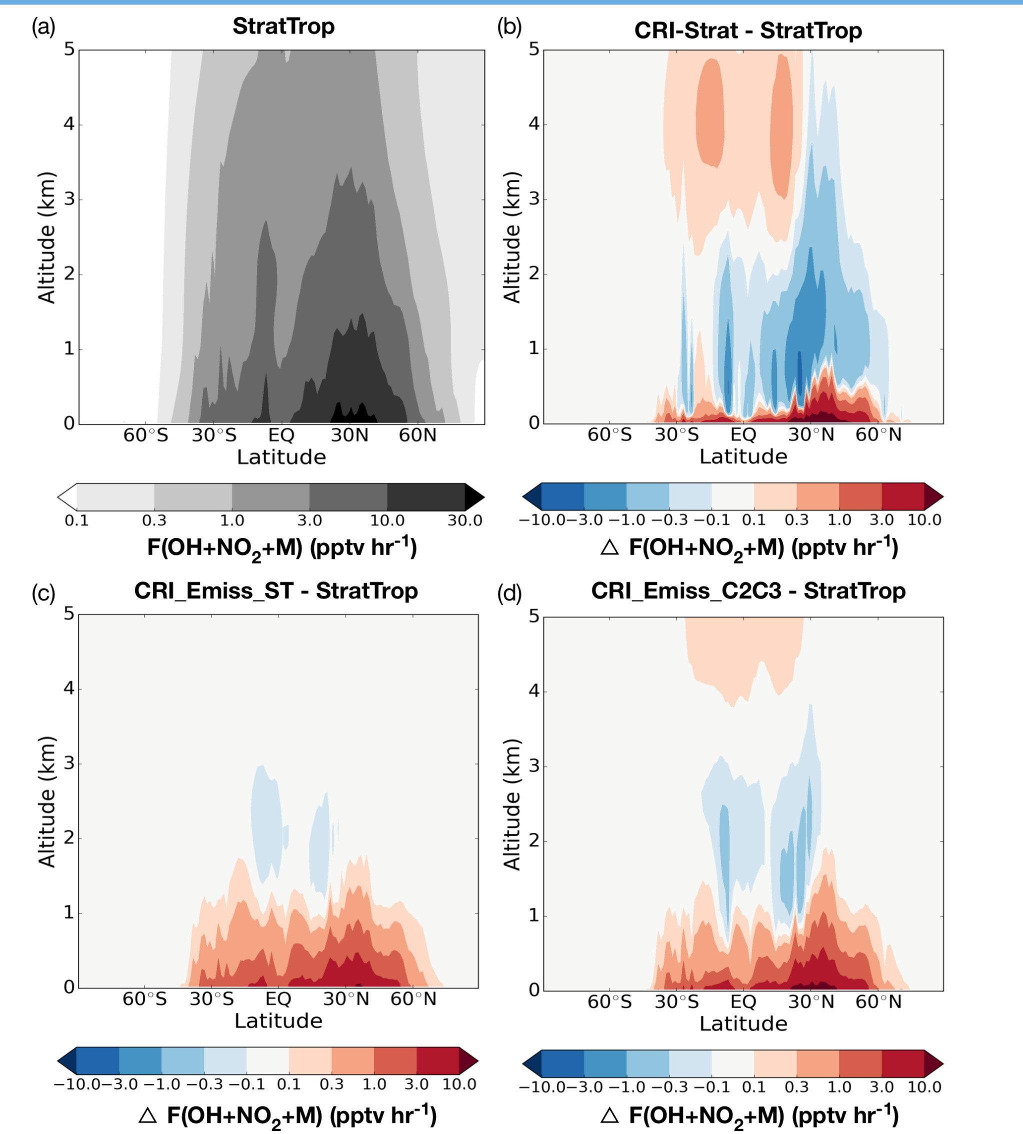
$NOy = NOx + NOz$

- CRI-Strat with ST emissions has much less NOx **and** NOz in the troposphere
- Due to small differences in HOx/NOx reaction rate coefficients:
- Faster production of HONO2 in boundary layer – faster loss via dry deposition

Differences in termolecular reaction rates Ratio CRI-Strat/StratTrop



HONO2 production



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Summary

- Comprehensive CRI-Strat mechanism, with detailed NMVOC chemistry built from CRIv2.1-R5, implemented in UKCA.

Pros:

- Much more detailed representation of VOCs, full use of emission inventory data
- **Traceability** of Ozone forming potential to Master Chemical Mechanism
- Improved aromatic and BVOC oxidation chemistry
  - Can be used to improve links between chemistry scheme and SOA formation
  - **Likely to have greater benefits at high resolution**

Cons:

- Slower and more complex to run/analyse, runs ~1.8x slower. However, this is still efficient enough for long-term (10yr+) and high-res runs to be possible.
- Does not necessarily "improve" O3, CO and other metrics against observations (highlights structural errors in the model).

Email: sa847 at cam.ac.uk

CRI-Strat 2: New isoprene chemistry and some inorganic rate changes

ST / CS

C_5H_8 + OH → ISOPO2

ISOPO2 + NO / NO_3 / RO_2 → MACR + MVK

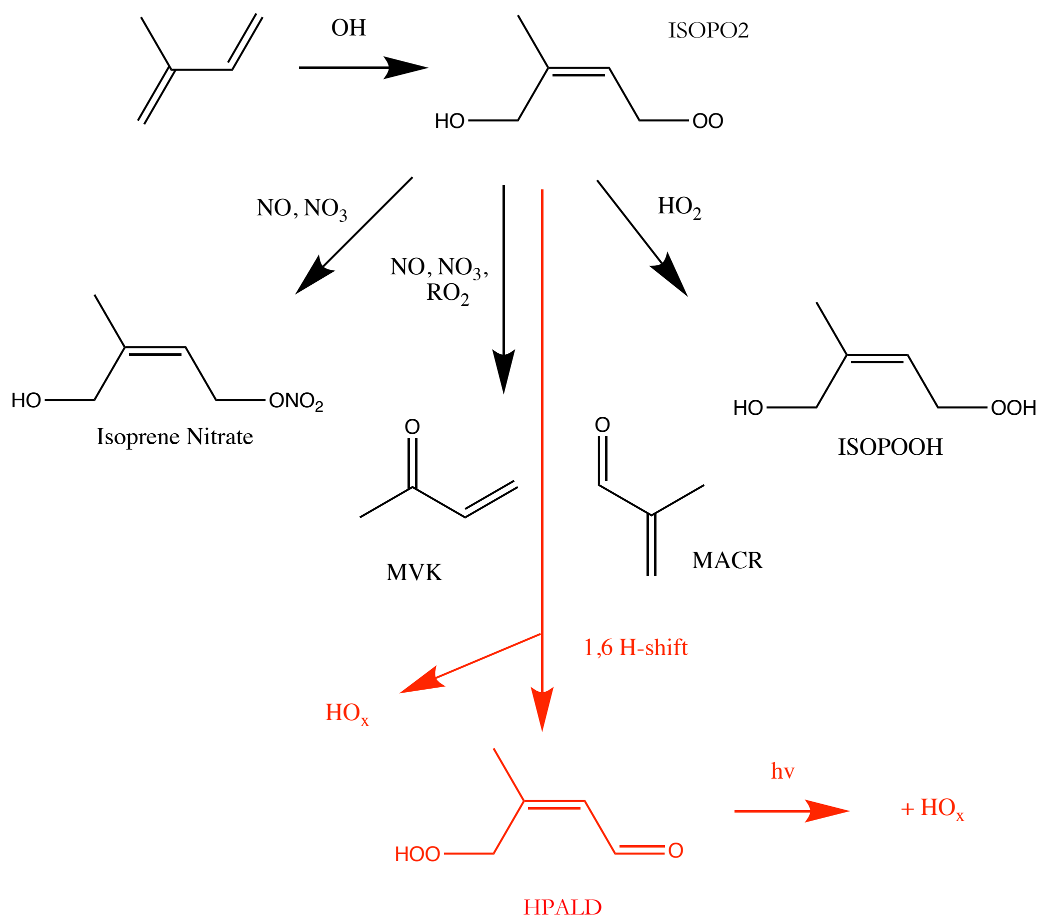
ISOPO2 + HO_2 → ISOPOOH

ISOPO2 + NO / NO_3 → Isoprene Nitrate

CS2

ISOPO2 → HPALDs + HO_2

HPALDs + hν → HO_x + …



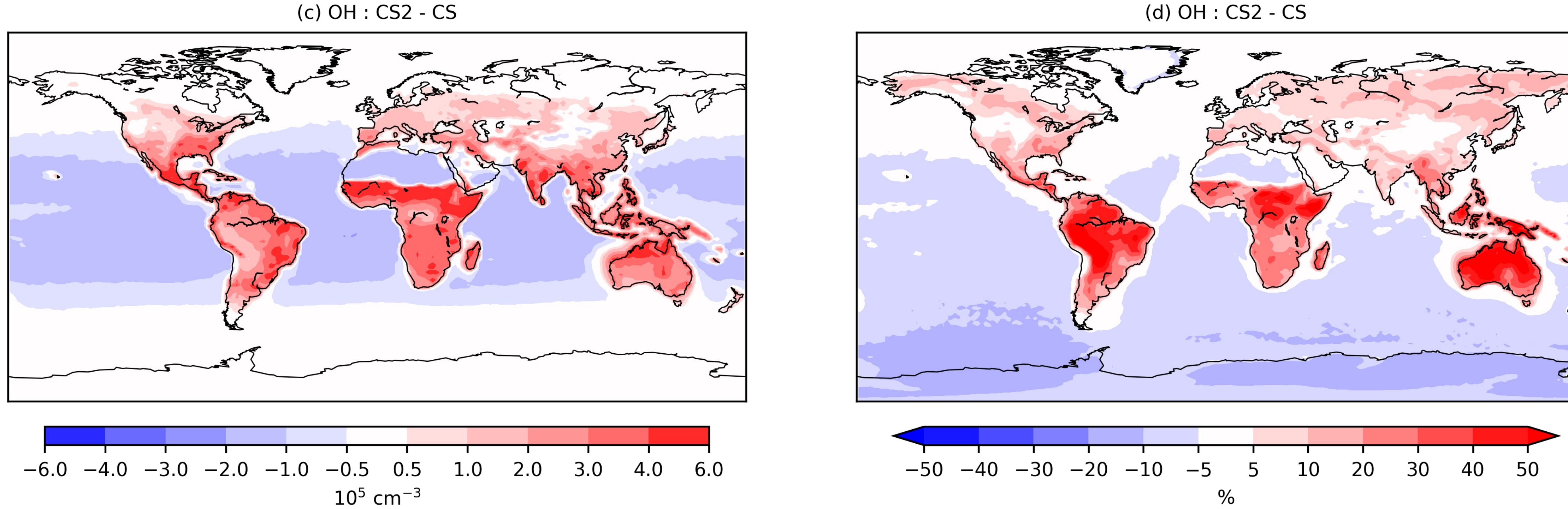
Mechanism Comparison: CRI-Strat vs. CRI-Strat 2

CS2 run time increases by ~6% relative to CS (cf. ~80% increase from ST to CS)
1 month free-running UKESM AMIP ≈ 1 hr 50 min

	CRI-STRAT (CS)	CRI-STRAT 2 (CS2)
Tropospheric Chemistry Scheme	CRI v2.1 (Jenkin et al., 2008, Watson et al., 2008, Utembe et al., 2010)	CRI v2.2 (Jenkin et al., 2019)
Stratospheric Chemistry Scheme	Stratospheric chemistry (Morgenstern et al., 2009)	Stratospheric chemistry (Morgenstern et al., 2009)
No. of Species	219	228 (+9)
No. of Bimolecular Reactions	536	582 (+46)
No. of Termolecular Reactions	36	44 (+8)
No. of Photolysis Reactions	128	140 (+12)

New species include IEPOX and HMML (SOA precursors) and HPALD (HPUCARB12).

Low Altitude OH: CRI-Strat vs. CRI-Strat 2



Implementing CRI-Strat 2

https://code.metoffice.gov.uk/doc/um/latest/papers/umdp_084.pdf

Select i_ukca_chem = 59 (CRI-Strat chemistry)

Then set i_ukca_chem_version >= 119

Same emissions as CRI-Strat

Summary

Updated CRIv2.2 has been added by James Weber. Offers several advantages:

- Updates to reaction rate coefficients - traceable to MCMv3.3.1
- Improved isoprene chemistry to reflect latest understanding of HOx recycling and IEPOX formation
- Useful for understanding oxidising capacity and SOA formation – being used for investigating changes to aerosol forcing

CRI-Strat (CRIv2.1-R5) is useable in version UM from version 11.7, first committed in ticket #4231, bug fix #5523.

See Archer-Nicholls et al., JAMES, 2021 doi:10.1002/essoar.10505092.1)

CRI-Strat2 paper: Weber et al., Geosci. Model Dev., 2021, Doi:10.5194/gmd-14-5239-2021

Email: sa847 at cam.ac.uk

Extra Slides

CRI vs StratTrop chemistry - details

Scenario	Mechanism	NMVOC Emissions (Tg C yr^{-1})
CRI-Strat	CRI-Strat	1012 Tg C yr^{-1} - CRI speciation
StratTrop	StratTrop	762 Tg C yr^{-1} - ST speciation
CRI-S_STEmiss	CRI-Strat	762 Tg C yr^{-1} - ST speciation
CRI-S_C2C3ExpEmiss	CRI-Strat	762 Tg C yr^{-1} - CRI speciation

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

But how much does it all cost?...

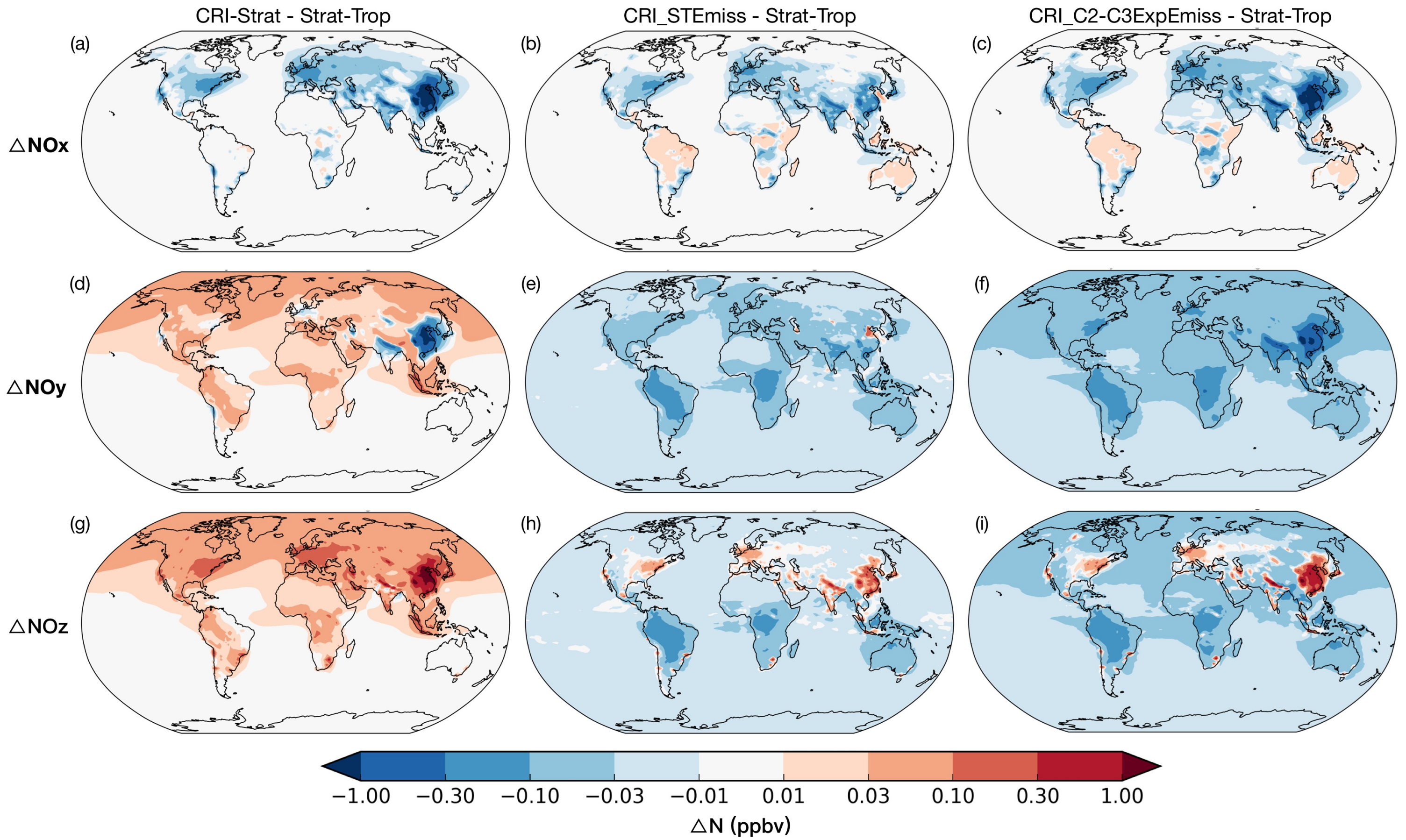
Average Wallclock times per month at N96e (1.875°×1.25° L85) after 200 months on 432 cores

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!

Boundary Layer NOy



In polluted environments, HNO3 formed faster in CRI-Strat => Greater loss in hot spots

In CRI runs with same amount of NMVOCs, leads to net loss of NOy

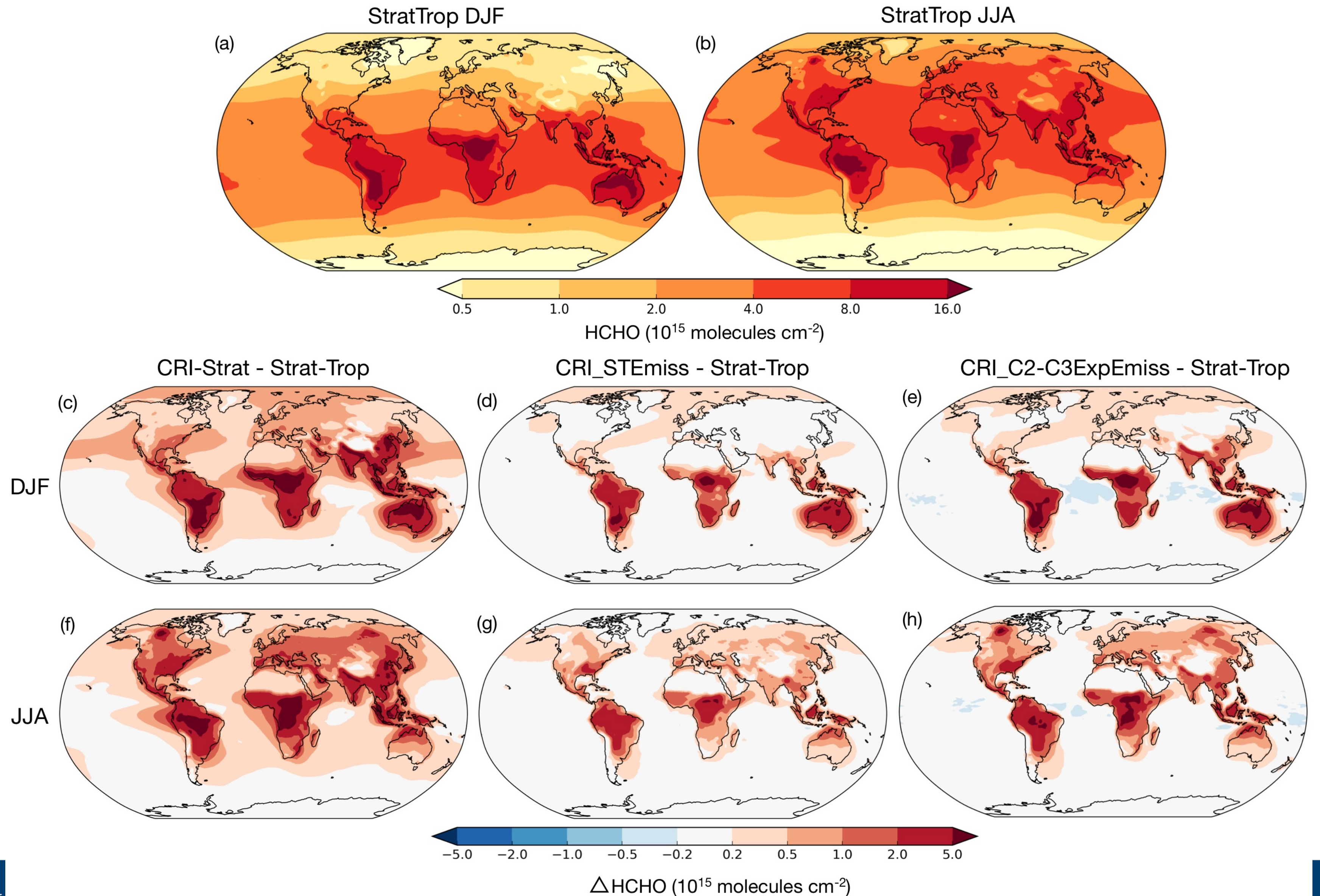
In CRI-Strat: extra NMVOCs mean more NOx stored in long-lived reservoirs => increased NOz

NOx = NO+NO2

$NOz = NO_3 + 2N_2O_5 + HNO_3 + PAN + RNO_3 + \ldots$

NOy = NOx + NOz

HCHO Tropospheric Column



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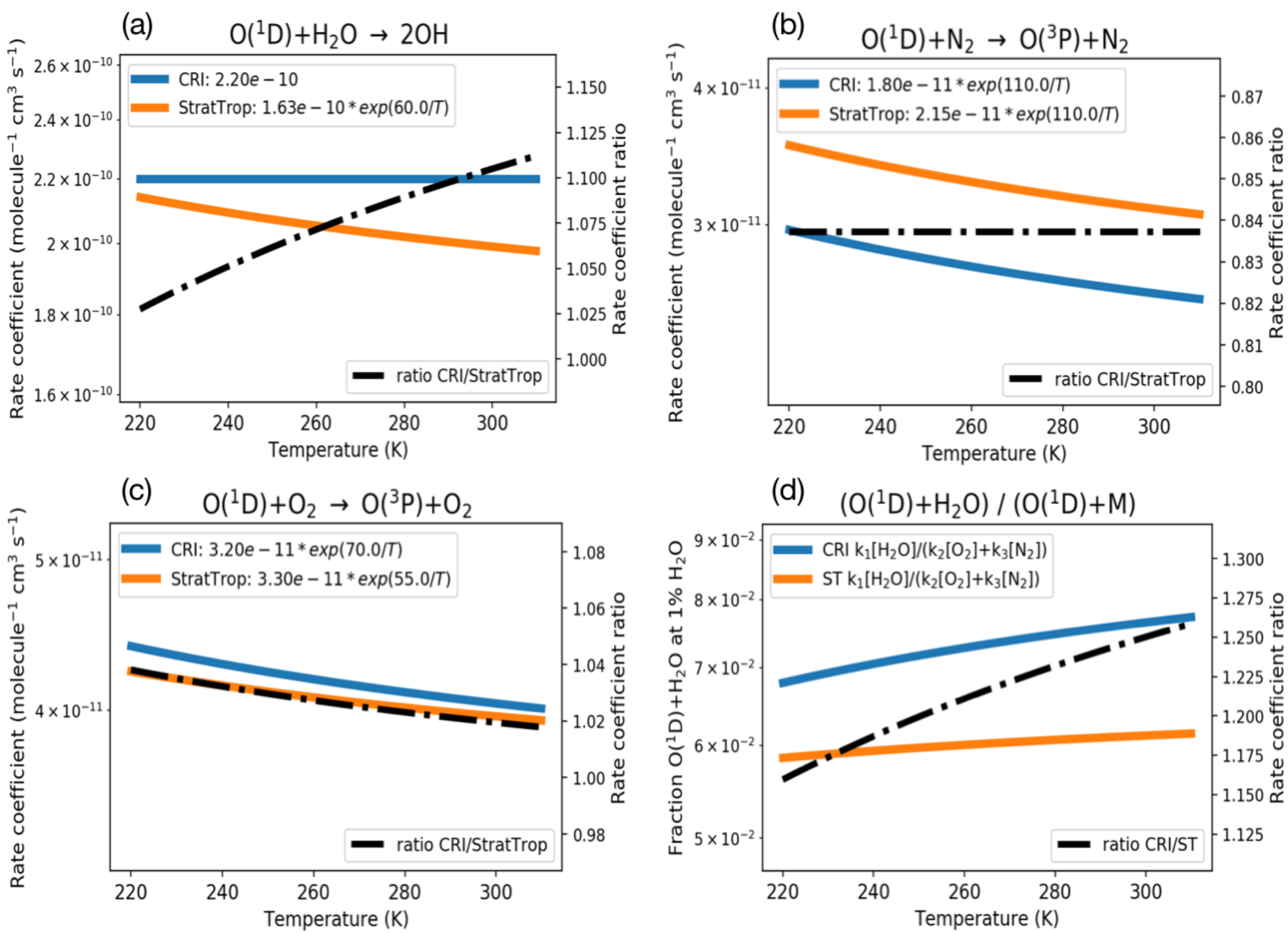
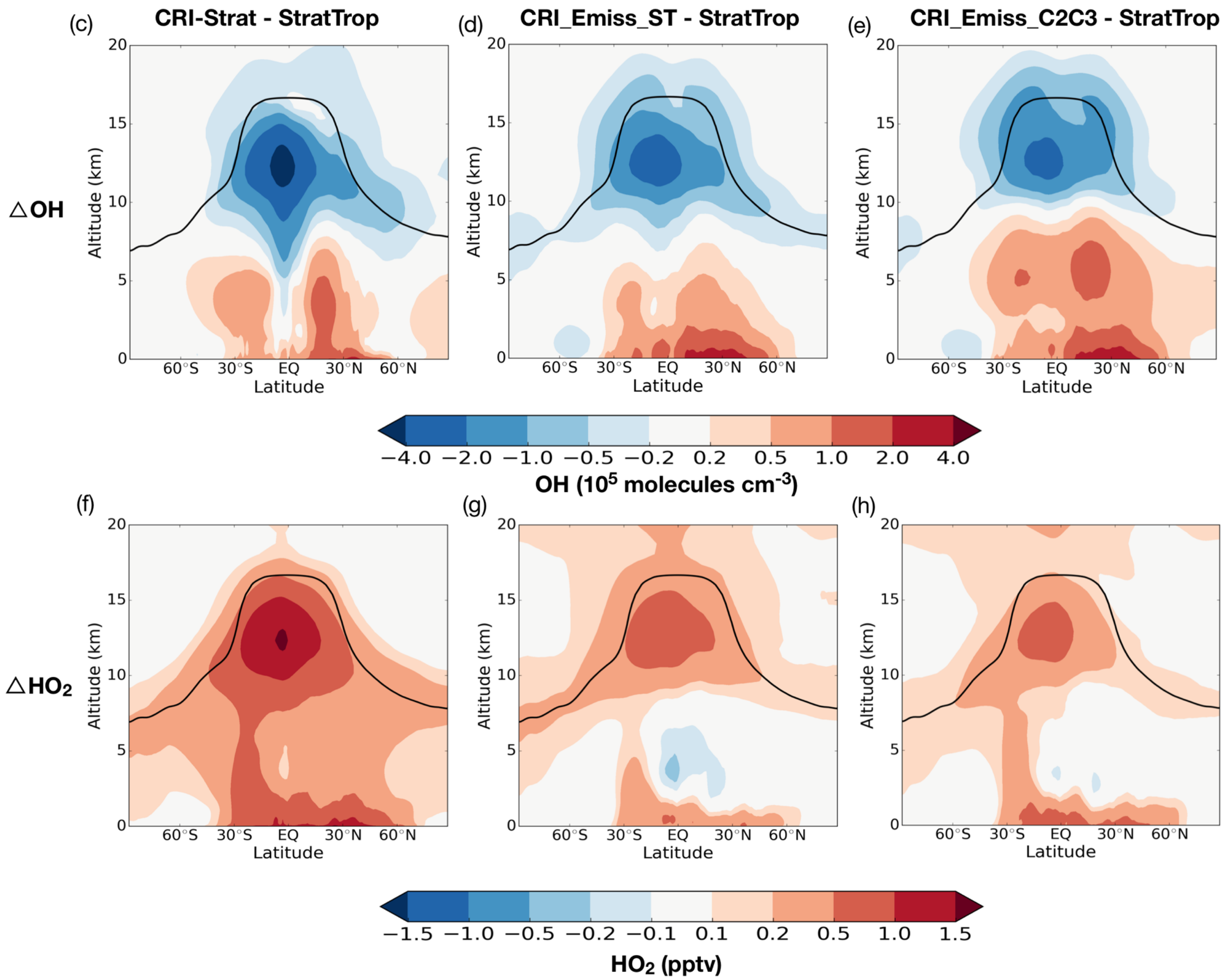
O(1D) reaction rate comparisons



- Overall, O(1D) ~20-25% more likely to react with H2O in CRI
- More HOx production and Ox loss
- Difference due to different sources for reaction rate coefficients (IUPAC vs JPL)

OH and HO2



Tropospheric HOx budget

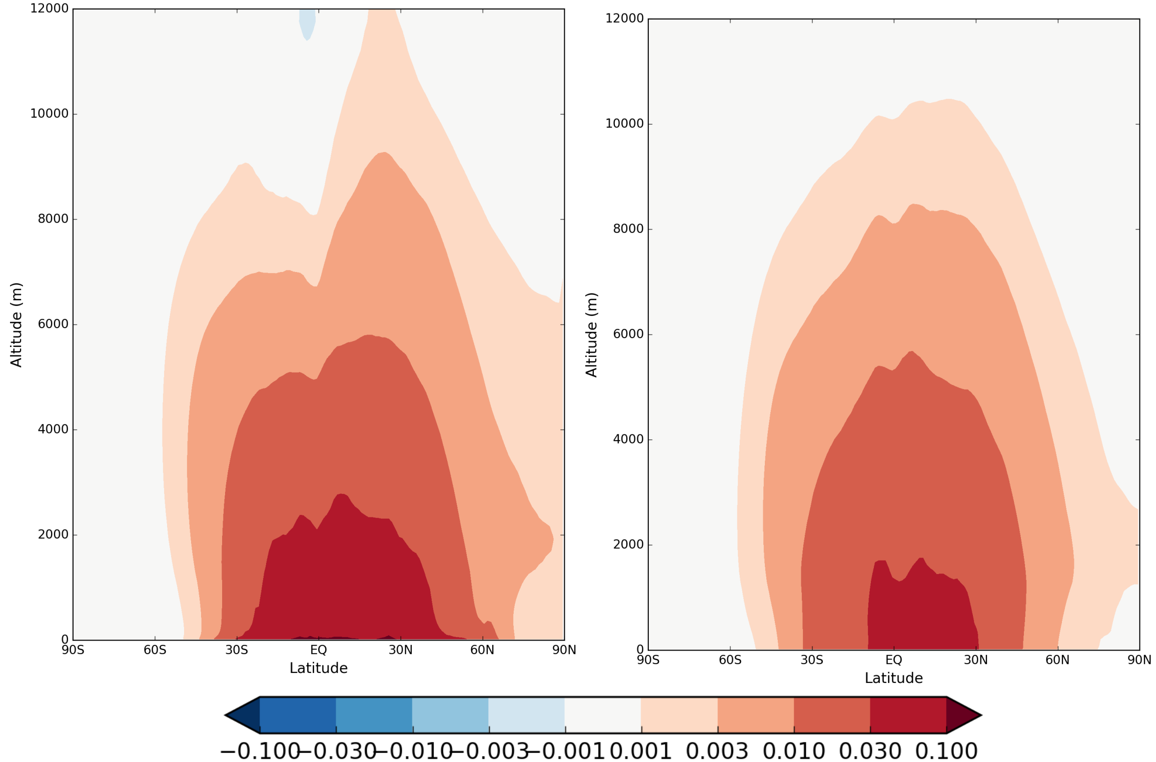
	CRI-Strat	StratTrop	CRI_Emiss_ST	CRI_Emiss_C2C3
[OH] (10^6 molecules cm^{-3})	1.335	1.339	1.348	1.375
OH NH:SH ratio	1.38	1.35	1.4	1.4
[HO_2] (pptv)	6.27	5.90	6.02	6.06
OH : HO_2 ratio (%)	1.49	1.67	1.61	1.63
CH_4 lifetime W.R.T. OH (years)	7.77	8.13	7.71	7.60
$HO_2 + HO_2$ flux (P mole $year^{-1}$)	60.5	32.2	38.8	39.9

NOy budget

	CRI-Strat	StratTrop	CRI_Emiss_ST	CRI_Emiss_C2C3
NO_y Burden (Tg N)	1.112	1.018	0.950	0.910
NO_x Burden (Tg N)	0.115 (10.3%)	0.152 (14.9%)	0.136 (14.3%)	0.131 (14.4%)
NO_z Burden (Tg N)	0.998 (89.7%)	0.866 (85.1%)	0.814 (85.7%)	0.779 (85.6%)
$HONO_2$ Burden (Tg N)	0.509 (45.8%)	0.513 (50.4%)	0.506 (53.2%)	0.512 (56.2%)
Other inorganic NO_z (Tg N)	0.021 (1.9%)	0.018 (1.7%)	0.018 (1.9%)	0.019 (2.1%)
PANs (Tg N)	0.367 (33.0%)	0.296 (29.1%)	0.245 (25.8%)	0.206 (22.7%)
$RONO_2$ (Tg N)	0.061 (5.5%)	0.039 (3.9%)	0.038 (4.0%)	0.035 (3.9%)
$CH_3O_2NO_2$ (Tg N)	0.008 (0.7%)	N/A	0.007 (0.7%)	0.007 (0.7%)
Nitrophenols (Tg N)	0.031 (2.8%)	N/A	0.0	0.0
Total NO_x Emissions (Tg N $year^{-1}$)	61.5	61.5	61.5	61.5
Total NO_y Deposition (Tg N $year^{-1}$)	63.0	62.9	63.0	63.0
Inferred STT (Tg N $year^{-1}$)	1.46	1.40	1.43	1.44
NO_x Dry deposition (Tg N $year^{-1}$)	6.83 (10.8%)	7.70 (12.2%)	7.36 (11.7%)	7.25 (11.5%)
$HONO_2$ Wet deposition (Tg N $year^{-1}$)	29.0 (46.0%)	30.1 (47.8%)	30.1 (47.8%)	30.0 (47.7%)
$HONO_2$ Dry deposition (Tg N $year^{-1}$)	22.0 (34.9%)	21.6 (34.3%)	22.3 (35.5%)	22.4 (35.6%)
Other inorganic NO_z deposition (Tg N $year^{-1}$)	1.21 (1.9%)	0.97 (1.6%)	1.04 (1.6%)	1.08 (1.7%)
PANs dry deposition (Tg N $year^{-1}$)	1.70 (2.7%)	1.28 (2.0%)	0.894 (1.4%)	0.918 (1.5%)
$RONO_2$ deposition (Tg N $year^{-1}$)	2.09 (3.3%)	1.30 (2.1%)	1.22 (2.0%)	1.28 (2.0%)
Nitrophenol deposition (Tg N $year^{-1}$)	0.22 (0.4%)	N/A	0.0	0.0
NO_y deposition lifetime (days)	6.44	5.91	5.51	5.28
$HONO_2$ deposition lifetime (days)	3.65	3.62	3.53	3.57
PANs deposition lifetime (days)	78.9	84.5	100.1	82.0
$RONO_2$ deposition lifetime (days)	10.7	11.0	11.4	9.99

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

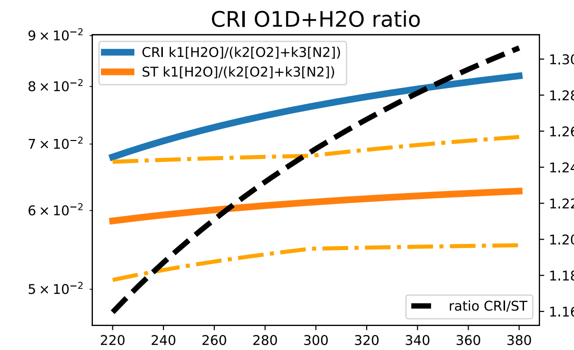
Difference in Ox Loss | Difference in O[1]D+H2O Flux



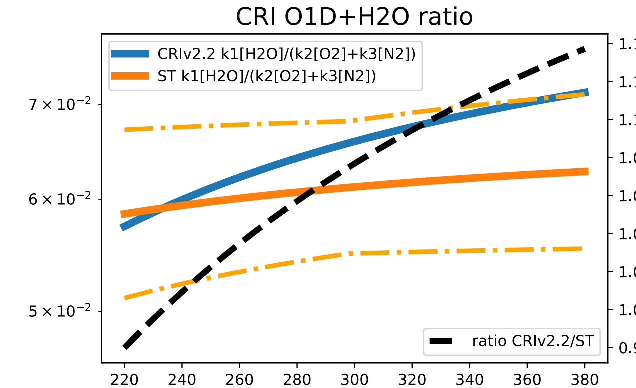
Increased Ox loss in CRIv2 almost entirely driven by faster O1D + H2O flux

CRIv2.2 has updated rate much closer to StratTrop

CRIv2 & StratTrop



CRIv2.2 & StratTrop



Ratio Flux (O[1]D+H2O)/(O[1]D+M)

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