Modeling Investigation of Volatile Methyl Siloxane (VMS) Oxidation, SOA Formation, and Aging Using CESM2, MUSICAv0

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Presentation Overview

- **Introduction & Motivation**

  → What are VMS and why do they matter?
- **Model Set up**

  → We used CAM-chem and MUSICA with updated chemistry.
- **Simulation Scenarios**

  → Goal: Four MUSICA cases explore oxidation and aging effects.

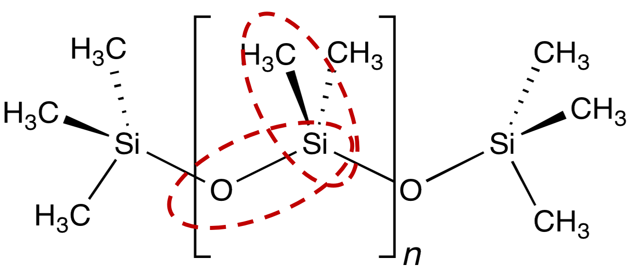
    → What we have: CAM-chem cases
- **Results & Evaluation**
- **Key Takeaways**
- **Future Work**

  → Higher resolution and refined mechanisms are planned.

What are Volatile Methyl Siloxanes (VMS)?

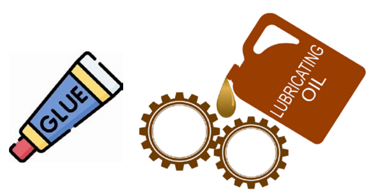
Synthetic, high-volume chemicals used in cosmetics and industry, entirely human-made compounds

Synthesis:



PDMS
Alternating Si --- O atoms with attached methyl groups (--- CH3)

Applications:



Personal Care Products (PCP), Industrial lubricants, glue, detergents

cVMS:

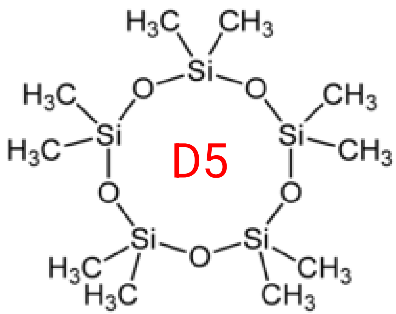
D4

D5

D6

What is Known about Atmospheric Fate of VMS?

A few to several days of lifetime



95% OH

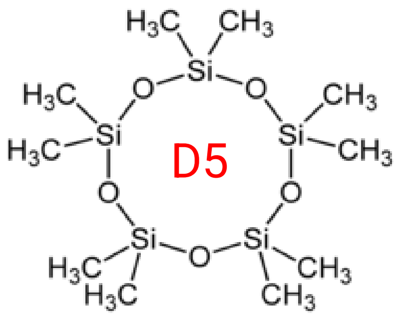
5% Cl

Volatile (>90% in atmosphere)

- Global D5 ~ 0.1 Tg per year vs global anthropogenic Benzene ~ 5.6 Tg per year.
- **Long-range transport**
- Classified as **very persistent and very bioaccumulative (vPvB)** under the Stockholm Convention on Persistent Organic Pollutants (2023)

What is Known about Atmospheric Fate of VMS? Aerosol Formation?

A few to several days of lifetime



95% OH

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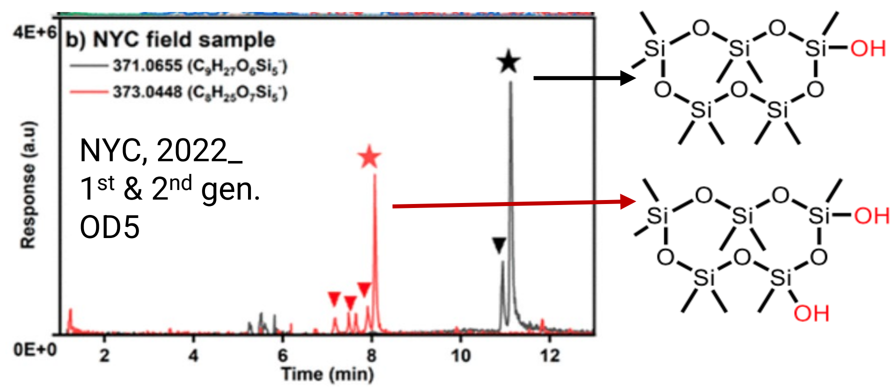

Meepage et al., *Environ. Sci. Technol Air*. 2024

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Multigenerational oxidation.

Why do we need to model cVMS?

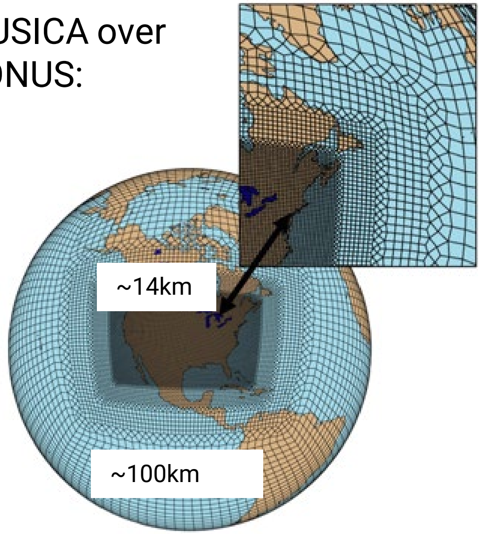
- **Widespread use and emissions** and **long-range transport.**
- **Bioaccumulation and environmental persistence concerns**; research on fate and transport needs to extend to oxidation products and aerosols, and not just be confined to the parent compounds.
- **Available gas and particle concentrations** to compare against in **NYC 2022 (NYC-METS)**.
- Parent and daughter compounds proposed as **tracer of PCP**, but specific daughter molecules, lifetime, and phase partitioning are needed.

Multi-Scale Infrastructure for Chemistry and Aerosols (MUSICAv0) Updated with cVMS chemistry

Community Atmosphere Model with Chemistry (**CAM-chem**) component with **MUSICAv0** configuration.

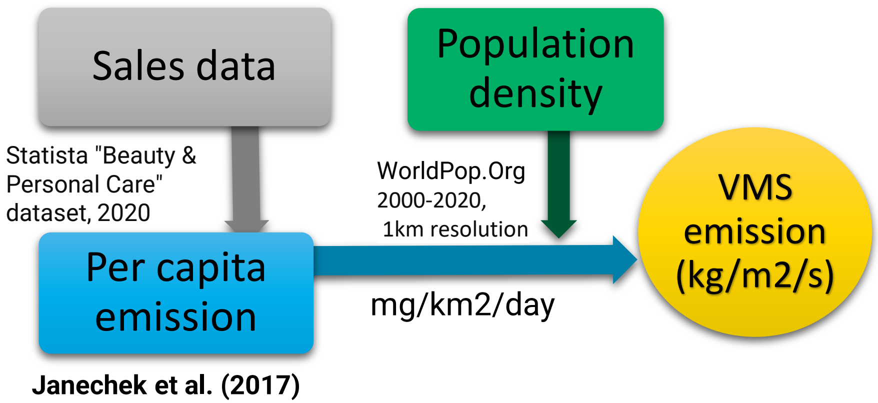
- Met. (T, U, V) nudged to MERRA2
- Anthropogenic emission: CAMSv6.2
- Biomass Burning emission: QFED2.5_FINN
- cVMS emission: Brunet, Mohammadi, et al. (2025)
  - 1 deg for CAM-chem simulations
  - 10 km emission regridded to MUSICA resolution
- Reaction mechanisms:
  - **CAM-chem** simulations: aging effect without Si conservation
  - **MUSICA**: updated mech. With multigenerational and aging with Si conservation

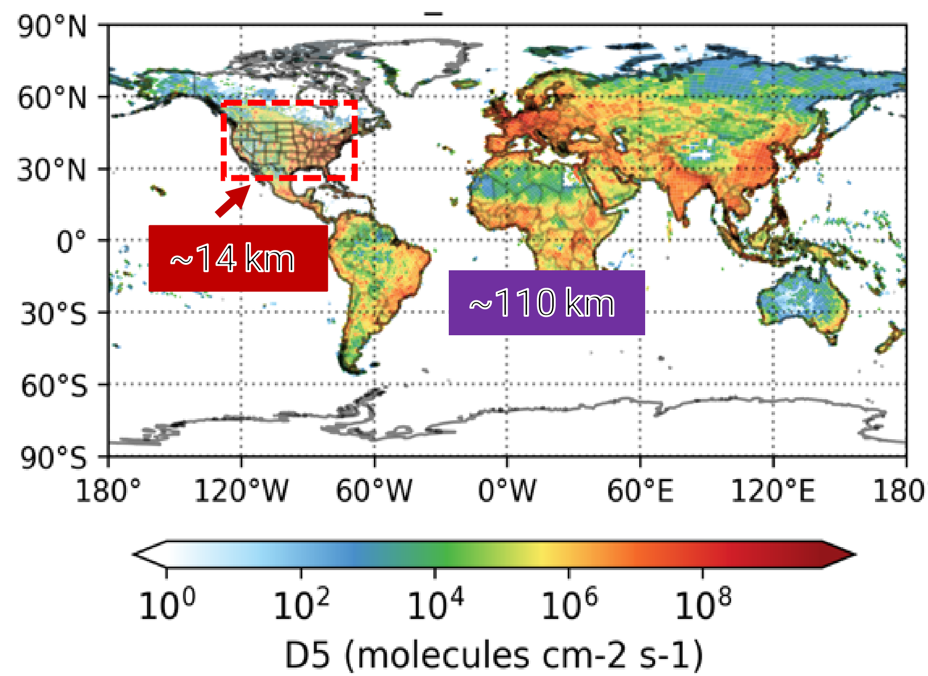
MUSICA over CONUS:



https://wiki.ucar.edu/display/MUSICA

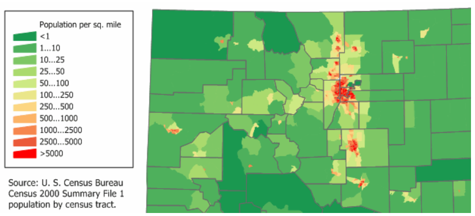
10 × 10 km cVMS Emission Data from Brunet et al. (2024) were Mapped onto the MUSICA Grid (ne0CONUSne30x8).

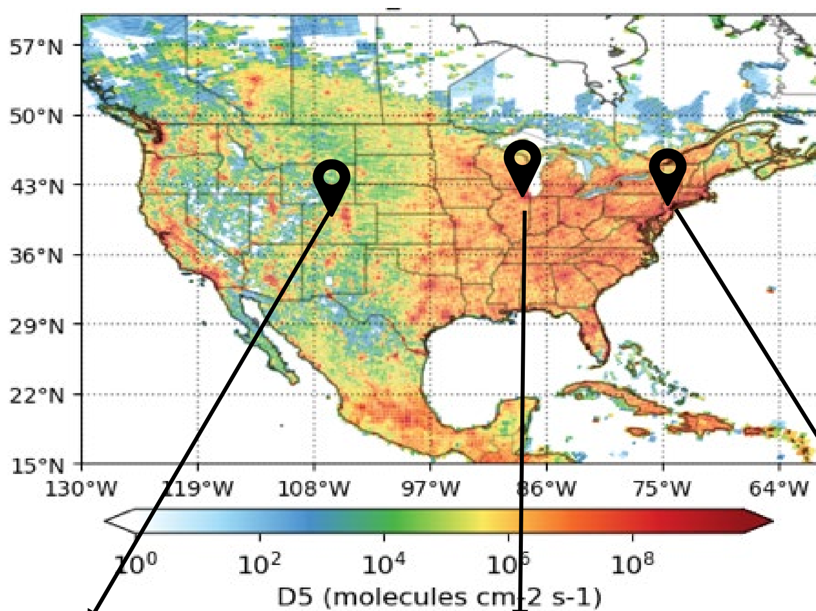




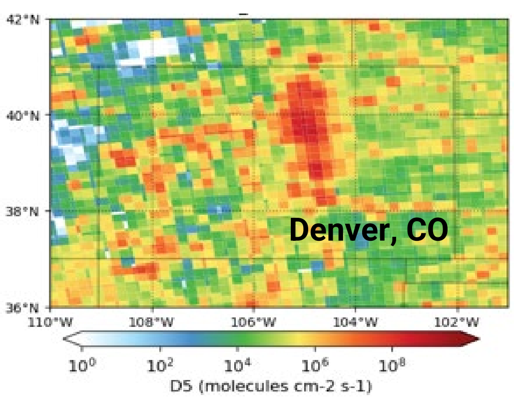
Per capita emissions rates for the rest of the world were calculated by normalizing the U.S. per capita emissions using each country's personal care product sales revenue.

MUSICA Grid D5 emission over CONUS

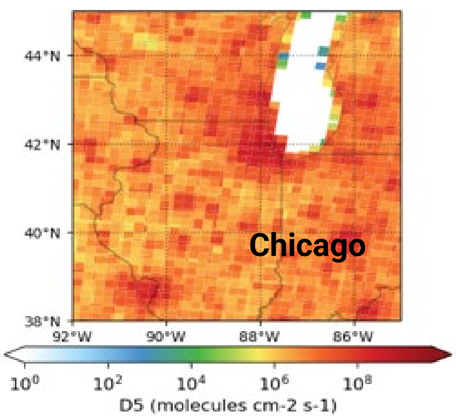




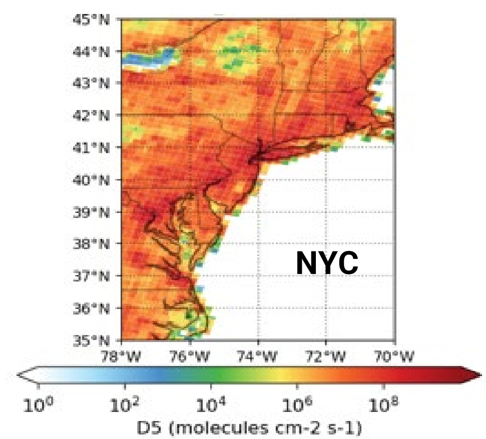
2.5e7 molec cm-2 s-1



2.3e8 molec cm-2 s-1

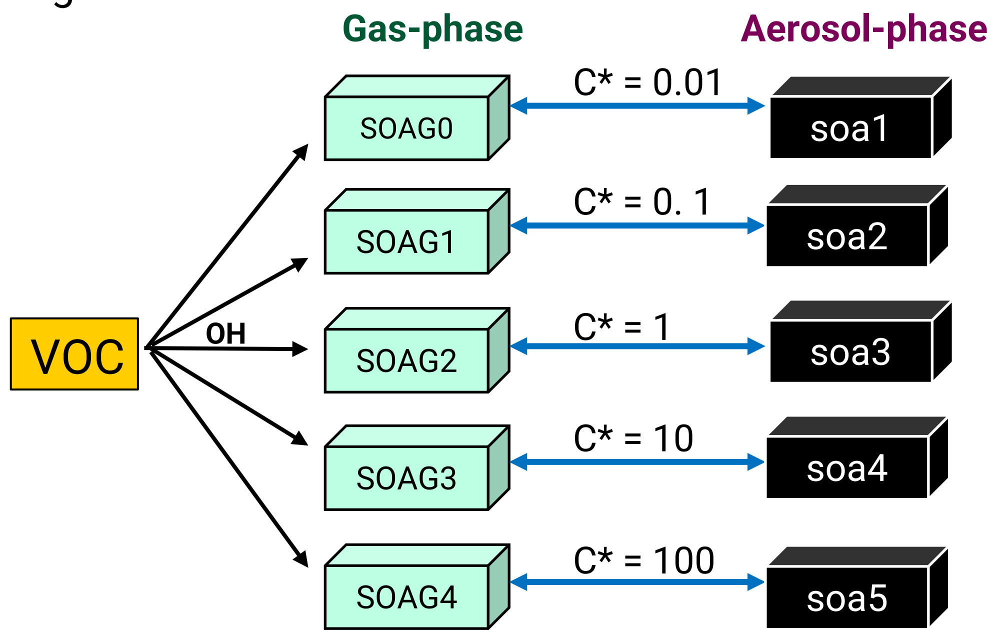


2.9e9 molec cm-2 s-1



SOA Formation in CAM-chem: Volatility Basis Set (VBS) Approach

VBS tracks oxidation products by volatility, distributing mass across bins to simulate gas-particle partitioning.



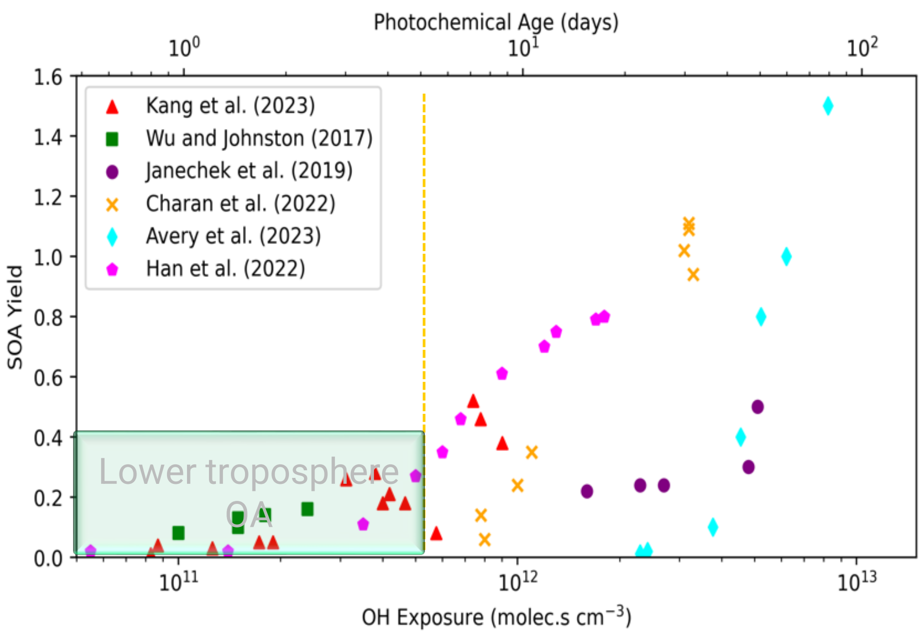
C*: Saturation vapor pressure (ug m^{-3})
SOAG mw in CEAM= 250 g/mol (C15H38O2)

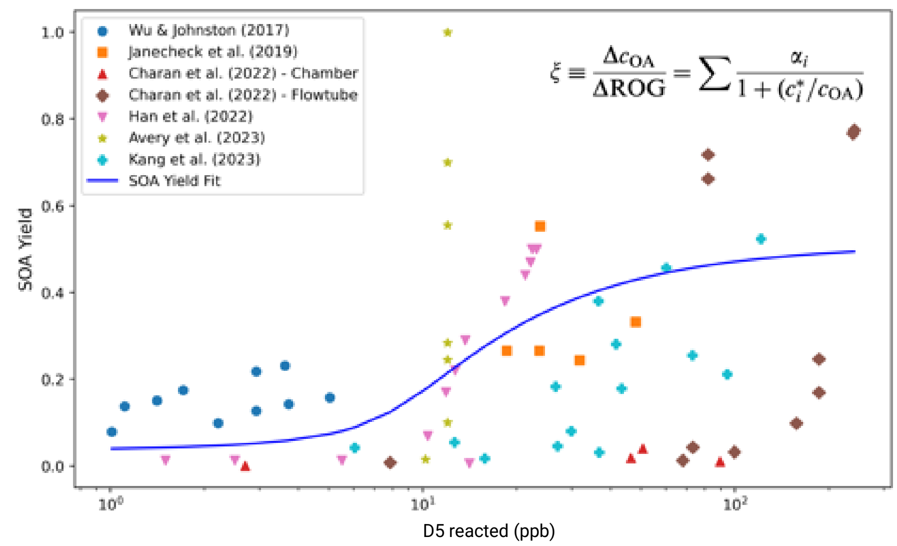
$$VOC + OH \rightarrow VOC + OH + \alpha_1 * SOAG0 + \alpha_2 * SOAG1 + \alpha_3 * SOAG2 + \alpha_4 * SOAG3 + \alpha_5 * SOAG4$$

Molar yields

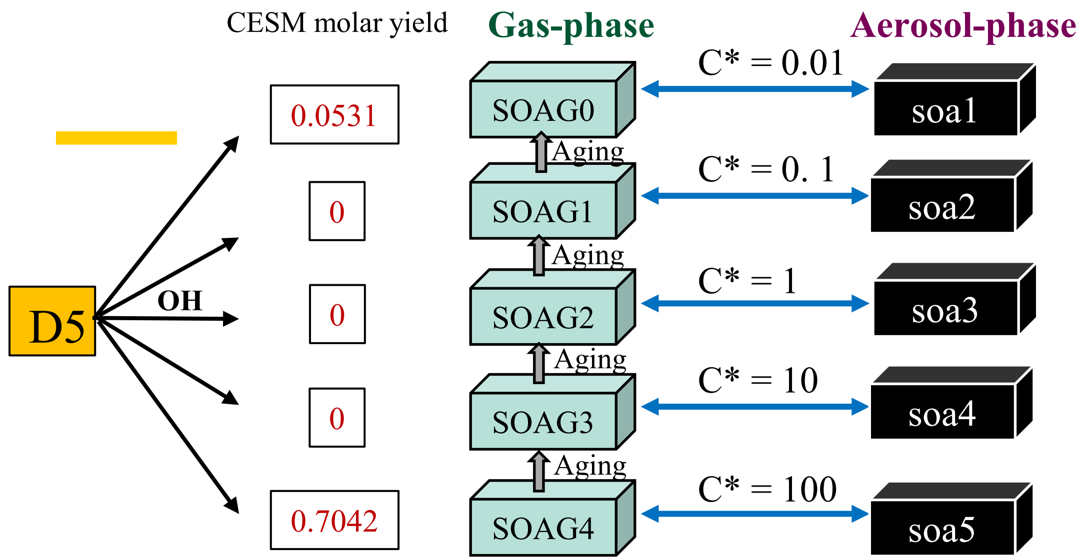
D5 Derived SOA Yield; Experimental Works

Best Molar Yield (α) Chosen via Nonnegative Linear Least Squares

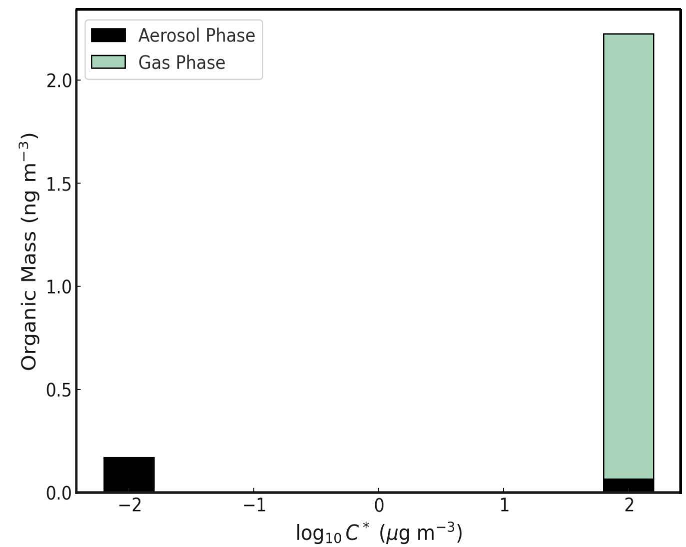




D5-drived SOA Explicitly Represented in Extended version of VBS



VMS product MW of 373 g mol^{-1} (vs. the parent mass of 371)



Mass partitions mainly into:
SOAG0 (low volatility, high SOA potential) and **SOAG4 (high volatility, low SOA potential)**

CESM species	Source	
	CESM Default	CESM with cVMS SOA modeling
SOAGff	fossil fuel	fossil fuel + biomass burning
SOAGbb	biomass burning	D5
SOAGbg	biogenic	biogenic

D5-SOA Formation + Aging Reaction Mechanisms and Simulations Scenarios

- D5 oxidation reaction: $\mathbf{D5 + OH \rightarrow OD5}$

- Explicit D5-SOA formation in model based on VBS and molar yields of SOAGs:

$$\mathbf{D5 + OH \rightarrow D5 + OH + 0.0531 * SOAGbb0 + 0.7041 * SOAGbb4}$$

- D5-SOA aging – considering functionalization only (no fragmentation): mass gain, lower volatility:

$$\mathbf{SOAGbb4 + OH \rightarrow OH + SOAGbb3}$$
$$\mathbf{SOAGbb3 + OH \rightarrow OH + SOAGbb2}$$
$$\mathbf{SOAGbb2 + OH \rightarrow OH + SOAGbb1}$$
$$\mathbf{SOAGbb1 + OH \rightarrow OH + SOAGbb0}$$

- Simulation scenarios to evaluate aging effects (CAM-chem):

Case	Case Name	CONUS Resolution	Period	D5 Emission	D5 Gas	D5 Aerosol	Aging
C1	f09_f09_mg17_ic	1 deg	2021-2022	On	On	On	Off
C2	f09_f09_mg17-d5soa	1 deg	2022 Jul-Aug	On	On	On	Off
C3	f09_f09_mg17-d5soa_aging	1 deg	2022 Jul-Aug	On	On	On	on

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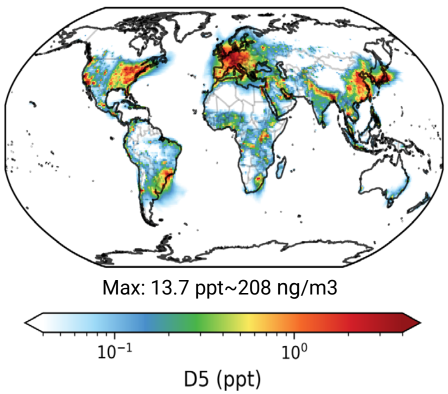
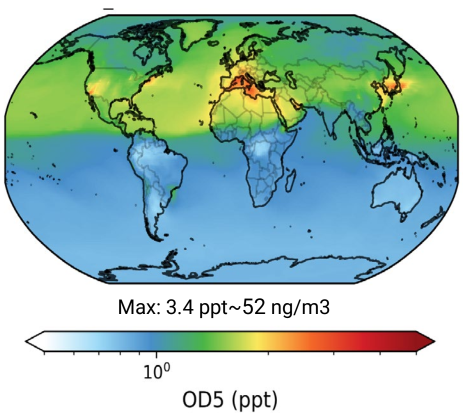
Global and Regional Distribution of D5 Species and Total Organic Aerosol - Case C3 (Aging)– July 2022

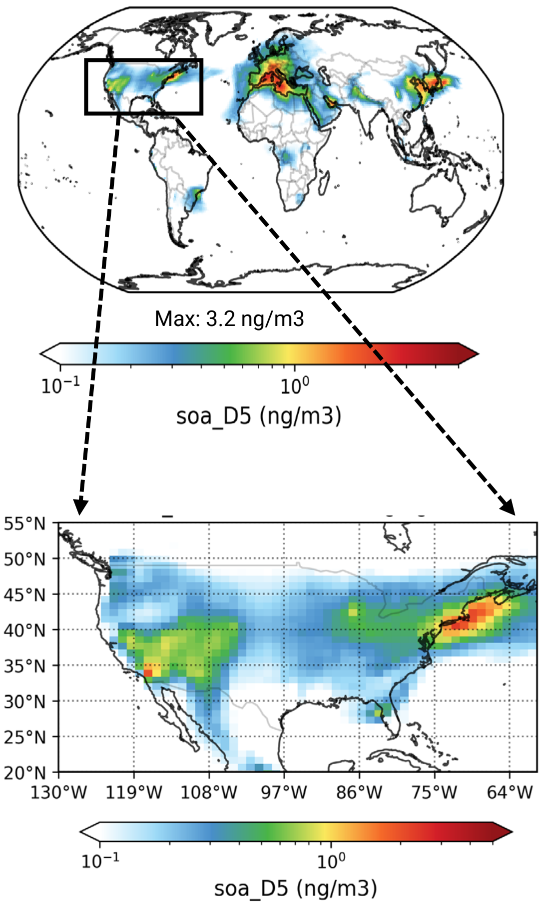
D5



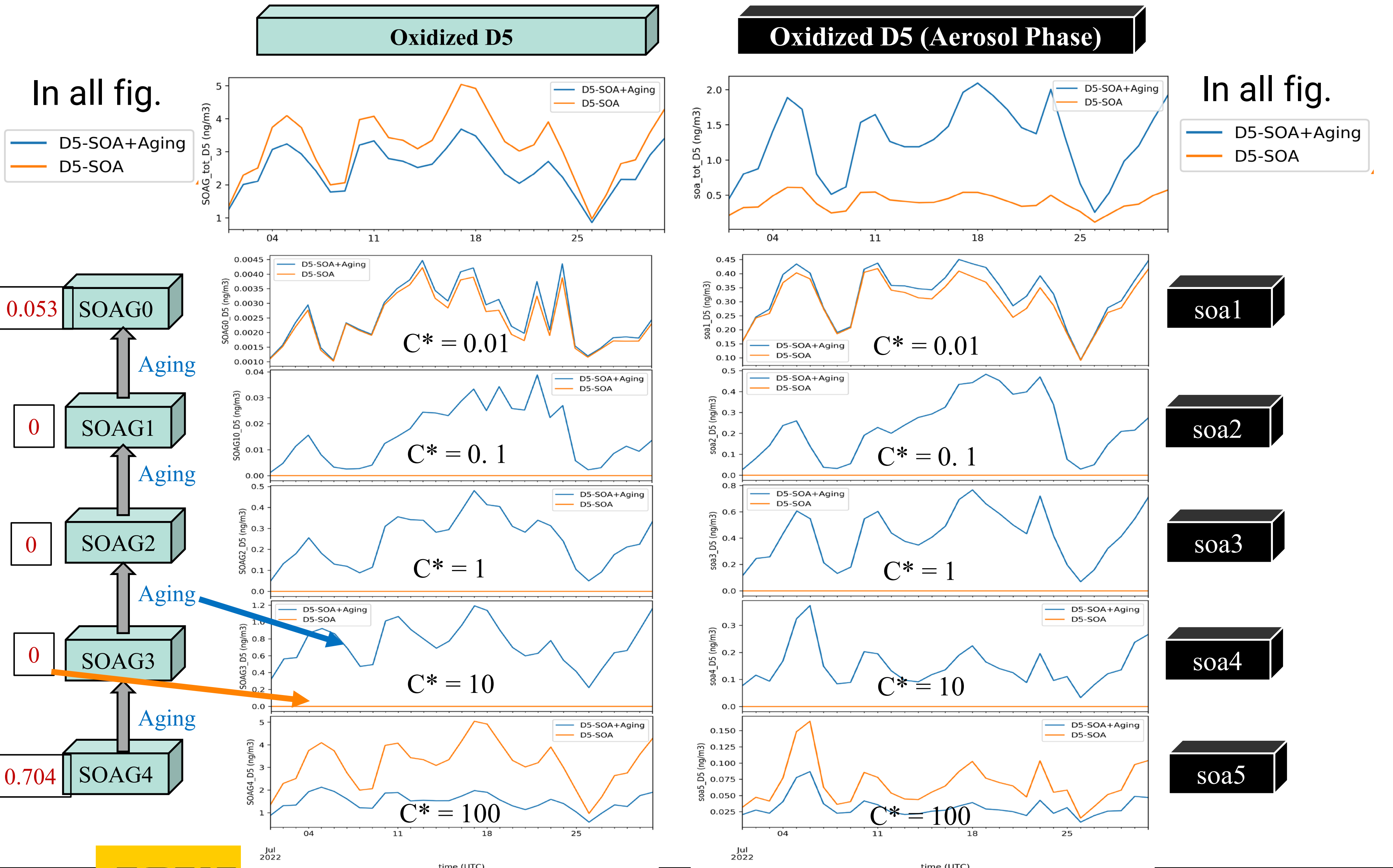
Oxidized D5



D5-soa$_{total}$

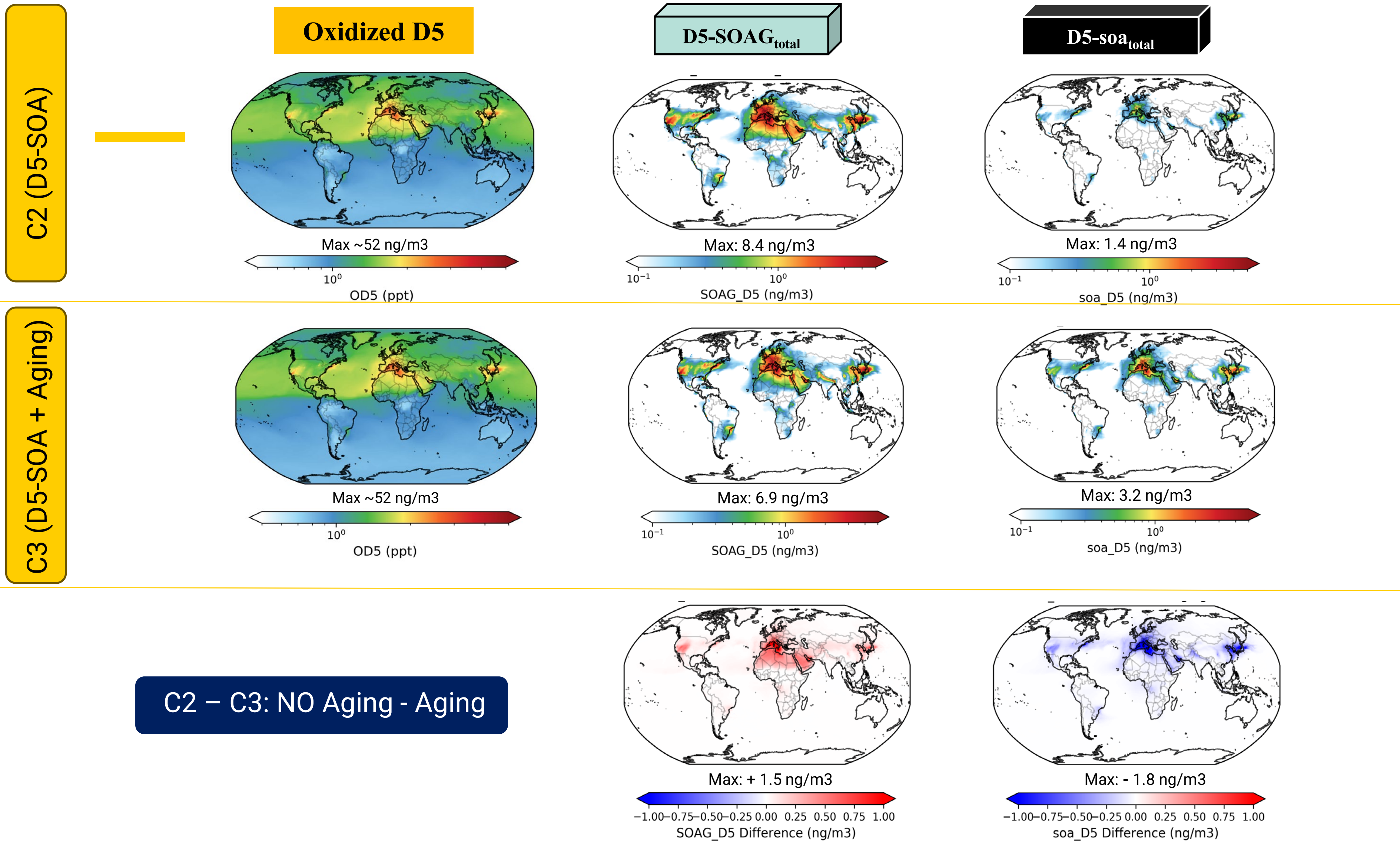


Diurnal Profile of D5 Species (SOAGbb and soabb) _ Case C2 and C3 (Aging effect on SOA formation of D5)_ NYC (July 2022)



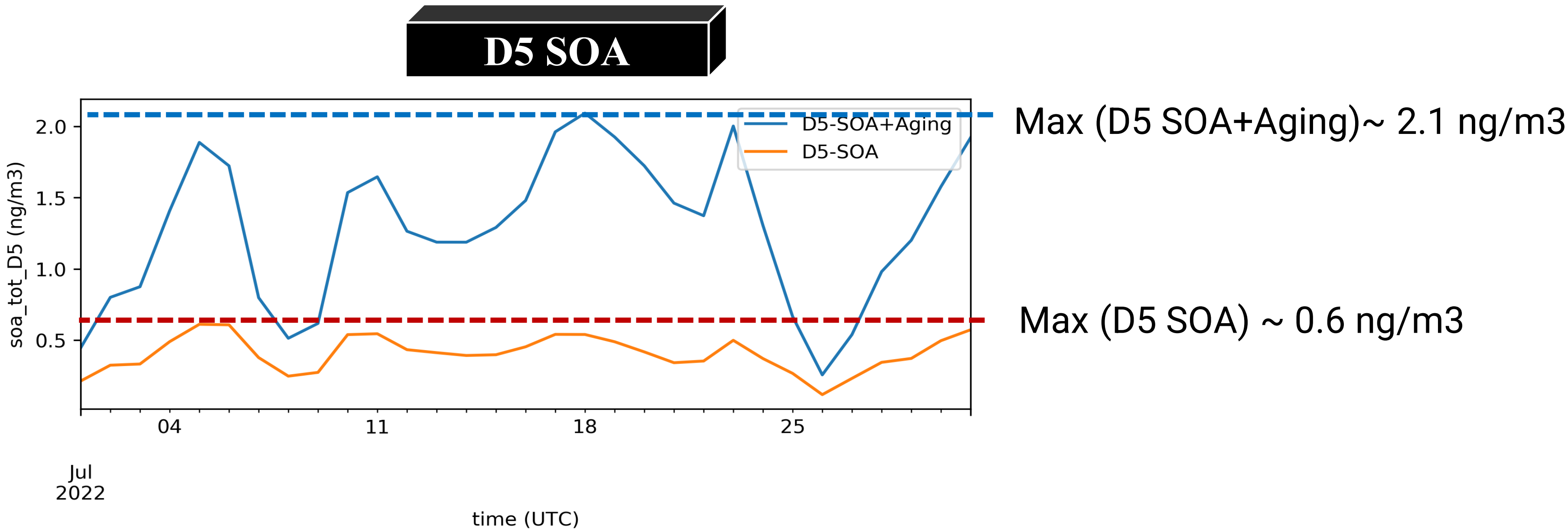
Aging increases SOA levels consistently across diurnal cycle

Spatial Distribution of D5 Species- Case C2 and C3 (Aging effect on SOA formation of D5)_ July 2022



Aging reduces SOAG concentrations by ~1.5 ng/m³ and increases SOA by ~1.8 ng/m³, reflecting the transfer of mass from gas to particle phase during aging.

Model Evaluation: Comparison of Model's With(out) Aging D5-derived SOA with Observations in NYC (July 2022)

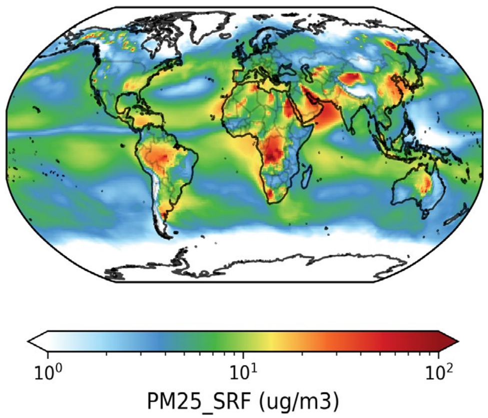


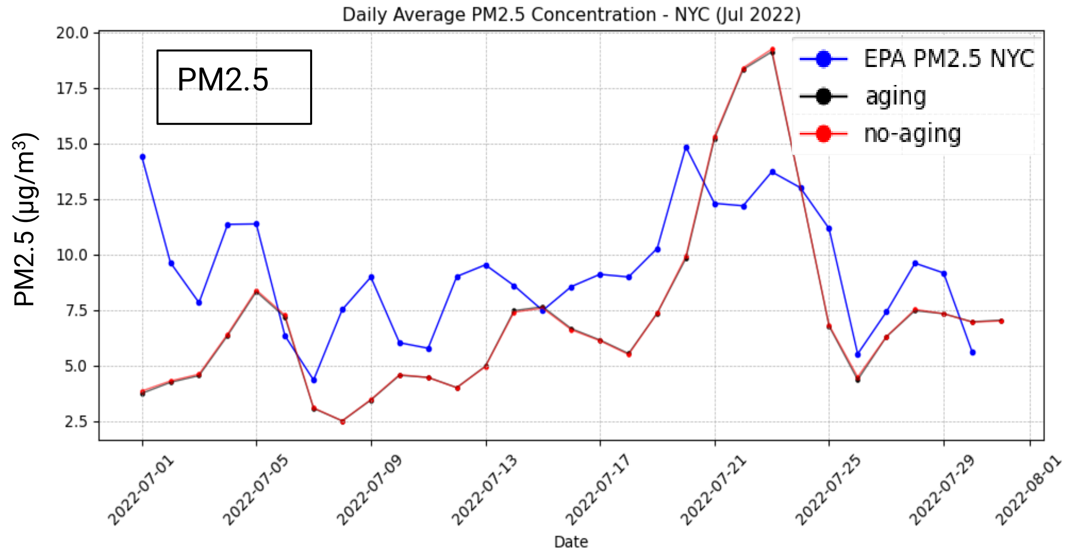
Oxidized D5 in particle phase during the NYC-METS sampling campaign in Jul 2022, after applying artifact correction, is ~ **6.6 ng/m³** (n=4). (Meepage et al)

Model underestimates D5 SOA by a factor of ~3.
We have not yet apportioned the error to **emissions, SOA yields, mechanisms, resolution effects, or even analytical uncertainty**.
Additional investigation of analysis refinements, compound ratios and temporal patterns underway.

Model Evaluation: Comparison of Model's With(out) Aging PM2.5 and O3 with Observations in NYC (July 2022)

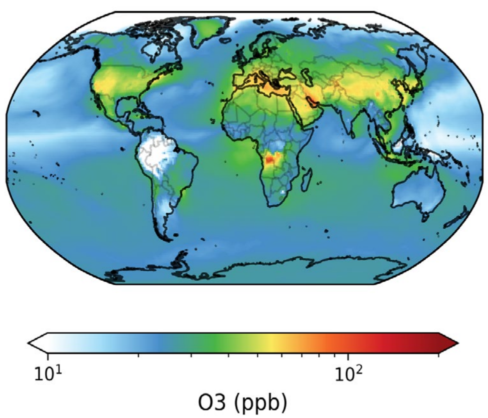
PM2.5

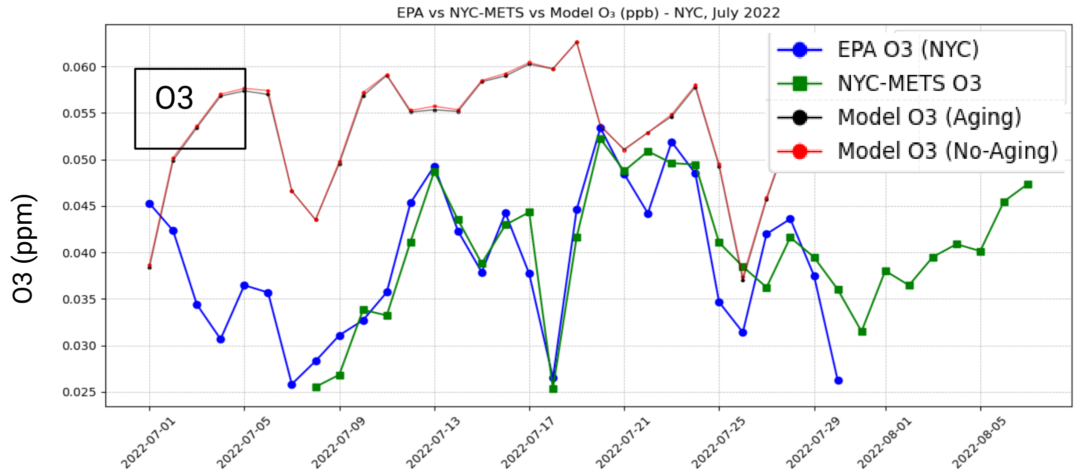




The model generally **underestimates $PM_{2.5}$ by 1–5 μg/m³**, with **good agreement in daily trends**.

O3





The model **overpredicts O_3** especially in early Jul, often linked to overestimated VOC/NO_x chemistry, insufficient scavenging, and simplified cloud or convection processes.

D5 aging shows minimal influence on ozone and PM2.5.

Key Takeaways (CAM-chem simulations):

- **Urban and Hemispheric Trends**
  D5 peaks in urban areas, especially in the Northern Hemisphere (dense population and PCP usage); Despite localized emissions, OD5 is also found in rural and remote regions, showing **long-range cVMS transport**.
- **Molar Yield & Volatility Partitioning**
  D5 oxidation products span five volatility bins, with most mass in SOAG0 and SOAG4 — showing distinct aerosol formation paths.
- **D5 SOA Formation and Aging Effects**
  Aging shifts D5 mass to aerosol phase and model shows high sensitivity to aging, but its impact on $PM_{2.5}$ and O_3 is small.
- **Model Performance Insight**
  Model underestimates D5 SOA by ~3×,
  highlighting the need for better mechanisms or resolution — goals of upcoming MUSICA runs.
  It captures diurnal variability of $PM_{2.5}$ and O_3, but **underestimates $PM_{2.5}$** and **overestimates O_3**, consistent with known CAM-chem biases related to VOC/NO_x chemistry and coarse spatial resolution.

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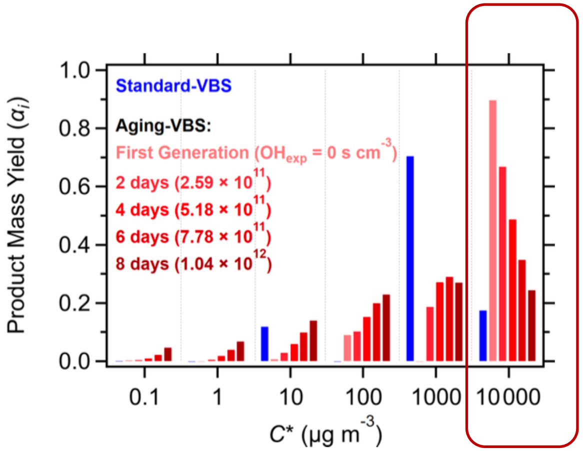
Looking Forward:



Kang et al., Atmos. Chem. Phys., 2023

Next Steps:

- High-resolution MUSICA simulations (14 km)
- **Updated D5 chemistry to be mass conservative for silicon and multi-generational mechanisms more consistent with experimental data**, especially at low OH exposures. Initial oxidation will lead to virtually no aerosol, and multiple reactions with OH are required to build up SOA. Based on Kang et al. (2023) and our experiments with the Browne group at CU Boulder.

Expected Improvement:

- Refined resolution should improve results for New York City NYC-METS campaign from summer 2022.
- Model-observation comparison of product distribution and phase (siloxanol, di-siloxanol, tri-siloxanol, etc.) will constrain the various mechanisms and VBS choices used across the cases.

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Future Work:
Planned MUSICA Simulations to Evaluate D5 Chemistry and Aging

Preliminary results shown today are from CAM-chem (C1-C3).

IC for MUSICA cases

cVMS Cases

Case	Case Name	CONUS Resolution	Period	cVMS Emissions	cVMS Gas	cVMS Aerosol	Aging
C1	CAM-chem	1 deg	2021-2022	On	On	On	On
M1	MUSICA –BASE CASE	14 km	Jul-Aug 2022	Off	Off	Off	Off
M2	MUSICA - GAS			On	On	Off	Off
M3	MUSICA - SOA			On	On	On	Off
M4	MUSICA –SOA-Multi-gen.-Aging			On	On	On	On

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Thank you!

Questions?

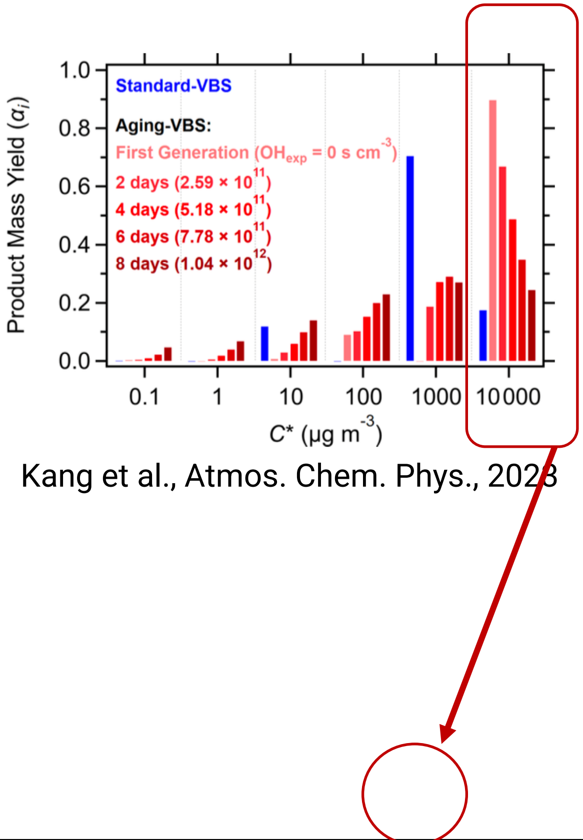
Future Work:
Refined mechanism according to Kang et al. 2023; D5 + OH products stay volatile at first, but multigenerational oxidation lowers volatility → SOA forms.

Chemical mechanisms for cVMS are implemented with the following goals:
(1) mass conservative for silicon; and
(2) consistent with experimental data.

$$D_5 + OH \rightarrow VOP_{rep} + \gamma_{HCHO} HCHO \quad \left(k_{D_5+OH} = 2.0 \times 10^{-12}\, cm^3\, s^{-1}\right) \quad (R6)$$

$$VOP_{rep} + OH \rightarrow VOP_{rep} + \gamma_{HCHO} HCHO \quad (k_{D_5+OH}) \quad (R7)$$

$$HCHO + OH \rightarrow \quad \left(k_{HCHO+OH} = 8.5 \times 10^{-12}\, cm^3\, s^{-1}\right) \quad (R8)$$



Kang et al., Atmos. Chem. Phys., 2023

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Future Work:
Refined mechanism according to Kang et al. (2023)

D5-SOA

D5-SOA with multigenerational aging of oxidation products