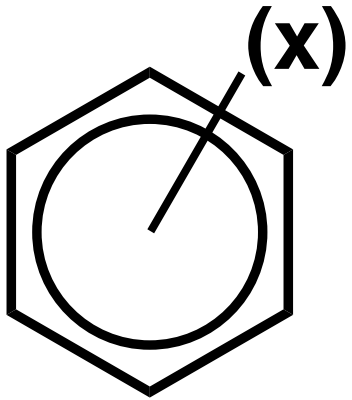
Intercomparison & optimization of aromatic oxidation mechanisms



Kelvin Bates[1]

with Ke Li[1], Daniel Jacob[1], Peter Ivatt[2], Mat Evans[2], Yingying Yan[3], & Jintai Lin[3]

[1]Harvard U. [2]U. York [3]Peking U.

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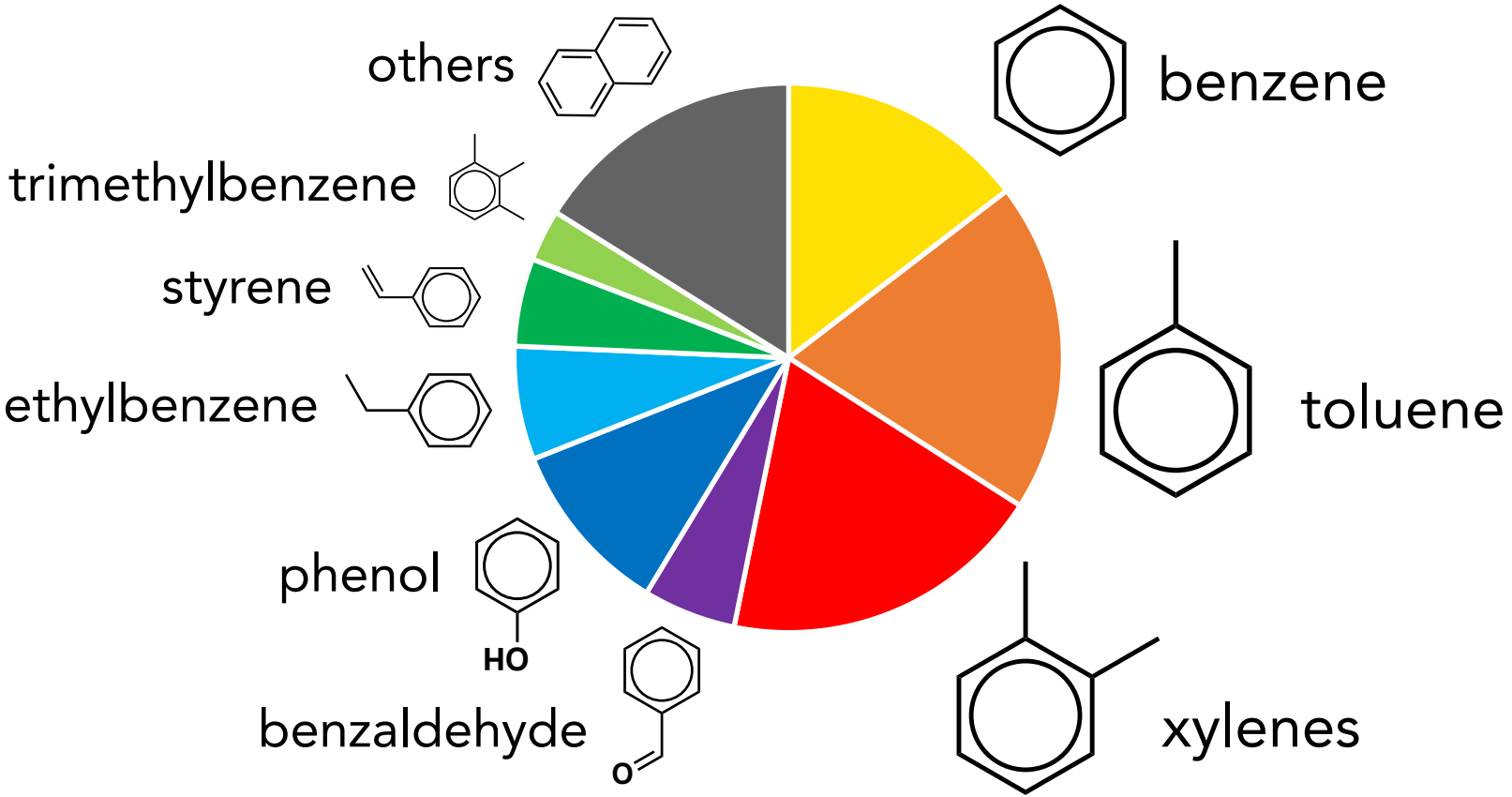
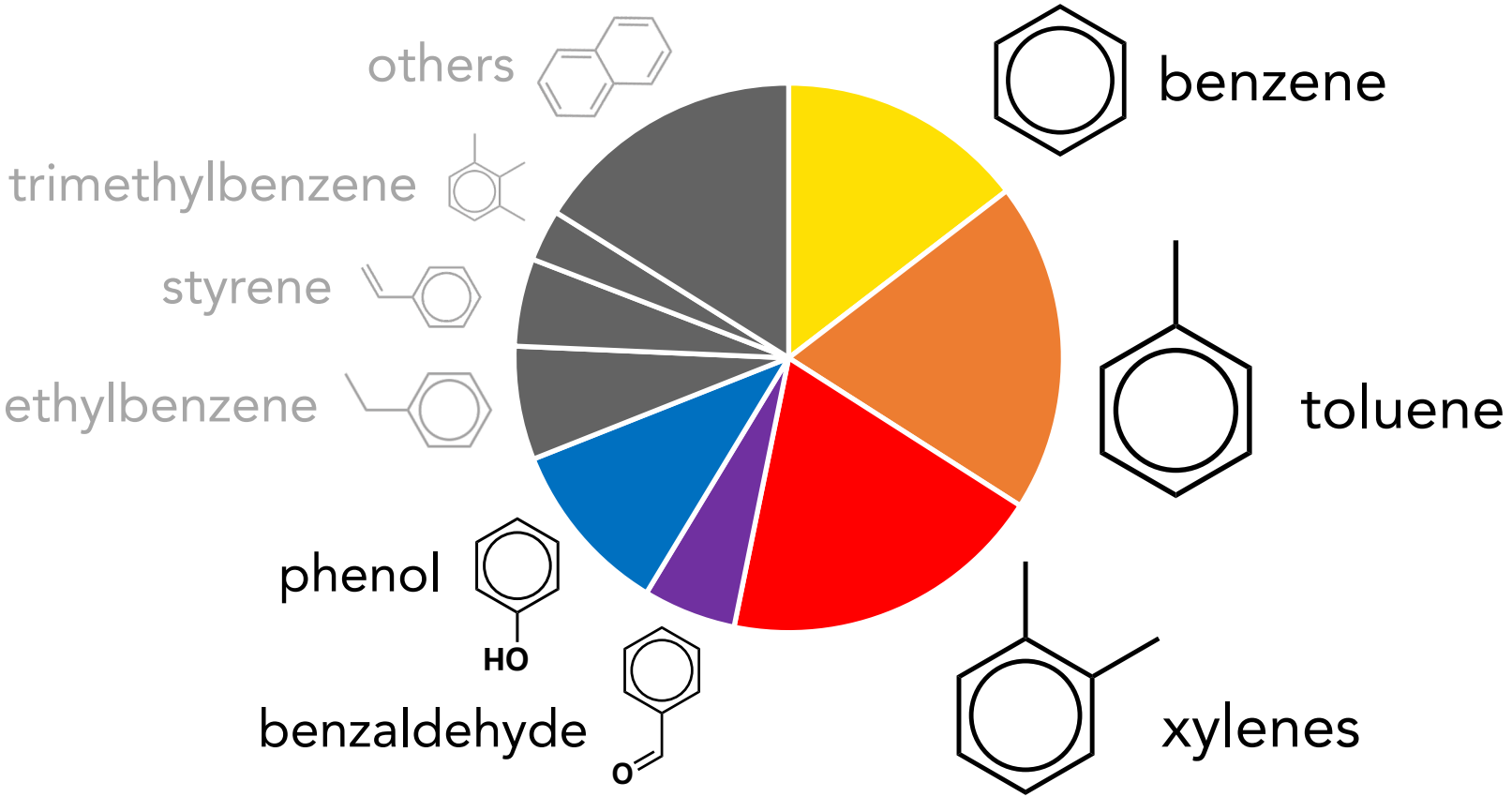
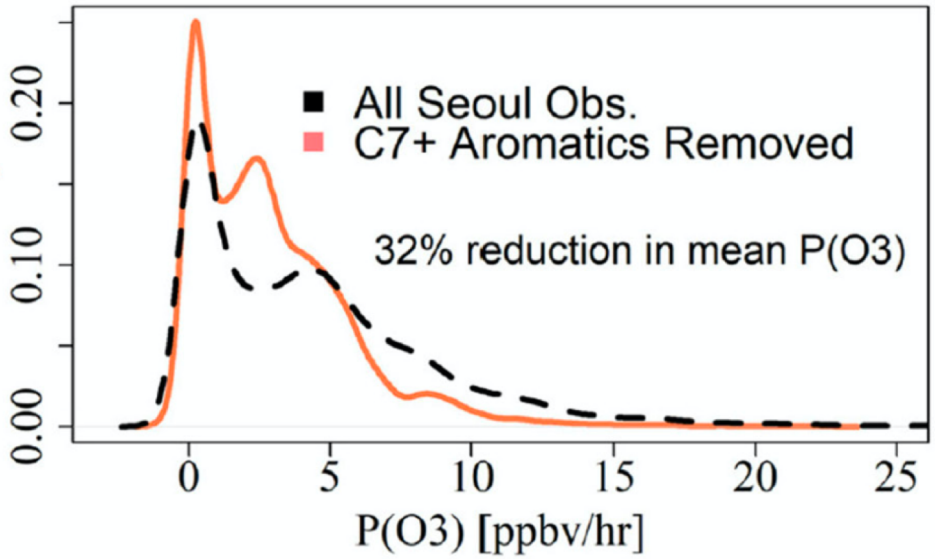
Atmospheric aromatics by emitted mass



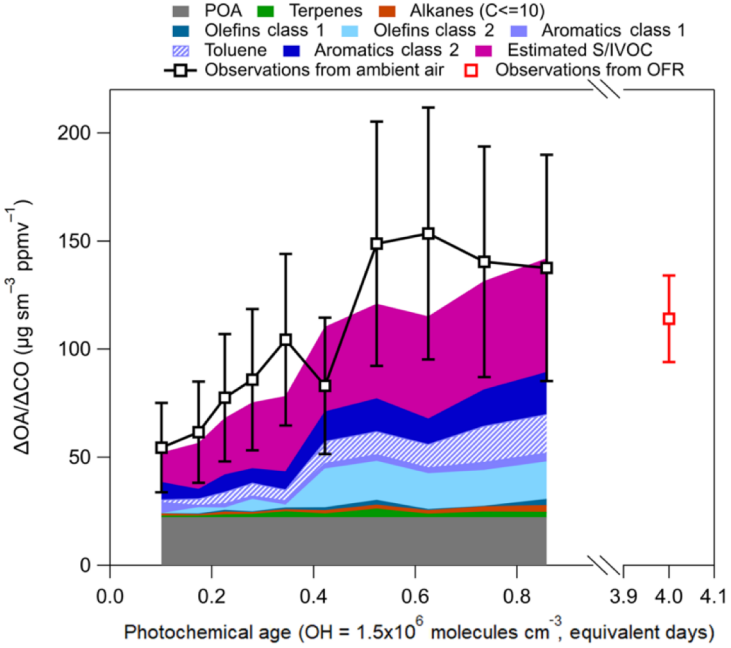
Atmospheric aromatics by emitted mass



Aromatics contribute to local & regional ozone and particulate pollution

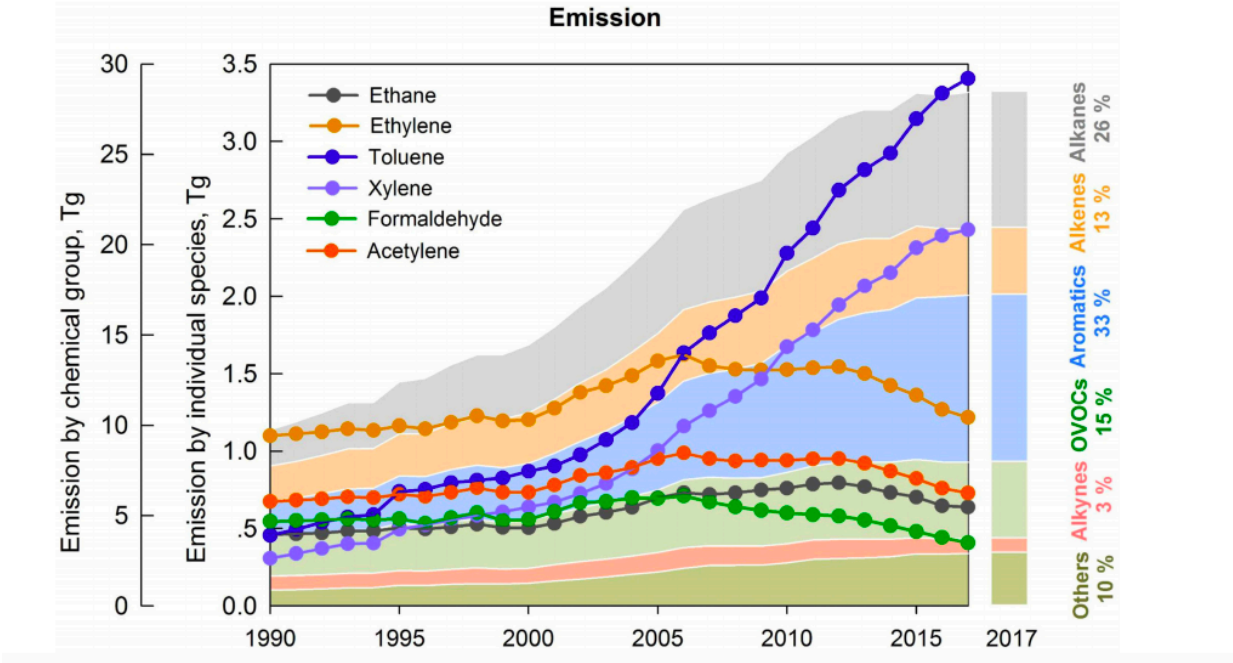


Schroeder *et al.* 2020



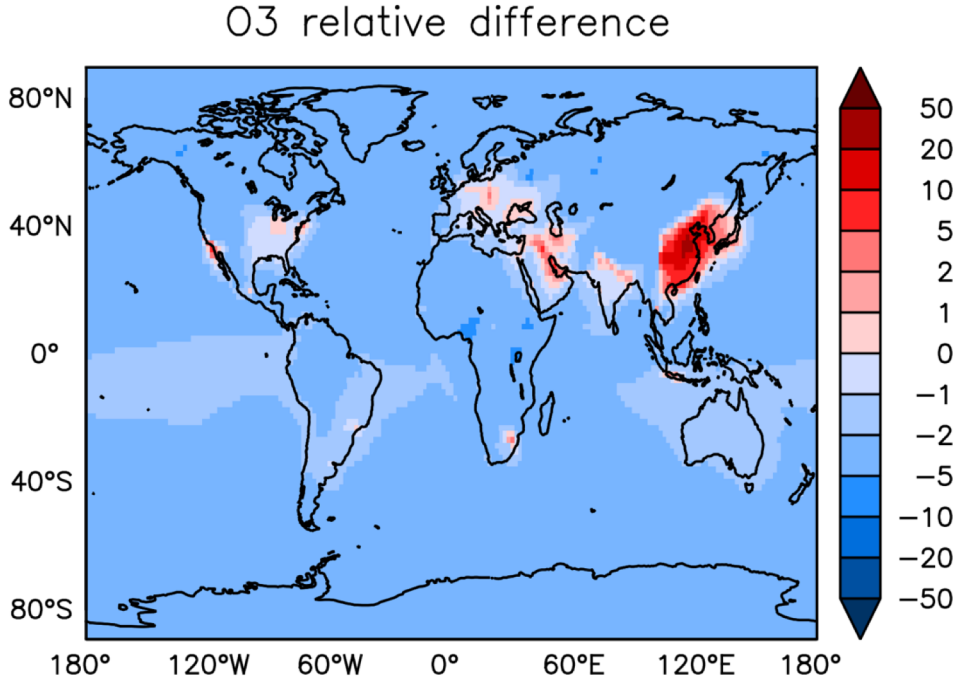
Nault *et al.* 2018

Aromatics account for an increasing fraction of VOC emissions



Li *et al.* 2019

Models show a wide range of results for regional & global impacts of aromatic oxidation



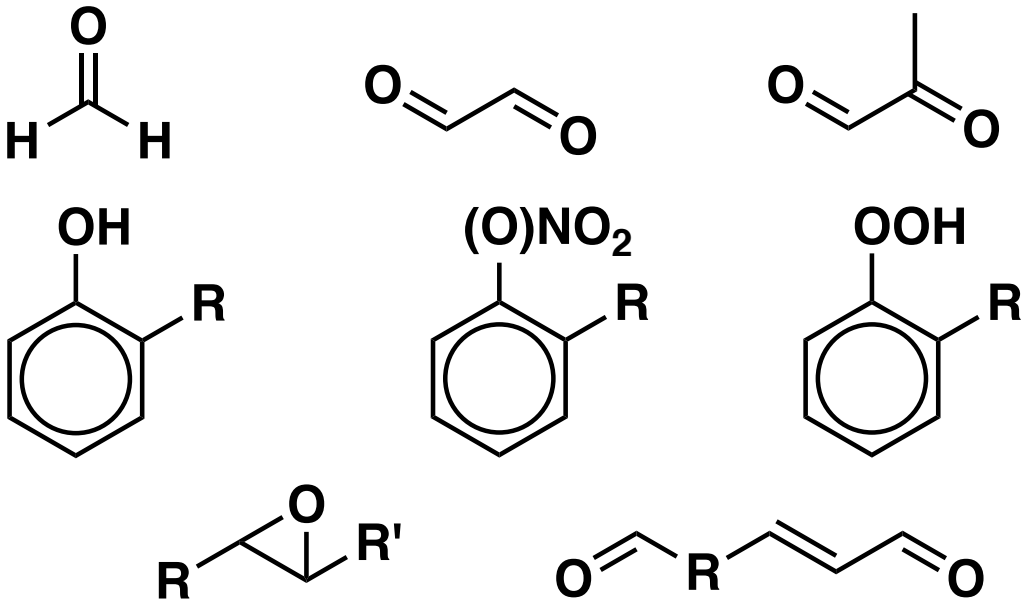
Taraborrelli *et al.* 2020

"Our results for ozone differ both in magnitude and sign compared to the global study by Yan *et al.* (2019)."

Our goal:

To develop a mechanism for the major aromatics that…

- accurately simulates short- & long-term product yields



Our goal:

To develop a mechanism for the major aromatics that…

- accurately simulates short- & long-term product yields
- accurately simulates effects on HO_x, NO_x, and ozone
- retains major classes of intermediates
- conserves carbon
- minimizes complexity (# of species and reactions)

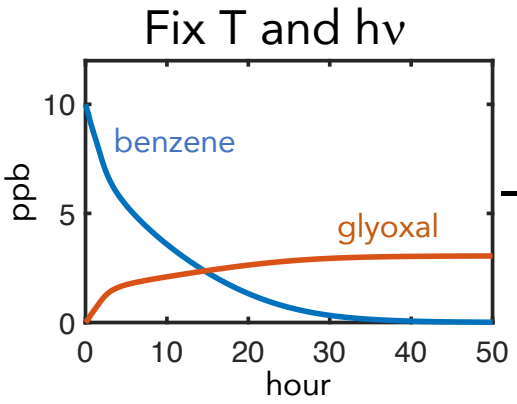
Our method:

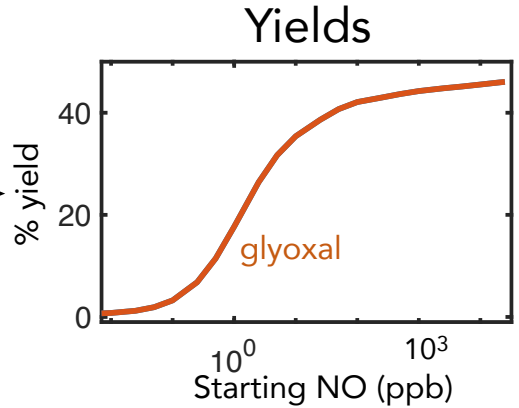
- Design a new simple mechanism from experimental outcomes and previous mechanisms
- Compare short-term product yields using simulated chamber experiments
- Compare long-term yields and outcomes by simulating aromatic chemistry in ambient conditions
- Iteratively adjust the mechanism to optimize simulated outcomes

Box modeling for mechanism comparisons

1. Chamber

Initial species:
- aromatic
- NO_x
- H_2O_2 or HONO

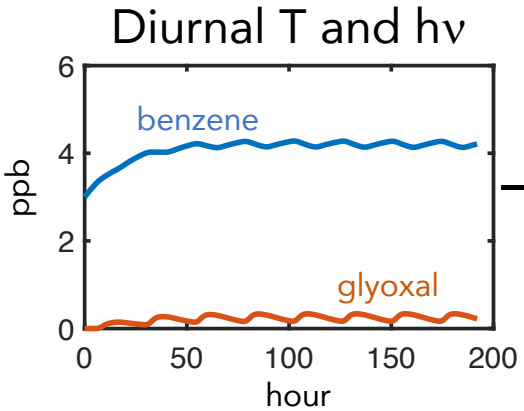


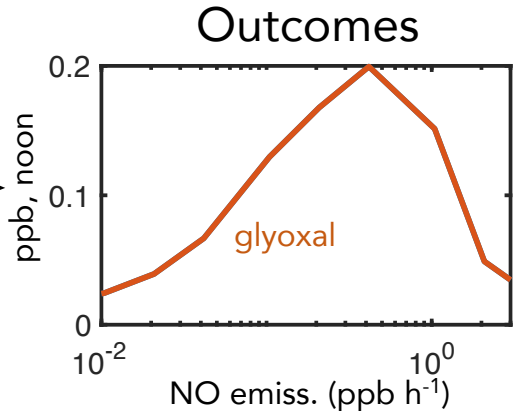


2. Ambient

Continuous emissions:
- aromatic(s)
- NO
- background

Mixing out (τ = 1 d)





Results: chamber yield comparisons

Models

Mechanism	Species	Reactions
GEOS-Chem	6	10
MOZART	13	43
SAPRC	55	374
RACM2	34	115
MCM	1271	3788
MECCA	229	666
New	**19**	**49**

Experiments

- Arey et al. (2009)
- Atkinson et al. (1983)
- Atkinson et al. (1989)
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- Atkinson et al. (1994)
- Baltaretu et al. (2009)
- Bandow et al. (1985)
- Becker et al. (1997)
- Berndt et al. (1999)
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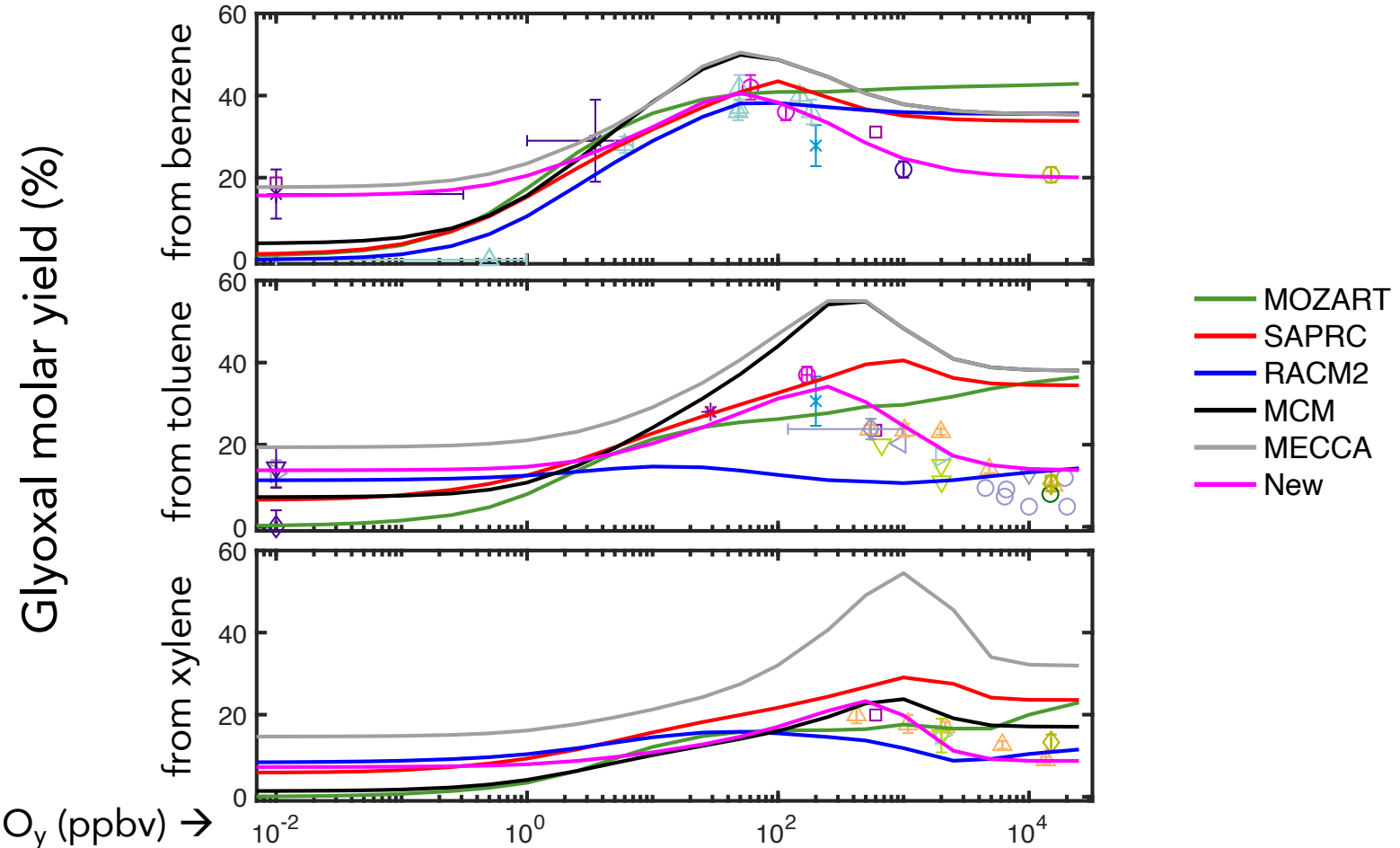
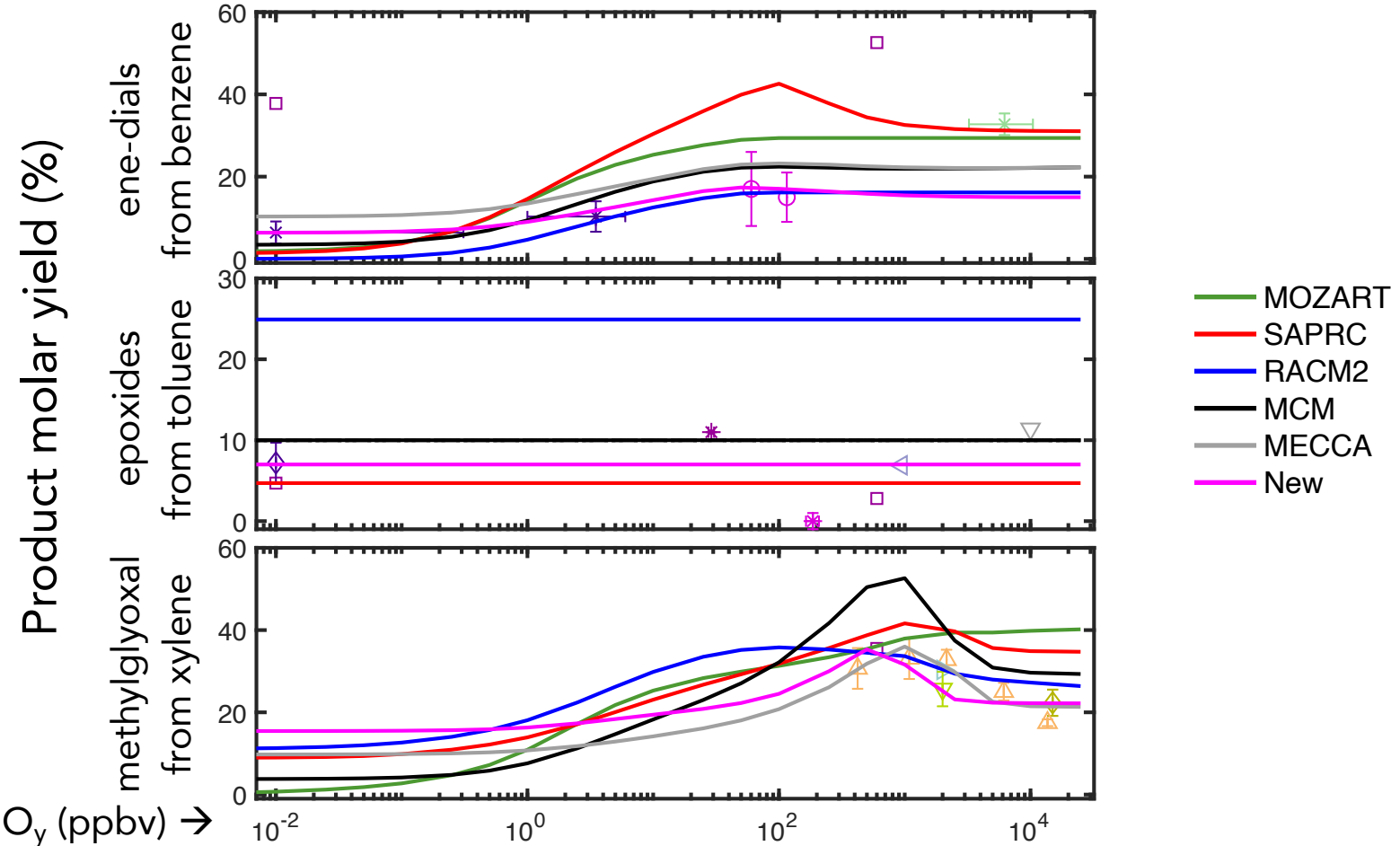
- Birdsall et al. (2011)
- Bjergbakke et al. (1996)
- Dumdei et al. (1988)
- Gery et al. (1985)
- Gomez Alvarez et al. (2007)
- Ji et al. (2017)
- Klotz et al. (1998)
- Klotz et al. (2002)
- Leone et al. (1985)
- Martin et al. (2005)
- Moschonas et al. (1998)
- Nishino et al. (2010)
- Noda et al. (2009)
- Seuwen et al. (1996)
- Shepson et al. (1984)
- Smith et al. (1998)
- Tuazon et al. (1984)
- Tuazon et al. (1986)
- Volkamer et al. (2001)
- Wu et al. (2014)
- Zaytsev et al. (2019)

Results: chamber yield comparisons



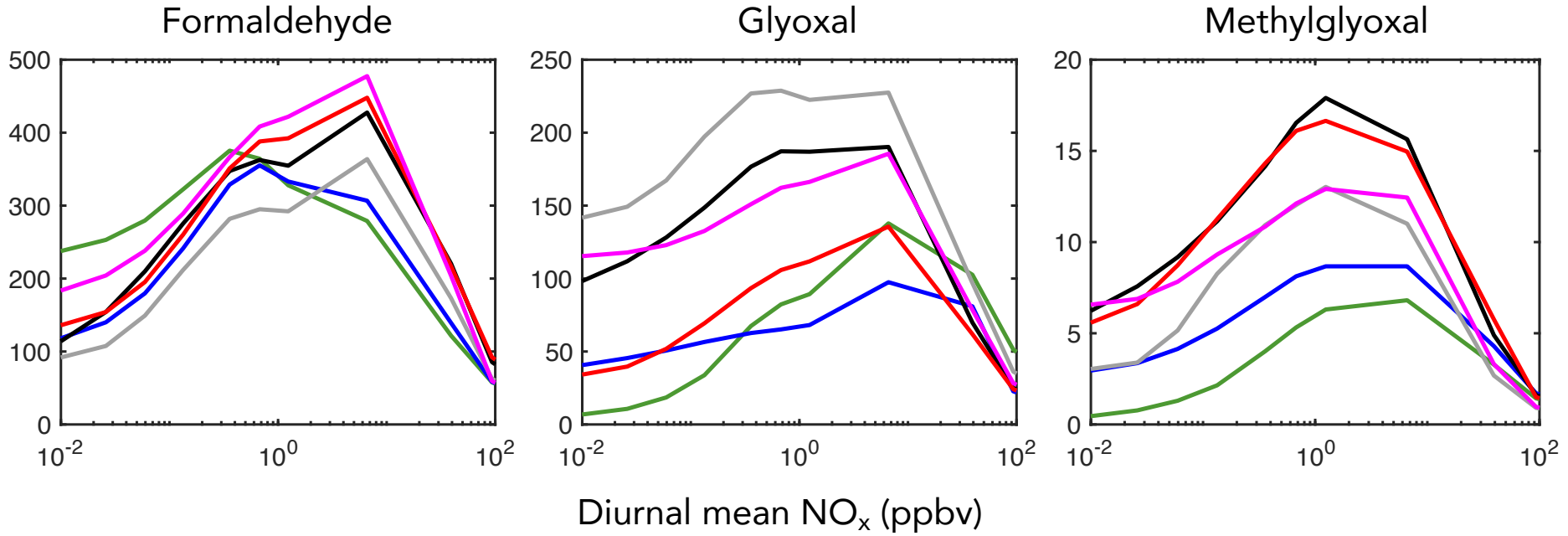
Results: chamber yield comparisons



Results: ambient comparisons

MOZART
SAPRC
RACM2
MCM
MECCA
New

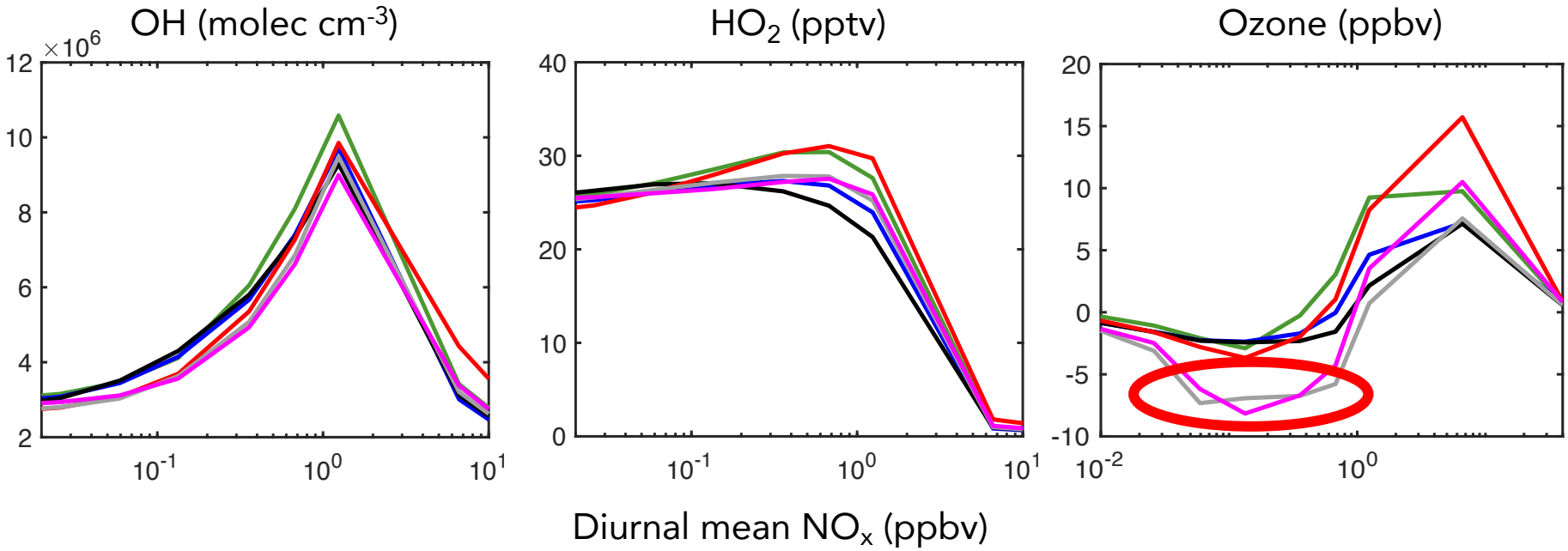
Mixing ratios (pptv, enhancement over background)
from mixed aromatics, day eight



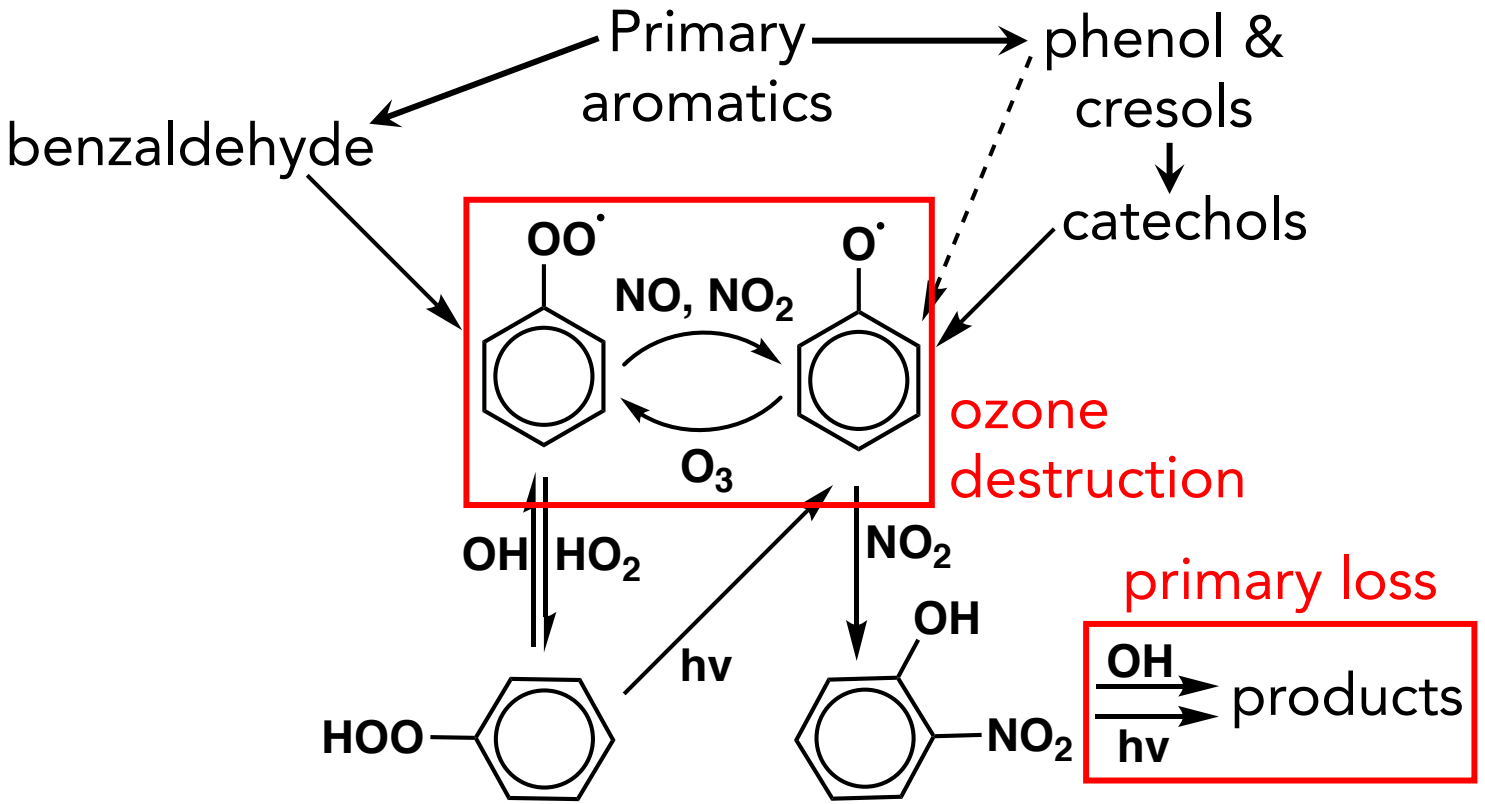
Results: ambient comparisons

MOZART
SAPRC
RACM2
MCM
MECCA
New

Enhancement over background
from benzene, noon, day eight

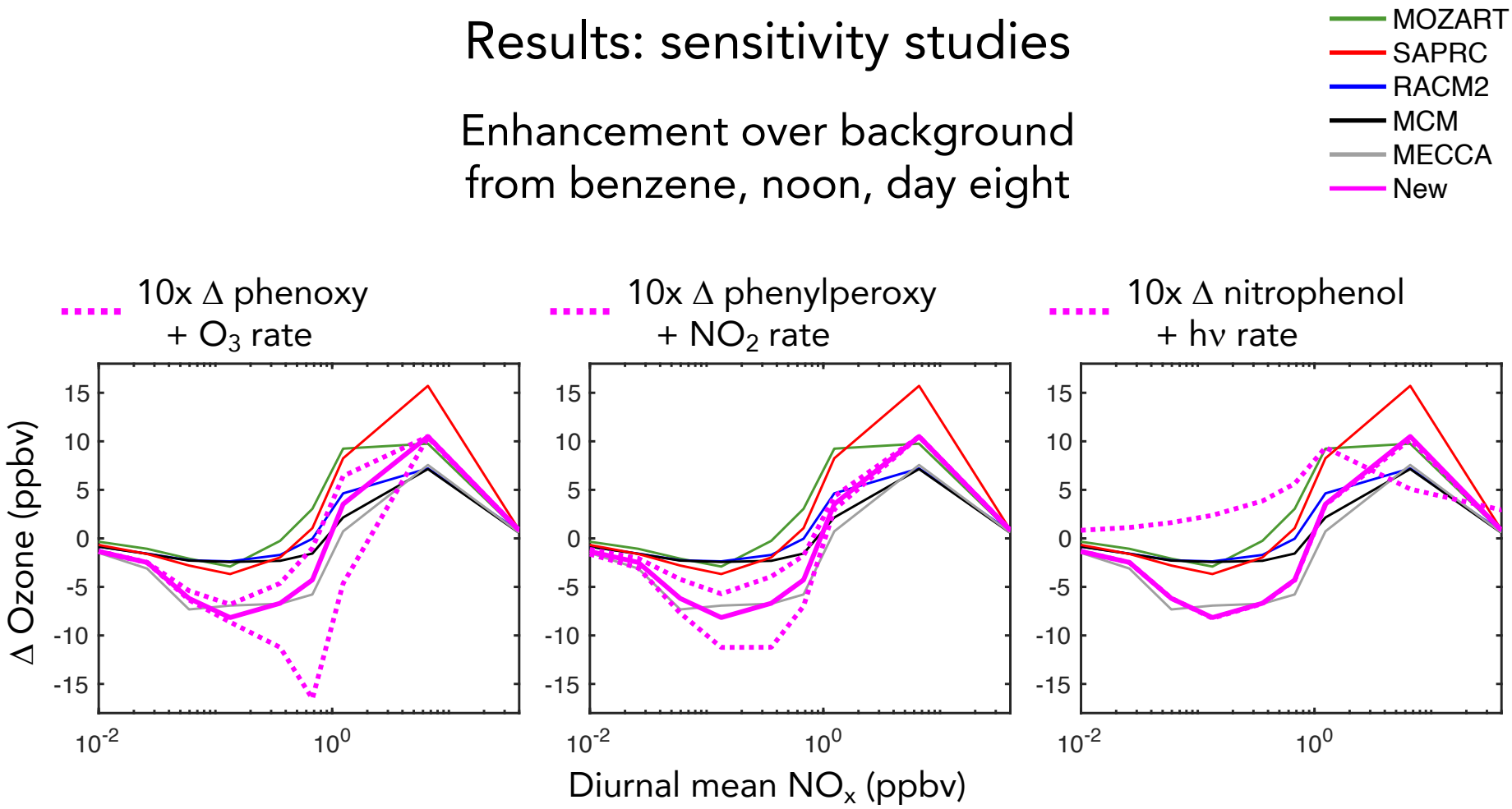


Results: ambient comparisons



Results: sensitivity studies

Enhancement over background from benzene, noon, day eight



Take-aways:

- Key outcomes and intermediates of aromatic oxidation can be satisfactorily simulated with a simple mechanism (<20 species, <50 reactions)

- Careful representation of the phenylperoxy-phenoxy radical system is crucial for ozone outcomes

- Substantial uncertainties remain, especially in later-generation chemistry

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