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# Impact of C<sub>1</sub>-C<sub>3</sub> alkyl nitrate chemistry on tropospheric ozone: box and global model perspectives

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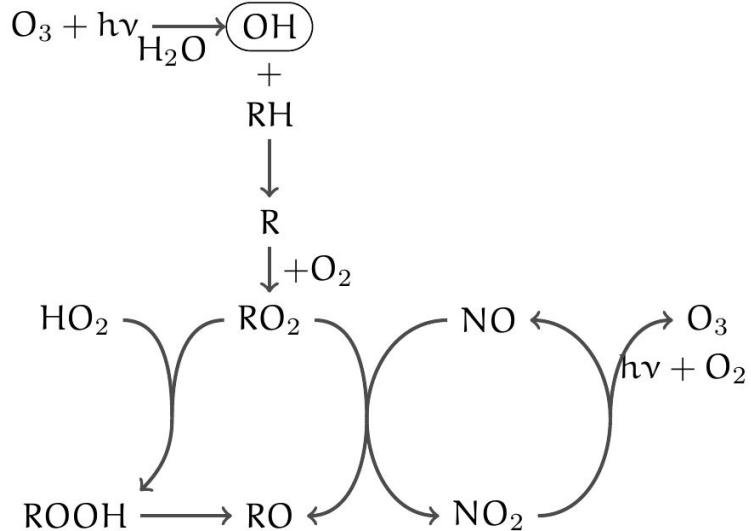
<sup>2</sup>National Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, UK



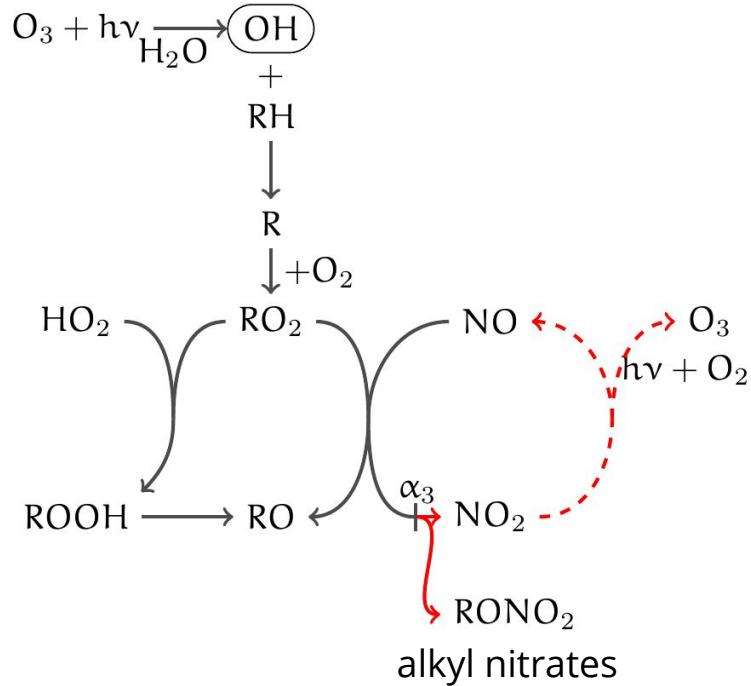
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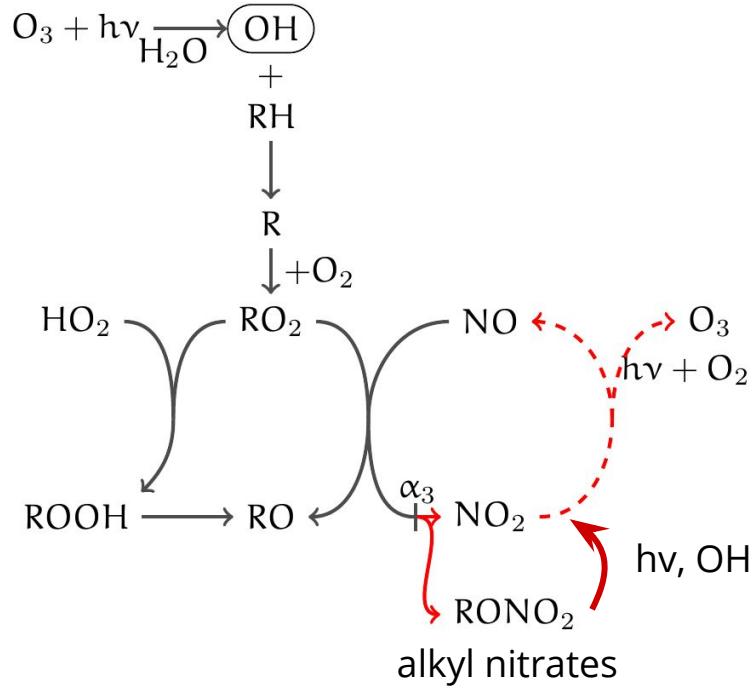
# Introduction



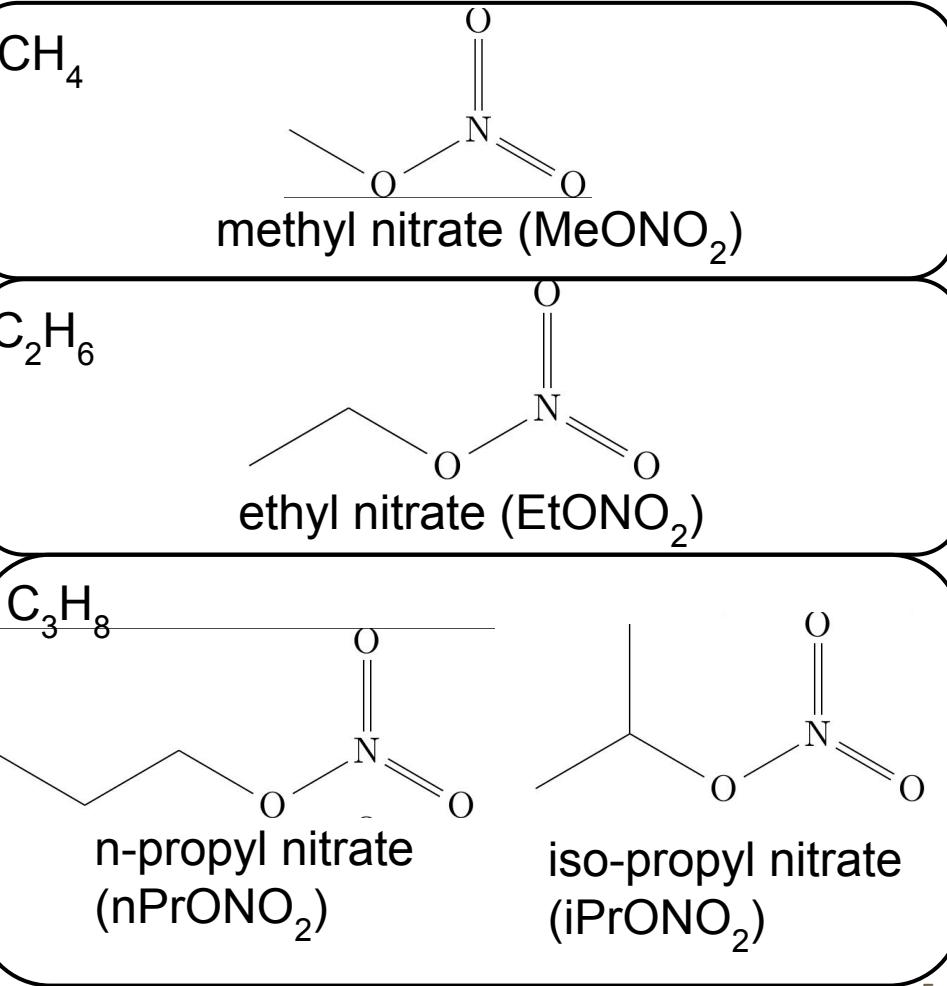
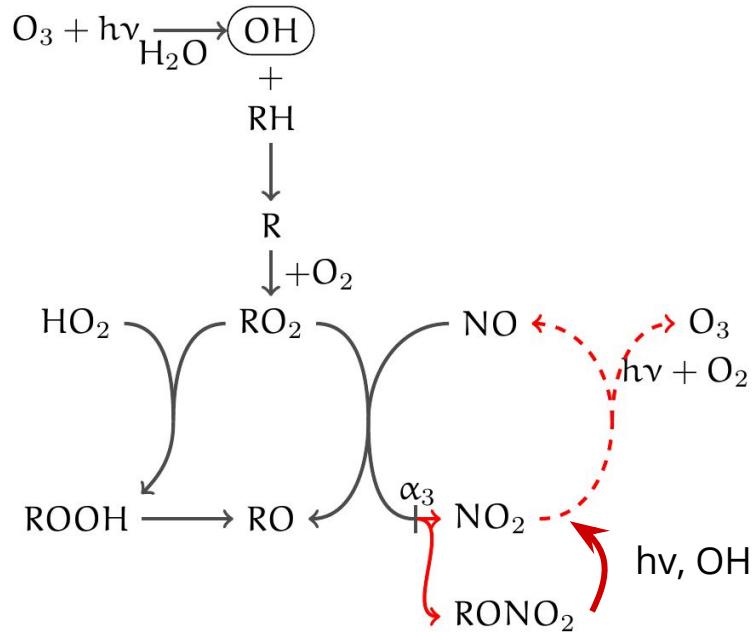
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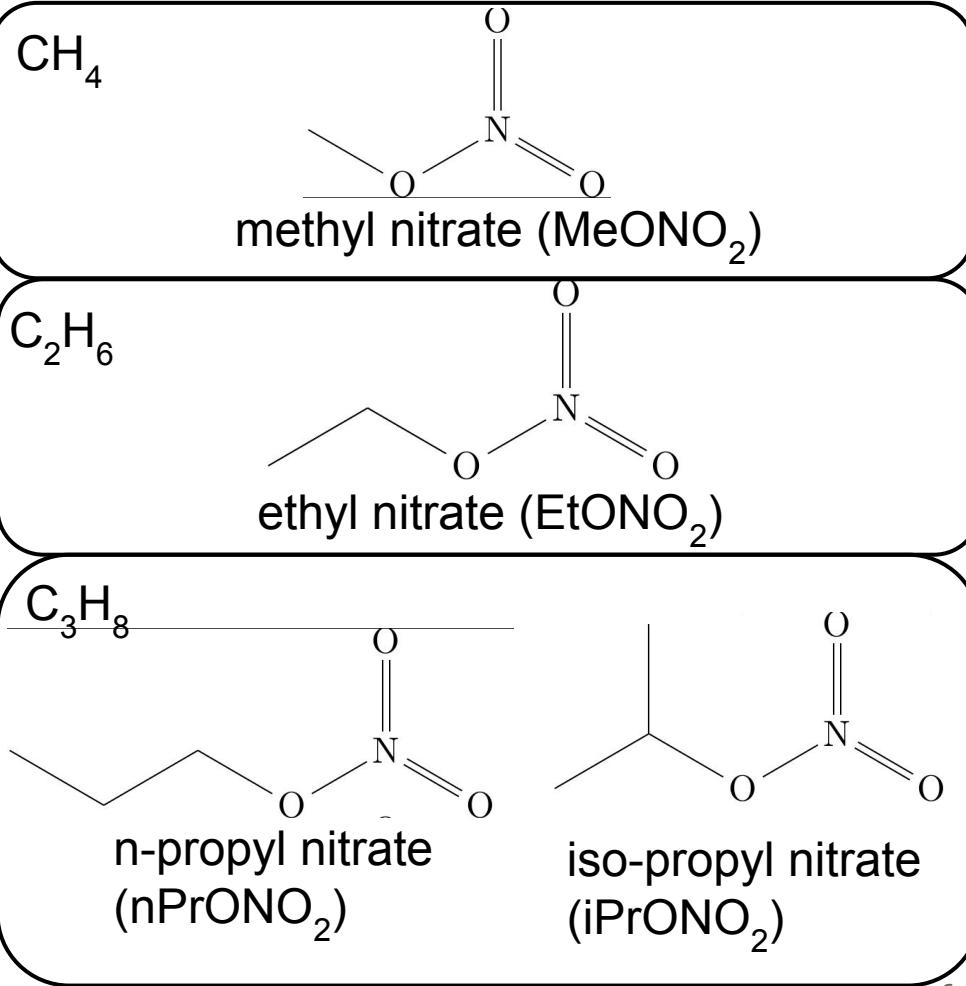
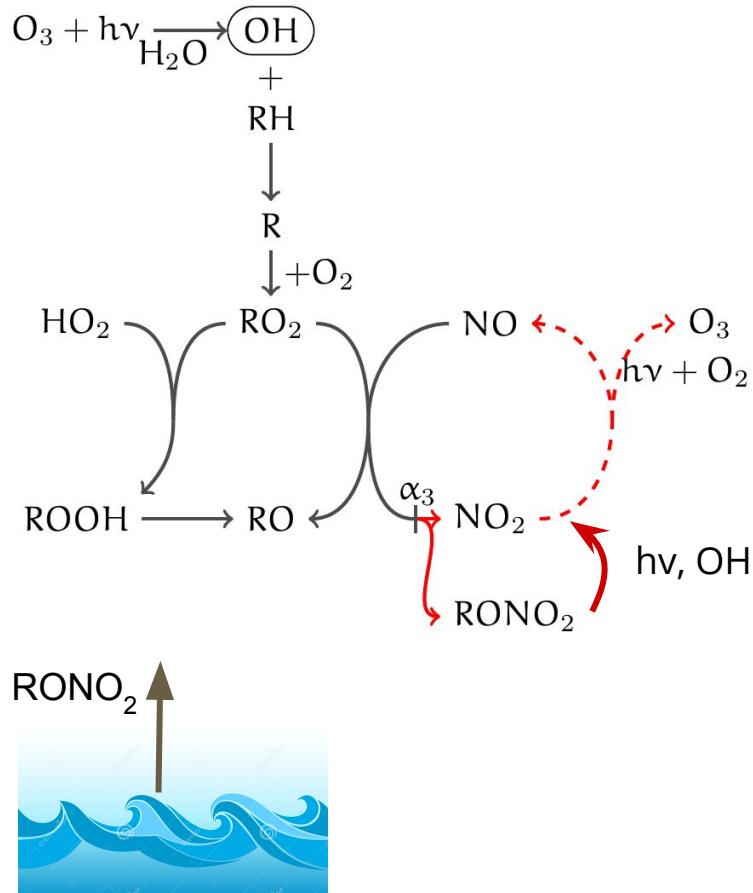
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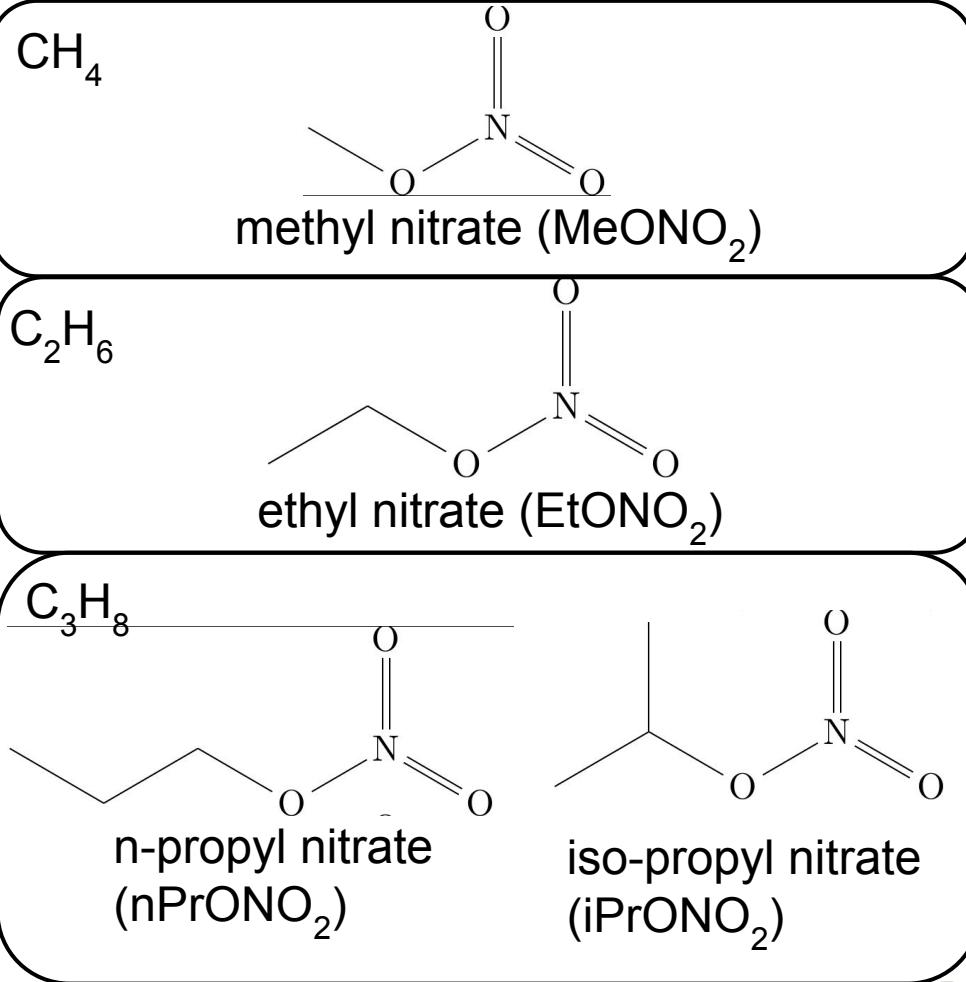
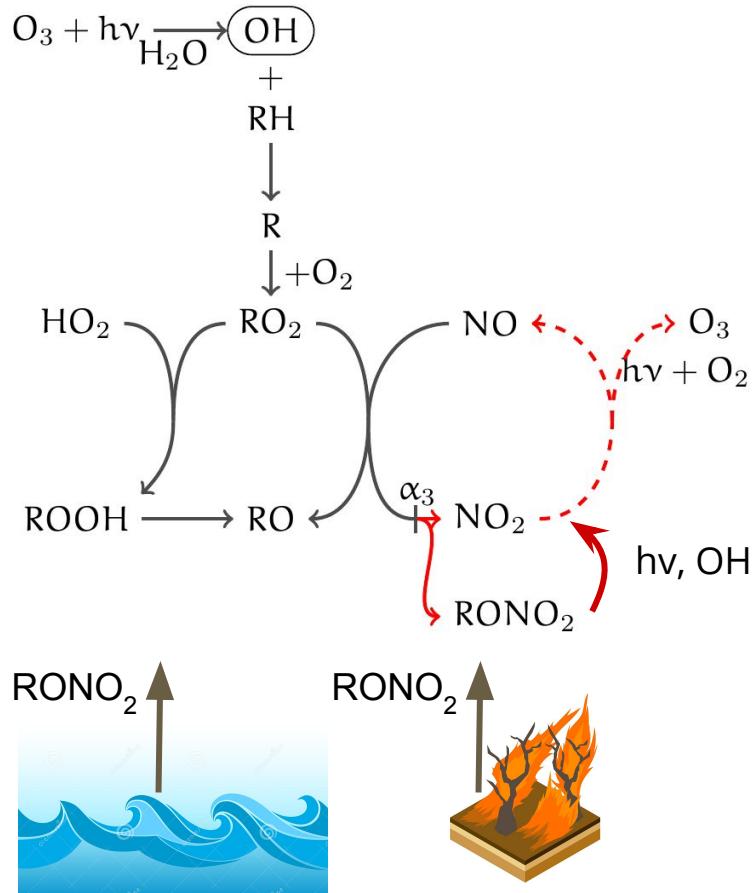
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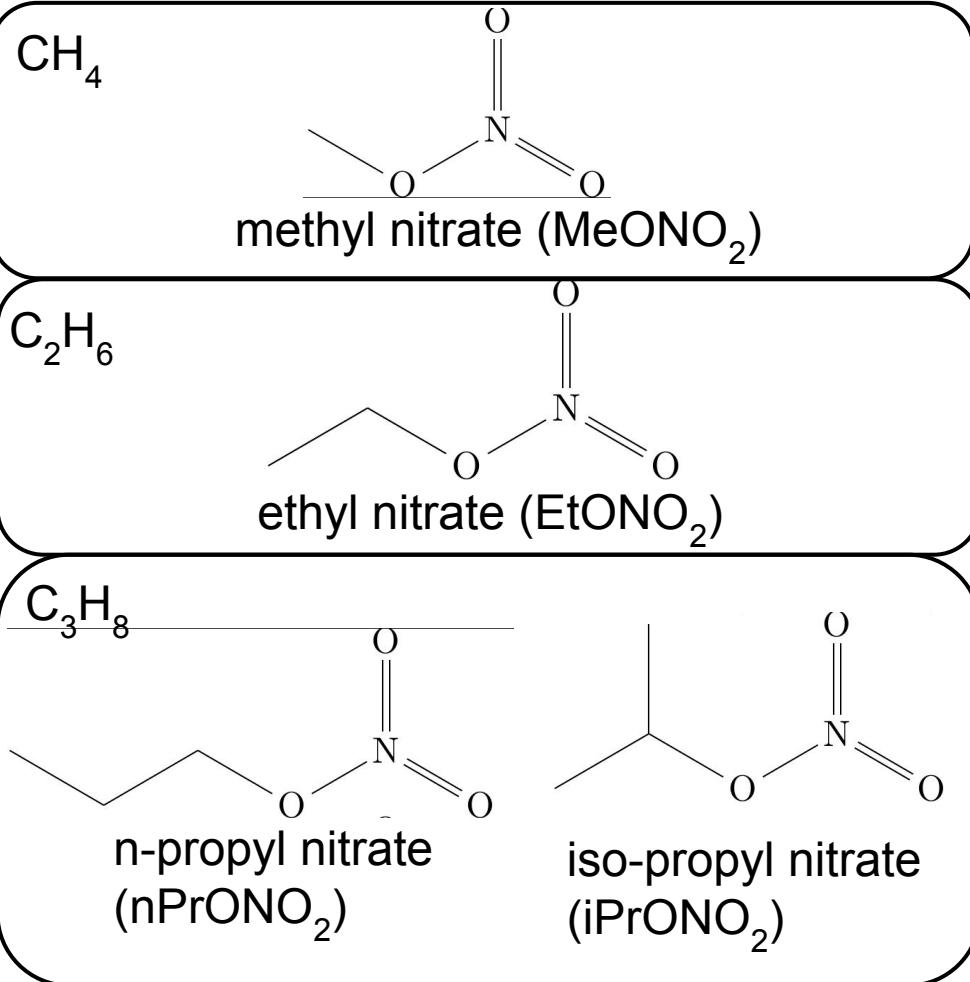
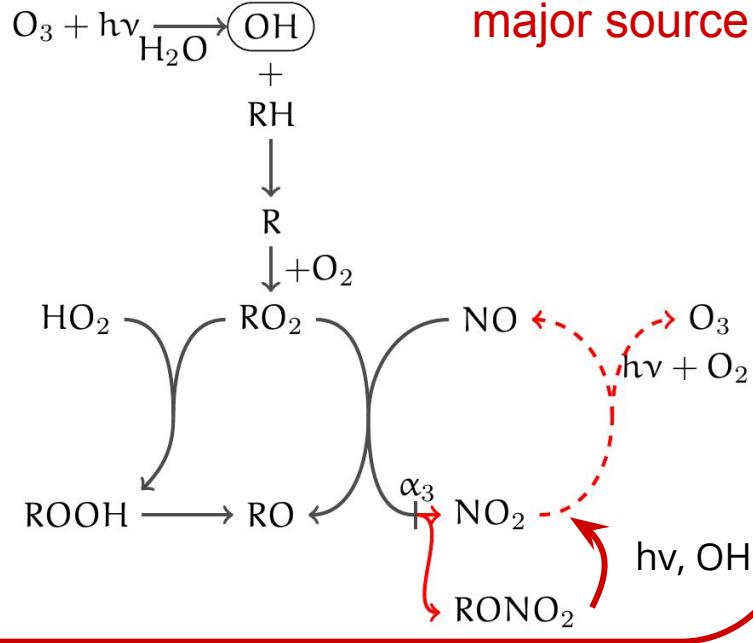
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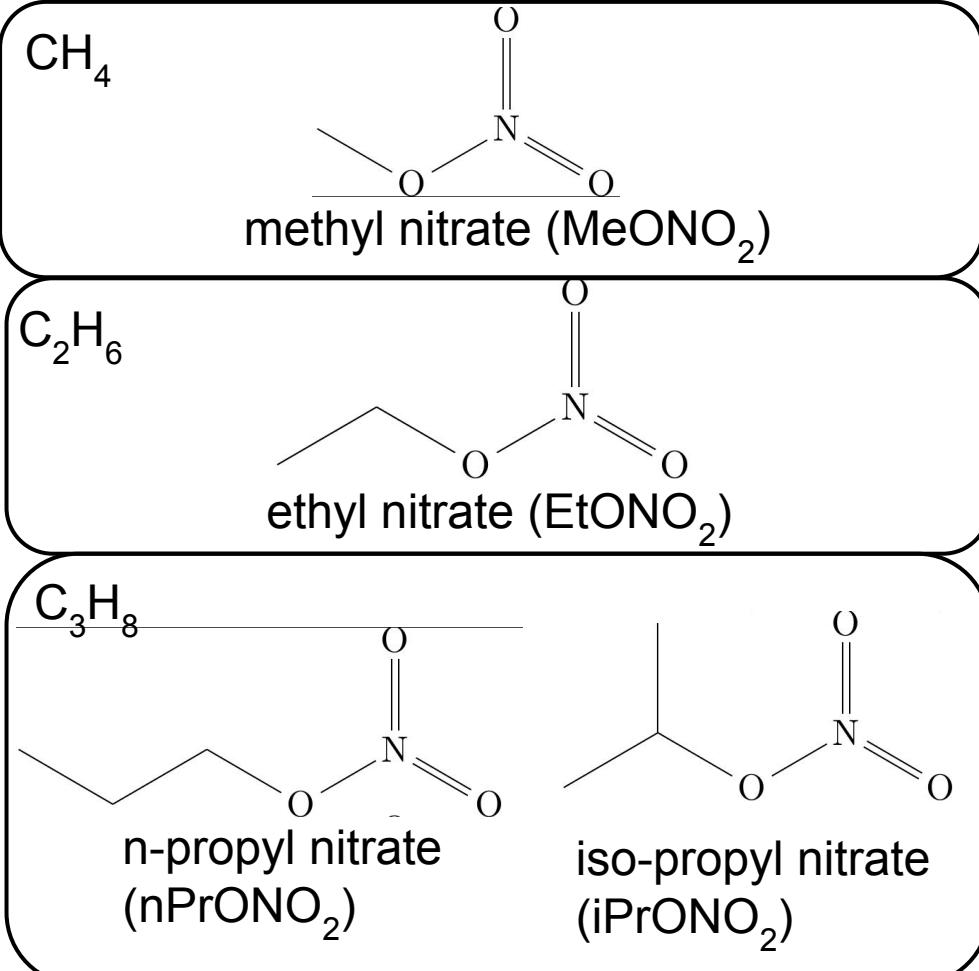
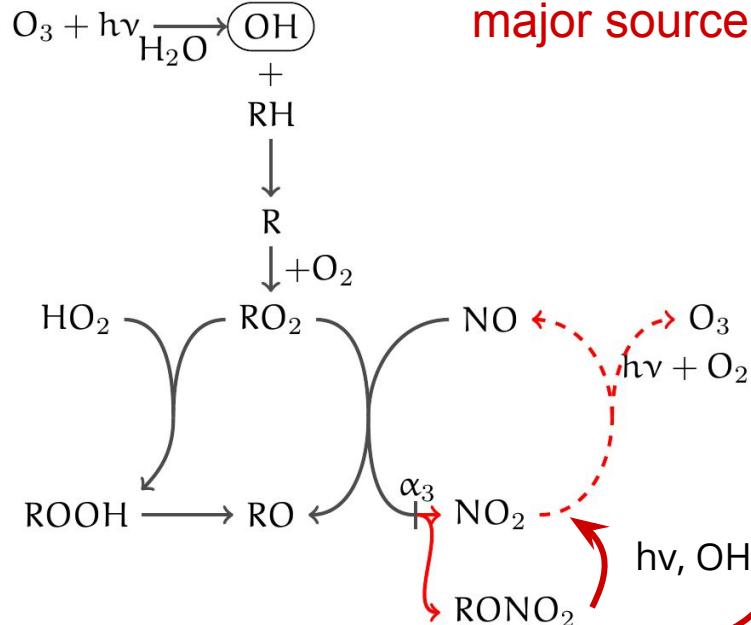
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# Global 3D modelling studies with RONO<sub>2</sub> so far...

Study	Model name	Model type	Simulation	Chemical scheme
Neu2008	UCI	CTM	year 2000	Wild2003
Williams2014	TM5	CTM	year 2008	CB05
Khan2015	STOCHEM-CRI	CTM	year 1998	CRI v2-R5
Fisher2018	GEOS-Chem	CTM	year 2013	GEOS-Chem
this study	UM-UKCA	CCM	10-year mean	CheST

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All studies had a different representation of RONO<sub>2</sub> sources

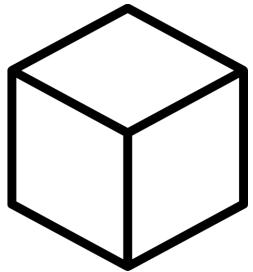
# Objectives

- develop a chemical mechanism with C<sub>1</sub>-C<sub>3</sub> RONO<sub>2</sub>
- test it against a benchmark
- implement the mechanism into a global 3D model
- add oceanic emissions
- add biomass burning emissions

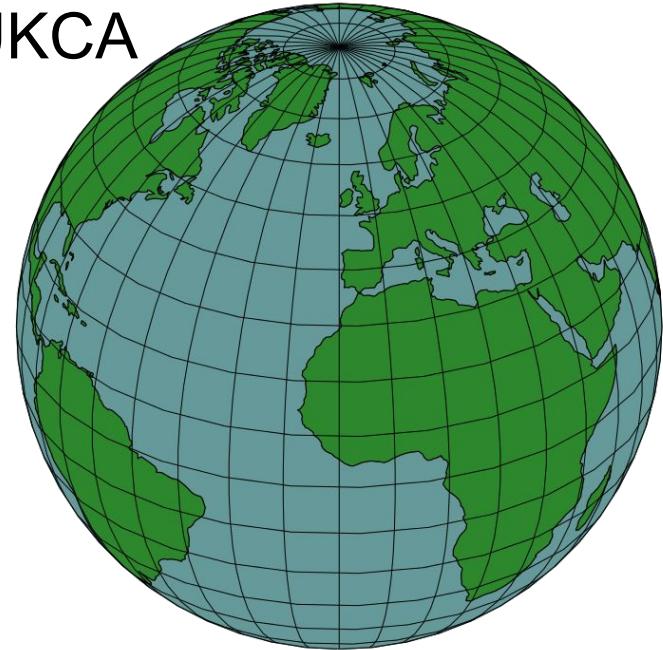
# Methods

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Box model

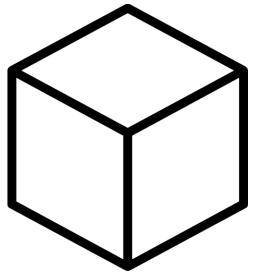


UM-UKCA

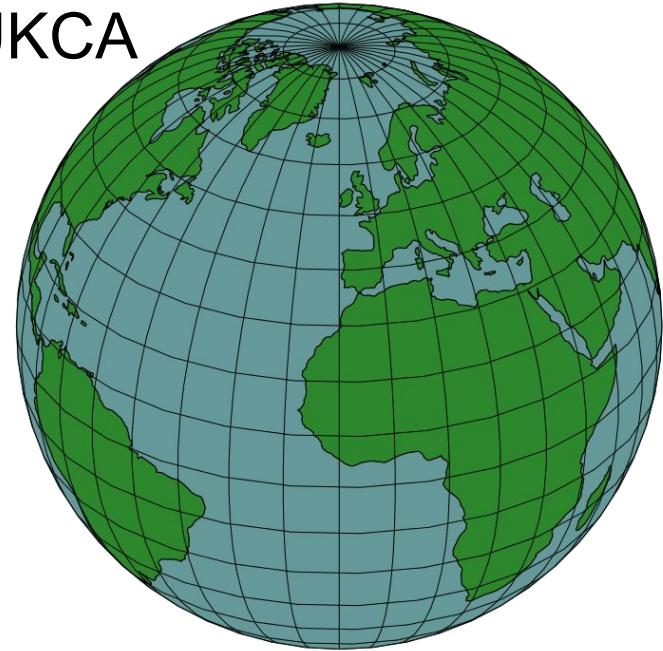


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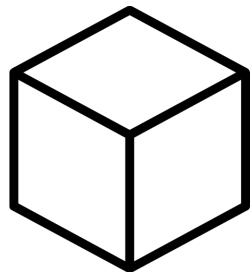
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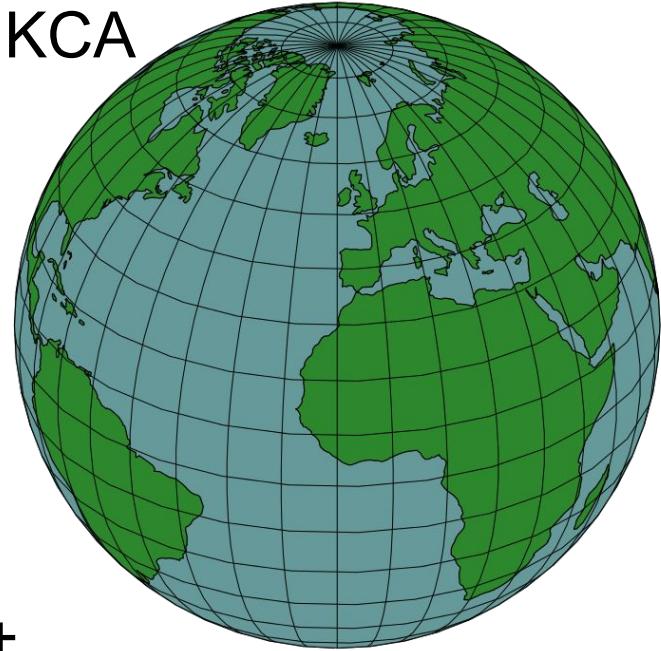
CheST

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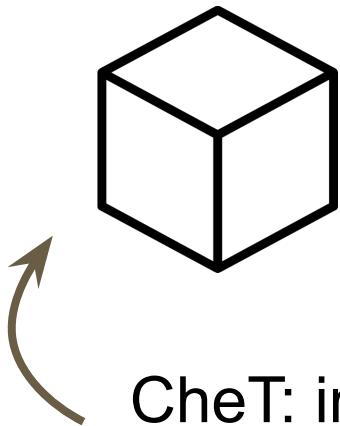
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 $C_1$ - $C_3$  alkanes +  
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CheST

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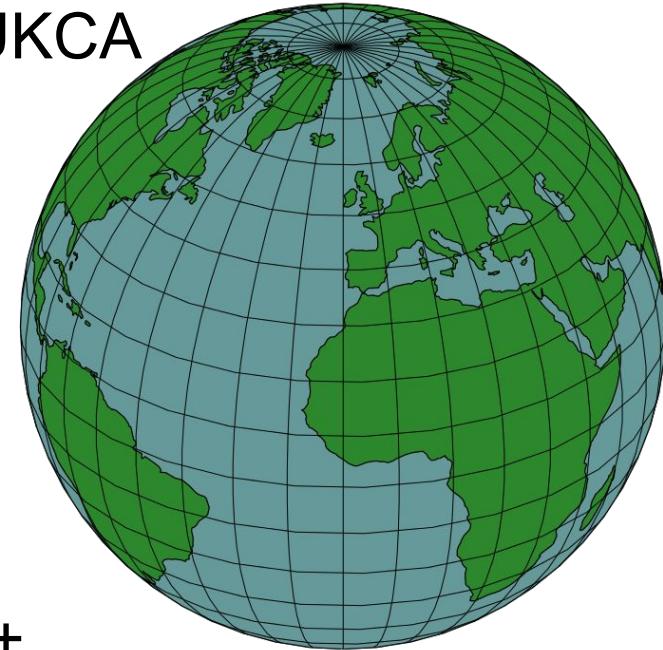
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testing against MCM\*



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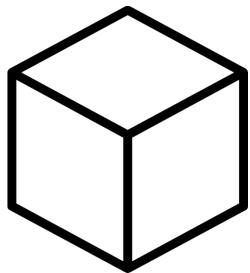
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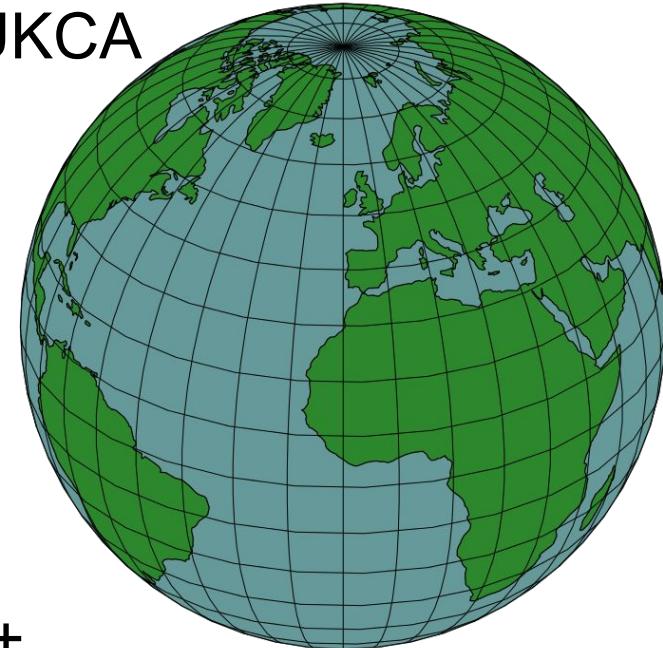
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} exactly like in MCM

# UKCA experiments

# UKCA configuration

Version	7.3
Resolution	$2.5^\circ \times 3.75^\circ$ , 60 levels
Meteorology	free running
Emissions	RCP8.5 scenario
Boundary conditions	SSTs, sea-ice annual cycle
Initial conditions	year 2000
Run lengths	10 years

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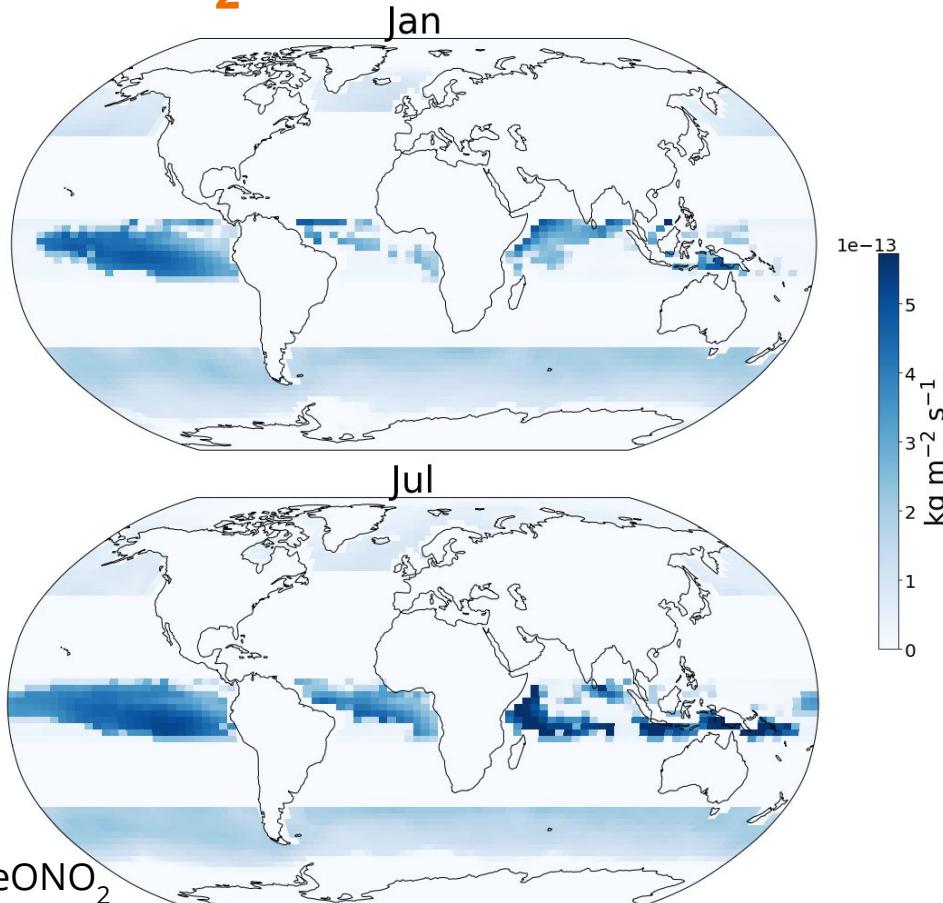
Are changes in the model chemical state statistically significant?

- use perpetual year simulations

# UKCA experiments

Experiment	Description
BASE	Updated CheST without MeONO <sub>2</sub>
OCEAN	C <sub>1</sub> -C <sub>2</sub> RONO <sub>2</sub> oceanic emissions & photochemical loss
BB	C <sub>1</sub> -C <sub>3</sub> RONO <sub>2</sub> biomass burning emissions & photochemical loss
CHEM* (historical)	MeONO <sub>2</sub> photochemical production & loss
RONO <sub>2</sub> dry deposition switched on in all experiments except CHEM*	

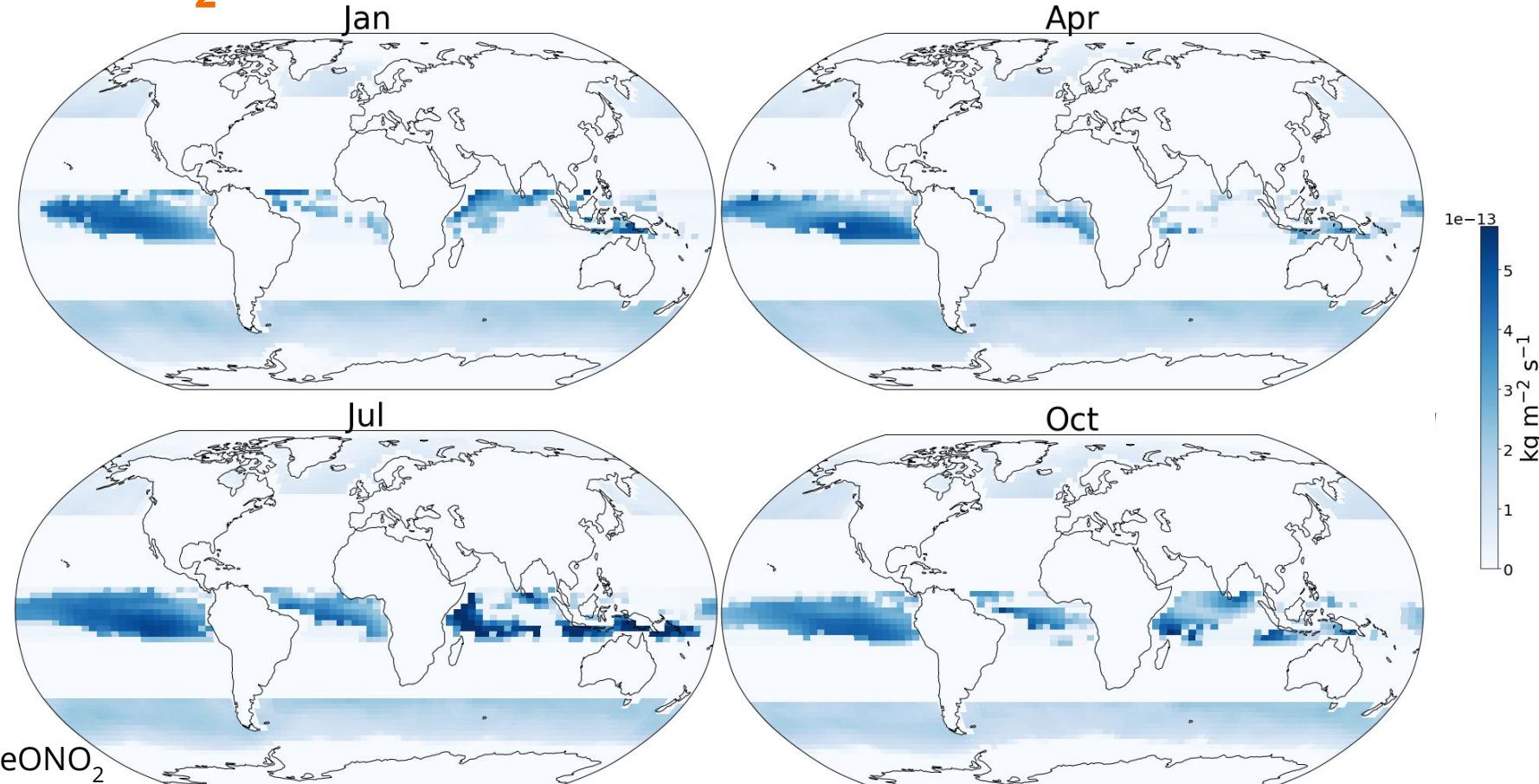
# $\text{RONO}_2$ oceanic emissions



- In GEOS-Chem, Fisher et al. (2018) implemented  **$\text{C}_1\text{-}\text{C}_2 \text{ RONO}_2$  air-sea exchange**
- it was driven by changes in:
  - wind speed
  - SST
  - nitrite availability
- included seasonal and spatial variability

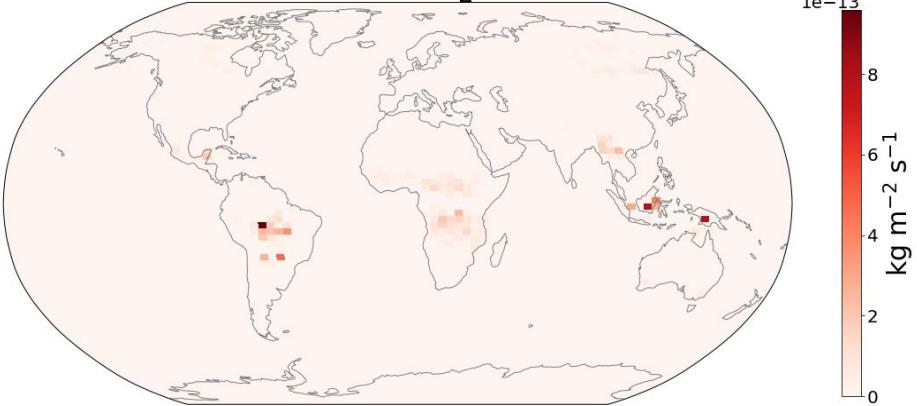
**We implemented  $\text{C}_1\text{-}\text{C}_2 \text{ RONO}_2$  oceanic emissions modelled by GEOS-Chem into UKCA.**

# $\text{RONO}_2$ oceanic emissions

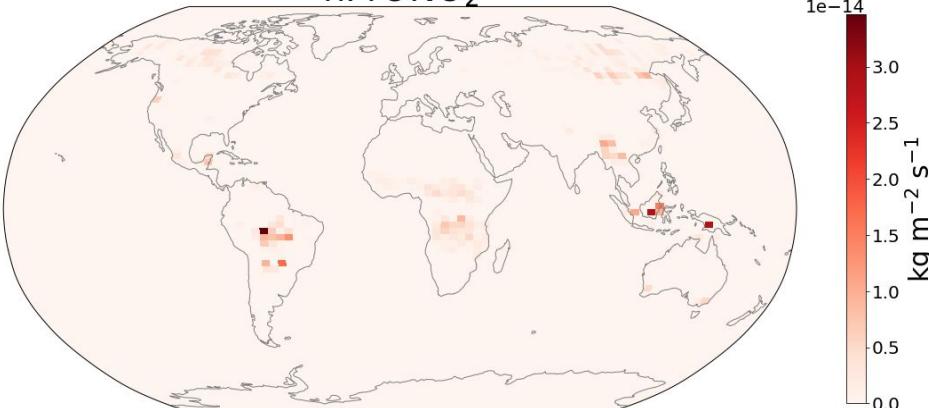


# $\text{RONO}_2$ , biomass burning emissions

MeONO<sub>2</sub>



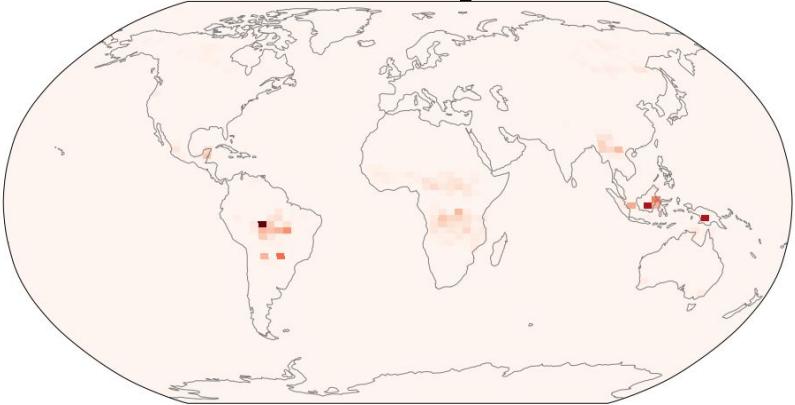
nPrONO<sub>2</sub>



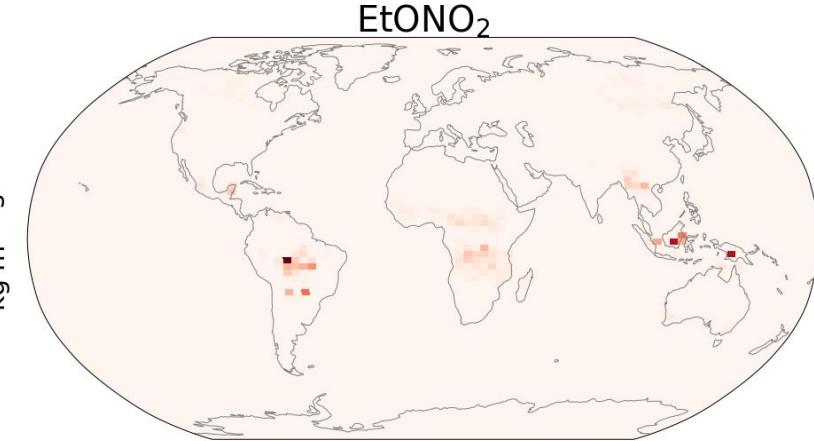
- Used Global Fire Emissions Database (GFED) data on dry matter emissions
- Applied emission factors for C<sub>1</sub>-C<sub>3</sub> RONO<sub>2</sub> from Akagi et al. (2011) for **fires in:**
  - **tropical forest**
  - **savanna**
  - **boreal forest**
  - **extratropical forest**
- Calculated 20-year mean monthly emissions
- implemented into UKCA

# $\text{RONO}_2$ biomass burning emissions

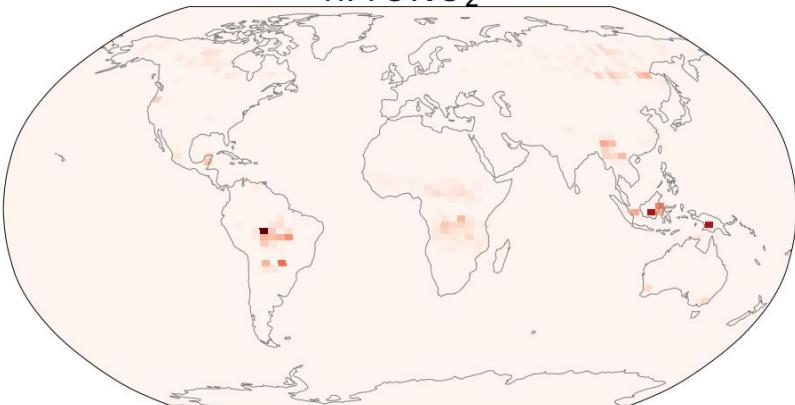
$\text{MeONO}_2$



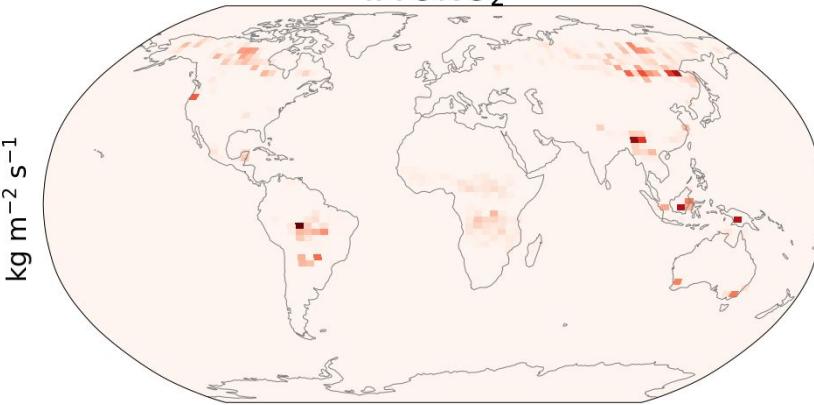
$\text{EtONO}_2$



$\text{nPrONO}_2$



$\text{iPrONO}_2$



# Global RONO<sub>2</sub> emissions per year

Emissions, Gg N yr <sup>-1</sup>	MeONO <sub>2</sub>	EtONO <sub>2</sub>	nPrONO <sub>2</sub>	iPrONO <sub>2</sub>
oceanic	141	24	-	-
biomass burning	10	5	0.3	2

Simpson et al. (2002): C<sub>1</sub>-C<sub>4</sub> RONO<sub>2</sub> BB emissions: ~18 Gg N yr<sup>-1</sup>

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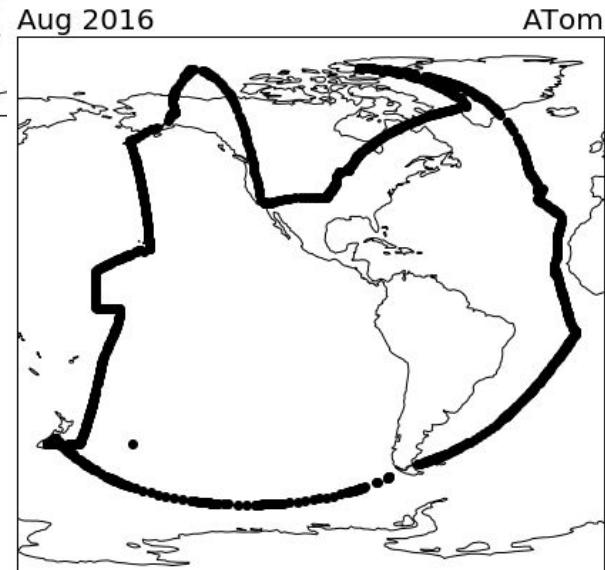
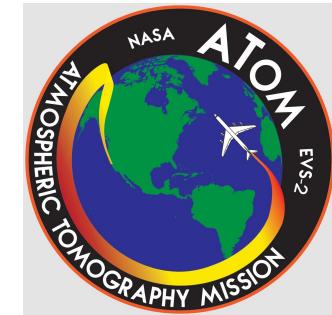
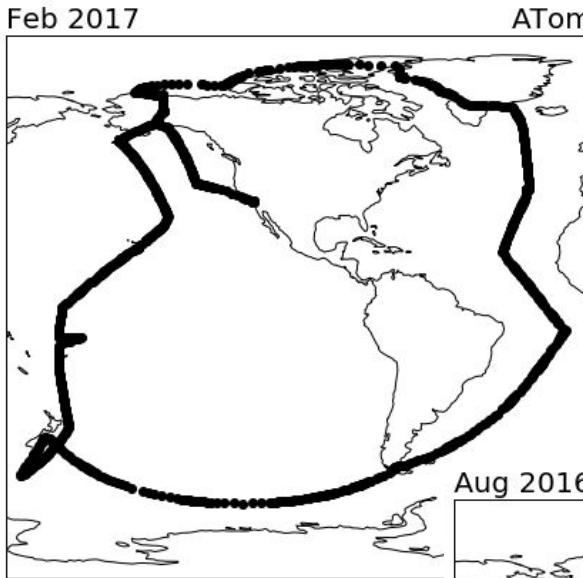
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NASA's Atmospheric Tomography (ATom) mission

- flights occurred in each of 4 seasons from 2016 to 2018
- profiles from 0.2 to 12 km

Here we used:

- ATom-1 (Jul-Aug 2016)
- ATom-2 (Jan-Feb 2017)



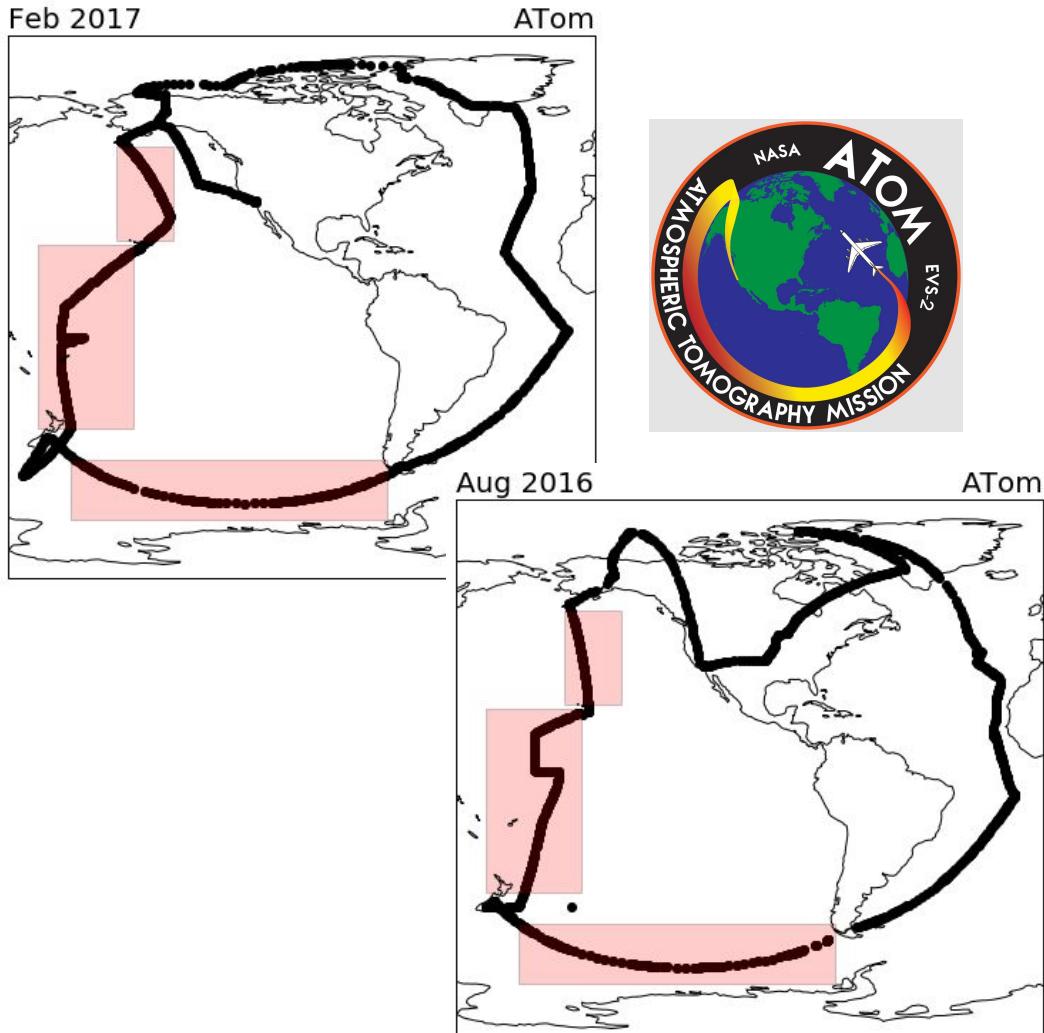
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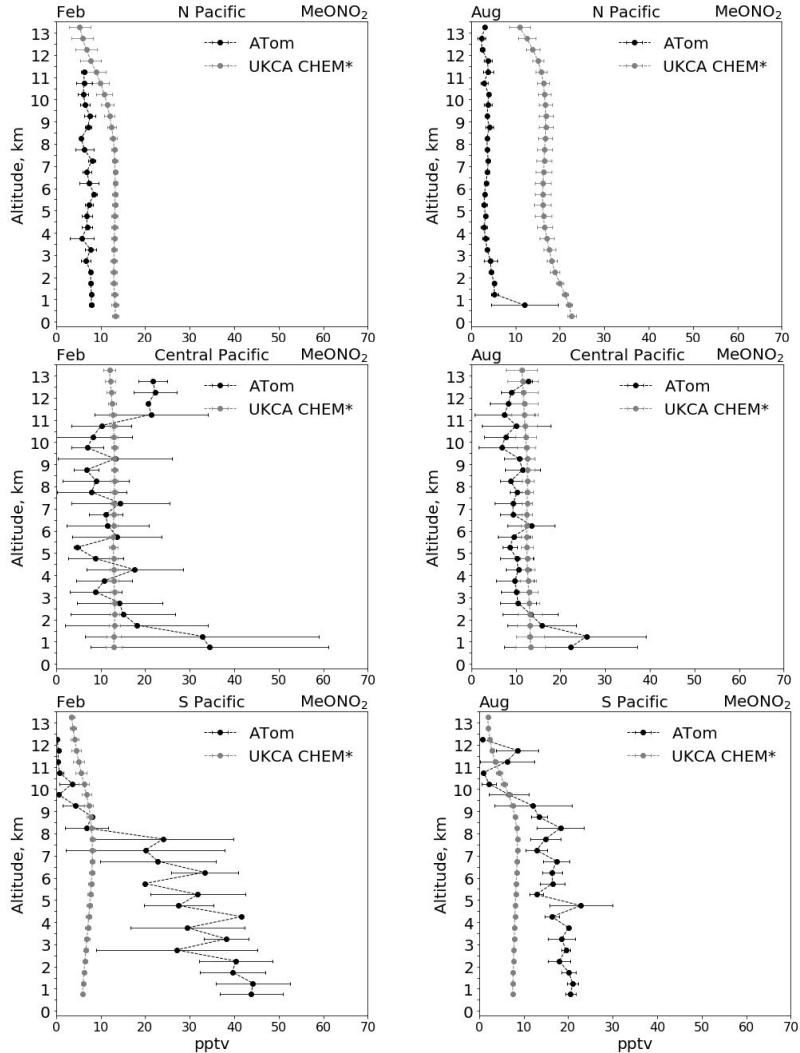
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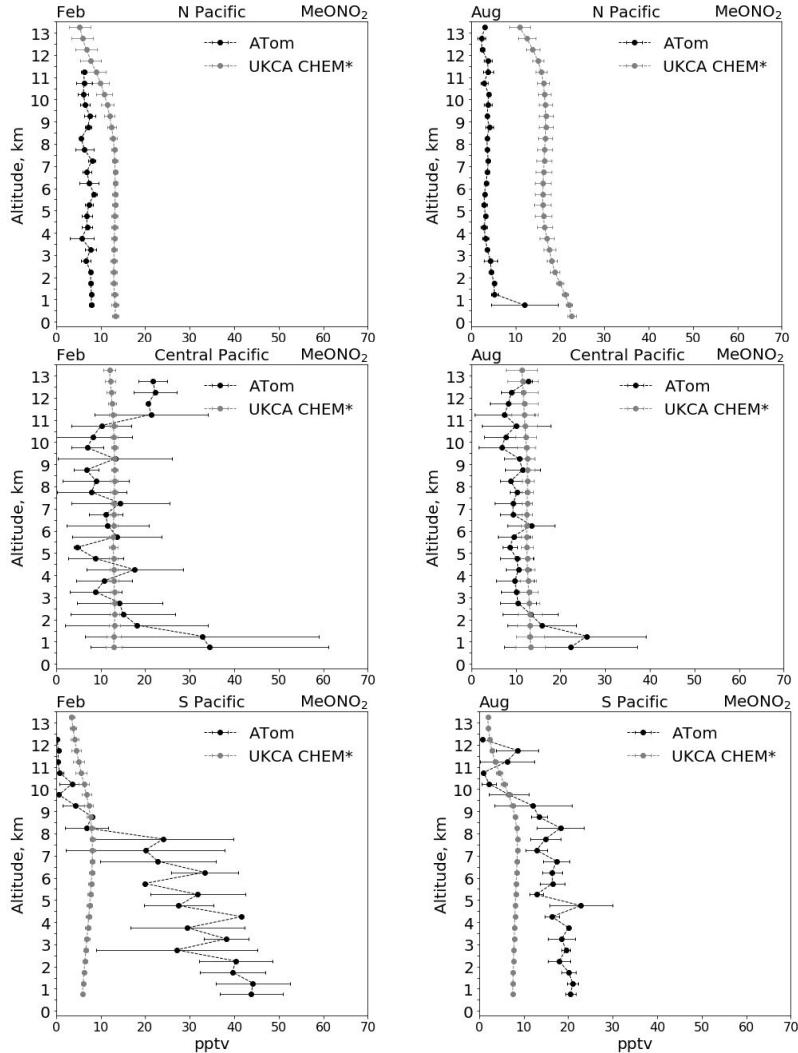


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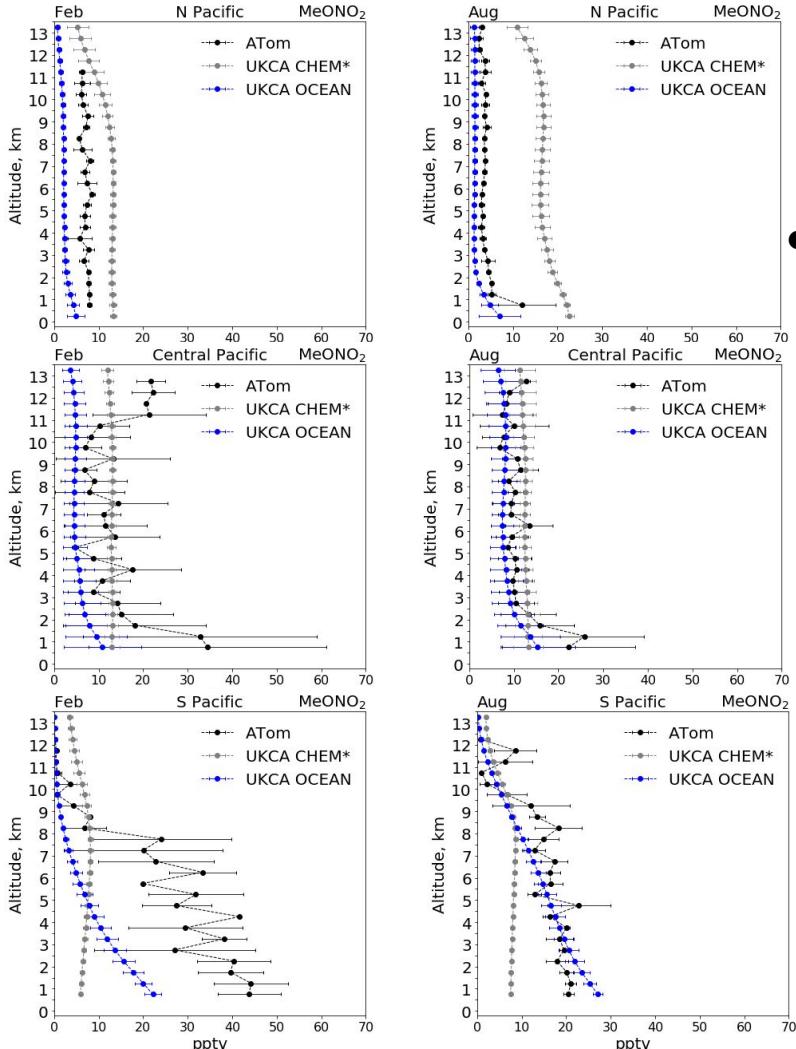
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- UKCA's  $\text{MeONO}_2$  seasonality is opposite to ATom's
- CHEM\* suggests a missing oceanic source over the equator and Southern Ocean



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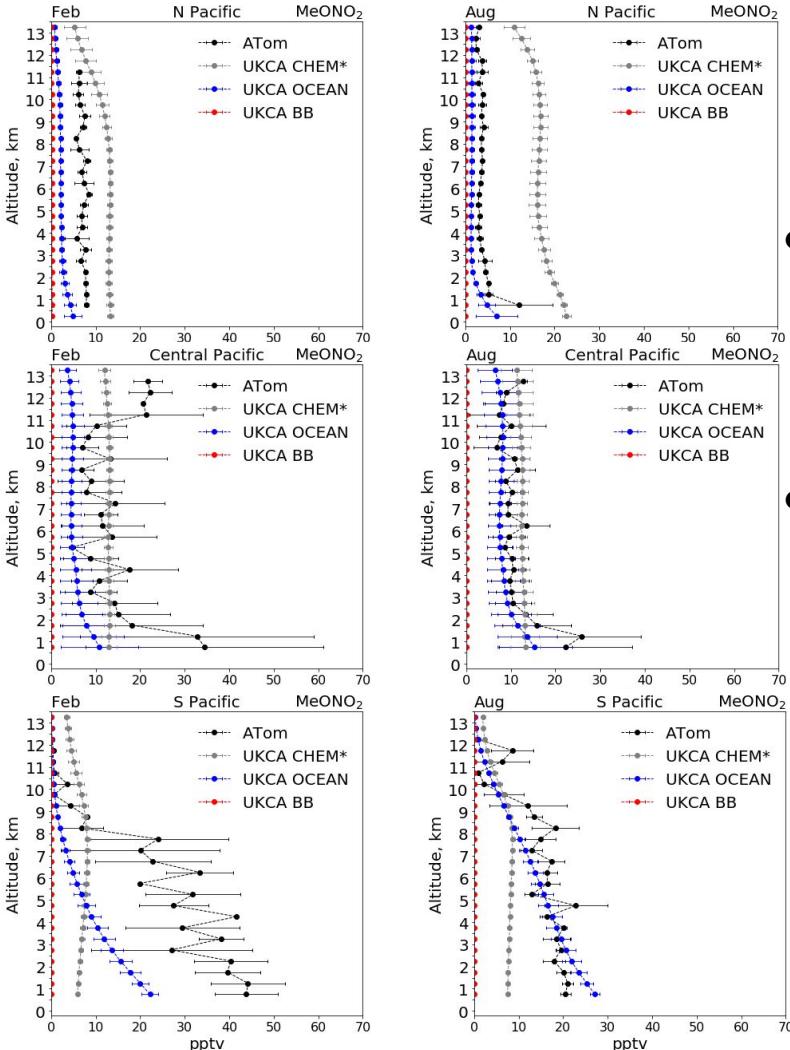
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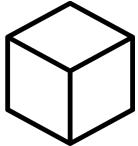
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- BB  $\text{MeONO}_2$  contribution is small

# Impacts of RONO<sub>2</sub> chemistry

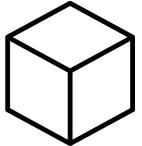
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  - O<sub>3</sub>, OH, HO<sub>2</sub> were lower by 2% in runs with RONO<sub>2</sub> (without isoprene)
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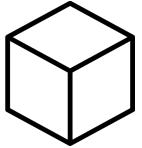


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	OCEAN	BB
O <sub>3</sub> burden, Tg		
Williams et al. (2014)	335.3 ( <b>+0.30%</b> )	
this study*	274.54 ( <b>+0.46%</b> )	273.25 ( <b>-0.007%</b> )
CH <sub>4</sub> lifetime, yr		
Neu et al. (2008)	9.28 (-1.7%)	
Williams et al. (2014)	8.40 ( <b>-0.24</b> )	
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\*10-year average using 125 ppb ozonopause

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All of these are global means,  
**but what happens locally?**

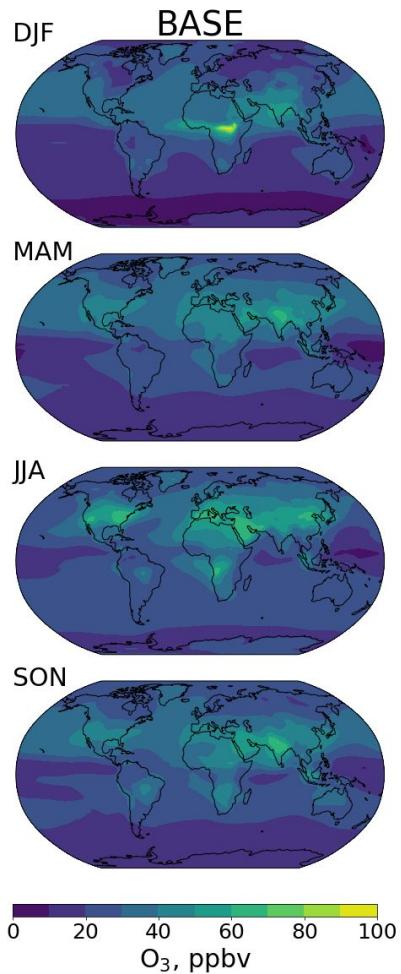
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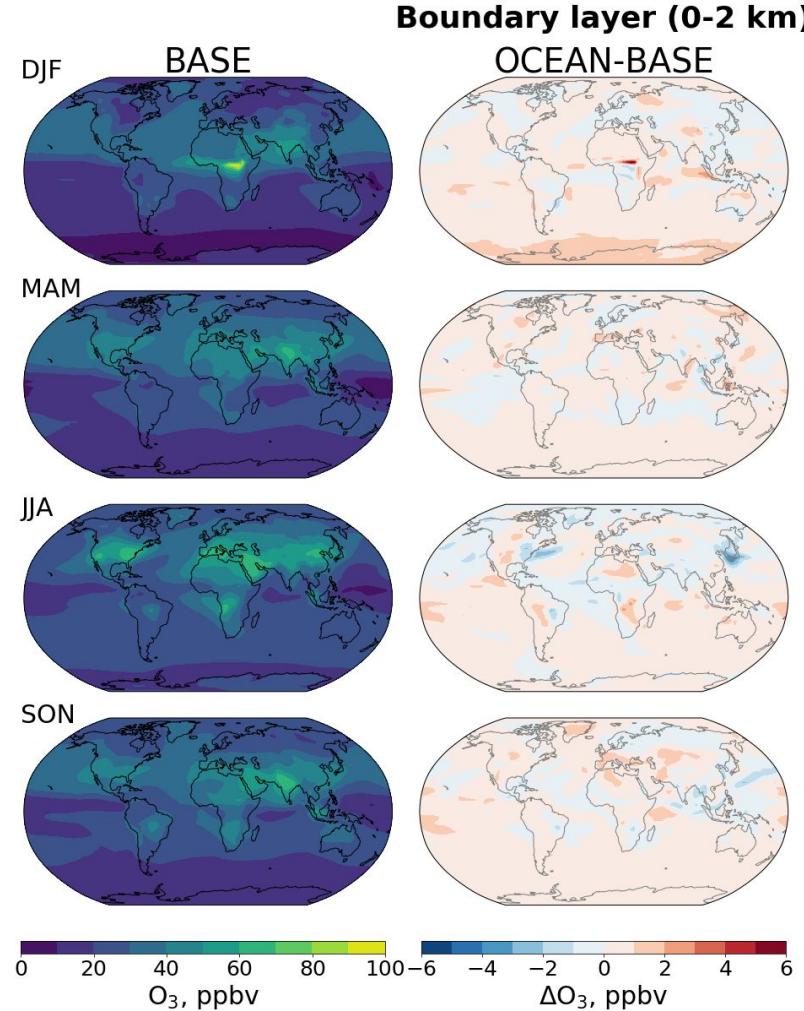
# Impact of oceanic RONO<sub>2</sub> on O<sub>3</sub>

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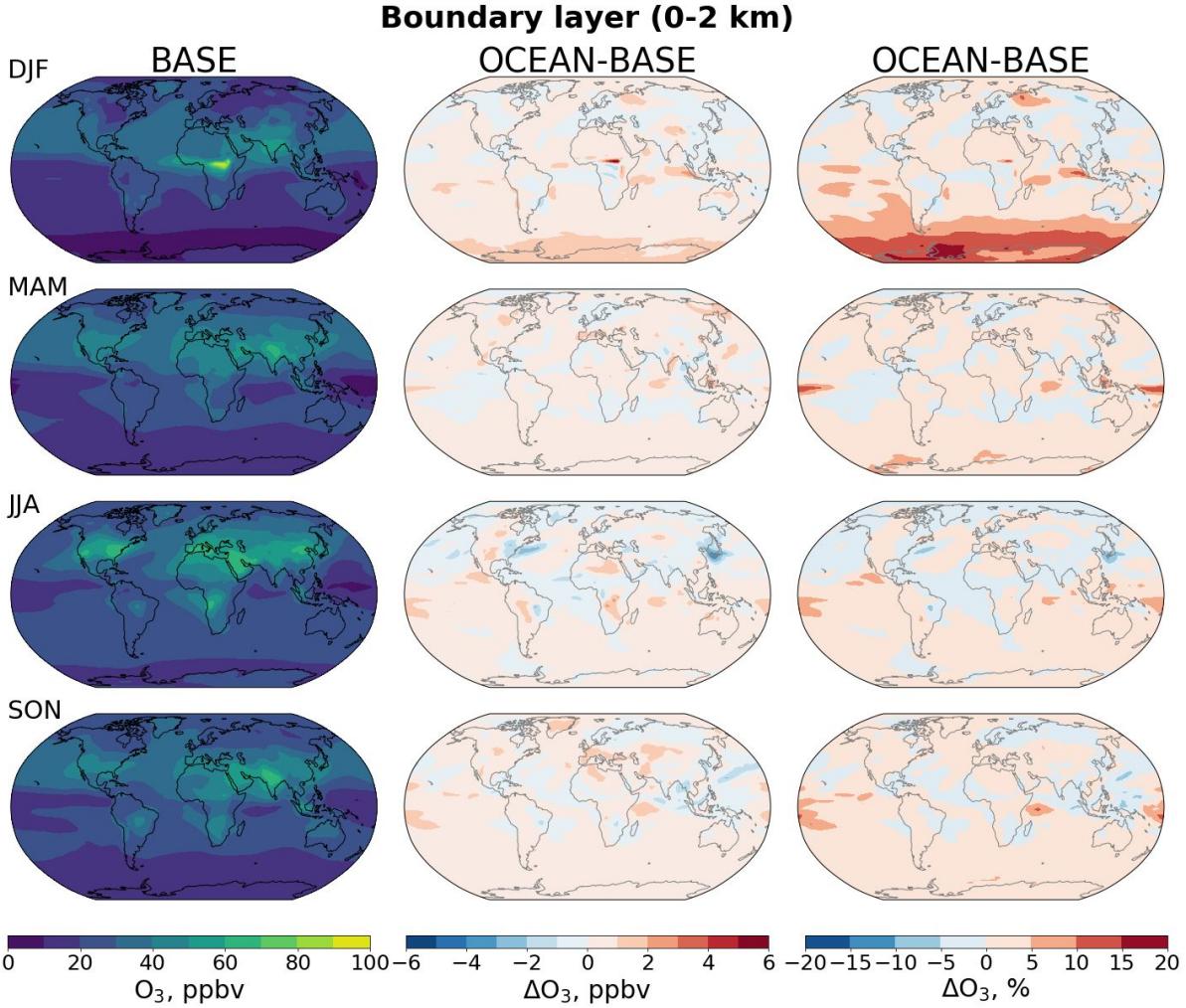
Boundary layer (0-2 km)



# Impact of oceanic RONO<sub>2</sub> on O<sub>3</sub>

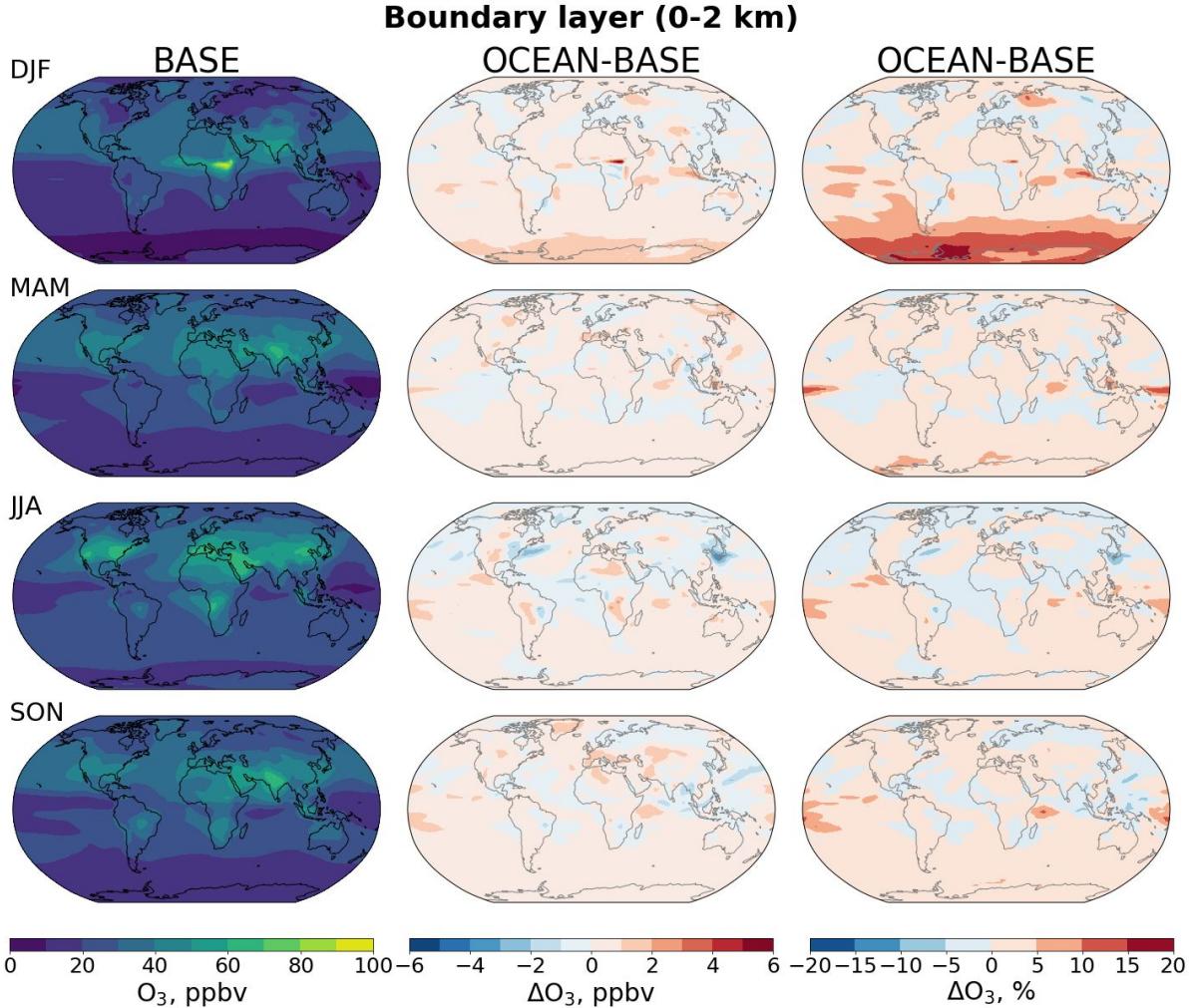


# Impact of oceanic RONO<sub>2</sub> on O<sub>3</sub>



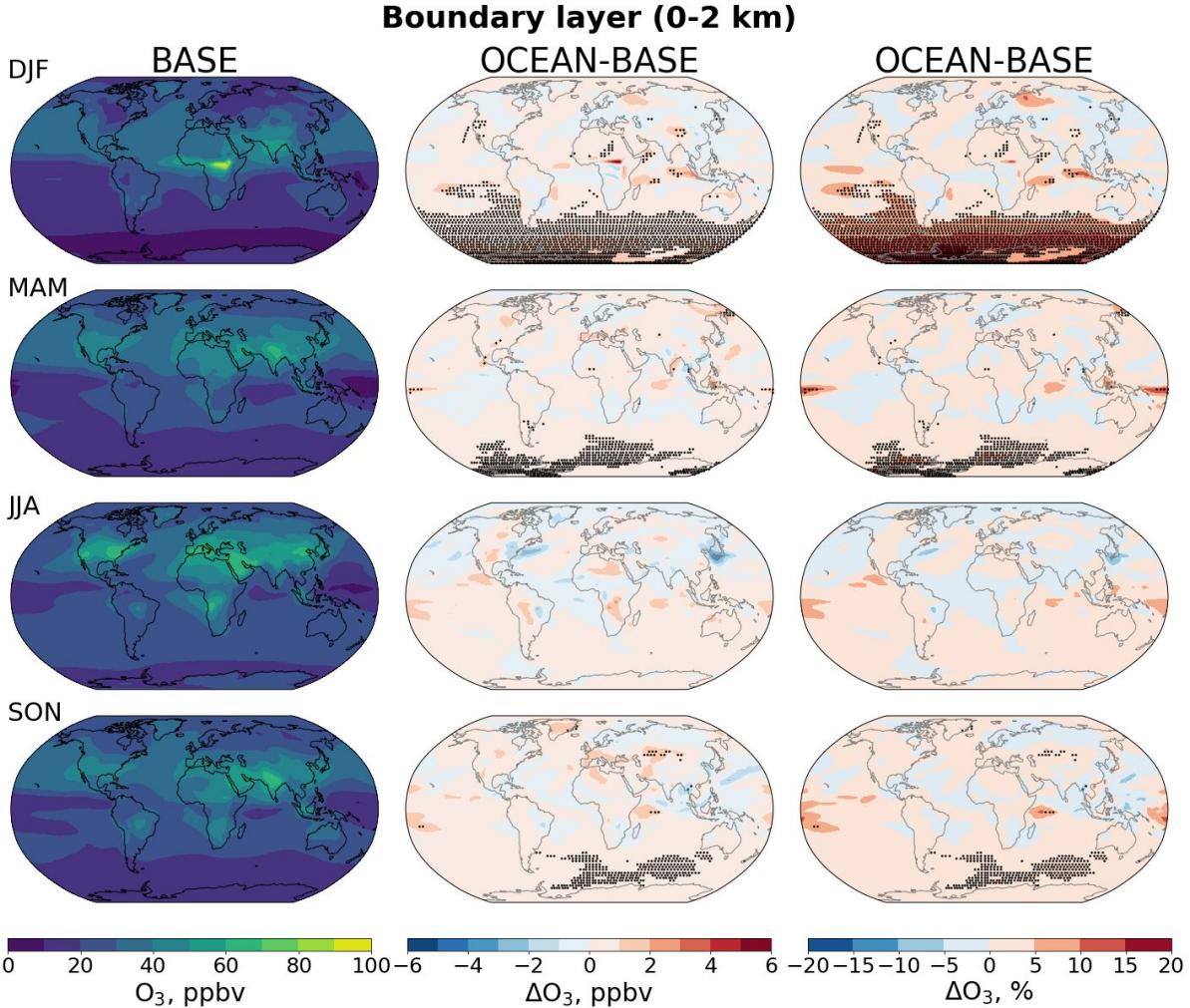
# Impact of oceanic RONO<sub>2</sub> on O<sub>3</sub>

- increase over the Southern Ocean by up to 20% (< 2 ppb)



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- increase over the Southern Ocean by up to 20% (< 2 ppb)
- statistically significant in all seasons except JJA



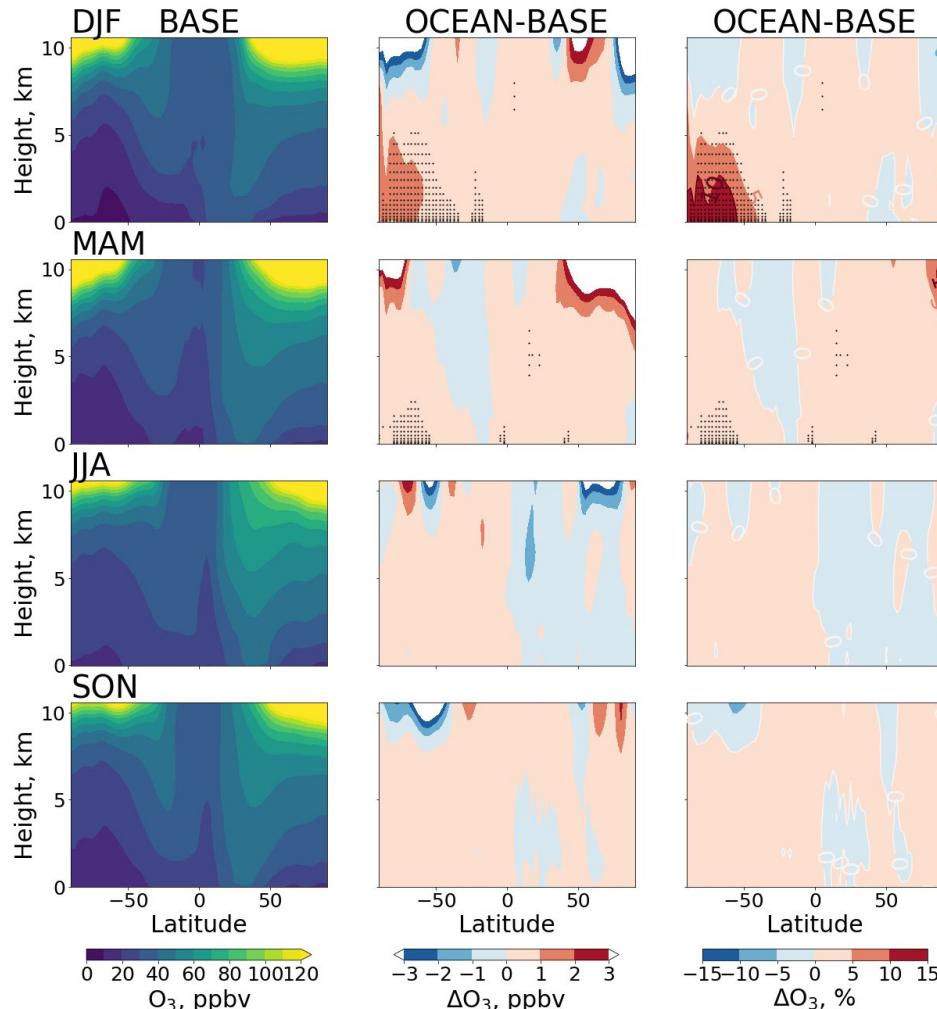
# Impact of oceanic RONO<sub>2</sub> on O<sub>3</sub>

- increase over the Southern Ocean by up to 20% (< 2 ppb)
- statistically significant in all seasons except JJA

zonal mean (0-10 km)

# Impact of oceanic RONO<sub>2</sub> on O<sub>3</sub>

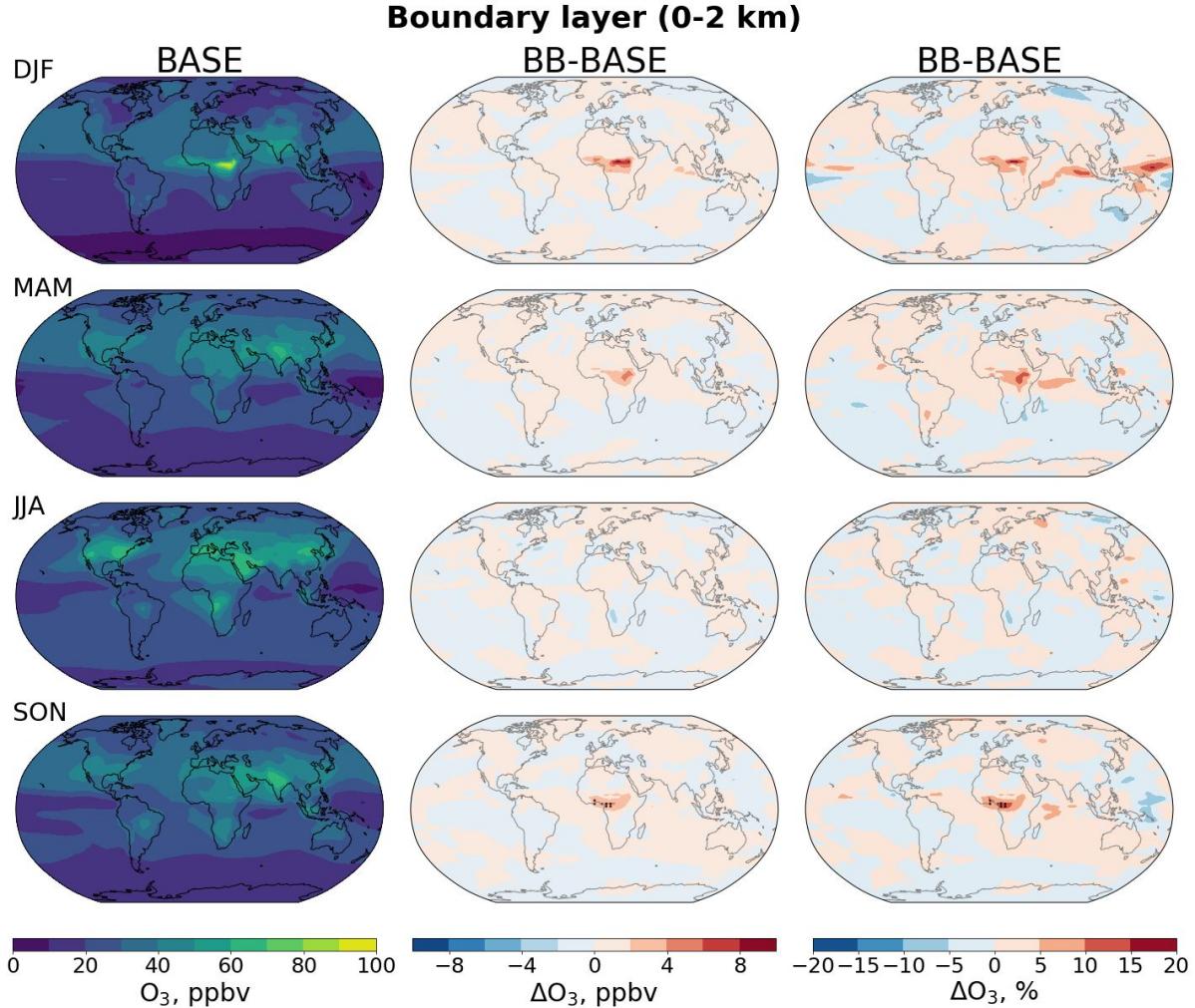
- increase over the Southern Ocean by up to 20% (< 2 ppb)
- statistically significant in all seasons except JJA
- signal persists up to 3-5 km in DJF and MAM



# Impact of BB RONO<sub>2</sub> on O<sub>3</sub>

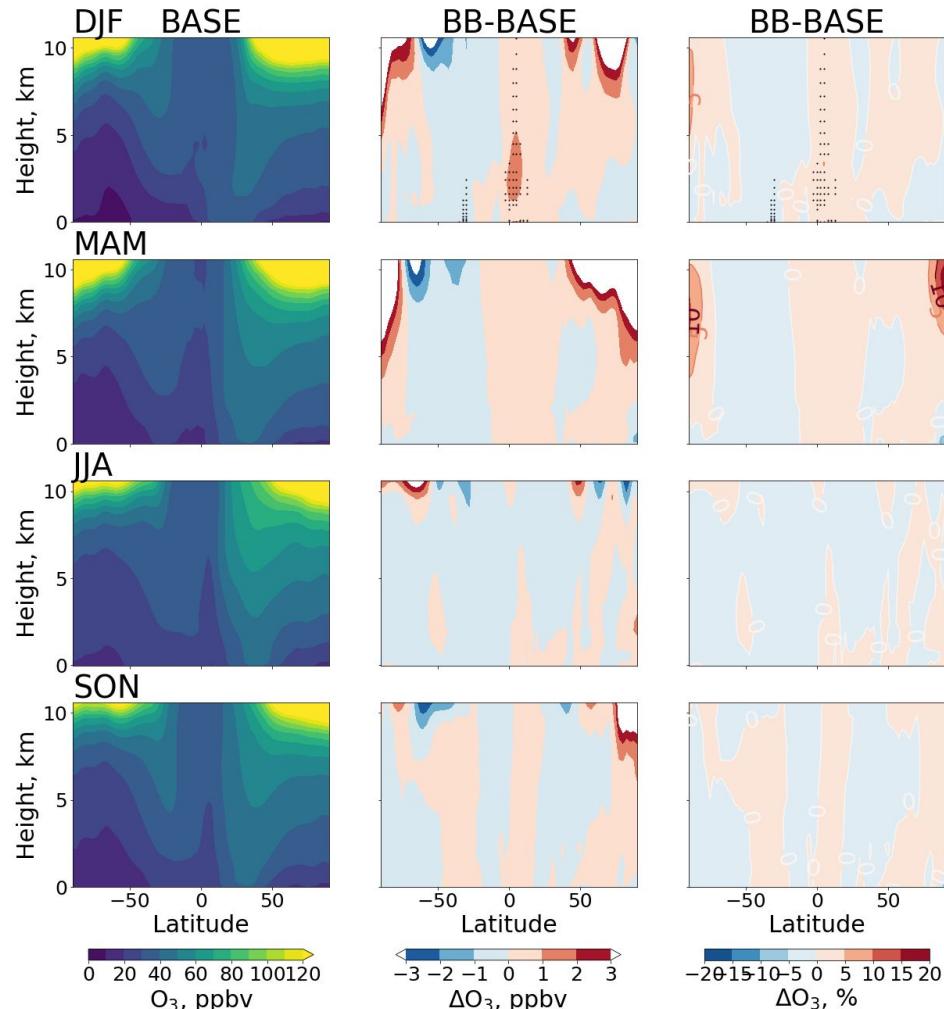
# Impact of BB RONO<sub>2</sub> on O<sub>3</sub>

- increase over the equatorial Africa by up to 20% (< 6 ppb)



# Impact of BB RONO<sub>2</sub> on O<sub>3</sub>

- increase over the equatorial Africa by up to 20% (< 6 ppb)
- statistically significant in DJF up to 10 km



# Conclusions

- We updated UKCA's CHeST chemical kinetics and added C<sub>2</sub>-C<sub>3</sub> RONO<sub>2</sub> chemistry explicitly.
- When compared to ATom, UKCA overestimates MeONO<sub>2</sub>, especially in August.
- Implemented monthly varying emissions of:
  - oceanic C<sub>1</sub>-C<sub>2</sub> RONO<sub>2</sub> modelled by GEOS-Chem,
  - biomass burning C<sub>1</sub>-C<sub>3</sub> RONO<sub>2</sub> derived from GFED.
- UKCA model state is sensitive to oceanic and biomass burning RONO<sub>2</sub> emissions:
  - Southern Ocean area is sensitive to oceanic RONO<sub>2</sub> emissions:
    - NO<sub>x</sub> increases up to 160% (< 700 ppt),
    - O<sub>3</sub> increases by up to 20% (< 2 ppb) in DJF, MAM, SON.
  - equatorial Africa region is sensitive to RONO<sub>2</sub> biomass burning emissions:
    - NO<sub>x</sub> increases by up to 80% (< 800 ppt),
    - O<sub>3</sub> increases by up to 20% (< 6 ppb) in DJF.

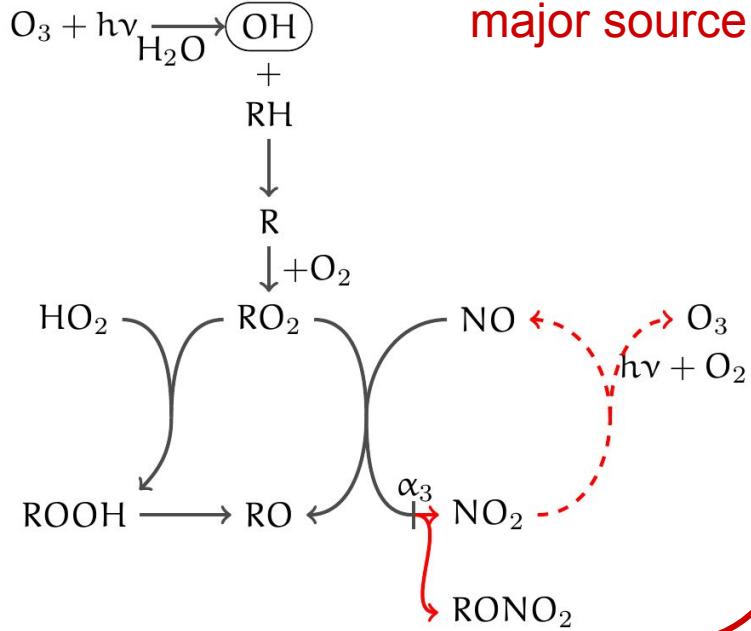
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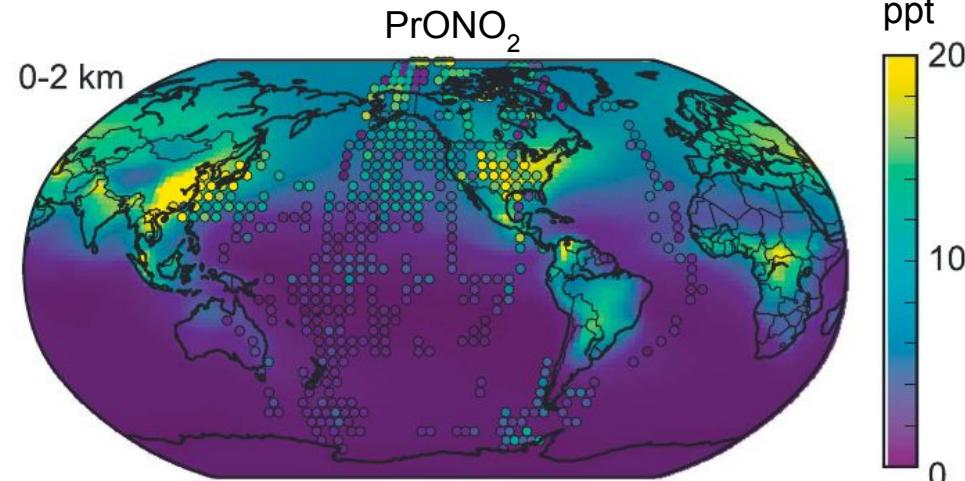
Thank you!

# Extra

# Introduction



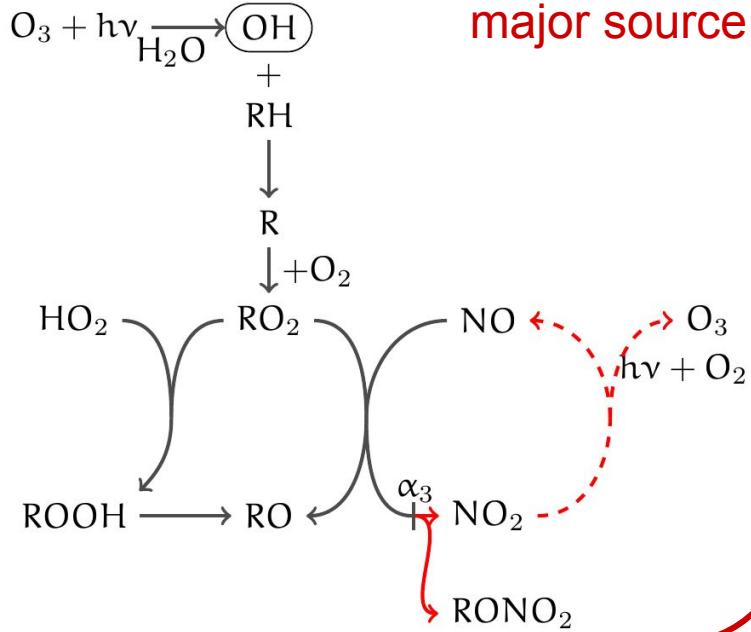
- PrONO<sub>2</sub> are produced mostly photochemically



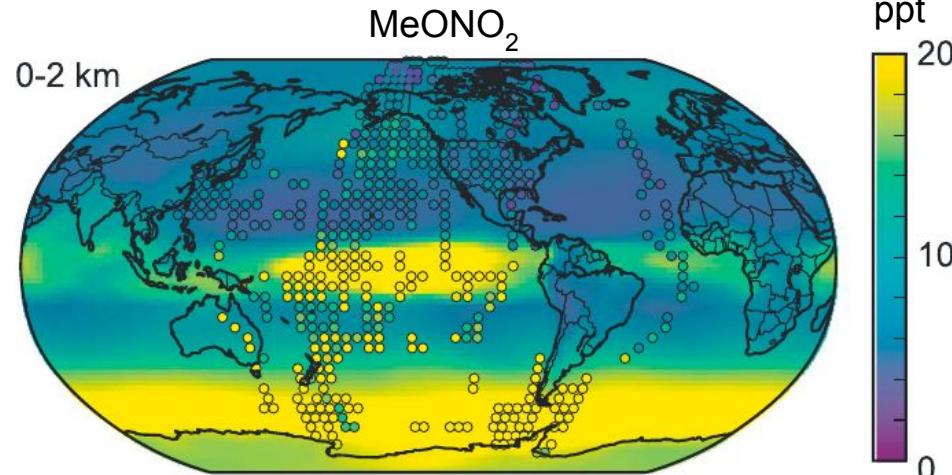
Annual mean distribution of PrONO<sub>2</sub>.  
20 years of aircraft observations were averaged  
over all flight days and over a horizontal  
resolution of 4°×5° for visibility.

Credit: Fisher et al. (2018)

# Introduction



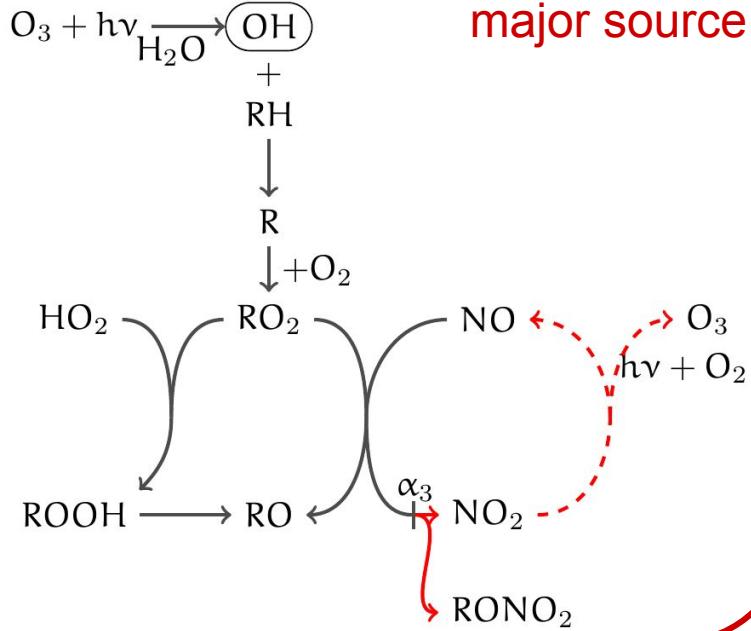
- MeONO<sub>2</sub> has strong oceanic sources in the Central Pacific and Southern Oceans



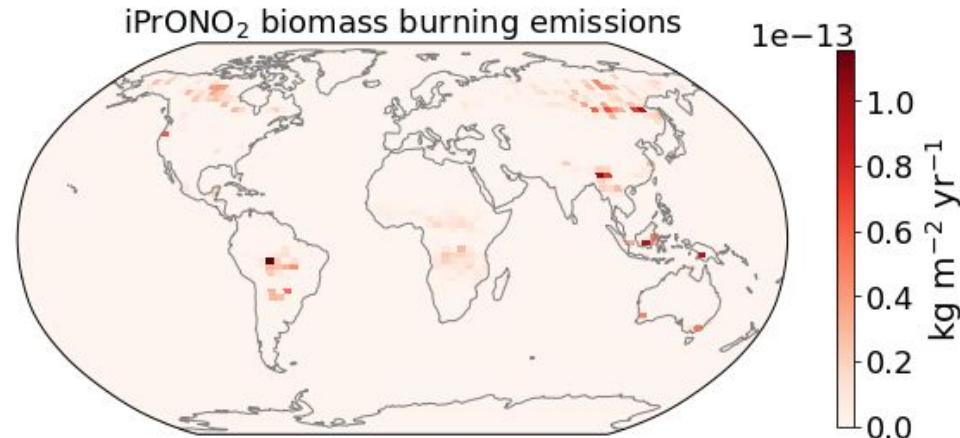
Annual mean distribution of MeONO<sub>2</sub>.  
20 years of aircraft observations were averaged over all flight days and over a horizontal resolution of  $4^\circ \times 5^\circ$  for visibility.

Credit: Fisher et al. (2018)

# Introduction



- RONO<sub>2</sub> biomass burning emissions depend on the type of fuel burned



20-year average annual mean distribution of iPrONO<sub>2</sub> biomass burning emissions derived from the GFED data (Akagi et al. (2011)).

this study

# Implementation of C<sub>1</sub>-C<sub>3</sub> RONO<sub>2</sub>

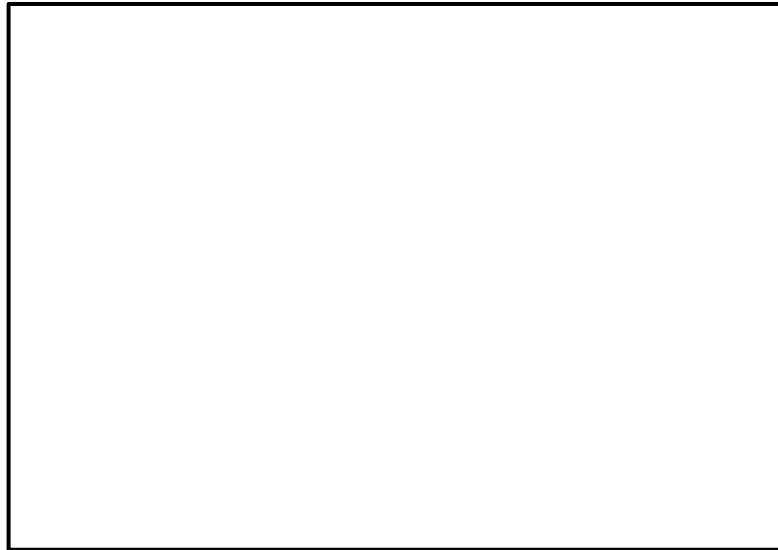
	MeONO <sub>2</sub>					EtONO <sub>2</sub>					nPrONO <sub>2</sub>					iPrONO <sub>2</sub>				
	CH prod	CH loss	DD	OC	BB	CH prod	CH loss	DD	OC	BB	CH prod	CH loss	DD	OC	BB	CH prod	CH loss	DD	OC	BB
Neu2008	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
Williams 2014	█	█	WD	Neu	█	OR GNT R	OR GN TR	WD	█	█	OR GNT R	OR GN TR	WD	█	█	OR GNT R	OR GN TR	WD	█	█
Khan2015	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
Fisher2018	█	█	█	air-sea	█	█	█	█	air-sea	█	█	█	█	air-sea	█	█	█	█	█	air-sea
this study	█	█	█	Fisher	GF ED	█	█	█	Fisher	GF ED	█	█	█	?	█	GF ED	█	█	█	?

# Steady state box model

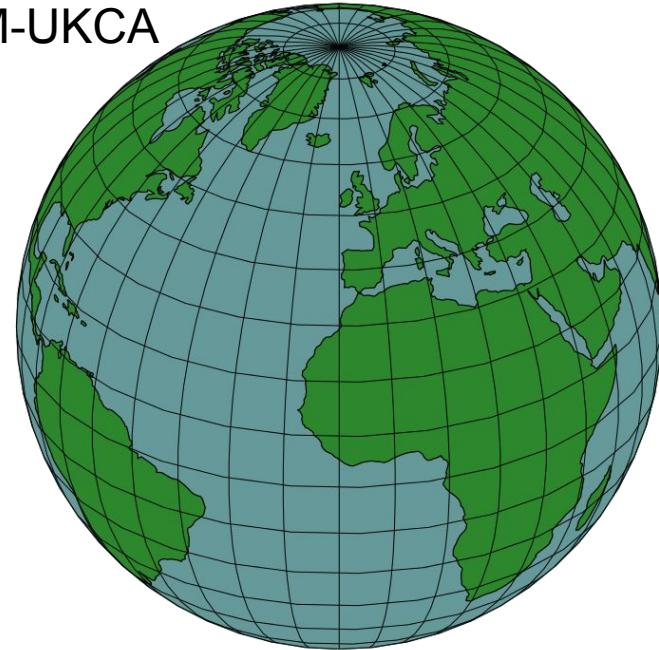
Temperature	298 K
Pressure	1000 hPa
Relative humidity	50%
Cloud cover	No clouds
Julian day	172 (21 June)
Latitude	45N
Solar declination angle	23.44
Initial concentration	O <sub>3</sub> 40 ppb, CO 100 ppb, CH <sub>4</sub> 1800 ppb
Run time	6 months

# Methods

Box model



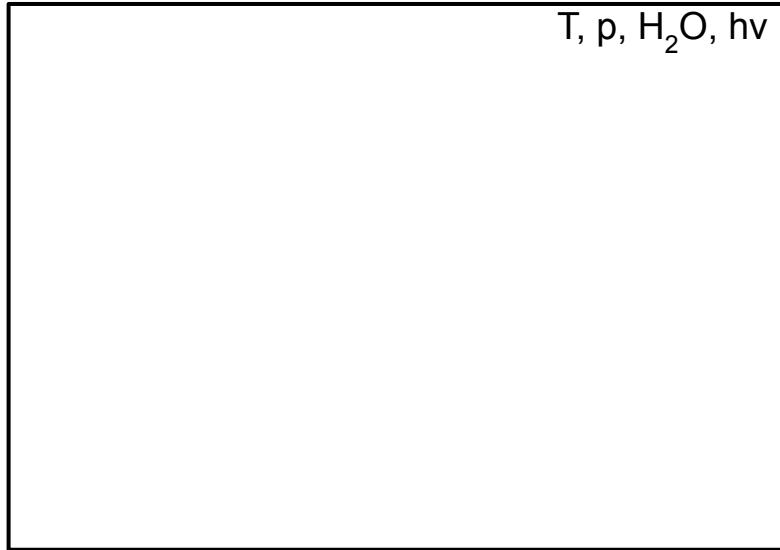
UM-UKCA



CheT

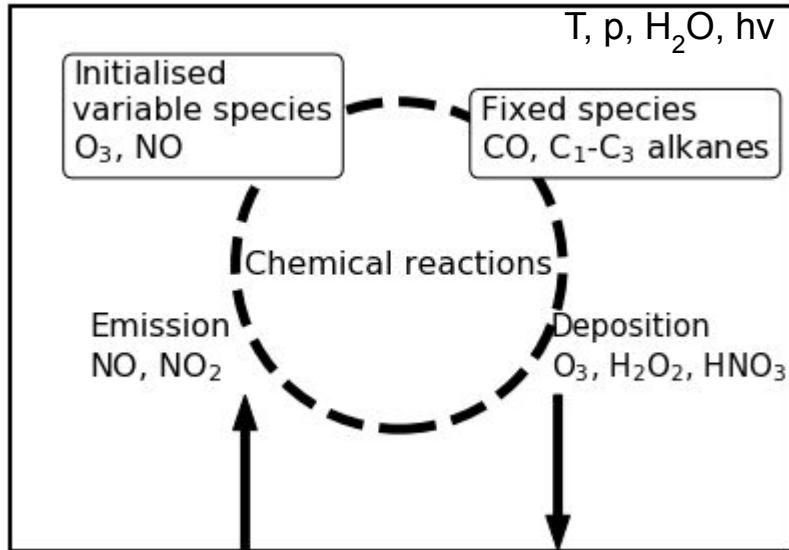
CheST: inorganic chemistry +  
 $C_1$ - $C_3$  alkanes +  
isoprene

# Steady state box model

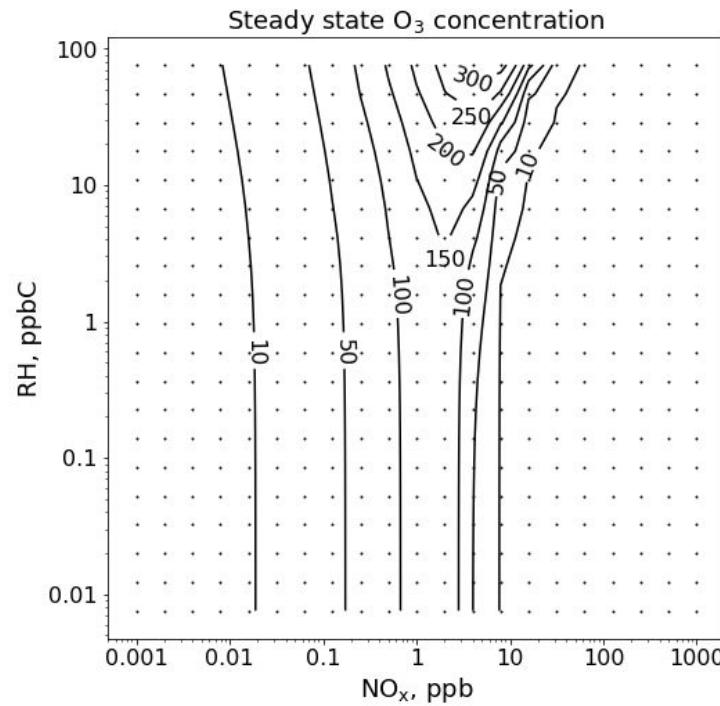
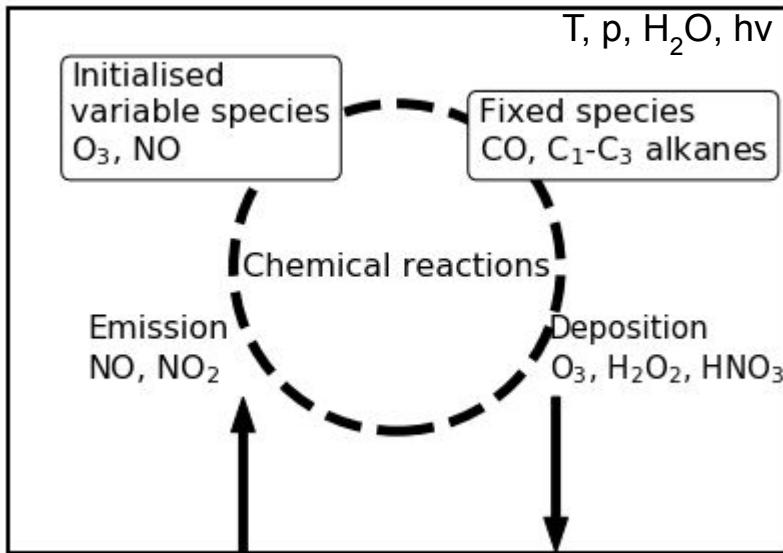


T, p, H<sub>2</sub>O, hν

# Steady state box model

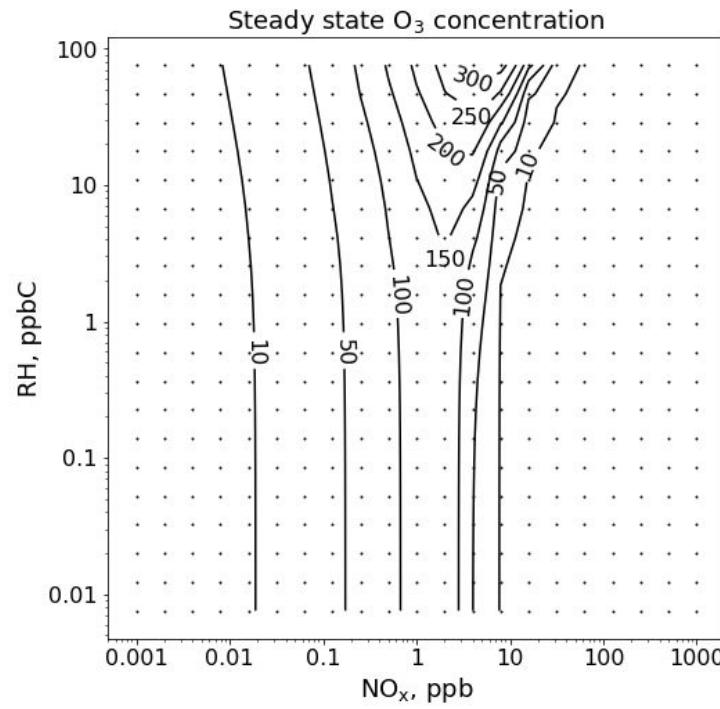
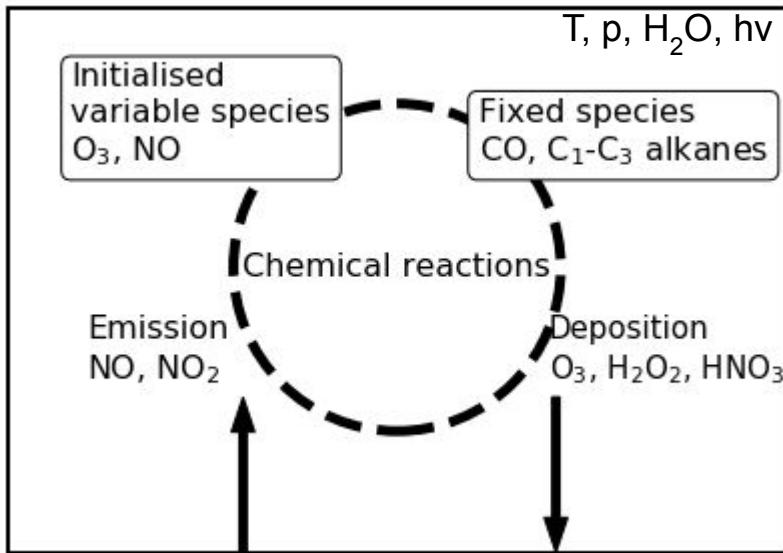


# Steady state box model



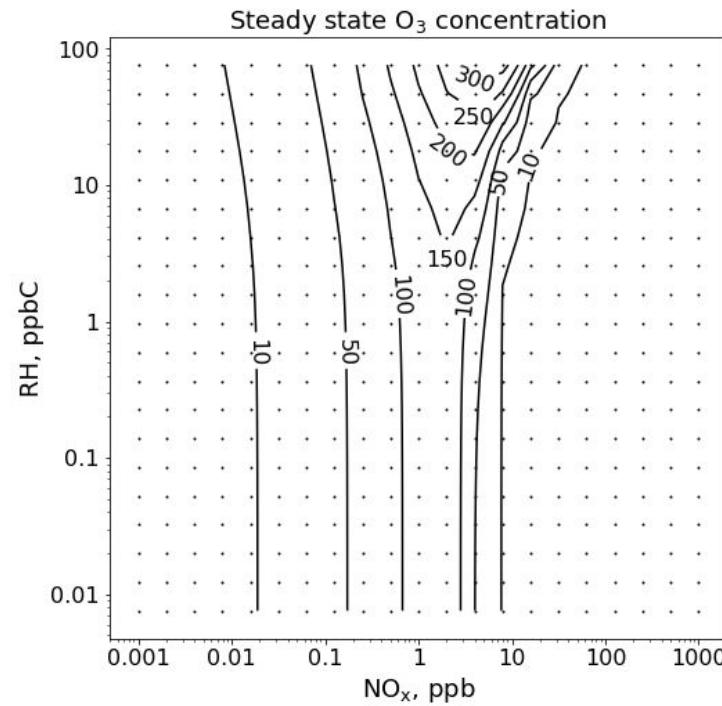
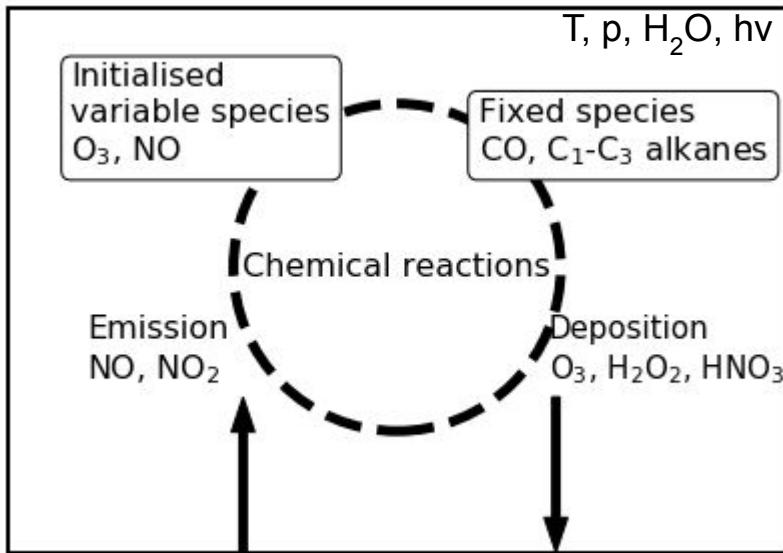
- To reach steady state,  $O_3$  precursors ( $NO_x$  and NMHC) were kept constant

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- $21 NO_x \times 20$  NMHC combinations considered in one experiment

# Steady state box model



- To reach steady state,  $O_3$  precursors ( $NO_x$  and NMHC) were kept constant
- $21 NO_x \times 20$  NMHC combinations considered in one experiment
- Chemical mechanisms were compared using isopleths plots of 24 hour average concentrations of various species

# Updating chemical kinetics

## Benchmark mechanism:

Master Chemical Mechanism (MCM) -  
a near-explicit chemical mechanism of O<sub>3</sub>  
generation during VOCs degradation in the  
boundary layer (Jenkin et al., 1997).

Inorganic + C<sub>1</sub>-C<sub>3</sub> RH oxidation requires:

	Species	Reactions
MCM	97	303
CheT	47	120

Updated bimolecular reactions:

1. HO<sub>2</sub>+EtCO<sub>3</sub>=O<sub>2</sub>+EtCO<sub>3</sub>H
2. **HO<sub>2</sub>+O<sub>3</sub>=OH+O<sub>2</sub>+O<sub>2</sub>**
3. iPrOO+NO<sub>3</sub>=Me<sub>2</sub>CO+HO<sub>2</sub>+NO<sub>2</sub>
4. MeOO+MeOO=HO<sub>2</sub>+HO<sub>2</sub>+HCHO+HCHO (\*)
5. MeOO+MeOO=MeOH+HCHO+O<sub>2</sub> (\*)
6. NO<sub>3</sub>+HCHO=HNO<sub>3</sub>+HO<sub>2</sub>+CO
7. nPrOO+NO<sub>3</sub>=EtCHO+HO<sub>2</sub>+NO<sub>2</sub>
8. **OH+CH<sub>4</sub>=H<sub>2</sub>O+MeOO**
9. **OH+HO<sub>2</sub>NO<sub>2</sub>=H<sub>2</sub>O+NO<sub>2</sub>+O<sub>2</sub>**
10. **OH+HONO=H<sub>2</sub>O+NO<sub>2</sub>**
11. OH+MeOOH=H<sub>2</sub>O+MeOO
12. OH+MGLY=MeCO<sub>3</sub>+CO+H<sub>2</sub>O
13. OH+OH=H<sub>2</sub>O+O<sub>3</sub>P

Updated termolecular reactions:

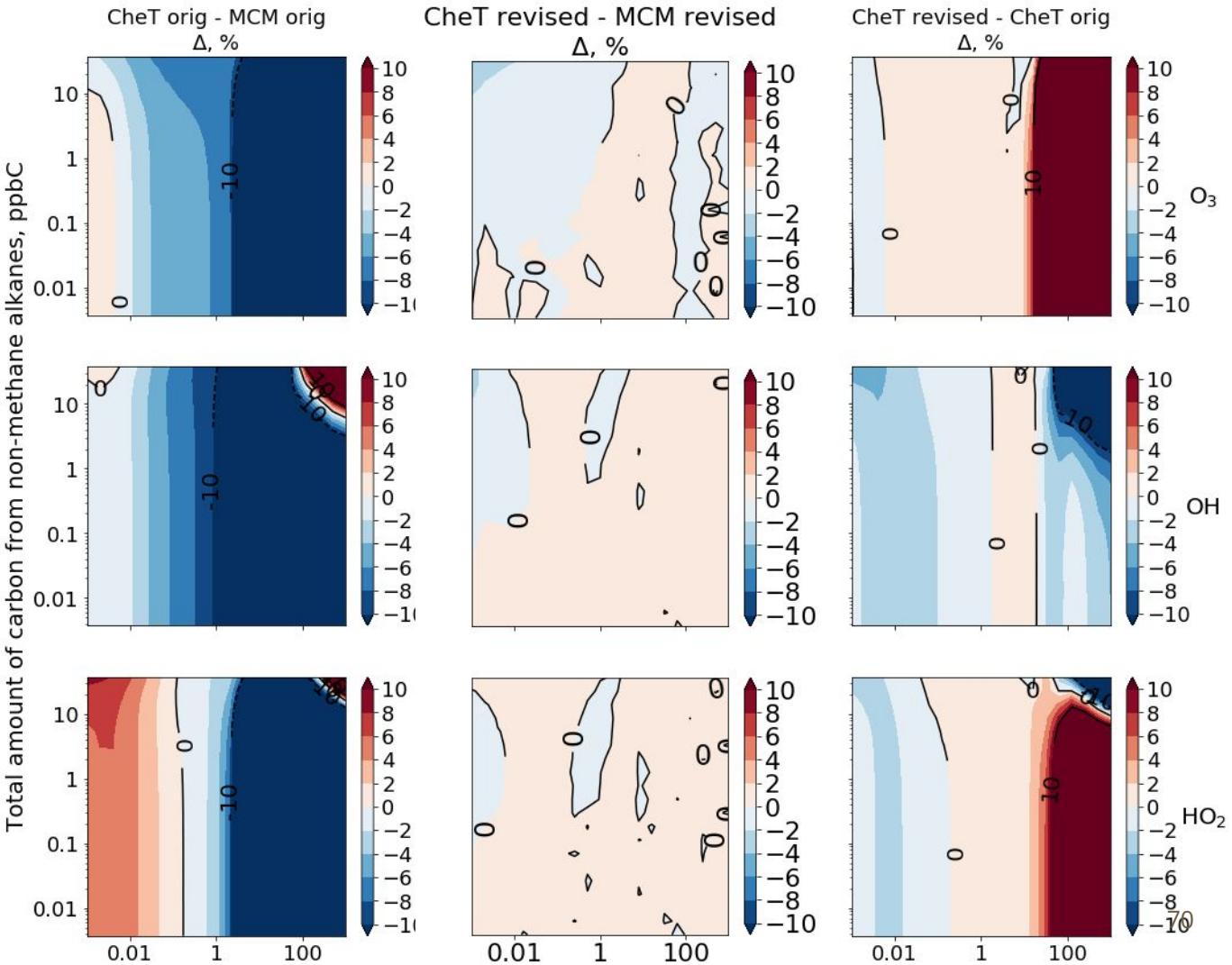
1. EtCO<sub>3</sub>+NO<sub>2</sub>=PPAN+M
2. HO<sub>2</sub>+NO<sub>2</sub>=HO<sub>2</sub>NO<sub>2</sub>+M
3. MeCO<sub>3</sub>+NO<sub>2</sub>=PAN+M
4. NO+NO=NO<sub>2</sub>+NO<sub>2</sub> (\*)
5. **NO<sub>2</sub>+NO<sub>3</sub>=N<sub>2</sub>O<sub>5</sub>+M**
6. O+NO=NO<sub>2</sub> (\*)
7. O+NO<sub>2</sub>=NO<sub>3</sub> (\*)

IUPAC vs JPL

(\*) box model only

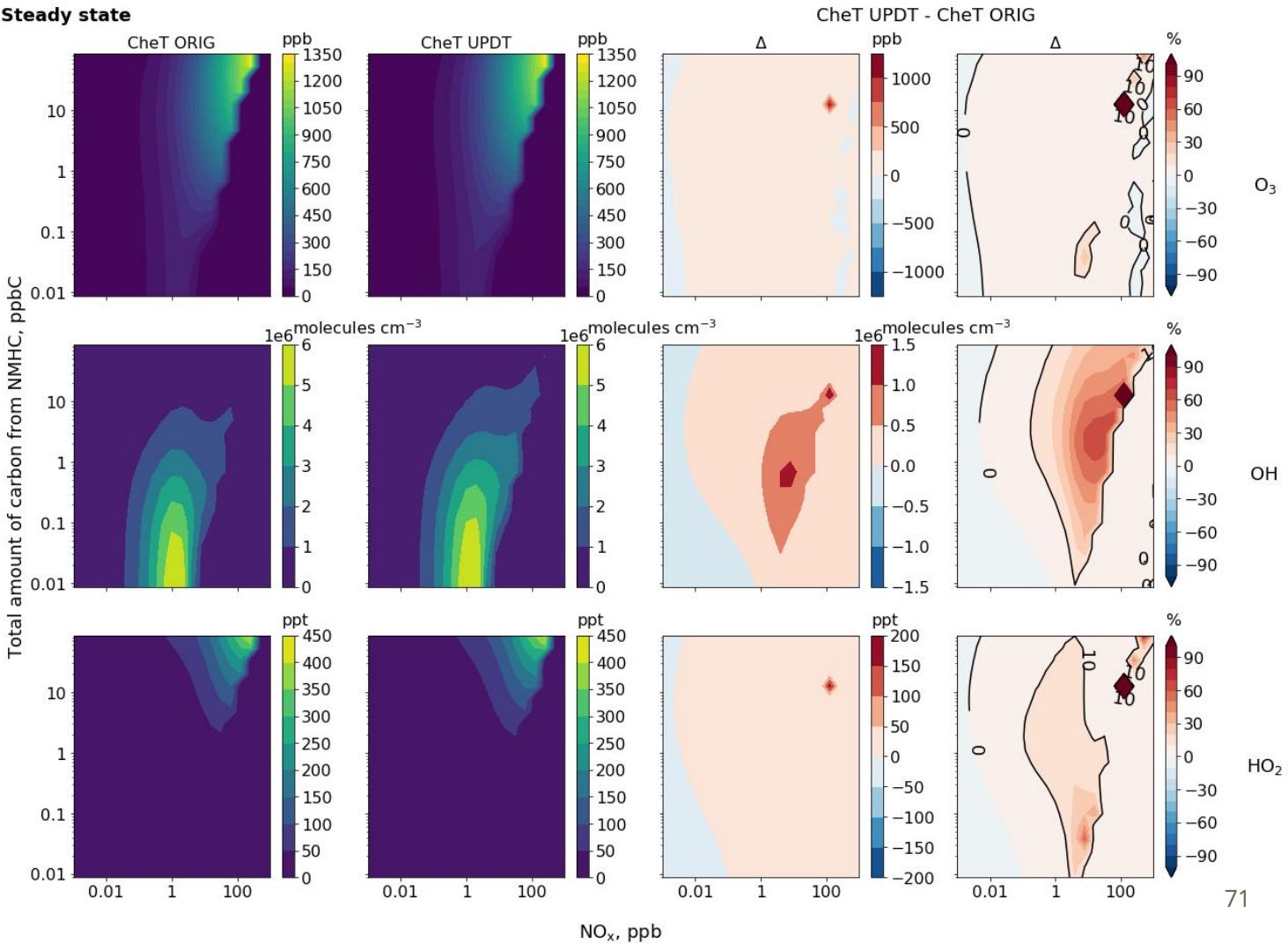
# Results: box

- Updating inorganic and C<sub>1</sub>-C<sub>3</sub> RH chemistry eliminates the differences in oxidants between mechanisms in a box model
- Updated CheT predicts higher O<sub>3</sub>, HO<sub>2</sub> and lower OH at high NO<sub>x</sub> but elsewhere it's similar to original



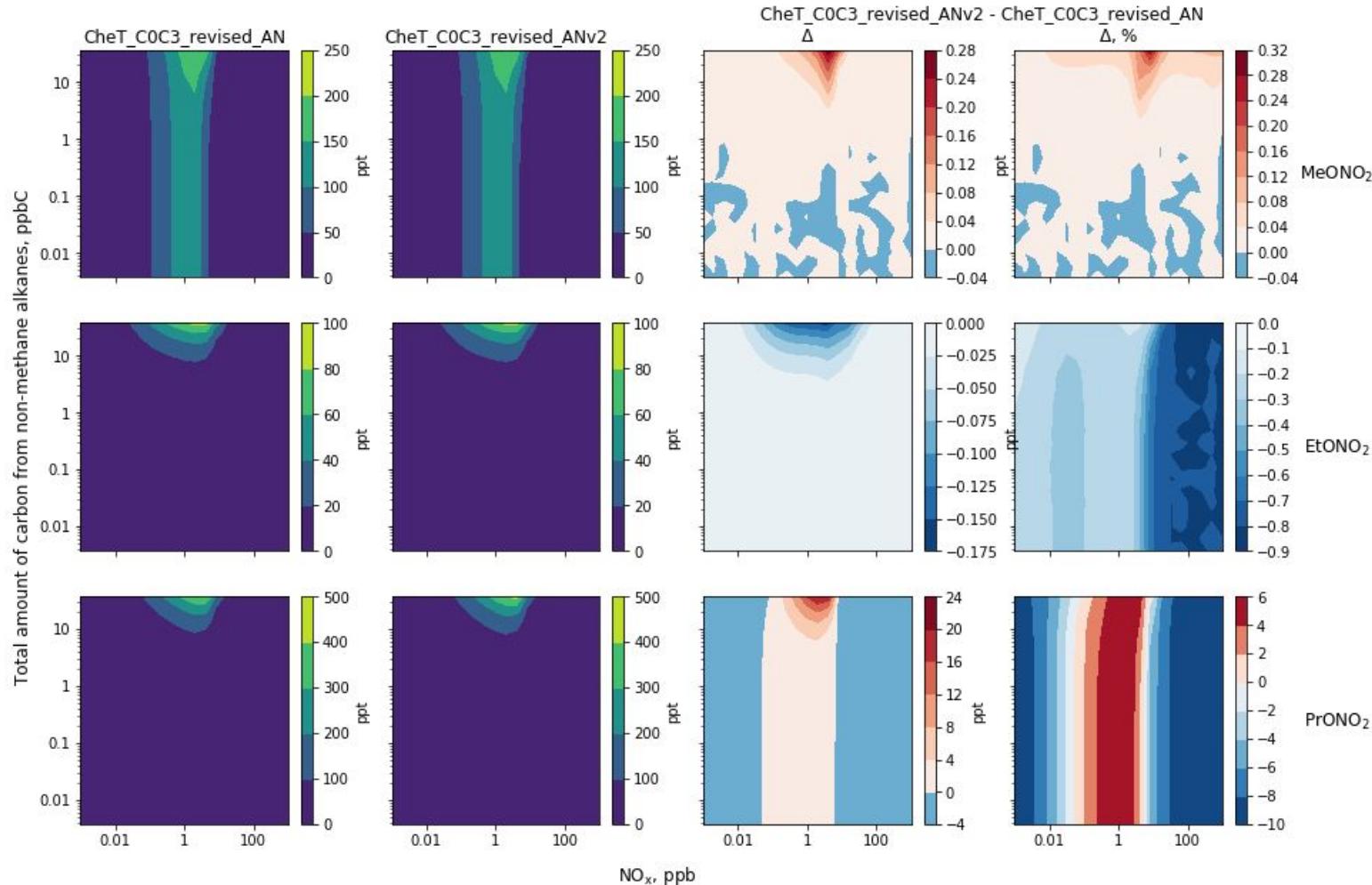
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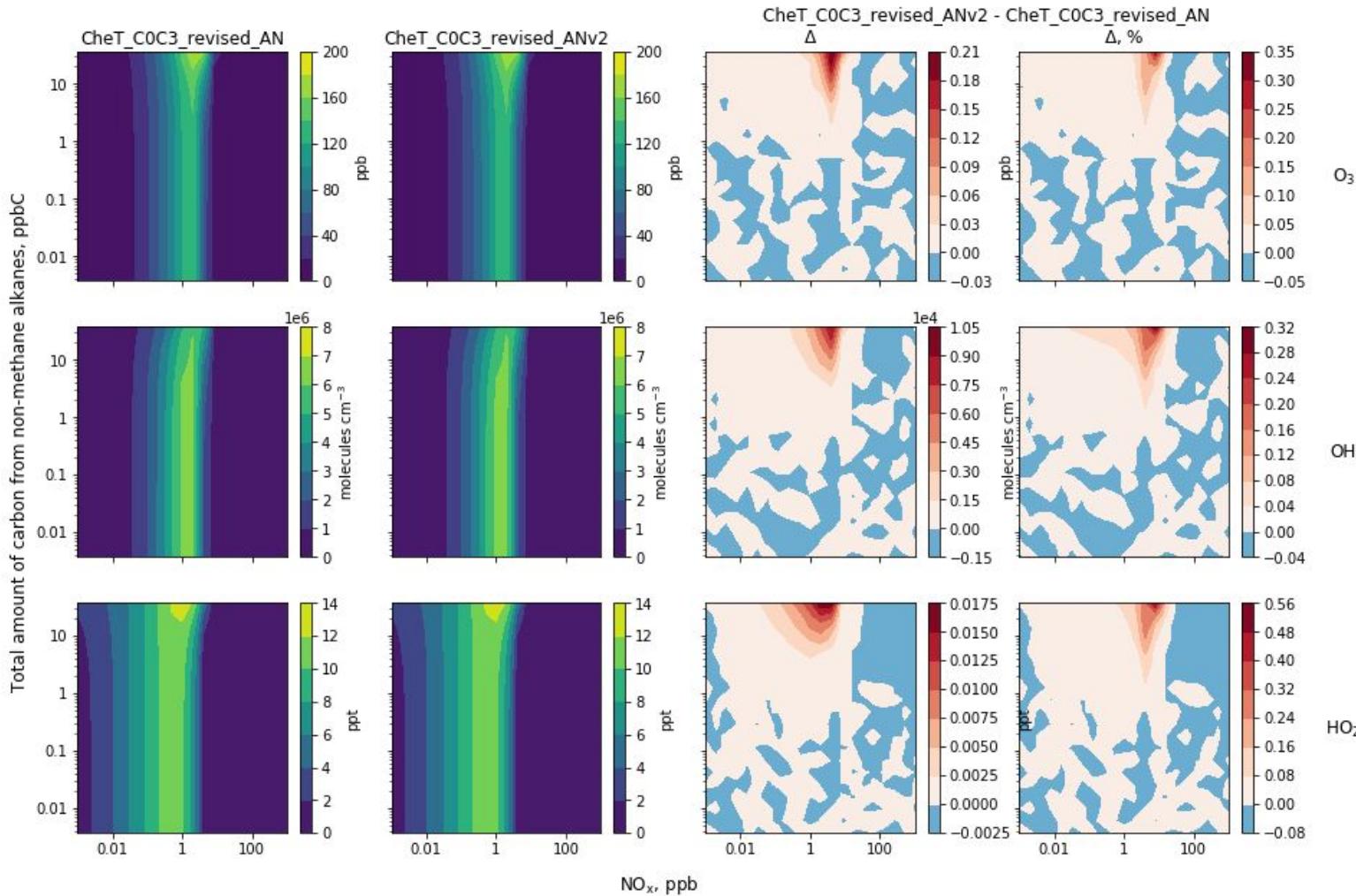
**Steady state**



# Versions of PrONO<sub>2</sub> chemistry

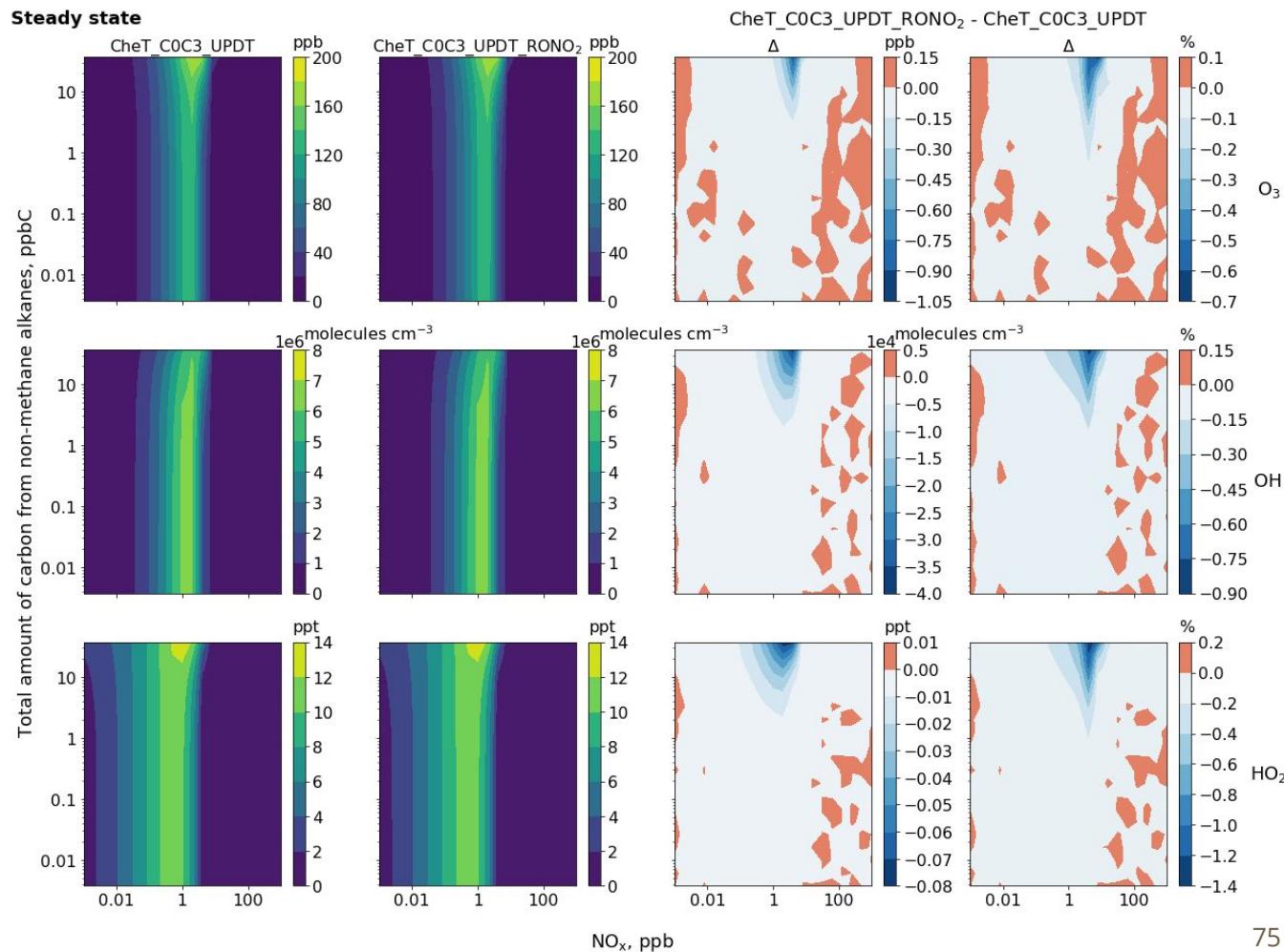
MCM/CheT_C0C3_revised_AN/base	CheT_C0C3_revised_ANv2	CheT_C0C3_revised_ANv3
$n\text{PrOO} + \text{NO} = n\text{PrONO}_2$ 2.90e-12*exp(350/T)*0.020 $i\text{PrOO} + \text{NO} = i\text{PrONO}_2$ 2.70e-12*exp(360/T)*0.042 $n\text{PrONO}_2 + \text{OH} = \text{EtCHO} + \text{NO}_2 + \text{H}_2\text{O}$ 5.8e-13 $i\text{PrONO}_2 + \text{OH} = \text{Me}_2\text{CO} + \text{NO}_2 + \text{H}_2\text{O}$ 6.20e-13*exp(-230/T) $n\text{PrONO}_2 + h\nu = \text{EtCHO} + \text{NO}_2 + \text{HO}_2$ 1.75e-06 $i\text{PrONO}_2 + h\nu = \text{Me}_2\text{CO} + \text{NO}_2 + \text{HO}_2$ 2.93e-06	$n\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.90e-12*exp(350/T)*0.020 $i\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.70e-12*exp(360/T)*0.042 $\text{PrONO}_2 + \text{OH} = \text{Me}_2\text{CO} + \text{NO}_2 + \text{H}_2\text{O}$ 6.20e-13*exp(-230/T) $\text{PrONO}_2 + h\nu = \text{Me}_2\text{CO} + \text{NO}_2 + \text{HO}_2$ 2.93e-06*	$n\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.90e-12*exp(350/T)*0.020 $i\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.70e-12*exp(360/T)*0.042 $\text{PrONO}_2 + \text{OH} = 0.62*\text{EtCHO} + 0.38*\text{Me}_2\text{CO} + \text{NO}_2 + \text{H}_2\text{O}$ 5.8e-13 $\text{PrONO}_2 + h\nu = 0.4*\text{EtCHO} + 0.6*\text{Me}_2\text{CO} + \text{NO}_2 + \text{HO}_2$ 2.93e-06*
<ul style="list-style-type: none"> <li>production rates of n- and i-propyl nitrate at 298 K are different by a factor of 2 (nPrONO<sub>2</sub> 1.88e-13, iPrONO<sub>2</sub> 3.80e-13)</li> <li>iPrONO<sub>2</sub> OH oxidation is temperature dependent</li> <li>iPrONO<sub>2</sub> photolysis is 1.67 times bigger than nPrONO<sub>2</sub></li> <li>products of n- and i-propyl nitrate oxidation and photolysis are different, with different lifetimes and impacts on the rest of the chemistry           <ul style="list-style-type: none"> <li>Me<sub>2</sub>CO is longer lived than EtCHO</li> <li>EtCHO -&gt; EtOO -&gt; EtONO<sub>2</sub></li> <li>Me<sub>2</sub>CO -&gt; MeOO -&gt; MeONO<sub>2</sub></li> </ul> </li> </ul>	<p>*In UKCA: <math>j(\text{MeONO}_2)</math></p> <ul style="list-style-type: none"> <li>produce one propyl nitrate instead of two</li> <li>branching ratio for iPrOO production from C<sub>3</sub>H<sub>8</sub>+OH is 0.736, so iPrOO should be more abundant</li> <li>use iPrONO<sub>2</sub> OH oxidation and photolysis for lumped PrONO<sub>2</sub> chemistry because iPrOO is more abundant</li> </ul> <p>Problems:</p> <ul style="list-style-type: none"> <li>overestimation of PrONO<sub>2</sub>, Me<sub>2</sub>CO, MeOO and MeONO<sub>2</sub></li> <li>underestimation of EtCHO, EtOO and EtONO<sub>2</sub></li> </ul>	<p>*In UKCA: <math>j(\text{MeONO}_2)</math></p> <ul style="list-style-type: none"> <li>produce one propyl nitrate instead of two</li> <li>produce both EtCHO and Me<sub>2</sub>CO during PrONO<sub>2</sub> oxidation and photolysis, with yields derived from the ratio of the corresponding reaction rate coefficients</li> <li>use nPrONO<sub>2</sub> oxidation and iPrONO<sub>2</sub> photolysis rate for PrONO<sub>2</sub> as an upper limit</li> </ul> <p>Problems:</p> <ul style="list-style-type: none"> <li>severe underestimation (up to -160 ppt) of PrONO<sub>2</sub> despite it being produced from nPrOO+NO and iPrOO+NO due to high PrONO<sub>2</sub>+OH/hv rate</li> <li>negative bias in O<sub>3</sub> (up to -700 ppt)</li> </ul>
	CheT_C0C3_revised_ANv4	
	$n\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.90e-12*exp(350/T)*0.020 $i\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.70e-12*exp(360/T)*0.042 $\text{PrONO}_2 + \text{OH} = 0.62*\text{EtCHO} + 0.38*\text{Me}_2\text{CO} + \text{NO}_2 + \text{H}_2\text{O}$ (5.8e-13+6.20e-13*exp(-230/T))/2 $\text{PrONO}_2 + h\nu = 0.4*\text{EtCHO} + 0.6*\text{Me}_2\text{CO} + \text{NO}_2 + \text{HO}_2$ (1.75e-06+2.93e-06)/2*	$n\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.90e-12*exp(350/T)*0.020 $i\text{PrOO} + \text{NO} = \text{PrONO}_2$ 2.70e-12*exp(360/T)*0.042 $\text{PrONO}_2 + \text{OH} = 0.62*\text{EtCHO} + 0.38*\text{Me}_2\text{CO} + \text{NO}_2 + \text{H}_2\text{O}$ 5.8e-13 $\text{PrONO}_2 + h\nu = 0.4*\text{EtCHO} + 0.6*\text{Me}_2\text{CO} + \text{NO}_2 + \text{HO}_2$ 2.93e-06*
	<p>*In UKCA: <math>j(\text{MeONO}_2)</math></p> <ul style="list-style-type: none"> <li>EtONO<sub>2</sub>, EtCHO, Me<sub>2</sub>CO and O<sub>3</sub> bias is the same as in v3, up to -700 ppt for O<sub>3</sub> in O<sub>3</sub> production regime (mid NOx-high RH)</li> <li>MeONO<sub>2</sub>, PrONO<sub>2</sub> bias is smaller, but to -70 ppt for PrONO<sub>2</sub> in O<sub>3</sub> production regime (mid NOx-high RH)</li> </ul>	



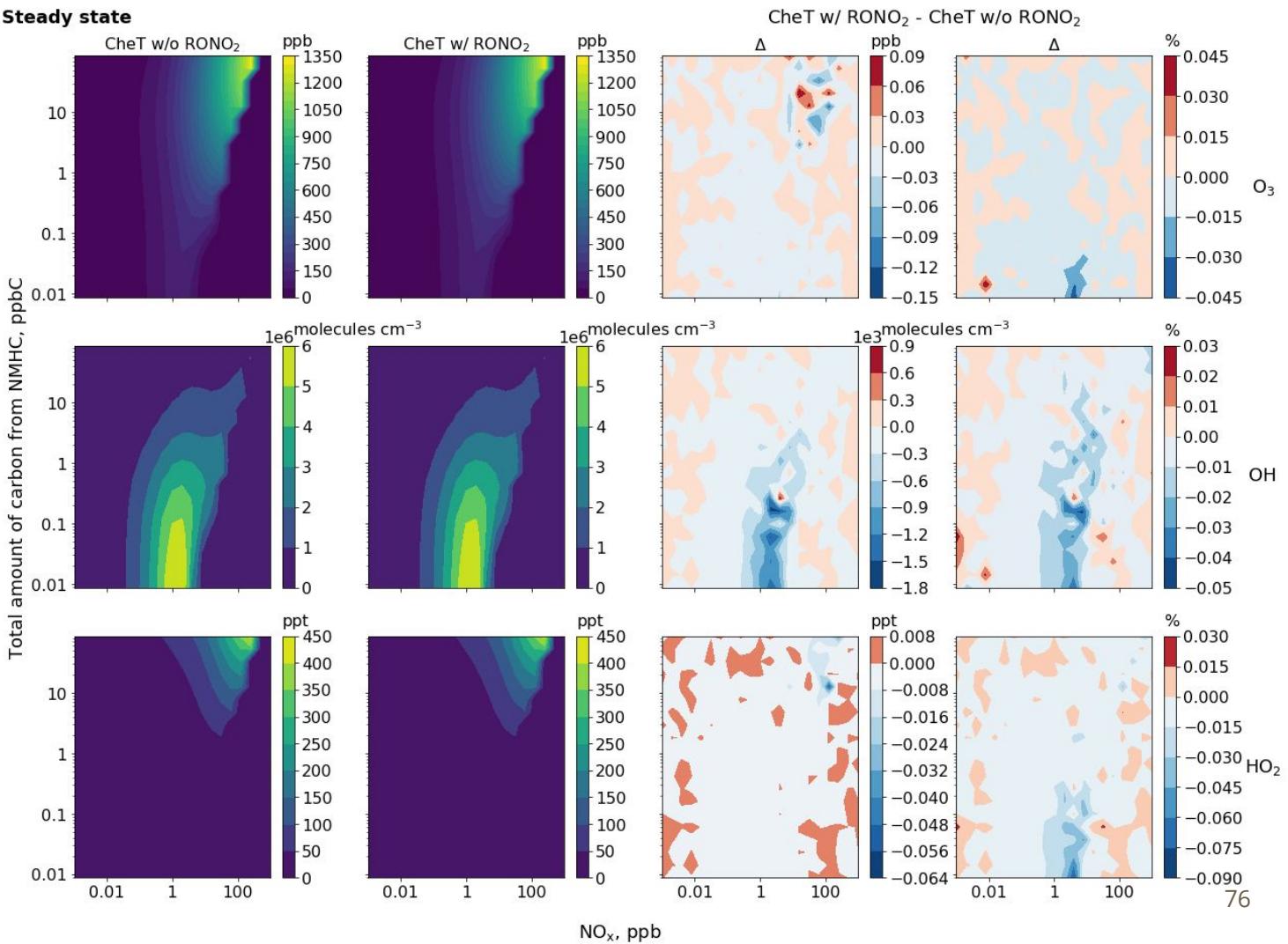


# Results: box

- Addition of C<sub>1</sub>-C<sub>3</sub> RONO<sub>2</sub> changes steady state O<sub>3</sub>, OH and HO<sub>2</sub> by no more than 2%
- At mid NOx-high RH conditions C<sub>1</sub>-C<sub>3</sub> RONO<sub>2</sub> reduce O<sub>3</sub> by ~1 ppb (where baseline O<sub>3</sub> is ~180 ppb)



# Results: box



# UKCA experiments

Experiment	Description
BASE	Updated CheST without MeONO <sub>2</sub>
CHEM	C <sub>1</sub> -C <sub>3</sub> RONO <sub>2</sub> photochemical production & loss
OCEAN	C <sub>1</sub> -C <sub>2</sub> RONO <sub>2</sub> oceanic emissions & photochemical loss
BB	C <sub>1</sub> -C <sub>3</sub> RONO <sub>2</sub> biomass burning emissions & photochemical loss
ALL	C <sub>1</sub> -C <sub>3</sub> RONO <sub>2</sub> photochemical production & loss + both types of emissions
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RONO <sub>2</sub> dry deposition switched on in all experiments	

# Metrics

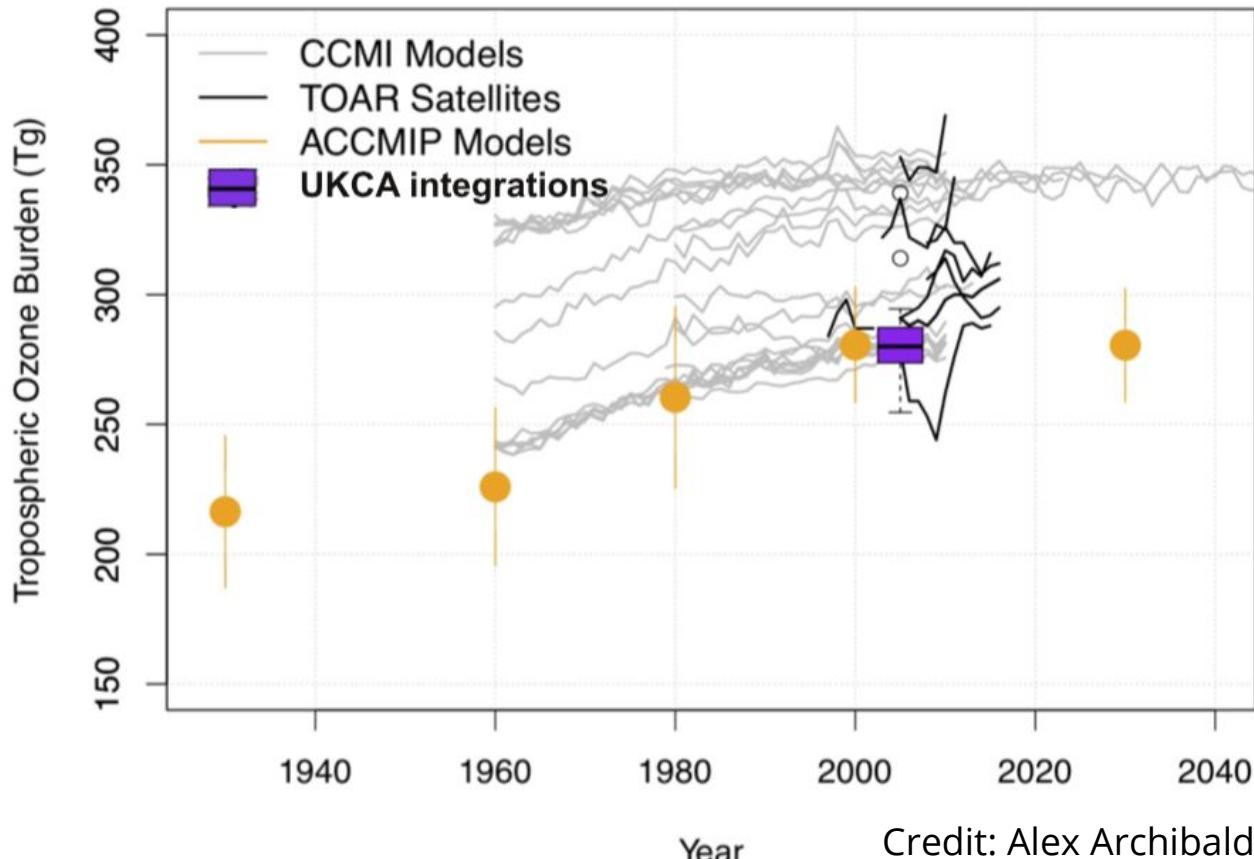
Name	O3 burden, Tg/yr	CH4 burden, Tg/yr	CH4 lifetime, yr	NH/SH annual OH	MeONO2, Gg/yr	EtONO2, Gg/yr	nPrONO2, Gg/yr
BASE	246.56±2.05	3855.72±91.98	8.68±0.18	1.35±0.02	0.88±2.64	0.00±0.00	0.00±0.00
OCEAN	247.63±1.95	3845.95±86.12	8.59±0.17	1.34±0.02	55.58±1.79	9.49±0.16	0.00±0.00
BB	246.58±1.97	3864.29±93.91	8.68±0.18	1.35±0.02	1.08±2.64	0.11±0.00	0.004±0.000

10-year average 60S60N using chemical troposphere (125 ppb O3) and  $f(K)^*[CH_4]^*[OH]$

# Metrics

## Comparison of models and TOAR data (+/-60 deg.) (using 125 ppb ozonopause)

Name	O <sub>3</sub> burden, Tg/yr	CH <sub>4</sub> Tg
BASE	246.56±2.05	384
OCEAN	247.63±1.95	384
BB	246.58±1.97	386
10-year average 60S-60N using TOAR Satellites		



Year

Credit: Alex Archibald

# Statistical tests

1. Shapiro-Wilk test for normality.
2. if data is normally distributed:
  - a. Paired samples t-test
- else:
  - b. Wilcoxon signed-rank test
3. Control false discovery rate to better interpret multiple hypothesis tests.

# $\text{RONO}_2$ emission factors from biomass burning

$\text{RONO}_2$	tropical forest	savanna	crop residue	pasture maintenance	boreal forest	temperate forest	extratropical forest
$\text{MeONO}_2$	$8.29 \times 10^{-3}$ ( $1.60 \times 10^{-2}$ )	$5.1 \times 10^{-4}$ ( $3.7 \times 10^{-4}$ )	-	-	$2.83 \times 10^{-3}$	-	$2.83 \times 10^{-3}$
$\text{EtONO}_2$	$5.70 \times 10^{-3}$	$3.51 \times 10^{-4}^*$	-	-	$1.78 \times 10^{-3}$	-	$1.78 \times 10^{-3}$
$\text{nPrONO}_2$	$3.00 \times 10^{-4}$	$1.85 \times 10^{-5}^*$	-	-	$3.23 \times 10^{-4}$	-	$3.23 \times 10^{-4}$
$\text{iPrONO}_2$	$3.00 \times 10^{-4}$	$6.15 \times 10^{-5}^*$	-	-	$3.23 \times 10^{-3}$	-	$3.23 \times 10^{-3}$

From Akagi et al. (2011) Table 1.

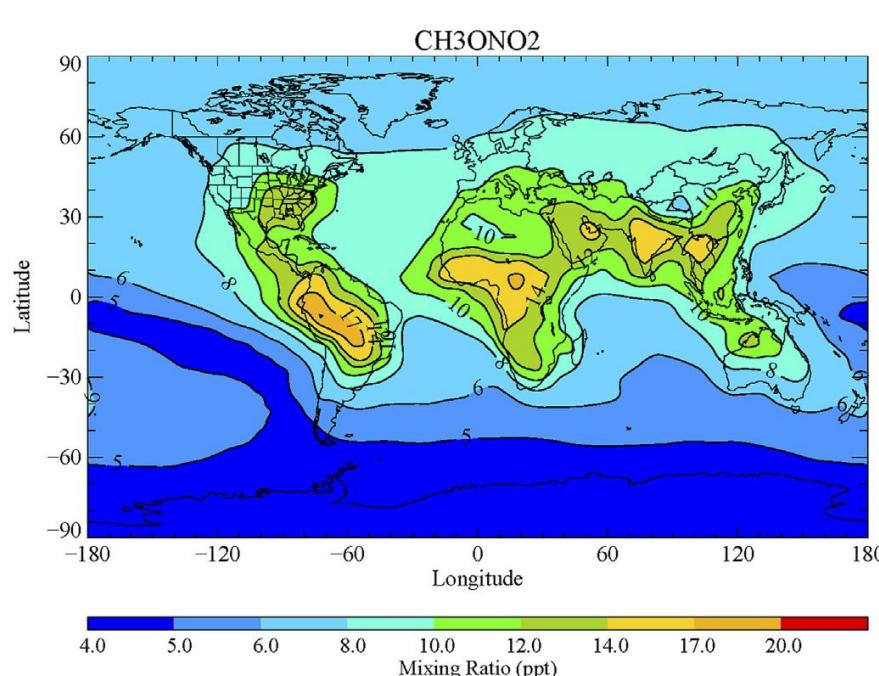
\*calculated in this work

# $\text{RONO}_2$ burdens

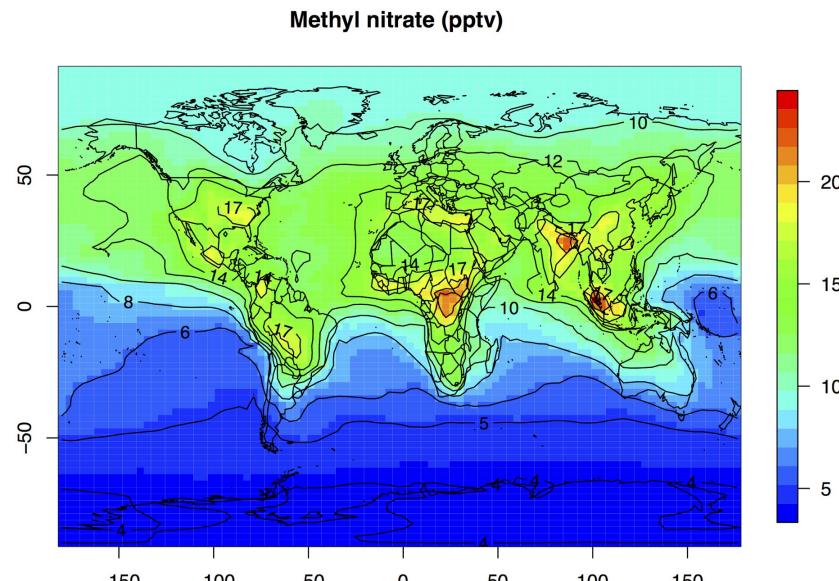
$\text{RONO}_2$ burden, Gg N	OCEAN	BB
Neu et al. (2008)	28.7 MeONO <sub>2</sub> 6.3 EtONO <sub>2</sub>	-
Williams et al. (2014)	0.3 ORGNIT	-
Khan et al. (2015)	-	1.1 MeONO <sub>2</sub> 0.4 EtONO <sub>2</sub> 0.02 nPrONO <sub>2</sub> 0.08 iPrONO <sub>2</sub>
this study*	66.16 MeONO <sub>2</sub> 11.47 EtONO <sub>2</sub>	1.21 MeONO <sub>2</sub> 0.11 EtONO <sub>2</sub> 0.004 nPrONO <sub>2</sub>

\*10-year average using 125 ppb ozonopause

# Primary results: methyl nitrate from CHEM run

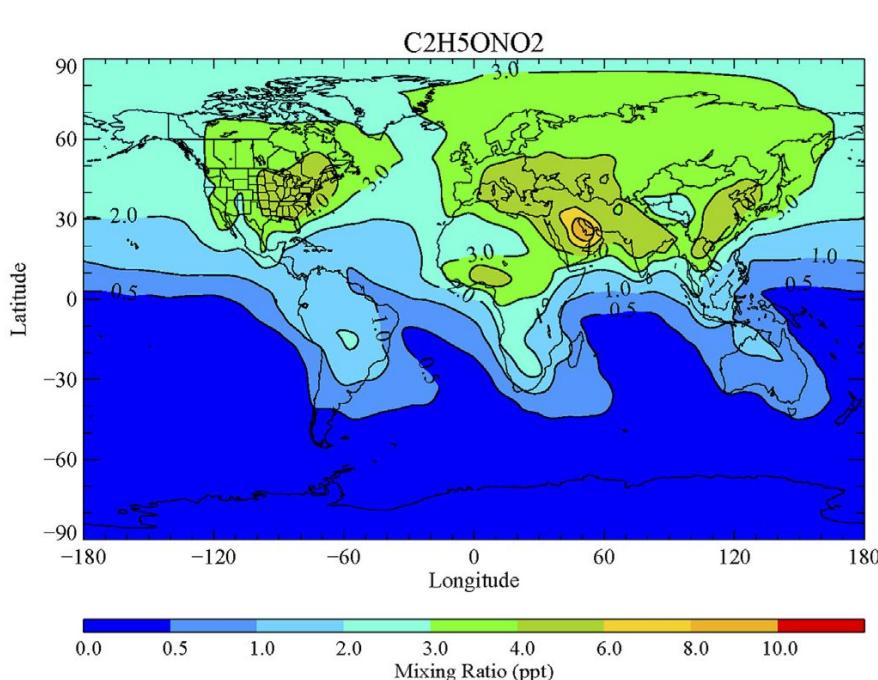


Credit: Khan et al. (2015)

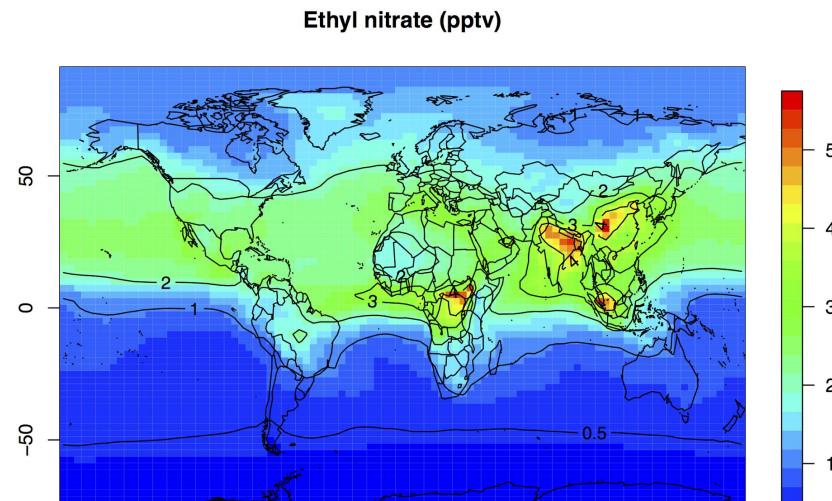


Credit: Paul Griffiths

# Primary results: ethyl nitrate from CHEM run

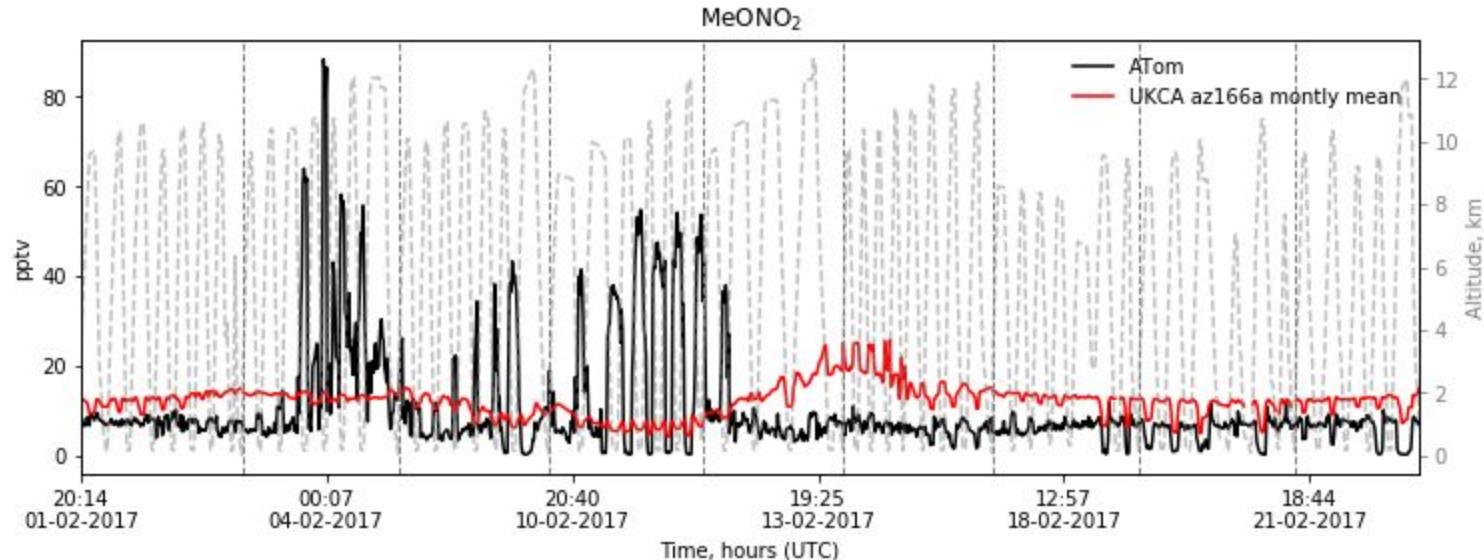
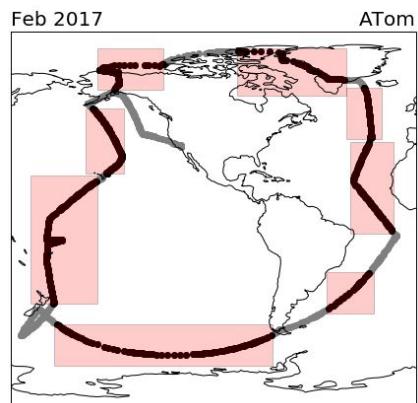


Credit: Khan et al. (2015)

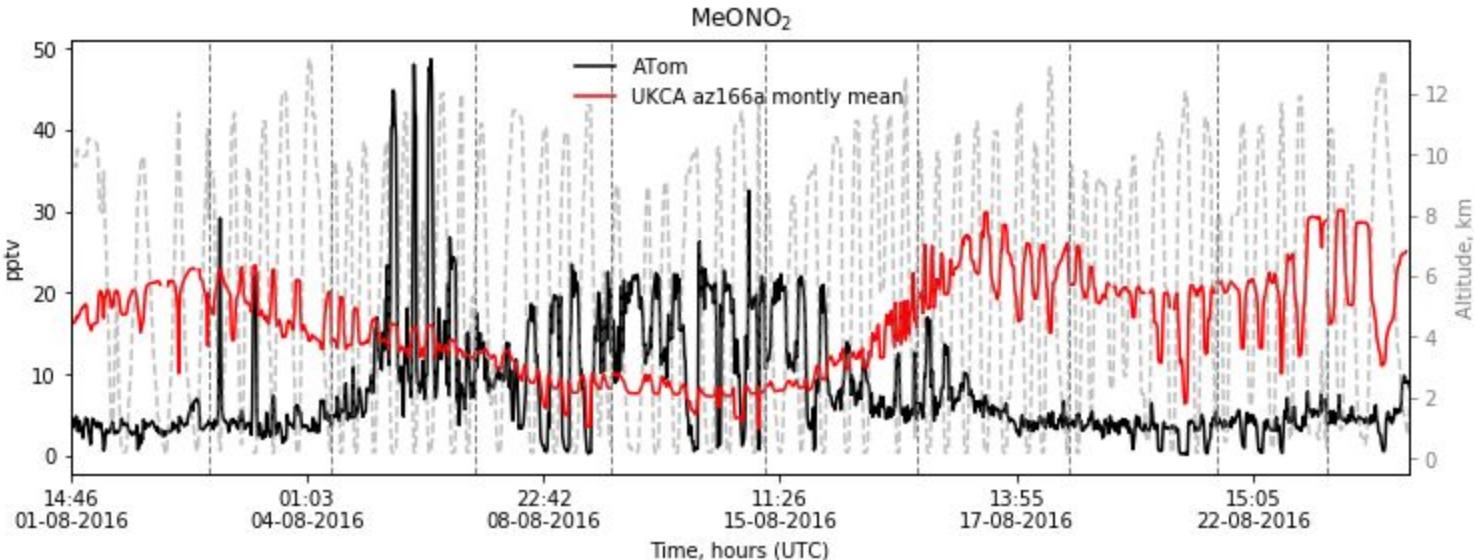
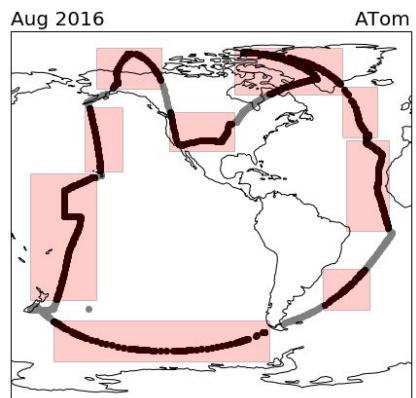


Credit: Paul Griffiths

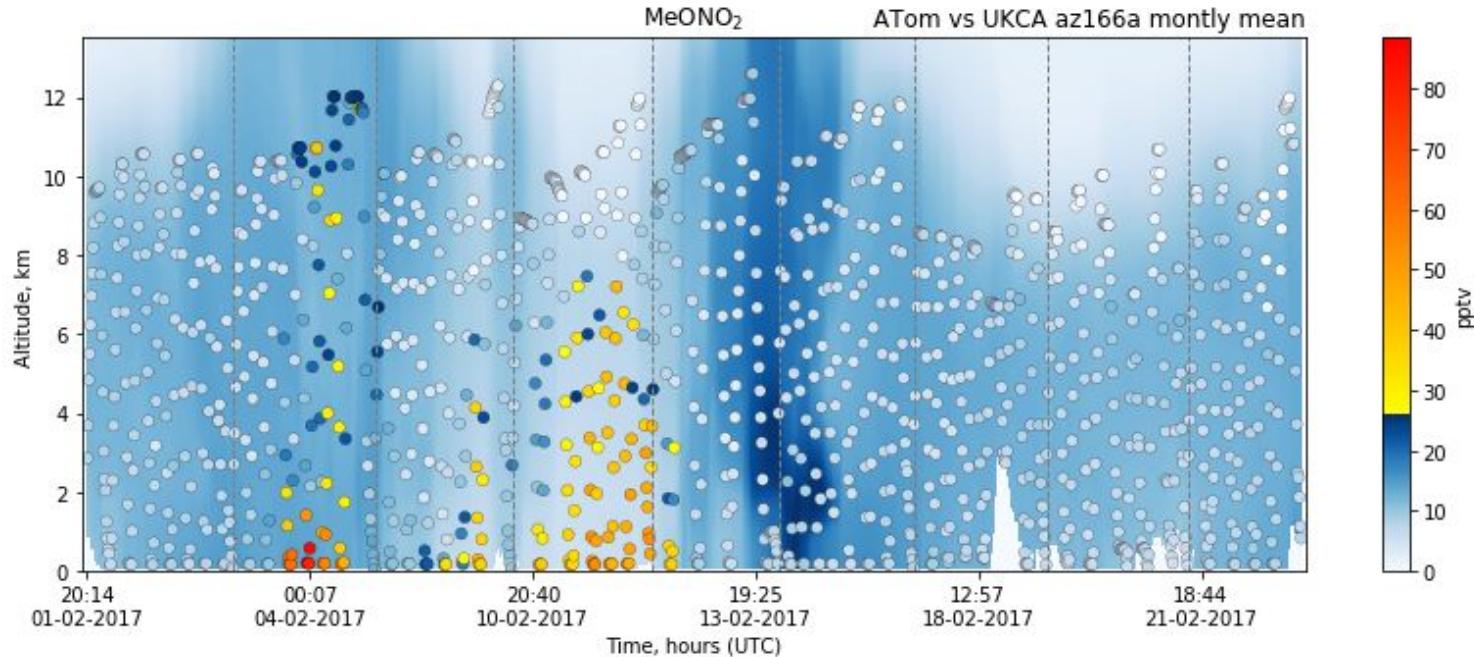
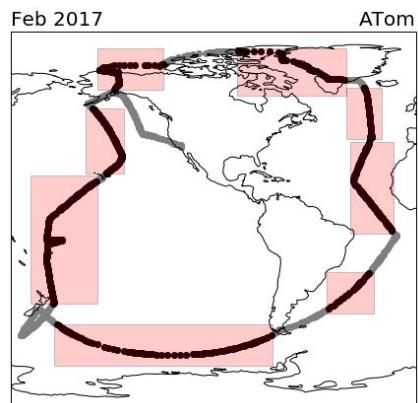
# Validation



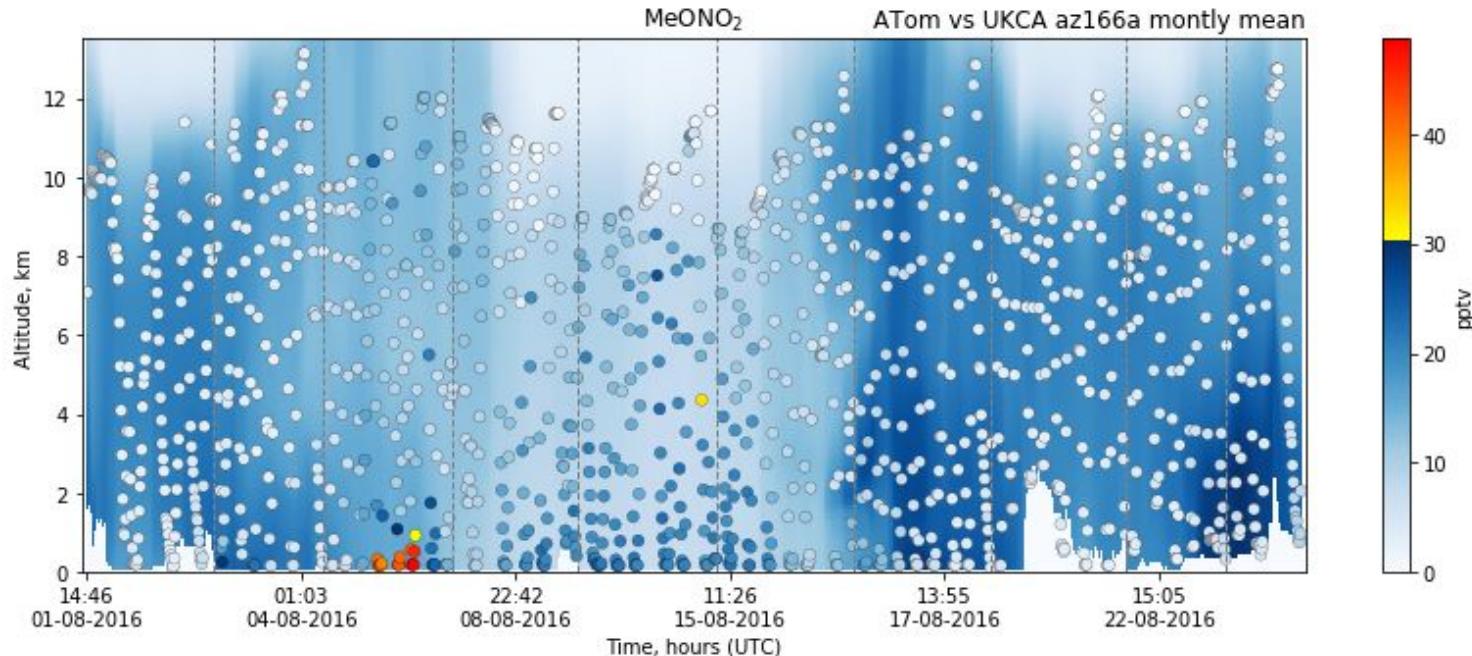
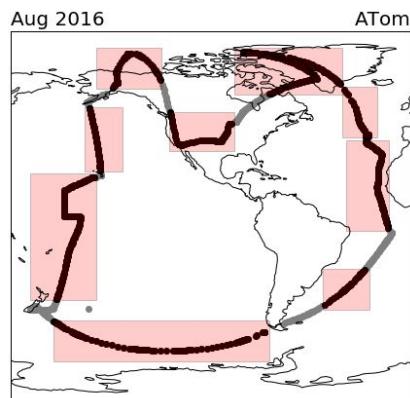
# Validation



# Validation

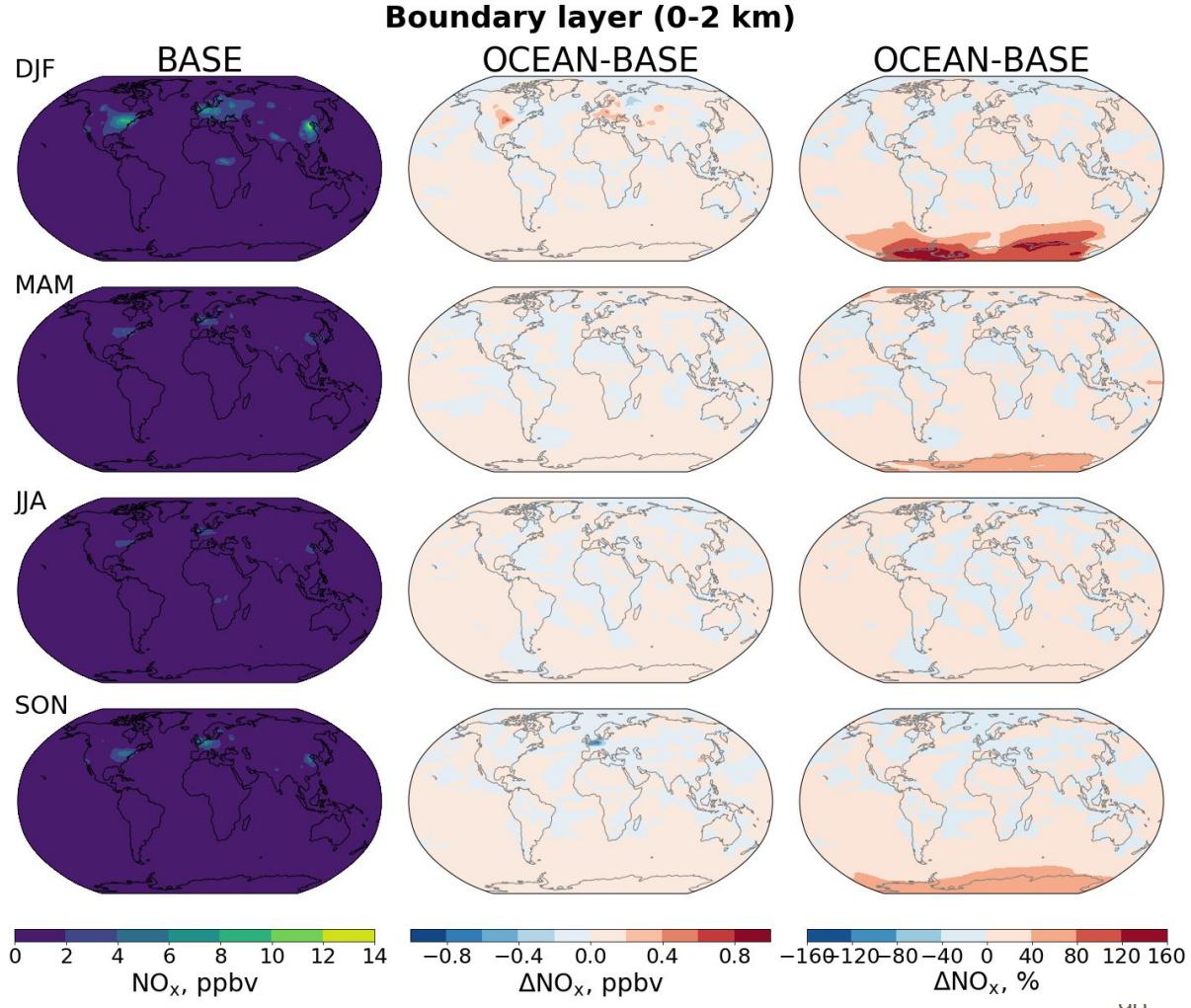


# Validation



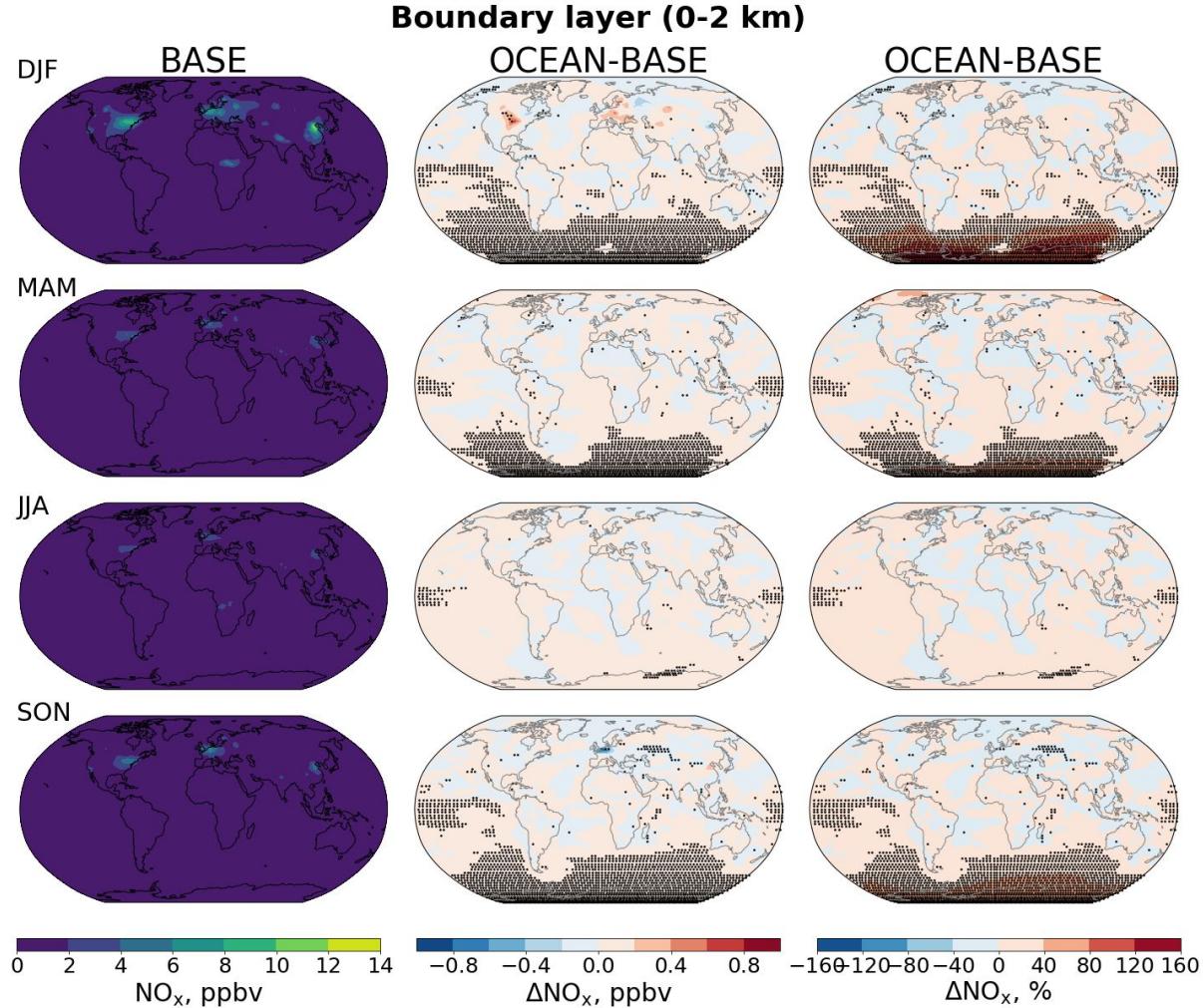
# Impact of oceanic RONO<sub>2</sub> on NO<sub>x</sub>

- increase over the Southern Ocean by up to 160% (< 700 ppt)



# Impact of oceanic RONO<sub>2</sub> on NO<sub>x</sub>

- increase over the Southern Ocean by up to 160% (< 700 ppt)
- statistically significant in all seasons except JJA



# Impact of BB RONO<sub>2</sub> on NO<sub>x</sub>

- increase over the equatorial Africa by up to 80% (< 800 ppt)
- statistically significant in DJF and SON

