Evaluating an Isoprene SOA Kinetic Model Using Laboratory and Field Measurements

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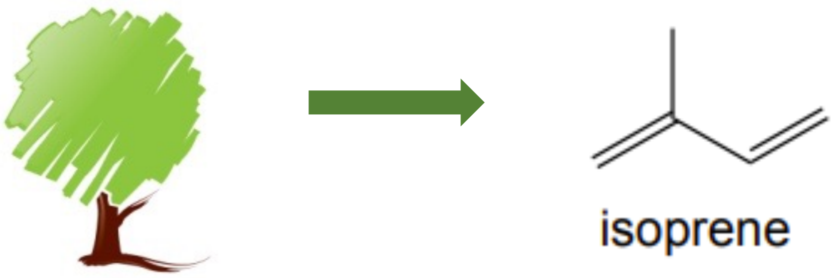
AGS-2037698

Motivation: Why isoprene



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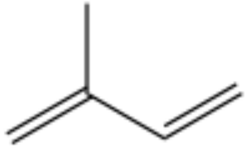

isoprene

VOCs	Emission Inventory (Tg/yr)
Isoprene	**500 - 600**
Terpenes	100 - 150
Other BVOCs	400 - 500
Anthropogenic	100 -150

Guenther et al., *Atmos. Chem. Phys.*, **2006**, 6, 3181

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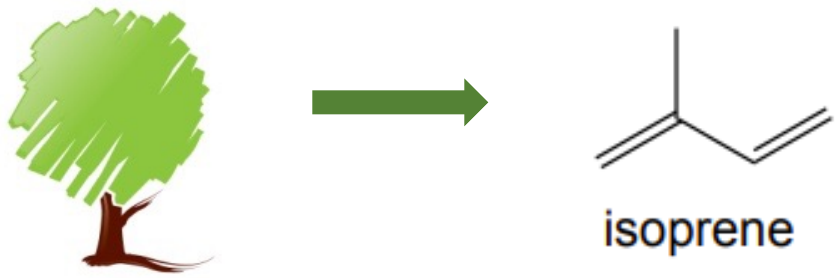

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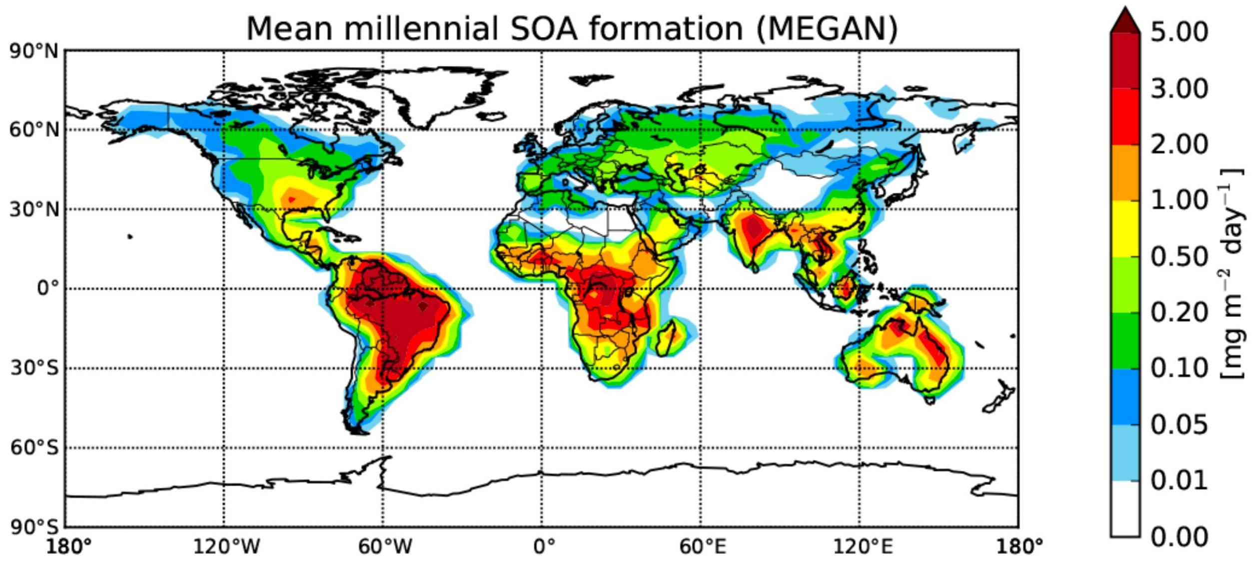

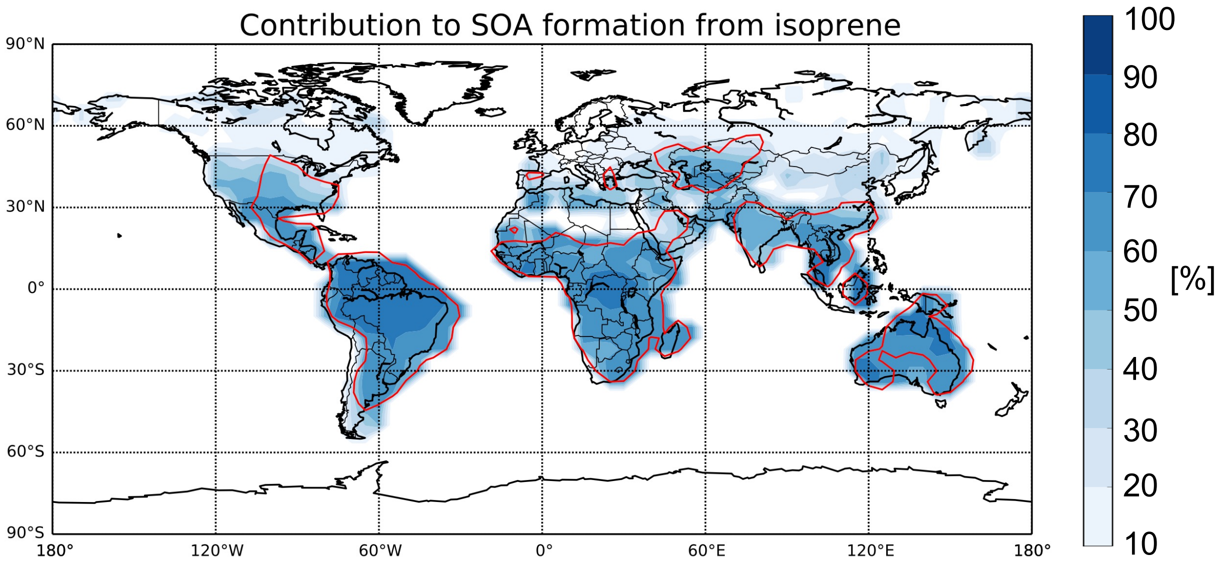

Motivation: Why still isoprene

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Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene

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Reactive intermediates revealed in secondary organic aerosol formation from isoprene

Jason D. Surratt[a], Arthur W. H. Chan[a], Nathan C. Eddingsaas[a], ManNin Chan[b], Christine L. Loza[a], Alan J. Kwan[b], Scott P. Hersey[b], Richard C. Flagan[a,b], Paul O. Wennberg[b,c], and John H. Seinfeld[a,b,1]

[a]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125[b]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125[c]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125

Edited by Barbara J. Finlayson-Pitts, University of California, Irvine, Irvine, CA, and approved November 23, 2009 (received for review September 30, 2009)

Molecular-level studies

Field observations

Claeys et al., *Science*, **2004**, 303, 1173; Paulot et al., *Science*, **2009**, 325, 730; Surratt et al., *Proc. Natl. Acad. Sci.*, **2010**, 107, 6640

Motivation: Why still isoprene

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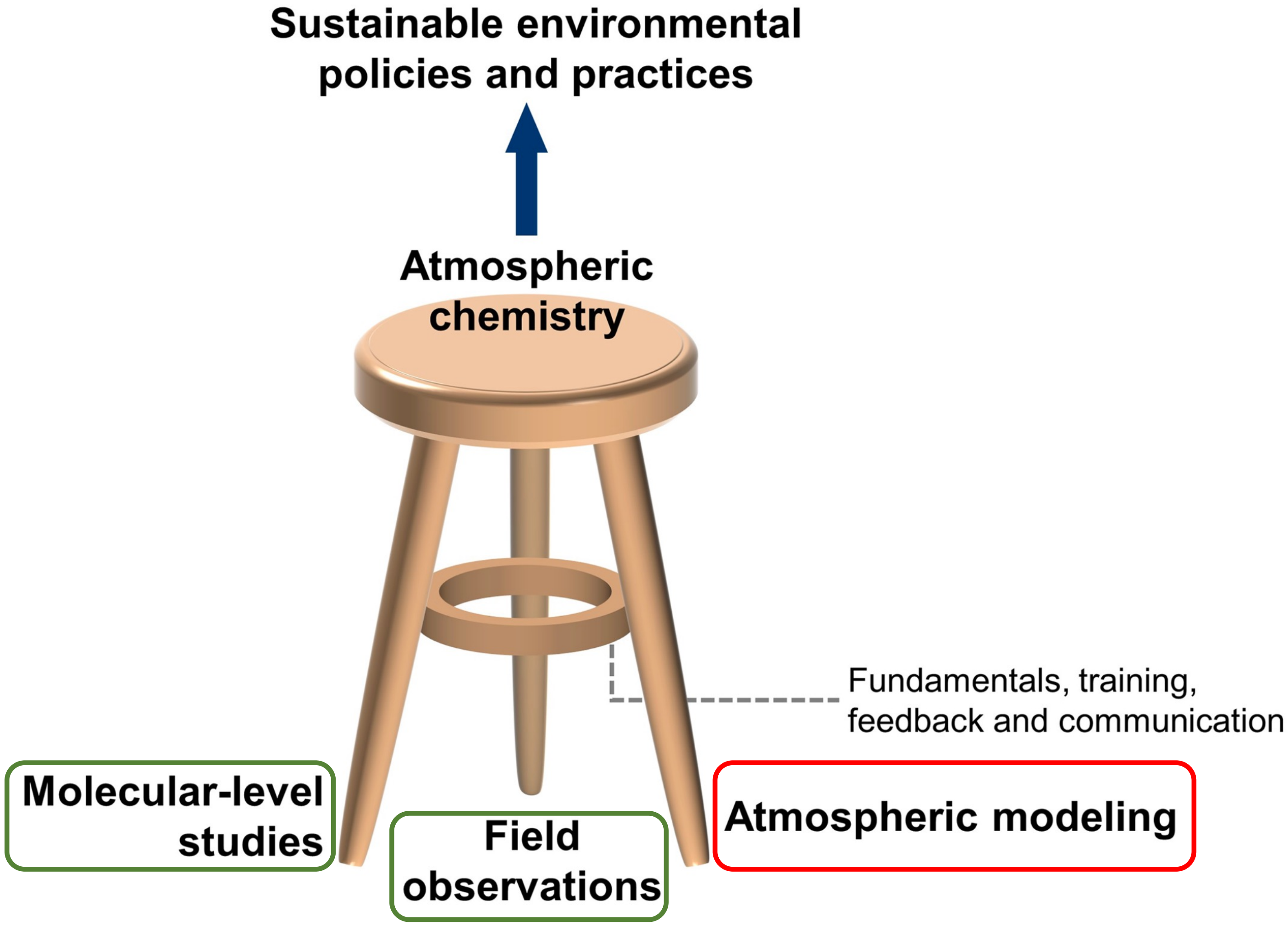

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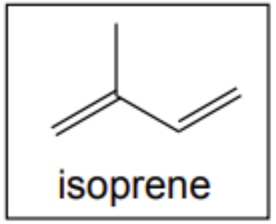
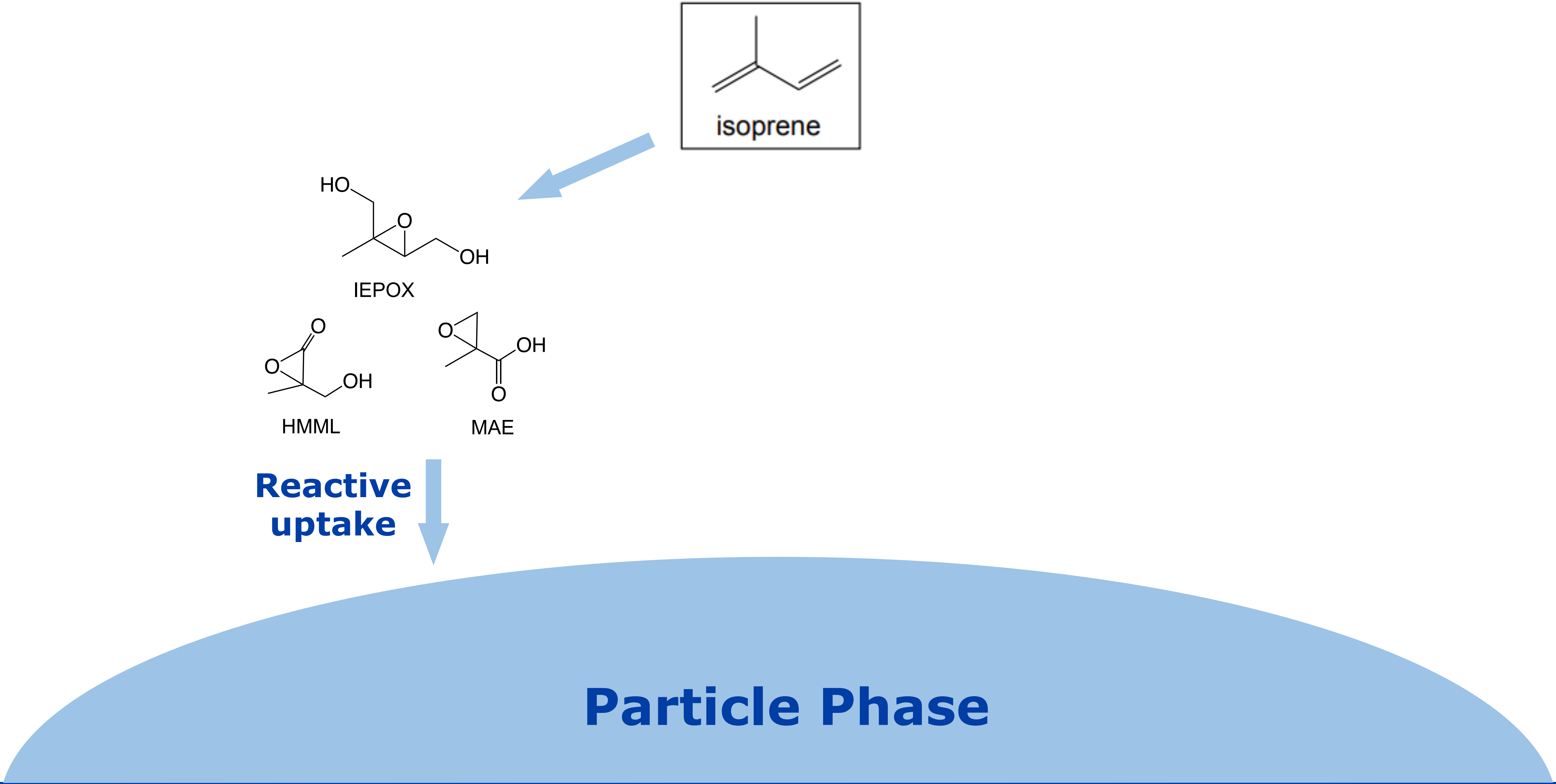
Abbatt and Ravishankara, *Atmos. Chem. Phys.*, **2023**, 23, 9765

Isoprene SOA Formation



Particle Phase

Isoprene SOA Formation



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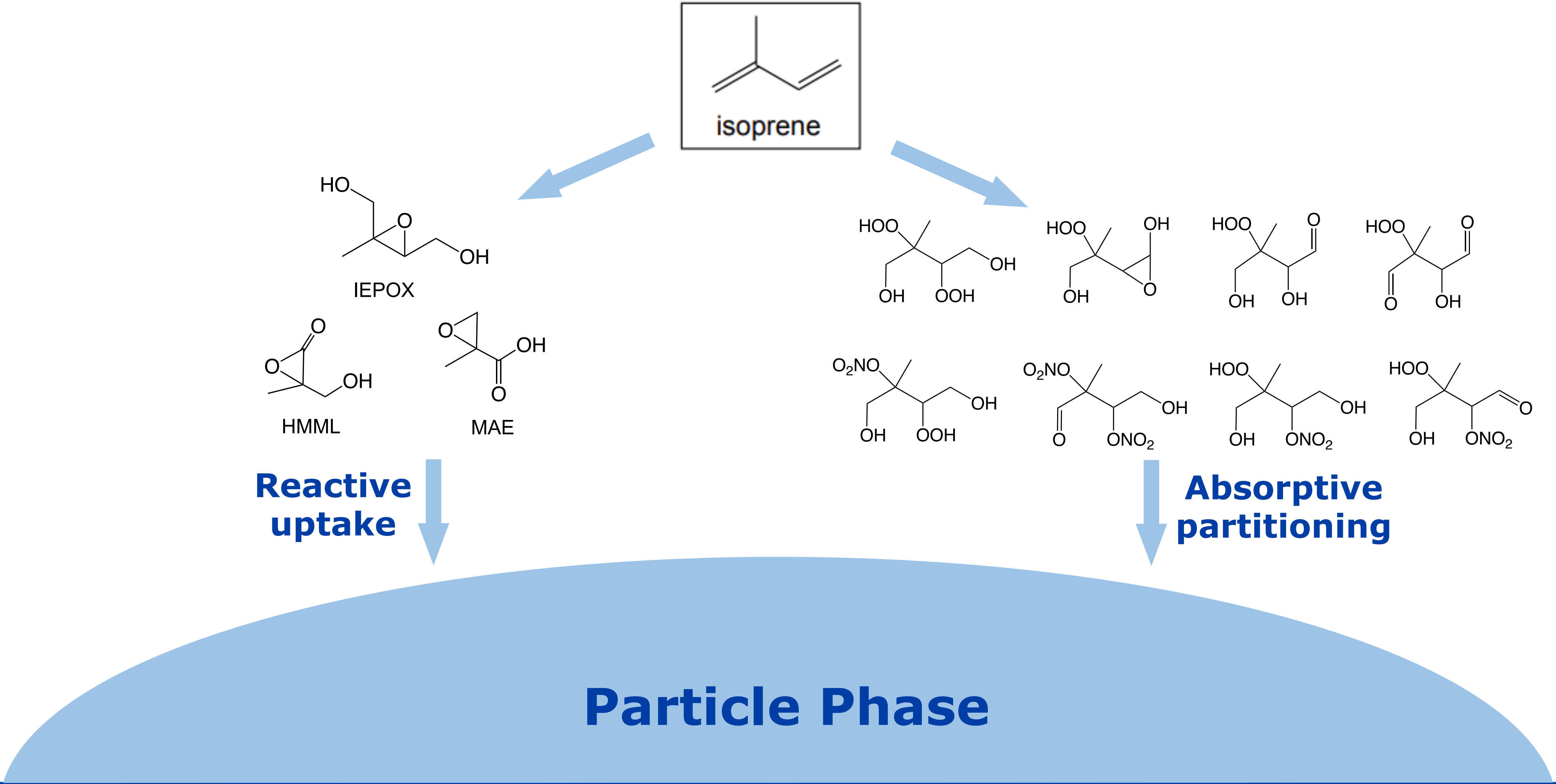

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Liu et al., *Environ. Sci. Technol.*, **2016**, 50, 9872; Lee et al., *Proc. Natl. Acad. Sci.*, **2016**, 113, 1516; Schwantes et al., *Atmos. Chem. Phys*, **2019**, 19, 7255

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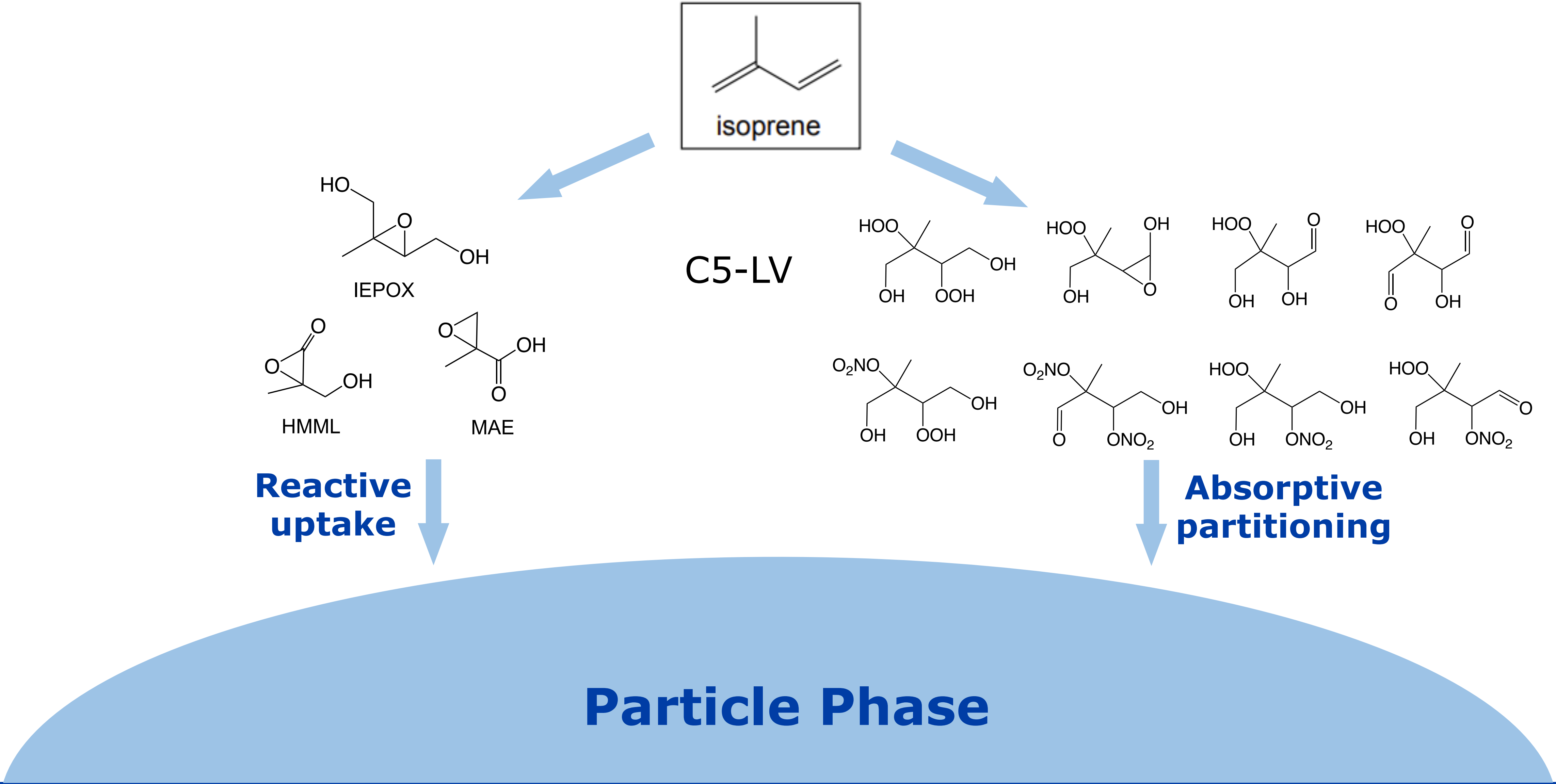

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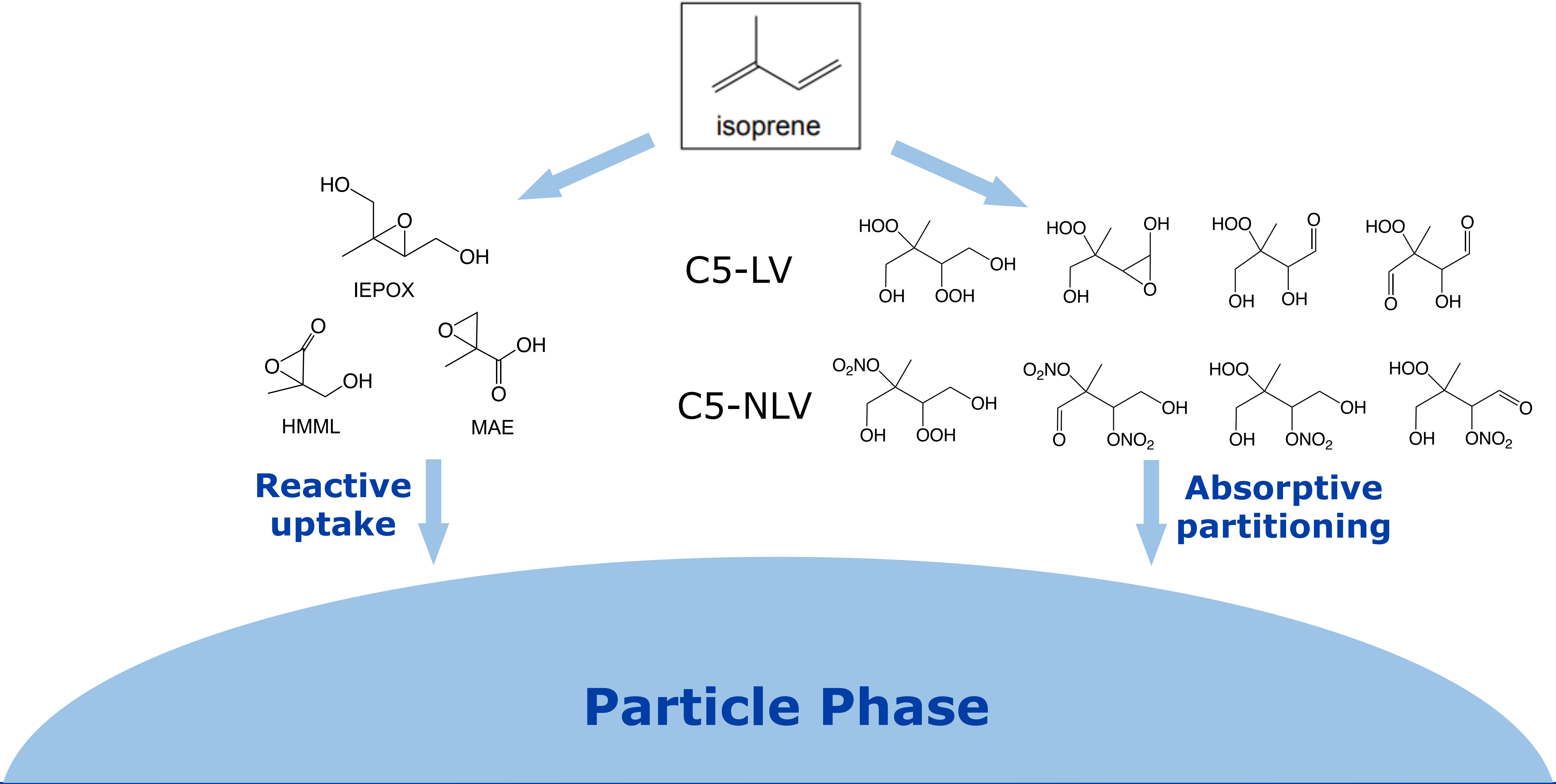

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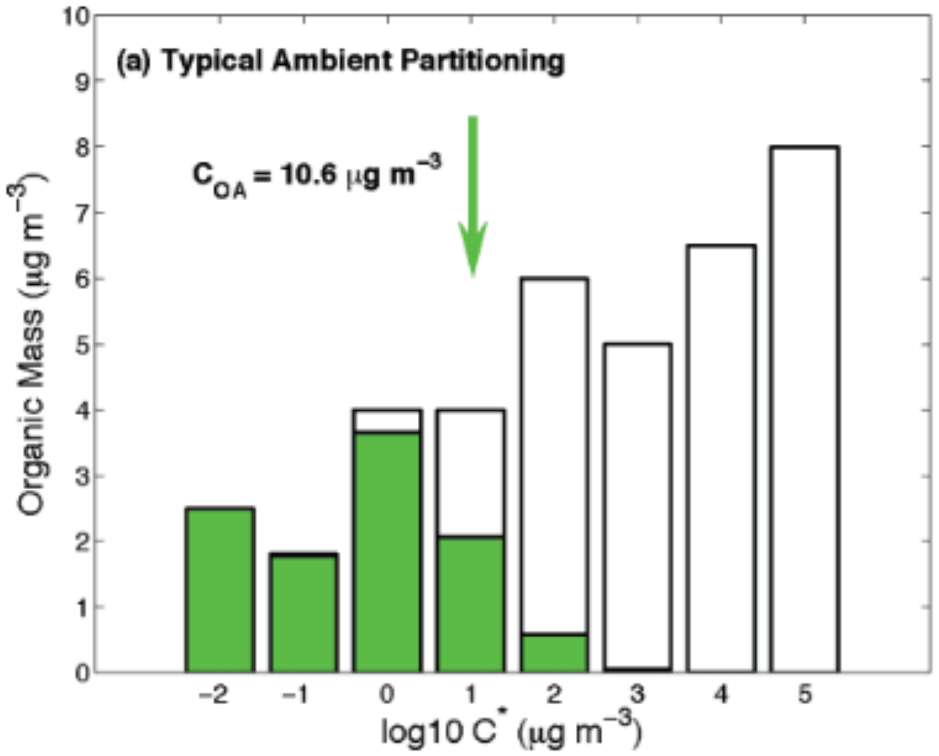
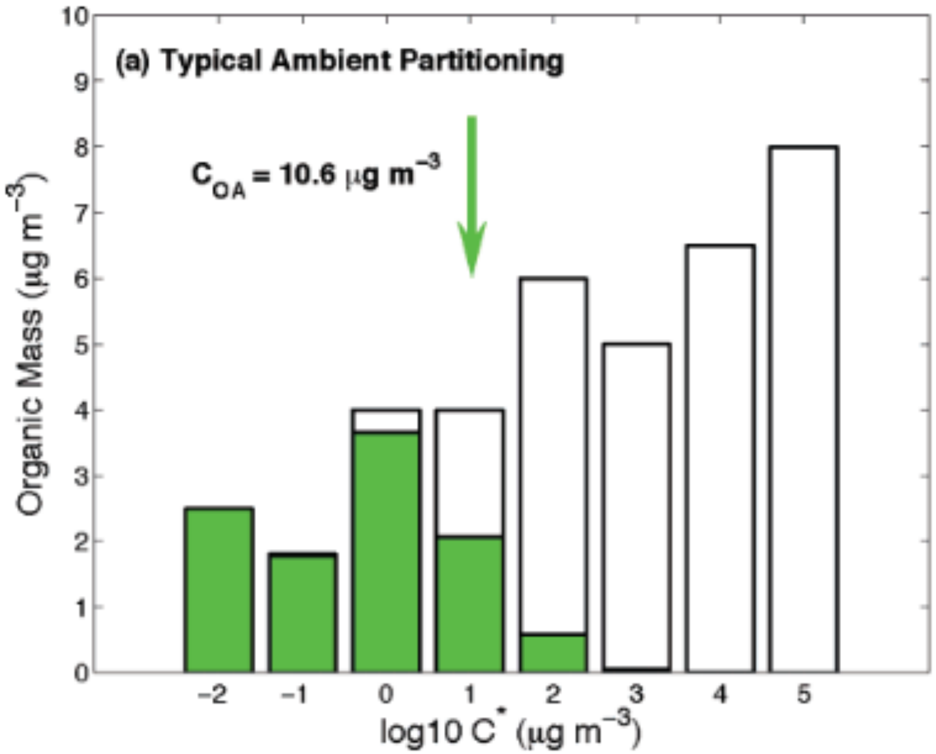
Isoprene SOA Formation Modeling

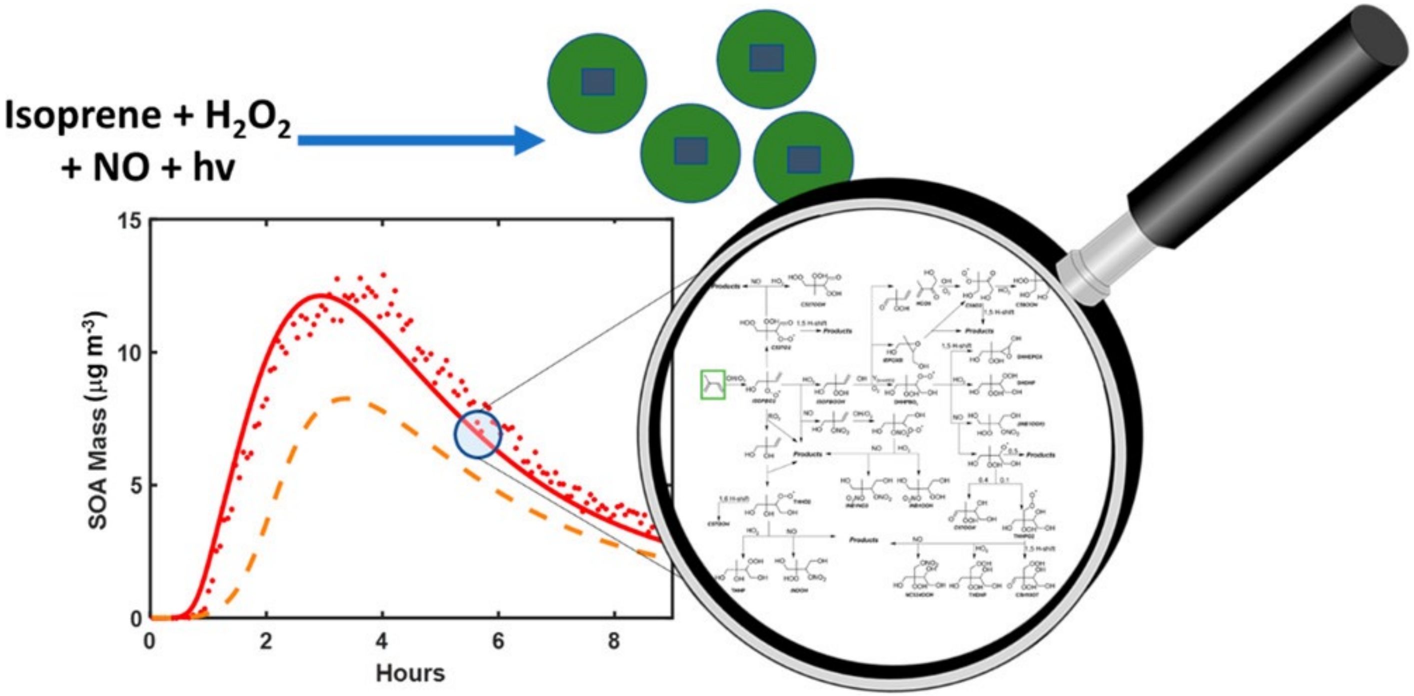


- Highly simplified;
- Parameterization based on chamber-derived SOA;
- No molecular information.

Donahue et al., *Environ. Sci. Technol.*, **2006**, 40, 2635

Isoprene SOA Formation Modeling





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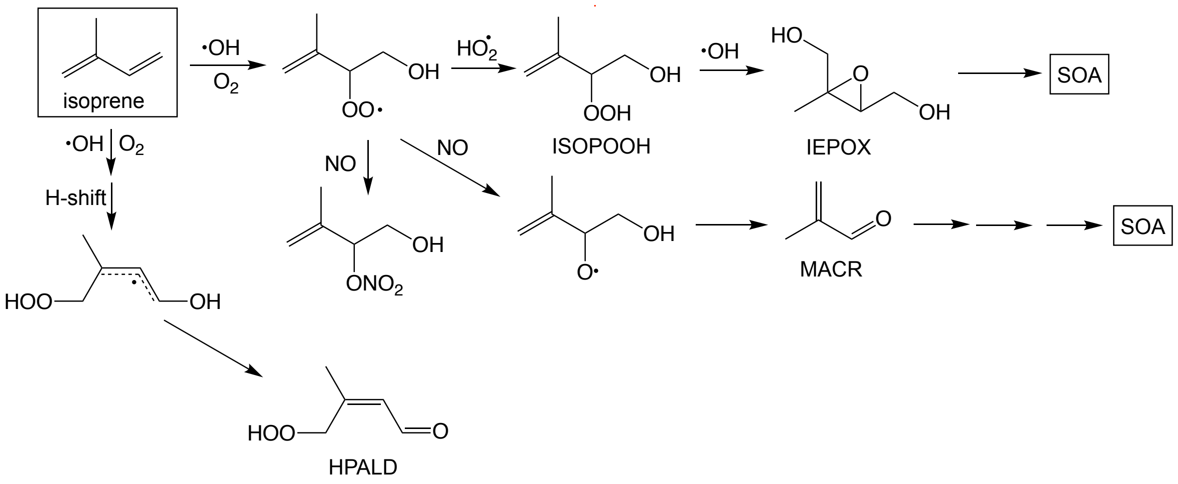
- Too large to implement;
- The isomeric-level details are sometimes unnecessary

Multiphase Isoprene SOA Kinetic Modeling



Shen et al., *in prep.*

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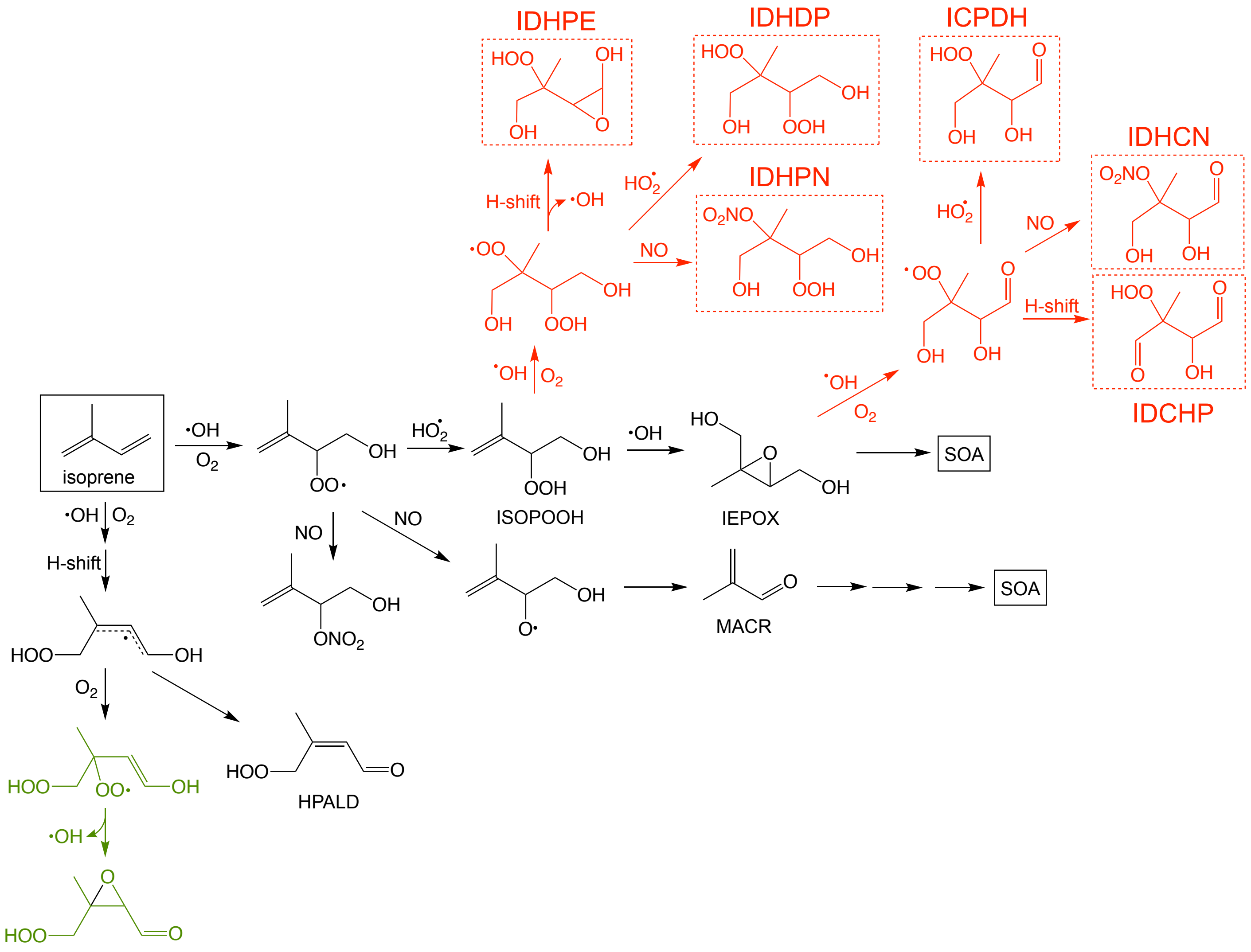

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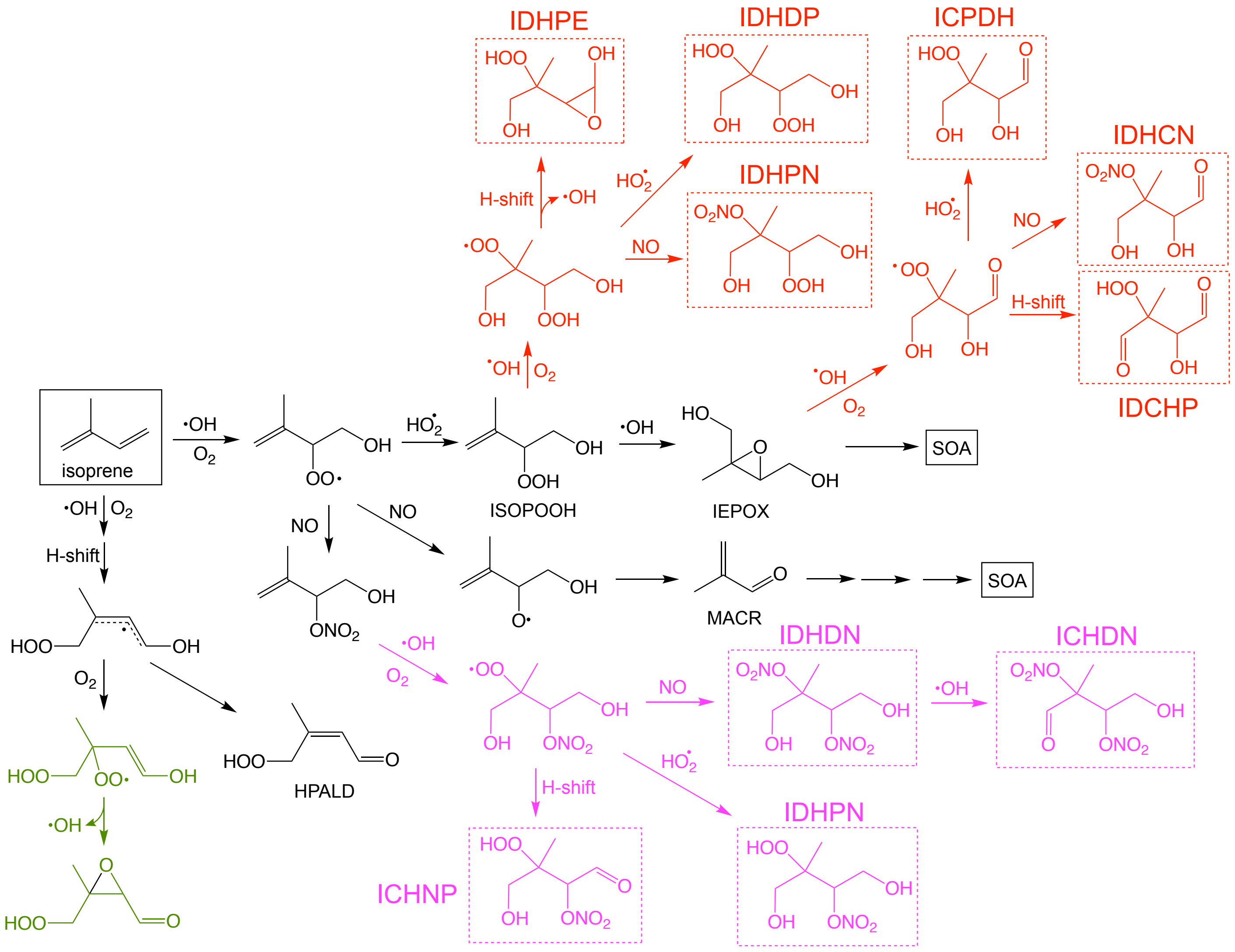

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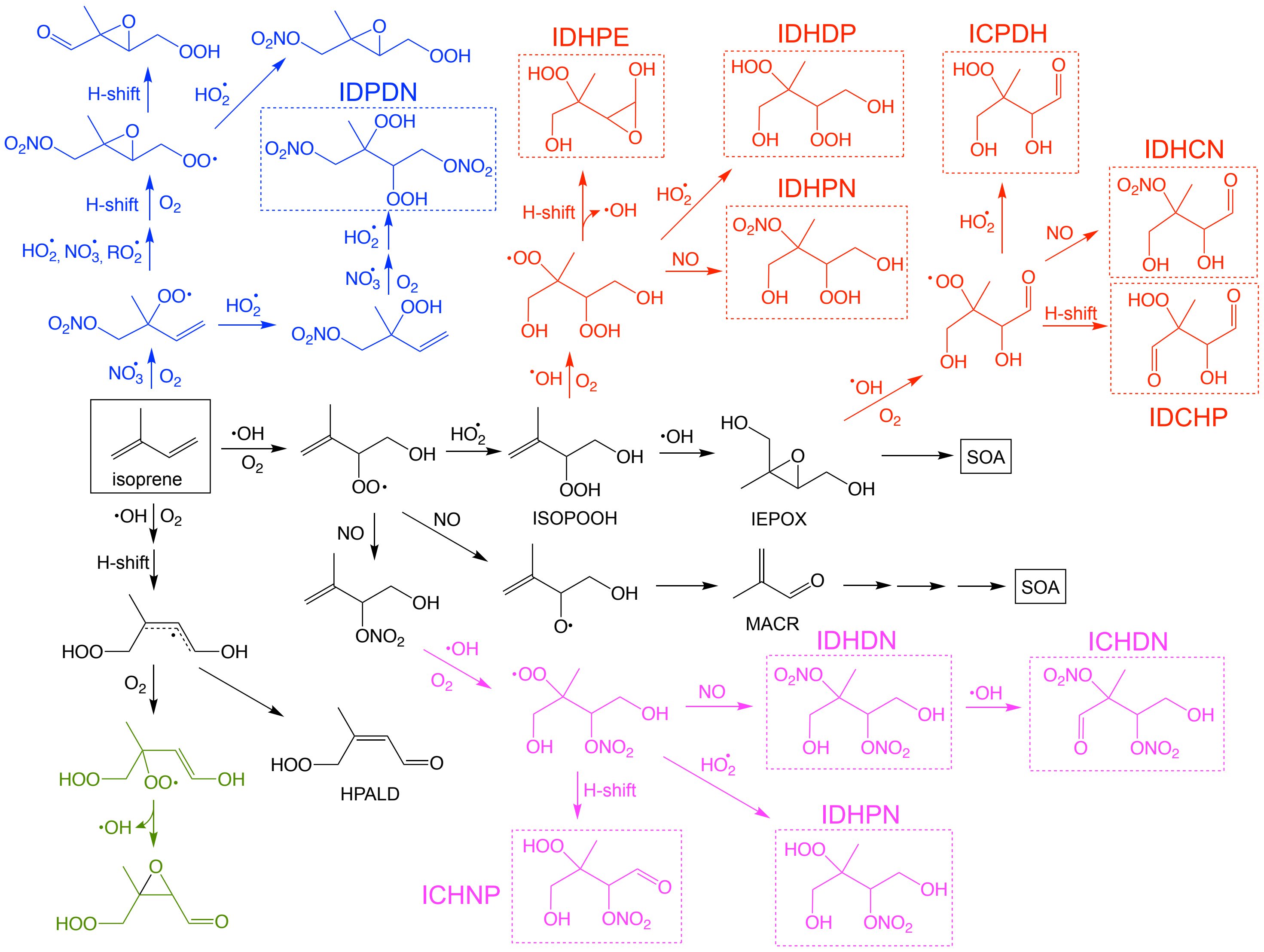

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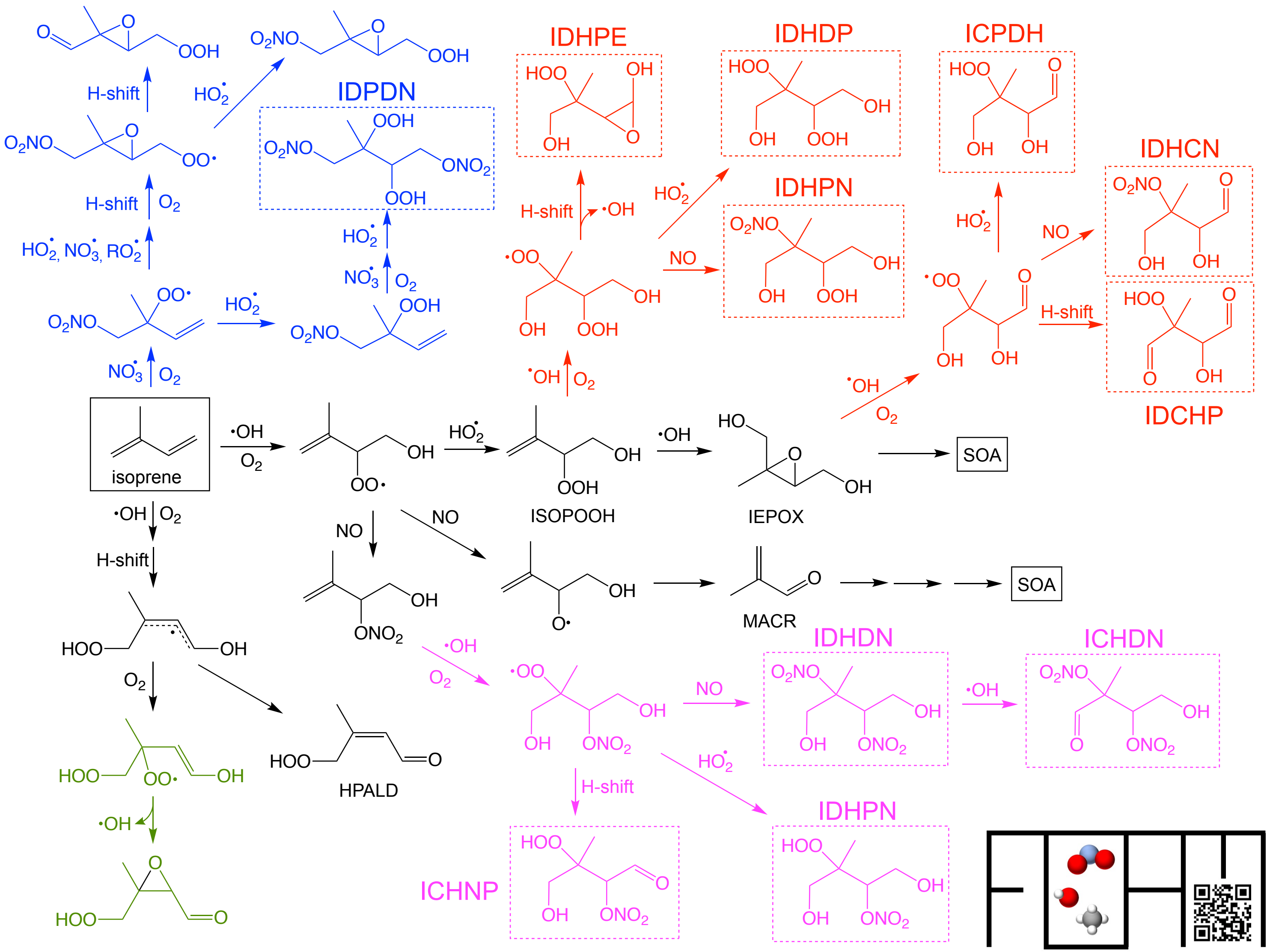

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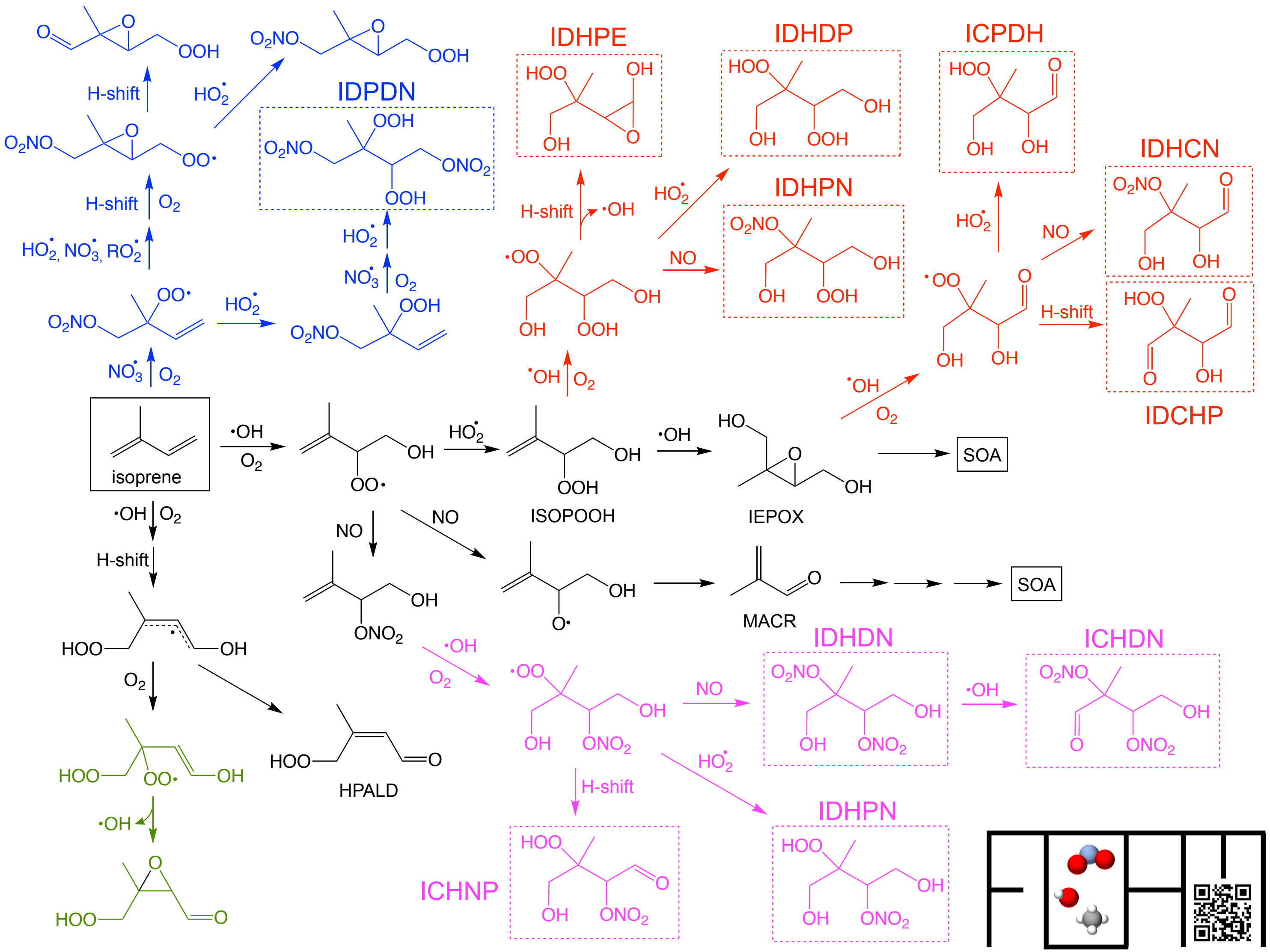

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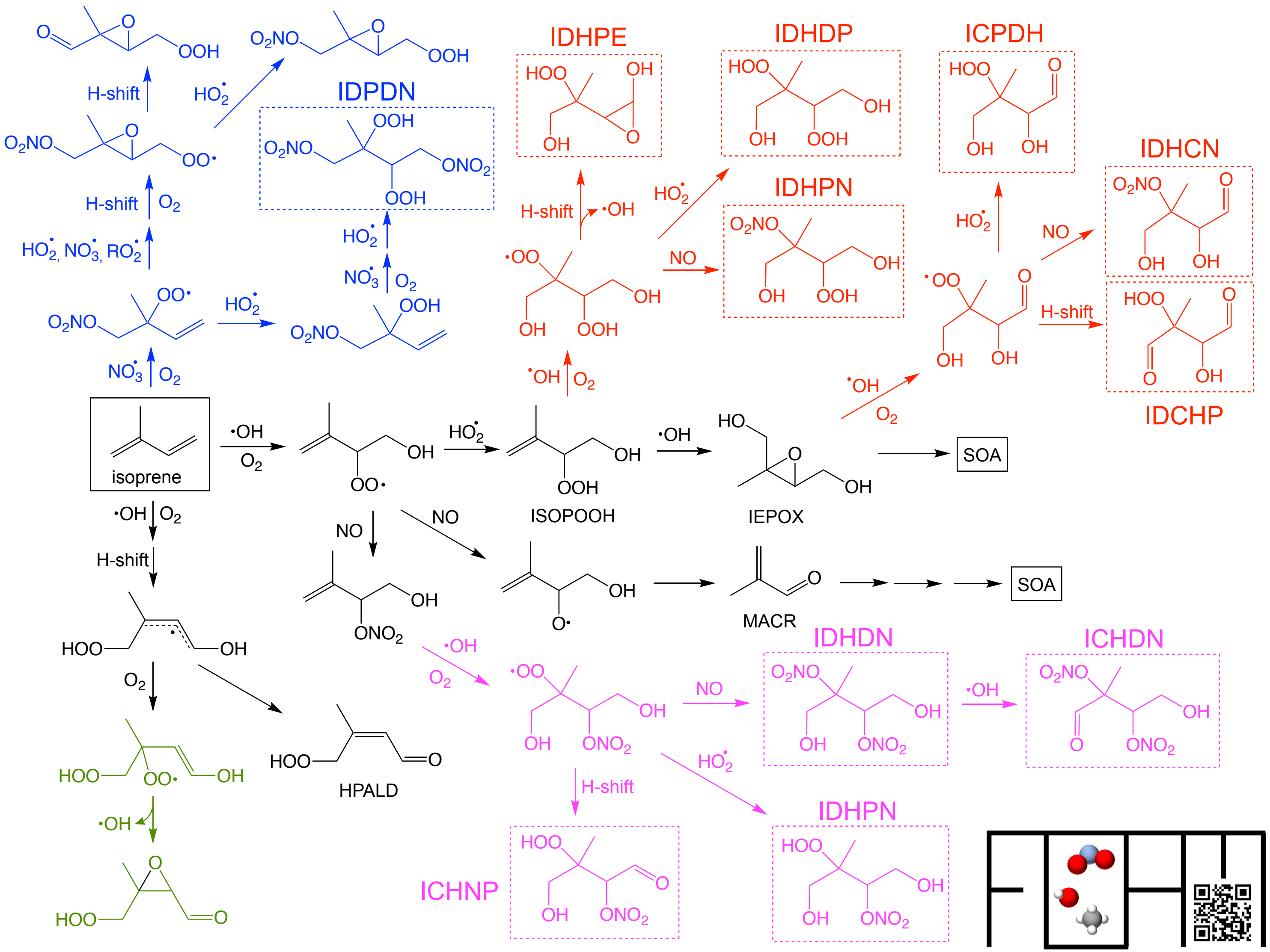

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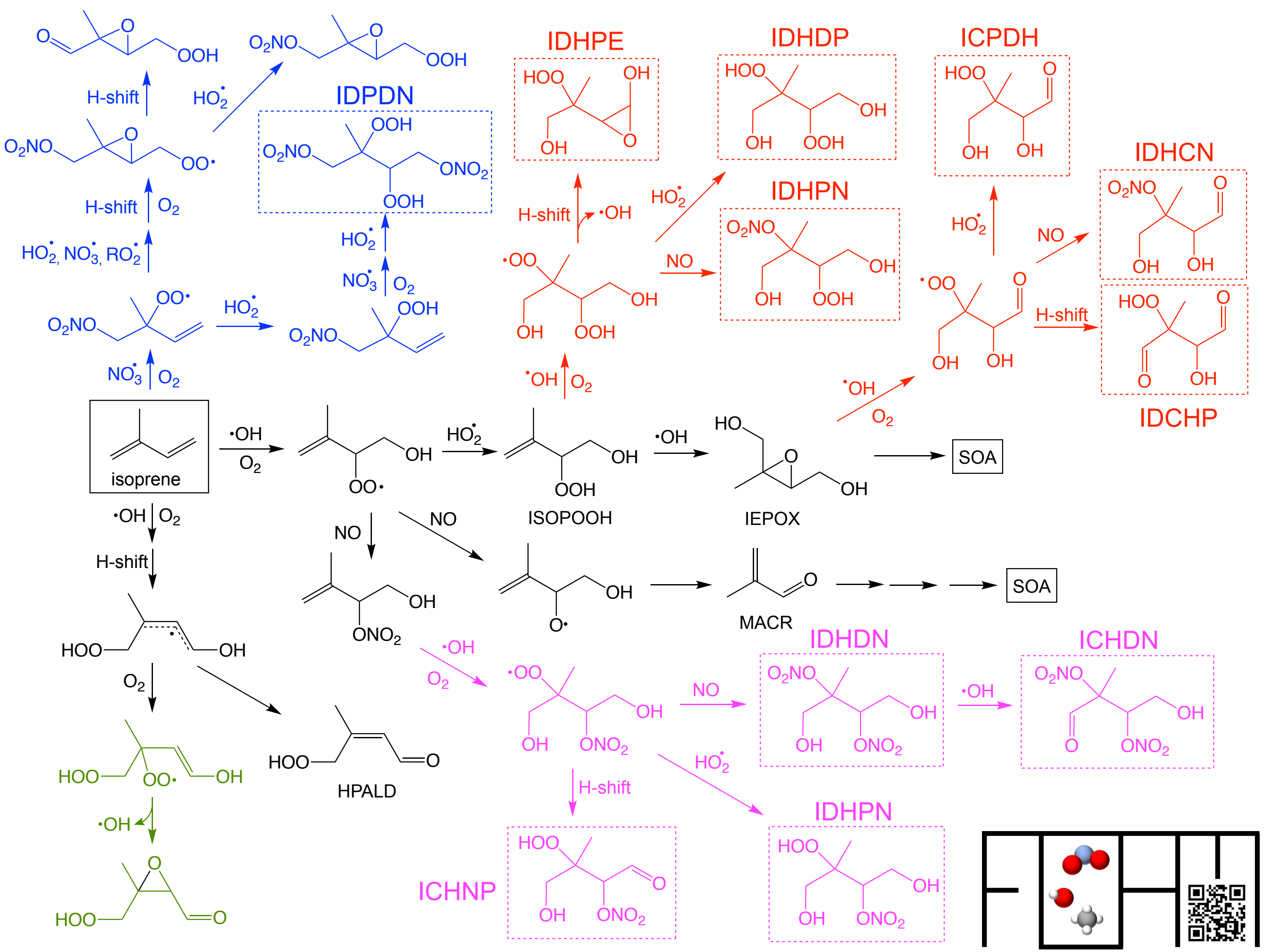

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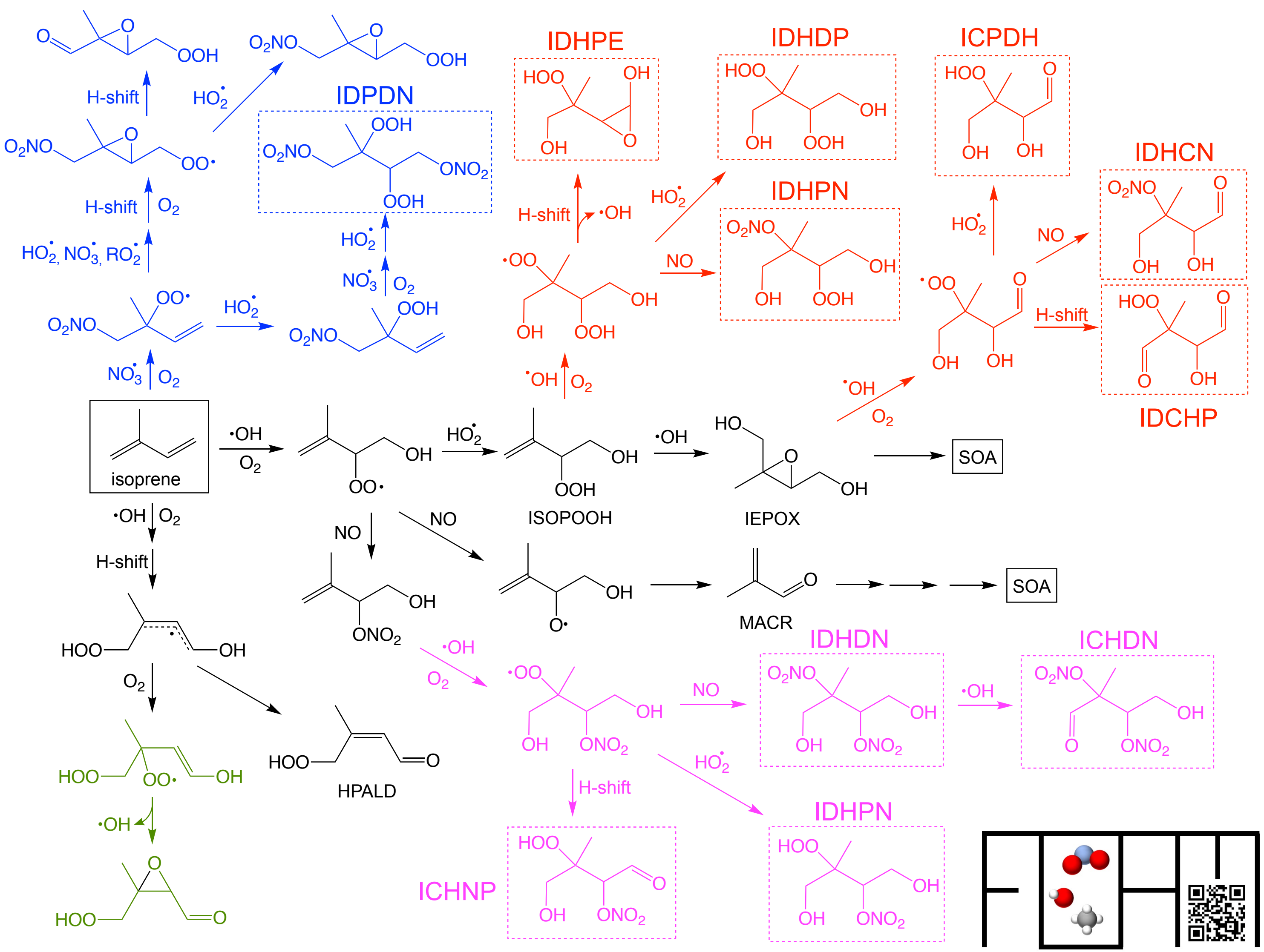

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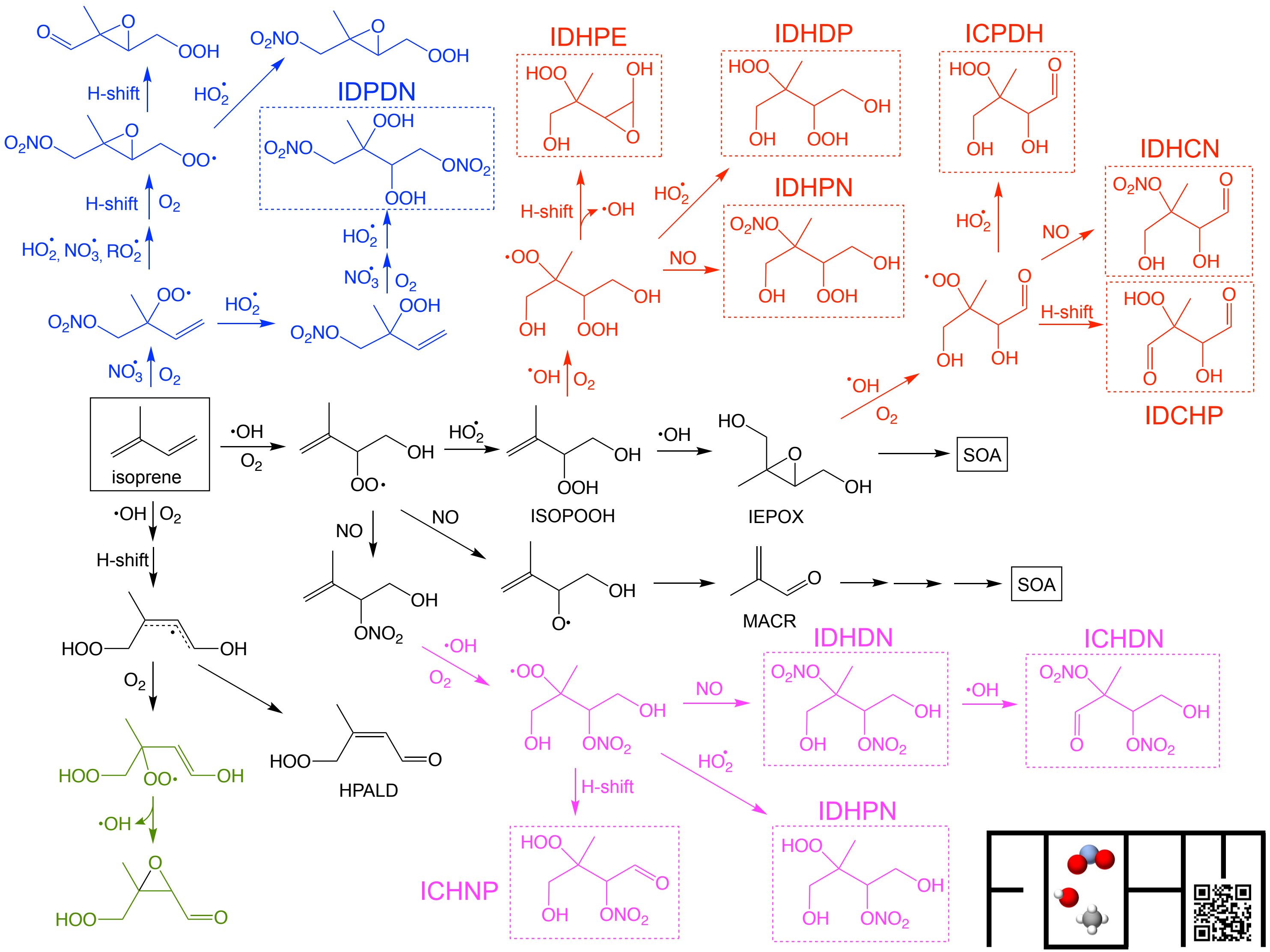

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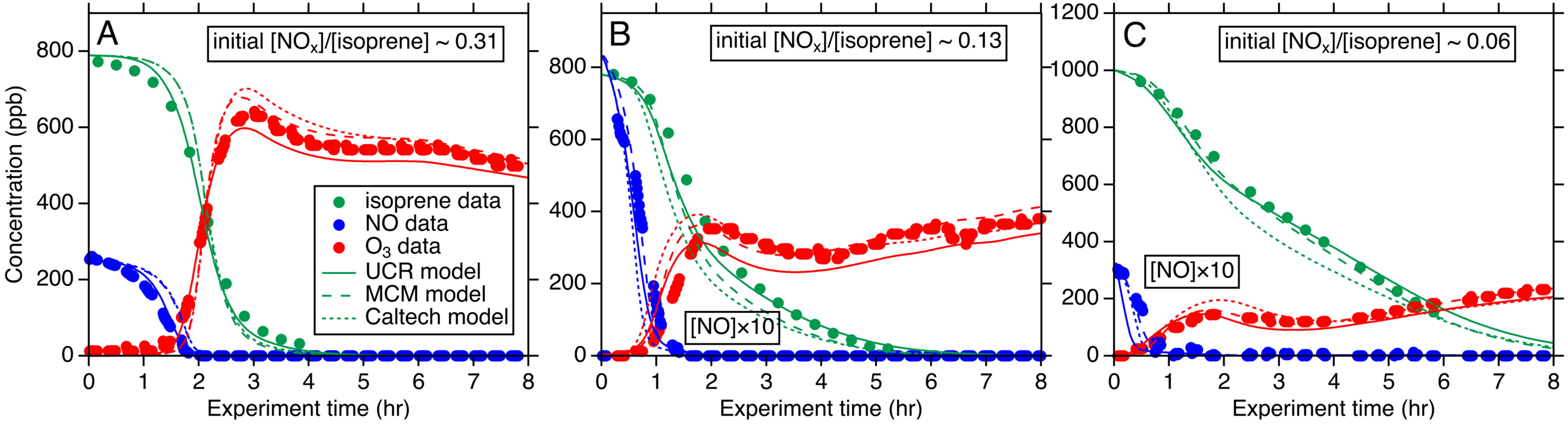
- Epoxides undergo reactive uptake (in the presence of aqueous/acidic sulfate);
- Low-volatility products undergo absorptive gas-particle partitioning;
- Particle-phase photolysis (for hydroperoxides) and hydrolysis (for organic nitrates);

Shen et al., *in prep.*

Wennberg et al., *Chem. Rev.*, **2018**, 118, 3337; Vereecken et al., *Phys. Chem. Chem. Phys.*, **2021**, 23, 5496

Evaluation with Chamber Experiments

Gas-phase



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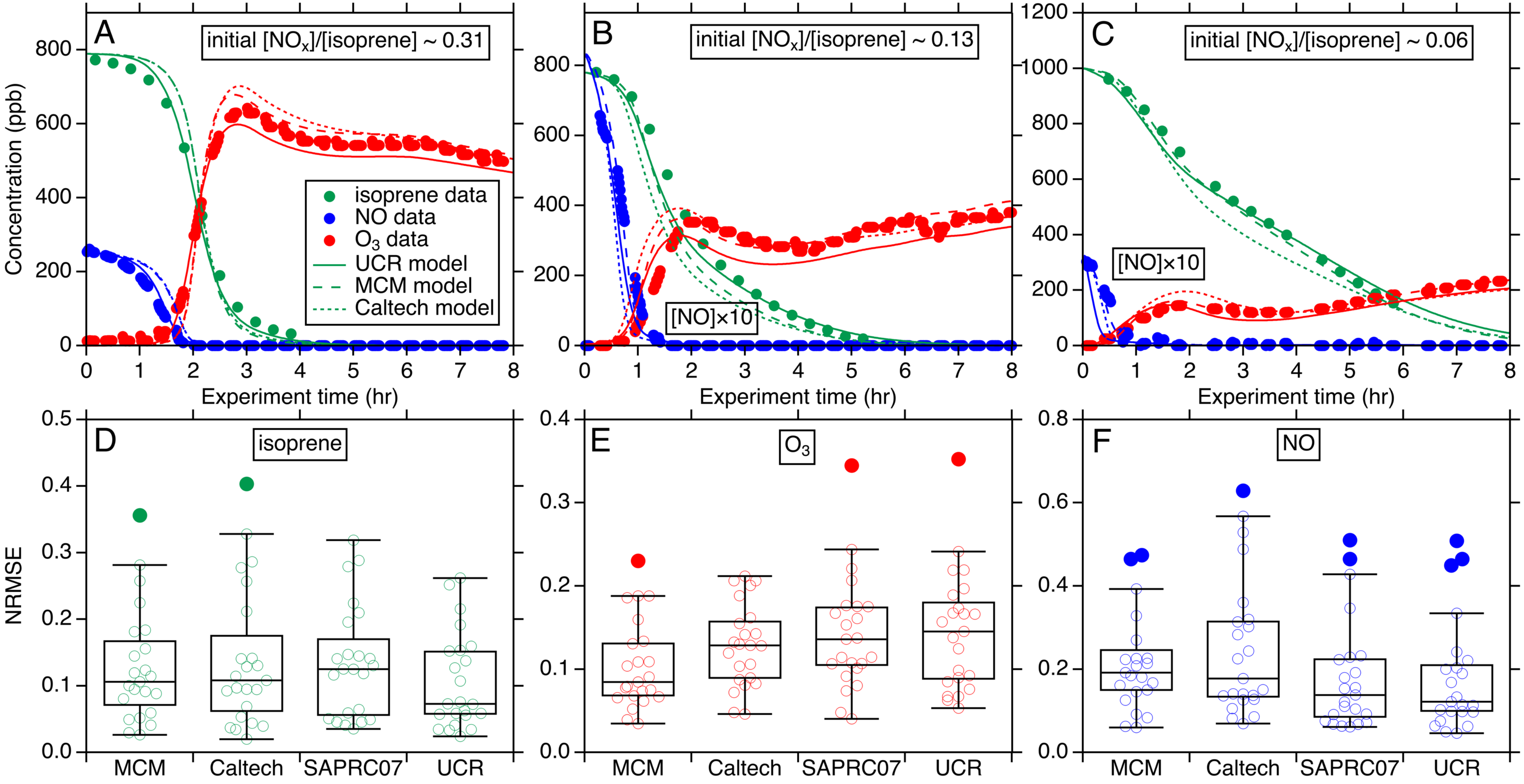

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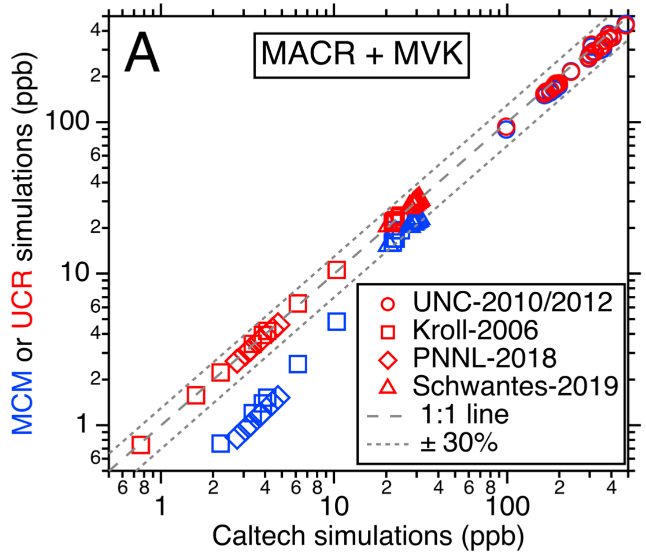

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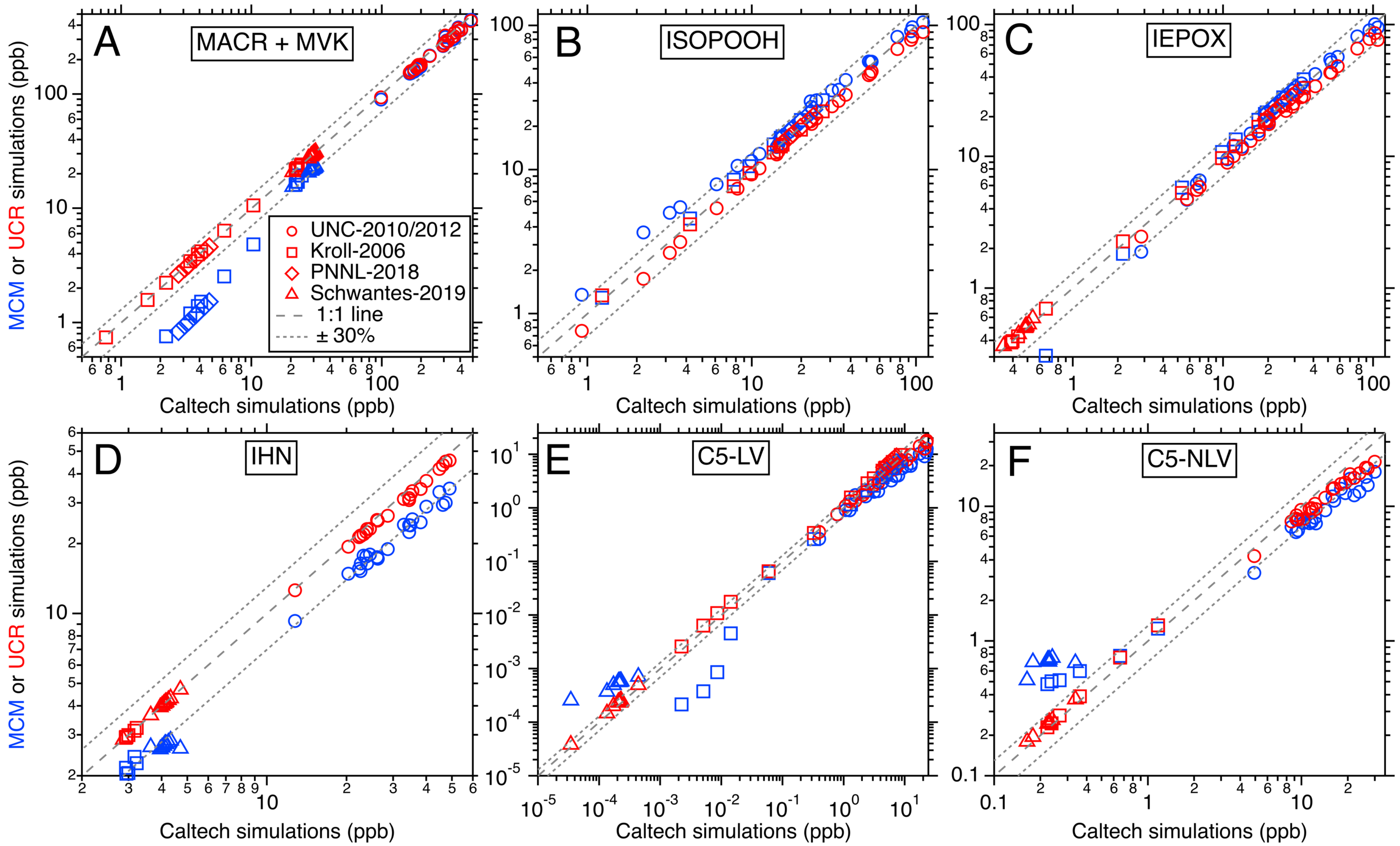

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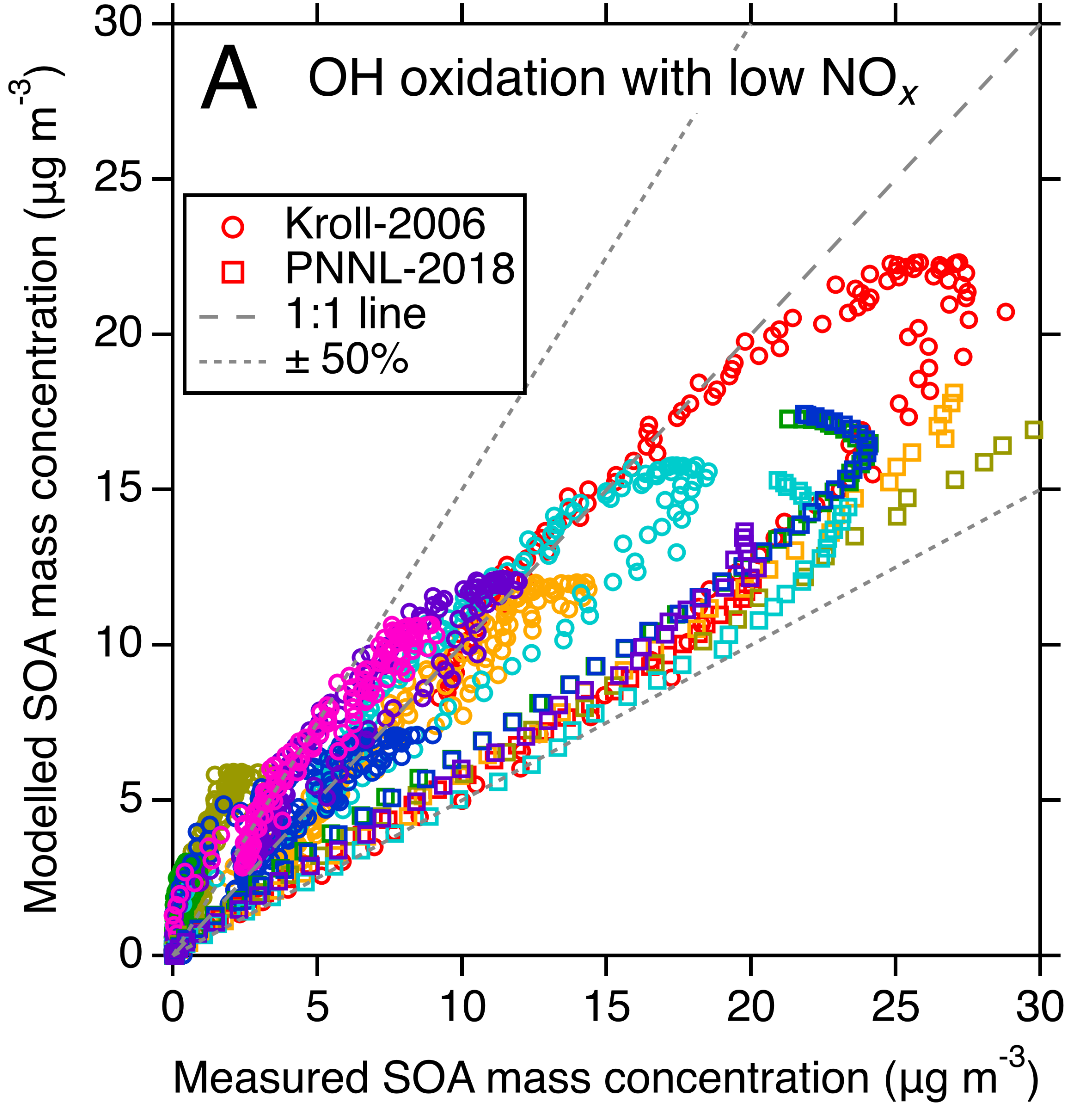
Evaluation with Chamber Experiments

SOA

Evaluation with Chamber Experiments

SOA



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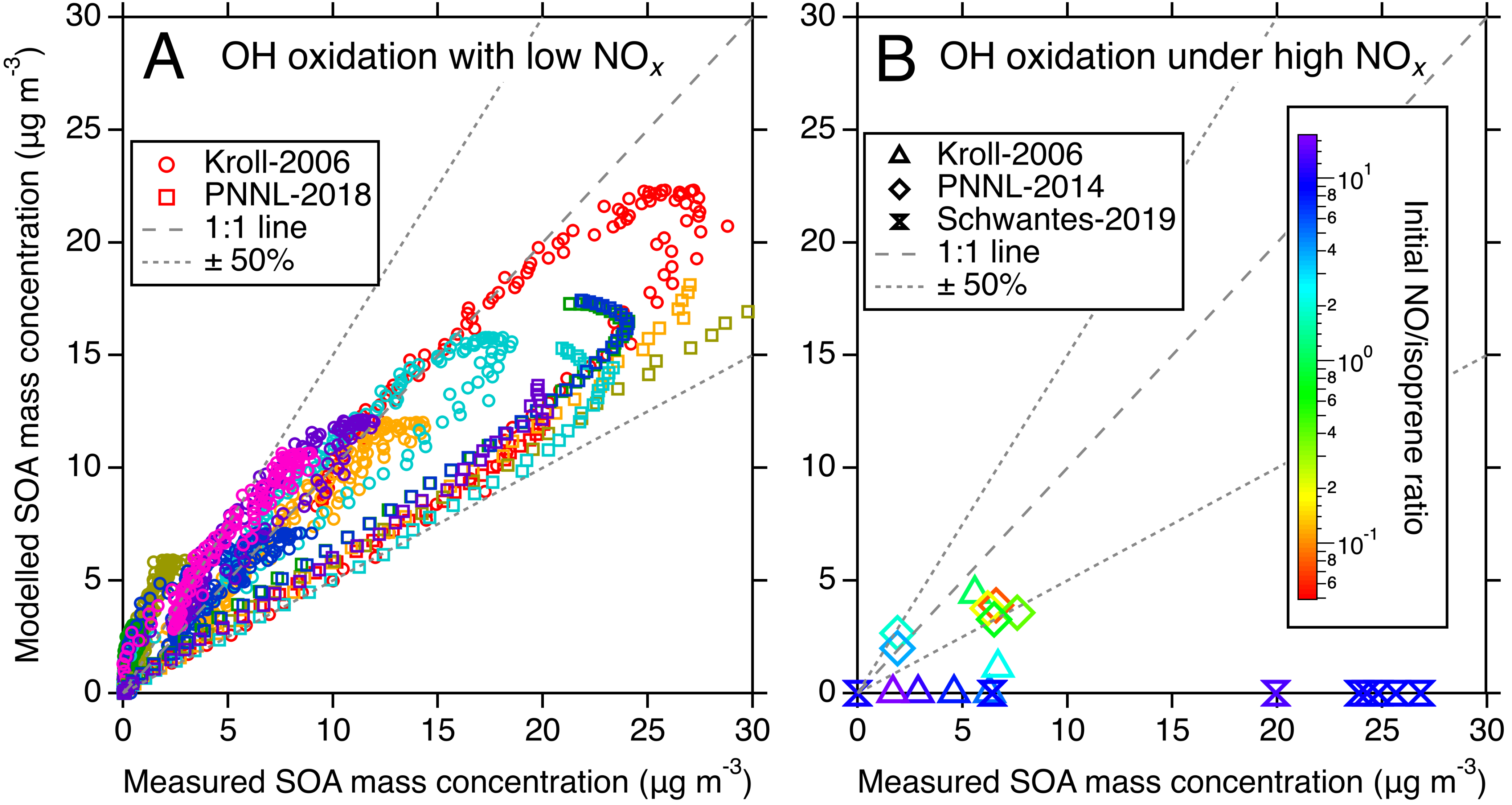

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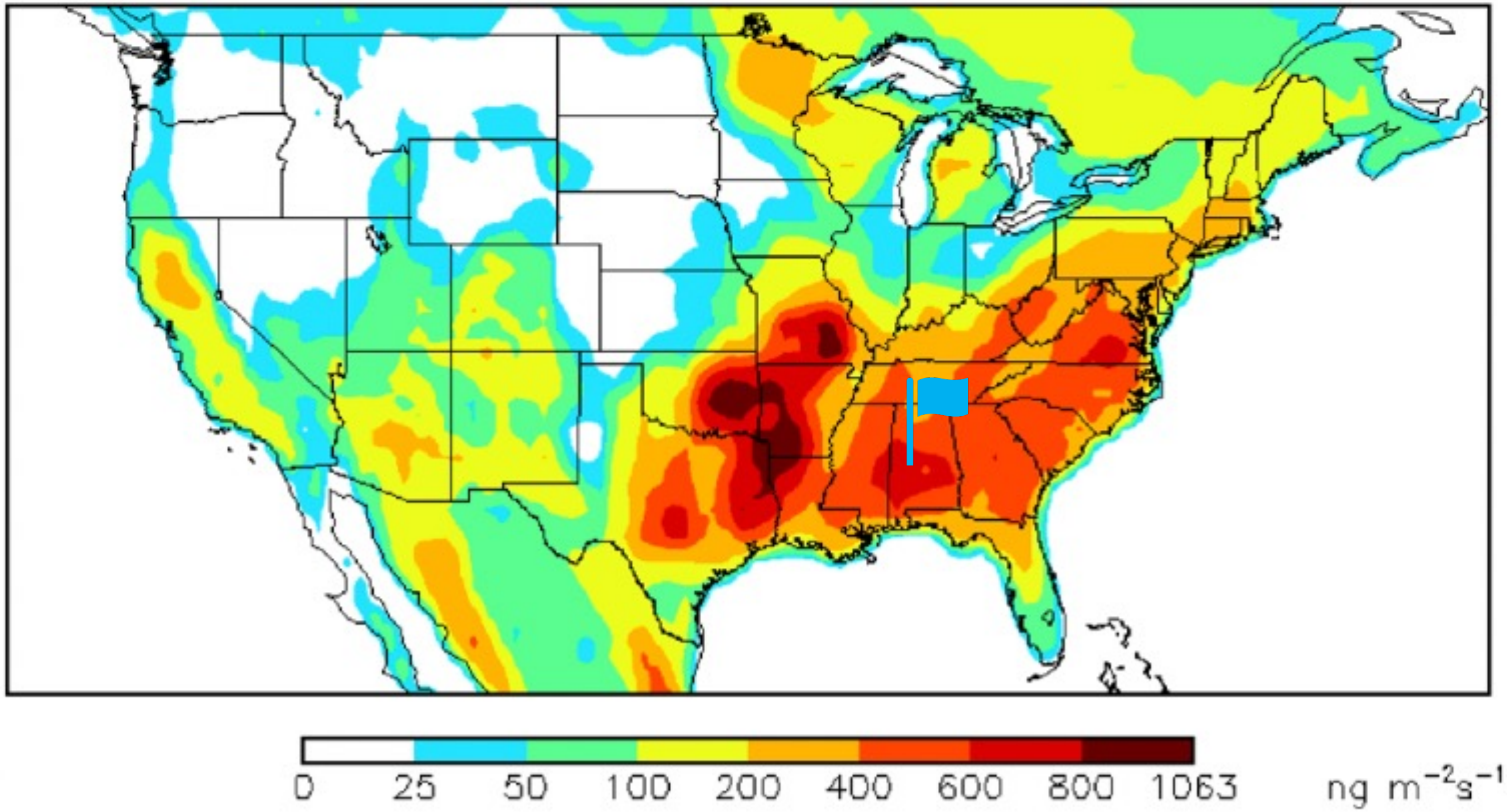
Evaluation with SOAS Field Measurements

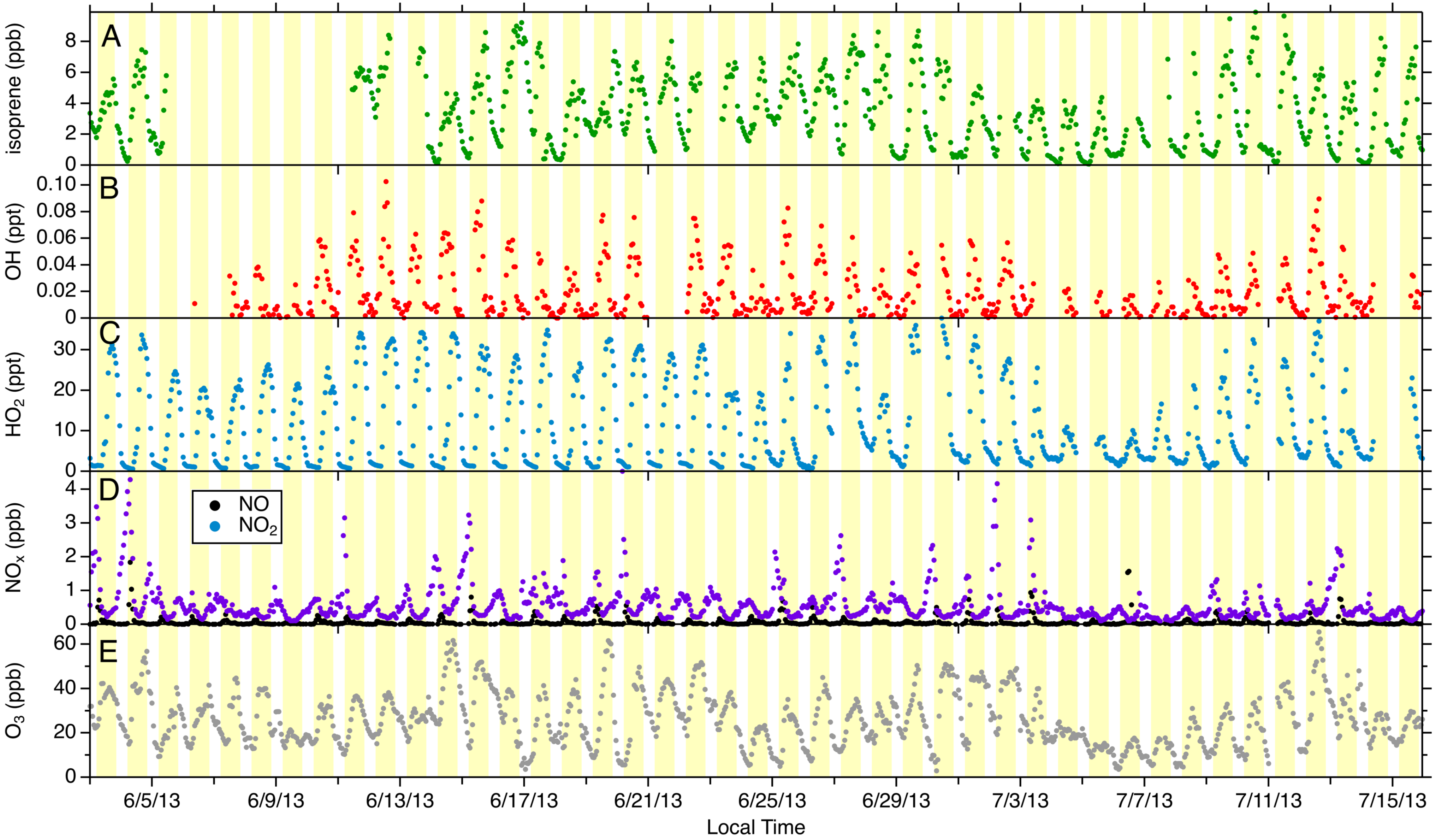
SOAS
Southern Oxidant & Aerosol Study



Isoprene emission

Evaluation with SOAS Field Measurements

Measurement constraints



Shen et al., *in prep.*

Evaluation with SOAS Field Measurements

Other considerations

- Dry and wet depositions (*Nguyen et al., Proc. Natl. Acad. Sci., 2015, 112, E392; Bi and Isaacman-Vanwertz, Environ. Sci.: Atmos. 2022, 2, 1526*);

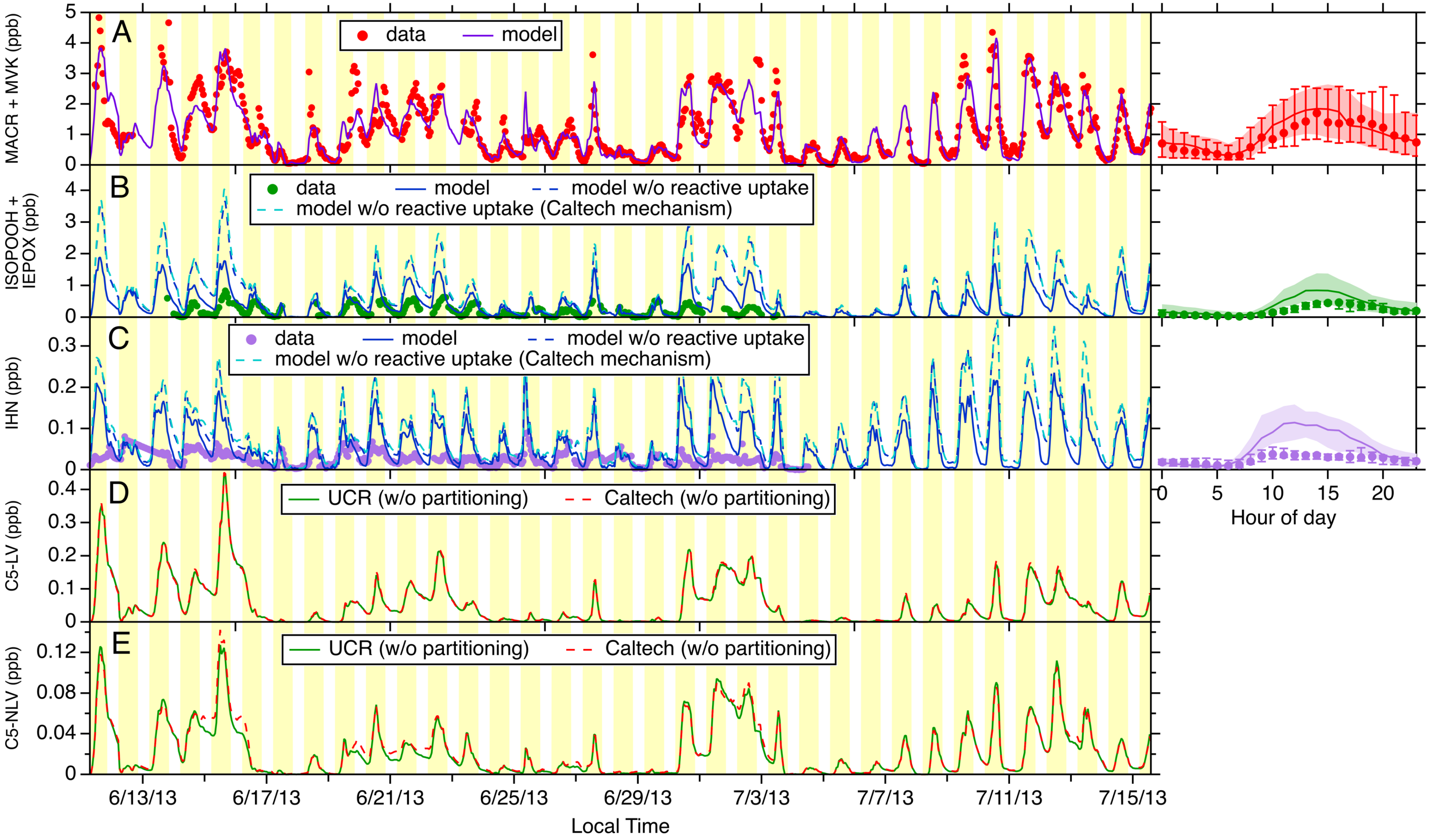
- Dilution (*Kaiser et al., Atmos. Chem. Phys. 2016, 16, 9349*);

- Aqueous-phase uptake (*Isaacman-Vanwertz et al., Environ. Sci. Technol., 2016, 50, 9952; Vasquez et al., Proc. Natl. Acad. Sci., 2020, 117, 33011*);

- Aerosol phase state (*Shiraiwa et al., Nature Comm., 2017, 8, 15002; Schmedding et al., Atmos. Chem. Phys., 2020, 20, 8201*);

Evaluation with SOAS Field Measurements

Gas-phase comparisons



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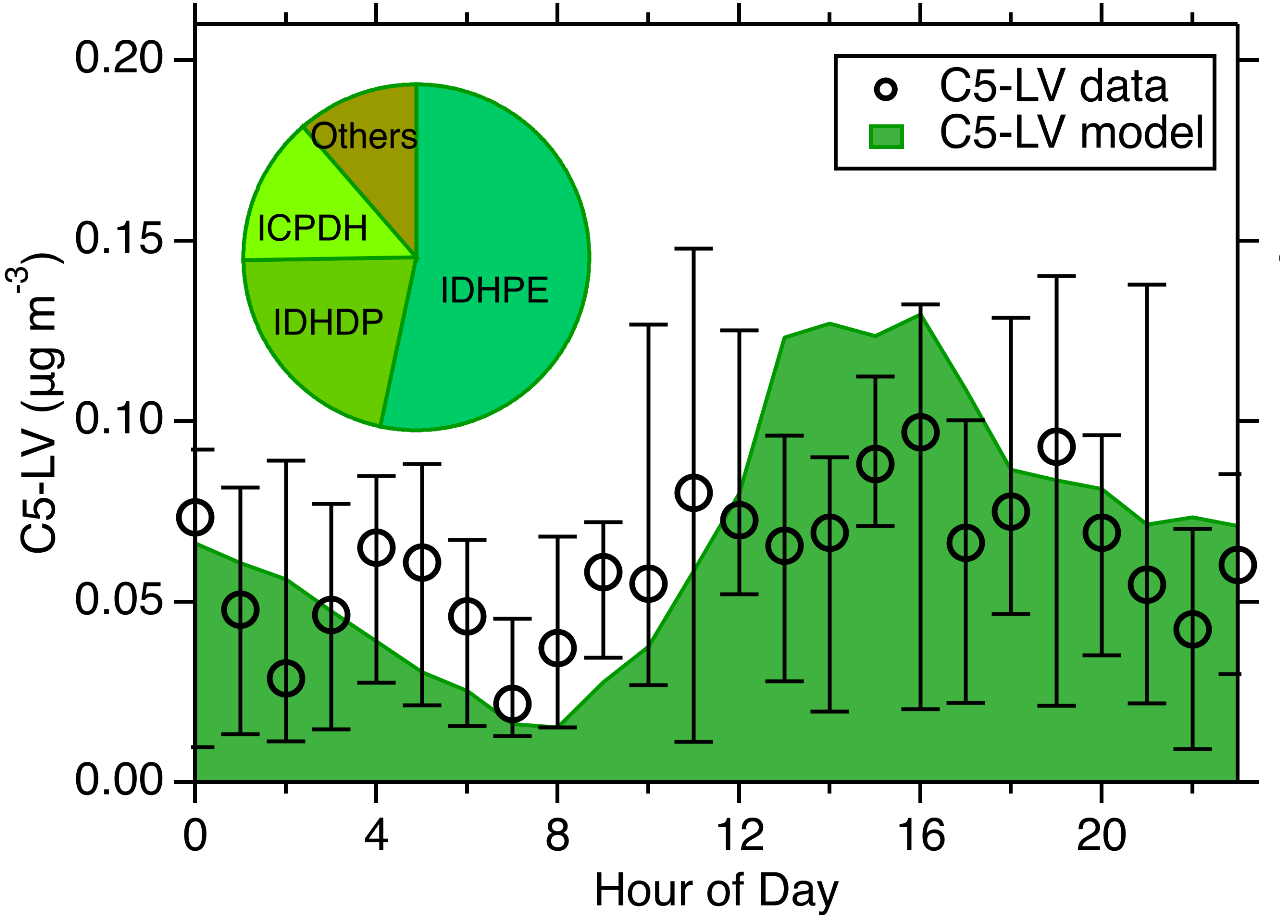
Evaluation with SOAS Field Measurements

SOA comparisons



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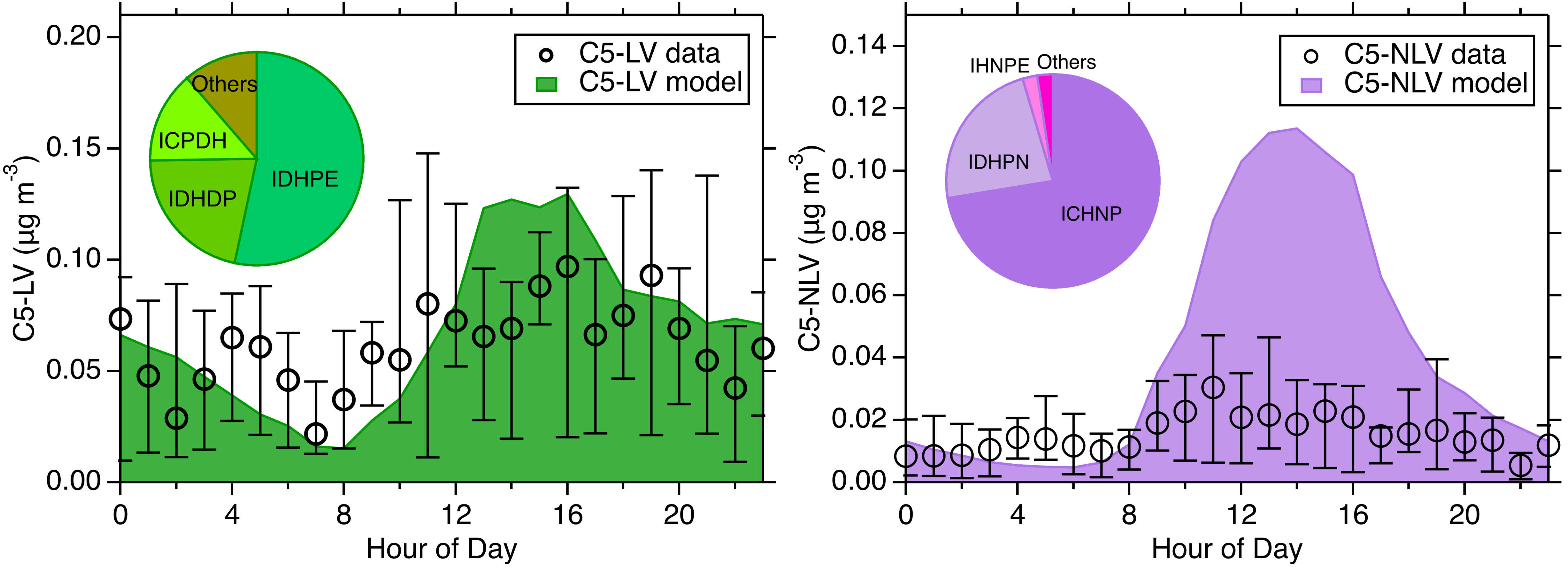

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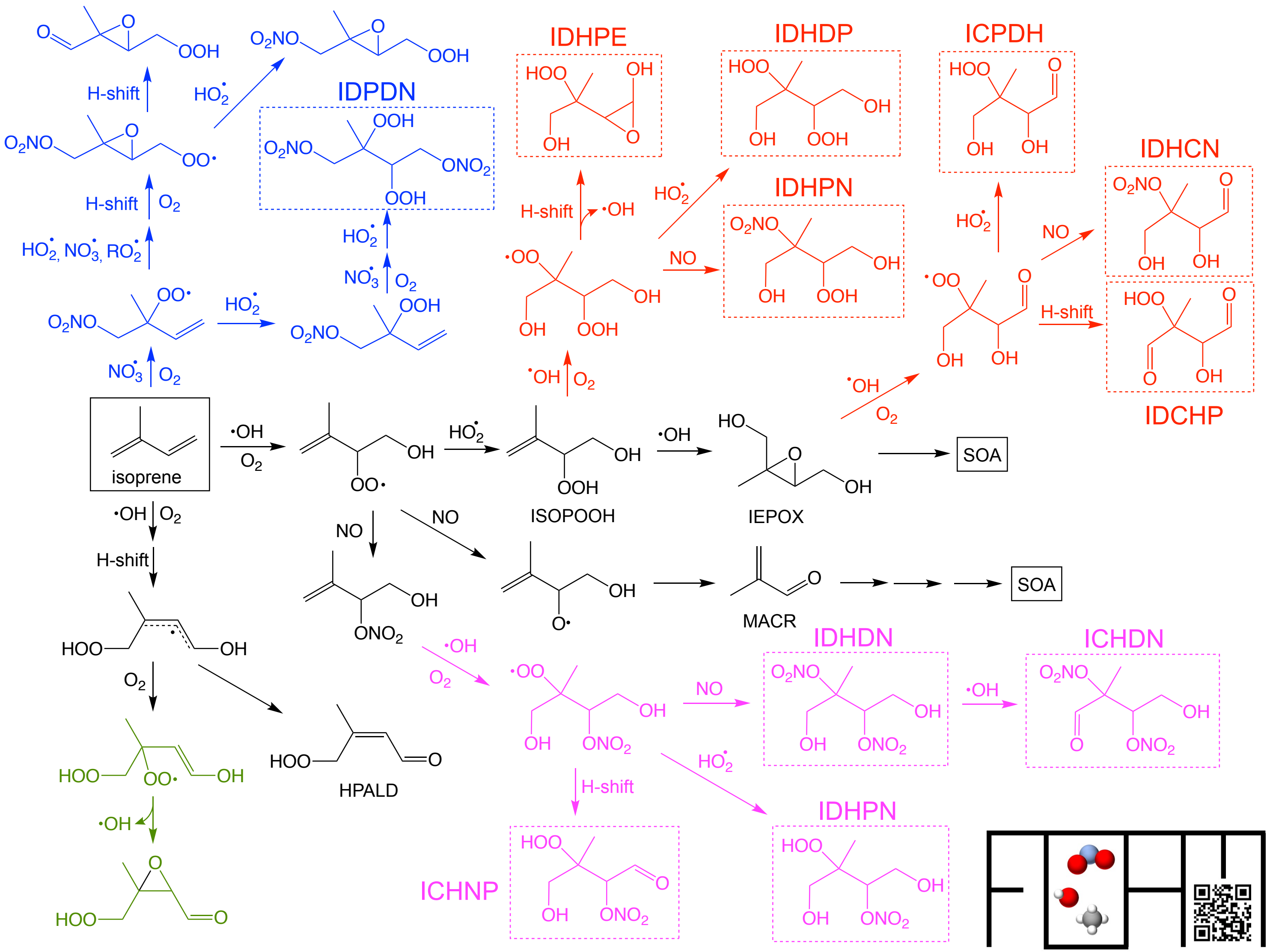

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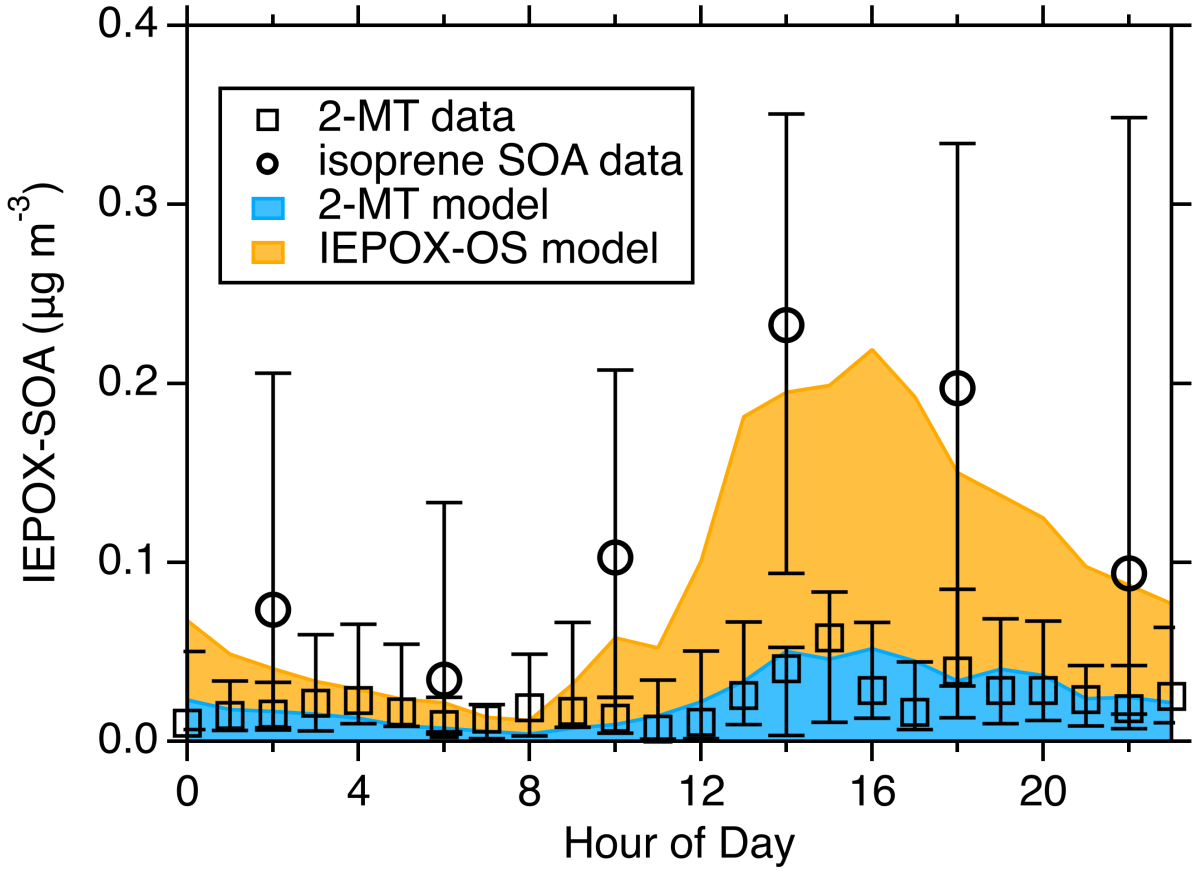

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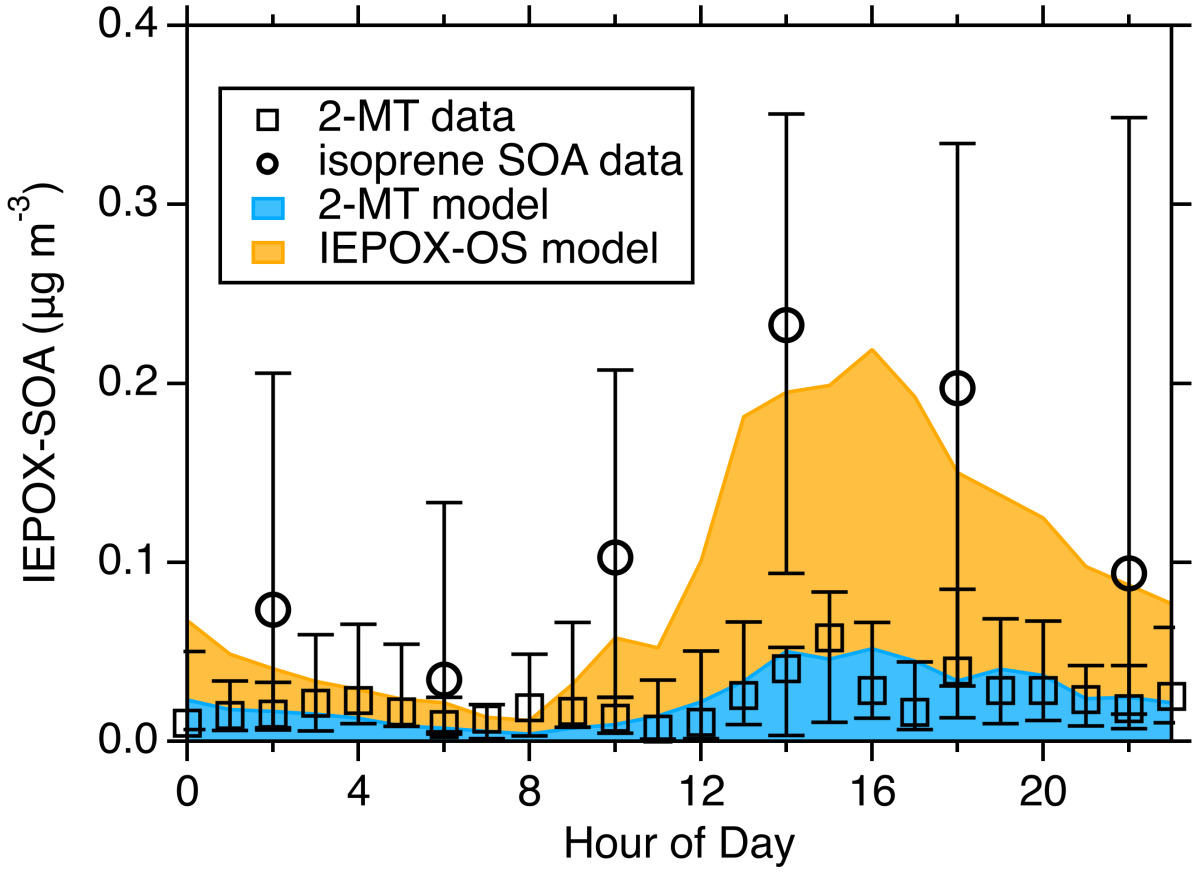
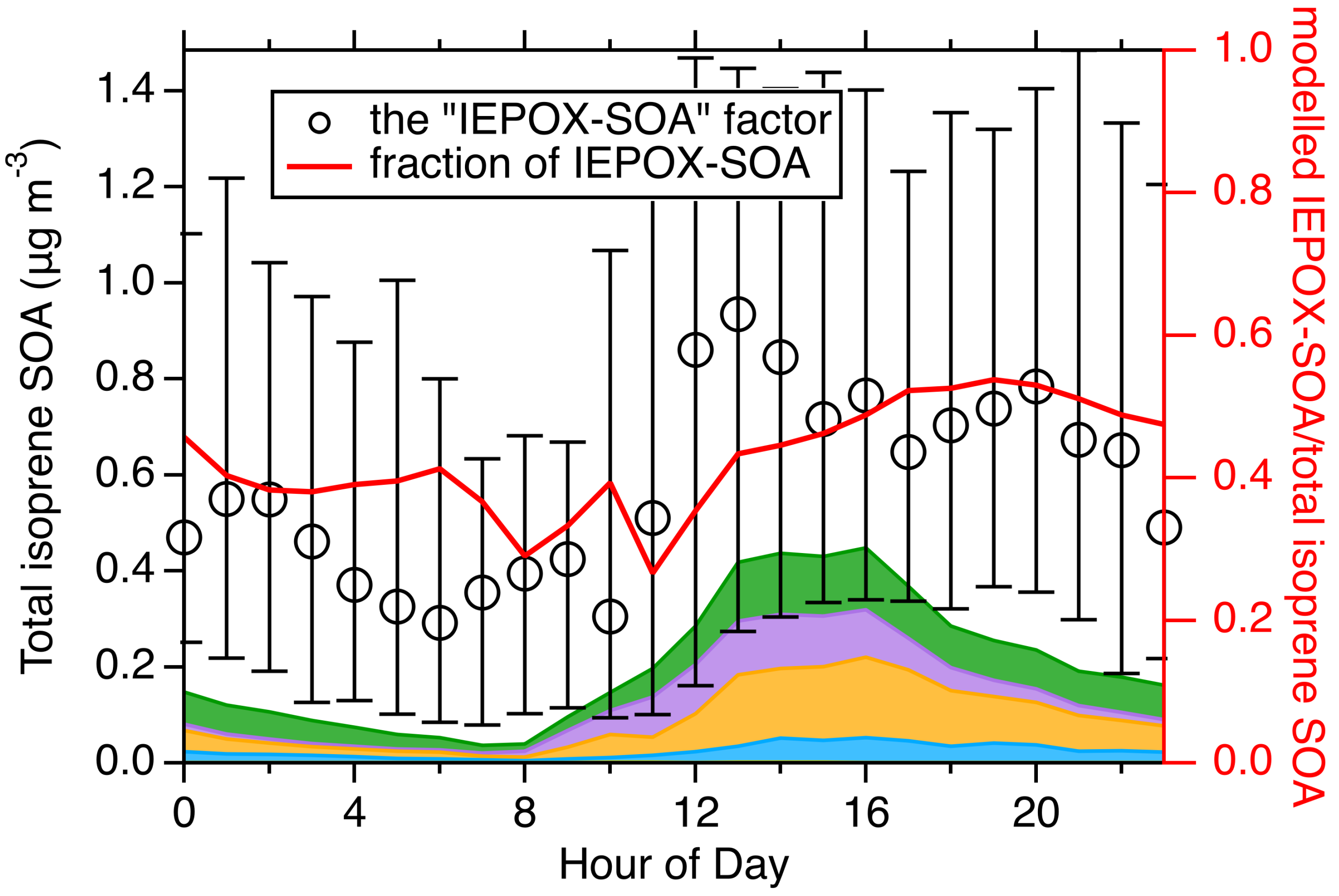


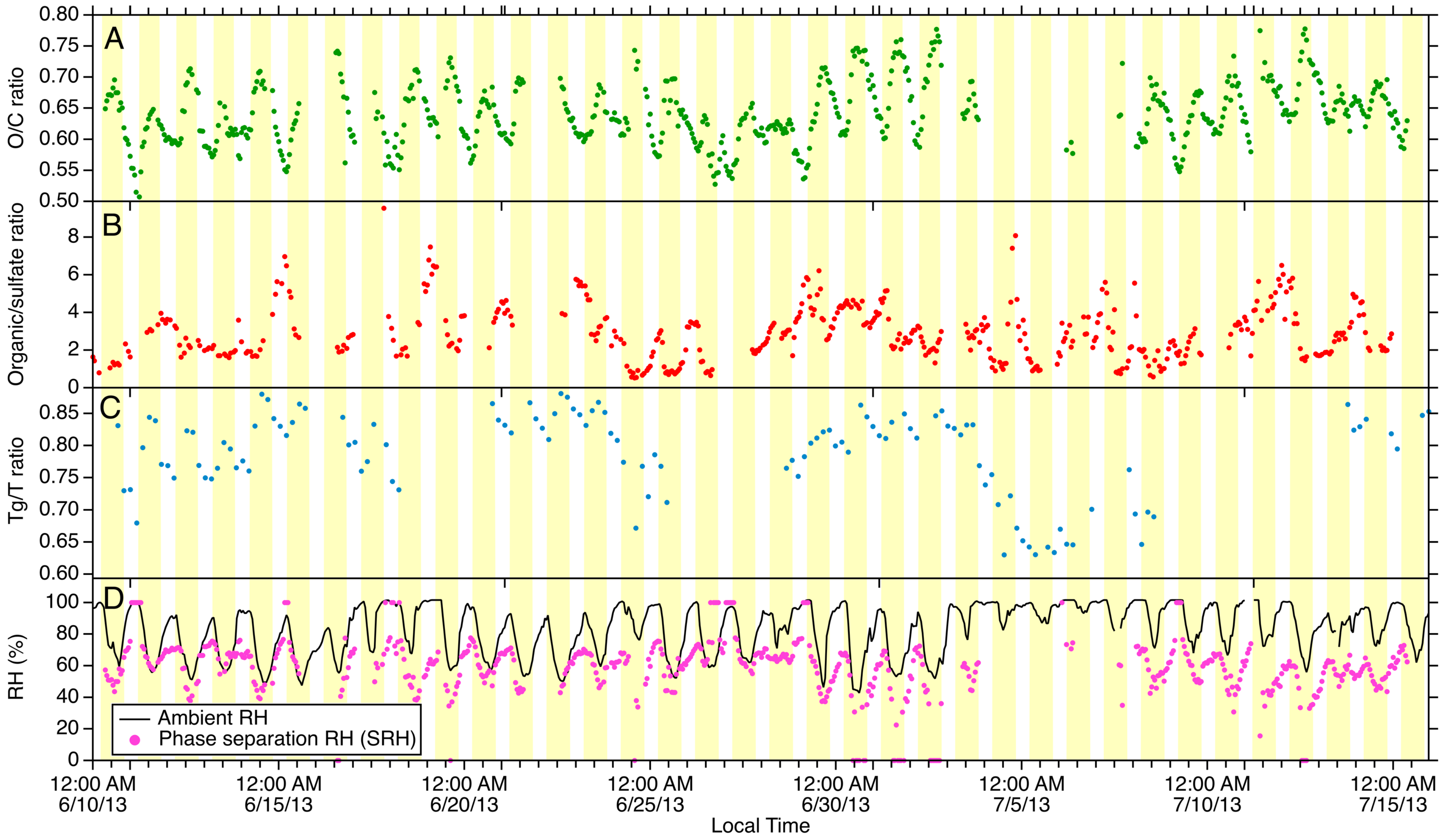


Summary

- A new condensed isoprene mechanism. Consistency with chamber experiments. Can be applied in large-scale regional models.
- The low-volatility pathway constitute a large fraction (~57%) in the field isoprene-SOA formation.
- Future study on specific conditions (e.g. the high-NOx condition) should be done fully understand the isoprene oxidation and SOA formation.

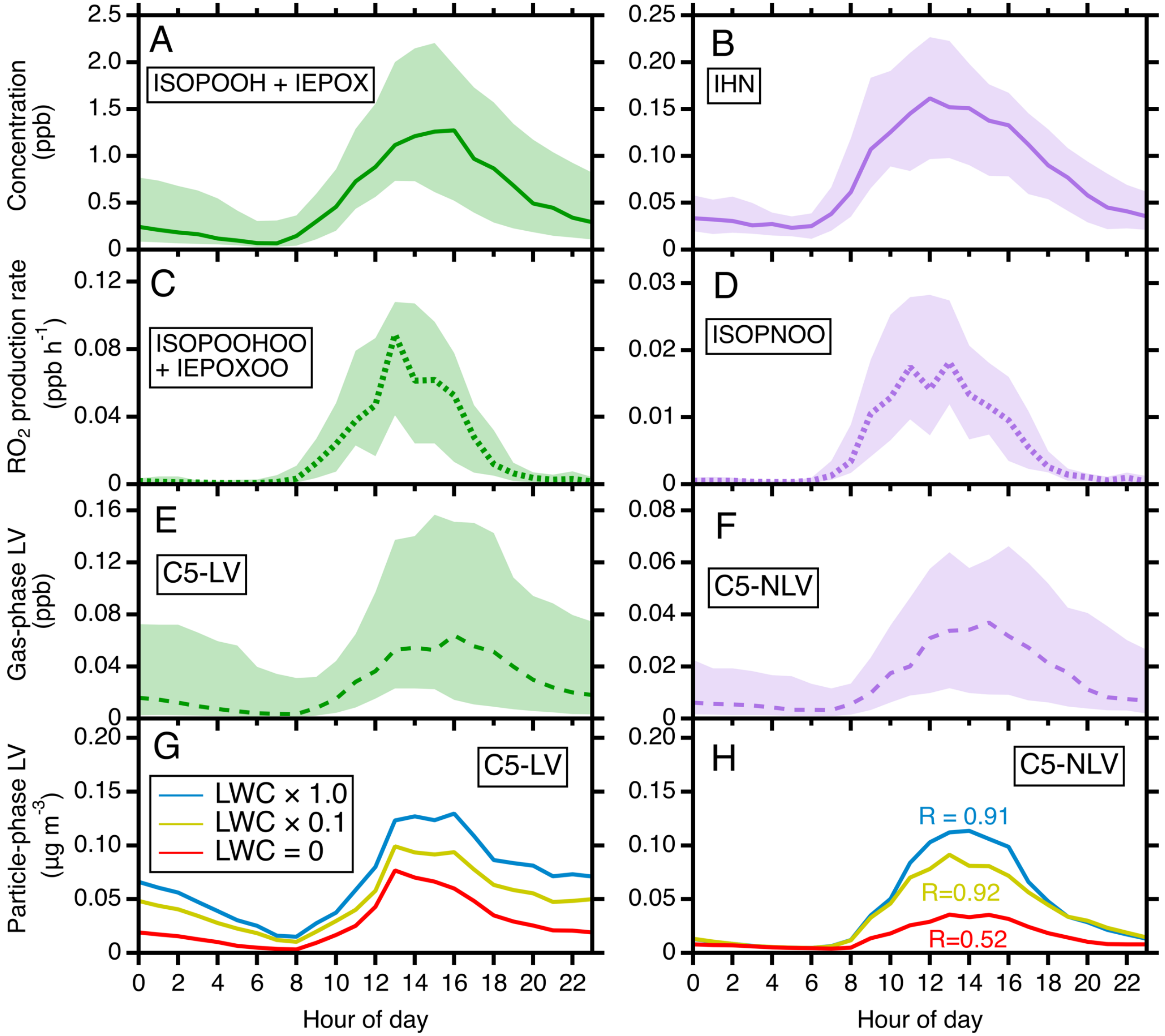
UCR

SRH vs. RH



A
B
C
D
O/C ratio
Organic/sulfate ratio
Tg/T ratio
RH (%)
0.80
0.75
0.70
0.65
0.60
0.55
0.50
8
6
4
2
0
0.85
0.80
0.75
0.70
0.65
0.60
100
80
60
40
20
0
Ambient RH
Phase separation RH (SRH)
12:00 AM 6/10/13
12:00 AM 6/15/13
12:00 AM 6/20/13
12:00 AM 6/25/13
12:00 AM 6/30/13
12:00 AM 7/5/13
12:00 AM 7/10/13
12:00 AM 7/15/13
Local Time

C5-LV vs. C5-NLV



LV vs. Reactive uptake