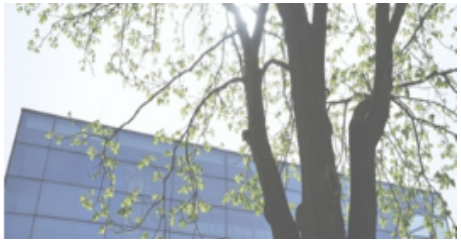



Tropospheric Ozone Production Pathways with Detailed Chemical Mechanisms

Jane Coates

1st July 2015

Outline

Action Points from Last Meeting

- Submit mechanism comparison paper to ACP. ✓
- Analysis for second paper outlining differences in O_3 production when using different VOC speciations for solvent sector emissions. ✓
- Modelling work for third paper. **In progress**
- Action plan timeline for finishing PhD. ✓

Outline

Paper Status

- Submitted to ACP on 10th April.
- Editing of the manuscript by Robert Harley.
- Accepted for discussion phase on 13th April.
- Manuscript appeared in ACPD forum till 24th June.
- Currently viewed **207** times.

Referee (William Stockwell) Comments

- 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.

Referee #2 Comments

- Generally positive review.

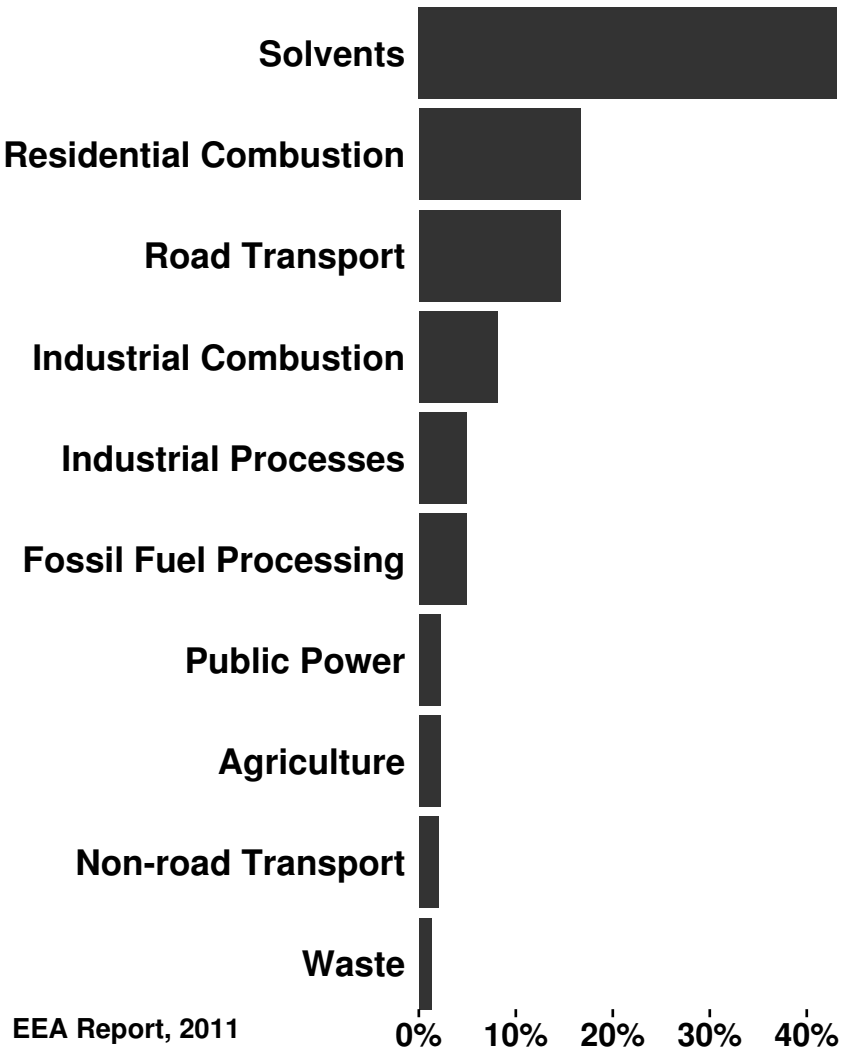
Outline

Main Research Question

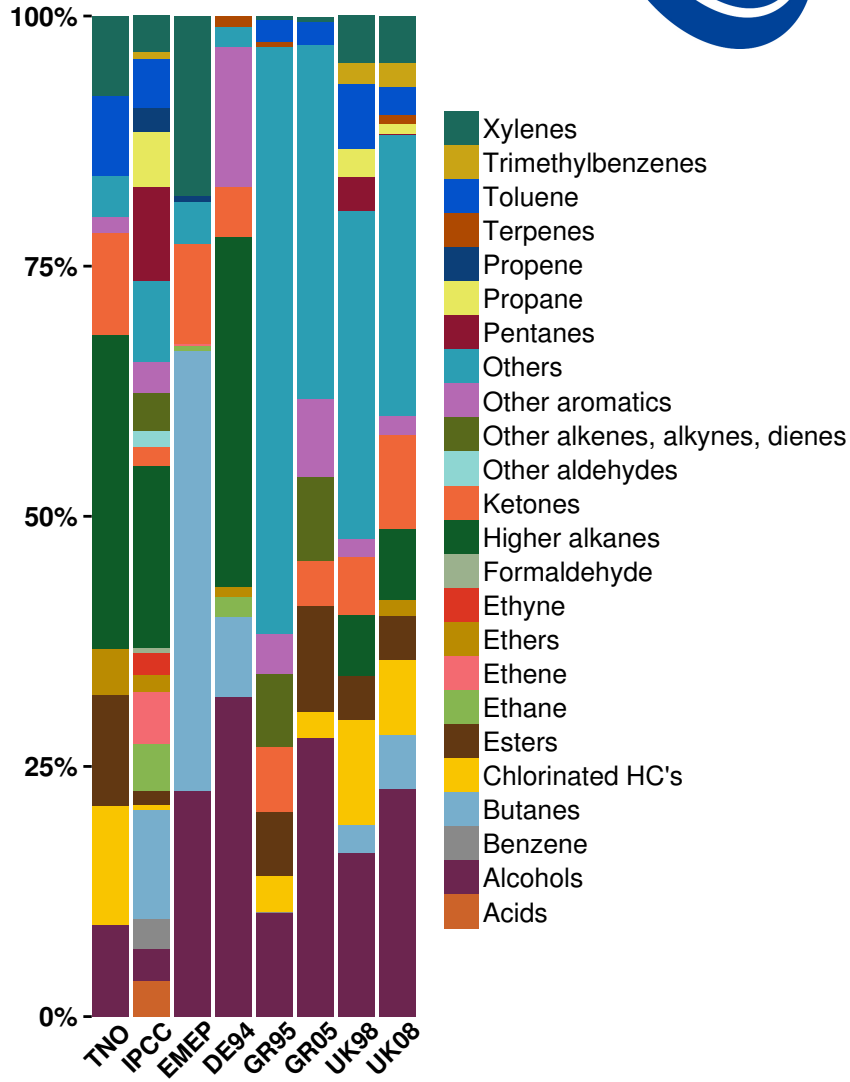
How does VOC speciation affect

O_3 concentrations in models?

Motivation



EEA Report, 2011

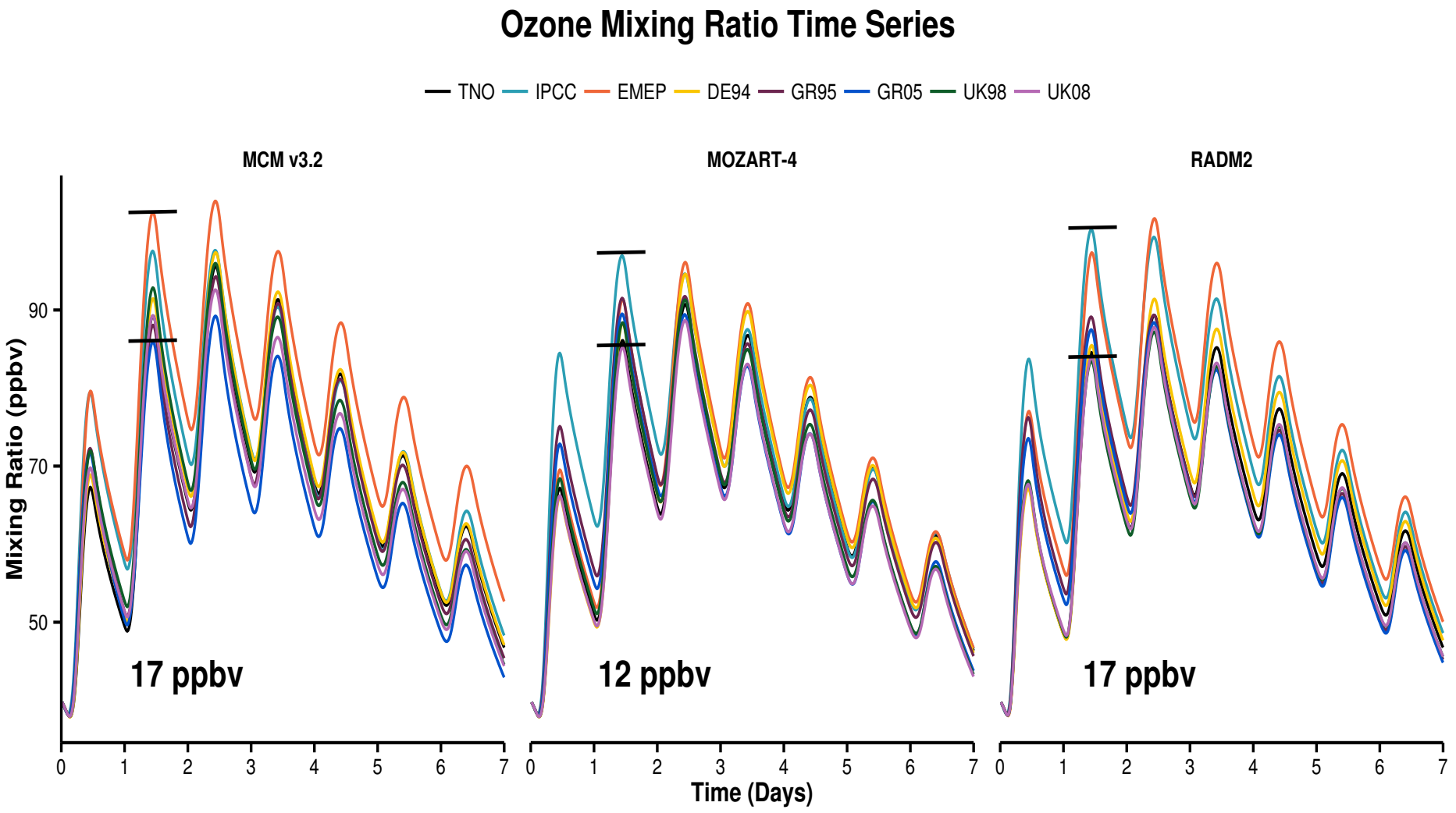


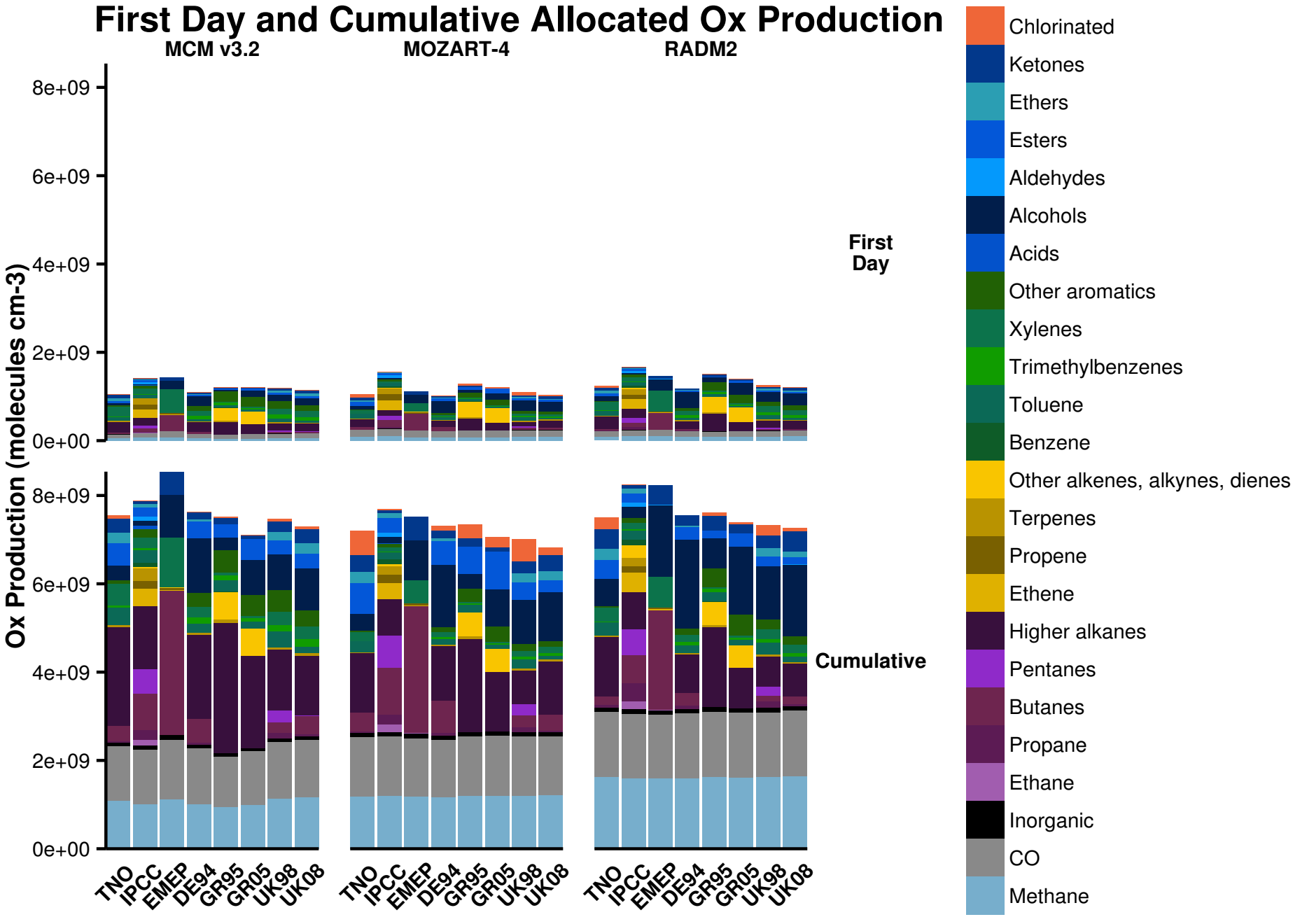
Compared Solvent Speciations

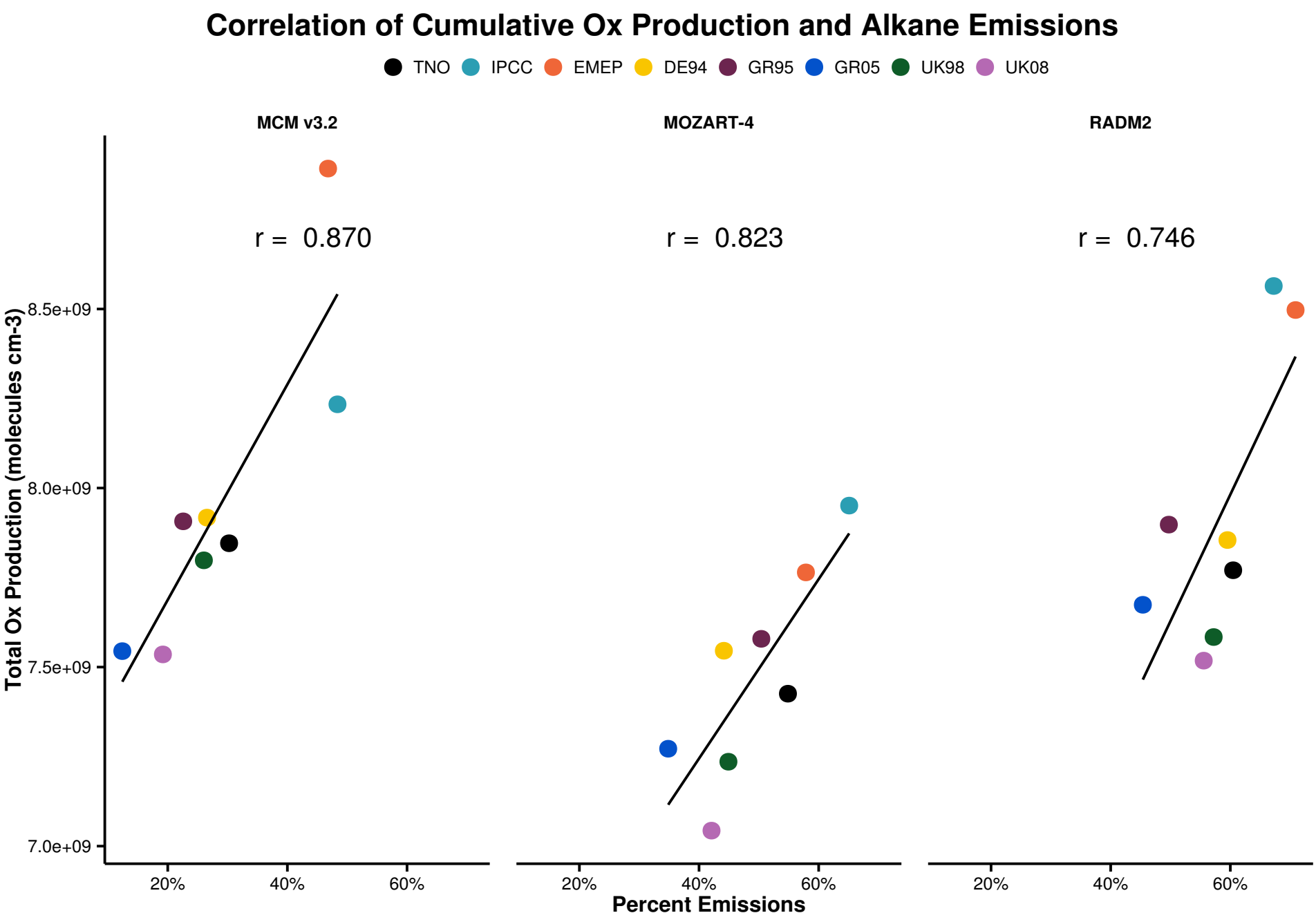
Speciation	**Reference**
TNO	[Builtjes et al., TNO Report, 2002]
IPCC	[Ehhalt et al., IPCC Report, 2001]
EMEP	[Simpson et al., ACP, 2010]
DE94	[Friedrich et. al., JAC, 2002]
GR95	[Sidiropoulos and Tsilingiridis, FEB, 2007]
GR05	[Sidiropoulos and Tsilingiridis, FEB, 2007]
UK98	[Goodwin, UK NAEI report,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

Boxmodel Setup

- MECCA boxmodel over 7 days.
- Idealised urban area of 1000 km^2.
- Total NMVOC emissions of 1000 ton/day [Warnecke et al., JGR, 2007].
- NMVOC emissions constant until noon of day 1.


Ozone Mixing Ratio Time Series
TNO
IPCC
EMEP
DE94
GR95
GR05
UK98
UK08
MCM v3.2
MOZART-4
RADM2
Mixing Ratio (ppbv)
90
70
50
17 ppbv
12 ppbv
17 ppbv
0
1
2
3
4
5
6
7
Time (Days)


First Day and Cumulative Allocated Ox Production
MCM v3.2
MOZART-4
RADM2
Ox Production (molecules cm-3)
8e+09
6e+09
4e+09
2e+09
0e+00
First Day
Cumulative
TNO
IPCC
EMEP
DE94
GR95
GR05
UK98
UK08
Chlorinated
Ketones
Ethers
Esters
Aldehydes
Alcohols
Acids
Other aromatics
Xylenes
Trimethylbenzenes
Toluene
Benzene
Other alkenes, alkynes, dienes
Terpenes
Propene
Ethene
Higher alkanes
Pentanes
Butanes
Propane
Ethane
Inorganic
CO
Methane


Correlation of Cumulative Ox Production and Alkane Emissions
TNO
IPCC
EMEP
DE94
GR95
GR05
UK98
UK08
MCM v3.2
MOZART-4
RADM2
r = 0.870
r = 0.823
r = 0.746
Total Ox Production (molecules cm-3)
8.5e+09
8.0e+09
7.5e+09
7.0e+09
20%
40%
60%
Percent Emissions

Paper Status

- Initial draft focussing on modelling work.
- Erika will be first author, paper will focus on comparison of solvent sector VOC speciations performed by Erika with the modelling results supporting.
- Updates from Erika.
- Journal
- Deadline for submission

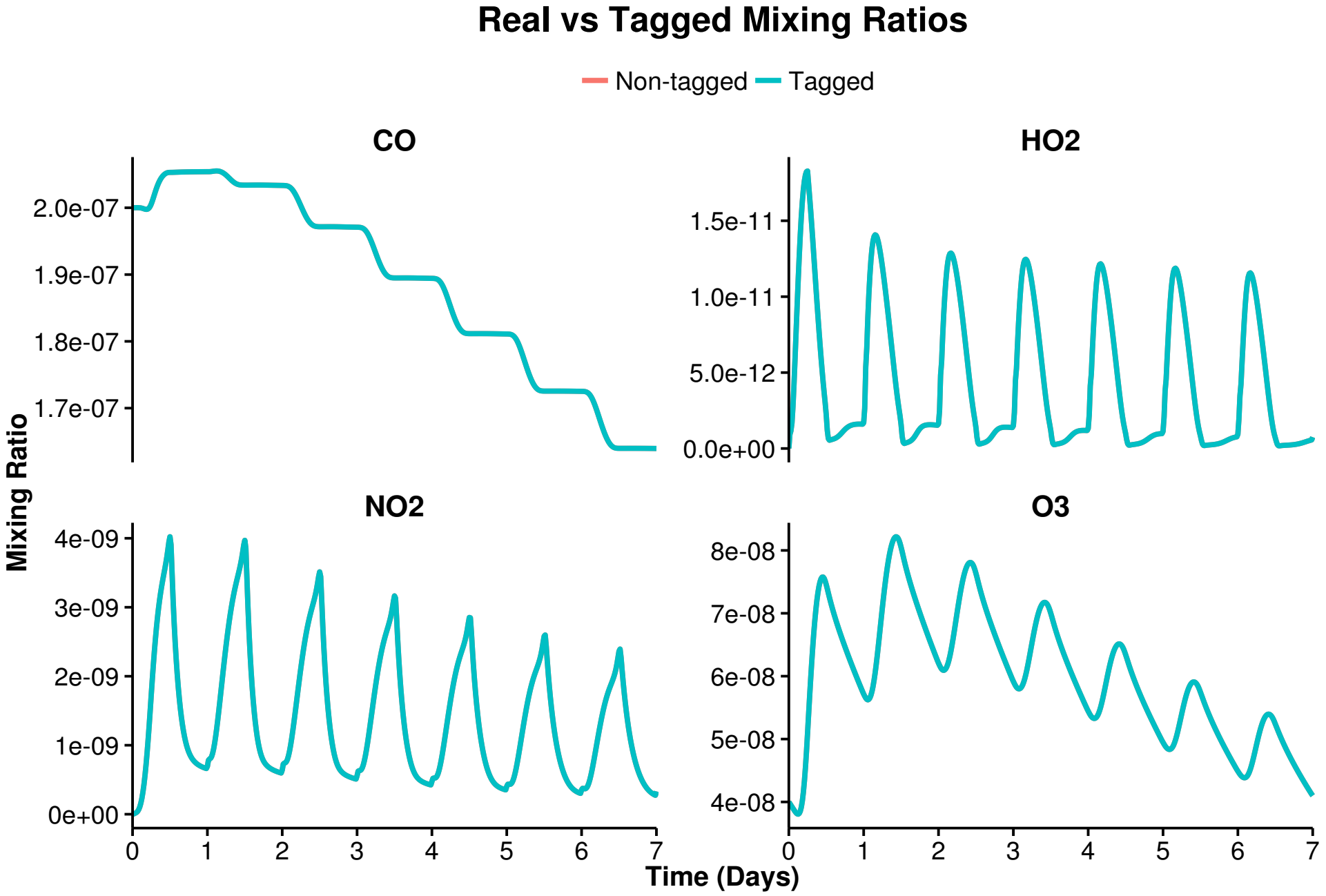
Outline

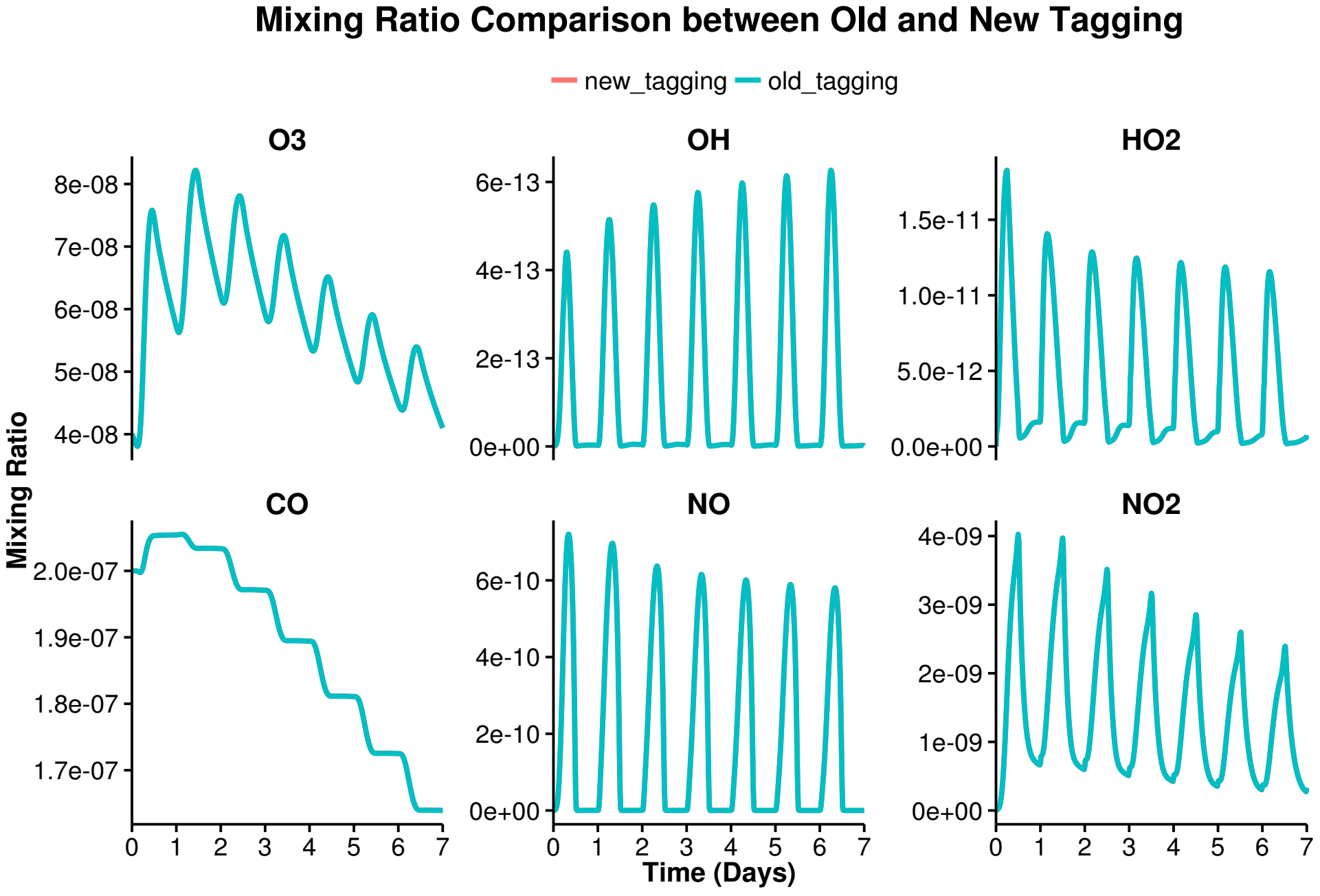
Main Research Question

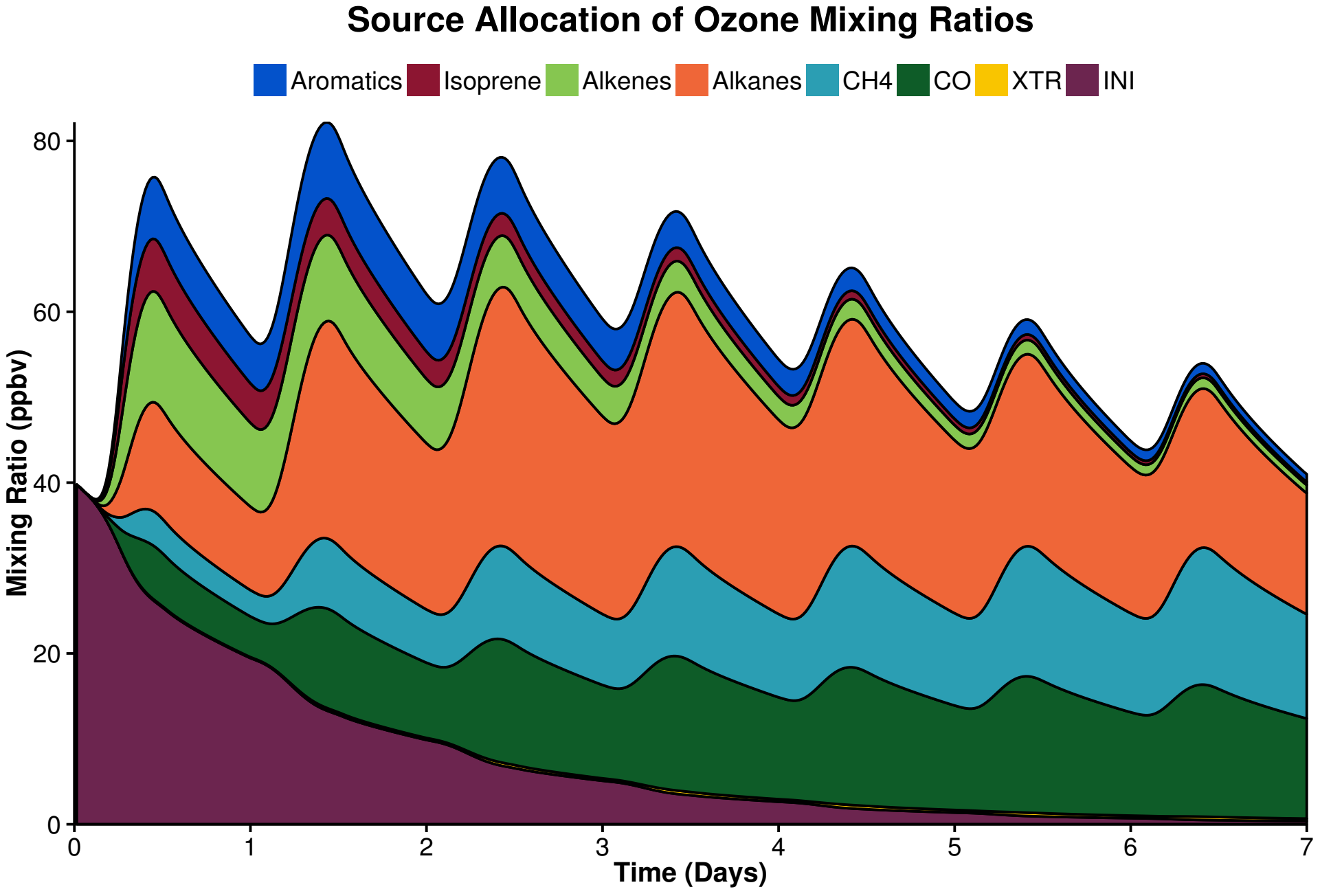
How sensitive are O_3 concentrations to non-chemical variables?

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.
- Same boxmodel set-up as in mechanism comparison study.

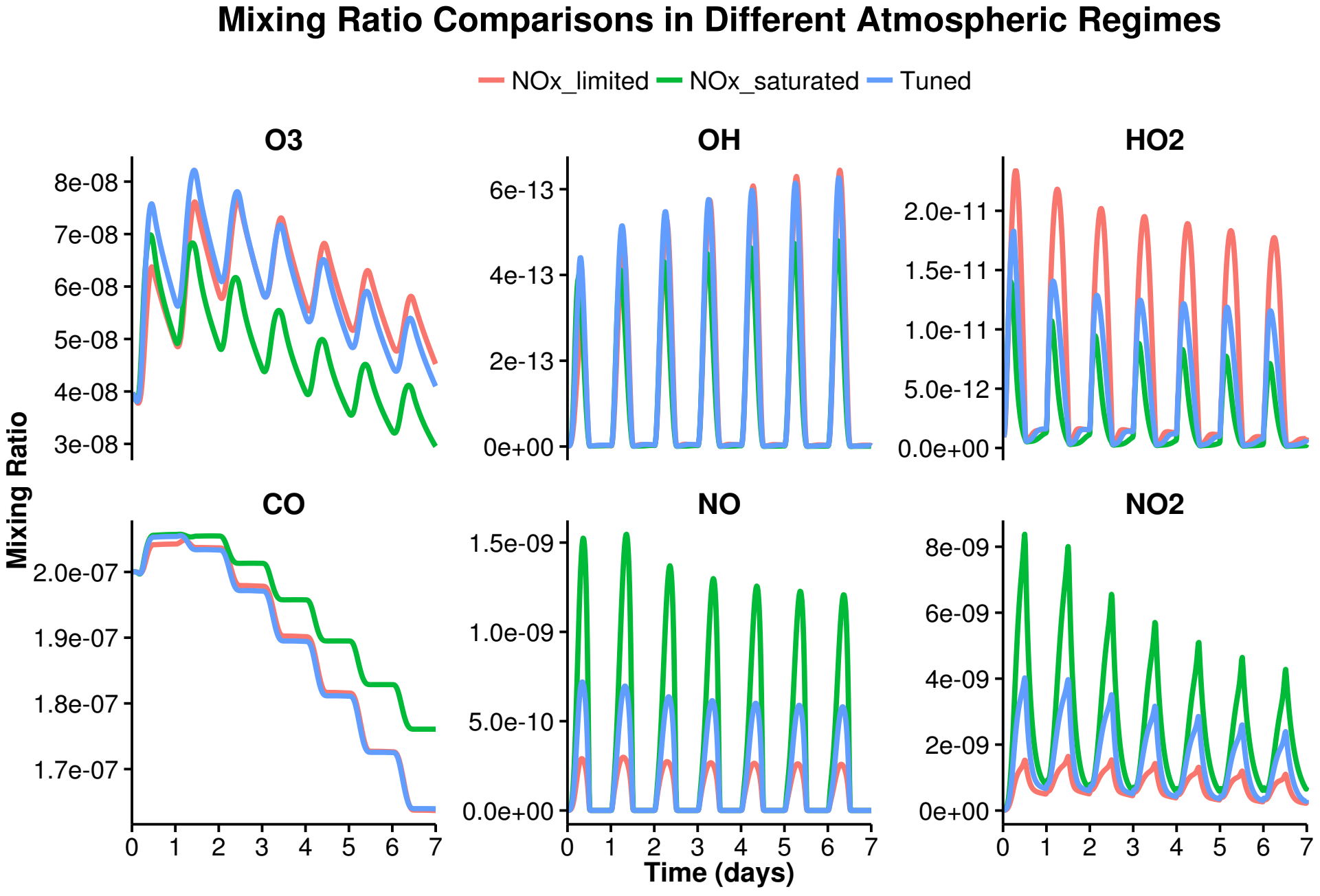

Real vs Tagged Mixing Ratios
Non-tagged
Tagged
CO
HO2
NO2
O3
Mixing Ratio
2.0e-07
1.9e-07
1.8e-07
1.7e-07
1.5e-11
1.0e-11
5.0e-12
0.0e+00
4e-09
3e-09
2e-09
1e-09
0e+00
8e-08
7e-08
6e-08
5e-08
4e-08
0
1
2
3
4
5
6
7
Time (Days)

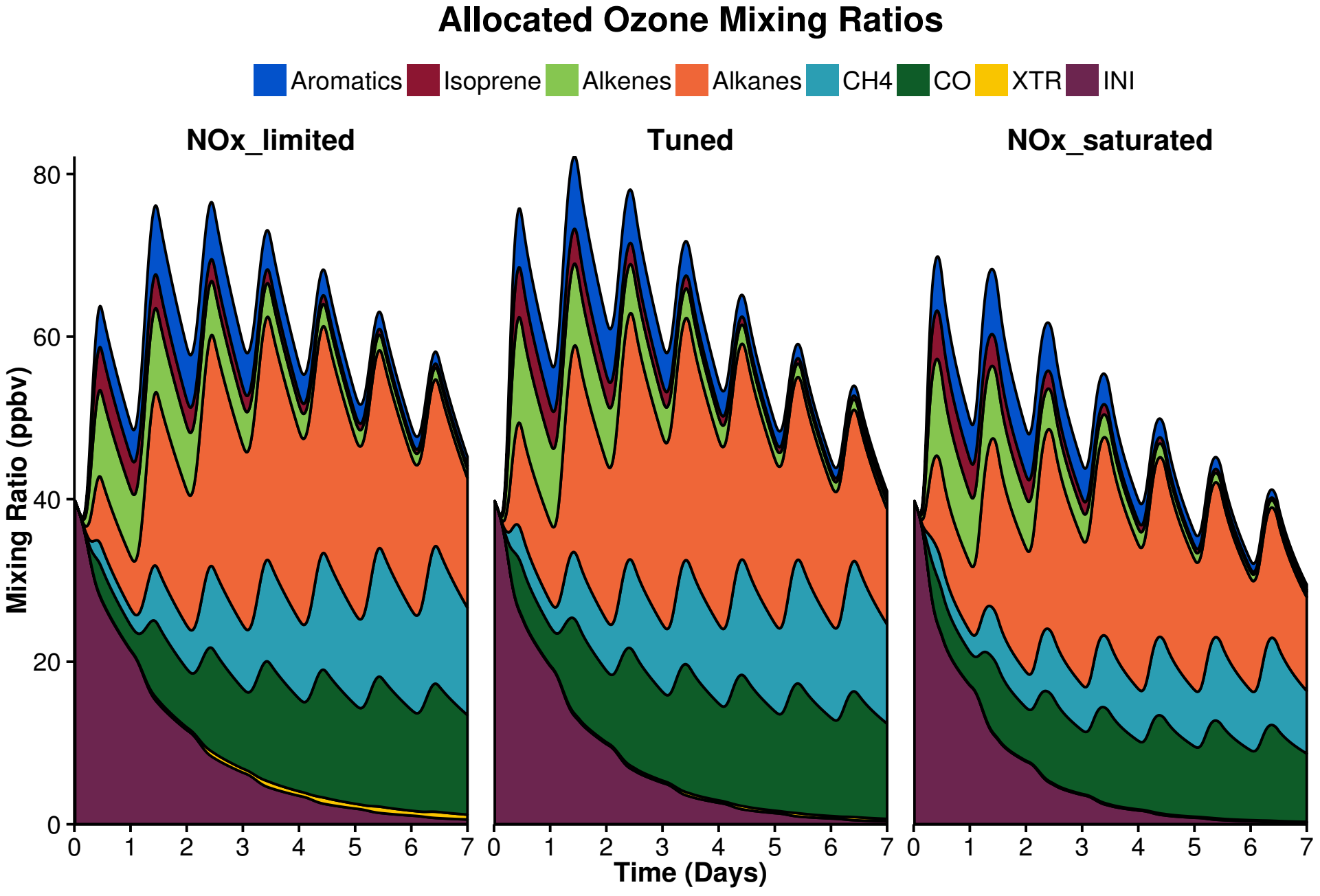

Mixing Ratio Comparison between Old and New Tagging
new_tagging
old_tagging
O3
OH
HO2
CO
NO
NO2
Mixing Ratio
Time (Days)
8e-08
7e-08
6e-08
5e-08
4e-08
6e-13
4e-13
2e-13
0e+00
1.5e-11
1.0e-11
5.0e-12
0.0e+00
2.0e-07
1.9e-07
1.8e-07
1.7e-07
6e-10
4e-10
2e-10
0e+00
4e-09
3e-09
2e-09
1e-09
0e+00
0 1 2 3 4 5 6 7


Source Allocation of Ozone Mixing Ratios
Aromatics
Isoprene
Alkenes
Alkanes
CH4
CO
XTR
INI
Mixing Ratio (ppbv)
0
20
40
60
80
0
1
2
3
4
5
6
7
Time (Days)

2. Low and High NO_x Conditions

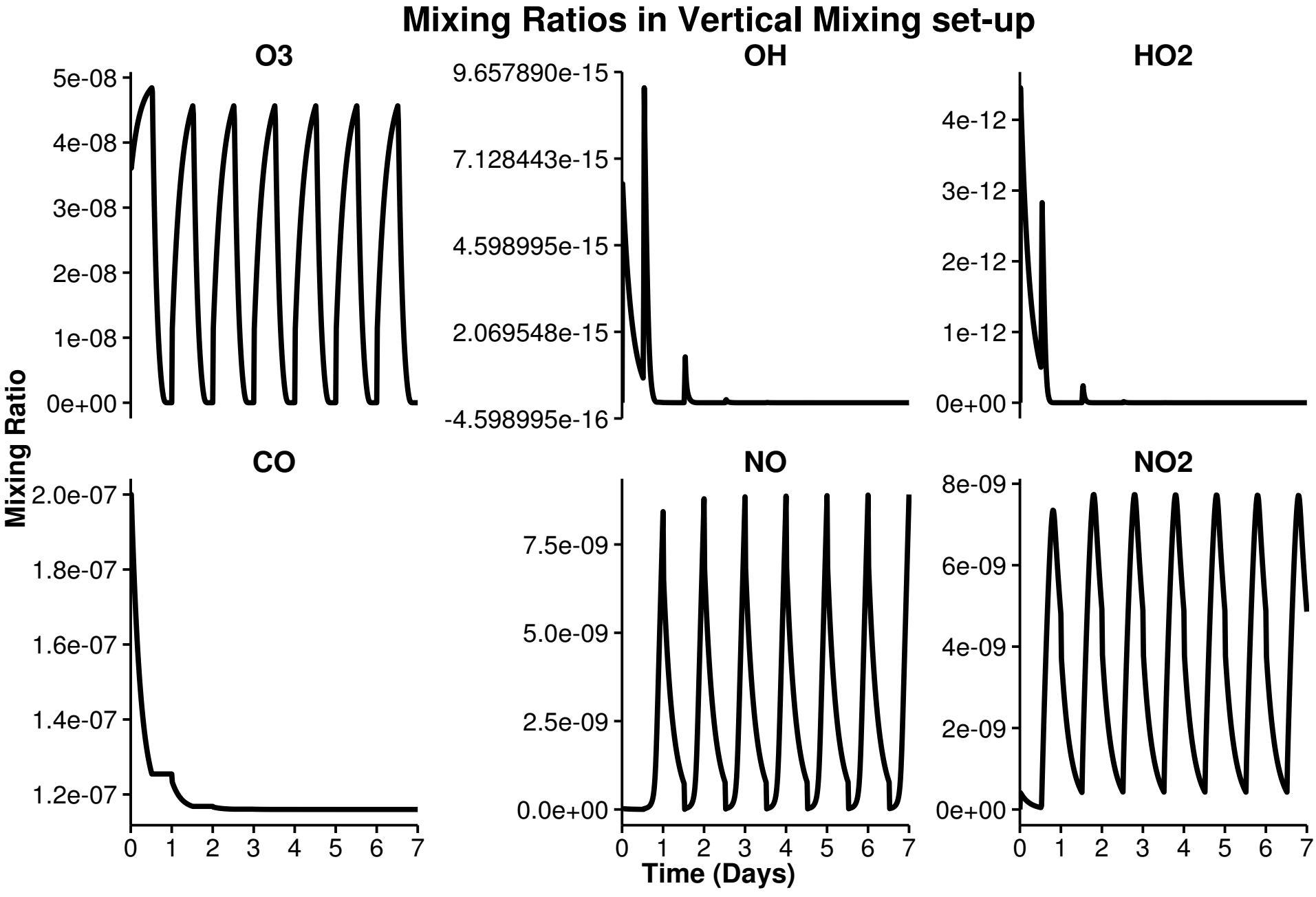
- Modelling rural (low) and polluted urban (high) NO_x conditions.
- MOZART-4 mechanism with VOC tagging approach.
- Same VOC emissions and boxmodel set-up as in mechanism comparison study.
- NO emissions calculated for maximum O_3 production scaled by
  - 0.5 for Low NO_x
  - 1.5 for High NO_x


Mixing Ratio Comparisons in Different Atmospheric Regimes
NOx_limited
NOx_saturated
Tuned
O3
OH
HO2
CO
NO
NO2
Mixing Ratio
Time (days)
8e-08
7e-08
6e-08
5e-08
4e-08
3e-08
6e-13
4e-13
2e-13
0e+00
2.0e-11
1.5e-11
1.0e-11
5.0e-12
0.0e+00
2.0e-07
1.9e-07
1.8e-07
1.7e-07
1.5e-09
1.0e-09
5.0e-10
0.0e+00
8e-09
6e-09
4e-09
2e-09
0e+00
0 1 2 3 4 5 6 7


Allocated Ozone Mixing Ratios
Aromatics
Isoprene
Alkenes
Alkanes
CH4
CO
XTR
INI
NOx_limited
Tuned
NOx_saturated
Mixing Ratio (ppbv)
0
20
40
60
80
0 1 2 3 4 5 6 7
Time (Days)

3. Vertical Mixing

- Same boxmodel set-up as VOC tagging approach.
- Initial VOC are kept constant till noon of the first day.
- Included diurnal cycle for PBL height.
- Vertical mixing with free troposphere approach as in Sandra Louren's thesis.
- Free troposphere mixing ratios for O_3 and CO from MATCH-MPIC model.


Mixing Ratios in Vertical Mixing set-up
O3
OH
HO2
CO
NO
NO2
Mixing Ratio
Time (Days)
5e-08
4e-08
3e-08
2e-08
1e-08
0e+00
9.657890e-15
7.128443e-15
4.598995e-15
2.069548e-15
-4.598995e-16
4e-12
3e-12
2e-12
1e-12
0e+00
2.0e-07
1.8e-07
1.6e-07
1.4e-07
1.2e-07
7.5e-09
5.0e-09
2.5e-09
0.0e+00
8e-09
6e-09
4e-09
2e-09
0e+00
0 1 2 3 4 5 6 7

4. Horizontal Mixing

- Same boxmodel set-up as VOC tagging approach.
- Implement horizontal mixing approach as in Sandra Louren's thesis.
- ??? what is the modelling case?

5. Temperature

- Current boxmodel setup uses constant temperature (293 K).
- Run boxmodel at 295 K, future scenario of a warmer climate.
- Compare O_3 between lower and higher temperatures.
- Based on recent review by Pusede et al., temperature impacts O_3 production through chemistry of alkyl nitrates (RONO2) and peroxy nitrates (RO2NO2).
- See which chemical mechanisms reflect the temperature dependance of this chemistry and its effect on O_3.

Outline

Finishing PhD

- Submit paper on Solvents Sector emissions by end-August 2015. TBC
- Finish paper on Sensitivity study by end-Dec 2015.
- Present Sensitivity study at AGU in December 2015.
- Hand in cumulative 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.