Comprehensive Accounting for Reactive Organic Carbon (ROC) Emissions from Residential Wood Combustion Processes

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BEN MURPHY

Center for Environmental Measurement and Modeling (CEMM)
Office of Research and Development (ORD)
U.S. EPA

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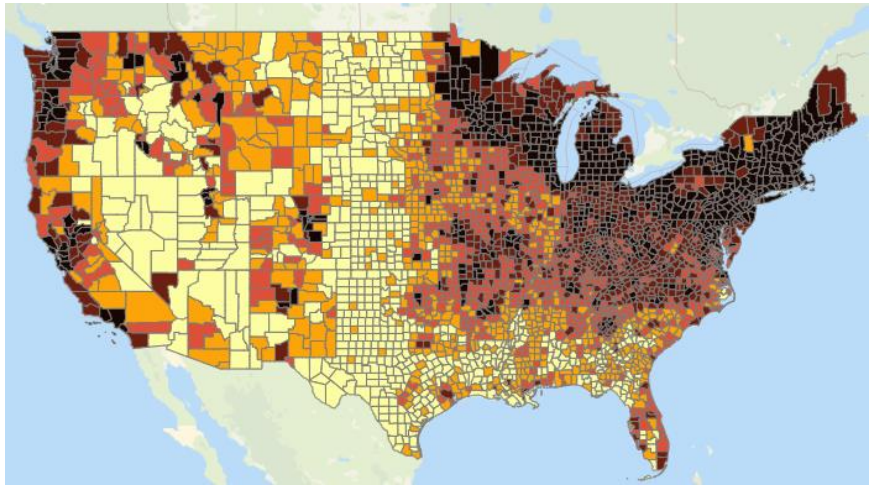
Residential Wood Combustion (RWC) Emissions

- Residential wood combustion is a significant source of multiple pollutants including PM, CO, and VOCs (both toxics and precursors to PM and O_3)
- Measuring wood smoke emissions and translating to models is challenging:
  - Fuel (wood species) vary
  - Fuel moisture and condition vary
  - Real-world operations vary
  - Standard test method procedures may introduce biases
  - Emissions chemical composition is complex

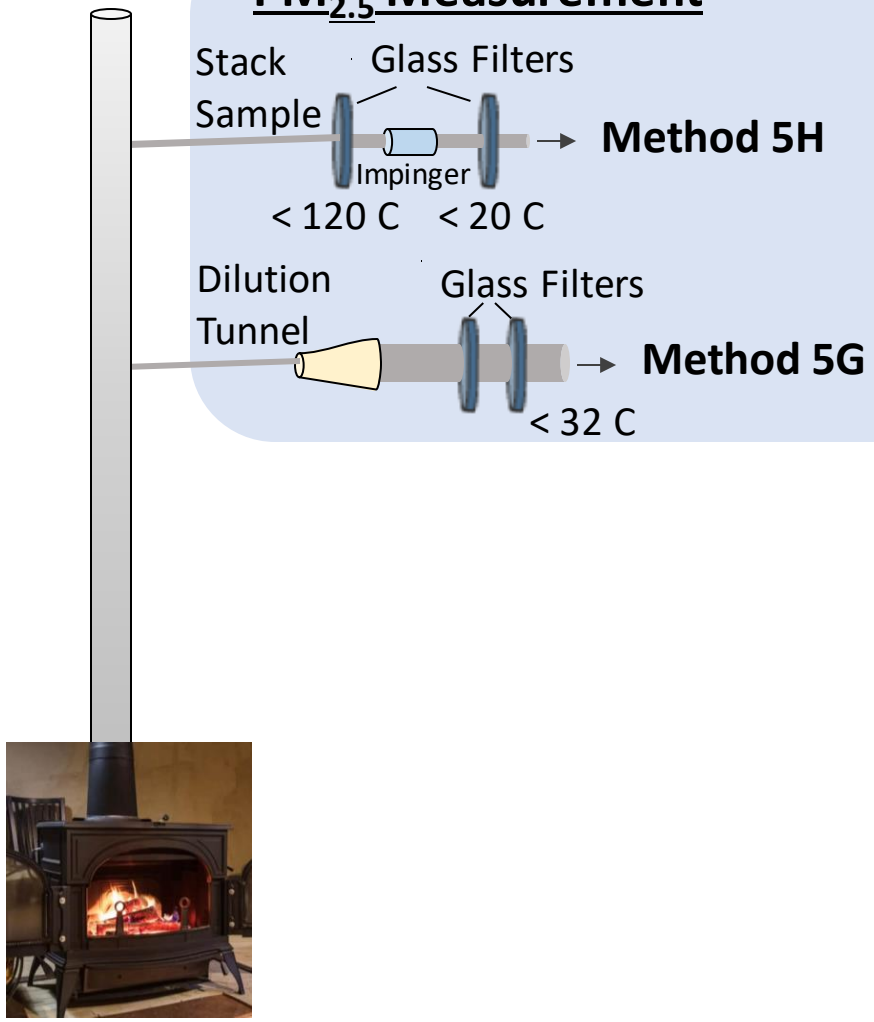


Residential Wood Sources $PM_{2.5}$ Emissions (tons/mi^2). EPA 2020 NEI Exploration Tool.

Pollutant	Annual 2020 Emissions [kt yr^{-1}]	Fraction of NEI 2020*
$PM_{2.5}$	484	20.0%
VOC	460	4.6%

*Excludes dust, biogenic, and fire (wild, prescribed and agriculture) sources

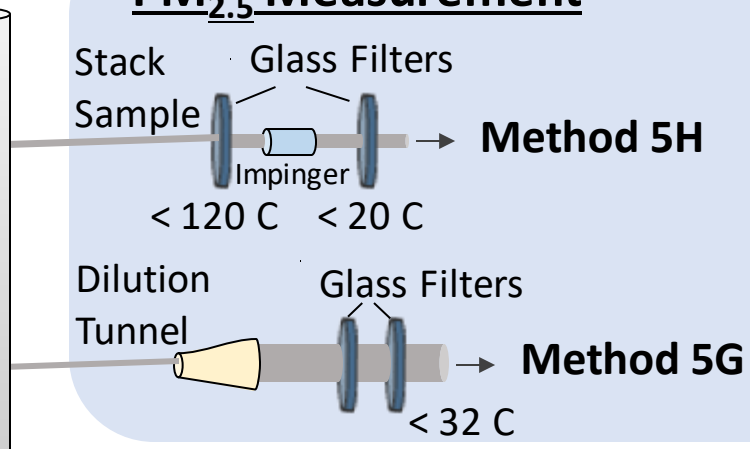
Standard methods for measuring RWC emission factors



- Glass filters collect PM mass
- Quartz Filters (not shown) measure OC and EC
- IVOCs and SVOCs may condense to the filter or break through
- *PM emission factor depends on the temperature and concentration of the sample (Robinson et al., 2011)*

Standard methods for measuring RWC emission factors

$PM_{2.5}$ Measurement



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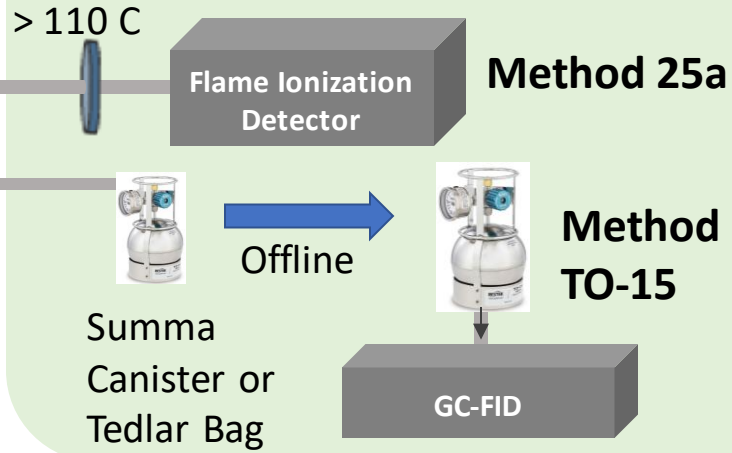
VOC Measurement



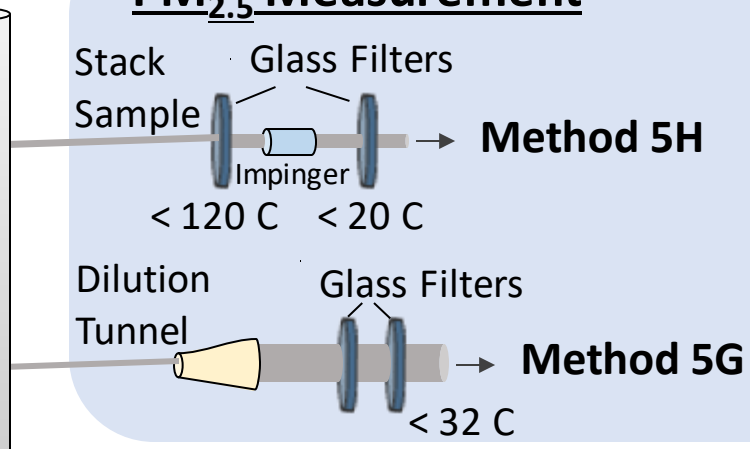
- Particles removed by the glass fiber filter before entering the Flame-Ionization Detector (FID).
- Uncertain losses to filters, canisters, and bags
- FID undercounts oxygenated carbons and doesn't count non-carbon atoms.
- *The total NMOG reported depends on definition and losses.*

These Methods are useful but may not capture the full extent of emissions.

Applying speciation profiles to these bulk metrics adds further uncertainties.

Standard methods for measuring RWC emission factors

$PM_{2.5}$ Measurement



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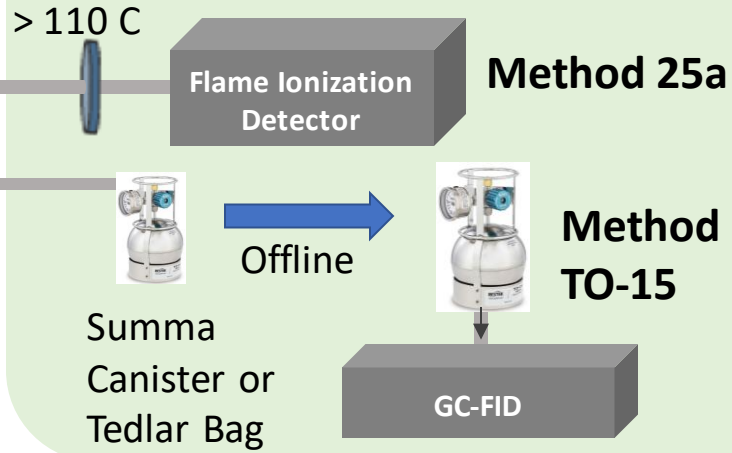

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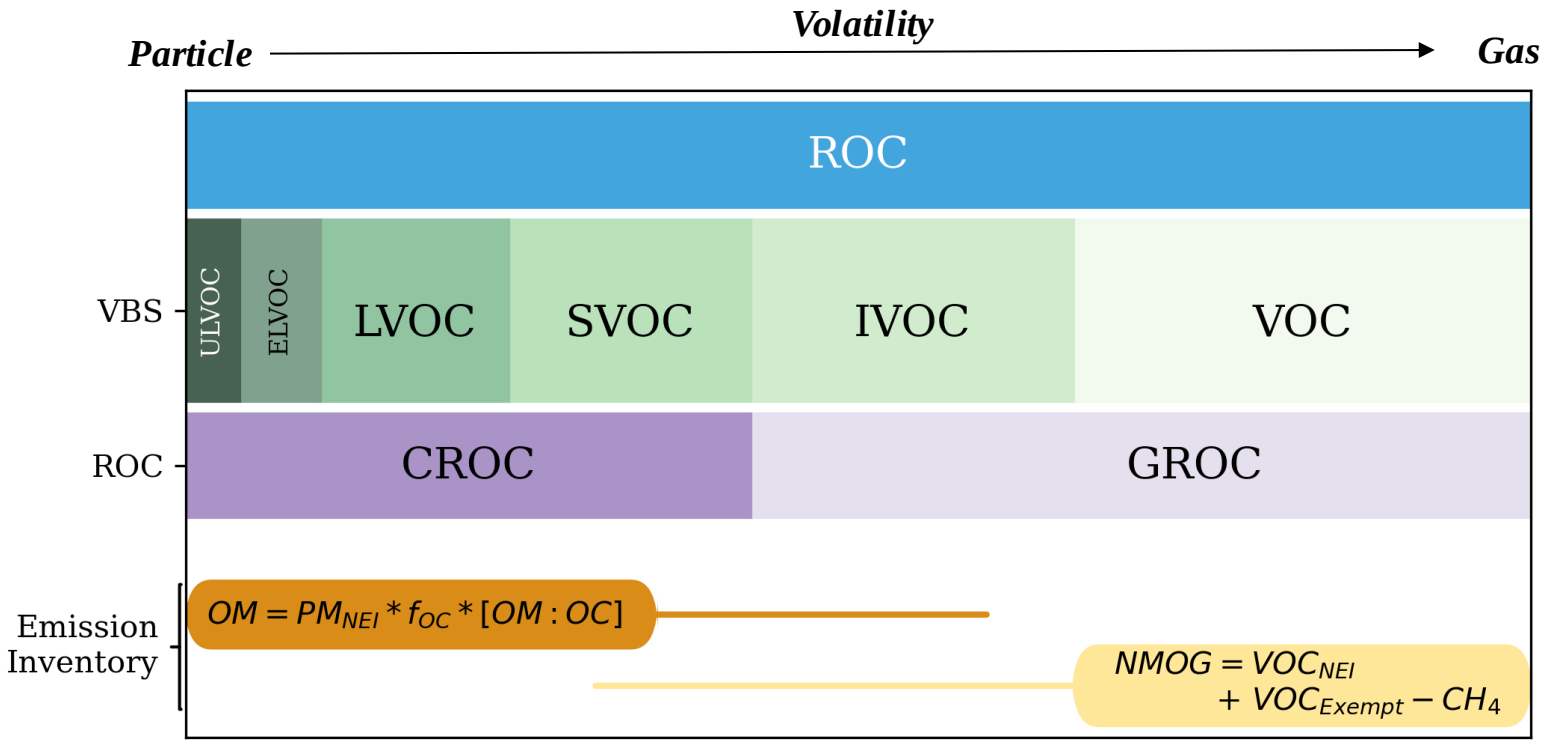
Research Questions:

1. Do these Methods account for the mass and character of all ***reactive organic carbon (ROC)*** emitted by wood-burning sources?
2. How can we translate these operational definitions of PM and VOC to standard definitions for use in the NEI and air quality modeling?
3. What is the impact on RWC carbon emissions and ambient organic aerosol?

Reactive Organic Carbon (ROC) Framework



- **CROC** (Condensable Reactive Organic Carbon) – compounds with volatility less than C20 (n-Eicosane).

  CROC = [SVOC + LVOC + ELVOC + ULVOC]

- **GROC** (Gaseous Reactive Organic Carbon) – compounds with volatility greater than C20.

  GROC = [IVOC + VOC]

- f_{OC} = organic carbon fraction from speciation profile
- OM:OC = ratio of non-carbon to carbon
- VOC_{Exempt} = gas-phase compounds exempted from the regulatory definition of VOC

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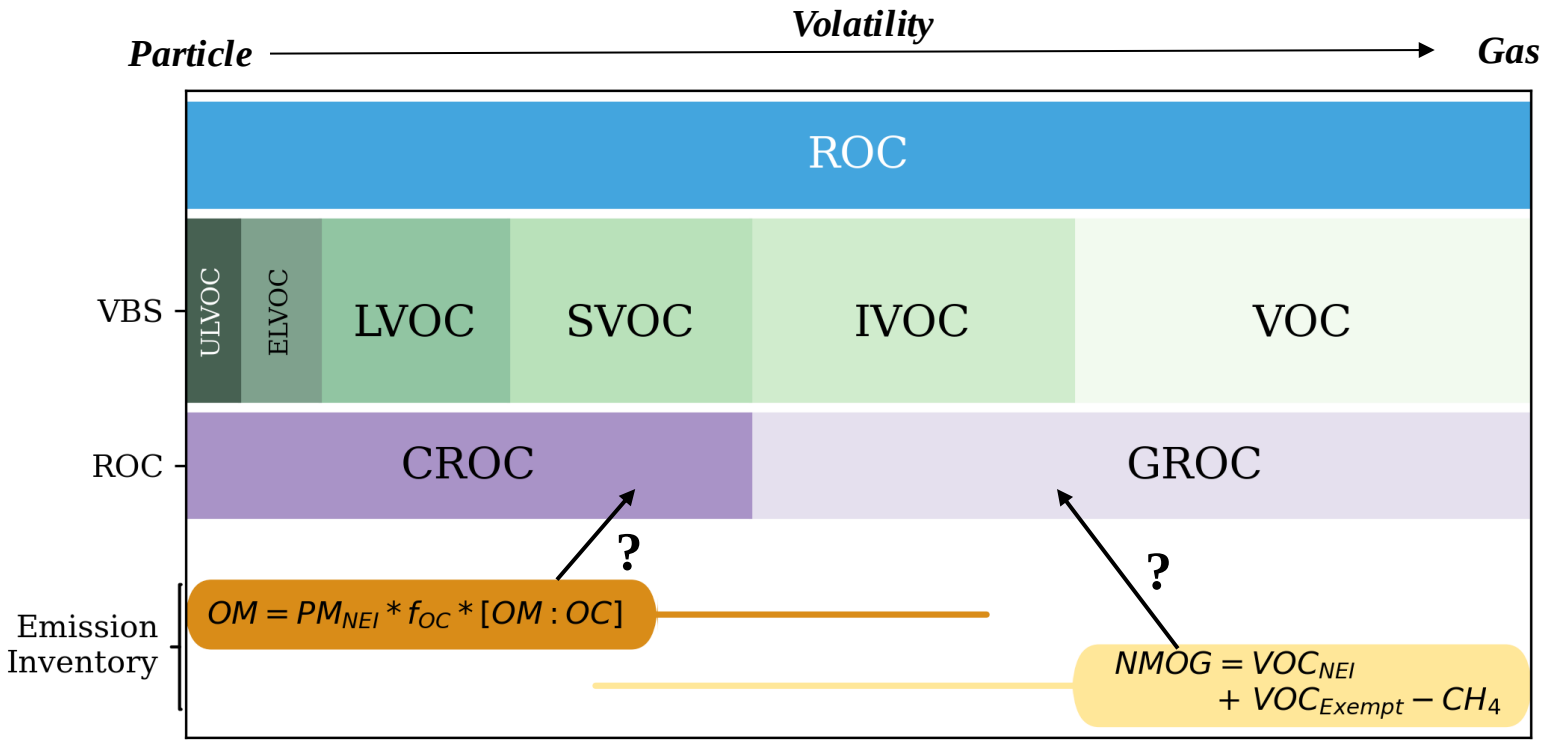

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Use a detailed speciation profile to simulate Test Method measurements

- 226 explicit species measured
- Semivolatile components quantified in both gas and particle phases.
- EC fraction = 1.4%
- NMOG/OM = 2.1
- Unresolved non-methane organic gas = 8.1%
- Unresolved particle = 61%

Fireplace pine smoke reported by Schauer et al. (2001) and Nolte et al. (2001)

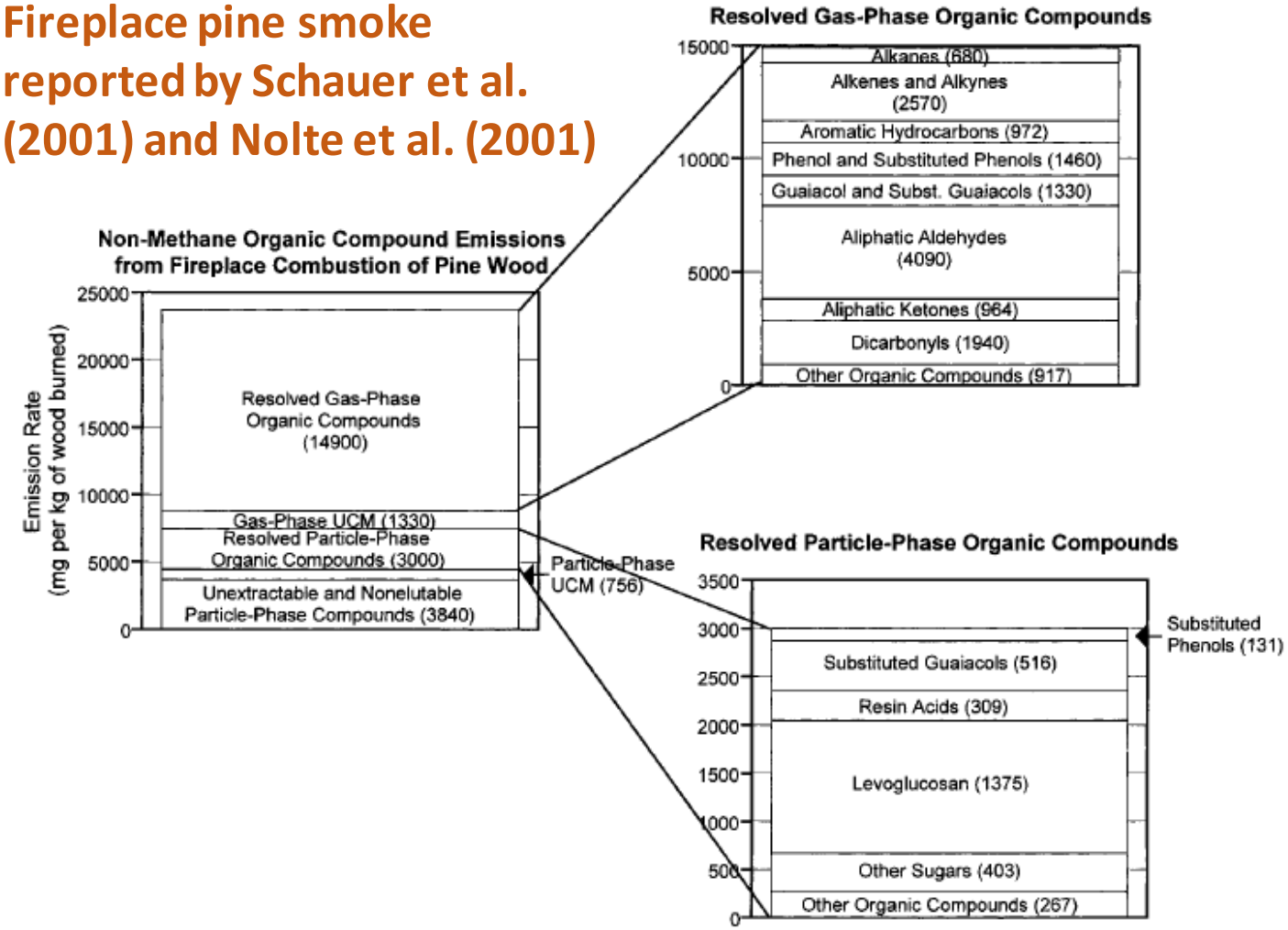
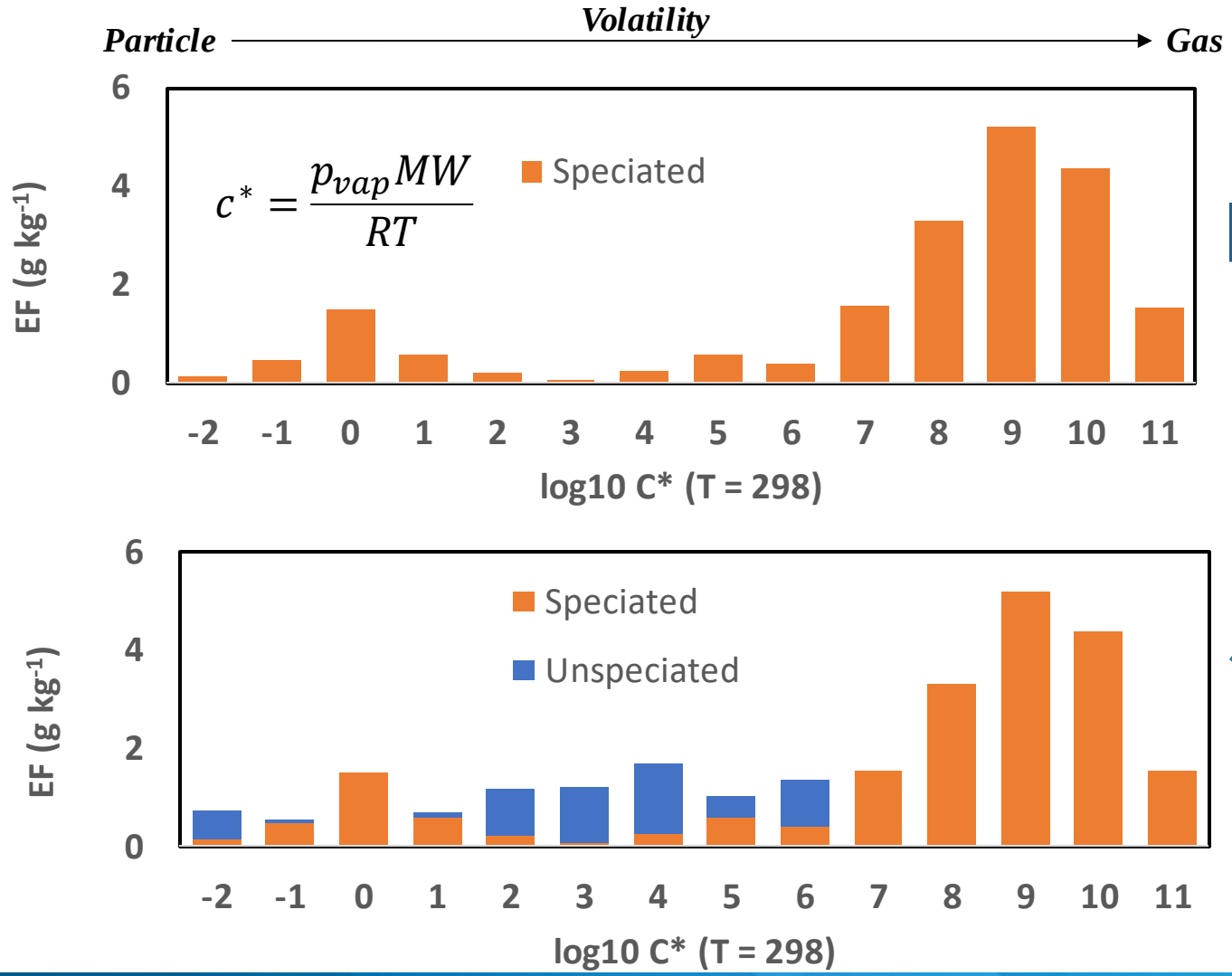
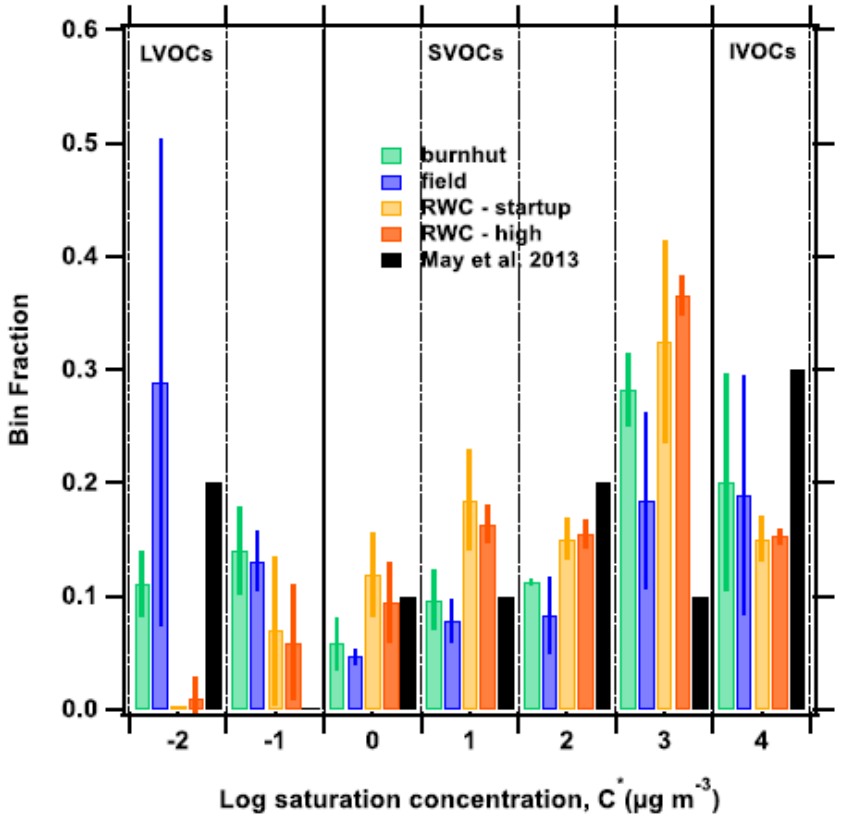


FIGURE 1. Mass balance on the non-methane organic compounds emitted from the fireplace combustion of pine wood.

Schauer et al. (2001): https://pubs.acs.org/doi/full/10.1021/es001331e
Nolte et al. (2001): https://pubs.acs.org/doi/full/10.1021/es001420r

Assign unspeciated mass to reproduce observed volatility trends





Woodsmoke volatility distribution (Sinha et al., 2022)

https://pubs.rsc.org/en/content/articlehtml/2023/ea/d2ea00080f

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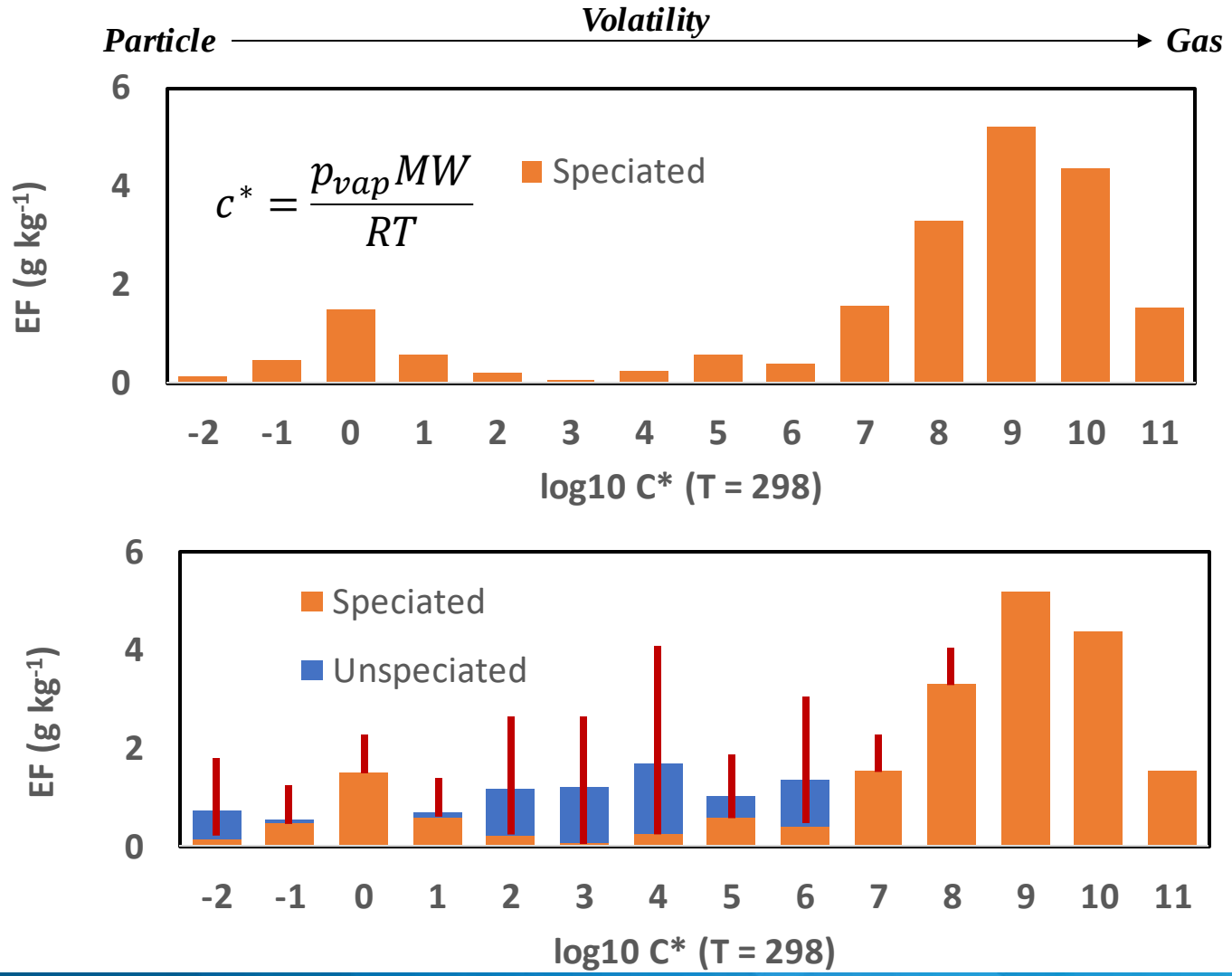
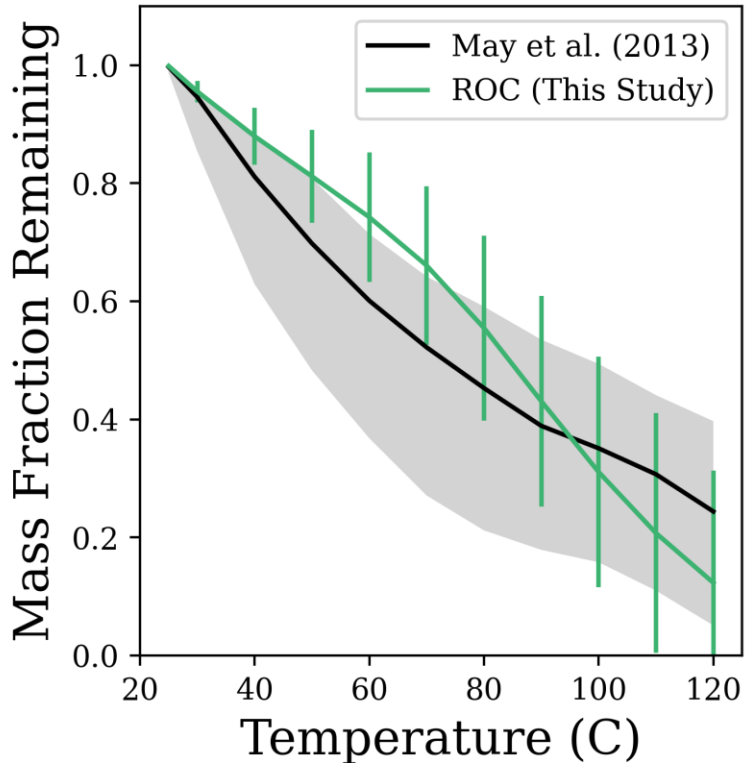


PM temperature sensitivity is similar to that observed in previous biomass burning studies



1,000 Monte Carlo Runs varying Unspeciated Emission Factors and O:C

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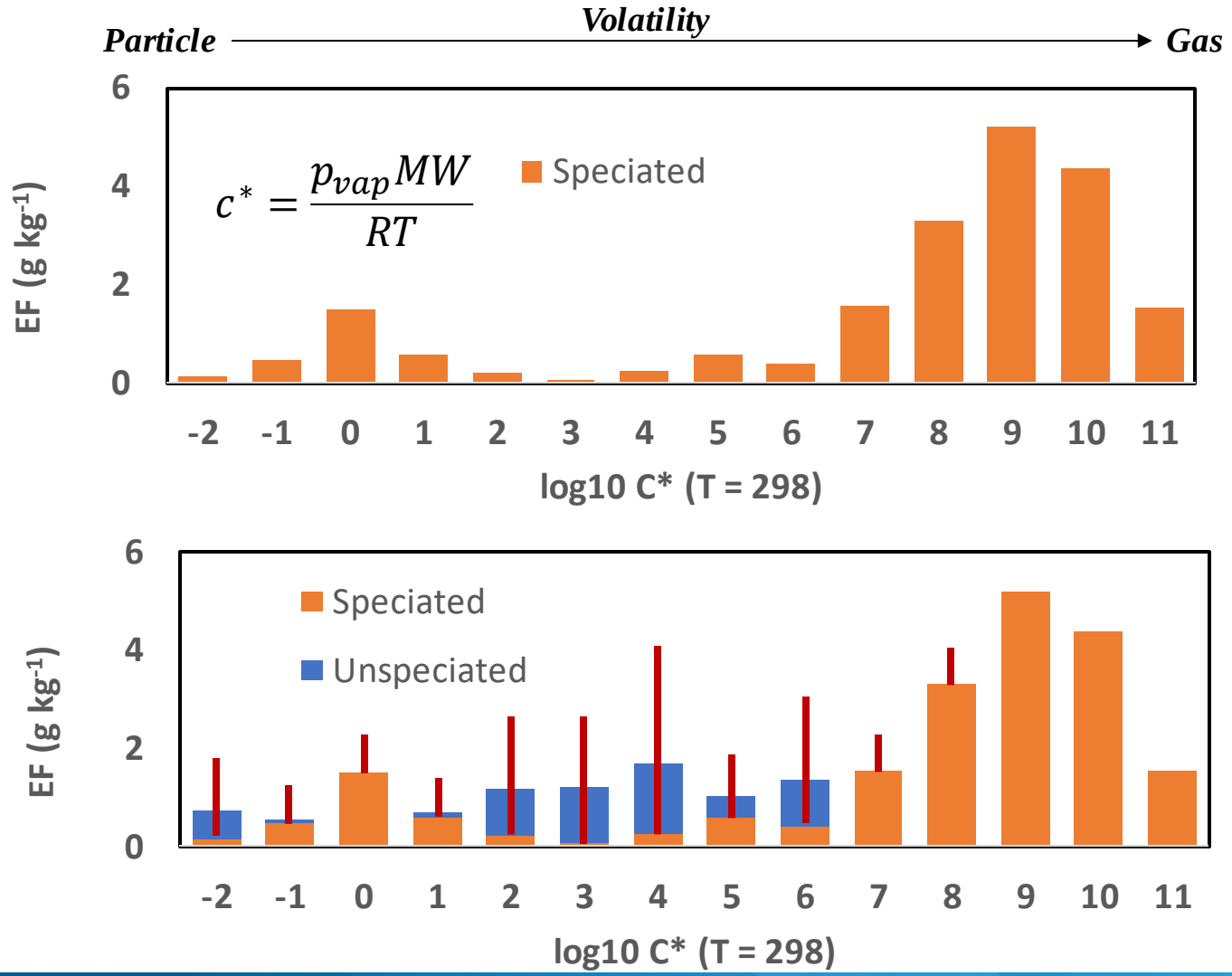

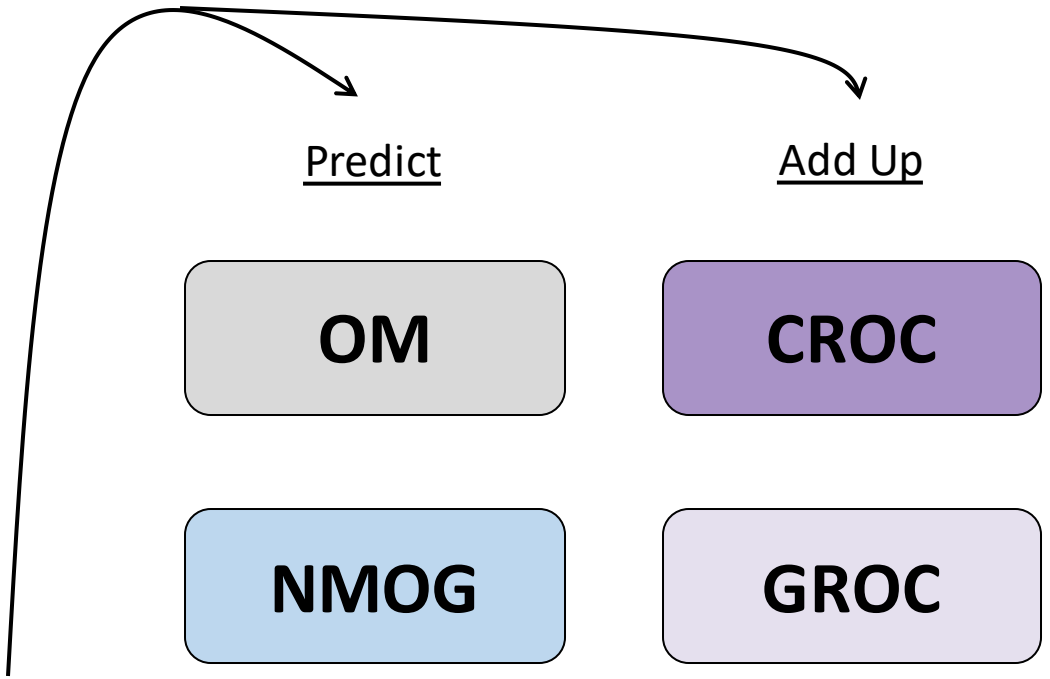

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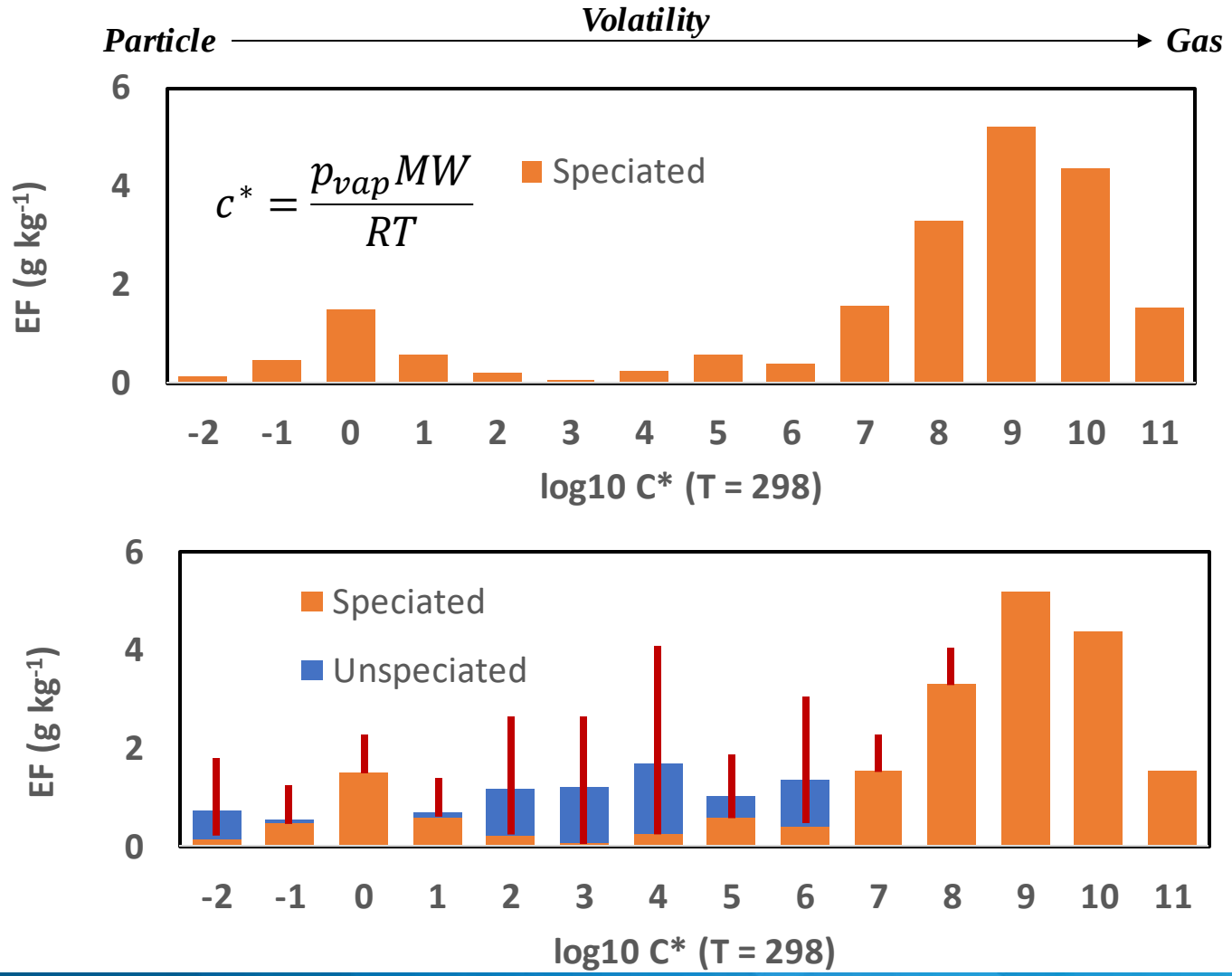

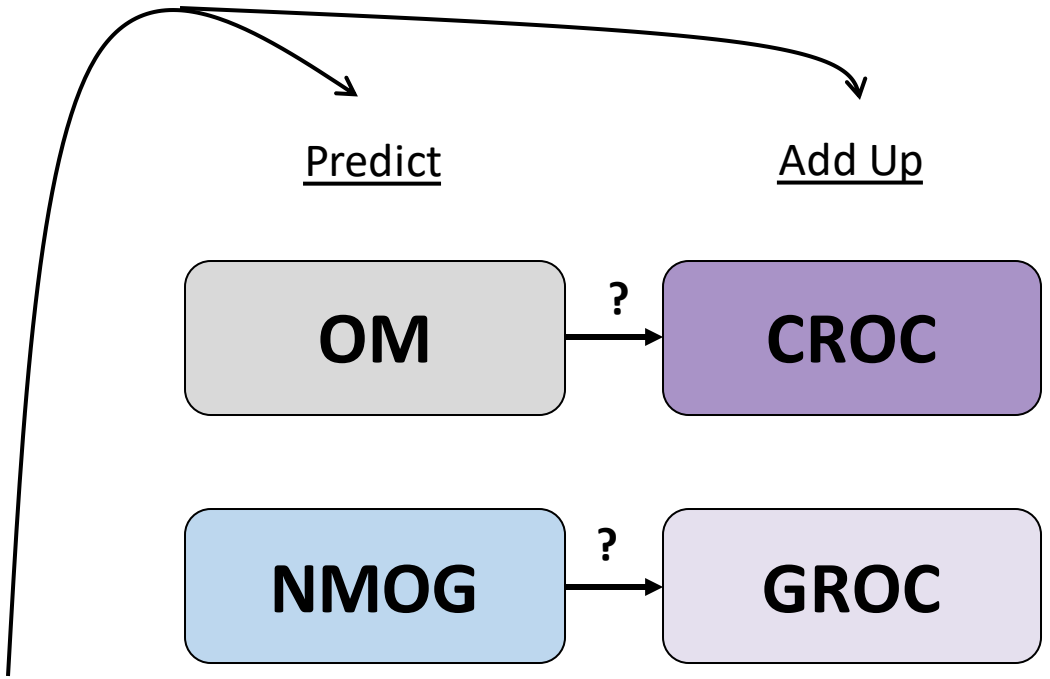

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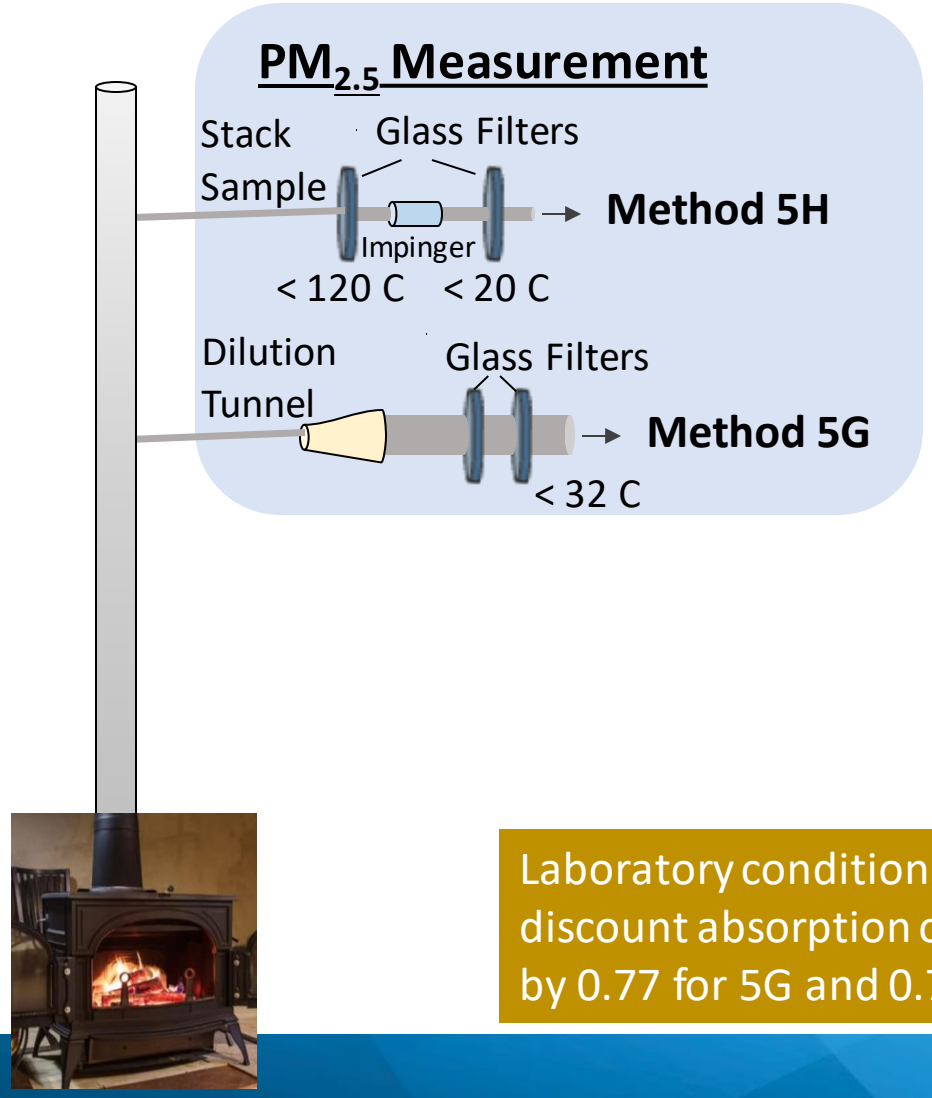
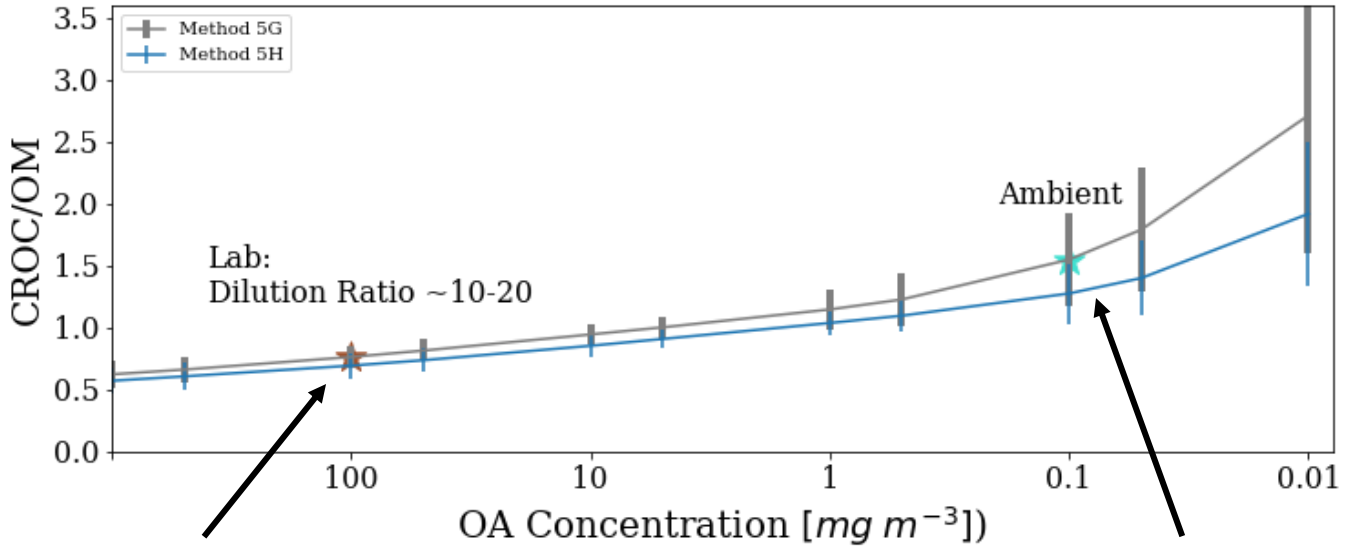
Impact of partitioning on Method 5G and 5H measurements



$$\text{CROC/OM} = \frac{\text{Sum EFs for CROC compounds from Schauer profile}}{\text{Calculate particle-phase EF given filter temperature and OA conc.}}$$



Laboratory conditions –need to discount absorption of IVOCs. Multiply by 0.77 for 5G and 0.72 for 5H.

Ambient conditions –need to add SVOCs broken through the filter. Multiply by 1.55 for 5G and 1.27 for 5H.

Impact of partitioning and functionality on FID detection

Method TO-15

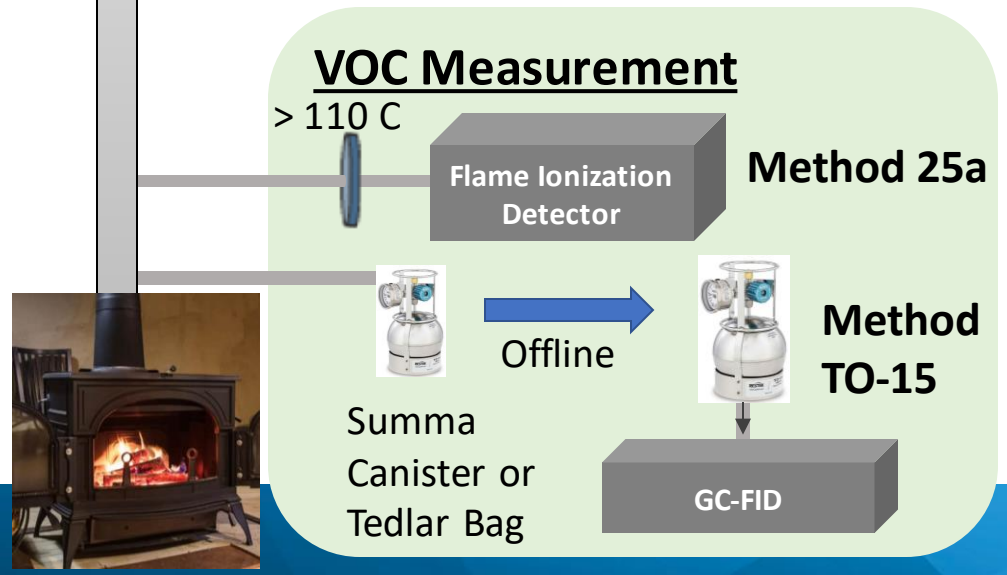
Canisters and bags:

VOCs ✓

IVOCs ✗

Lu et al., *Atmos, Chem and Phys.* 2018.
https://acp.copernicus.org/articles/18/17637/2018/

→ Temperature independent correction



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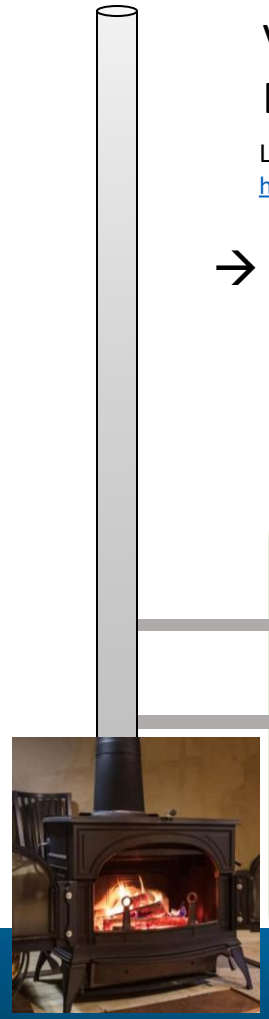
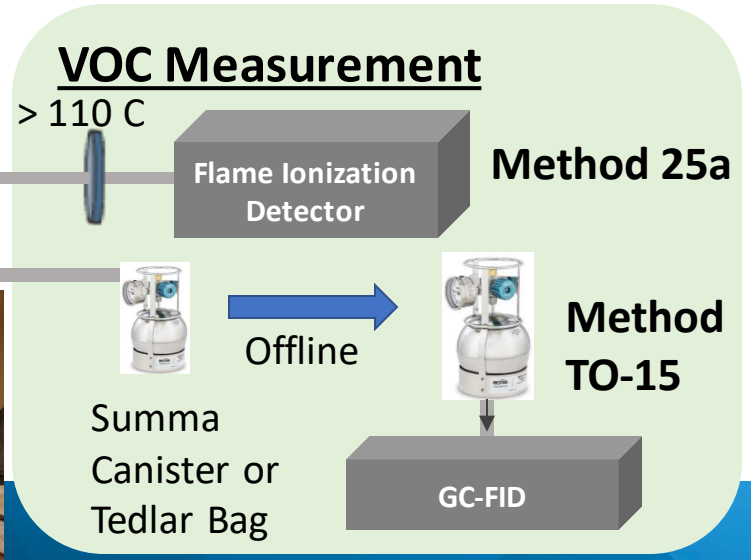
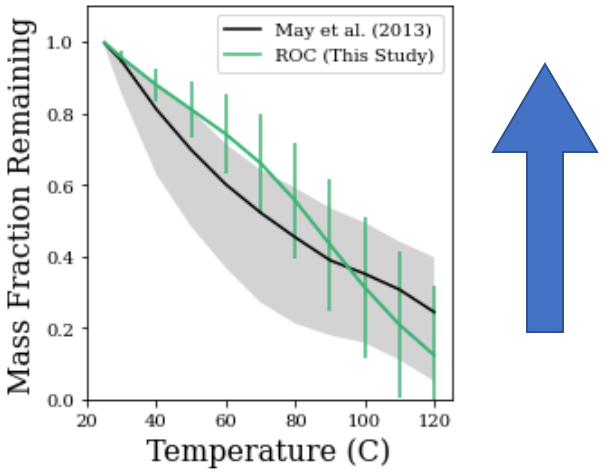


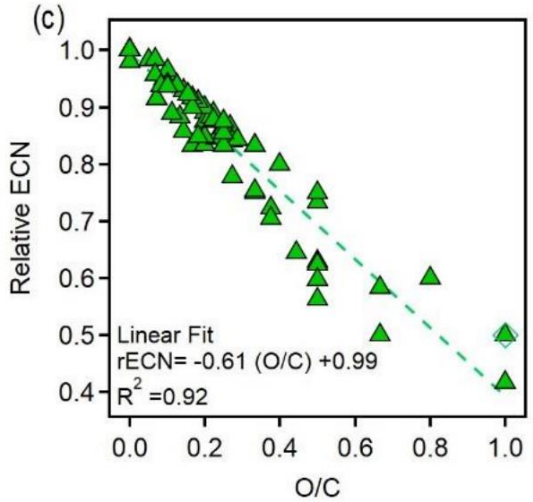


Method 25a

Inline FID with glass filter (110 C)



May et al., *Journal of Geophys. Res.* (2013)
https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/jgrd.50828



Hurley et al. *Atmos. Meas. Tech.* (2020)
https://amt.copernicus.org/preprints/amt-2020-44/amt-2020-44.pdf

Impact of partitioning and functionality on FID detection

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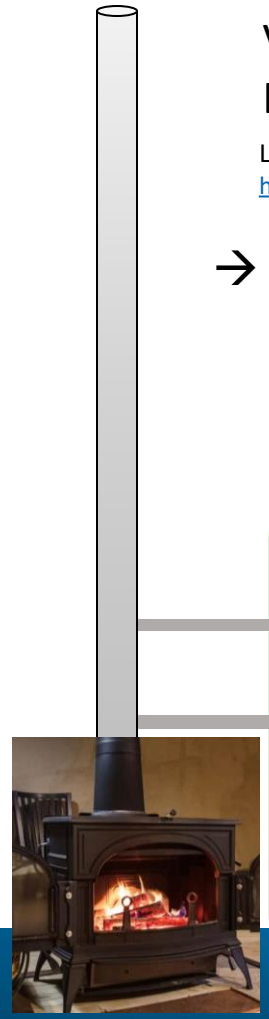
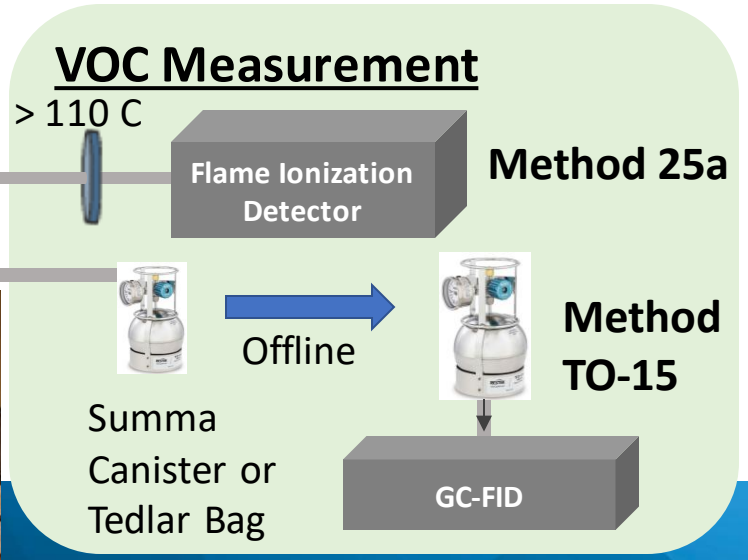
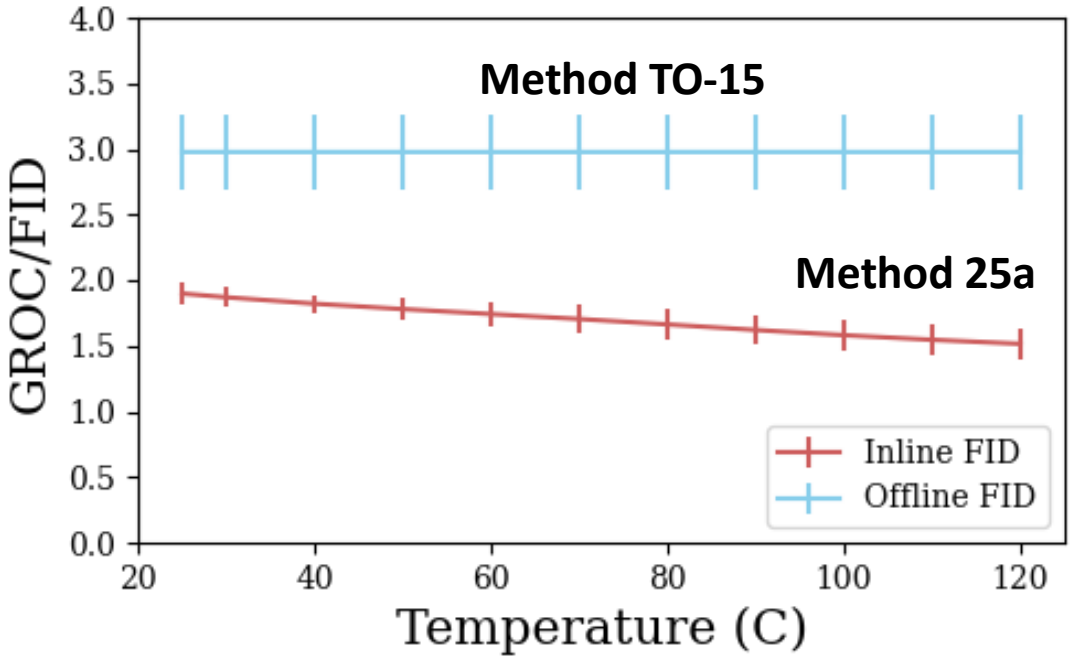




Method 25a

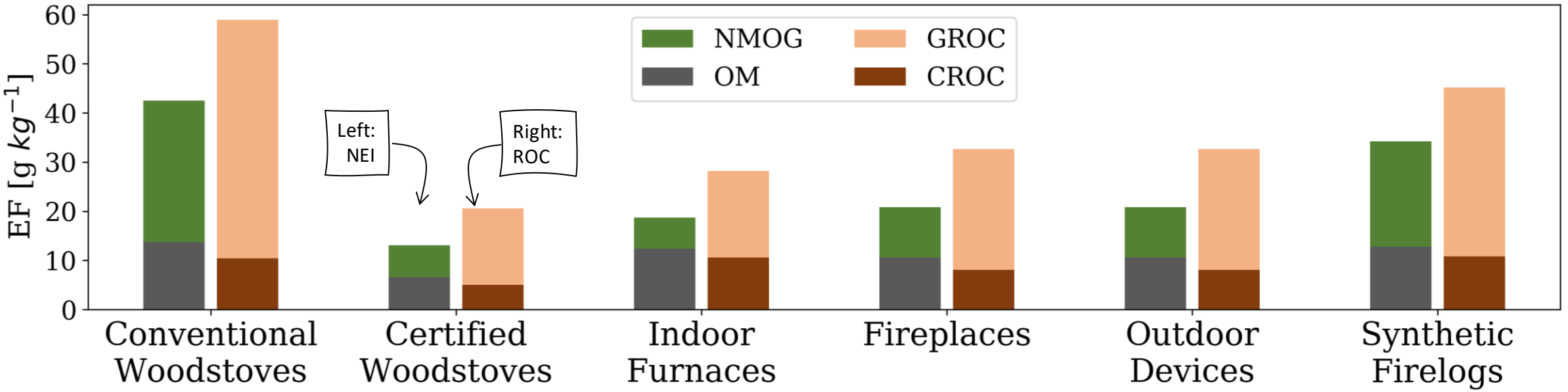
Inline FID with glass filter (110 C)



GROC/FID: Method TO-15 → Multiply by 3.0

Method 25a → Multiply by 1.6 (assuming 110 C)

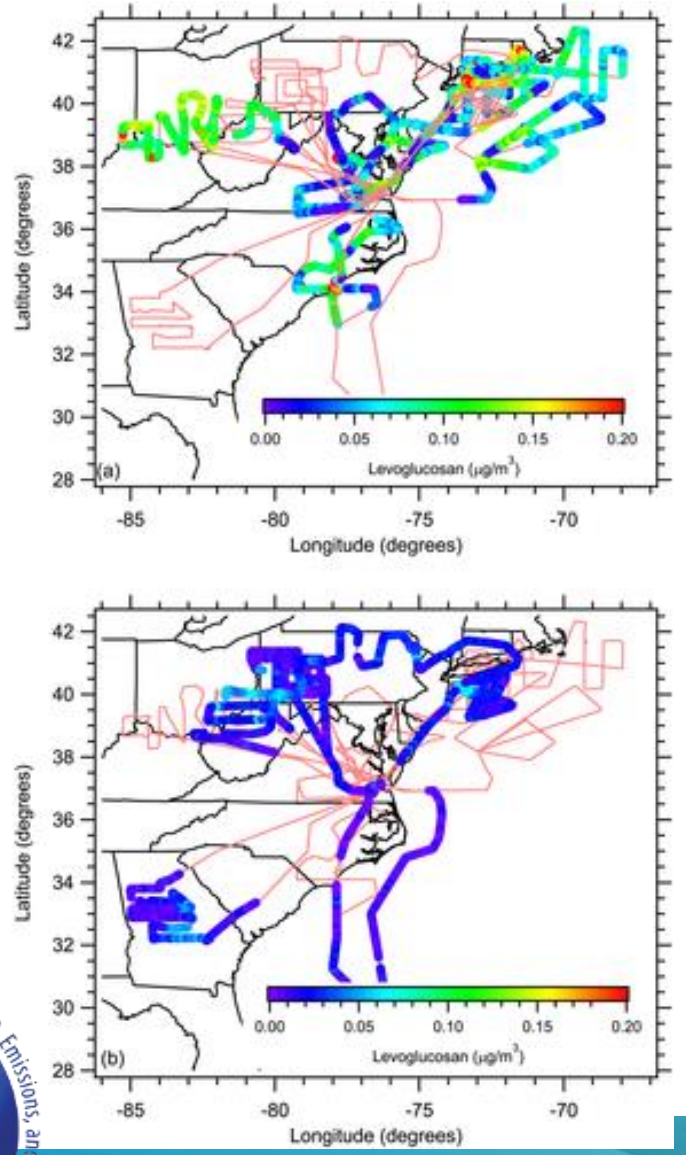
Impact of update on RWC emission factors



Total ROC increases (32-56%), but part of CROC will evaporate at ambient conditions.

Simulate WINTER Campaign with CMAQ

Levoglucosan Measurements



January 29 – March 13, 2015

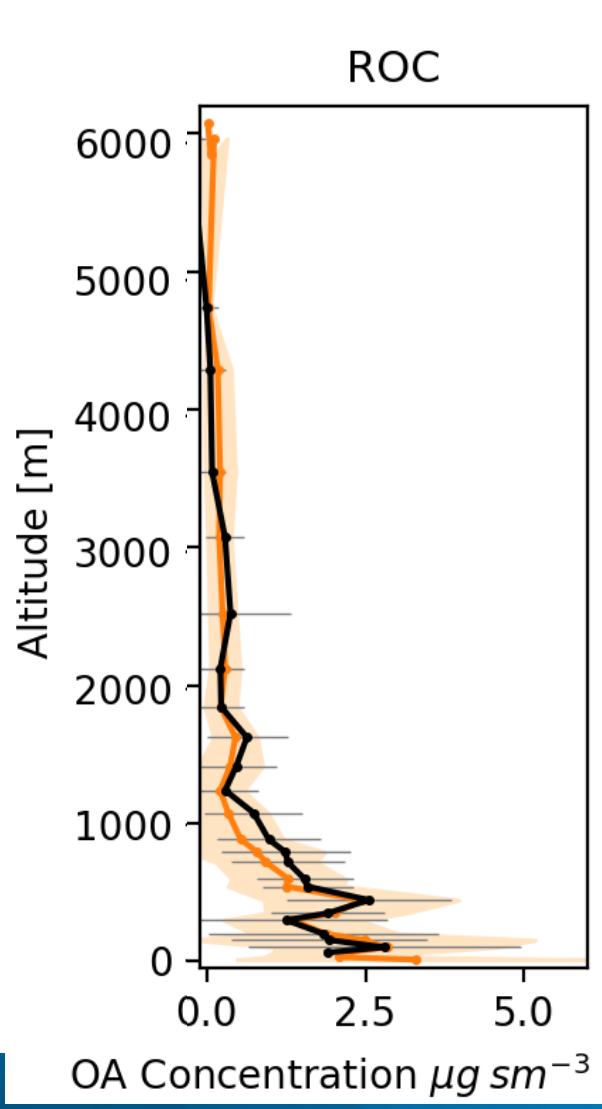
GEOS-Chem simulates OA, HOA, BBOA, and OOA well with semivolatile POA and SIMPLE SOA approaches (Schroder et al., 2018; Shah et al., 2019)

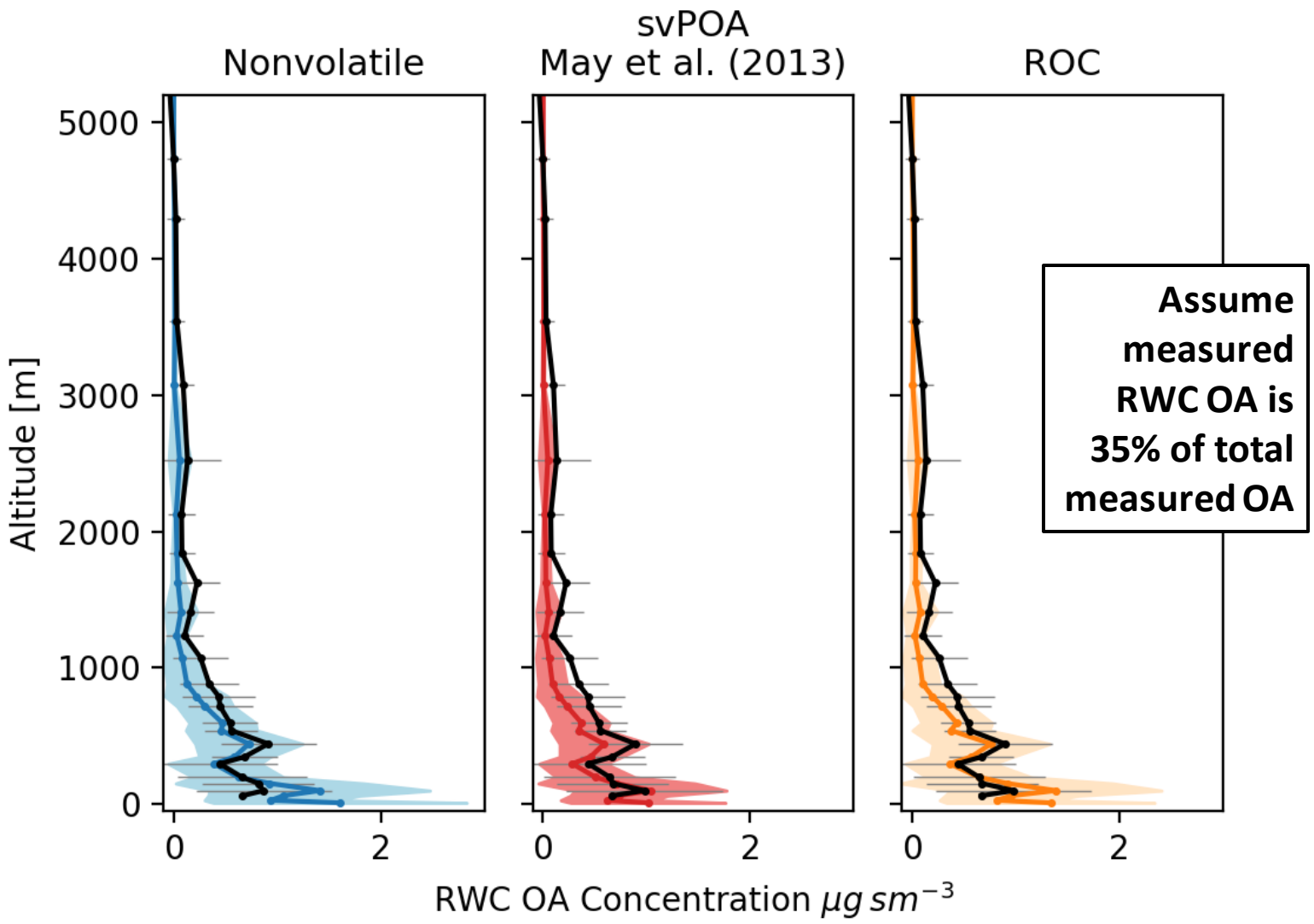
- 2011 NEI POA was reduced by 50% based on preliminary evaluations
- Residential Wood contributes 30-100% to the organic aerosol burden (Sullivan et al., *JGR*, 2019)

CMAQ Simulations

- EPA Air Quality Time Series Project (EQUATES) emissions for 2015
- Cases:
  1. Carbon Bond v6 with Nonvolatile POA
  2. Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM) with svPOA (May et al., 2013)
  3. CRACMM with new ROC emission factors

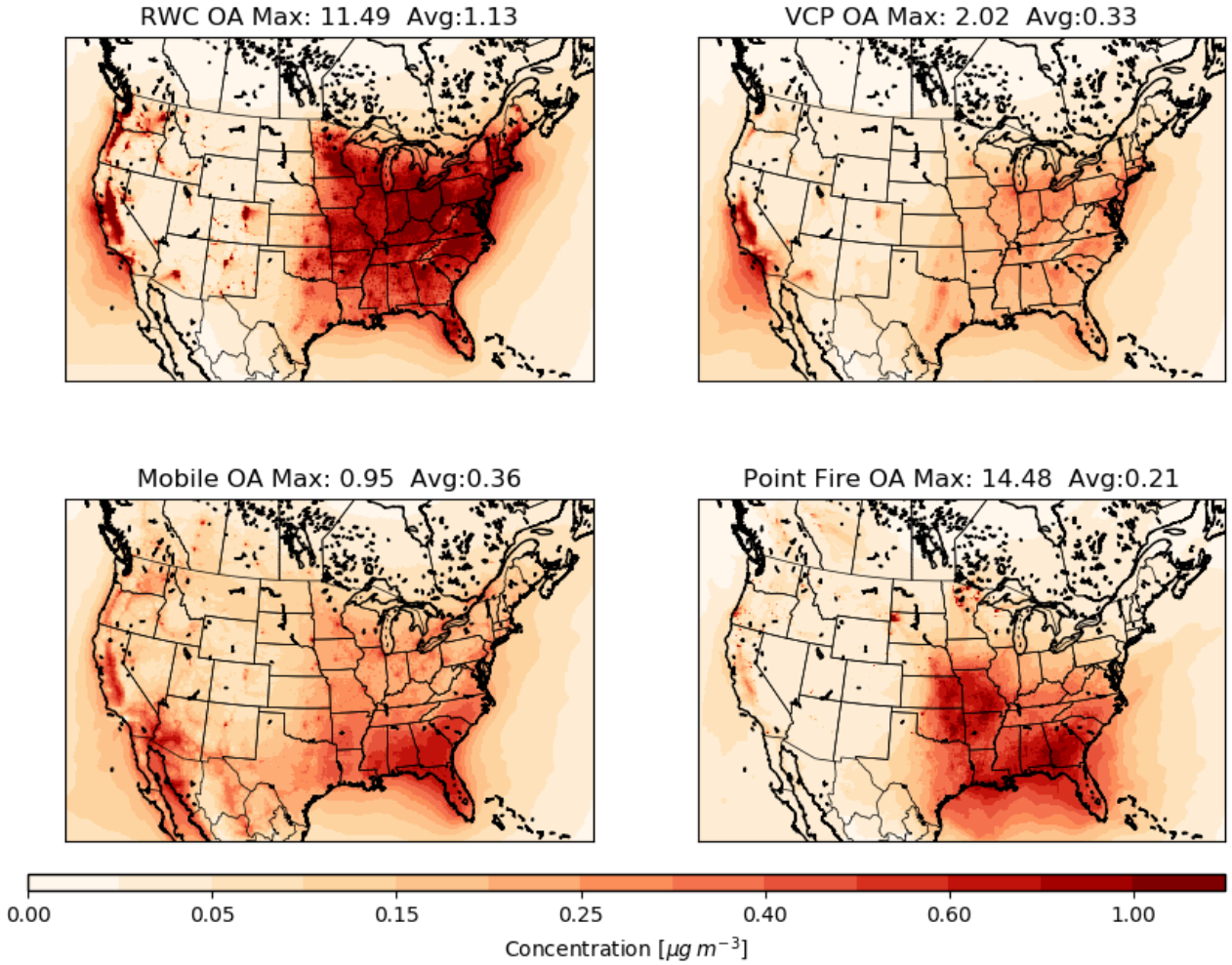
Impact of update on CMAQ predictions for WINTER Campaign

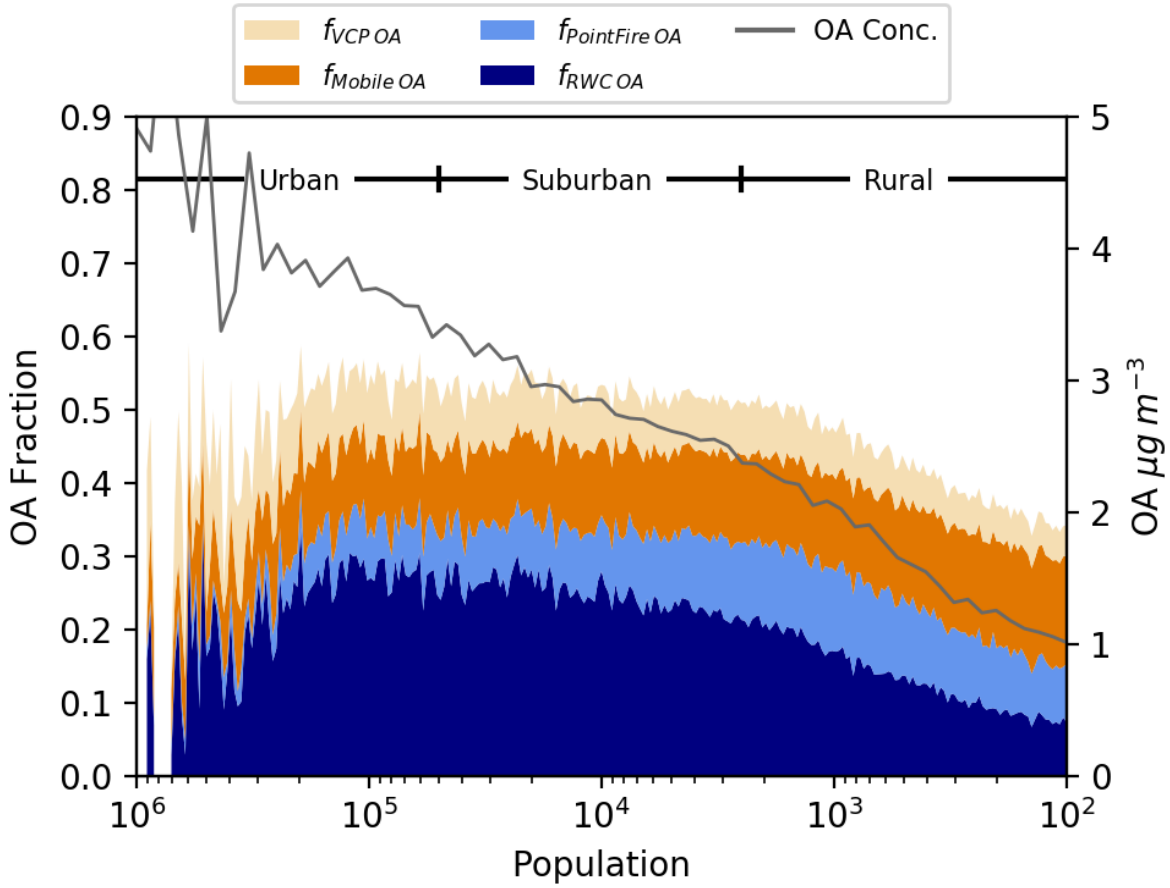




Assume measured RWC OA is 35% of total measured OA

Impact of update on CMAQ predictions for WINTER Campaign





*Averages are population-weighted

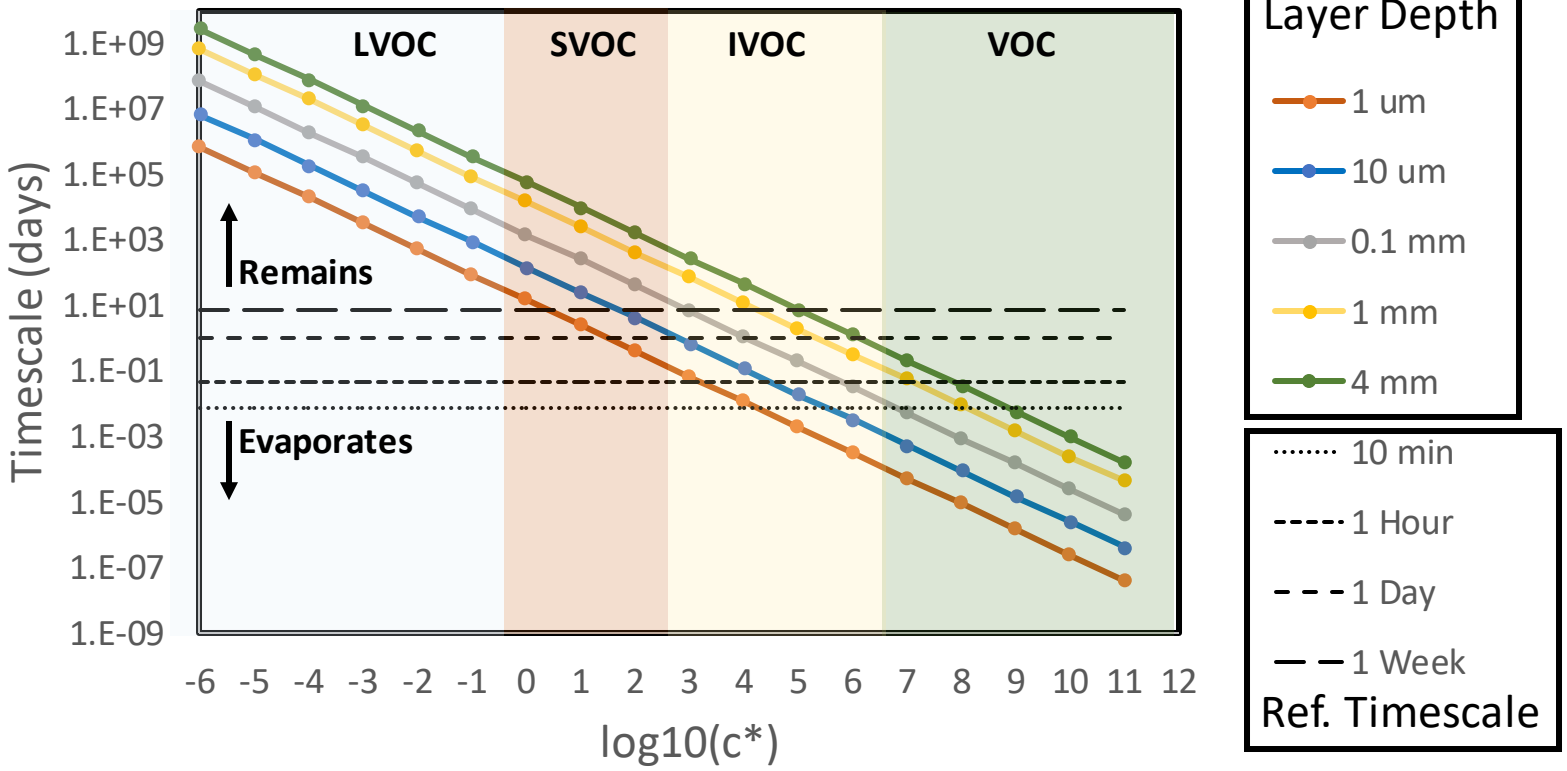
Summary

- Proposed revised emission factors for conventional wood stoves and similar combustion sources.
- Total ROC increases by 30-50%. This mass is potentially *missing* in the NEI.
- Wood-Burning OA in CMAQ averages 1.13 µg m^{-3} for Jan-Mar, 2015.
- HAP predictions are essentially unchanged.
- Filter handling is more complicated than treated here.

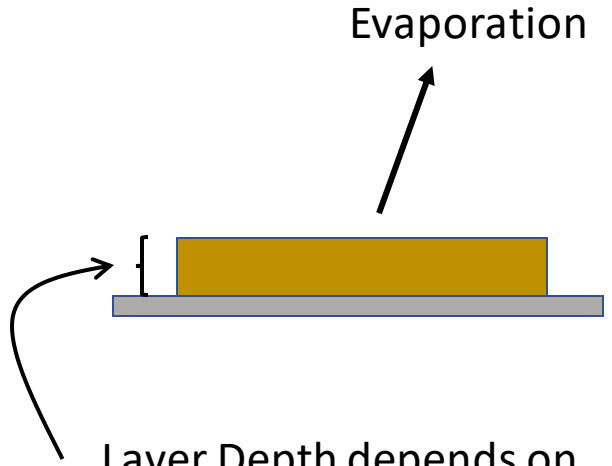
Contact: murphy.ben@epa.gov

Evaporation lifetimes of organic compounds during filter processing

Evaporation Timescales at Varying Depth

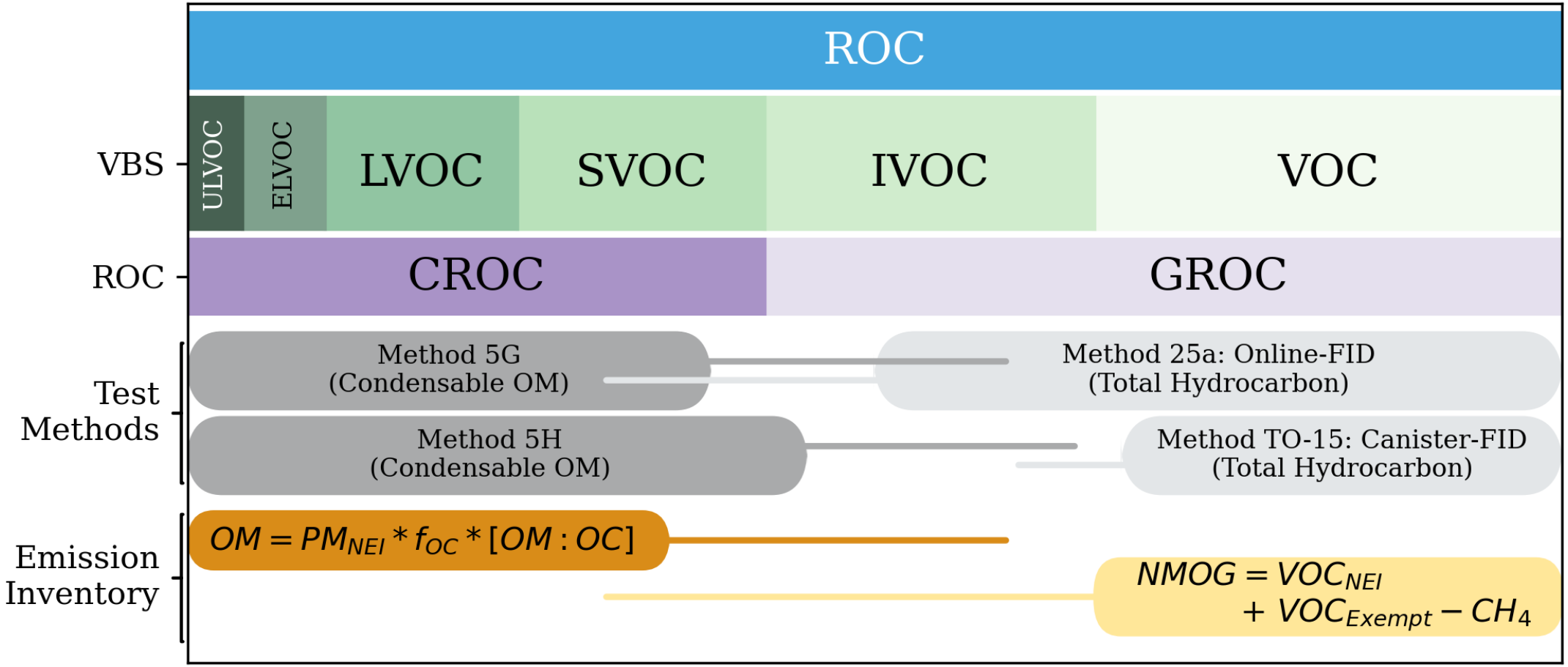


Filters offgas for 1-5 days before weighing.



Adapted evaporation timescale calculation from Seltzer et al. (*ACP,* 2021) designed for VCP emissions.

Relationship between ROC and Test Methods

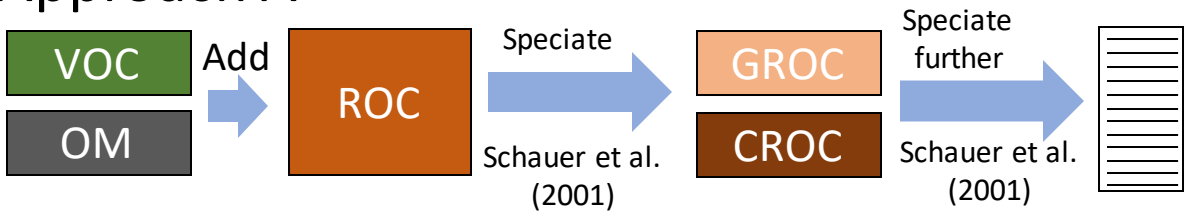


Determine Method basis for each RWC source

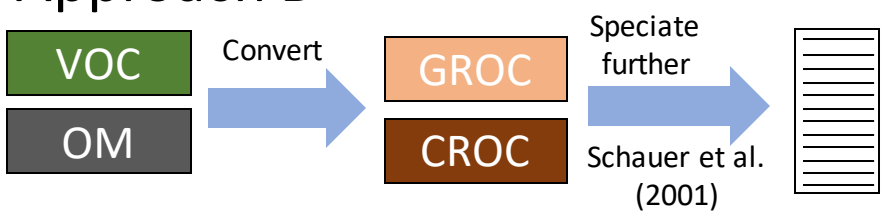
Reference 2020 NEI Technical Support Document, AP-42 and supporting studies.

SCC Description	Particulate	VOC	Approach
Conventional Woodstoves	Method 5H	Tedlar Bag (TO-15)	A
Certified Woodstoves	Method 5H	Tedlar Bag (TO-15)	A
Indoor Furnaces	Method 5G	Method 25a	B
Fireplaces	Method 5H	Canister (TO-15)	A
Outdoor Wood Burning Devices	Method 5H	Tedlar Bag (TO-15)	A
Synthetic Firelogs	Method 5G	Method 25a	B

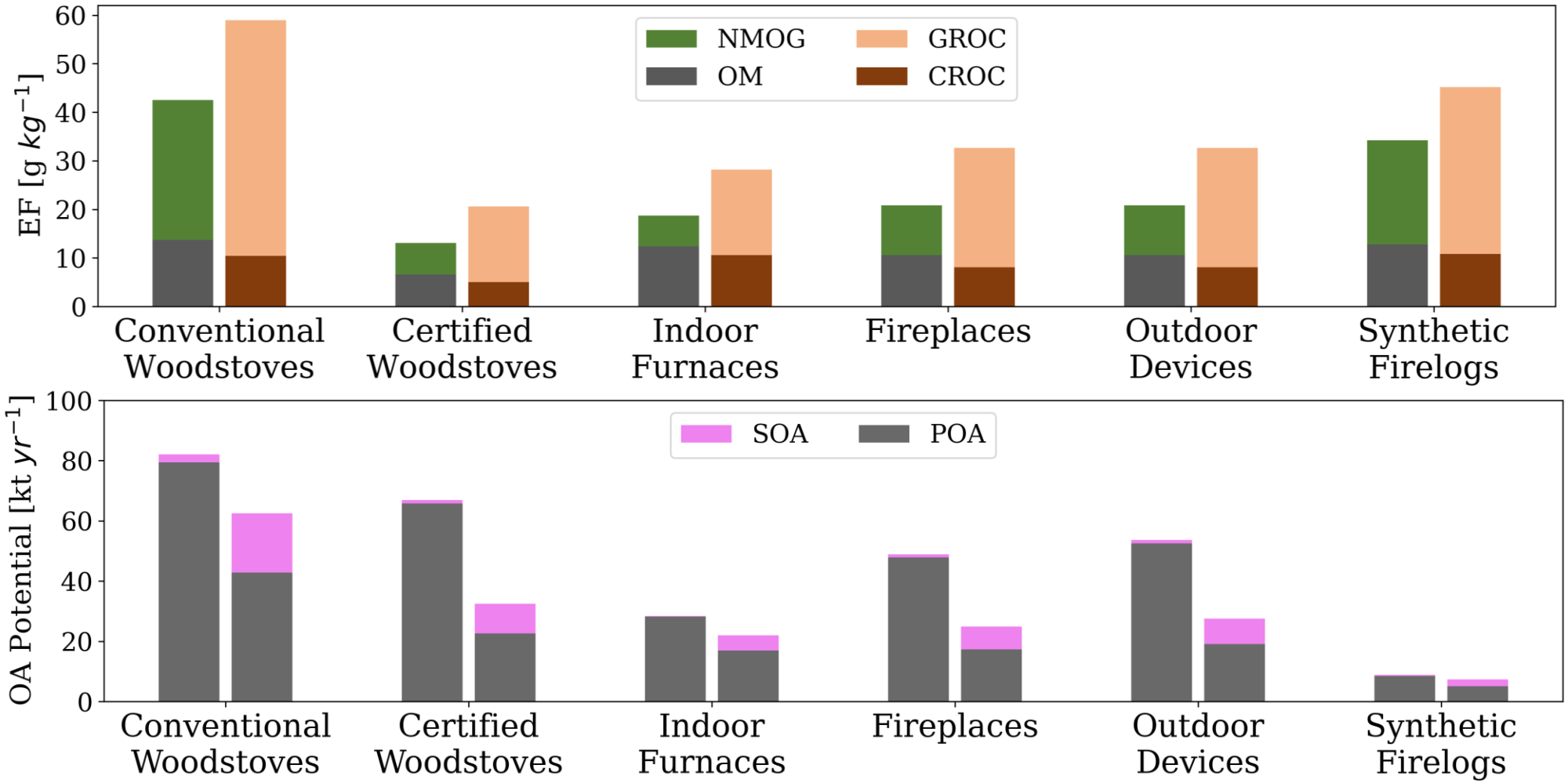
Approach A



Approach B

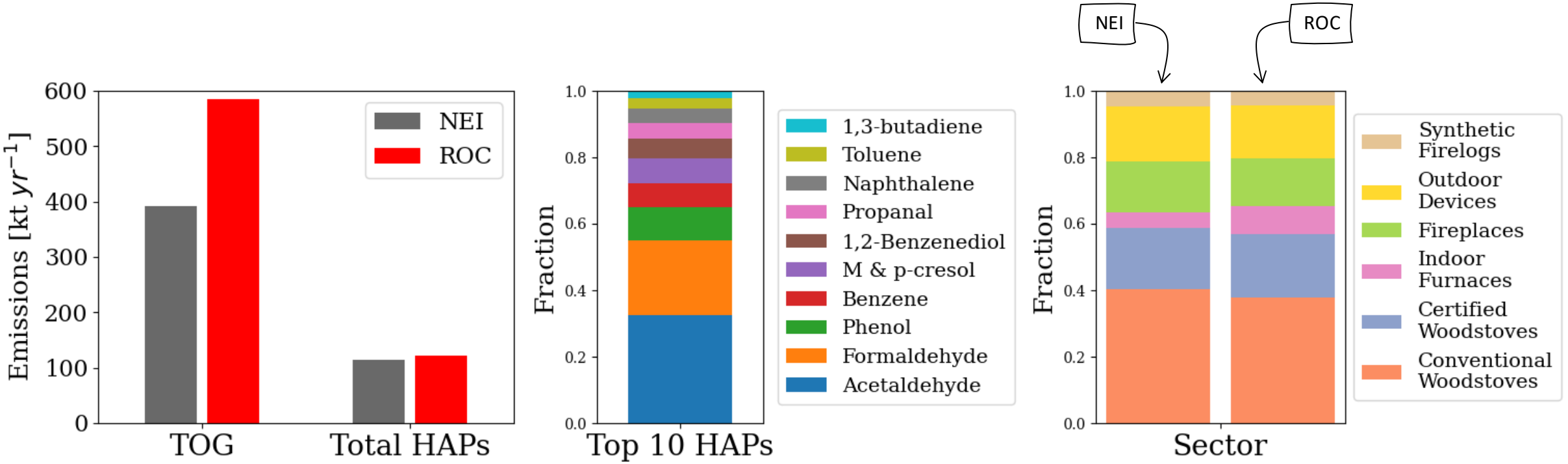


Impact of update on RWC emission factors and OA potential



Account for activity, POA partitioning and 1st-generation SOA yields

Impact of update on hazardous air pollutants



Total TOG emissions increase by 50% but HAP emissions stay roughly the same.