Accounting for Organic Compound Volatility in Standard Emissions Speciation Profiles, Databases and Models

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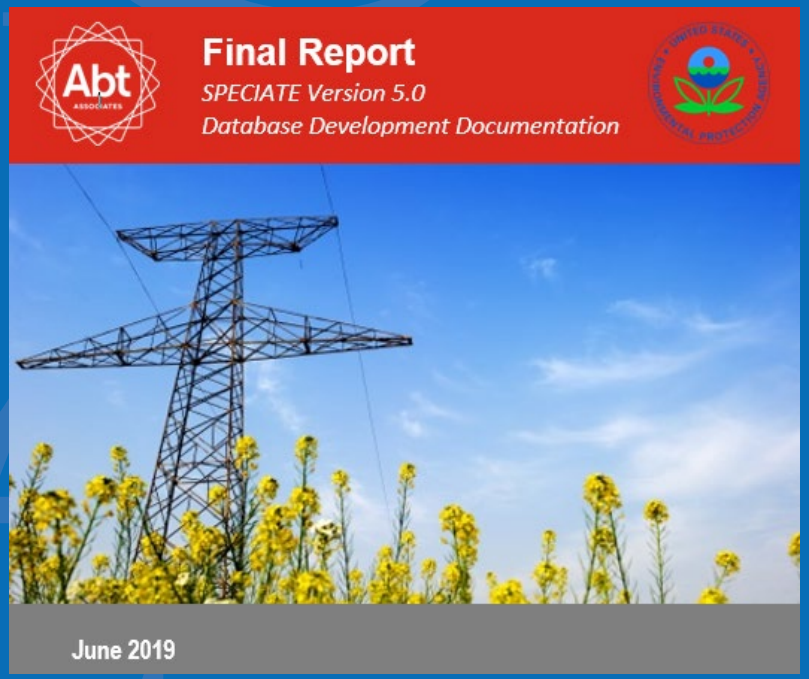

Emission Inventory Conference
Dallas Texas July 29-August 2, 2019

Office of Research and Development
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Outline

- What we have learned about semi-volatile VOCs and intermediate volatility VOCs (IVOCs) from the laboratory measurements of combustion
- Example of how Volatility Basis Set (VBS) improves air quality modeling
- Updates to SPECIATE for combustion profiles
- Where do we go from here

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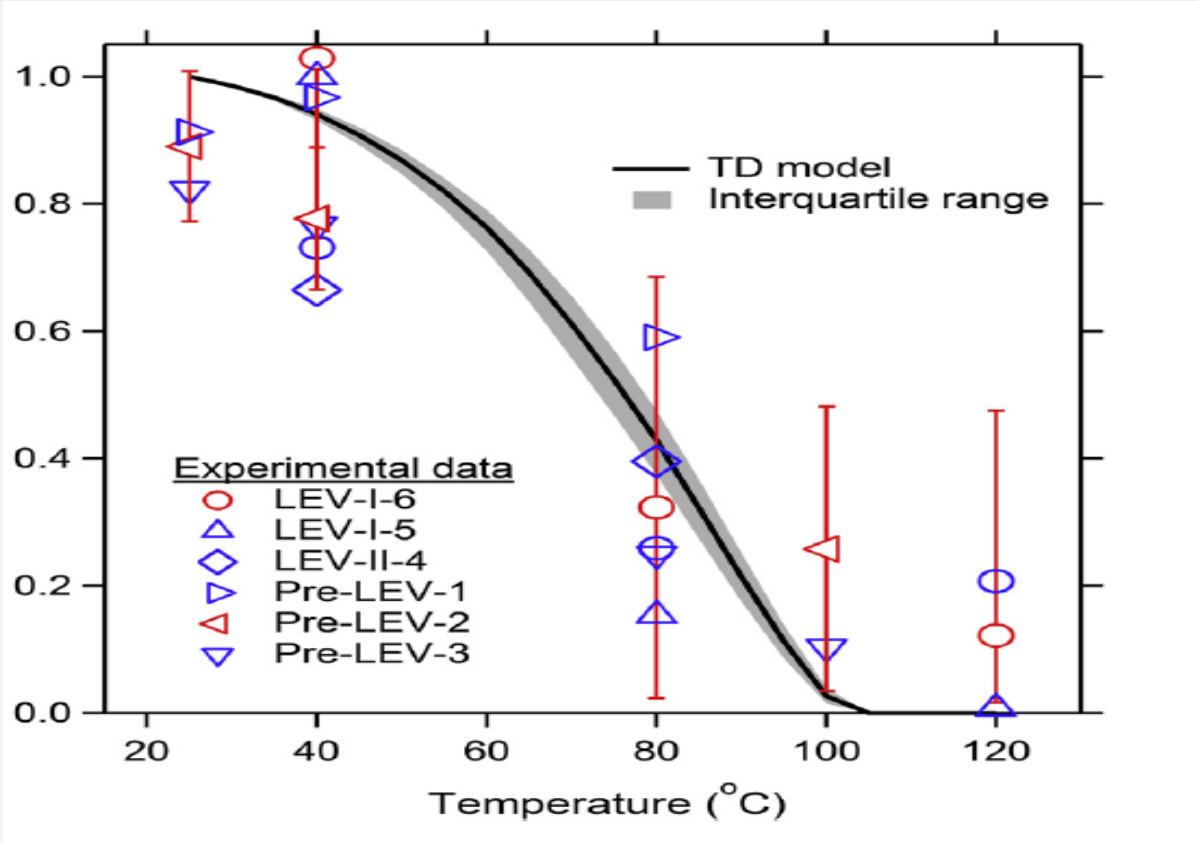
Definitions

- **VBS**: Volatility Basis Set (ordered from low to high volatility)
  - **LVOCs**: low volatility organic compound (particle at ambient conditions)
  - **SVOCs**: semi-volatile organic compounds
  - **IVOCs**: intermediate volatility organic compounds
  - **VOCs**: Volatile Organic Compounds as defined by EPA

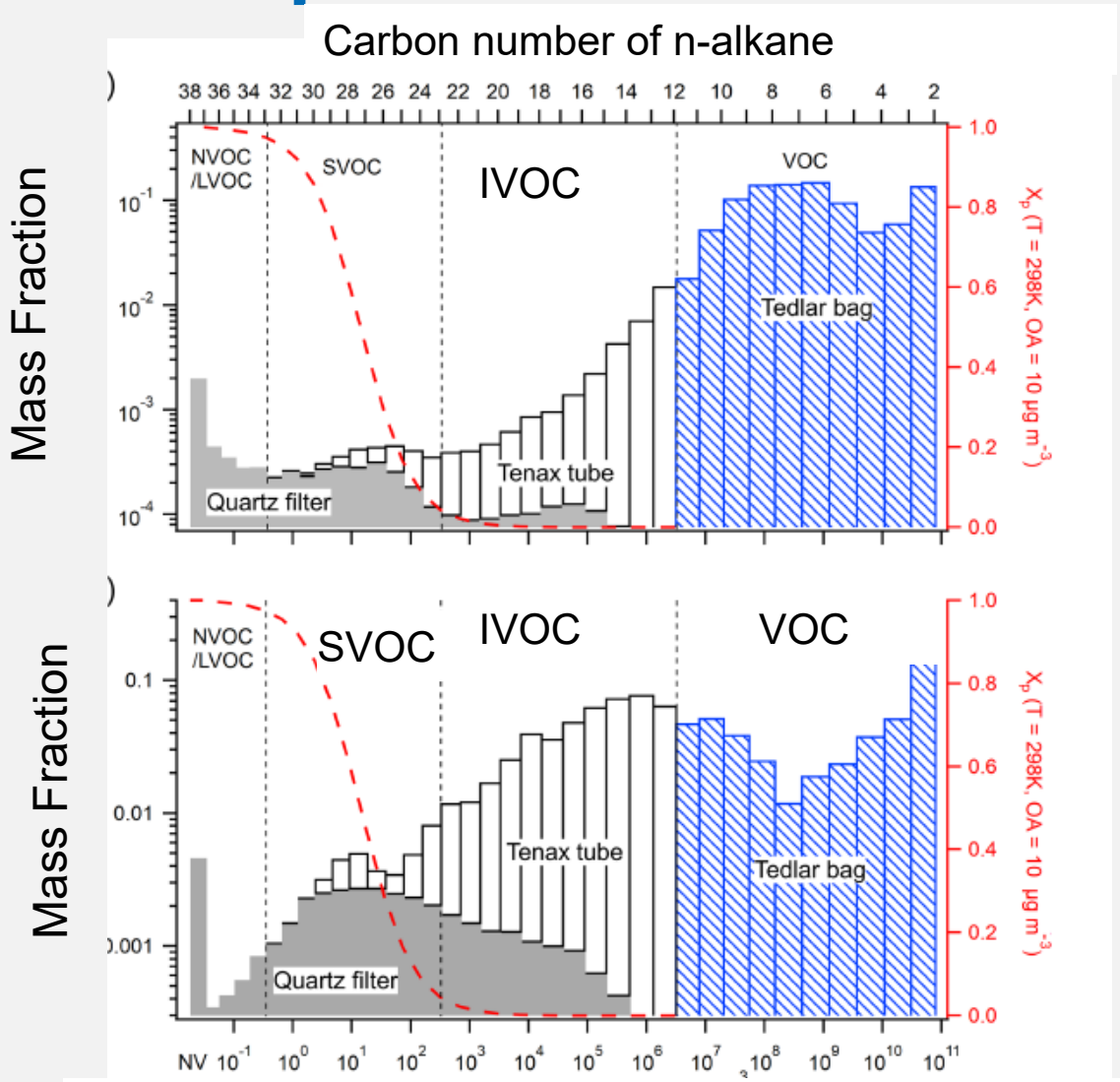
Chamber and Lab Measurements of Primary Organic Aerosol Gas-Particle Partitioning:

Particle emissions respond to temperature when measuring emission rates in a lab



May, et. al. "Gas-particle partitioning of primary organic aerosol emissions: (1) Gasoline vehicle exhaust' **Atmospheric Environment. 2013.**

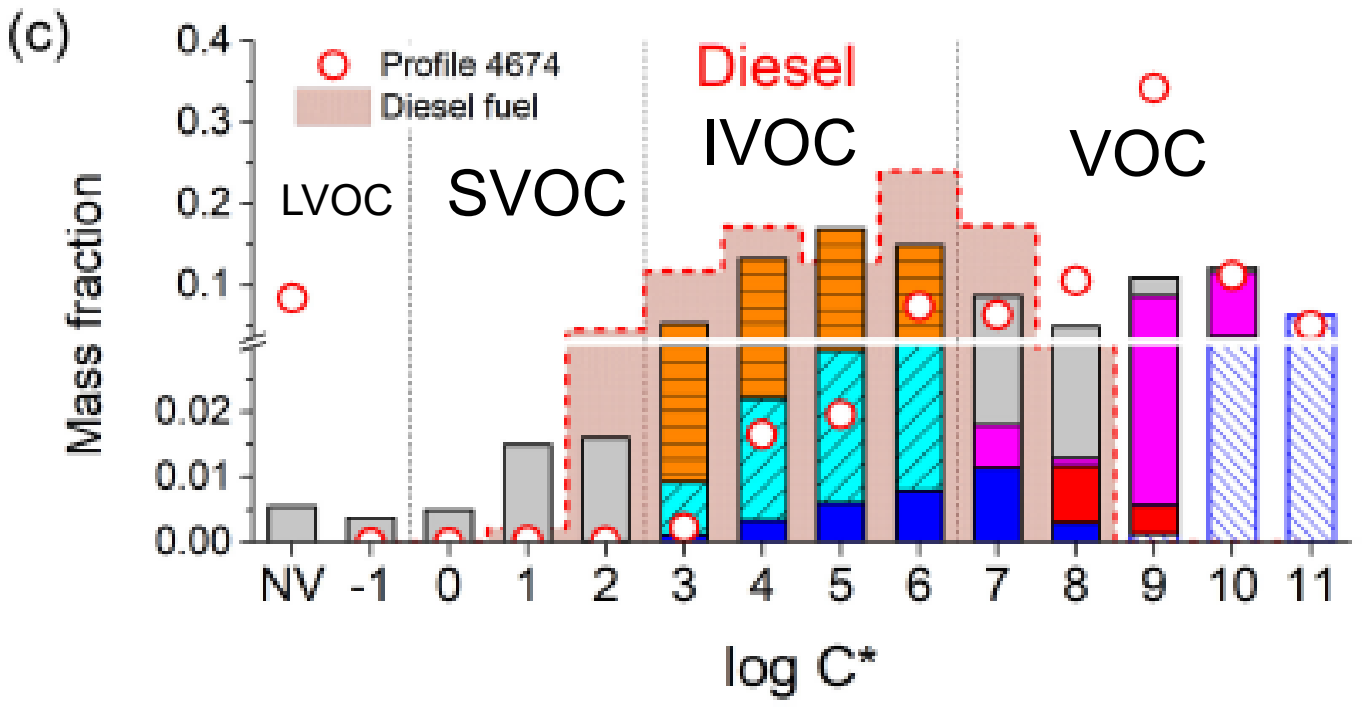
Accounting for intermediate volatility SOA precursors

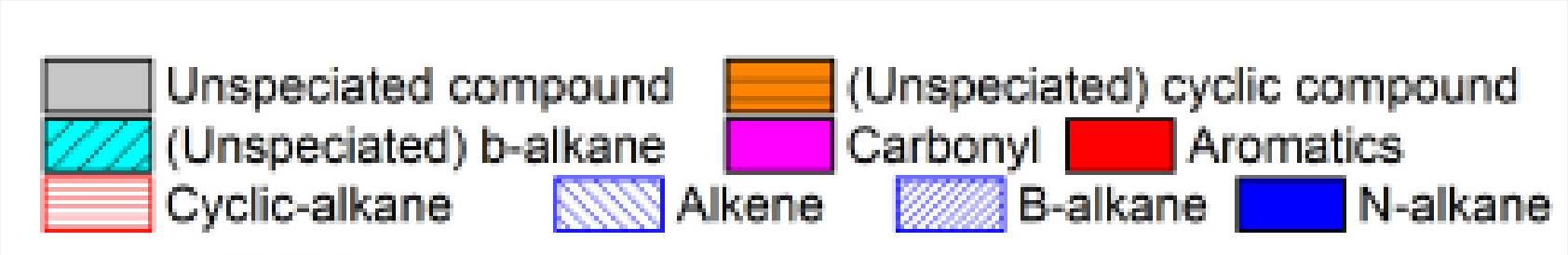


Lu, et. al. "Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic emissions." **Atmospheric Chemistry & Physics. 2018**

IVOC do not partition to the aerosol phase at ambient conditions

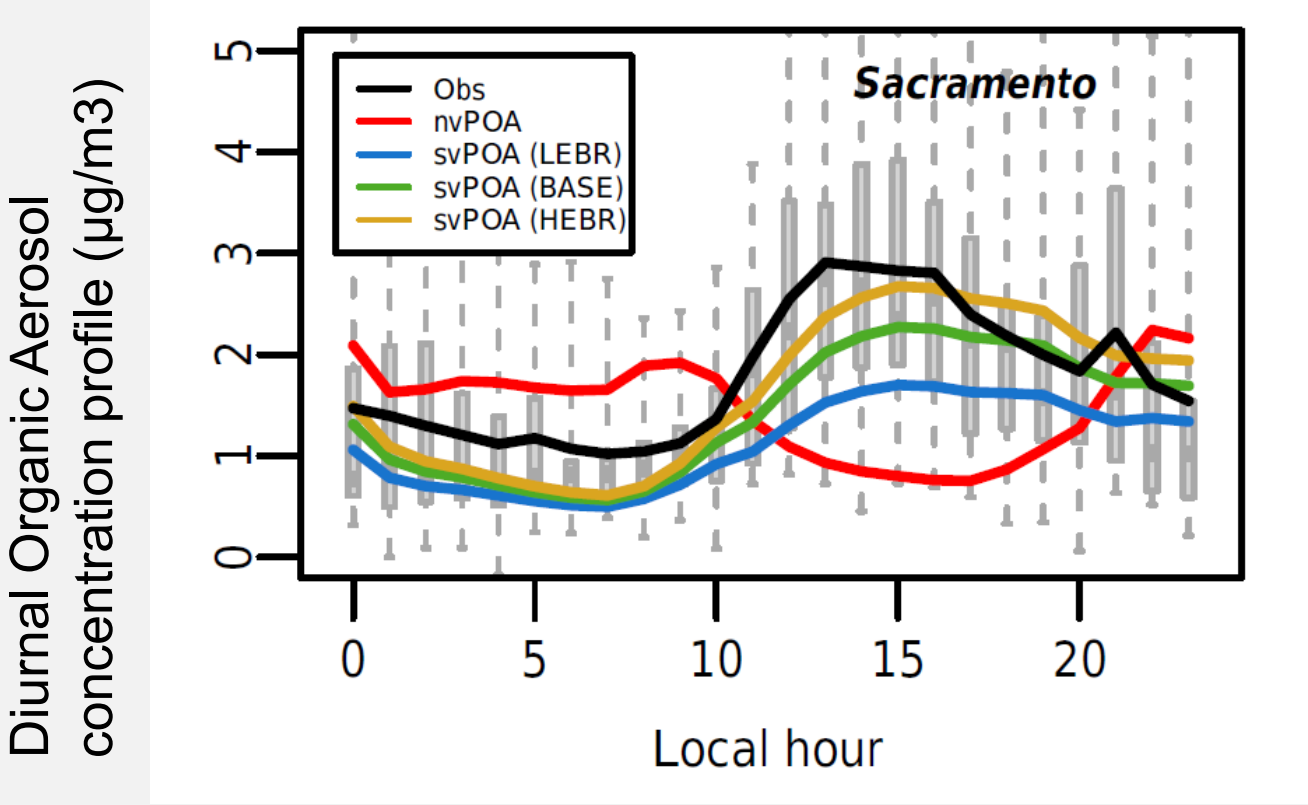
Median volatility distribution of organic emissions for on-road diesel engine





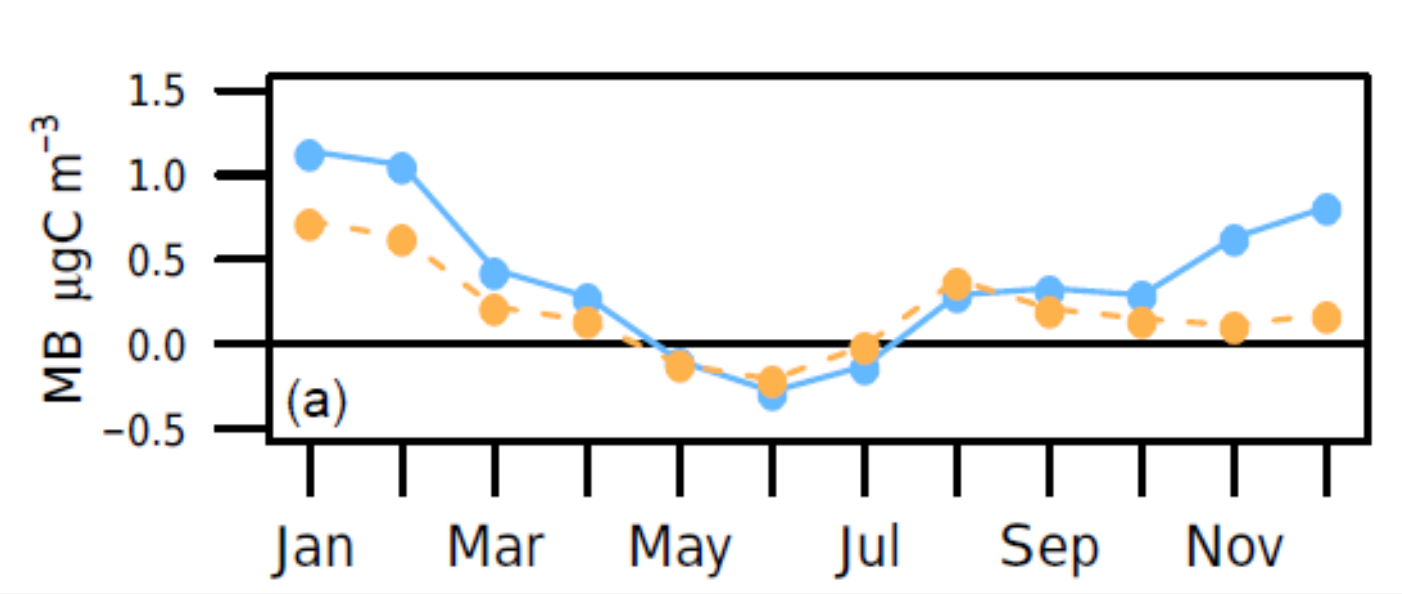
Lu Q, Zhao Y, Robinson AL. Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions. Atmospheric Chemistry and Physics. 2018 Dec 12;18(23):17637-54.

Accounting for organic aerosol volatility improves air quality model performance in CALNEX case



Murphy BN, Woody MC, Jimenez JL, Carlton AM, Hayes PL, Liu S, Ng NL, Russell LM, Setyan A, Xu L, Young J. Semivolatile POA and parameterized total combustion SOA in CMAQv5. 2: impacts on source strength and partitioning. Atmospheric Chemistry and Physics. 2017 Sep 20;17(18):11107-33.

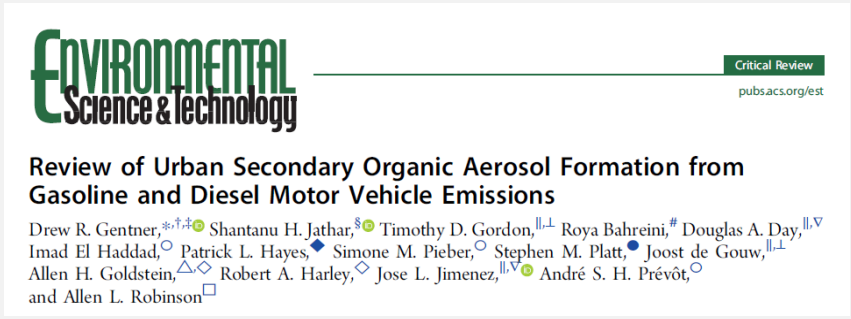
Accounting for organic aerosol volatility improves air quality model performance CONUS 2011 simulation



Organic Carbon mean bias the nvPOA (blue) and LEBR (orange) cases throughout the 2011 simulation.

Murphy BN, Woody MC, Jimenez JL, Carlton AM, Hayes PL, Liu S, Ng NL, Russell LM, Setyan A, Xu L, Young J. Semivolatile POA and parameterized total combustion SOA in CMAQv5. 2: impacts on source strength and partitioning. Atmospheric Chemistry and Physics. 2017 Sep 20;17(18):11107-33.

Therefore…



Environmental Science & Technology

Critical Review

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Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions

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- *Comprehensive emissions data:* The next generation of chemistry models will need more comprehensive emissions data. Historically, inventories have focused on including VOC because of their contribution to atmospheric reactivity and ozone formation. However, lower volatility species (e.g., IVOC) with lower emission rates disproportionally contribute to SOA formation. More measurements are needed of these emissions, and they need to be formally included in inventories.

- PM2.5 and VOC no longer independent pollutants from combustion sources and their lumping approach needs to be re-examined
- Organic combustion emissions need to be represented in a new paradigm: a continuum of volatility from little or none (particle) to complete volatility (gas)

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What we do now in CMAQ 5.3

- VBS profiles (that we have developed) are directly included into the model with the requirement that the emissions from a source with a VBS profile are a separate sector input. CMAQ does the speciation internally.
- However, it make better sense to do the VBS speciation (just like all other speciation) using SPECIATE, speciation tool, and SMOKE and then provided VBS speciated emissions to CMAQ.

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More information needed (depending on measurement method) when creating profiles for the SPECIATE database

- Profile Table
  - Sample temperature (i.e. filter)
  - Sample relative humidity
  - Particle Loading (i.e. concentration) (ug/m3)
  - Organic Loading (i.e. concentration) (ug/m3)
- Species Properties
  - Vapor pressure
  - Organic Matter/Organic Carbon (OM/OC) ratio

This information is needed so the VBS profile can be reconciled with emission factors (PM2.5 and VOC) that may have been measured under different conditions

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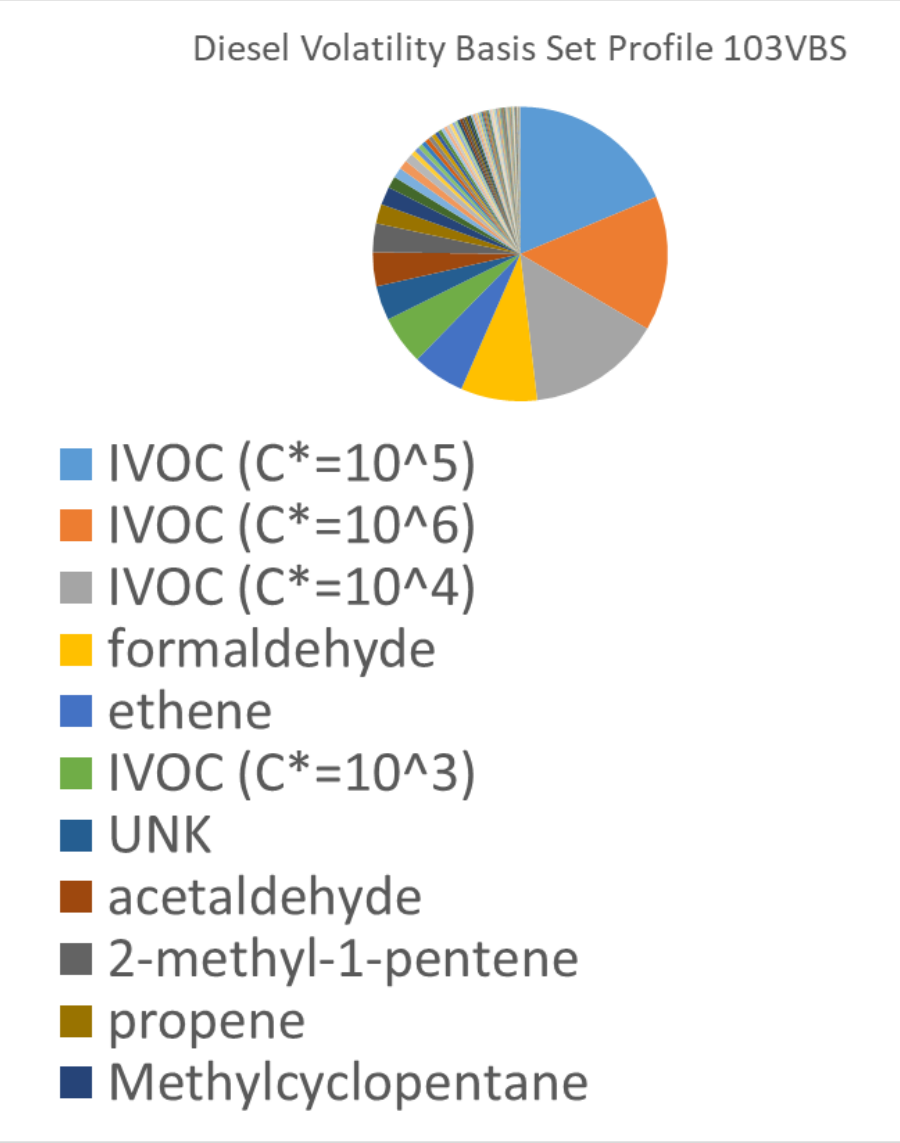
PM2.5 and VOC pollutants distributed into volatility bins (number of bins for each group)

- Particle
  - LVOC: 1 bins
  - SVOCs: 3 bins
- Gas
  - IVOCS: 6 bins {4 alkanes + 2 aromatics}
  - VOC: speciated (varies by source)

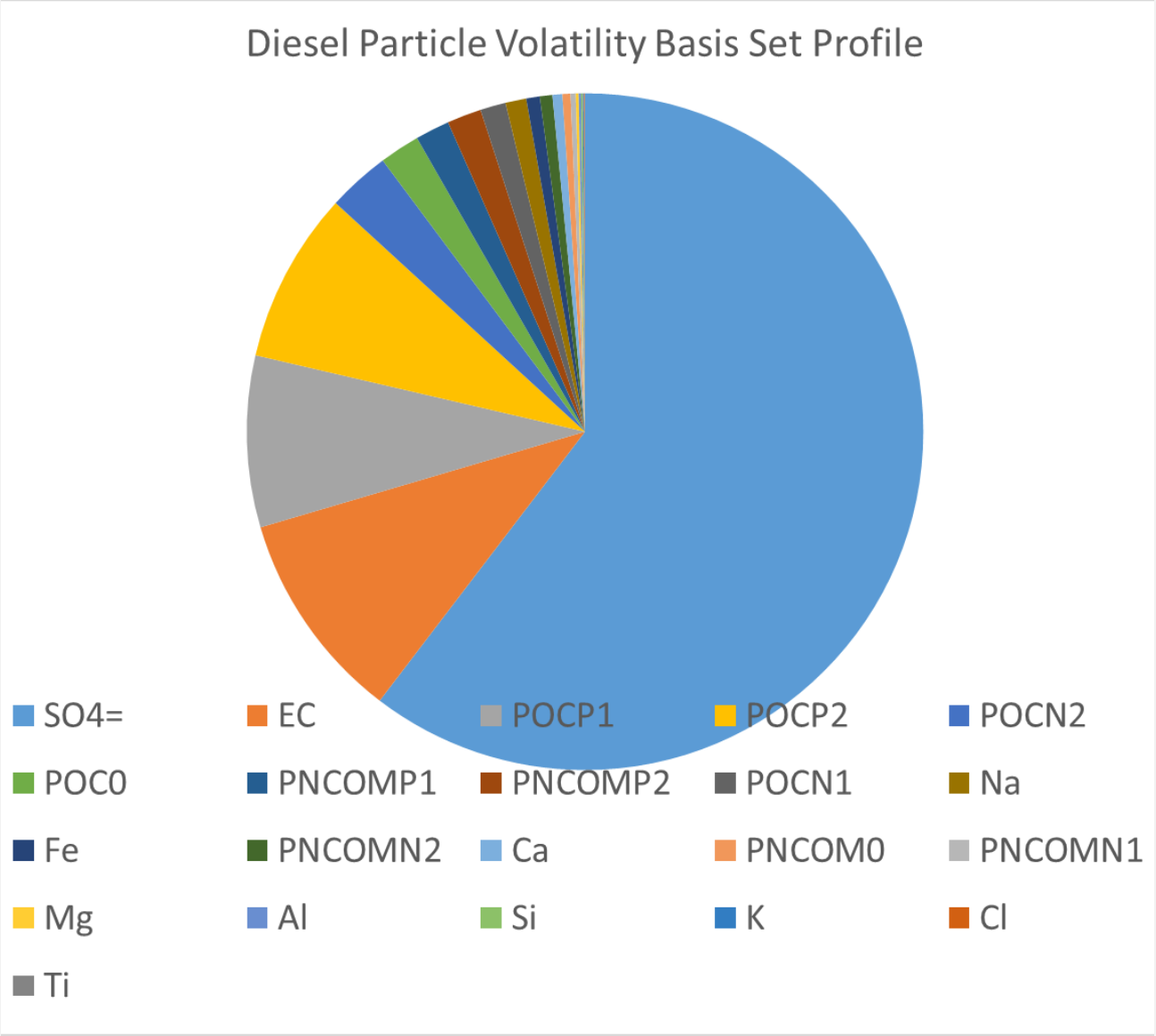
What does a VBS gas profile look like in SPECIATE?

Species	Fraction
IVOC (C*=10^5)	0.187
IVOC (C*=10^6)	0.148
IVOC (C*=10^4)	0.147
formaldehyde	0.084
ethene	0.058
IVOC (C*=10^3)	0.054
UNK	0.038



What does a VBS particle profile look like in SPECIATE?

PM2.5 component	Fraction
SO4=	59.9
EC	10.0
POCP1	8.1
POCP2	8.1
POCN2	3.0
POC0	1.9



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Where do we go from here?

Particulate organic carbon (POC) and particulate non carbon organic matter (PNCOM) need to be resolved into a more detailed set of species (based on volatility) that capture the physical and chemical properties so they can be modeled more accurately for all combustion sources

Organic Gases need to be resolved with more detail in the intermediate volatility (IVOC) range as well but we already have a master list of compounds which include IVOCS that we use in Speciation tool (Bill Carter's work)

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Where do we go from here?

- Compounds in the IVOC and VOC range should be in the VOC profiles
- Remaining compounds in SVOC and LVOC, etc should be in the PM2.5 profiles
- Both the PM2.5 profiles and the VOC profiles may be paired if the source has both particles and gases
- Over time, more explicit species (currently lumped) may be introduced in both PM2.5 and VOC profiles based on newer measurement techniques and improved understanding of the source profile.

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Questions?