Modeling Oxidation Products and Aerosol Formation from cyclic Volatile Methyl Siloxanes (cVMS) Using the MUSICA Framework

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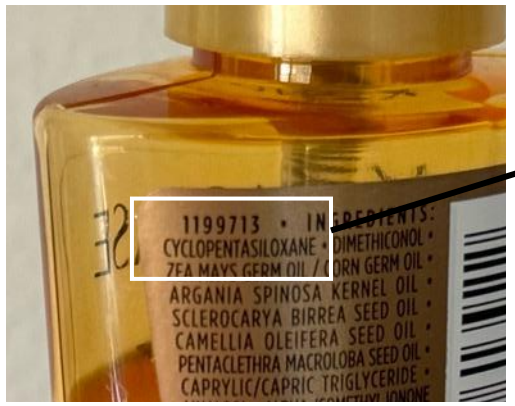
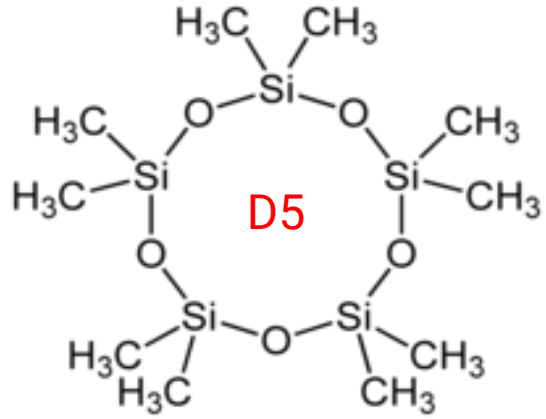
VMS are widely used human-made VCP



Cyclopentasiloxane

Personal care products



VMS

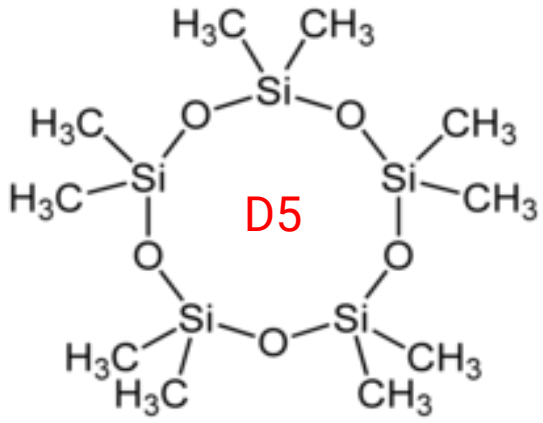
- Additive in personal care product
- Volatile (>90% in atmosphere)
- React with OH and Cl for a 4 to 10 days lifetime
- A global D5 ~ 0.153 Tg per year, distributed over major urban centers.
- Global anthropogenic Benzene ~ 5.6 Tg per year

IOWA

Brunet et al. (2024); Alton & Browne (2020) ; Gkatzelis et al., *Environ. Sci. Tech.*, 2021.
Mackay et al., *Environ. Toxic. Chem.*, 2015. Jiang et al., 2018

There are uncertainties on the role of personal care products in SOA concentration

Personal care products

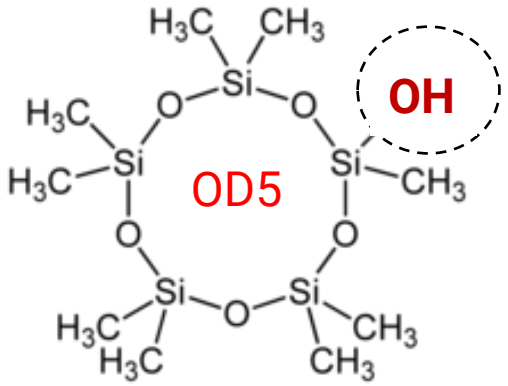


VMS

95% OH

5% Cl

k_{ox} = 2.1e-12 cm^3/molec/s



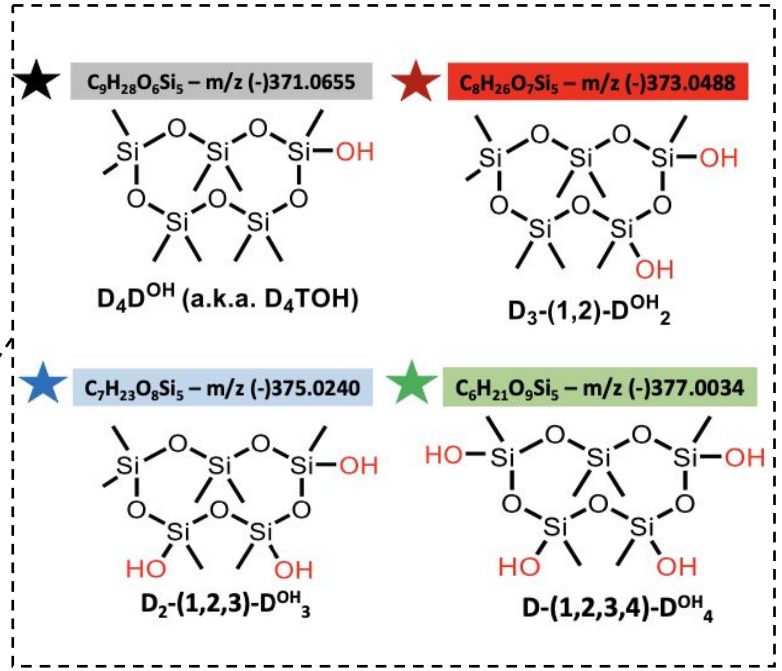
Main oxidation product
D5OH: siloxanol: **D4TOH**
+ other minor products

?

SOA

Aerosol Formation Evidence of VMS

Studies	Year	Experimental Condition
Latimar et al.,	1998	Chamber
Chandramouli and Kamens,	2001	Chamber
Bzdek et al.,	2014	Field
Wu and Johnston,	2016, 2017	Chamber
Janechek et al.,	2019	OFR
Milani et al.,	2021	Field
Han et al., Charan et al.,	2022	OFR Flow tube-Chamber
Avery et al., Kang et al.,	2023	OFR OFR
Meepage et al.,	2024	OFR - Field



Research Goals:

1. **SOA characterization:**

Establishing yields and chemical composition of VMS derived aerosol in OFR experiments and comparison to real ambient aerosols.

2. **Atmospheric Modeling:**

Estimating the fate of cVMS from PCPs upon oxidation over the US and rest of the world.

Team Science Work
SOA characterization

Charles Stanier

Ben McMillan

Carlos Gutierrez

Nate Massa

Betsy Stone

Jeewani Meepage

13 L OFR, Stanier Lab, UIowa

Team Science Work
VMS gas/aerosol analysis

Stone Research Group

Keri Hornbuckle

Rachel Marek

Chris Brunet

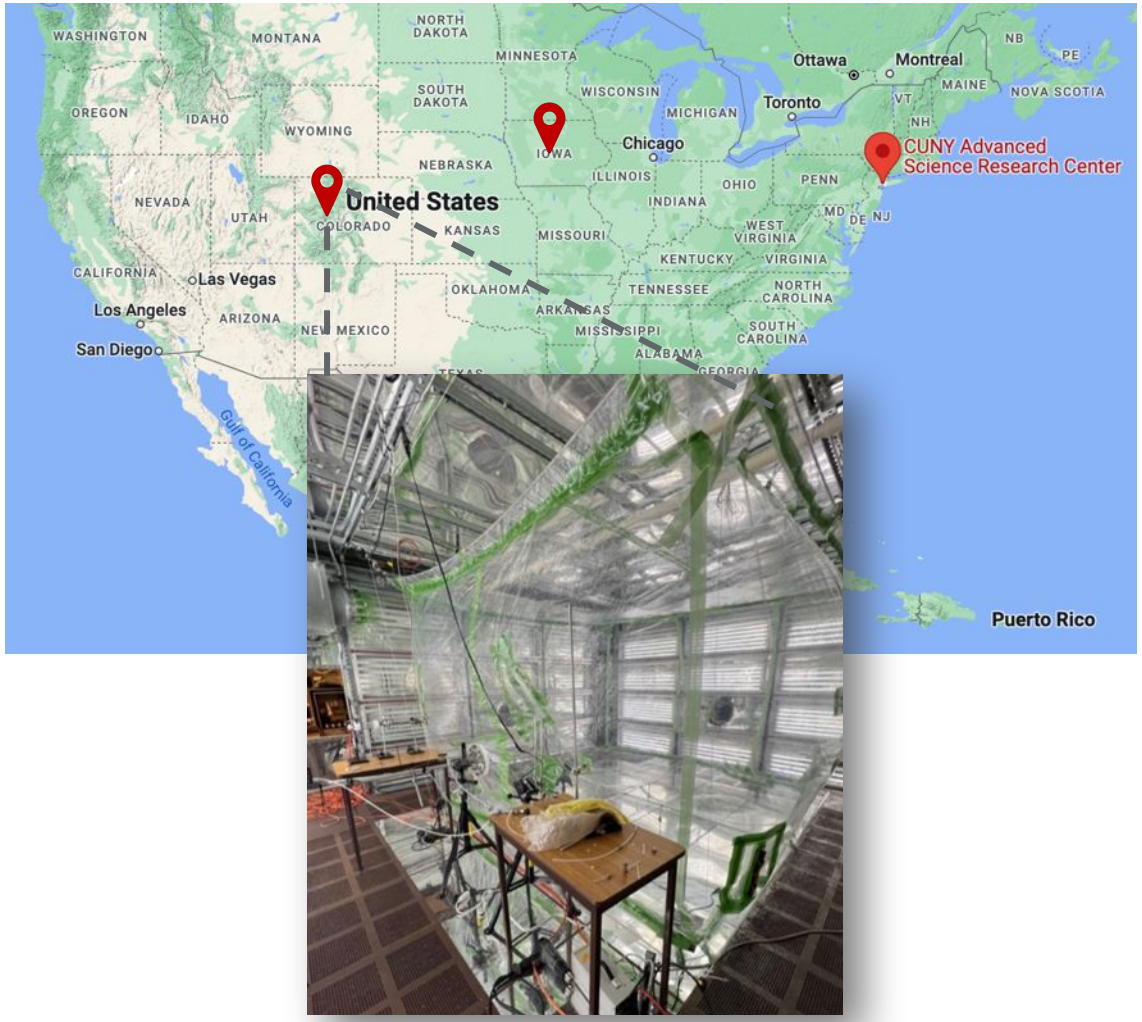
Advanced Science Research Center (ASRC) rooftop in the The City College of New York, Manhattan (July13 – Aug 4 , 2022)

Team Science Work
SOA characterization

Stanier/Stone Research Group

Eleanor. Browne

Hanalei Lewine



CU Environmental Chamber (CUEC)
Facility- 20 m3 FEP (Summer 2023)

Modeling cVMS and its SOA in MUSICA makes sense

- Continued interest in global distribution of parent and oxidation products due to **PBT** status.
- **Available gas and particle concentrations** to compare against in **NYC 2022**.
- Proposed as **tracer of PCP**; we need to know fate and distribution.

The Multi-Scale Infrastructure for Chemistry and Aerosols (MUSICA) V0 is a configuration of the Community Earth System Model (CESM)

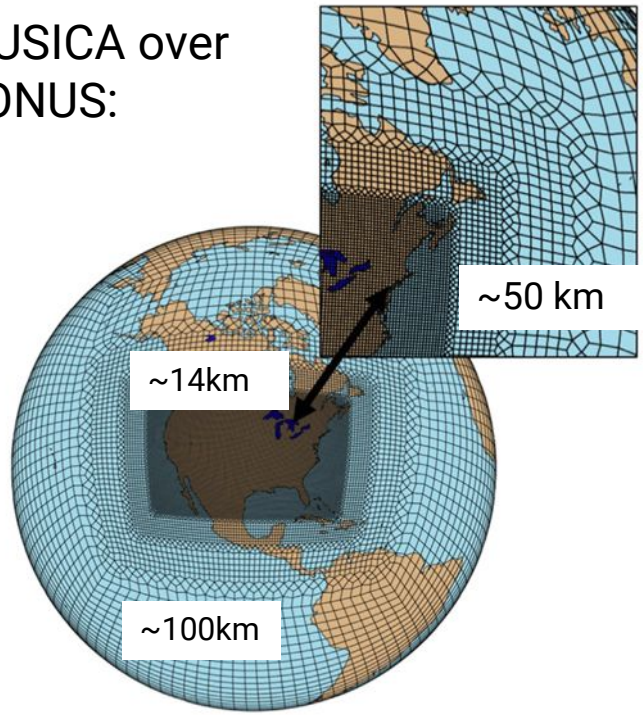
- CESM components:

CAM
(Community Atmosphere Model)

CAM-chem
(Community Atmosphere Model with Chemistry)

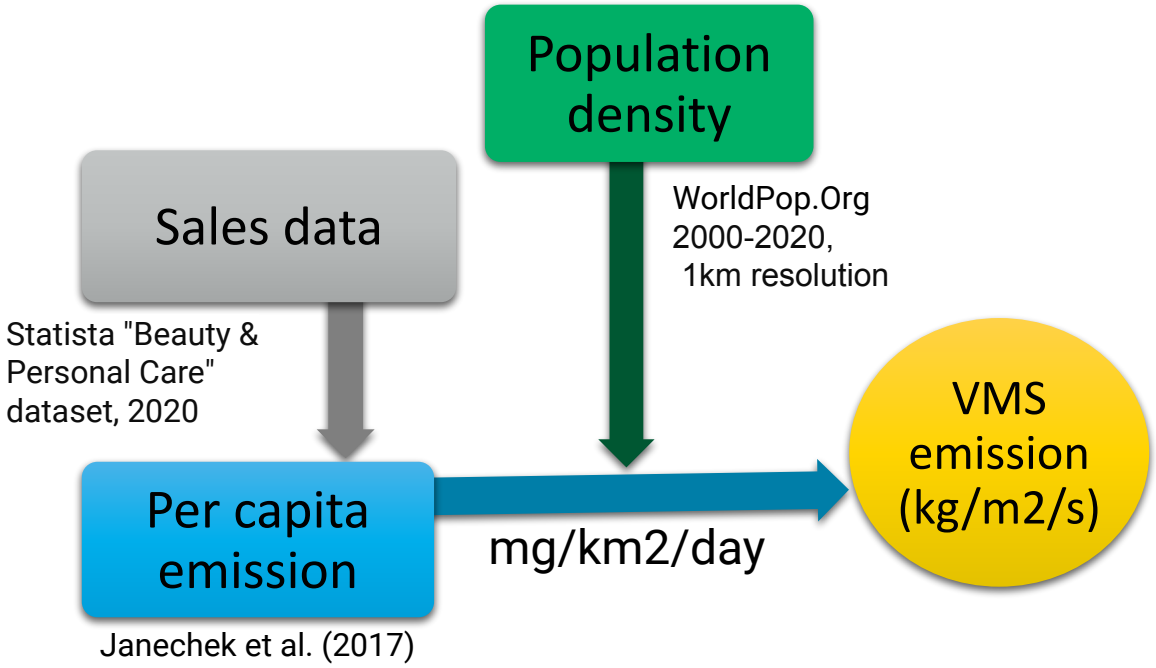
WACCM
(Whole Atmosphere Community Climate Model)

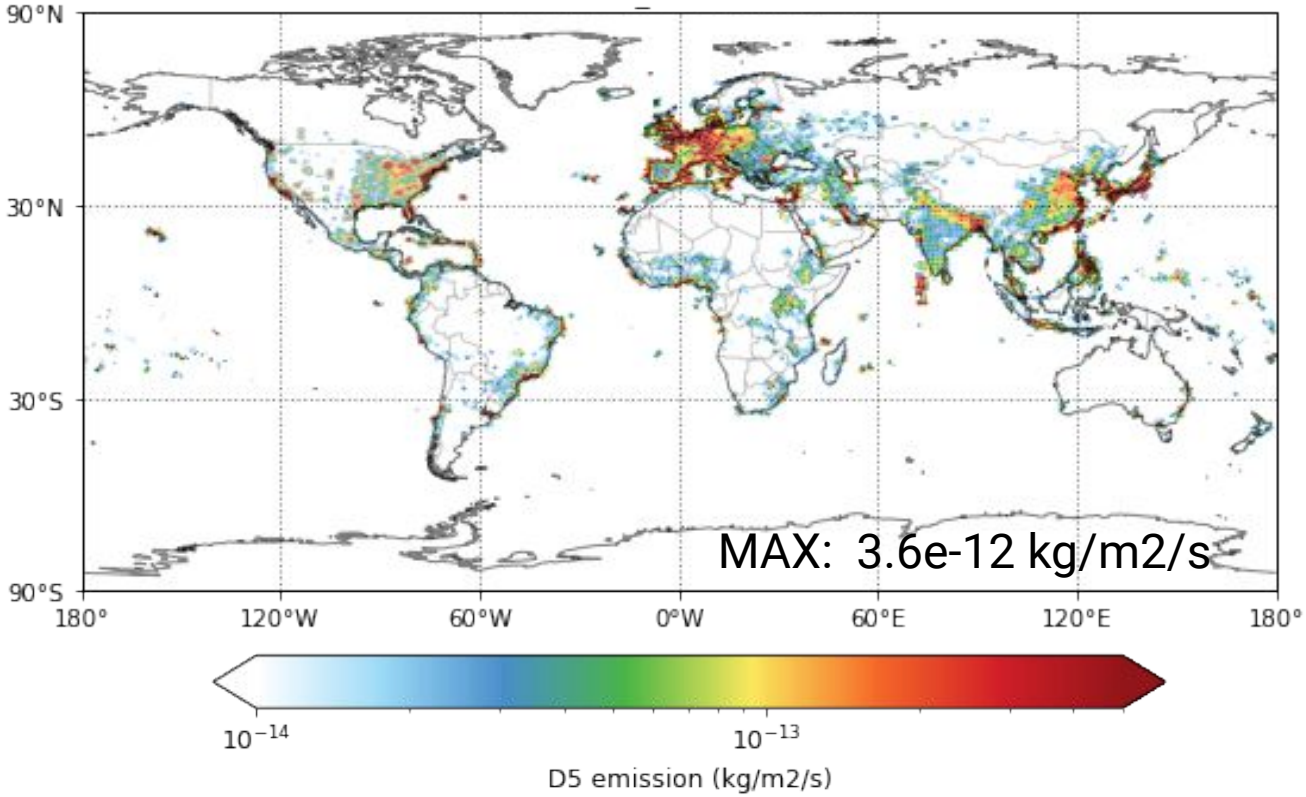
MUSICA over CONUS:



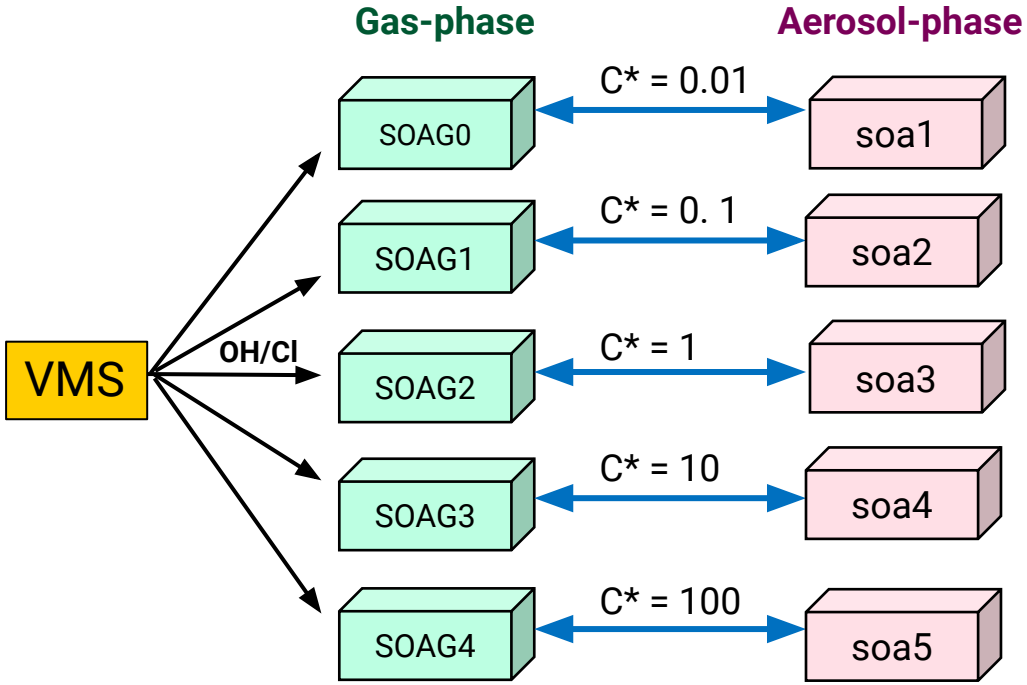
Spectral Element (SE - cubed sphere) dynamical core

Using VMS emission from Brunet et al. (2024)





SOA formation reactions in CAM-chem for different precursors sources is based on volatility basis set (VBS) and molar yields of SOAG formation

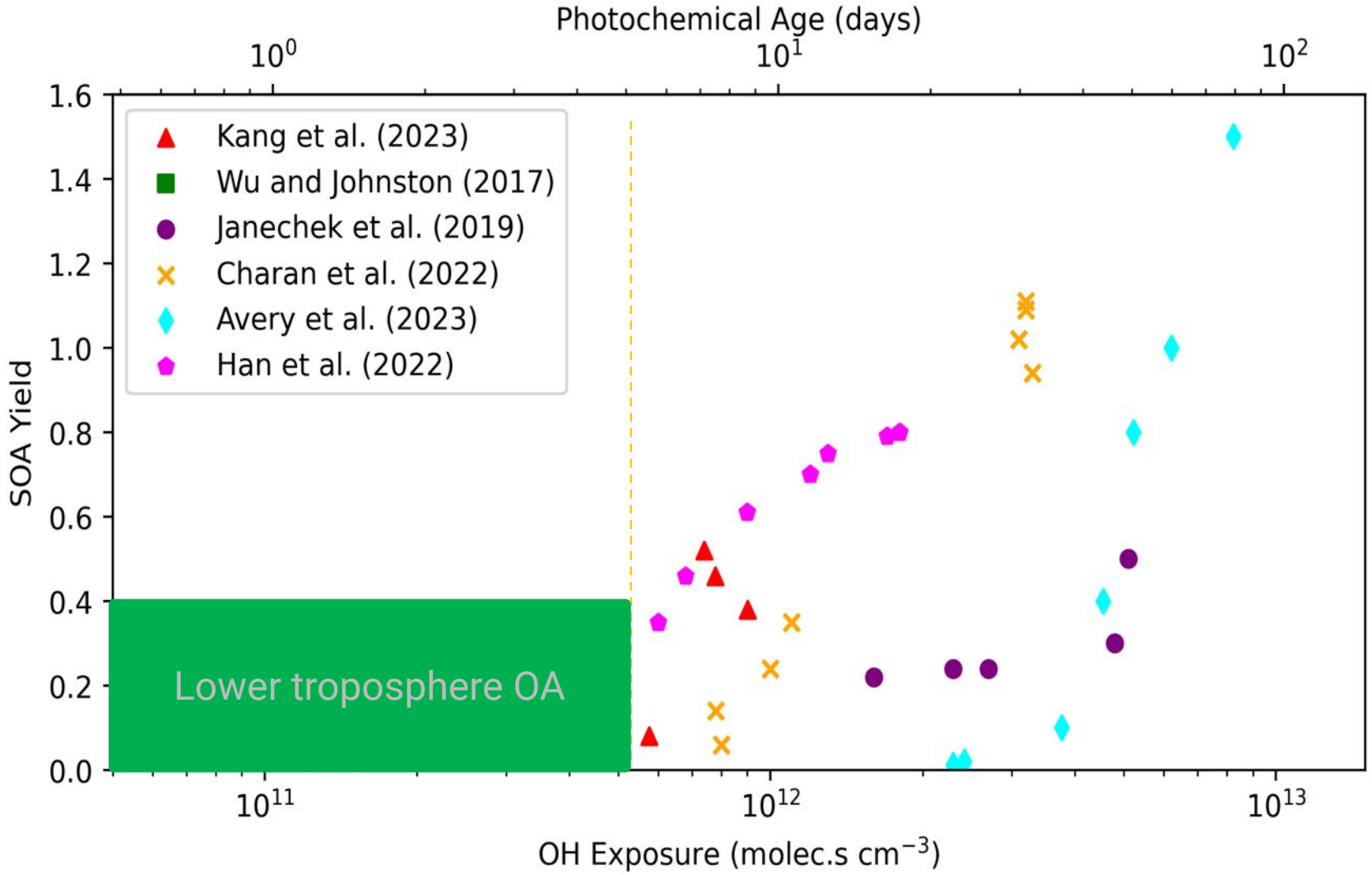


C*: Saturation vapor pressure (ug m^{-3})

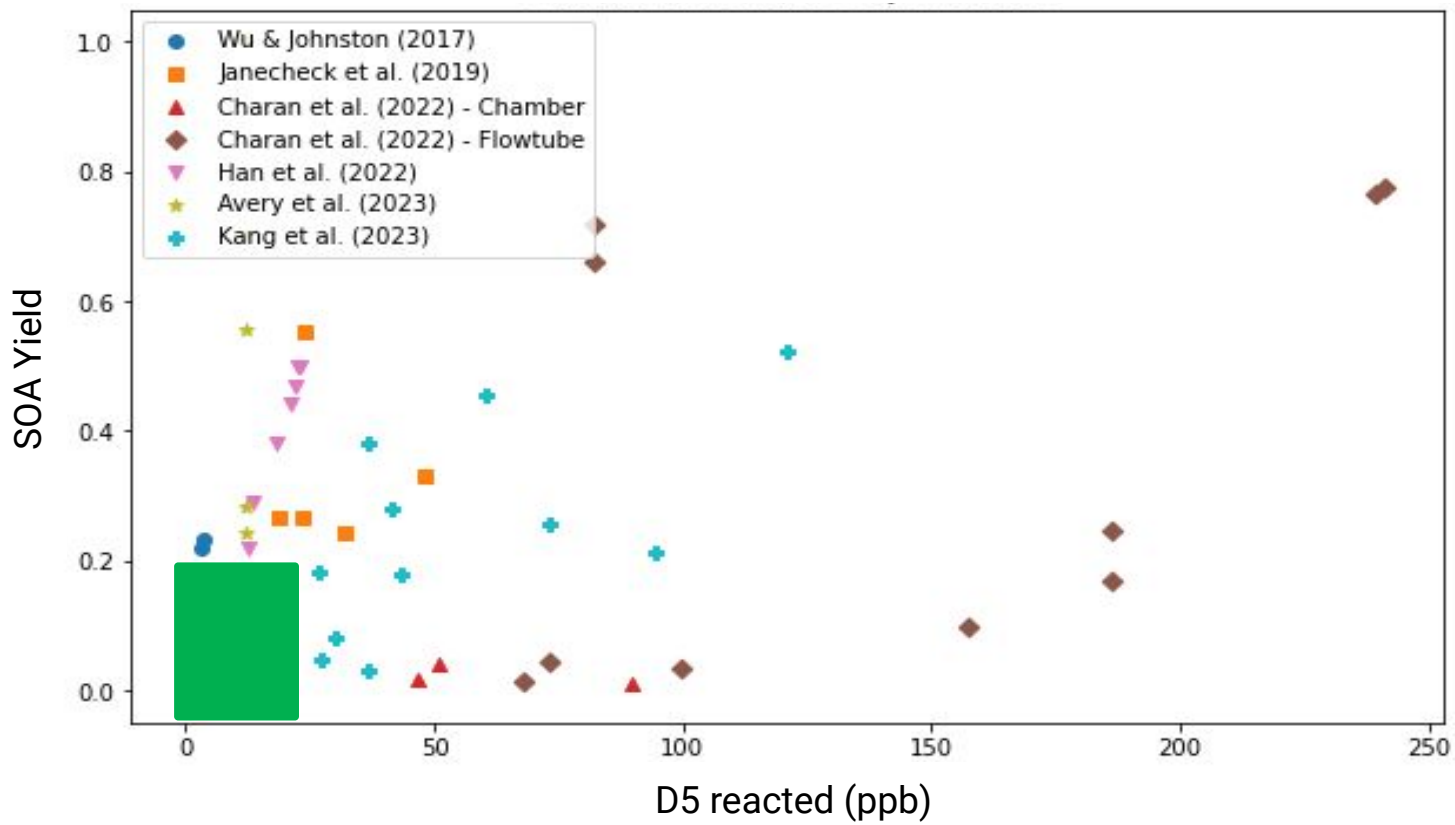
- T_{ref}=300 k
- SOAG molecular weight in CESM= 250 g/mol (based on $C_{15}H_{38}O_2$)

- D5 + OH = D5 + OH + α_0 SOAG0 + α_1 SOAG1 + α_2 SOAG2 + α_3 SOAG3 + α_4 SOAG4 k_{D5+OH}
- D4 + OH = D4 + OH + α_0 SOAG0 + α_1 SOAG1 + α_2 SOAG2 + α_3 SOAG3 + α_4 SOAG4 k_{D4+OH}
- D6 + OH = D4 + OH + α_0 SOAG0 + α_1 SOAG1 + α_2 SOAG2 + α_3 SOAG3 + α_4 SOAG4 k_{D6+OH}

D5 derived SOA yield vs OH_{exp} and equivalent photochemical age in the atmosphere

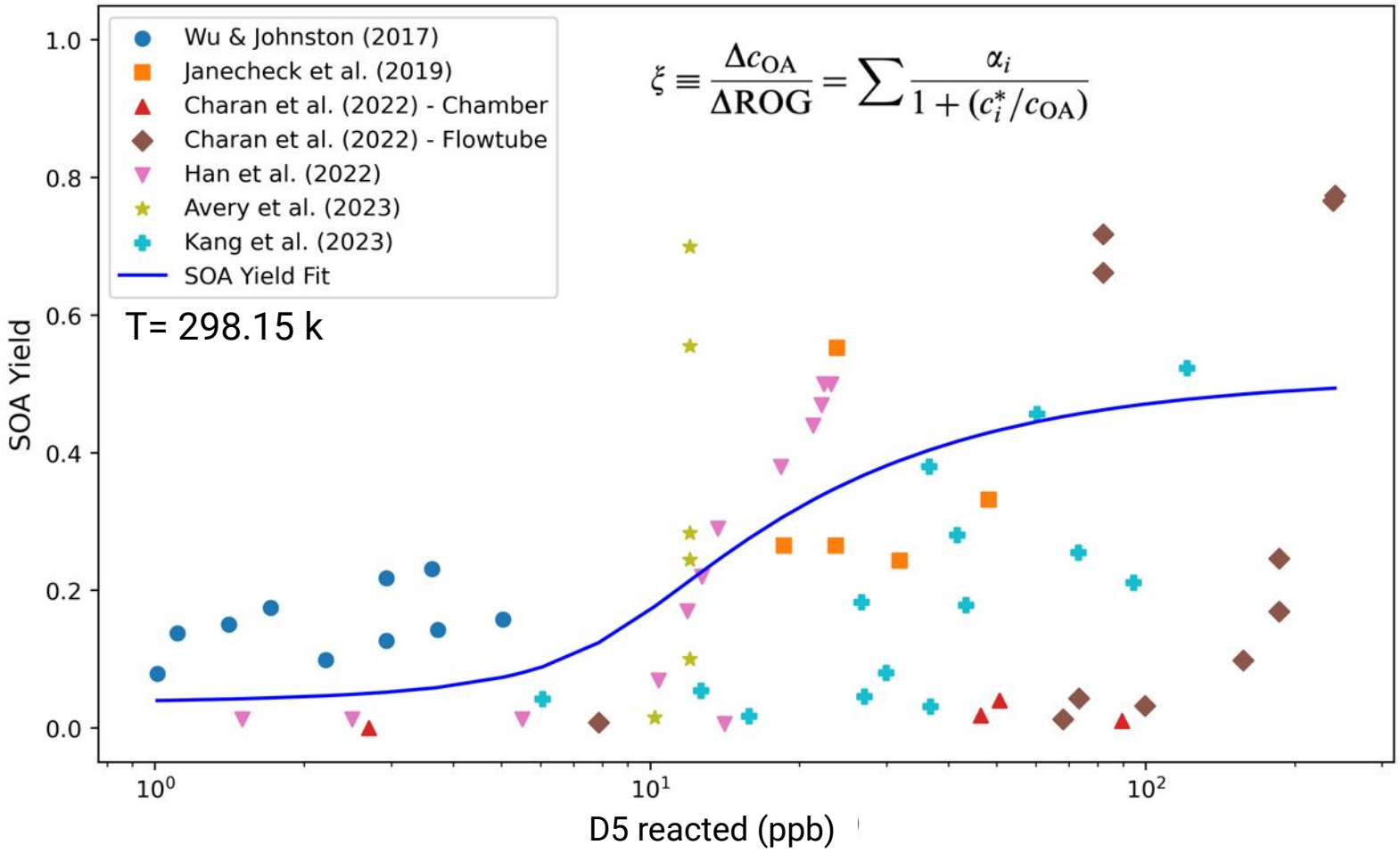


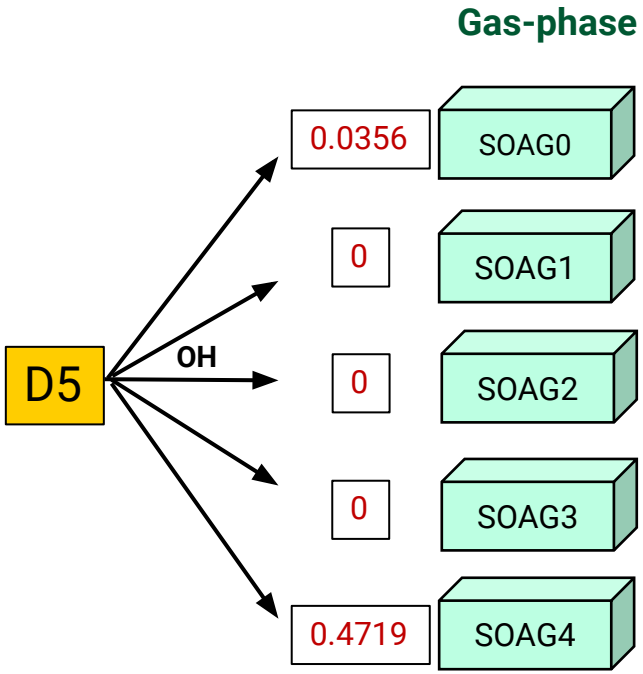
Fitting VBS molar yield (α) from experiments



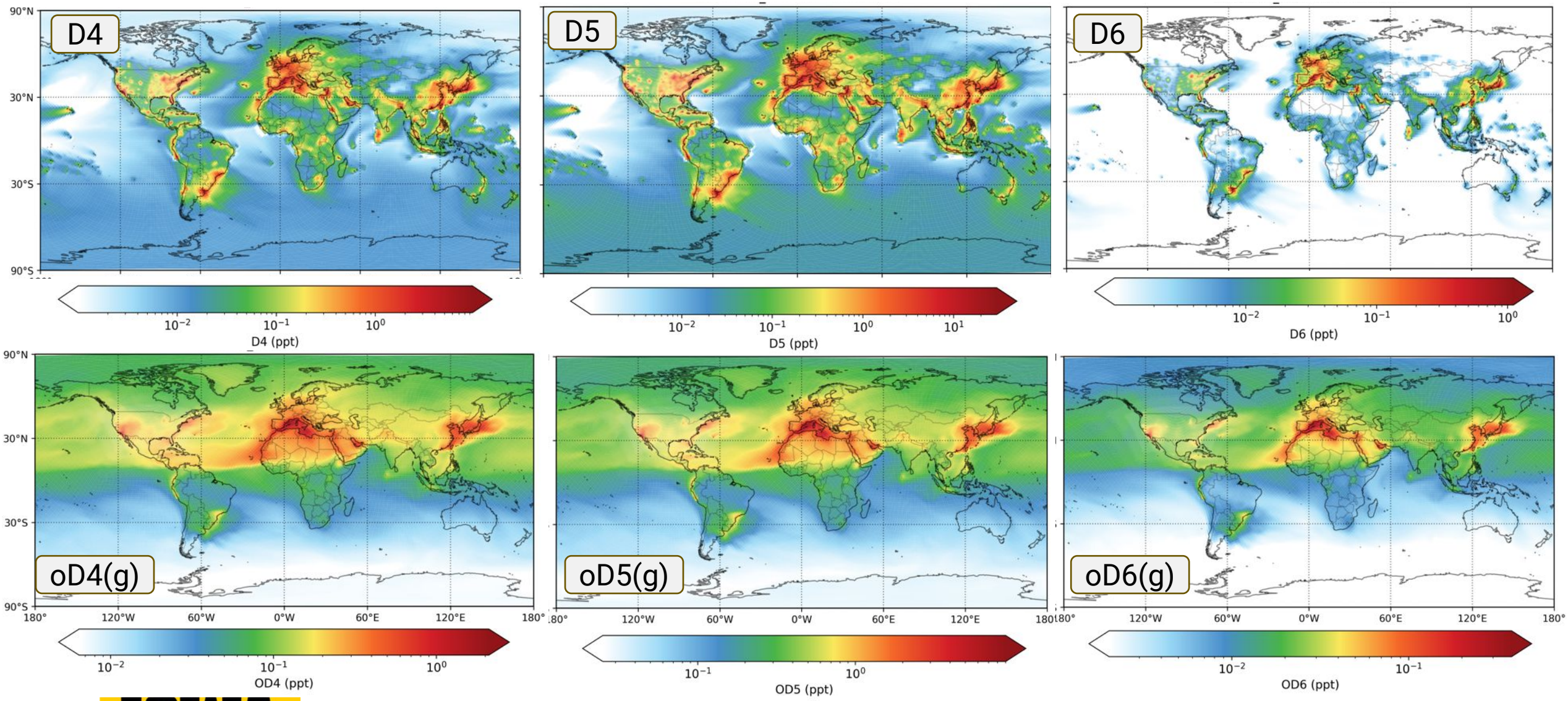
After estimating α, each of these experiments can be simulated to give aerosol mass concentration (C_{OA}) and yield

Best molar yield (α) chosen via nonnegative linear least squares

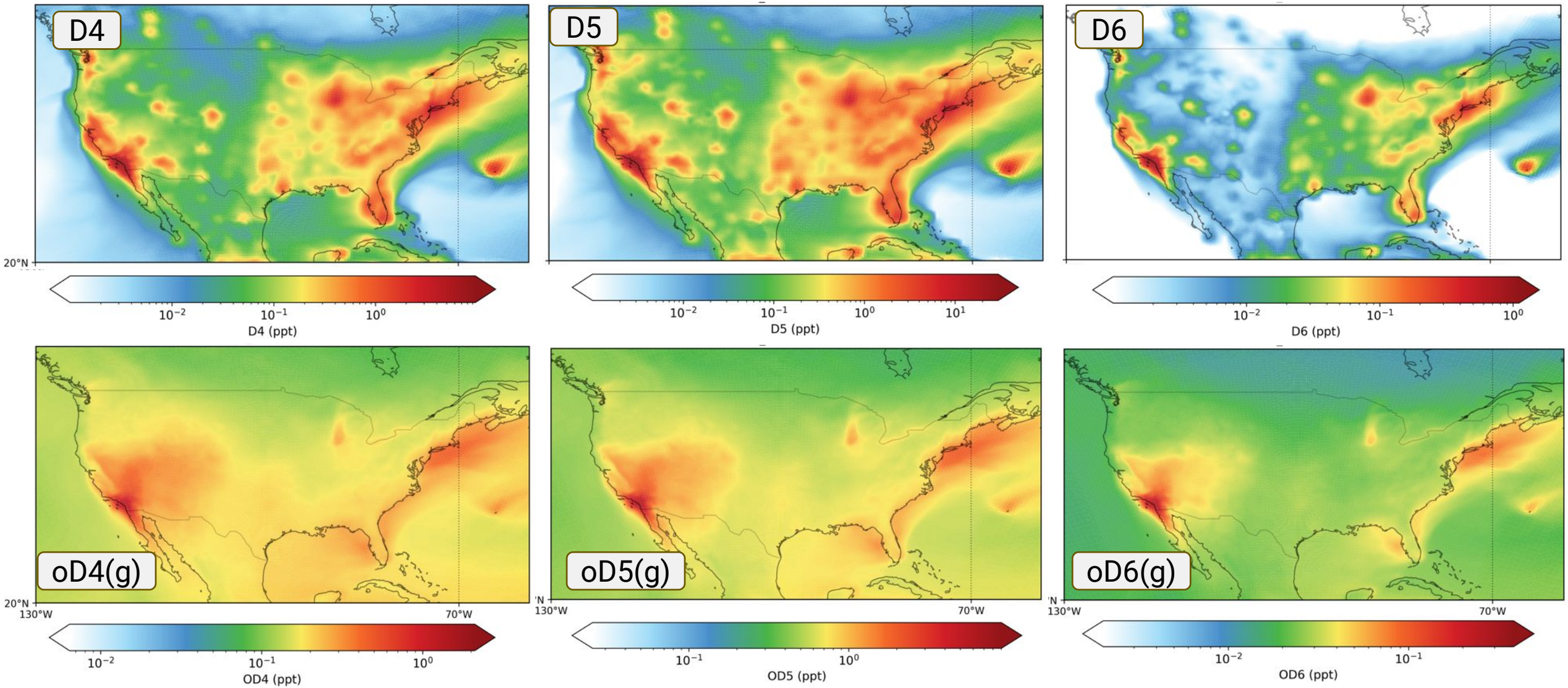




D4, D5, and D6 and OD4,OD5,OD6 global distribution July 13-Aug 6, 2022 (NYC-METS)

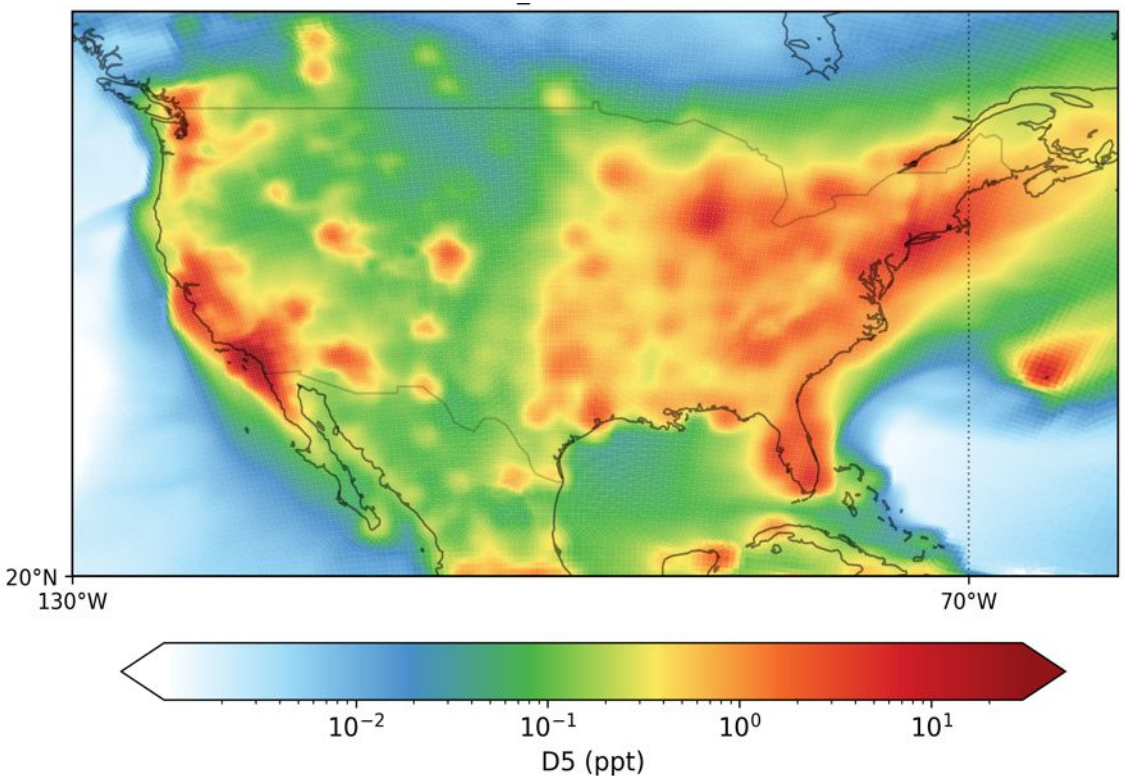


D4, D5, and D6 and OD4,OD5,OD6 CONUS distribution July 13-Aug 6, 2022 (NYC-METS)



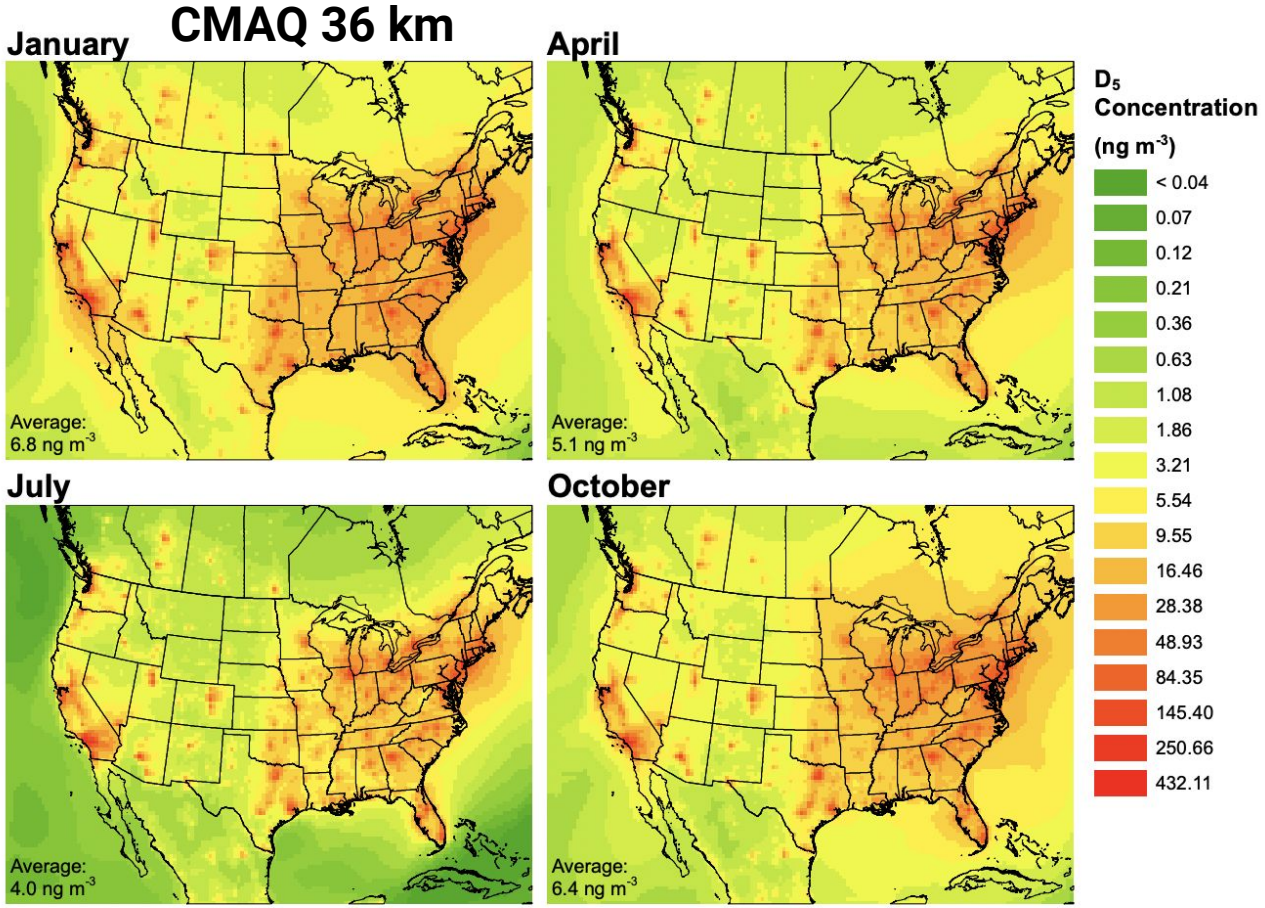
D5 CONUS distribution July 13-Aug 6, 2022 (NYC-METS) vs previous studies

MUSICA ~14 km



$[D5]_{MAX}$ ~ 450 ng m^{-3} in urban areas

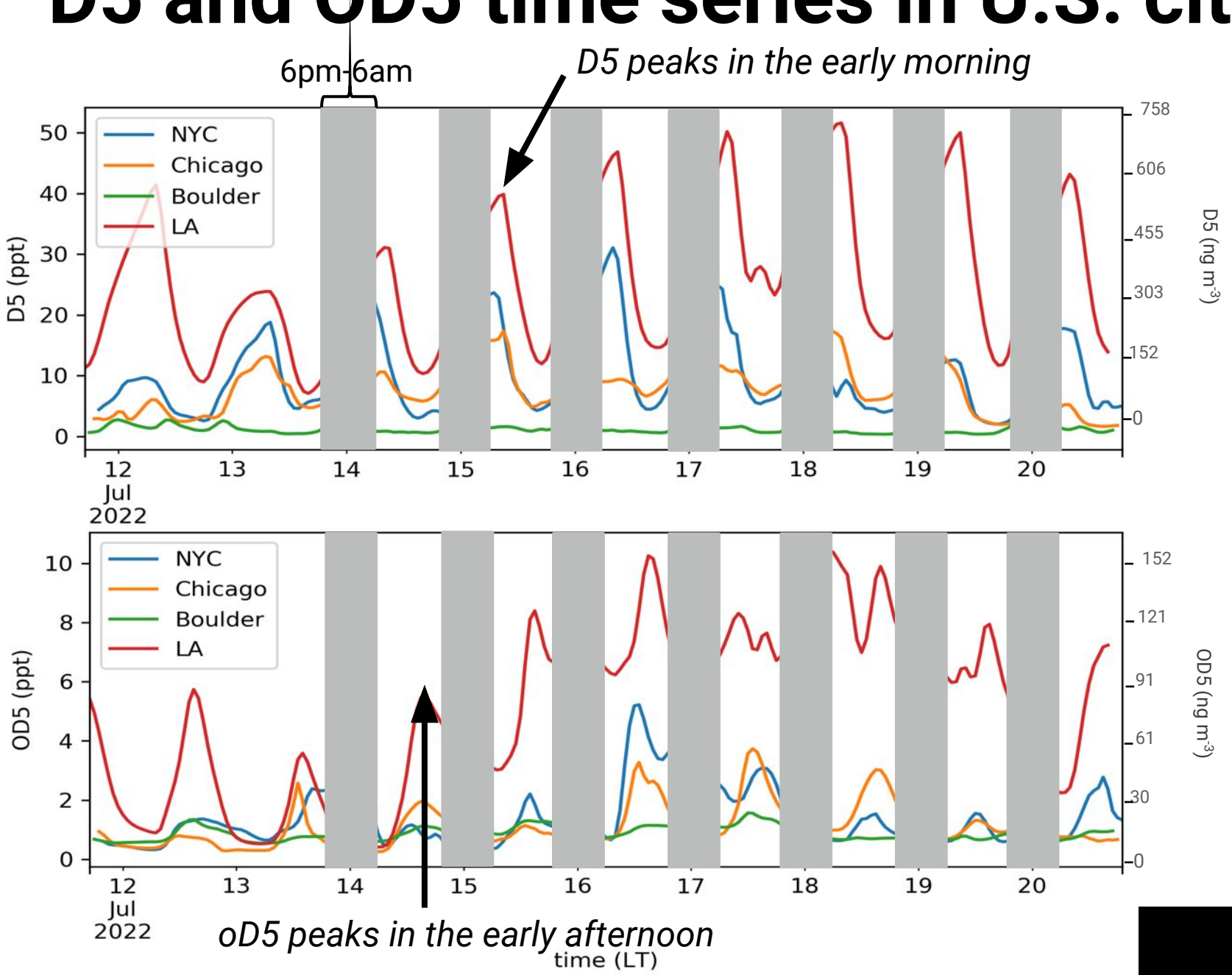
CMAQ 36 km

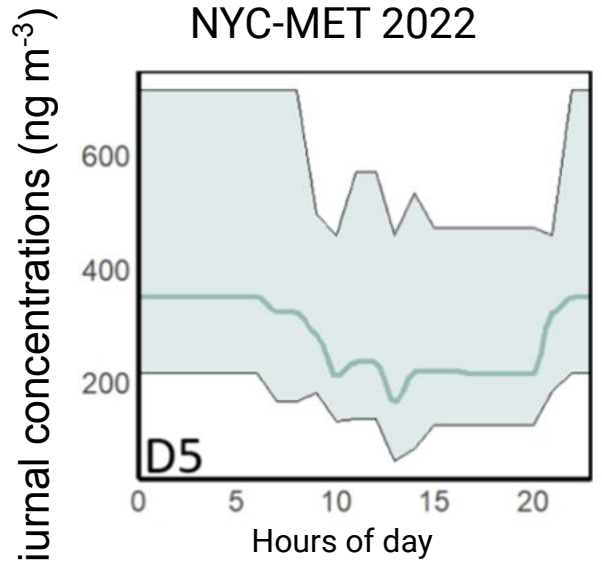


$[D5]_{MAX}$ ~ 430 ng m^{-3} in urban areas

Janechek et al. ACP, 2017

D5 and OD5 time series in U.S. cities





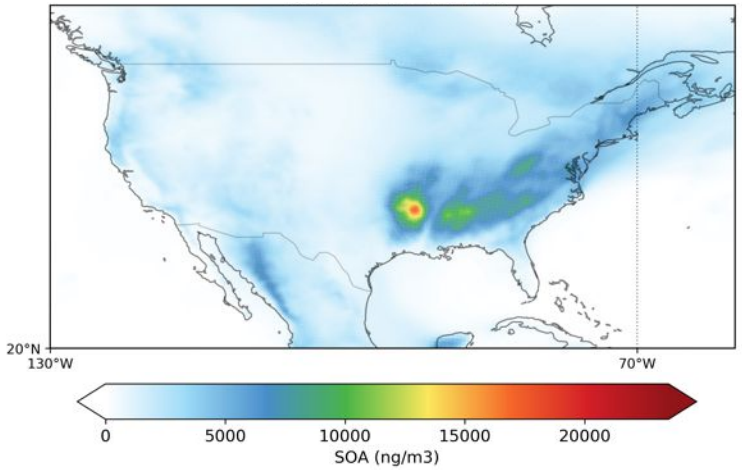
Brunet et al., *Environ. Sci. Technol*. 2024

Preliminary results - addition of VMS to the standard SOA mechanism significantly changes the overall modeled SOA - needs to be simulated explicitly

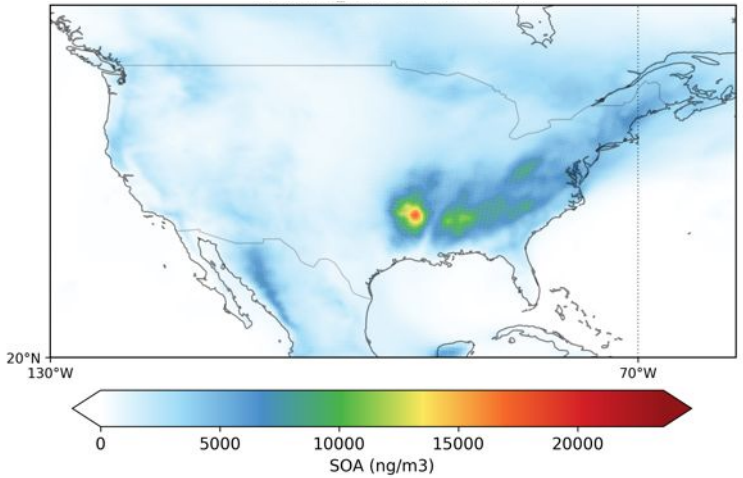
How D5-derived SOA is defined

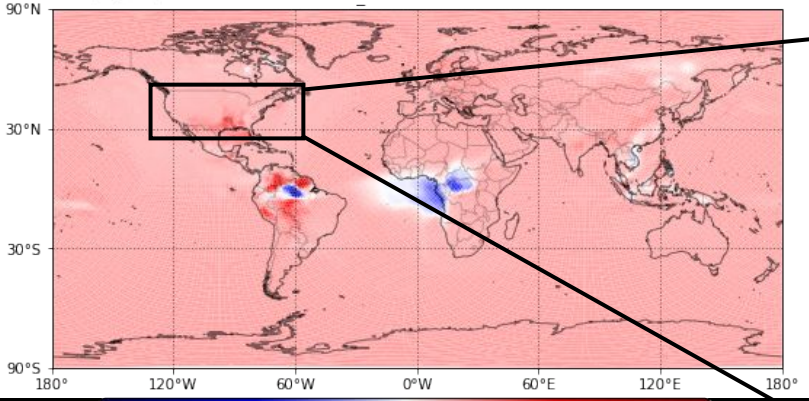
```
[D4_OH]          D4 + OH  -> OD4                                                    ; 1.01e-12
[D5_OH]          D5 + OH  -> OD5                                                    ; 1.55e-12
[D6_OH]          D6 + OH  -> OD6                                                    ; 1.92e-12
[OD5_OH_vbs]      D5 + OH  -> OH + 0.0356 (373/250)*SOAG0 + 0*SOAG1 + 0*SOAG2 + 0*SOAG3 + 0.4719(373/250)*SOAG4
[D5_OH_vbs]      D5 + OH  -> D5 + OH + 0.0531*SOAG0 + 0.7041*SOAG4 ; 1.55e-12
```

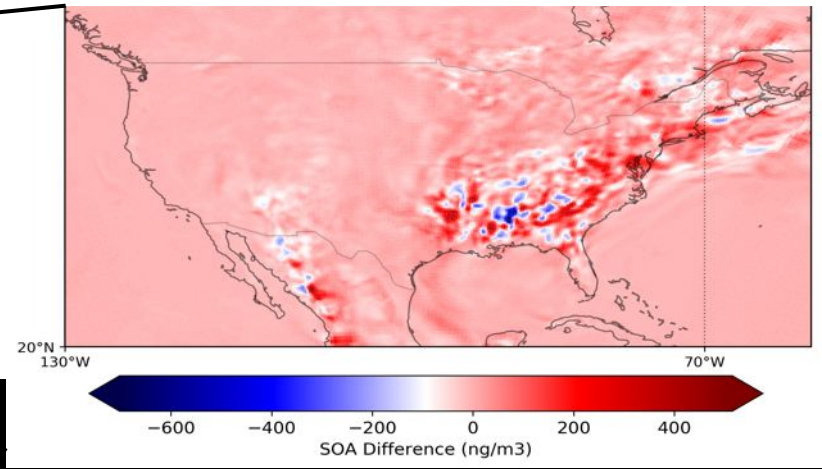
Total SOA in D5 gas+aerosol MUSICA simulation



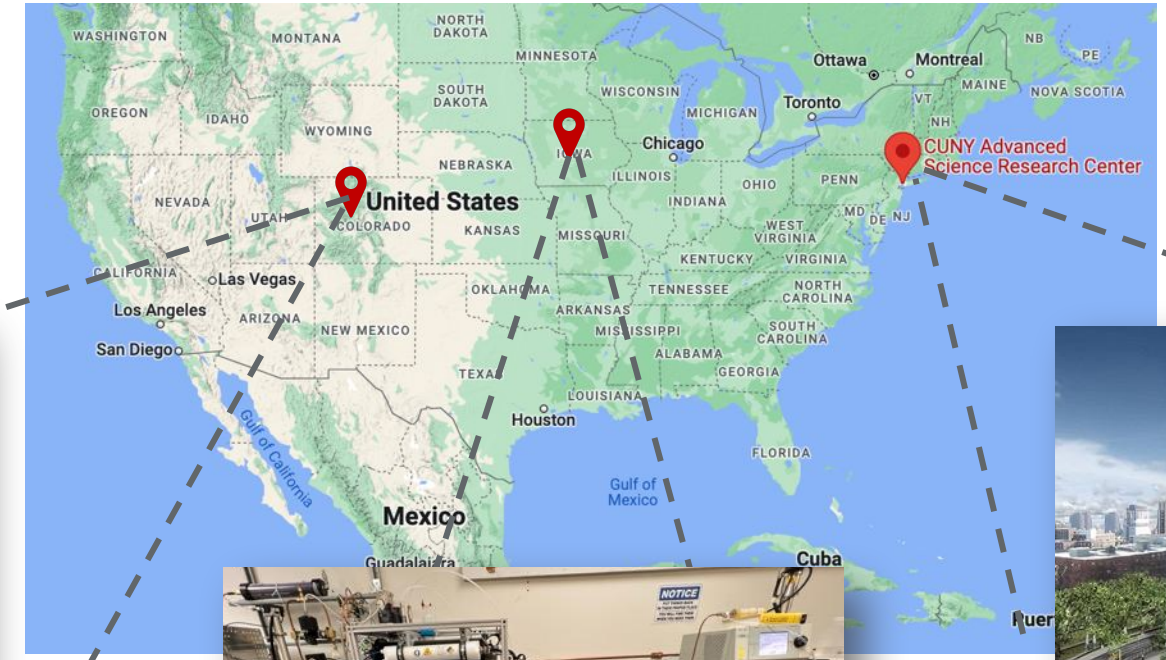
Total SOA in D5 gas-only MUSICA simulation







Future Direction: research outcomes are going to use for more atmospherically relavent simulation



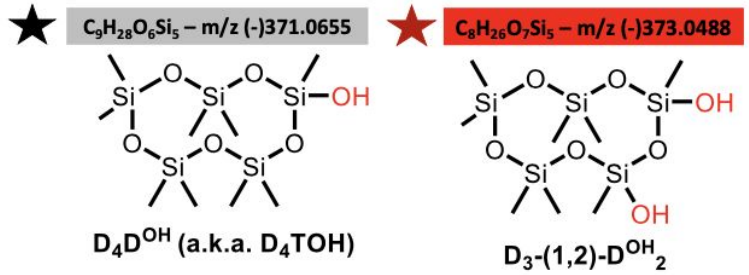
CU Environmental Chamber (CUEC) Facility- 20 m3 FEP (Summer 2023)

13 L OFR, University of Iowa

Advanced Science Research Center (ASRC) rooftop in the The City College of New York, Manhattan (July13 – Aug 8 , 2022)

Future Direction

- Multigenerational Aging; 1s2 and 2nd generation oxidation product in gas and SOA formation in the MUSICA model



Meepage et al., ACS *EST Air*, 2024

- Extended version of SOA parametrization in CAM-chem vs Standard SOA
- More careful consideration of reaction partner in low-NOx OFR/chamber studies (RO_2 + OH vs RO_2+HO_2) and SOA yield, as well as high-NOx condition

Thank you!

Questions?