United States Environmental Protection Agency

# Application of the Reactive Organic Carbon Framework to Modeling VOC and PM Emissions

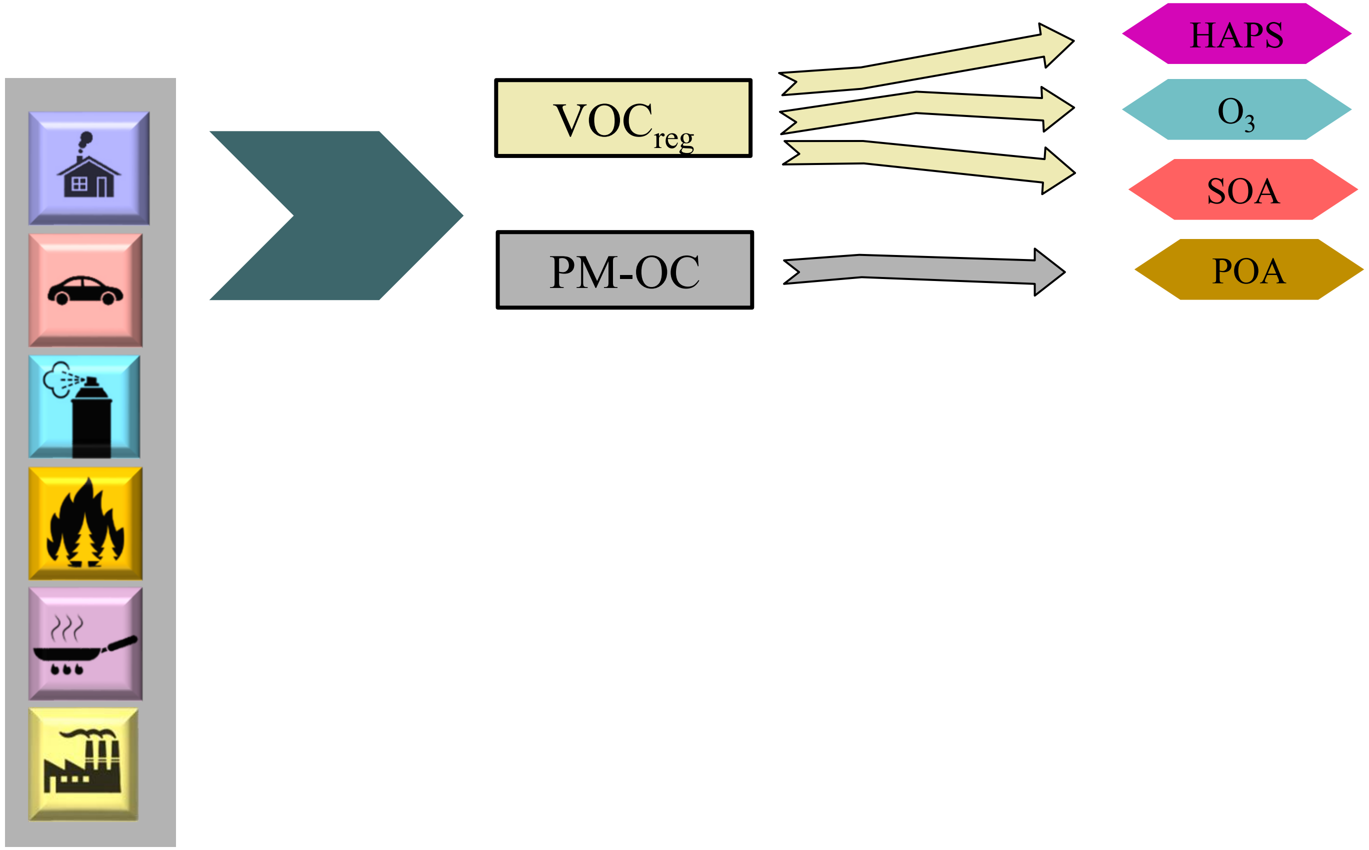
**Ben Murphy**[1], Karl Seltzer[2], Havala Pye[1], Emma D'Ambro[1], Colette Heald[3], and Jesse Kroll[3]

[1]Office of Research and Development, U.S. EPA , Research Triangle Park, NC
[2]Office of Air and Radiation, U.S. EPA, Research Triangle Park, NC
[3]Massachusetts Institute of Technology, Cambridge, MA



# Objectives of this Talk

- Review how conventional approaches for characterizing organic compound emissions are leaving important gaps when applied to PM and Ozone modeling.

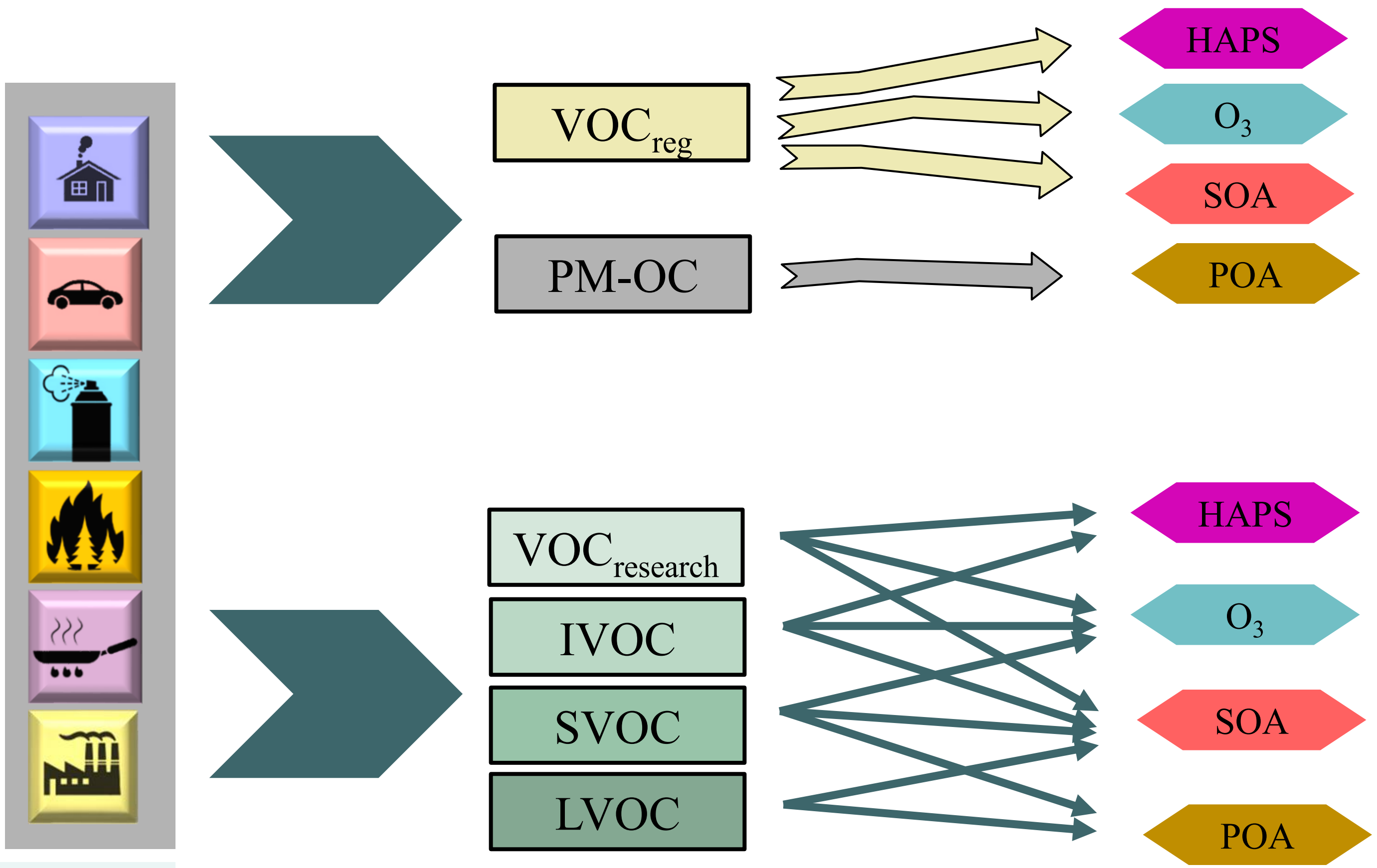



VOC$_{reg}$ – Regulatory Definition of Volatile Organic Compounds
PM-OC – Particulate Organic Compounds
HAPS – Hazardous Air Pollutants
SOA – Secondary Organic Aerosol
POA – Primary Organic Aerosol

United States Environmental Protection Agency

# Objectives of this Talk

- Review how conventional approaches for characterizing organic compound emissions are leaving important gaps when applied to PM and Ozone modeling.
- Demonstrate how the Reactive Organic Carbon framework can be applied to translate conventional data to more sophisticated chemical configurations.
- Share proposed steps for upgrading EPA emissions modeling tools and air quality models.




$VOC_{reg}$ – Regulatory Definition of Volatile Organic Compounds
PM-OC – Particulate Organic Compounds
HAPS – Hazardous Air Pollutants
SOA – Secondary Organic Aerosol
POA – Primary Organic Aerosol

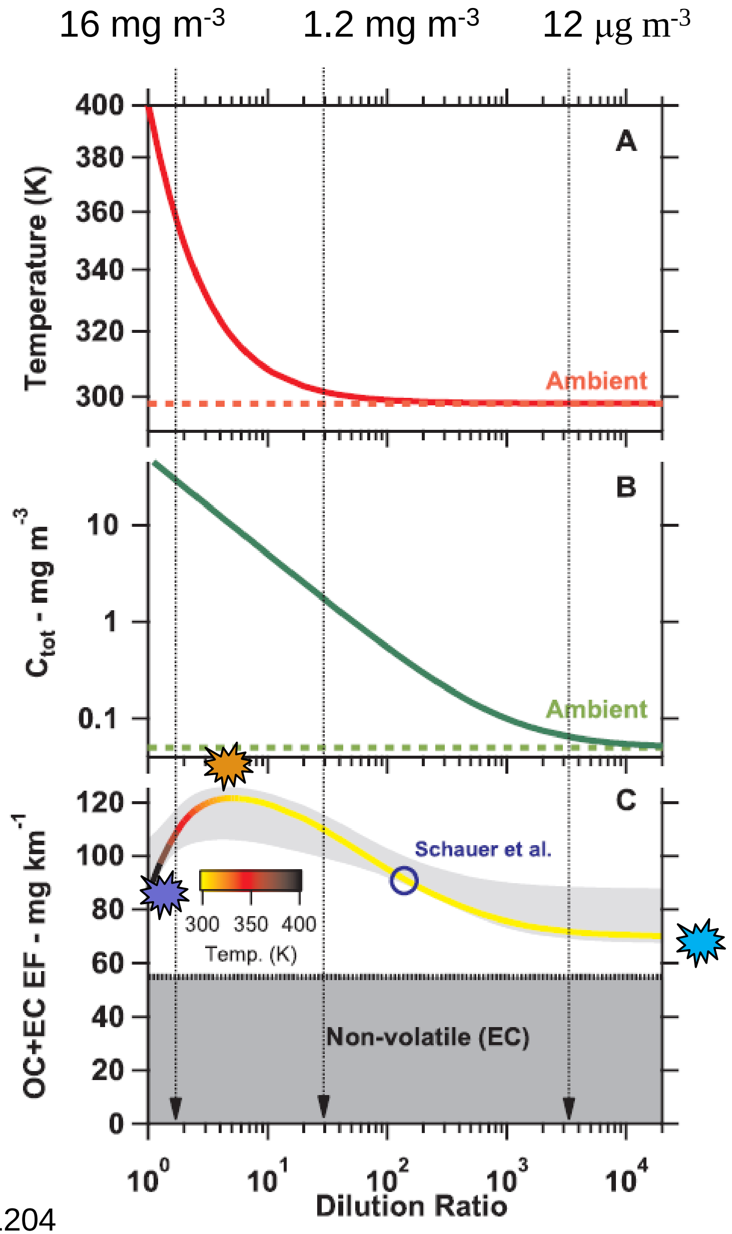
$VOC_{research}$ – All VOCs with saturation concentration > $10^6$ µg m$^{-3}$
IVOC – Intermediate Volatility Organic Compounds
SVOC – Semivolatile Organic Compounds
LVOC – Low Volatility Organic Compounds

# Getting to Know Our Inventoried Carbon Pollutants

## Particulate Organic Emissions (PM-OC)

- Based on PM Emission Factors (EF) multiplied by an OC weight percent from speciation profiles.
- OC is converted to organic mass in models using an assumed OM:OC.
- In systems with reported ‘Filterable’ and ‘Condensable’ PM, the total fine PM EF is assumed to be the sum of both quantities.
- Challenges for proper regional-scale air quality modeling:
    - Assumed to be nonvolatile in emission inventories
    - These PM-OC EFs are operationally defined at the test conditions rather than ambient or other set conditions

Filterable
Condensable
Ambient PM



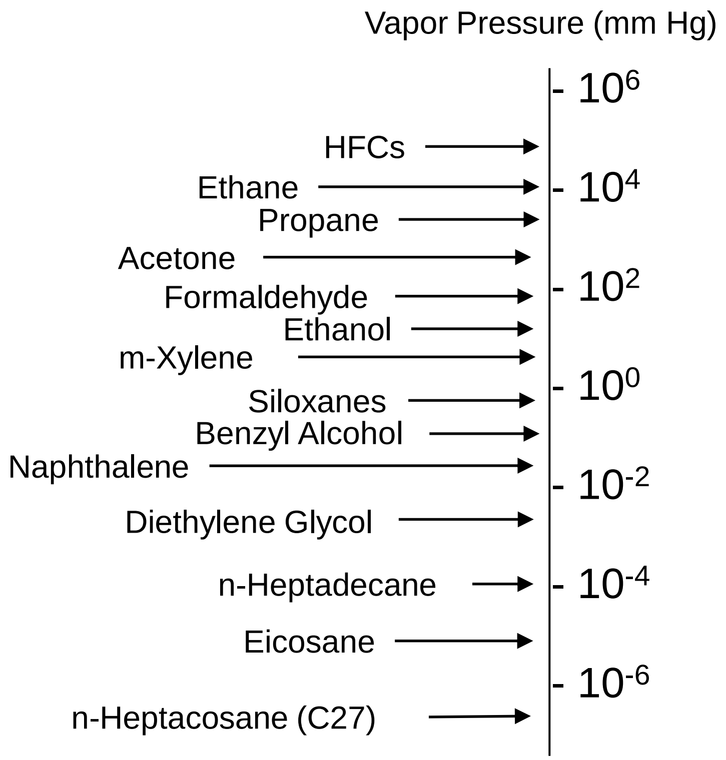



**Robinson et al., JA&WMA, 2011**: https://doi.org/10.3155/1047-3289.60.10.1204

# Getting to Know Our Inventoried Carbon Pollutants

## Volatile Organic Compounds (VOCs)

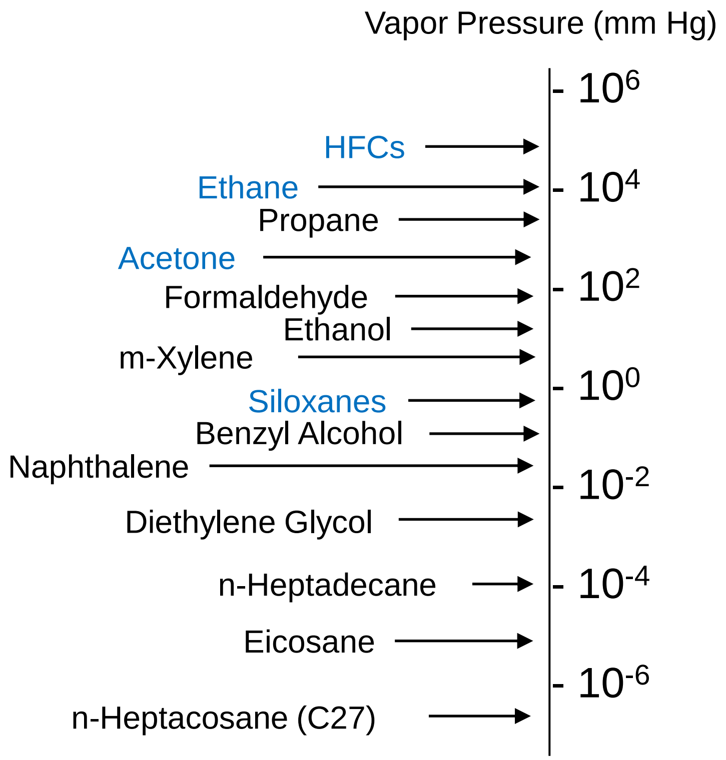
- 'VOC' includes compounds important for ozone formation.
- Measured EFs are combined with speciation profiles to estimate emissions of thousands of explicit species, which are translated to species in a chemical mechanism (e.g., Carbon Bond, SAPRC, RACM, etc.).



# Getting to Know Our Inventoried Carbon Pollutants

## Volatile Organic Compounds (VOCs)

- ‘VOC’ includes compounds important for ozone formation.
- Measured EFs are combined with speciation profiles to estimate emissions of thousands of explicit species, which are translated to species in a chemical mechanism (e.g., Carbon Bond, SAPRC, RACM, etc.).
- Challenges for proper regional-scale air quality modeling:
  - Compounds are exempted from the regulatory definition of VOC ($VOC_{reg}$) , often based on a determined low Maximum Incremental Reactivity (MIR) or OH reaction rate constant (kOH).




Potential for lower-volatility exempt compounds to contribute to SOA?

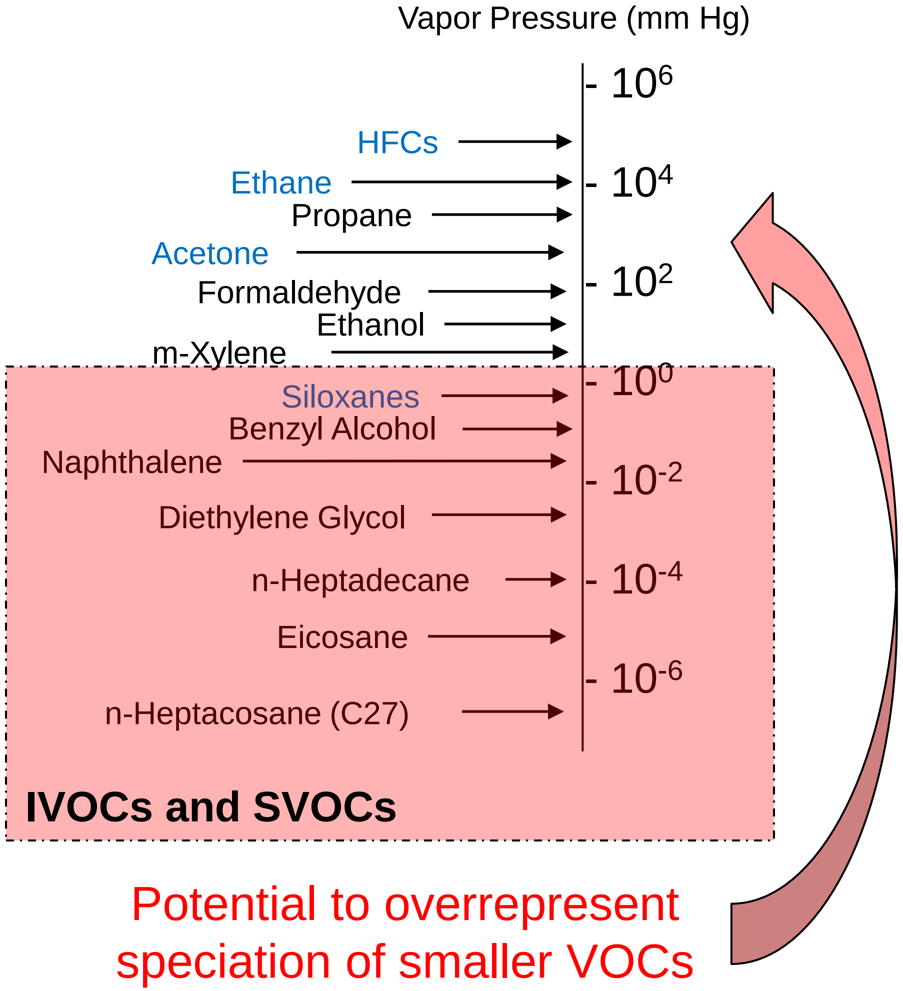


**40 CFR § 51.100:** https://ecfr.io/Title-40/Section-51.100
**Qin et al., Nature Sustainability, 2021**: https://doi.org/10.1038/s41893-020-00614-1

# Getting to Know Our Inventoried Carbon Pollutants

## Volatile Organic Compounds (VOCs)

- 'VOC' includes compounds important for ozone formation.
- Measured EFs are combined with speciation profiles to estimate emissions of thousands of explicit species, which are translated to species in a chemical mechanism (e.g., Carbon Bond, SAPRC, RACM, etc.).
- Challenges for proper regional-scale air quality modeling:
  - Compounds are exempted from the regulatory definition of VOC ($VOC_{reg}$) , often based on a determined low Maximum Incremental Reactivity (MIR) or OH reaction rate constant (kOH).
  - Complete speciation can be difficult to measure if significant condensation occurs in the sampling lines of an experimental setup.





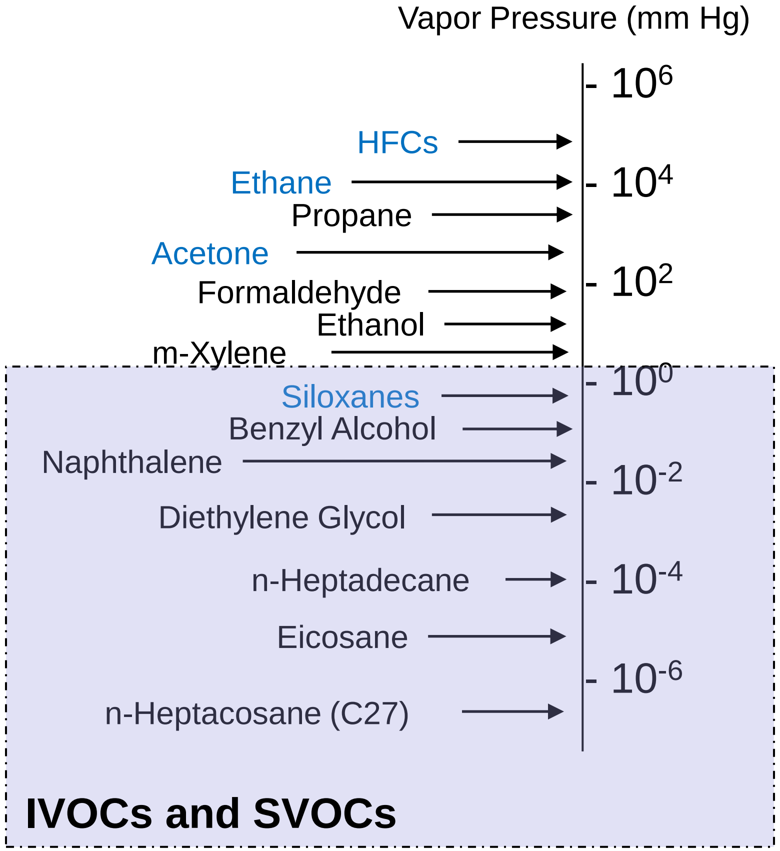

**Lu et al., ACP, 2020**: https://doi.org/10.5194/acp-18-17637-2018

EPA United States Environmental Protection Agency

# Getting to Know Our Inventoried Carbon Pollutants

## Volatile Organic Compounds (VOCs)

- ‘VOC’ includes compounds important for ozone formation.
- Measured EFs are combined with speciation profiles to estimate emissions of thousands of explicit species, which are translated to species in a chemical mechanism (e.g., Carbon Bond, SAPRC, RACM, etc.).
- Challenges for proper regional-scale air quality modeling:
  - Compounds are exempted from the regulatory definition of VOC ($VOC_{reg}$) , often based on a determined low Maximum Incremental Reactivity (MIR) or OH reaction rate constant (kOH).
  - Complete speciation can be difficult to measure if significant condensation occurs in the sampling lines of an experimental setup.
  - Chemical mechanisms additionally often disregard intermediate volatility and semivolatile compounds as irrelevant for ozone.




What is the potential impact on $O_3$ and SOA?

# Application of Integrated ROC Emissions Framework

| ROC | | | | | |
|---|---|---|---|---|---|
| $VOC_{research}$ | IVOC | SVOC | LVOC | ELVOC | ULVOC |

**ROC** – Reactive Organic Carbon[a]. All organic molecules in the atmosphere excluding methane. This is a comprehensive, coupled approach for modeling formation and evolution of organic gases and particles.

What is the potential impact of various classes of ROC compounds on ozone and OA formation?

Analyze data in existing SPECIATEv5.1[b].

Three example source categories:

- ❑ Residential Wood Burning
- ❑ Mobile
- ❑ Volatile Chemical Products



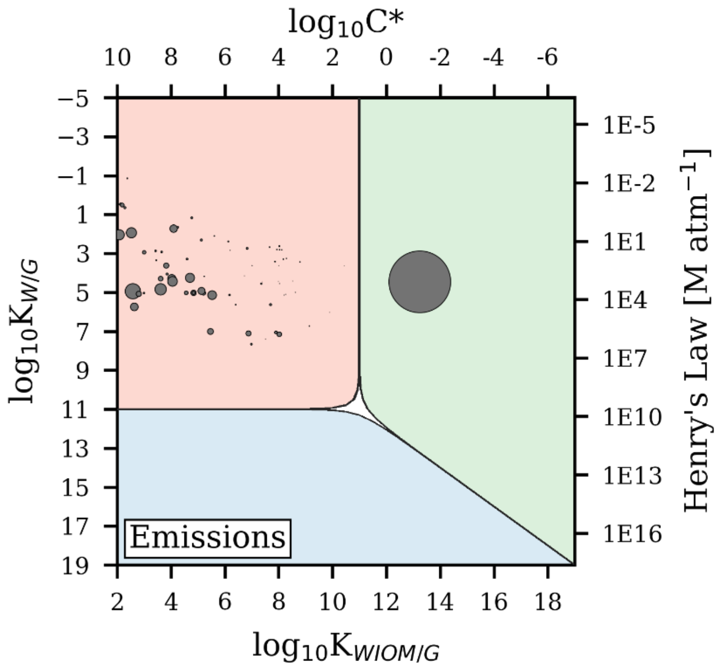
$VOC_{research}$ – All ROC compounds with saturation concentration ($C^*$) > $10^6$ µg $m^{-3}$

[a]Heald and Kroll, Science Advances, 2020: DOI: 10.1126/sciadv.aay8967
[b]SPECIATEv5.1: https://www.epa.gov/air-emissions-modeling/speciate

# Residential Wood Burning ROC Emissions

## Conventional Speciation Profile

VOC | IVOC | SVOC | LVOC




More likely to condense to water

Vapor
Organic Phase
@ $C_{OA}$ = 10 μg m$^{-3}$
Aqueous Phase
@ LWC = 10 μg m$^{-3}$

VOC = $VOC_{research}$

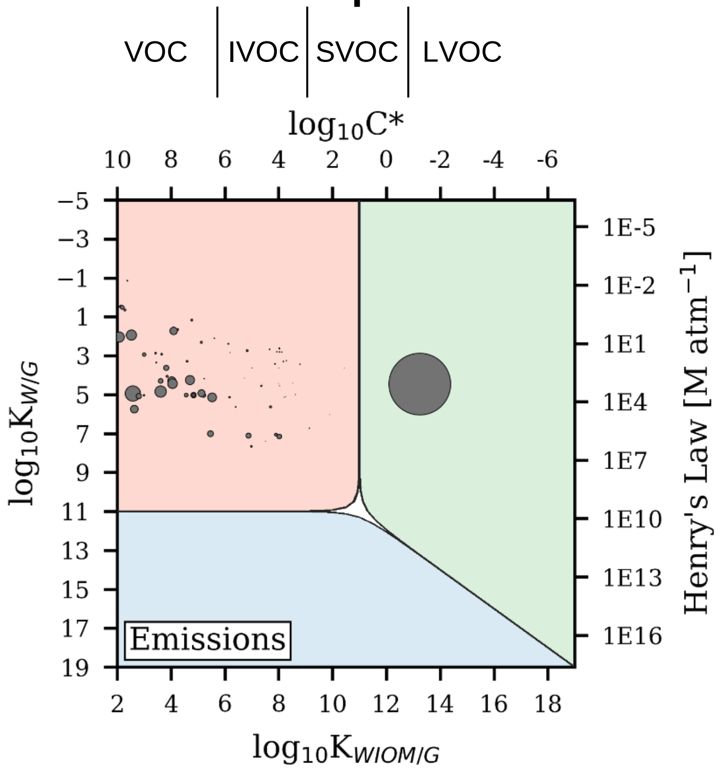
More likely to condense to Organic Particle phase



Wania et al., ACP: https://doi.org/10.5194/acp-15-3395-2015, 2015

# Residential Wood Burning ROC Emissions

## Conventional Speciation Profile



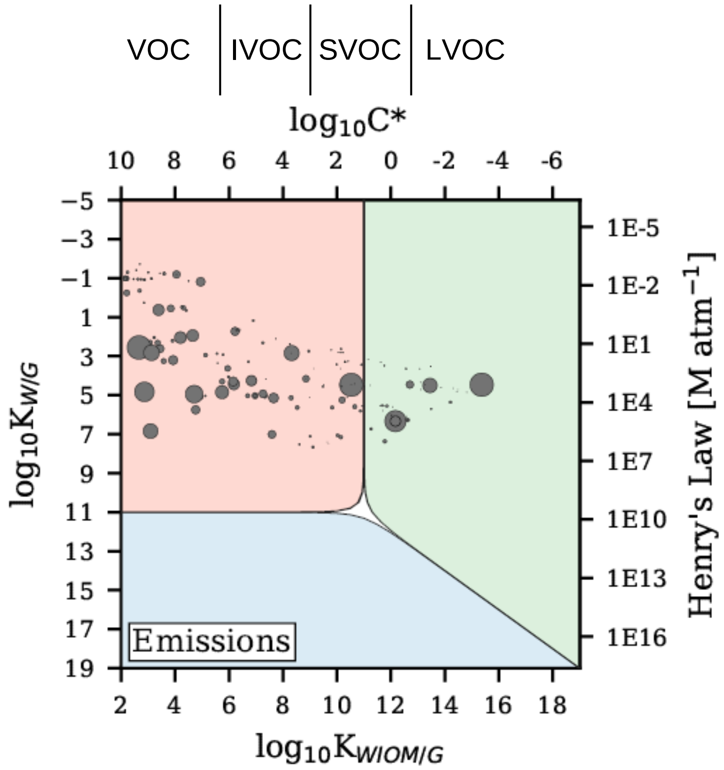

More likely to condense to water

Vapor
Organic Phase
@ $C_{OA}$ = 10 μg m$^{-3}$
Aqueous Phase
@ LWC = 10 μg m$^{-3}$

VOC = $VOC_{research}$

More likely to condense to Organic Particle phase

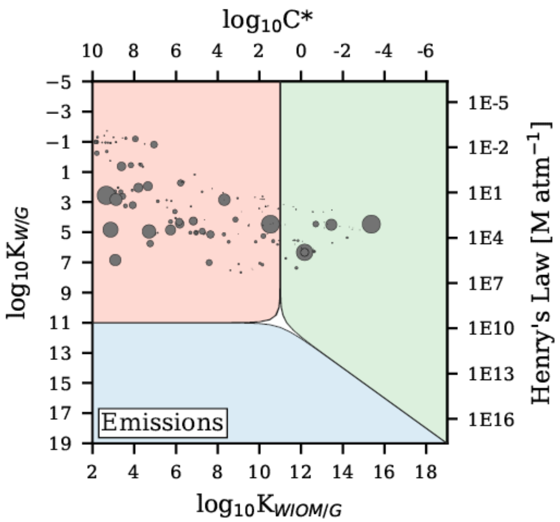
## Detailed Speciation Profile



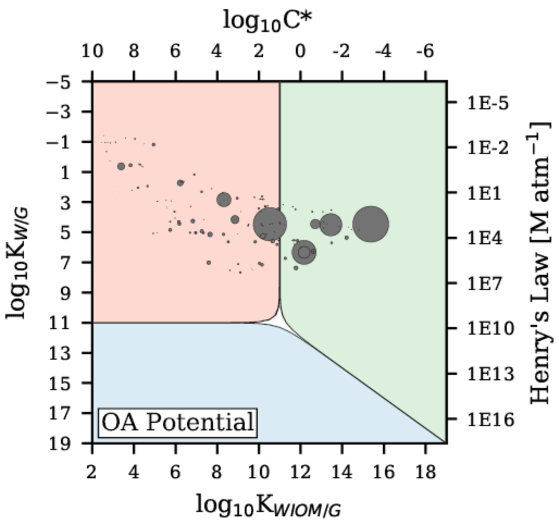

**Schauer et al., ES&T 2001:** 10.1021/es001331e
**Nolte et al., ES&T 2001:** 10.1021/es001420r

# Residential Wood Burning ROC Emissions

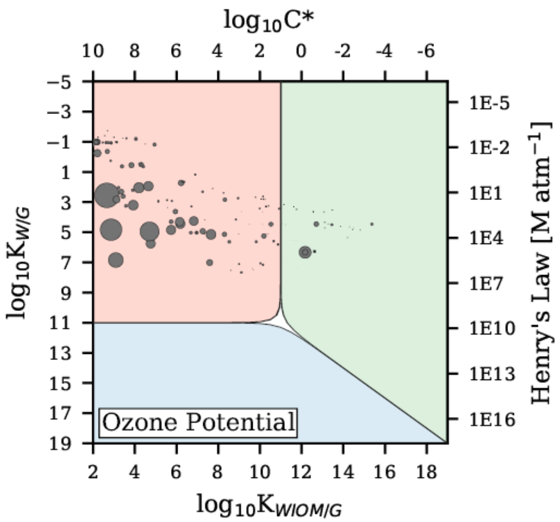
Emissions




Emissions weighted by OA potential




Emissions weighted by Ozone Potential (MIR)



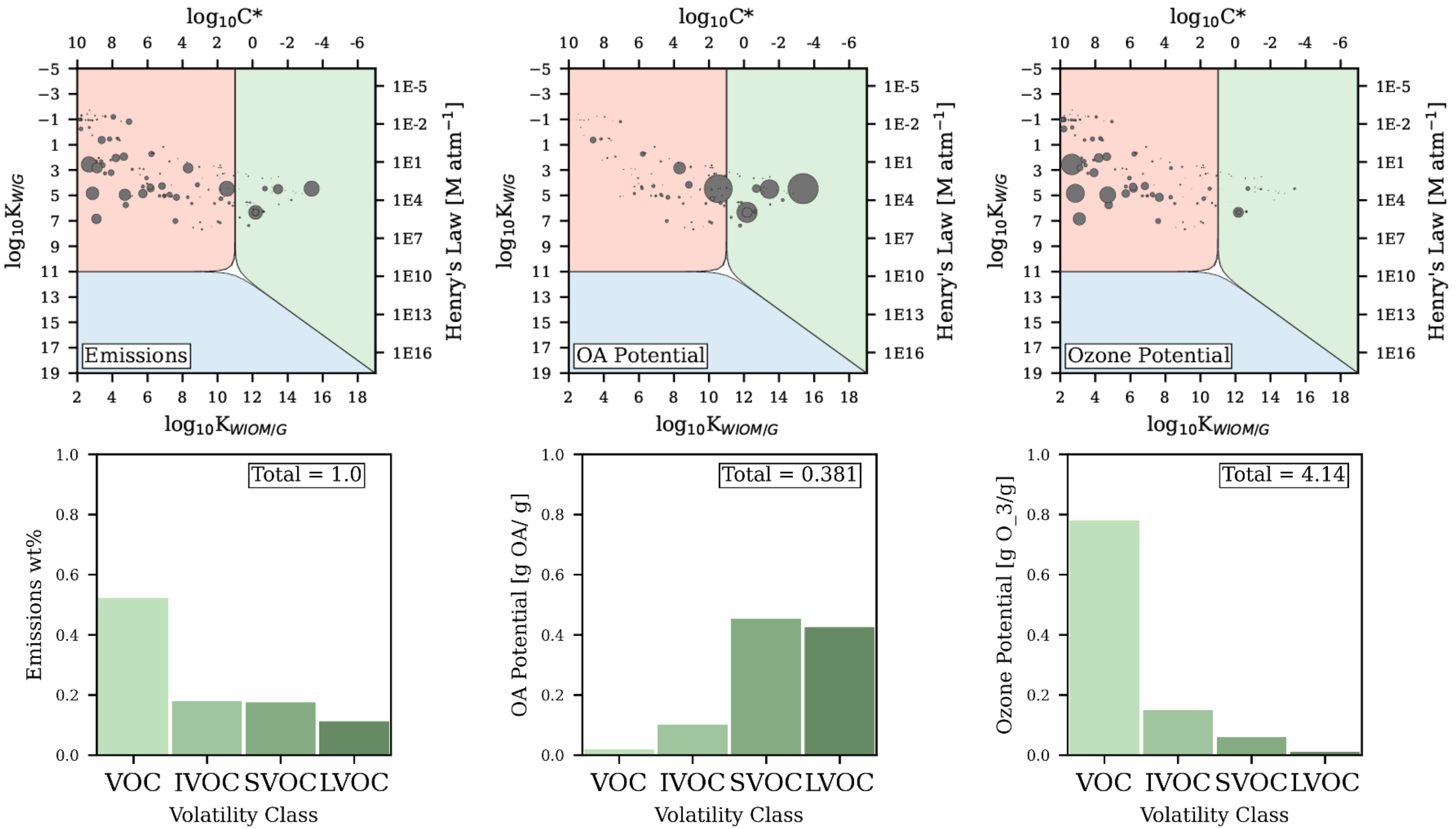

Vapor
Organic Phase
@ $C_{OA} = 10\ \mu g\ m^{-3}$
Aqueous Phase
@ $LWC = 10\ \mu g\ m^{-3}$

VOC = $VOC_{research}$

OA and Ozone potential were derived during the development of the Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM). Please see presentation by Havala Pye (2572, Development).

# Residential Wood Burning ROC Emissions

Emissions | Emissions weighted by OA potential | Emissions weighted by Ozone Potential (MIR)




Vapor
Organic Phase
@ $C_{OA}$ = 10 µg m$^{-3}$
Aqueous Phase
@ LWC = 10 µg m$^{-3}$

VOC = $VOC_{research}$

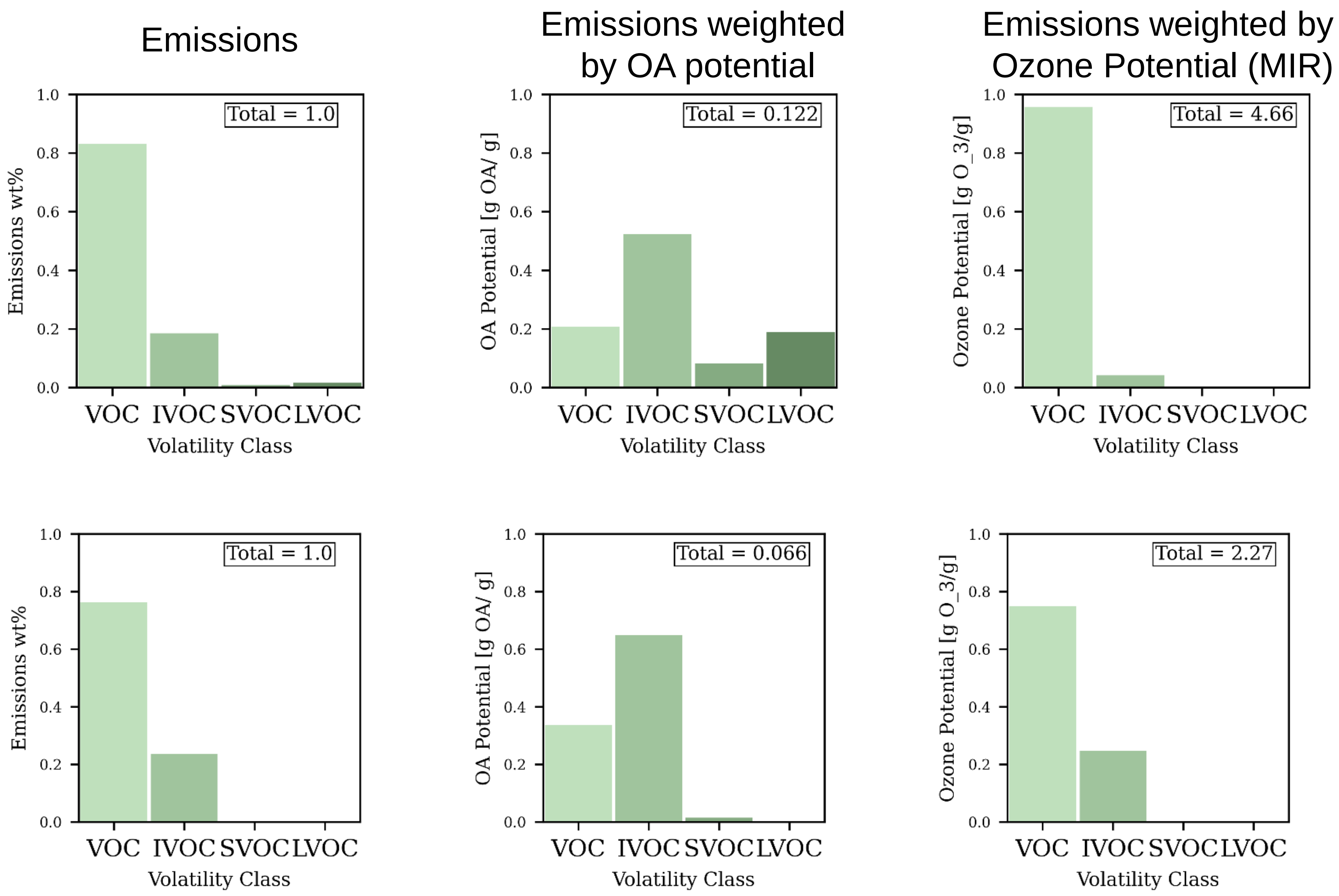


OA and Ozone potential were derived during the development of the Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM). Please see presentation by Havala Pye (2572, Development).

# Mobile Source and VCP ROC Emissions

Mobile

VCP




VOC = $VOC_{research}$

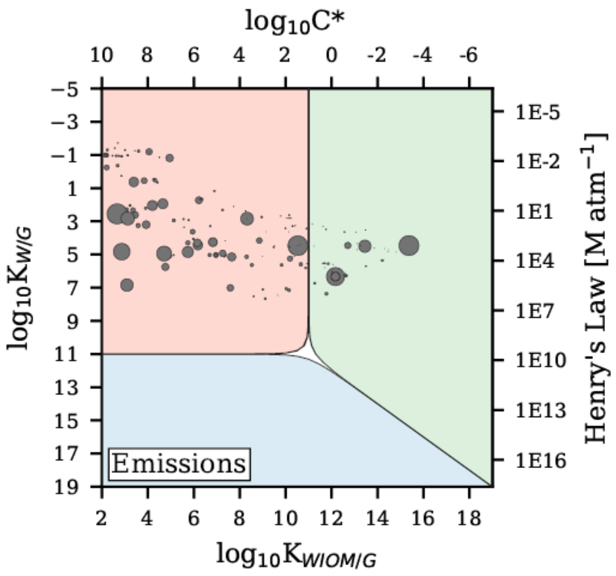


Please see presentations by Karl Seltzer (2573, Emissions) and Elyse Pennington (2662, Development) for more info on the development of VCP emissions, OA potential, and Ozone impacts.

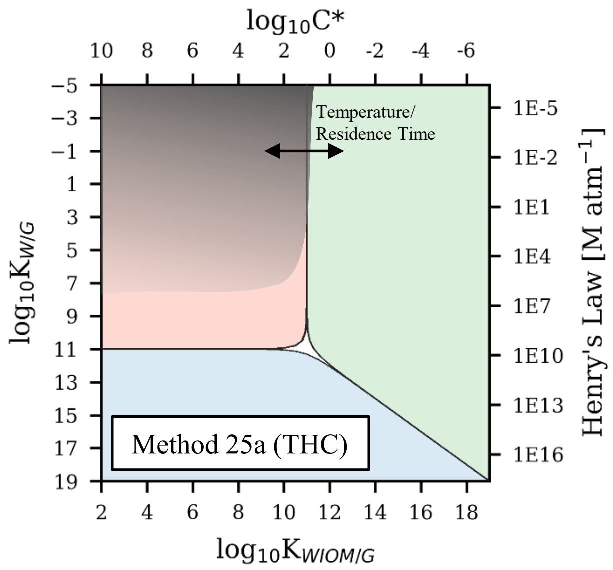
# The Problem With Operationally Defined Pollutants

United States Environmental Protection Agency

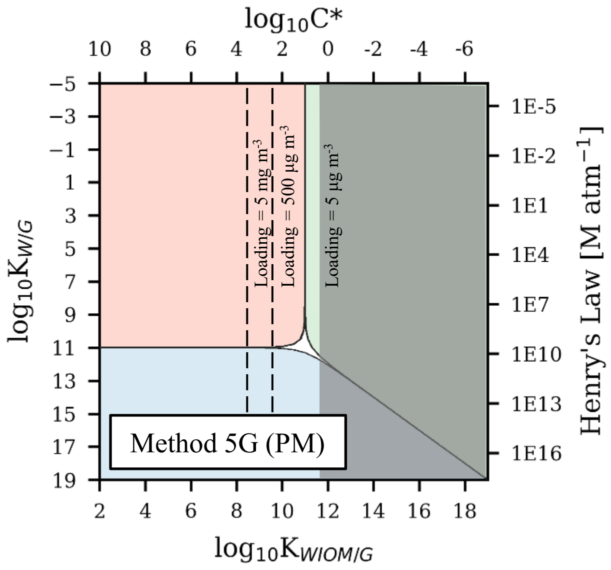
Emissions




VOC Method




PM-OC Method




Method 25a (Total Hydrocarbon) – Flame Ionization Detector with glass fiber filter in front. Line is heated to ~120 °C. Oxygenated groups are not detected.

Method 5G (PM) – Dilution tunnel. Cool flue gas to 32 °C prior to collection and filtration. Dilution ratio advised to be less than 150:1.

How much of the ROC space are available methods characterizing? How much consistency is there among samples?

→ We propose using fixed definitions to report VOC and PM-OC emission factors

Vapor
Organic Phase
@ $C_{OA}$ = 10 µg m$^{-3}$
Aqueous Phase
@ LWC = 10 µg m$^{-3}$

VOC = $VOC_{research}$



*Gray regions in Method plots are speculative, based on expert judgement. Need experiments to confirm.

# Proposed Systematic Definitions for ROC Pollutants

<table>
<tr><td colspan="6">ROC</td></tr>
<tr><td colspan="2">GROC</td><td colspan="4">CROC</td></tr>
<tr><td>$VOC_{research}$</td><td>IVOC</td><td>SVOC</td><td>LVOC</td><td>ELVOC</td><td>ULVOC</td></tr>
</table>

**GROC** – Gaseous Reactive Organic Carbon.

| | |
|---|---|
| Alkane $C^{\#}$ <= 22 (n-docosane) | $C^{*}$ >= 320 µg $m^{-3}$ |
| $P_{vap}$ >= 3 x $10^{-6}$ kPa | $T_{BP}$ <= ~350 ℃ |

**CROC** – Condensable Reactive Organic Carbon.

| | |
|---|---|
| Alkane $C^{\#}$ > 22 (n-docosane) | $C^{*}$ < 320 µg $m^{-3}$ |
| $P_{vap}$ < 3 x $10^{-6}$ kPa | $T_{BP}$ > ~350 ℃ |

# Proposed Systematic Definitions for ROC Pollutants

<table>
<tr><td colspan="6">ROC</td></tr>
<tr><td colspan="2">GROC</td><td colspan="4">CROC</td></tr>
<tr><td>$VOC_{research}$</td><td>IVOC</td><td>SVOC</td><td>LVOC</td><td>ELVOC</td><td>ULVOC</td></tr>
</table>

**GROC** – Gaseous Reactive Organic Carbon.

| | |
|---|---|
| Alkane $C^{\#}$ <= 22 (n-docosane) | $C^{*}$ >= 320 µg $m^{-3}$ |
| $P_{vap}$ >= 3 x $10^{-6}$ kPa | $T_{BP}$ <= ~350 ℃ |

**CROC** – Condensable Reactive Organic Carbon.

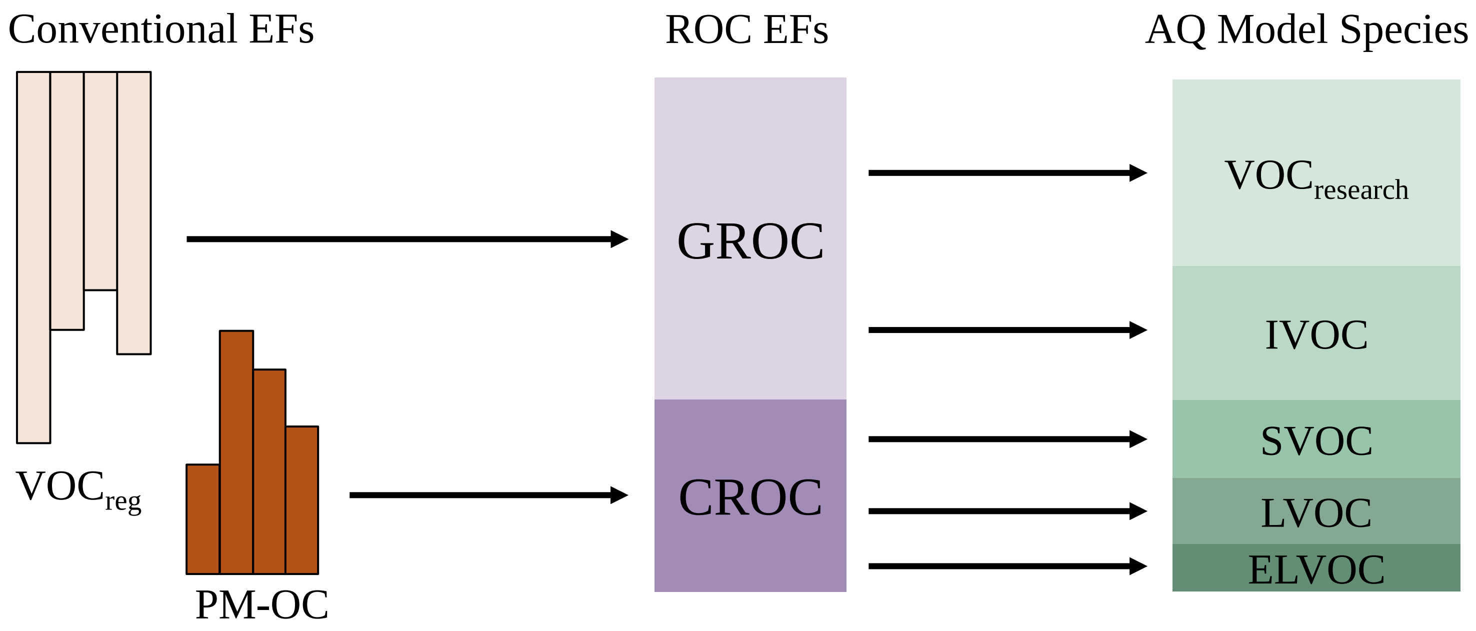
| | |
|---|---|
| Alkane $C^{\#}$ > 22 (n-docosane) | $C^{*}$ < 320 µg $m^{-3}$ |
| $P_{vap}$ < 3 x $10^{-6}$ kPa | $T_{BP}$ > ~350 ℃ |

ROC Framework connects:

conventional inventoried pollutants with operational variability

to

modern, volatility-resolved measurements and models.



# Proposed Upgrades to Emission Tools

## Short-Term:

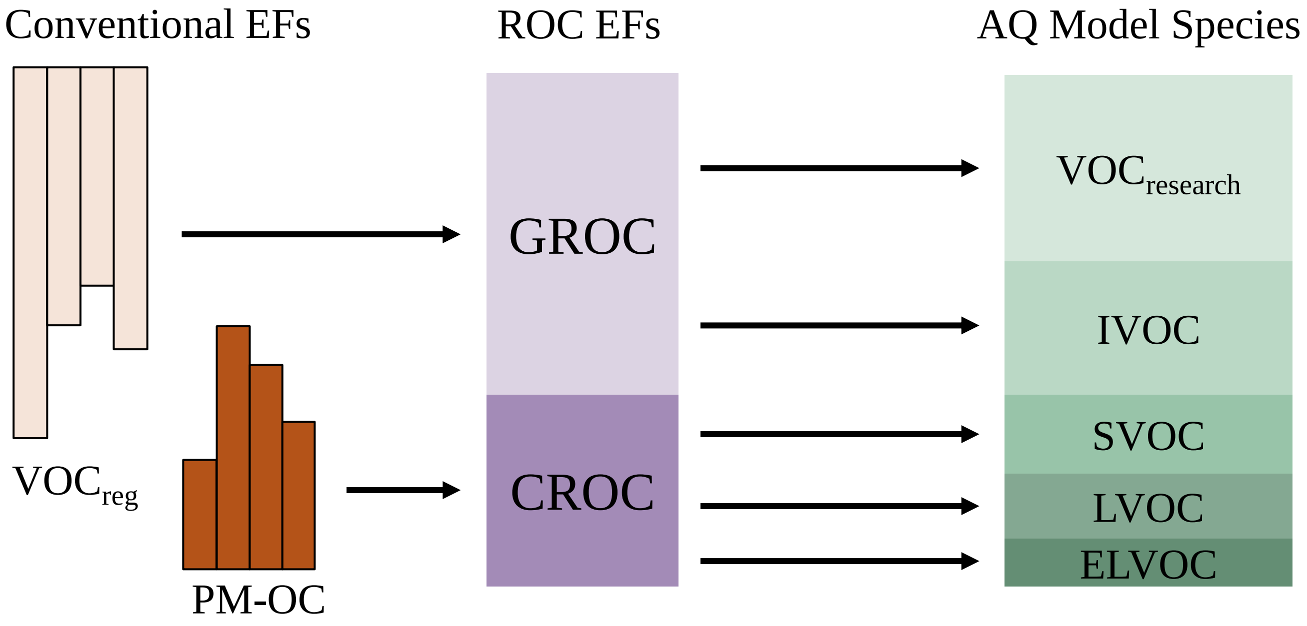
- Revise key speciation profiles in emission models to be consistent with GROC and CROC or Total ROC.
- Upgrade air quality model mechanisms to take advantage of modern speciation data[1].
- Future speciation profiles should be consistent with ROC, GROC, and CROC definitions.

## Medium-Term:

- Determine gaps between existing inventoried ($VOC_{reg}$ and PM) EFs and ROC (GROC and CROC) EFs.
- Apply corrections, if necessary. Default assumption is no correction.

## Long-Term:

- Continue updating EFs to ensure carbon mass is comprehensively captured via the ROC framework.
- Consider revisions to reference and test methods to better characterize organic gas- and particle-phase emissions.






[1]Please see CRACMM presentation by Havala Pye (2572, Development).

# Key Messages

**Reactive Organic Carbon (ROC)** provides a comprehensive framework for modeling impacts of organic compounds on criteria pollutants, among other goals.

Translation from conventional inventoried pollutants and speciation to ROC framework:

- is feasible utilizing new quantities, GROC and CROC.
- will help resolve issues of consistency among operationally defined metrics.
- will facilitate better capture of pollutant source attribution, exposure, and trends (i.e. get the right answer for the right reasons).

The following key source sectors are high priority:

| Source | Status | Reference |
|---|---|---|
| Volatile Chemical Products | Updated | Seltzer et al., ACP, 2021 |
| Mobile | Under review | Lu et al., ACP, 2020; Jathar et al., Atmos. Environ, 2020 |
| Residential Wood Burning | Under review | Schauer et al., 2001; Nolte et al., 2001; |
| Wildfires and Prescribed Fires | Under review | Koss et al., 2020; Hatch et al., 2017; Akherati et al., 2020 |
| Cooking | Needs review | Woody et al., ACP, 2016; Louvaris et al., 2017 |
| Industrial point sources | Needs review | Morino et al., ES&T, 2018 |

# Acknowledgements

**Contact:** murphy.ben@epa.gov

**Special Thanks to:**

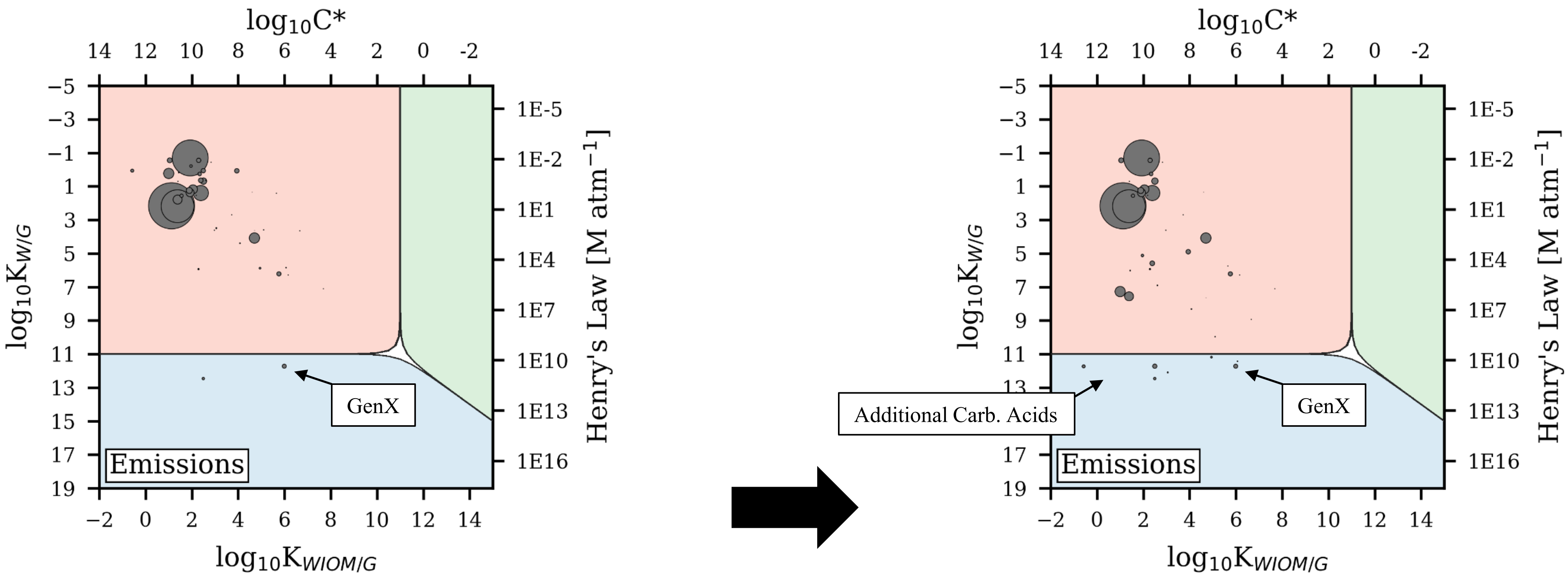
Amara Holder and George Pouliot
U.S. EPA Office of Research and Development

Madeleine Strum, Raymond Merrill, Alison Eyth, and Venkatesh Rao
U.S. EPA Office of Air Quality Planning and Standards

Darrell Sonntag
U.S. EPA Office of Transportation and Air Quality

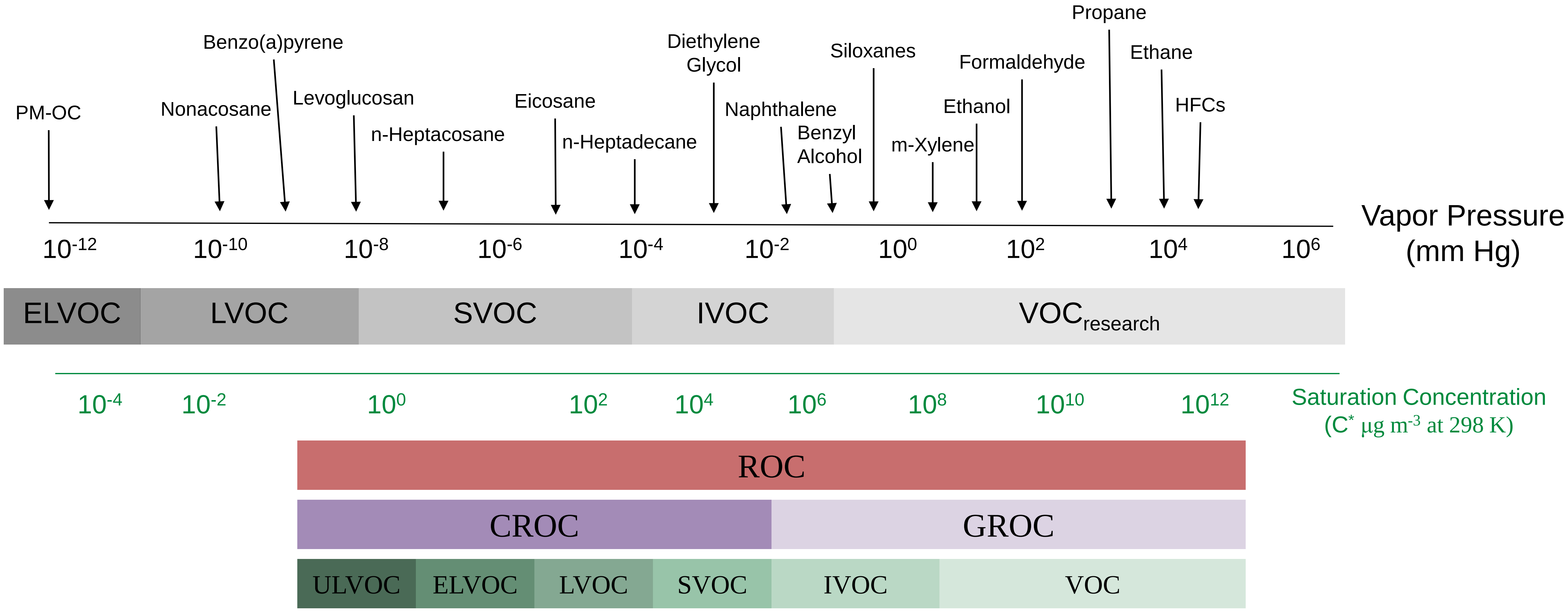
EPA Air, **Climate**, and Energy Research Program:
https://www.epa.gov/aboutepa/about-air-climate-and-energy-research-program

# Utility of Framework for Emerging Pollutants: PFAS



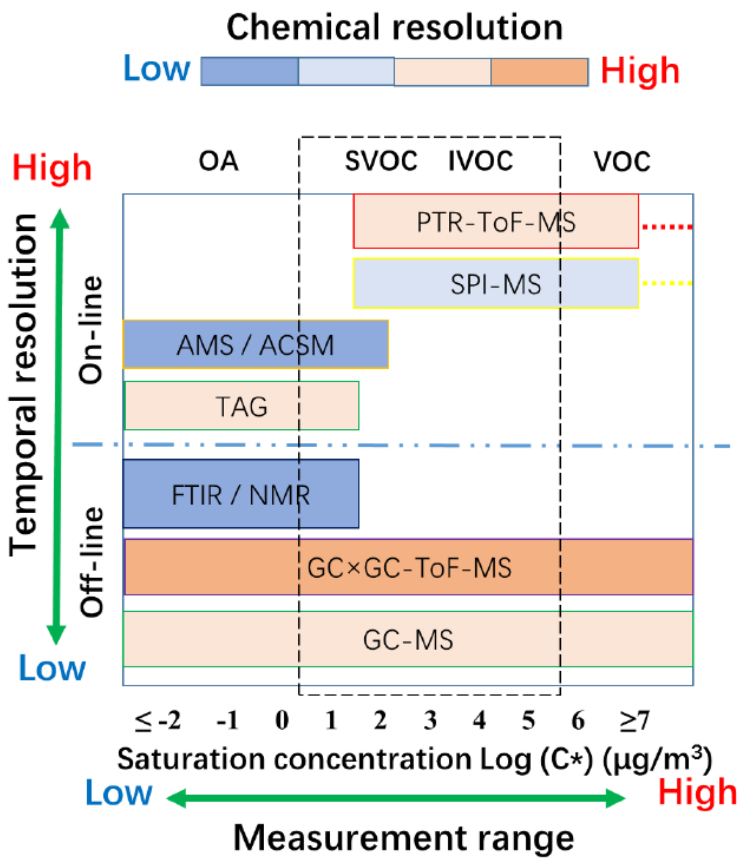

Many Acyl Fluoride compounds may undergo hydrolysis to form carboxylic acids, thus dramatically enhancing their water solubility (Henry's Law).

# Proposed Systematic Definitions for ROC Pollutants




ROC Framework connects conventional inventoried pollutants to modern volatility resolved measurements.

# Research methods for characterizing organic compounds



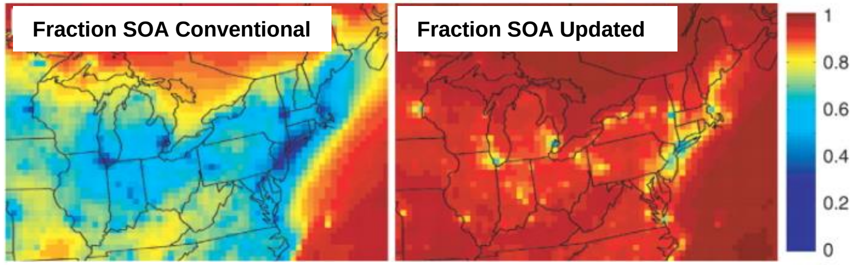

Cai et al., ES&T, 2019:
DOI: 10.1021/acs.est.9b00734

# Past studies worked within decoupled VOC/PM-OC system

**Treated POA semivolatile partitioning and SOA from IVOCs**

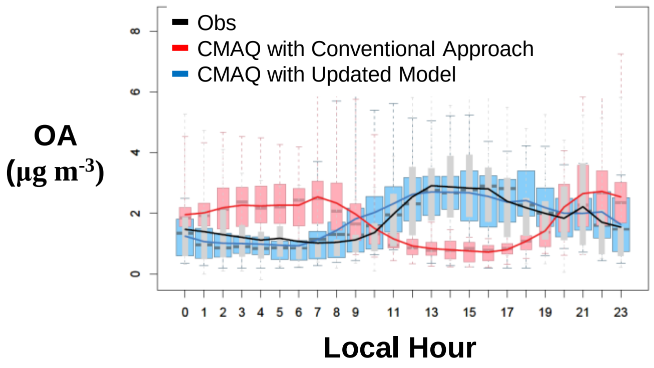
- IVOCs and SVOCs inferred from empirical (and uncertain) scale-factors applied to POA
- Large impact on SOA/OA ratio and spatiotemporal distribution of OA
- IVOCs and SVOCs largely ignored for ozone impacts

**Robinson et al., Science, 2007**: https://doi.org/10.3155/1047-3289.60.10.1204
**Tsimpidi et al., ACP, 2010:** https://doi.org/10.5194/acp-10-525-2010
**Koo et al., Atmos. Environ., 2014:** https://doi.org/10.1016/j.atmosenv.2014.06.031
**Zhao et al., Scientific Reports, 2016:** https://doi.org/10.1038/srep28815
**Woody et al., ACP, 2016:** https://doi.org/10.5194/acp-16-4081-2016
**Murphy et al., ACP, 2017:** https://doi.org/10.5194/acp-17-11107-2017




Northeast US, July 2001. Robinson et al., Science, 2007

**Sacramento, CA during CARES 2010**



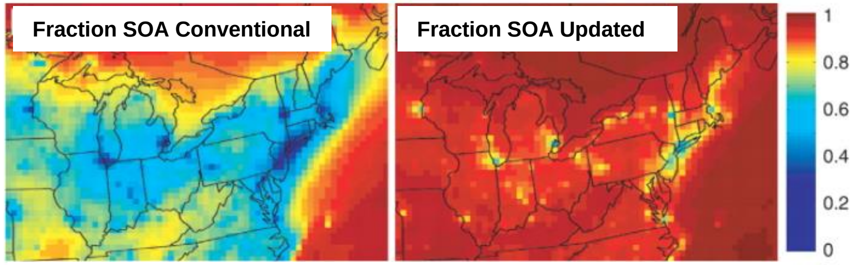

Murphy et al., ACP, 2017

# Past studies worked within decoupled VOC/PM-OC system

## Treated POA semivolatile partitioning and SOA from IVOCs

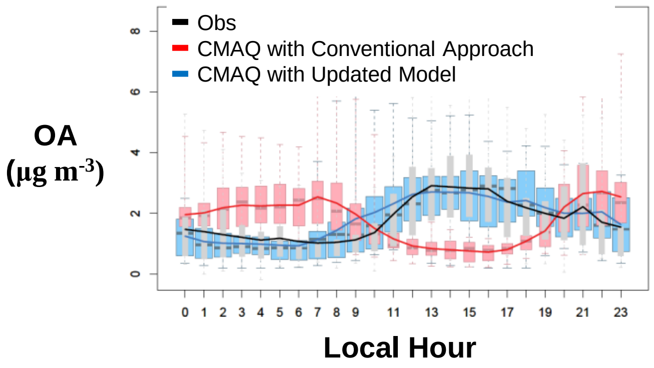
- IVOCs and SVOCs inferred from empirical (and uncertain) scale-factors applied to POA
- Large impact on SOA/OA ratio and spatiotemporal distribution of OA
- IVOCs and SVOCs largely ignored for ozone impacts

**Robinson et al., Science, 2007**: https://doi.org/10.3155/1047-3289.60.10.1204
**Tsimpidi et al., ACP, 2010:** https://doi.org/10.5194/acp-10-525-2010
**Koo et al., Atmos. Environ., 2014:** https://doi.org/10.1016/j.atmosenv.2014.06.031
**Zhao et al., Scientific Reports, 2016:** https://doi.org/10.1038/srep28815
**Woody et al., ACP, 2016:** https://doi.org/10.5194/acp-16-4081-2016
**Murphy et al., ACP, 2017:** https://doi.org/10.5194/acp-17-11107-2017




Northeast US, July 2001. Robinson et al., Science, 2007

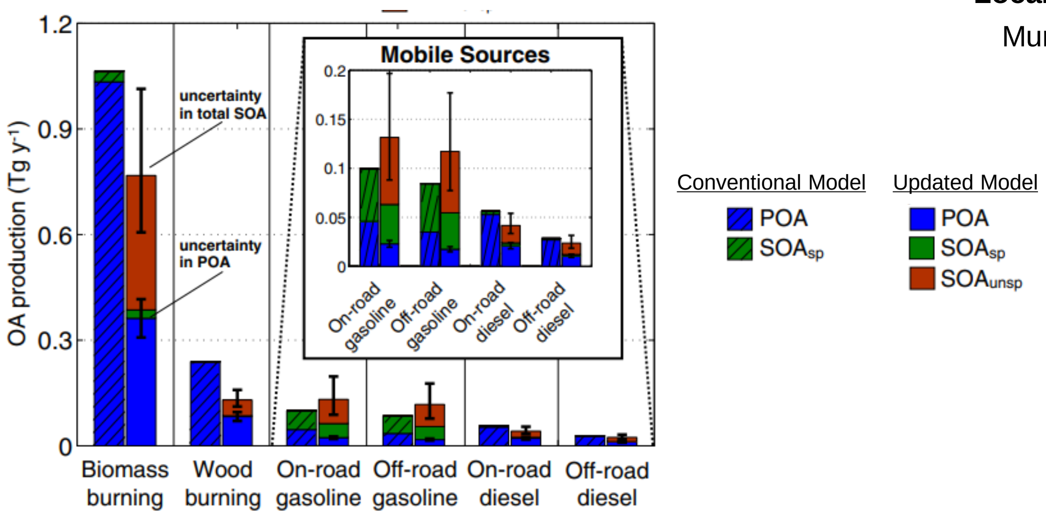
**Sacramento, CA during CARES 2010**




Murphy et al., ACP, 2017

## Updated to consider IVOC a component of VOC speciation

- More rigorous than POA scale factors
- OA source apportionment is impacted
- IVOCs and SVOCs largely ignored for ozone impacts

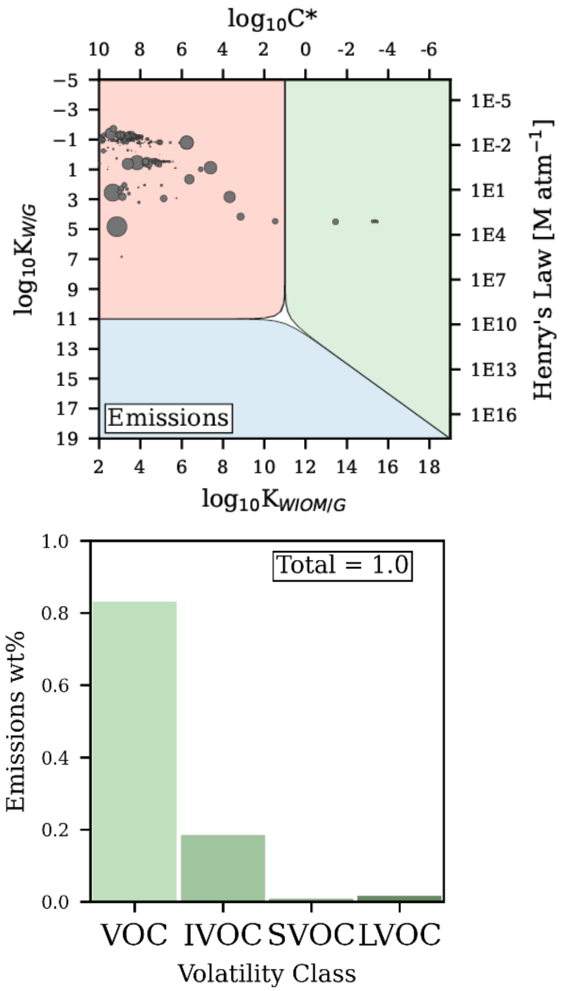



**Jathar et al., PNAS, 2014:**
https://doi.org/10.1073/pnas.1323740111

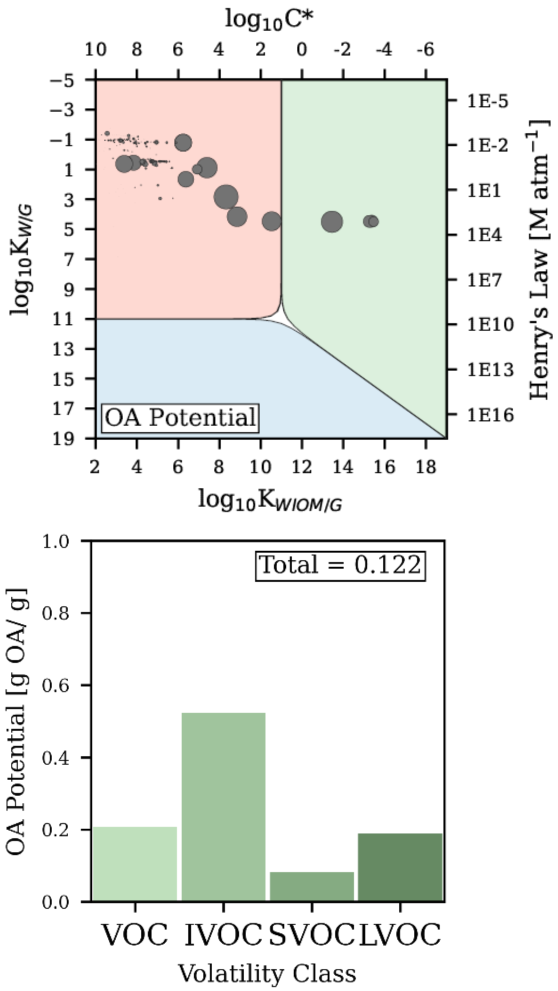
United States
Environmental Protection
Agency

# Mobile Source ROC Emissions

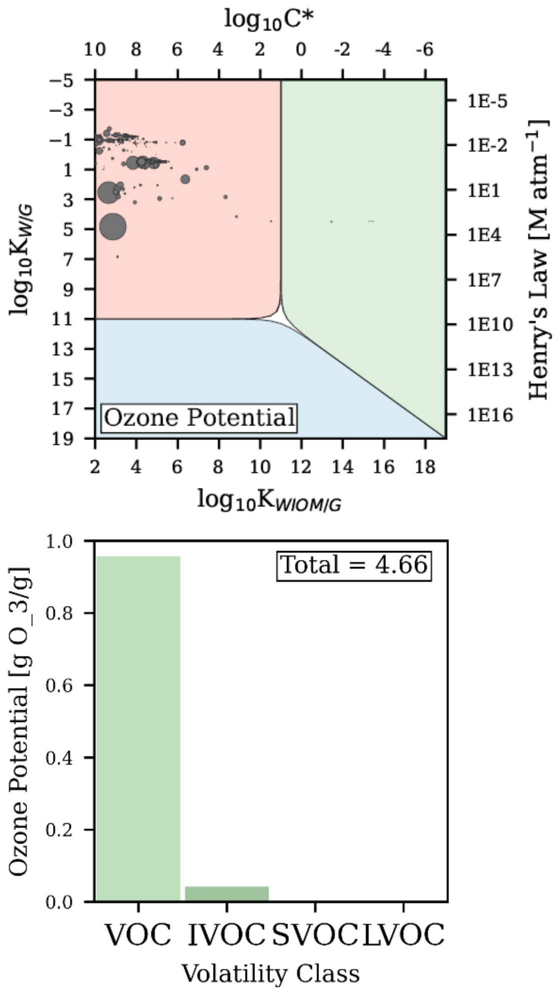
## Emissions




## Emissions weighted by OA potential




## Emissions weighted by Ozone Potential (MIR)



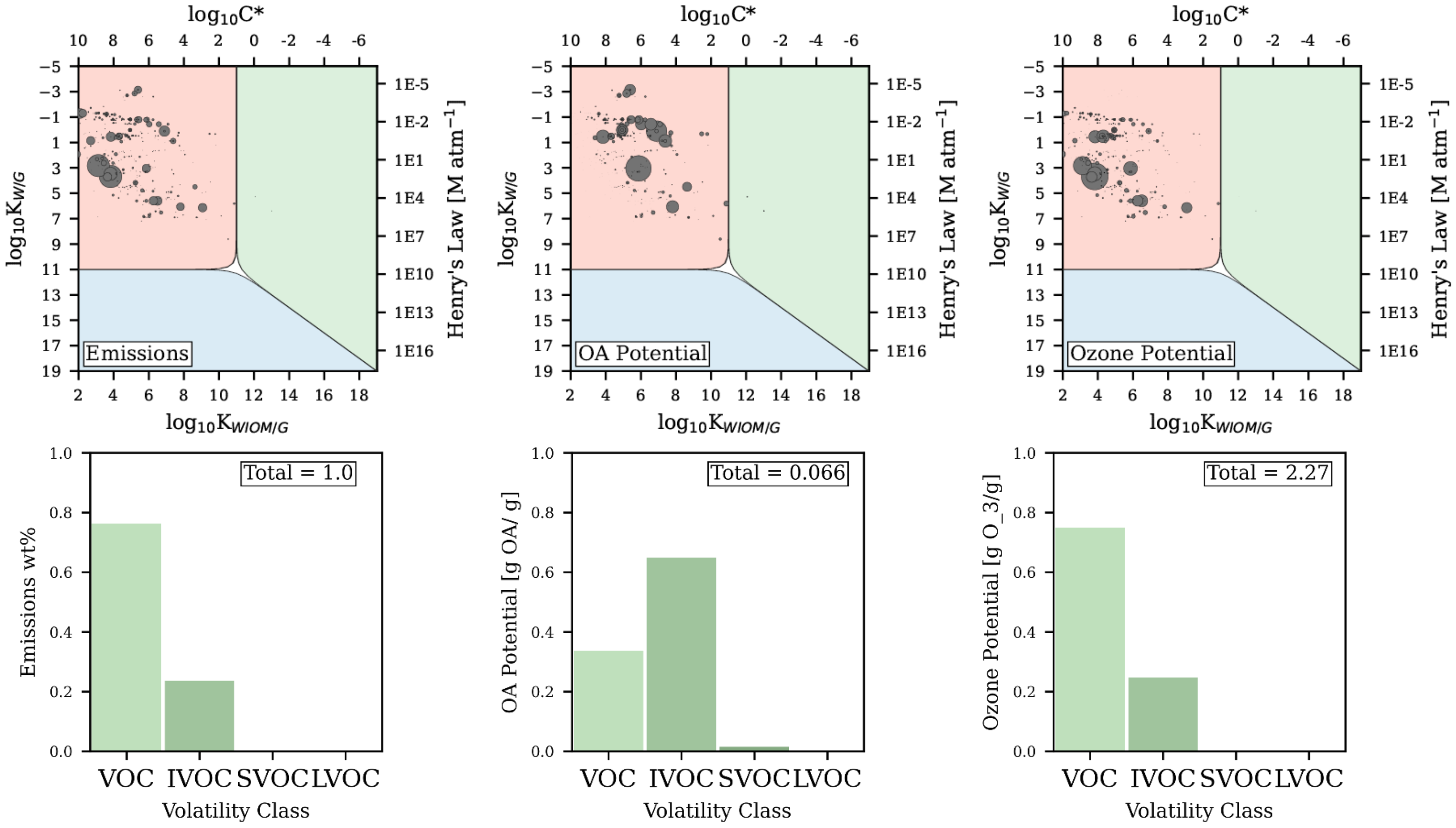

Vapor
Organic Phase
@ $C_{OA} = 10\ \mu g\ m^{-3}$
Aqueous Phase
@ $LWC = 10\ \mu g\ m^{-3}$

VOC = $VOC_{research}$

OA and Ozone potential were derived during the development of the Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM). Please see presentation by Havala Pye (2572, Development).

# Volatile Chemical Product ROC Emissions

Emissions | Emissions weighted by OA potential | Emissions weighted by Ozone Potential (MIR)




Vapor
Organic Phase
@ $C_{OA}$ = 10 μg $m^{-3}$
Aqueous Phase
@ LWC = 10 μg $m^{-3}$

VOC = $VOC_{research}$



Please see presentations by Karl Seltzer (2573, Emissions) and Elyse Pennington (2662, Development) for more info on the development of VCP emissions, OA potential, and Ozone impacts.