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

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

Accounting for intermediate volatility
SOA precursors


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

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

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.

Therefore...

- 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)
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.
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
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?

<table>
<thead>
<tr>
<th>Species</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVOC (C*=10^5)</td>
<td>0.187</td>
</tr>
<tr>
<td>IVOC (C*=10^6)</td>
<td>0.148</td>
</tr>
<tr>
<td>IVOC (C*=10^4)</td>
<td>0.147</td>
</tr>
<tr>
<td>formaldehyde</td>
<td>0.084</td>
</tr>
<tr>
<td>ethene</td>
<td>0.058</td>
</tr>
<tr>
<td>IVOC (C*=10^3)</td>
<td>0.054</td>
</tr>
<tr>
<td>UNK</td>
<td>0.038</td>
</tr>
</tbody>
</table>

Diesel Volatility Basis Set Profile 103VBS

- IVOC (C*=10^5)
- IVOC (C*=10^6)
- IVOC (C*=10^4)
- Formaldehyde
- Ethene
- IVOC (C*=10^3)
- UNK
- Acetaldehyde
- 2-Methyl-1-pentene
- Propene
- Methylcyclopentane
### What does a VBS particle profile look like in SPECIATE?

#### Diesel Particle Volatility Basis Set Profile

<table>
<thead>
<tr>
<th>PM2.5 component</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO4=</td>
<td>59.9</td>
</tr>
<tr>
<td>EC</td>
<td>10.0</td>
</tr>
<tr>
<td>POCP1</td>
<td>8.1</td>
</tr>
<tr>
<td>POCP2</td>
<td>8.1</td>
</tr>
<tr>
<td>POCN2</td>
<td>3.0</td>
</tr>
<tr>
<td>POC0</td>
<td>1.9</td>
</tr>
</tbody>
</table>
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).
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.
Questions?