United States Environmental Protection Agency

Presentation 2572

Integrating reactive organic carbon emissions into the Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM)

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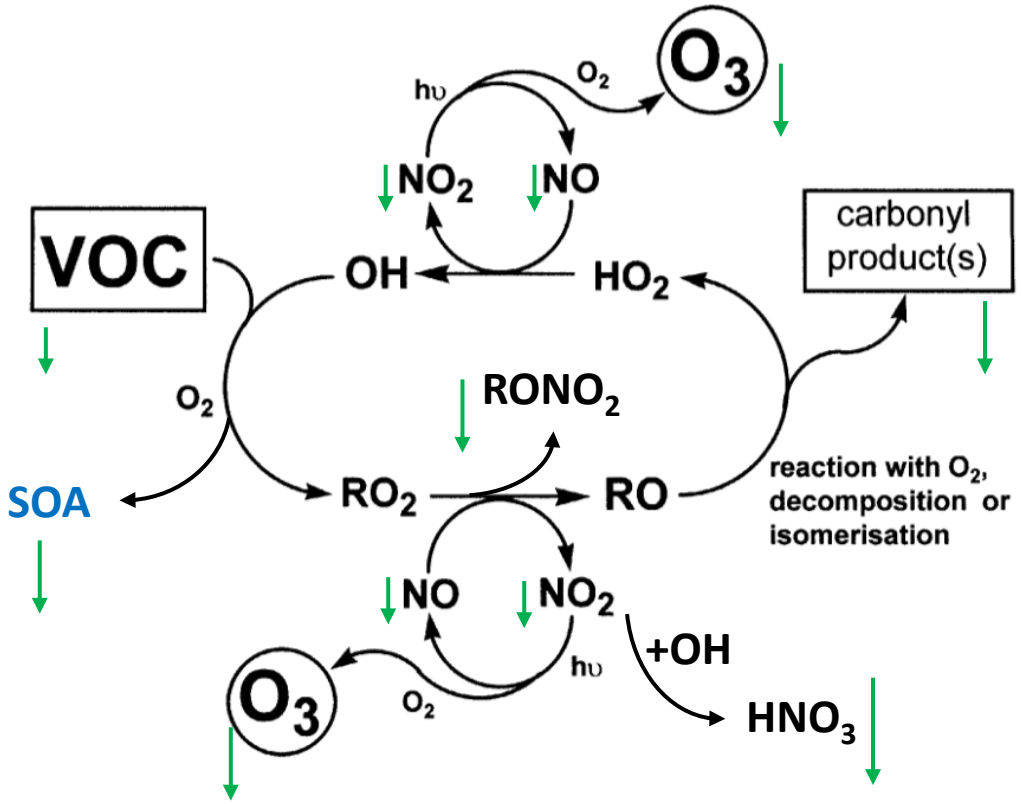
Chemical Mechanisms



Jenkin and Hayman *AE* 1999 with modification

- Traditionally include gas-phase NO_x-O_3-VOC chemistry (+SO_X)
- Require metadata (molecular weights, solubilities, vapor pressures, etc) to connect to other endpoints like secondary organic aerosol (SOA) and deposition
- Focus on the volatile subset of reactive organic carbon (ROC[1,2]) most relevant for gas phase pollutants like ozone

[1]ROC: All reactive organic carbon other than methane; includes gas and particulate organic compounds (Safieddine 2017 GRL)
[2]For more on ROC, see Ben Murphy's presentation 2618 (Emissions)

Integrating ROC emission information

Research Question

How might the design of mechanisms change if we considered:

- The composition of present-day ROC emissions of all volatilities
- Multiple endpoints (SOA, deposition, reactivity, toxicity)?

Hypothesis

We propose:

- Growing role of biomass burning and recognition of volatile chemical product (VCP[1]) emissions as well as role of specific toxic species in human health warrant additional species in the mechanism
- New species are needed at the lower-volatility end of the ROC spectrum (low, semi-, and intermediate volatility organic compounds, L/S/IVOC)

General Approach

Build on the history of RACM2 and develop the Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM)

[1]*For more information on VCPs, see Karl Seltzer's presentation 2573 (Emissions)*

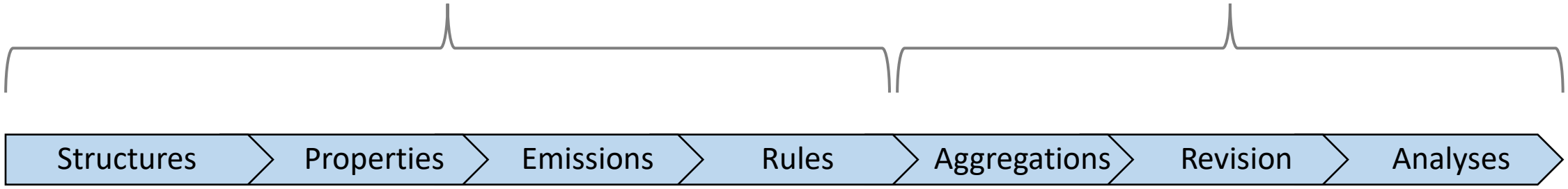
Methods

Individual ROC species level:

- Determine representative structures of all emissions
- Automate property estimation
- Determine abundance of individual ROC emissions
- Create rules for species mappings to the mechanism

Mechanism species level:

- Aggregate to mechanism species
- Revise mappings
- Analyze result

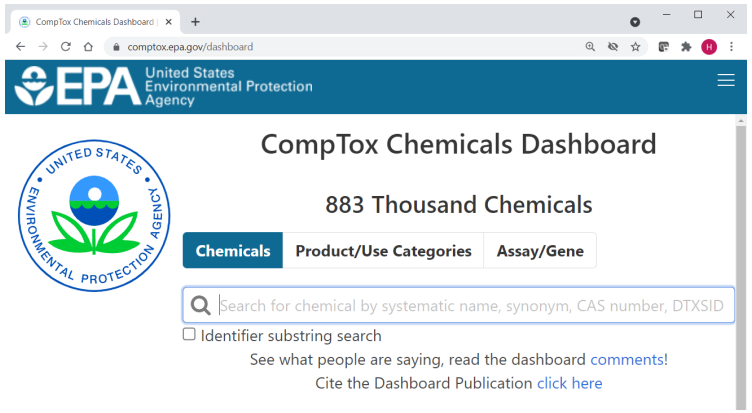


Representative Structures

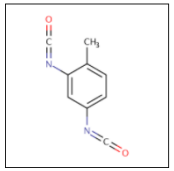
- Database of all (~3,000) known ROC emissions: SPECIATEv5.2 *(in development[1])*
- Map each species to a representative structure in the EPA Chemicals Dashboard
- Store identifiers (DTXSID) from dashboard in SPECIATE table

[1]See presentation 2632 by George Pouliot for information on the next SPECIATE release

https://comptox.epa.gov/dashboard

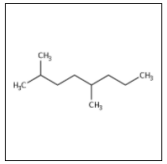


SPECIATE Species 154 (2,4-toluene diisocyanate) ↔



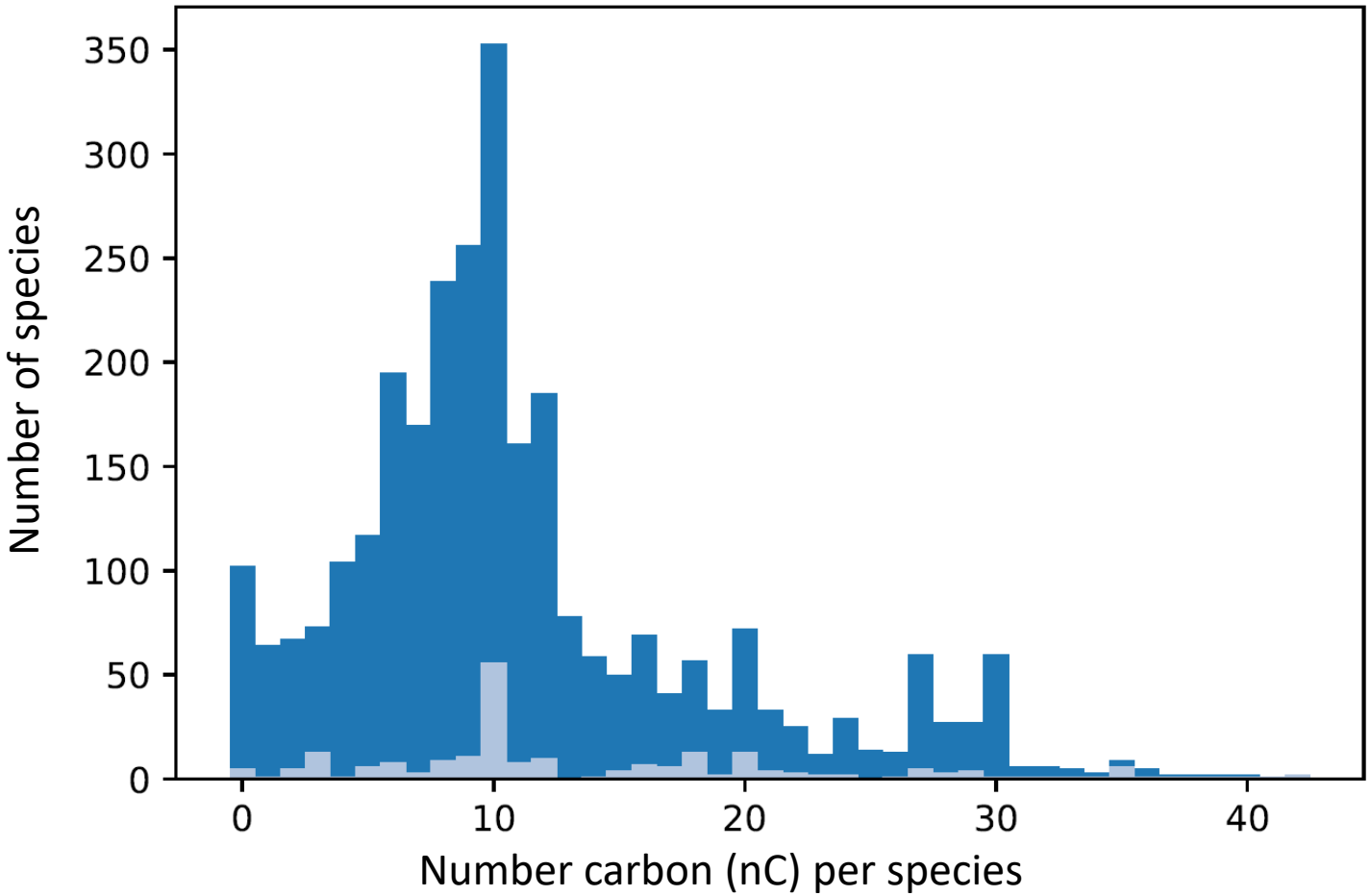
Toluene 2,4-diisocyanate
584-84-9 | DTXSID7026156
Searched by DSSTox Substance Id.

SPECIATE Species 151 (2,4-dimethyloctane) ↔



2,5-Dimethyloctane
15869-89-3 | DTXSID70871244
Searched by DSSTox Substance Id.

SPECIATE Database Coverage of ROC

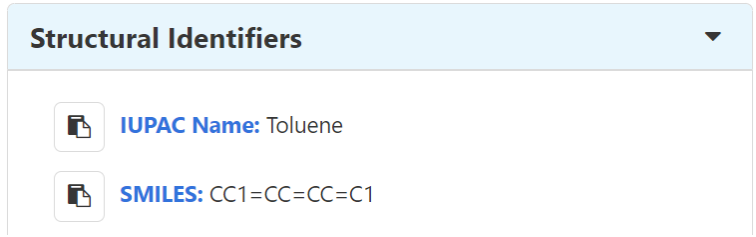


- SPECIATE contains many entries for the traditional volatile organic carbon range (nC<10)
- Uncertain compounds (light blue) tend to be represented by decane

As emissions characterization improves (particularly for S/IVOCs) → propagate information through to CRACMM

Property estimation

Basic info (chemical formula, SMILES) linked to DTXSID



OPEn quantitative structure-activity Relationship App (OPERA, Mansouri et al. 2018 *J. Cheminfo.*) for:
OH rate constant, vapor pressure, Henry's law coefficient;
Saturation concentrations (C*) calculated from vapor pressure

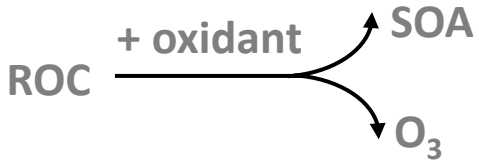
OPERA
OPEn (q)saR App

Open source (python) toolkit for cheminformatics: functional groups (e.g., furan, alcohol), aromaticity, and molecular structure

RDKit
Open-Source Cheminformatics and Machine Learning

Two pseudo-SARs

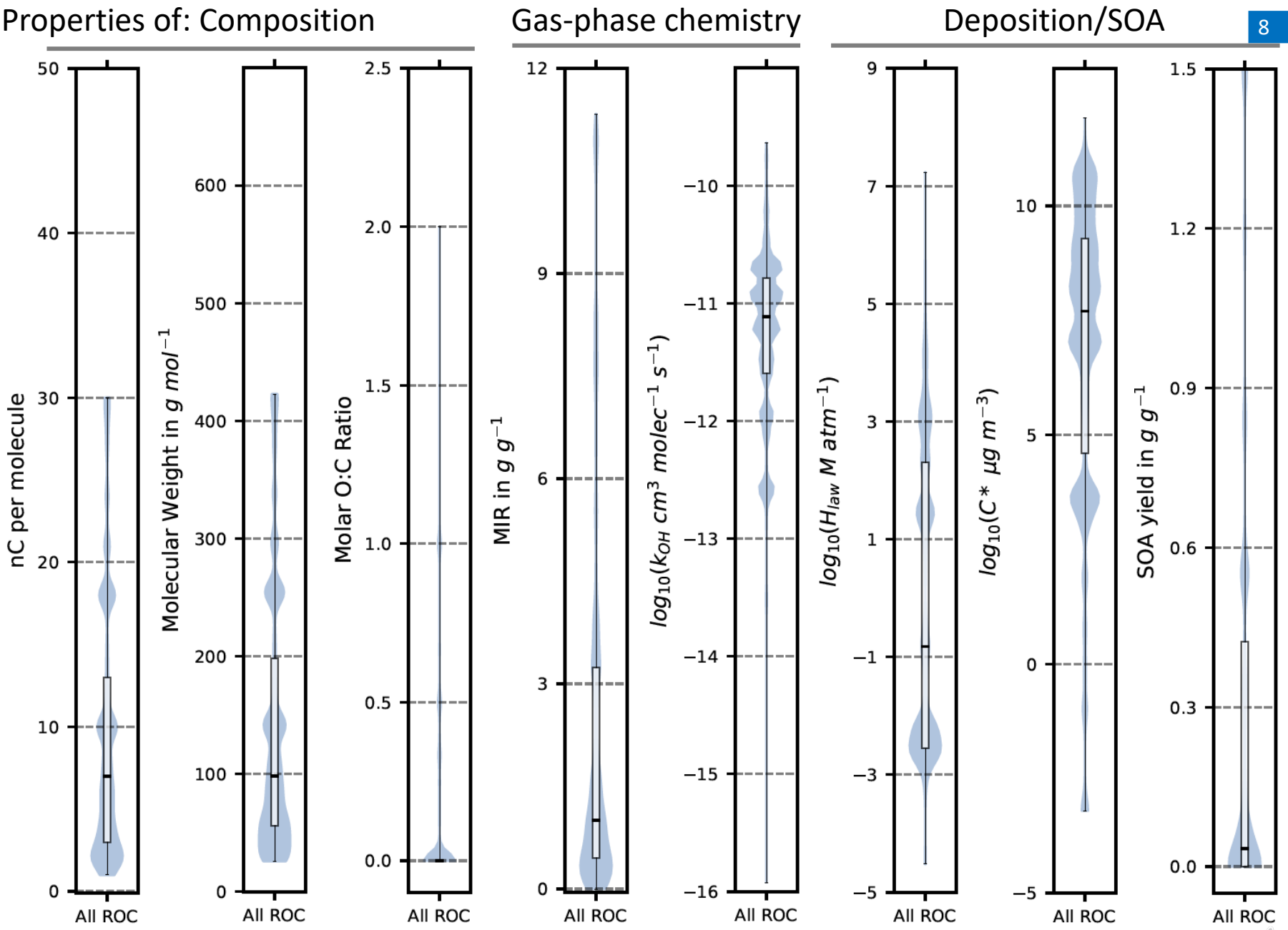
- Potential SOA yield
- Potential O_3 yield: Maximum Incremental Reactivity (MIR)



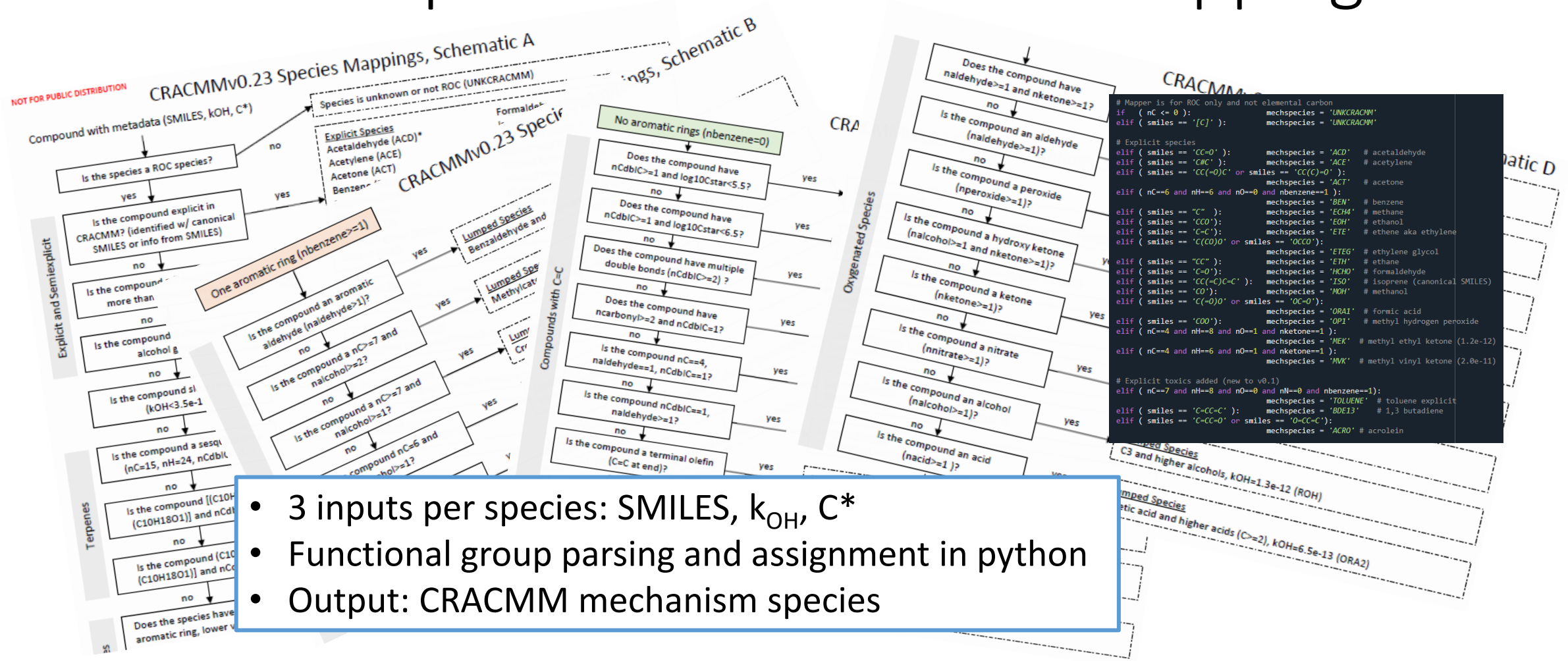
Emitted ROC

- Emission magnitude by species from EQUATES[1] for 2017 (and 2002)
- S/IVOCs from Murphy et al. (2017 *ACP*), Lu et al. (2020 *ACP*), & Jathar et al. (2014 *PNAS*)
- Emission magnitudes combined with estimated properties

[1]For more on EQUATES, see Kristen Foley's presentation 2588 (Applications)



Individual species to mechanism mapping



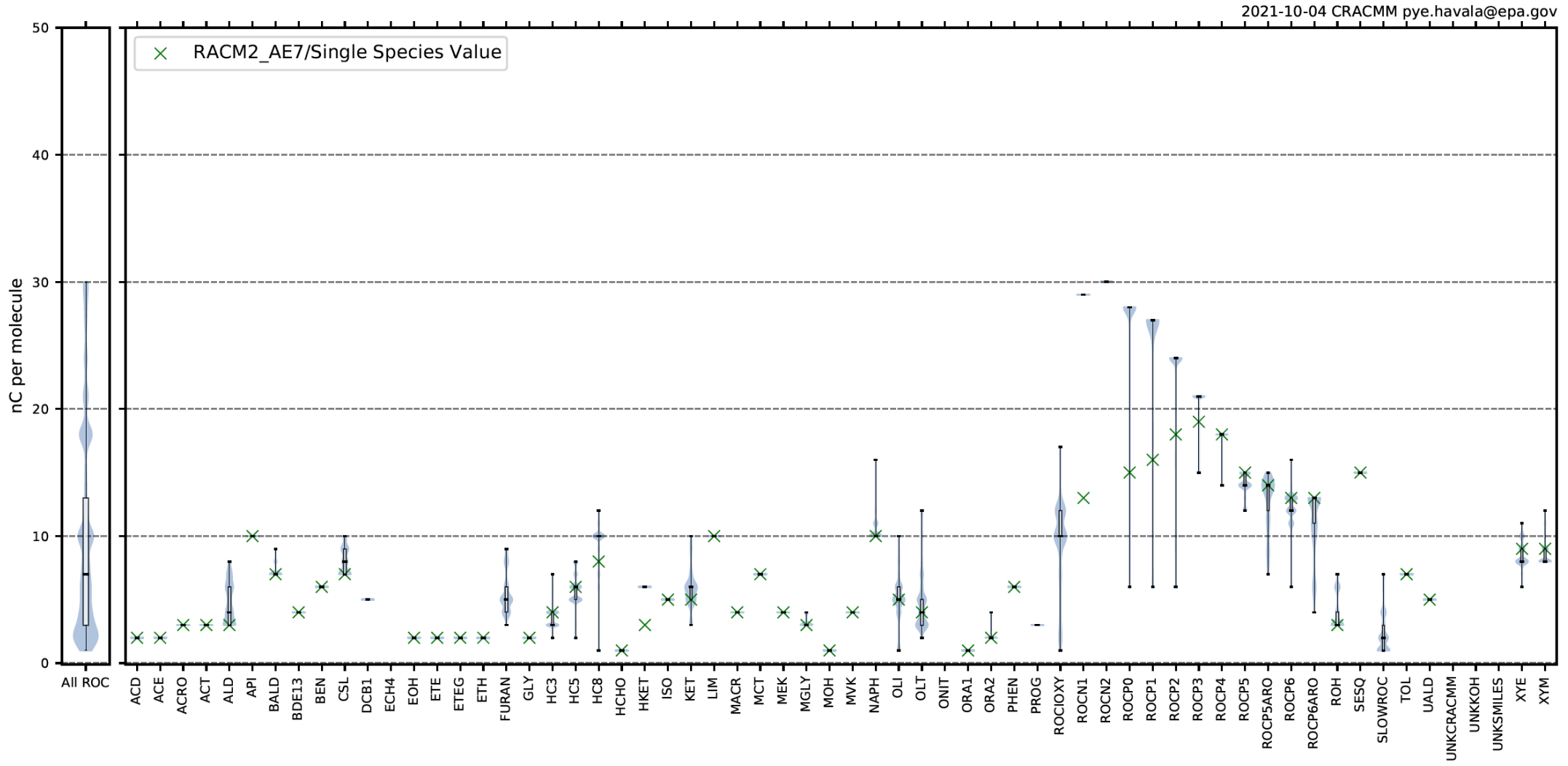

```
# Mapper is for ROC only and not elemental carbon
if   ( nC <= 0 ):                mechspecies = 'UNKCRACMM'
elif ( smiles == '[C]' ):        mechspecies = 'UNKCRACMM'

# Explicit species
elif ( smiles == 'CC=O' ):       mechspecies = 'ACD'   # acetaldehyde
elif ( smiles == 'C#C' ):        mechspecies = 'ACE'   # acetylene
elif ( smiles == 'CC(=O)C' or smiles == 'CC(C)=O' ):
                                 mechspecies = 'ACT'   # acetone
elif ( nC==6 and nH==6 and nO==0 and nbenzene==1 ):
                                 mechspecies = 'BEN'   # benzene
elif ( smiles == 'C'  ):         mechspecies = 'ECH4'  # methane
elif ( smiles == 'CCO'):         mechspecies = 'EOH'   # ethanol
elif ( smiles == 'C=C'):         mechspecies = 'ETE'   # ethene aka ethylene
elif ( smiles == 'C(CO)O' or smiles == 'OCCO'):
                                 mechspecies = 'ETEG'  # ethylene glycol
elif ( smiles == 'CC' ):         mechspecies = 'ETH'   # ethane
elif ( smiles == 'C=O'):         mechspecies = 'HCHO'  # formaldehyde
elif ( smiles == 'CC(=C)C=C' ):  mechspecies = 'ISO'   # isoprene (canonical SMILES)
elif ( smiles == 'CO'):          mechspecies = 'MOH'   # methanol
elif ( smiles == 'C(=O)O' or smiles == 'OC=O'):
                                 mechspecies = 'ORA1'  # formic acid
elif ( smiles == 'COO'):         mechspecies = 'OP1'   # methyl hydrogen peroxide
elif ( nC==4 and nH==8 and nO==1 and nketone==1 ):
                                 mechspecies = 'MEK'  # methyl ethyl ketone (1.2e-12)
elif ( nC==4 and nH==6 and nO==1 and nketone==1 ):
                                 mechspecies = 'MVK'  # methyl vinyl ketone (2.0e-11)

# Explicit toxics added (new to v0.1)
elif ( nC==7 and nH==8 and nO==0 and nN==0 and nbenzene==1):
                                 mechspecies = 'TOLUENE'  # toluene explicit
elif ( smiles == 'C=CC=C' ):     mechspecies = 'BDE13'    # 1,3 butadiene
elif ( smiles == 'C=CC=O' or smiles == 'O=CC=C'):
                                 mechspecies = 'ACRO' # acrolein
```

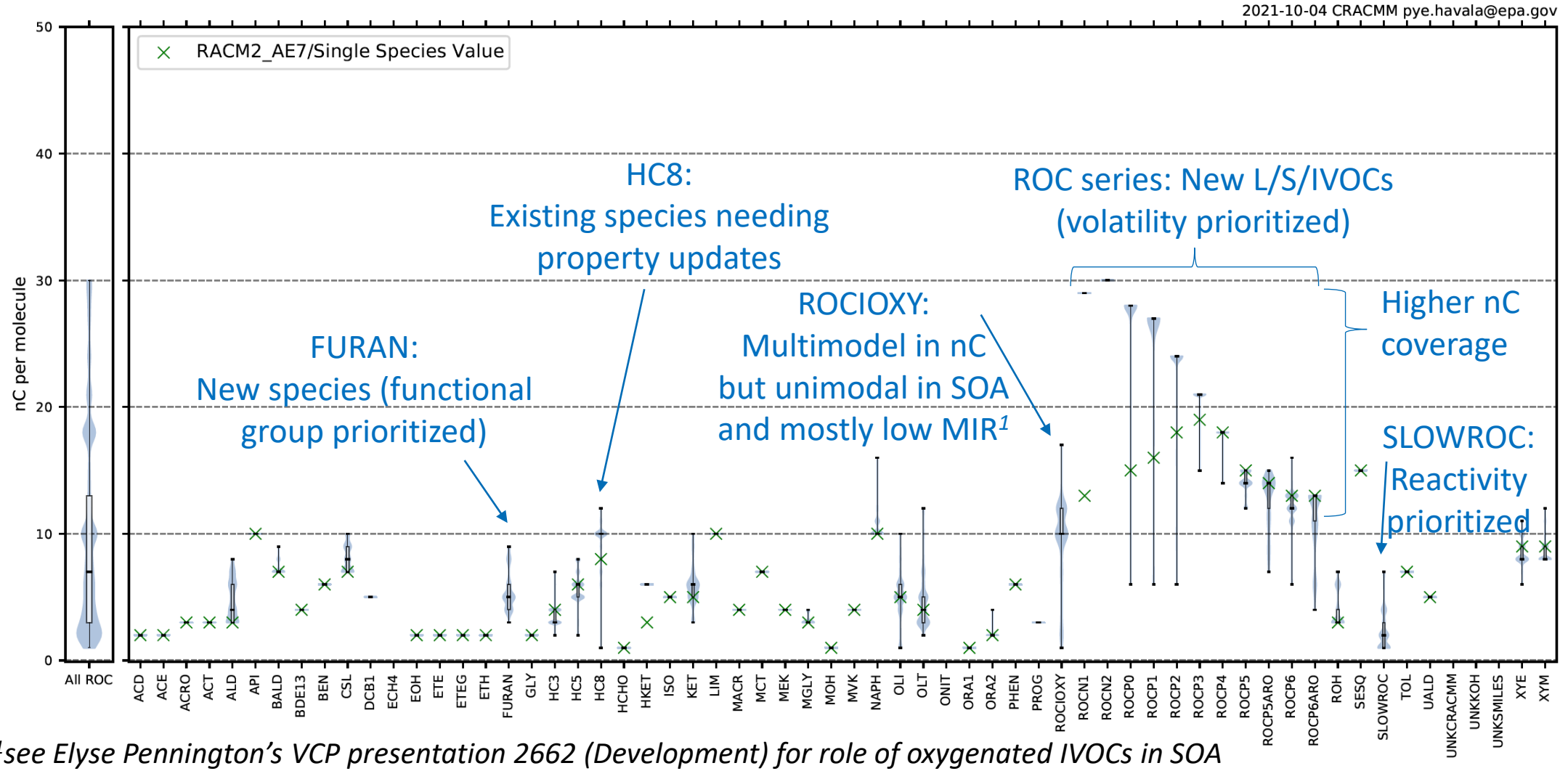
- 3 inputs per species: SMILES, k_{OH}, C*
- Functional group parsing and assignment in python
- Output: CRACMM mechanism species

Iterative visualization and revision of CRACMM



Structures | Properties | Emissions | Rules | Aggregations | Revision | Analyses

Iterative visualization and revision of CRACMM



[1]see Elyse Pennington's VCP presentation 2662 (Development) for role of oxygenated IVOCs in SOA

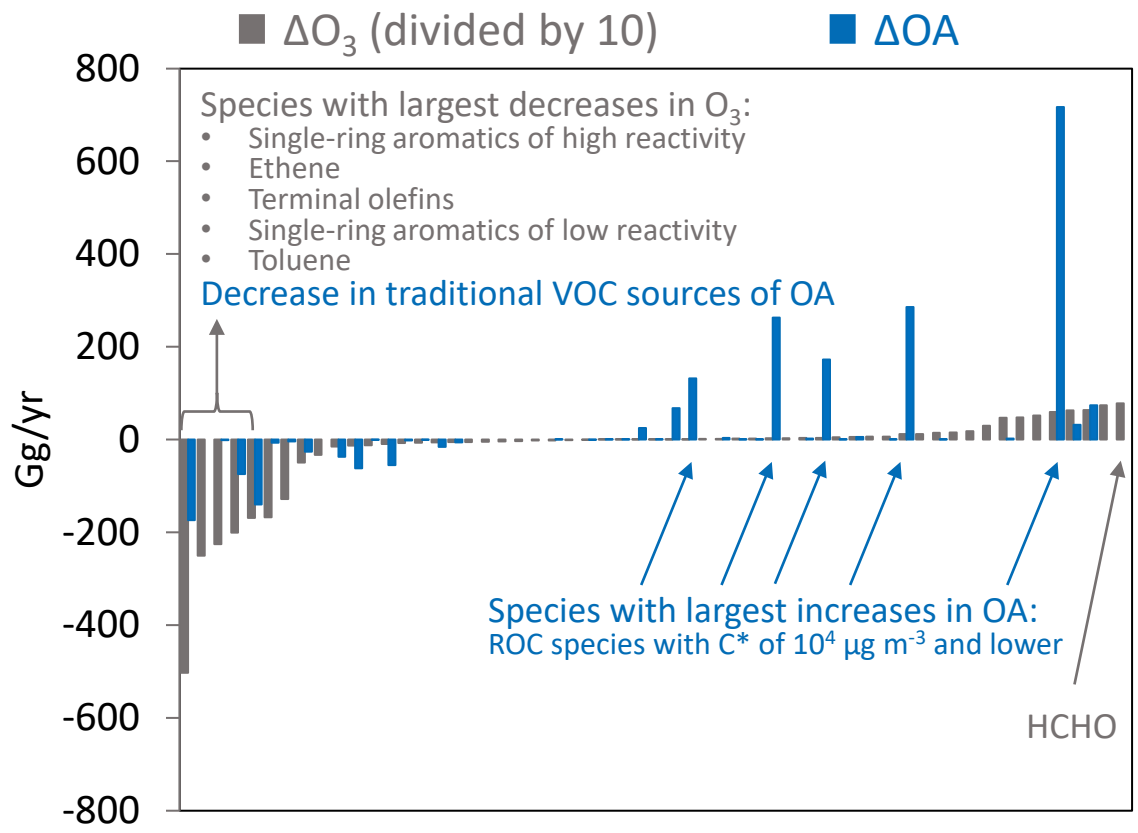
Structures | Properties | Emissions | Rules | Aggregations | Revision | Analyses

Final CRACMM Emissions

- Major updates reflect changing drivers of O_3 and OA formation in the U.S. and need to represent more diverse compounds:
  - Single ring aromatics were reorganized and reduced in count
  - L/S/IVOCs with alkane-like and aromatic-like behavior were added (functionality parsed)
  - More oxygenated species (e.g., furans, propylene glycol) were added
  - Explicit HAPs were added
  - Updates add 19 new species to RACM2

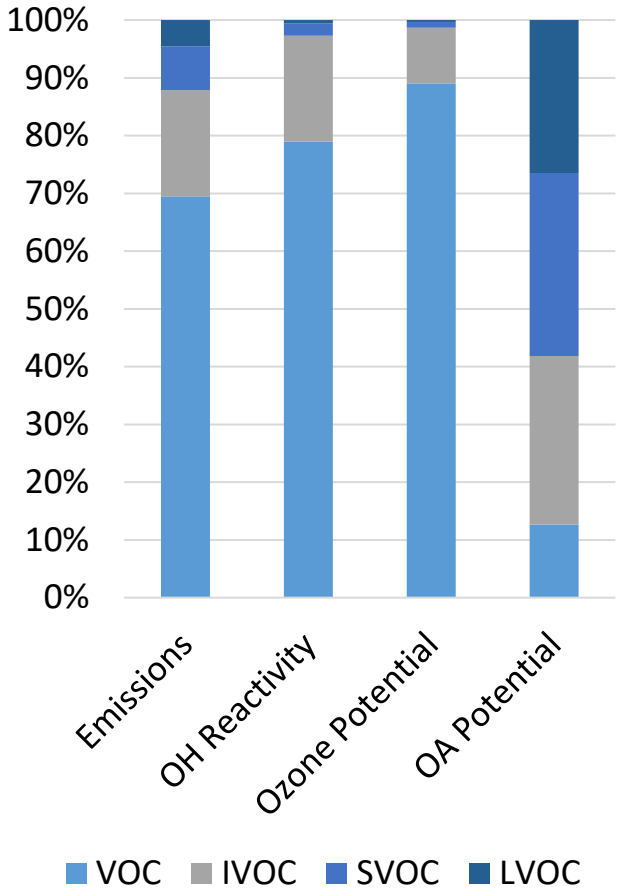
- After emission updates, CRACMM (256 species) is expected to have 15% *more* species than CB6r3_ae7 (222) & 7% *fewer* than SAPRC07tc_ae6 (276)

Change in Potential Production (2017-2002) by CRACMM Species



Potential for OA and O_3

VOC: $C^* \geq 10^{6.5}$ µg/m^3
IVOC: $10^{2.5} \leq C^* < 10^{6.5}$ µg/m^3
SVOC: $10^{-0.5} \leq C^* < 10^{2.5}$ µg/m^3
LVOC: $C^* < 10^{-0.5}$ µg/m^3



2017 U.S. conditions:

- 22 Tg/yr reactive organic carbon (ROC) emitted from non-biogenic activity*
  - 31% is an L/S/IVOC (sensitive to magnitude of wildland fire emissions)
  - Implication: Current gas-phase chemistry neglects 31% of ROC mass
- OH reactivity dominated by traditional VOCs, 21% from L/S/IVOCs
- 48 Tg/yr of O_3 formation potential (effective MIR of 2.2 g/g)
  - Fraction of O_3 potential in all L/S/IVOC species: 11% (effective MIR: 0.8 g/g)
  - Implication: ≥11% of O_3 formation potential is lost in historical methods**
- 5.6 Tg/yr OA formation potential (effective OA yield of 26%)
- L/S/IVOC contribution is expected to ***increase*** as emission datasets are improved

*includes fires and all types of wood burning, excludes biogenic sources. 12 Tg/yr without wood burning.
**when emissions are correctly estimated but mapped according to ae7 operational methods.

Summary

- Oxygenated and lower-volatility ROC species are of increasing importance for O_3 and OA production in the U.S.
- IVOCs are significant contributors to both O_3 and OA and often missing from chemical mechanisms
- Consideration of the current ROC emission composition resulted in new mechanisms species for:
  - Oxygenated ROC species
  - Higher carbon number/lower volatility surrogates
  - Explicit HAPs

Future work

- Release representative compound structures in SPECIATEv5.2
- Update chemical reactions in CRACMM within CMAQ to reflect the new emissions and other chemistry advances
- Evaluate CMAQ simulations with CRACMM over Northeast U.S. and finalize CRACMM v1.0
- Prepare CRACMM v1.0 for public distribution in fall 2022
  - Python tool repository including emission mapper
  - CRACMM archive of reactions and metadata for porting to other models
  - Release in CMAQv6 as research version

CRACMM Development Team

Chair: Havala Pye, EPA

Co-Chair: Becky Schwantes, NOAA/CIRES

Mechanism Developers:

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