



Tropospheric Ozone Production Pathways with Detailed Chemical Mechanisms

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1st July 2015

Previous Meeting Re-cap

Comparison of O_3 Production in Chemical Mechanisms

Impact of Solvent Speciations on O_3

Sensitivity of O_3 Production on Modelled Conditions

Timeline

Action Points from Last Meeting



- ▶ Submit mechanism comparison paper to ACP. ✓
- ▶ Analysis for solvent sector emissions model runs. ✓
- ▶ Modelling work for third paper. **In progress**
- ▶ Action plan timeline for finishing PhD. ✓

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Timeline

- ▶ Submitted to ACP on 10th April.
- ▶ Robert Harley is the editor.
- ▶ Accepted for discussion phase on 13th April.
- ▶ Manuscript appeared in ACPD forum till 8th July.

- ▶ Generally positive review.
- ▶ Commented that the older versions of the mechanisms should be considered as “relics of the past”.
- ▶ Manuscript gives the impression that we consider the MCM to be “correct”.
- ▶ Question on how much we learn about ozone production from more explicit versus less chemical mechanisms.

Previous Meeting Re-cap

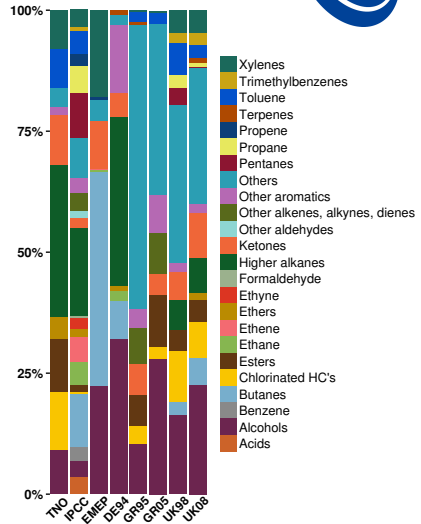
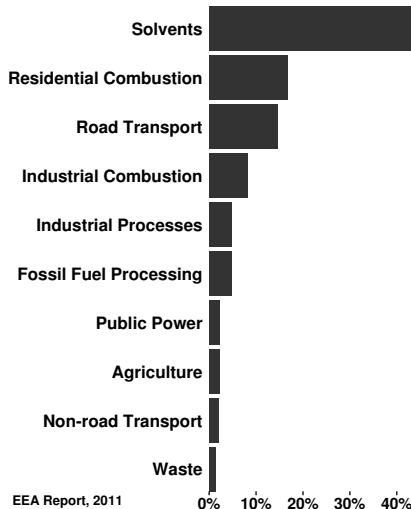
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Timeline

Motivation



Compared Solvent Speciations

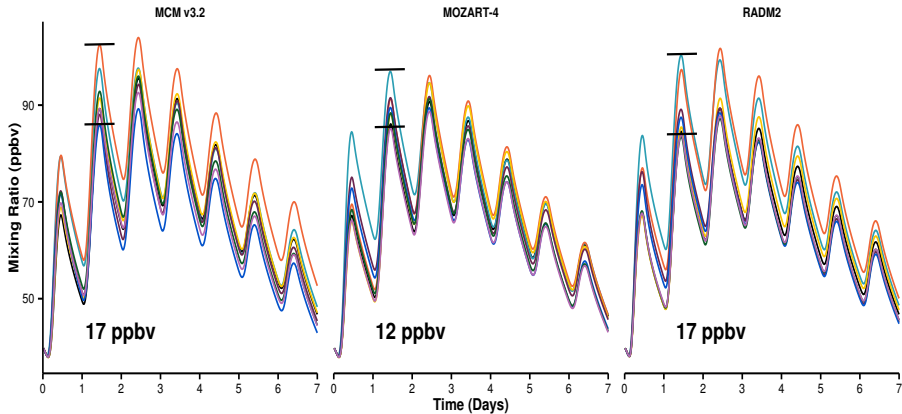
Speciation	Reference
TNO	[Builtjes et al., TNO Report, 2002]
IPCC	[Ehhalt et al., IPCC Report, 2001]
EMEP	[Simpson et al., ACP, 2010]
DE94	[Friedrich et. al., JAC, 2002]
GR95	[Sidiropoulos and Tsilingiridis, FEB, 2007]
GR05	[Sidiropoulos and Tsilingiridis, FEB, 2007]
UK98	[Goodwin, UK NAEI report, 2000]
UK08	[Murrells et al., UK NAEI Report, 2010]

- ▶ MECCA boxmodel over 7 days.
- ▶ Idealised urban area of 1000 km².
- ▶ NO source tuned for maximum ozone production.

- ▶ Solvent sector contributes 43 % to total NMVOC emissions (1000 tons/day) [Warnecke et al., JGR, 2007].
Total NMVOC emissions of 430 tons/day.
- ▶ NMVOC emissions constant until noon of day 1.
- ▶ Use different chemical mechanisms:
 - ▶ MCM v3.2,
 - ▶ MOZART-4,
 - ▶ RADM2.

Ozone Mixing Ratio Time Series

— TNO — IPCC — EMEP — DE94 — GR95 — GR05 — UK98 — UK08

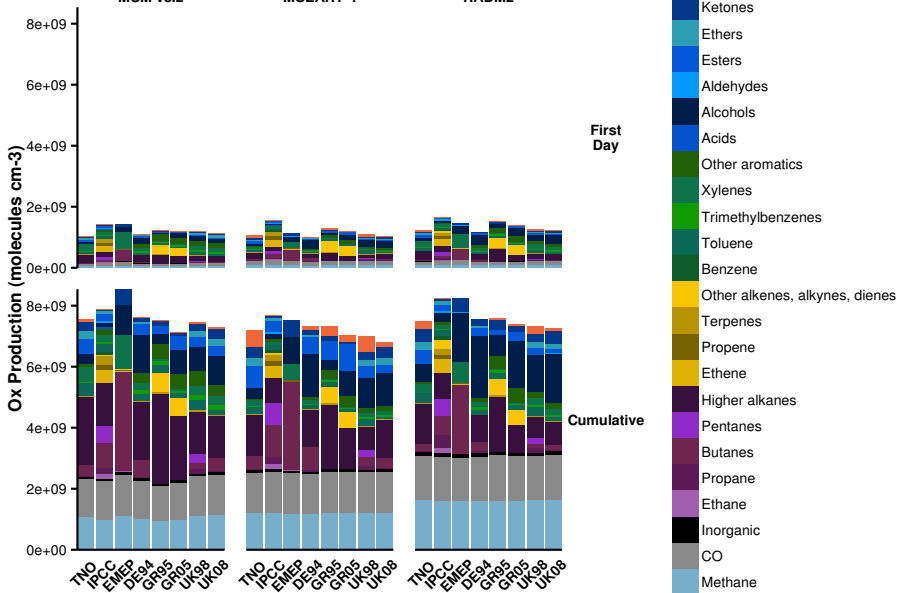


First Day and Cumulative Allocated Ox Production

MCM v3.2

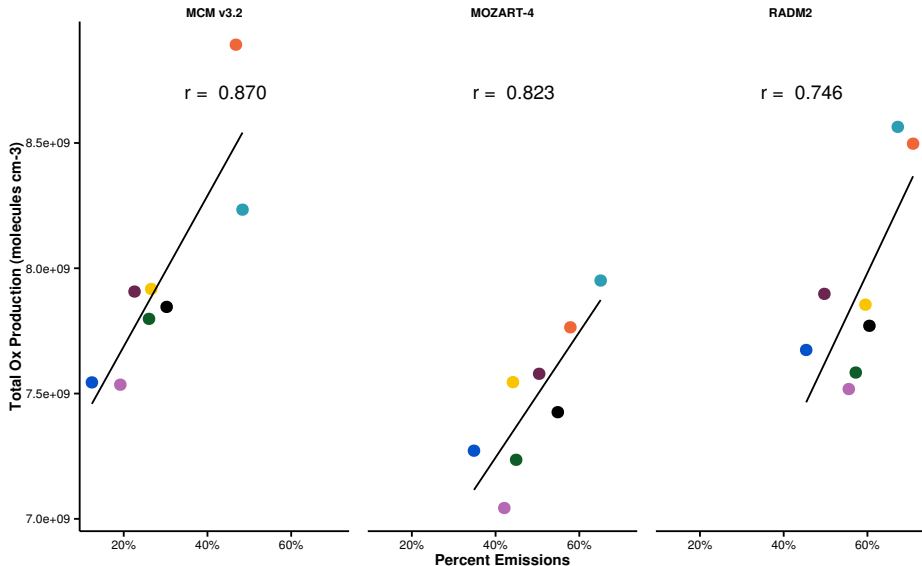
MOZART-4

RADM2

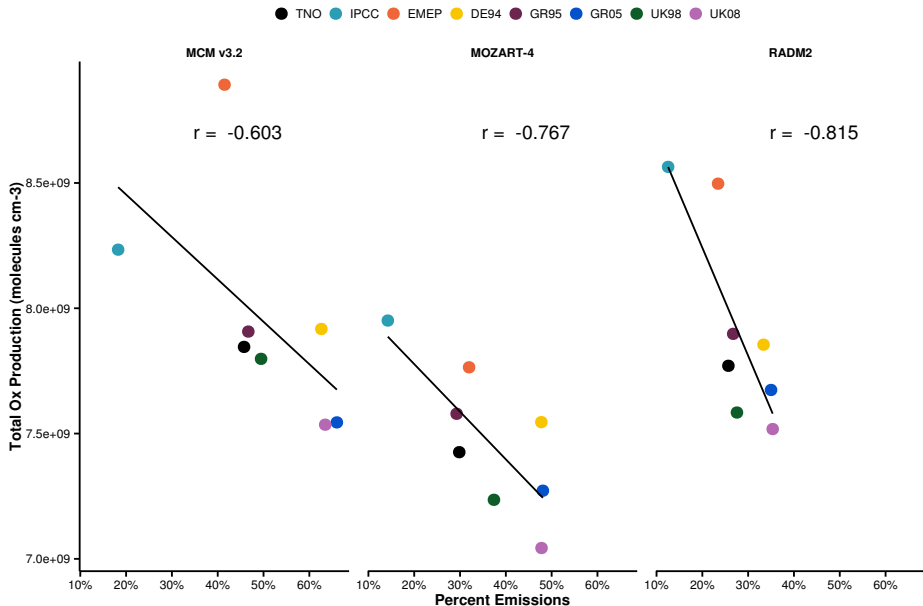


Correlation of Cumulative Ox Production and Alkane Emissions

● TNO ● IPCC ● EMEP ● DE94 ● GR95 ● GR05 ● UK98 ● UK08



Correlation of Cumulative Ox Production and Oxygenated Emissions



- ▶ Prepared an initial draft focussing on modelling work.
- ▶ Erika will be first author.
- ▶ Final paper will include more background information on comparing the different solvent sector speciations.
- ▶ Submit to Atmospheric Environment by end-August.

Previous Meeting Re-cap

Comparison of O_3 Production in Chemical Mechanisms

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Sensitivity of O_3 Production on Modelled Conditions

Timeline

- ▶ MECCA boxmodel over 7 days.
- ▶ Initial NMVOC typical of Los Angeles.
- ▶ NO source tuned for maximum O_3 production.

- ▶ Tagging follows organic products from VOC degradation
⇒ effects on O_3 production inferred from O_x production.
- ▶ Constant PBL height of 1 km
⇒ no vertical mixing.
- ▶ Constant temperature of 293 K.

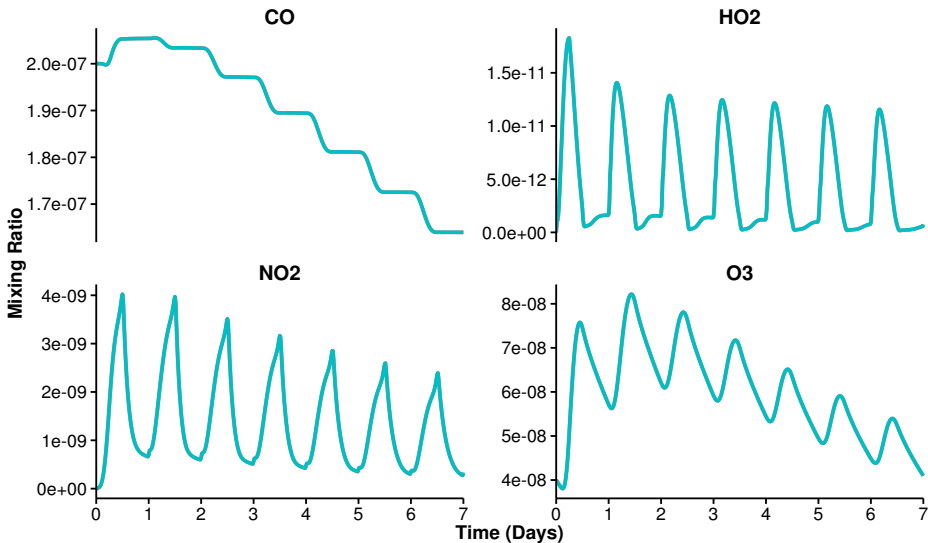
1. Tagging Approach



- ▶ VOC tagging approach implemented in global model by Shuai and Tim.
- ▶ Allows allocation of O_3 mixing ratios to source rather than comparing O_x production.
- ▶ Tagged MOZART-4 mechanism that was implemented in boxmodel for mechanism comparison study.

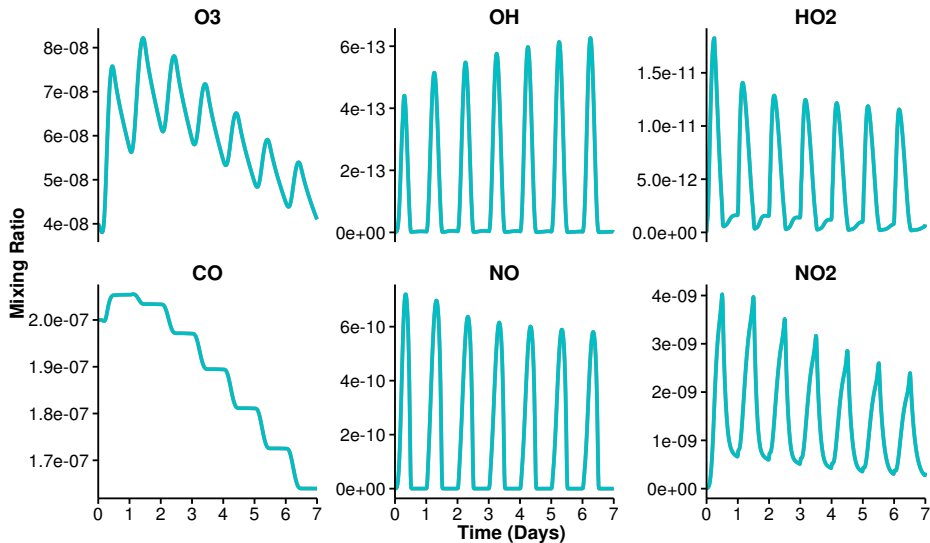
Real vs Tagged Mixing Ratios

Non-tagged Tagged



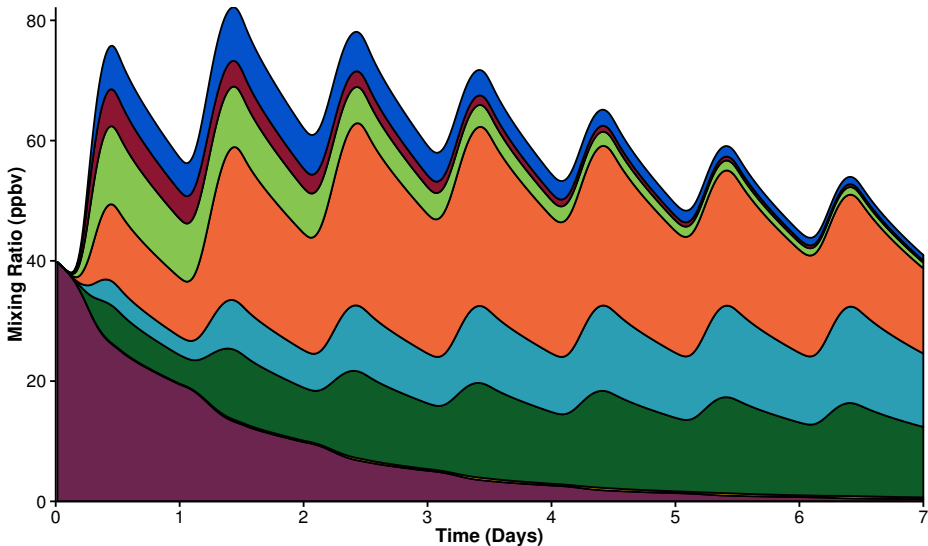
Mixing Ratio Comparison between Old and New Tagging

new_tagging old_tagging



Source Allocation of Ozone Mixing Ratios

Aromatics Isoprene Alkenes Alkanes CH₄ CO XTR INI



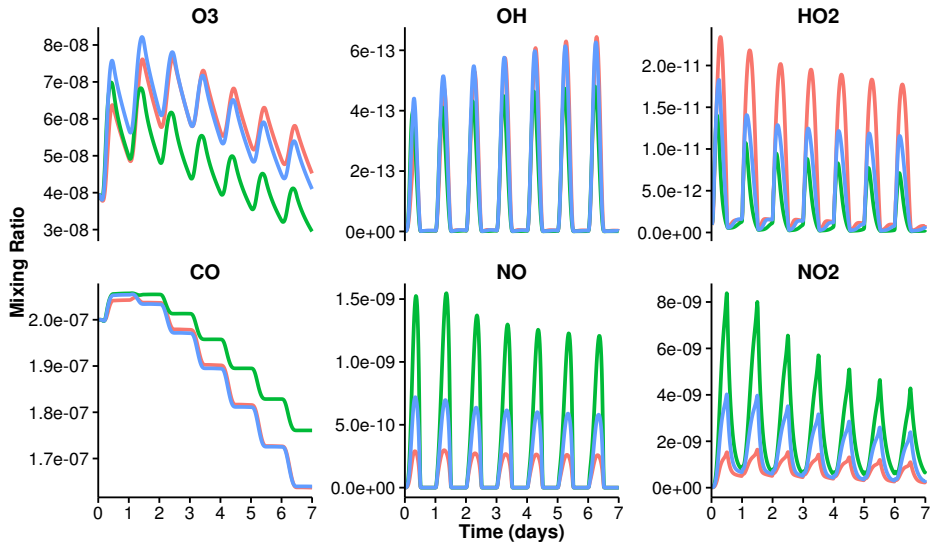
2. Low and High NO_x Conditions



- ▶ Modelling rural and polluted urban conditions.
- ▶ MOZART-4 mechanism with VOC tagging approach.
- ▶ NO emissions calculated for maximum O₃ production scaled
 - ▶ 0.5 for Low NO_x
 - ▶ 1.5 for High NO_x

Mixing Ratio Comparisons in Different Atmospheric Regimes

— NOx_limited — NOx_saturated — Tuned



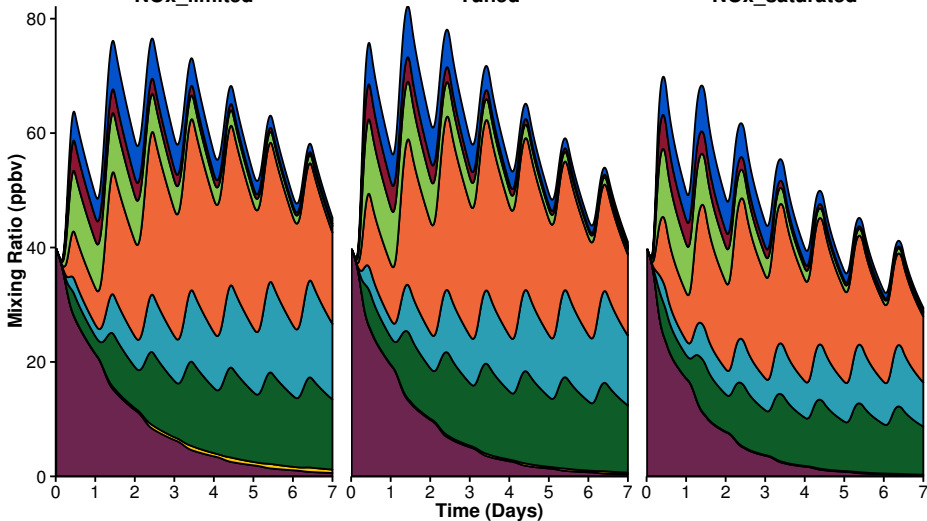
Allocated Ozone Mixing Ratios

Aromatics Isoprene Alkenes Alkanes CH₄ CO XTR INI

NO_x_limited

Tuned

NO_x_saturated

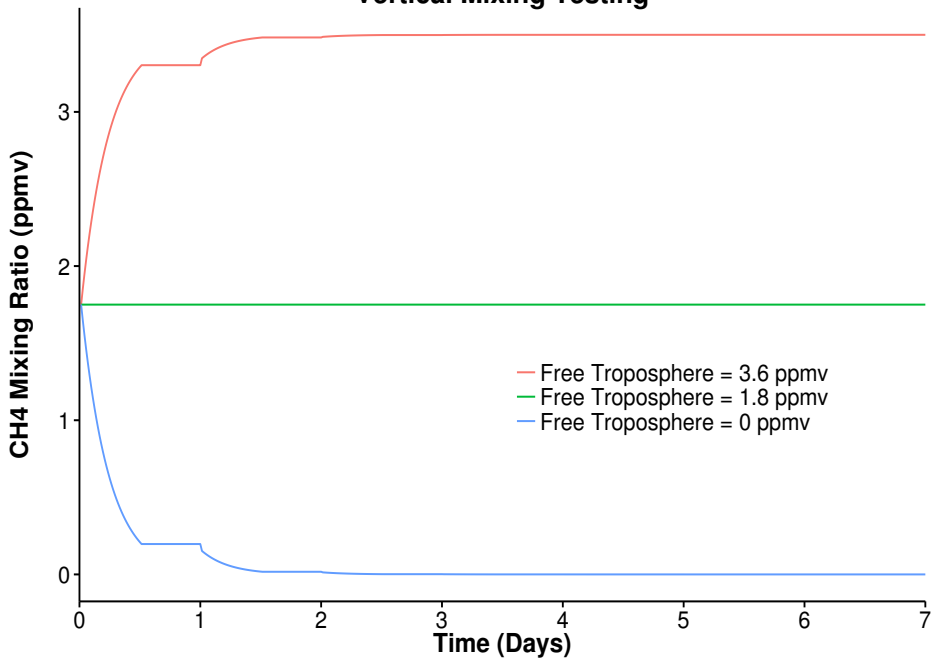


3. Vertical Mixing

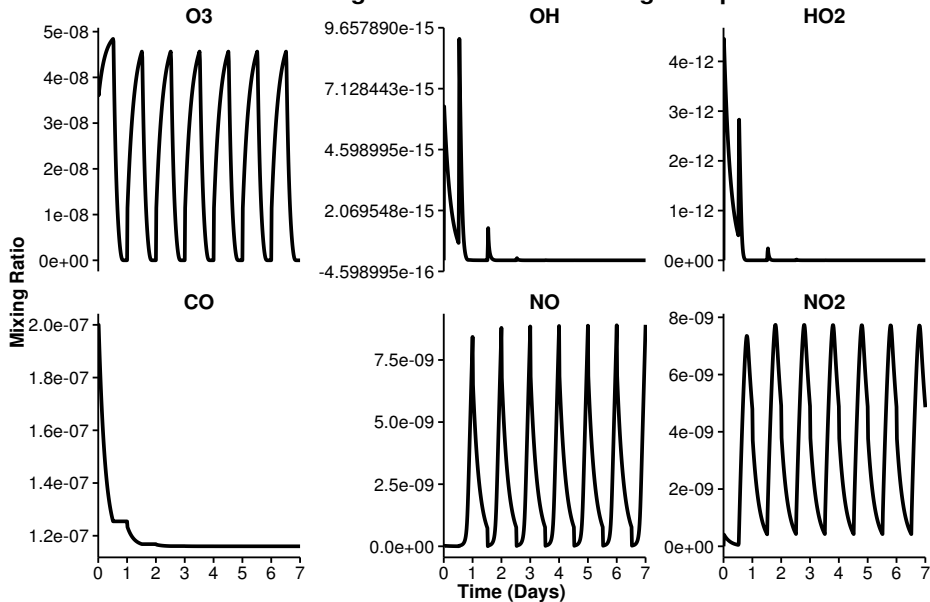


- ▶ Included diurnal cycle for PBL height from CARES measurement campaign.
- ▶ Vertical mixing with free troposphere approach from Sandra Louren's thesis.
- ▶ Free troposphere mixing ratios for O_3 and CO from MATCH-MPIC model.

Vertical Mixing Testing



Mixing Ratios in Vertical Mixing set-up



4. Temperature



- ▶ Run boxmodel at 295 K, scenario of a warmer climate.
- ▶ Compare O_3 between lower and higher temperatures.
- ▶ According to recent review by Pusede et al., temperature dependent chemistry of alkyl nitrates impacts O_3 production.
- ▶ Assess how this chemistry is represented in the chemical mechanisms used in comparison study.

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Timeline

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- ▶ Submit solvents sector emissions paper by end-August 2015.
 - ▶ Finish sensitivity study paper by end-Dec 2015.
 - ▶ Present sensitivity study at AGU in December 2015.
 - ▶ Hand in thesis to reviewers by end-April 2016.
 - ▶ Six weeks for reviewers to assess thesis.
 - ▶ Display graded thesis at FU Examinations Office for 2 weeks prior to thesis defense.
 - ▶ Defend thesis in July 2016.