The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the U.S. EPA.

EPA United States Environmental Protection Agency

Volatile Chemical Product Enhancements to Criteria Pollutants in the United States

Karl Seltzer,[1,2] Ben Murphy,[2] Elyse Pennington,[1,3] Chris Allen,[4] Kevin Talgo,[4] Havala Pye[2]

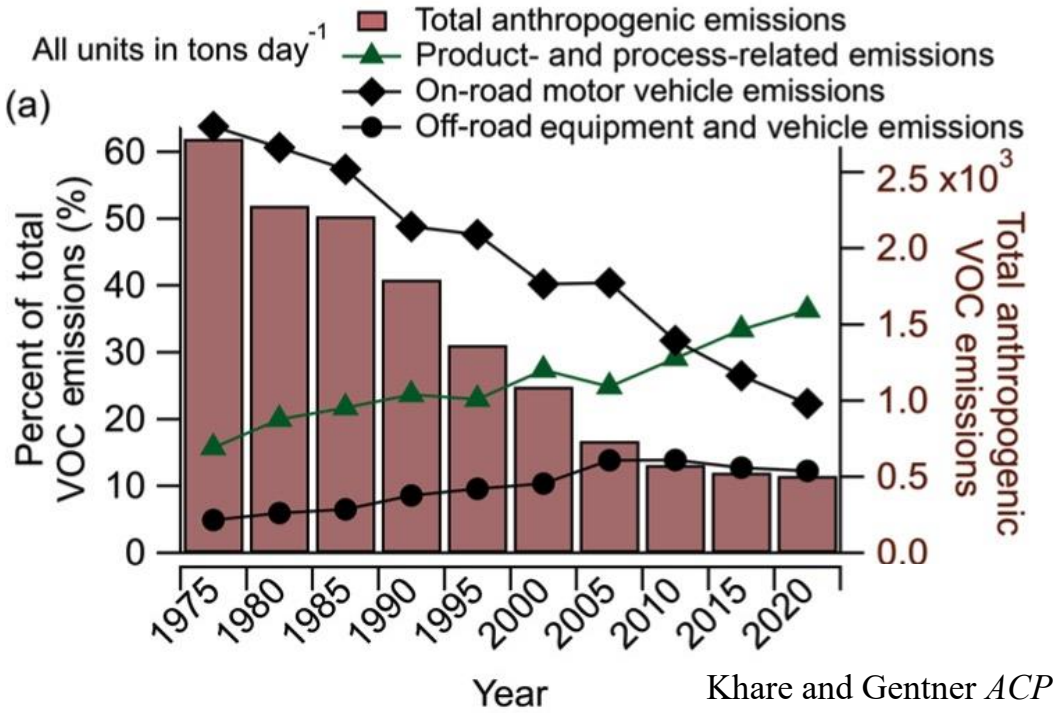
[1]ORISE Fellow, US Environmental Protection Agency, Research Triangle Park, NC
[2]US Environmental Protection Agency, Research Triangle Park, NC
[3]California Institute of Technology, Pasadena, CA
[4]General Dynamics Information Technology, Research Triangle Park, NC

Volatile Chemical Products

Broad category of non-point sources.

- Personal care products: lotions, deodorants, body sprays, hair/nail/bath products.
- Cleaners: household/commercial cleaners & degreasers, air fresheners, hand sanitizer.
- Adhesives & sealants: Carpet/tile/wood glues, sealants/caulking compounds.
- Pesticides: Household, institutional, and industrial.
- Paints & coatings: Paint, spray paint, commercial product coatings, paint thinners.
- Printing inks, dry cleaning fluids, oil & gas solvents.

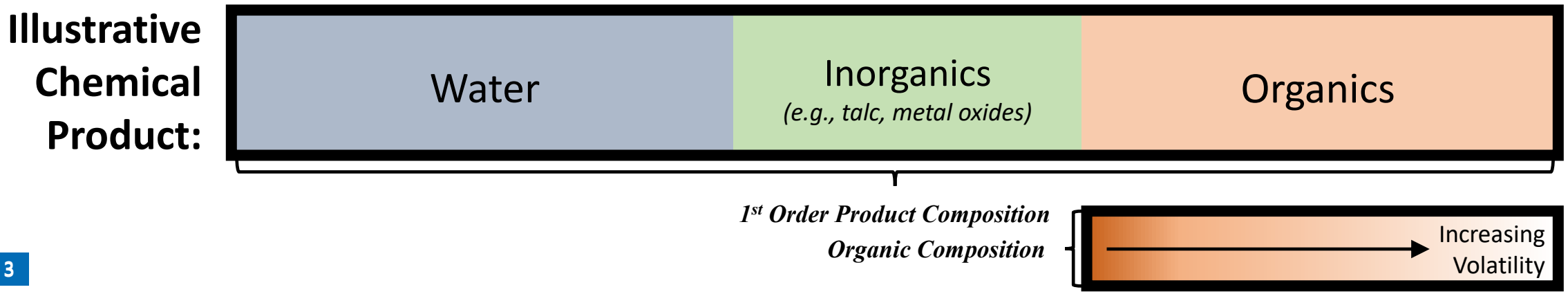
Chemical product emissions are becoming more important:



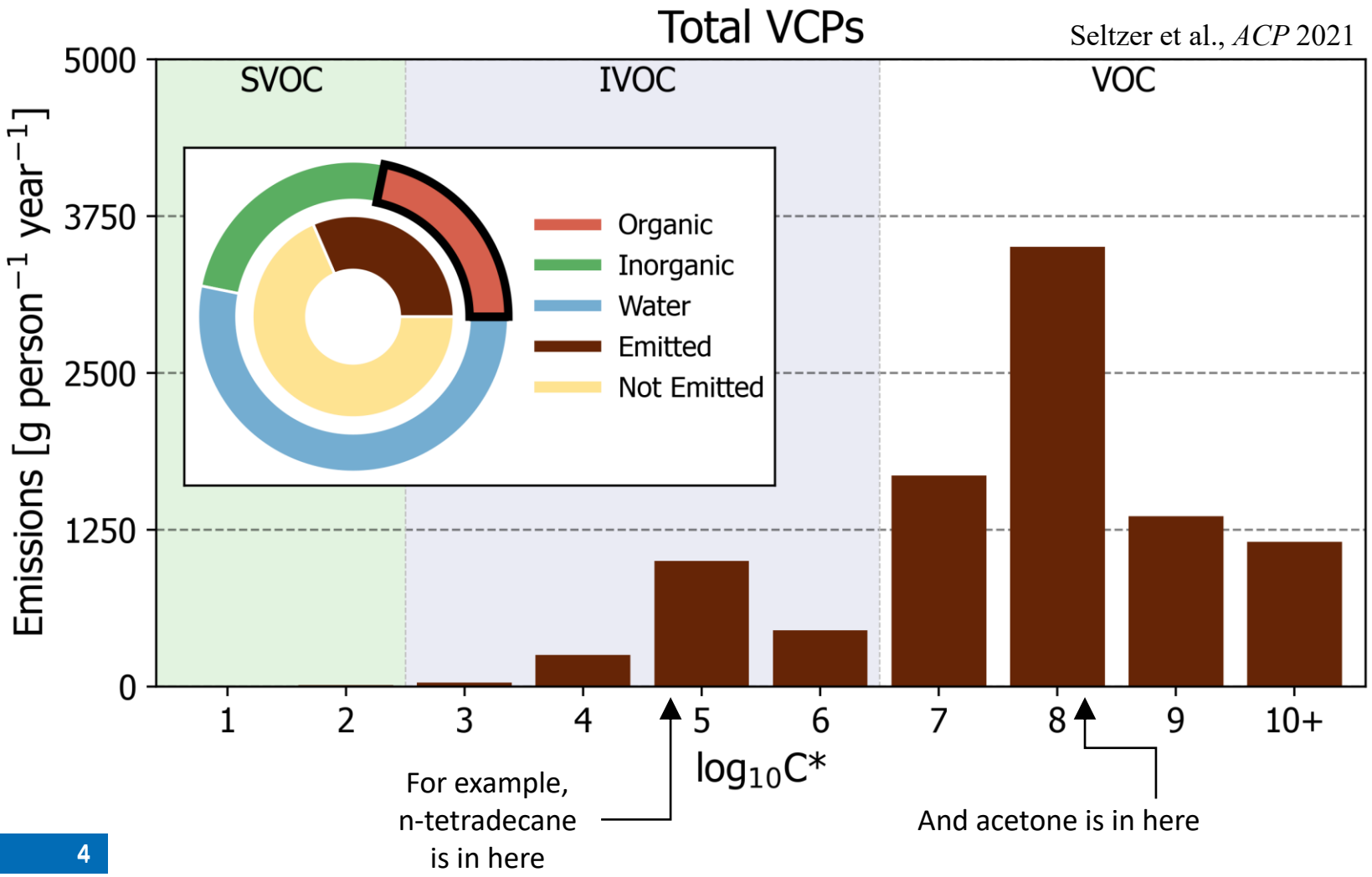
Khare and Gentner *ACP* 2018

Introducing VCPy

- New framework to model organic emissions from VCPs.
  - Publication: Seltzer et al., ACP, 2021
- Name derived from Volatile Chemical Products and Python.
- The magnitude and speciation of emissions is directly related to:
  i. The mass of chemical products used
  ii. The composition of these products
  iii. The physiochemical properties of their constituents that govern volatilization (evaporation timescale)
  iv. The timescale available for these constituents to evaporate (use timescale) →

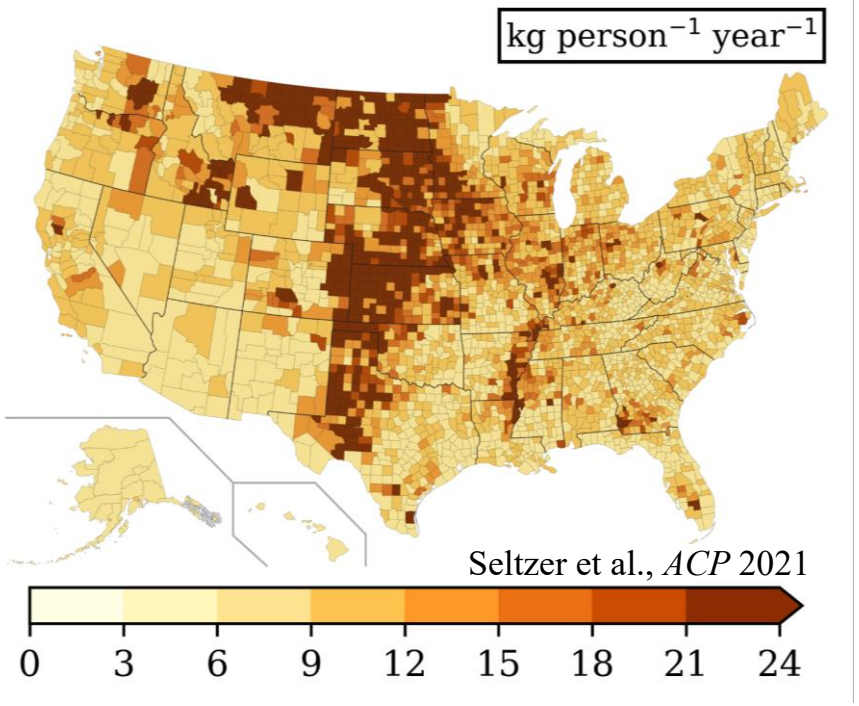


VCPy: Sector Emissions

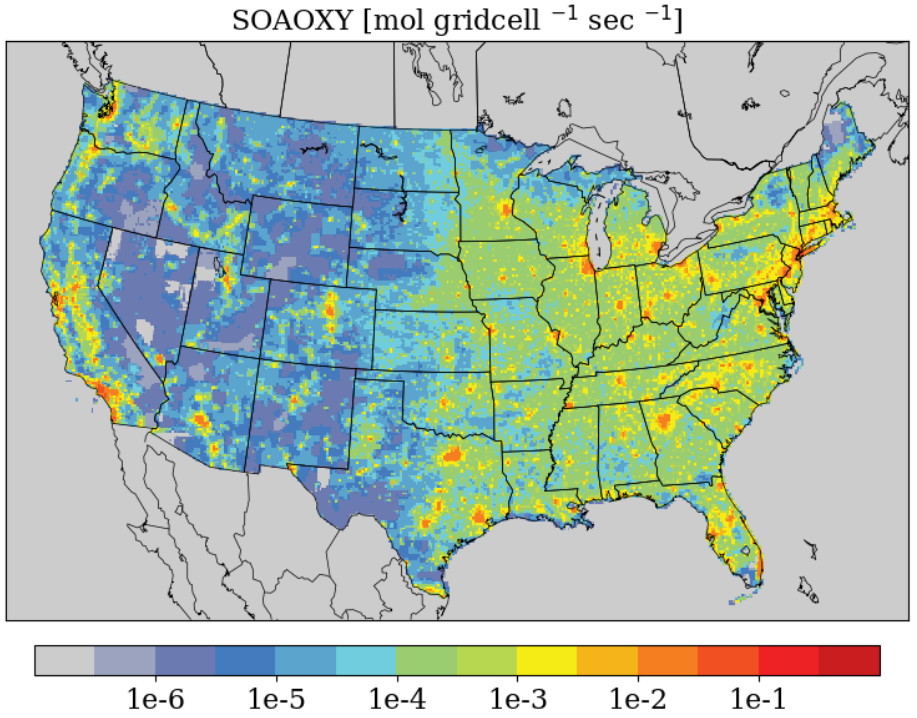


- National, per-capita organic emissions from VCPs are 9.5 kg person^{-1} year^{-1}.
- 20% of organic emissions from VCPs are IVOCs: SOA precursors.
- Predicted emissions reflect estimates of current usage and formulations.
- VCP emissions are complex: span 8+ orders of magnitude in saturation concentration.

Spatial Allocation of VCP Emissions



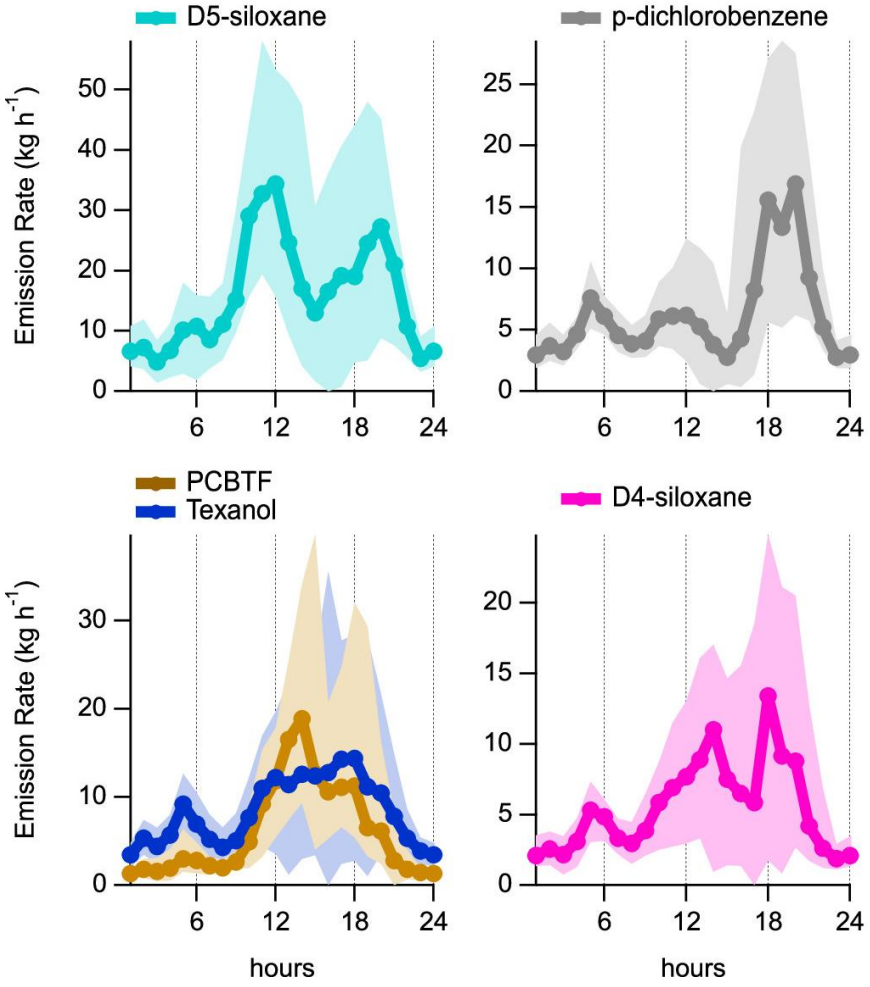
VCPy allocates emissions to the county-level using population, employment statistics, and other proxy datasets.



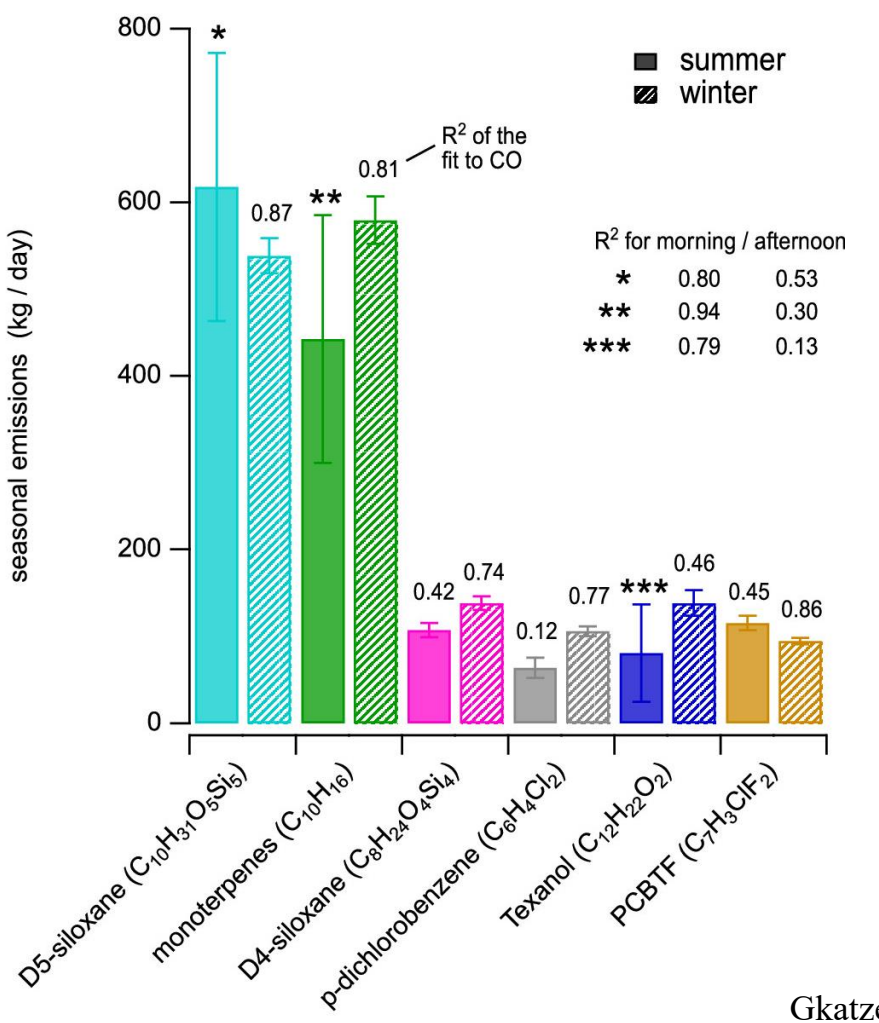
Additional post-processing to grid emissions for air quality modeling.

Temporal Allocation of VCP Emissions

Diurnal Profiles:



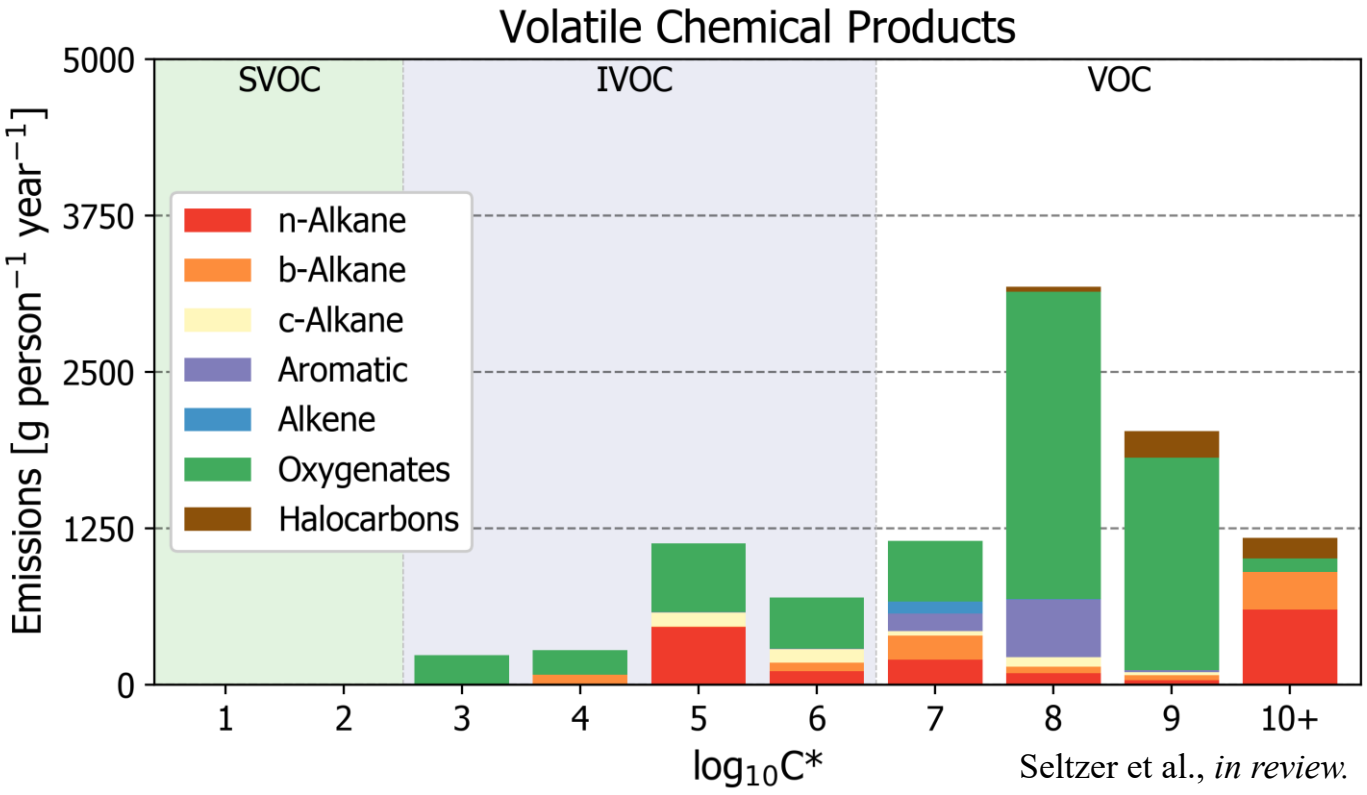
Seasonal Profiles:



Gkatzelis et al., *ES&T 2021*

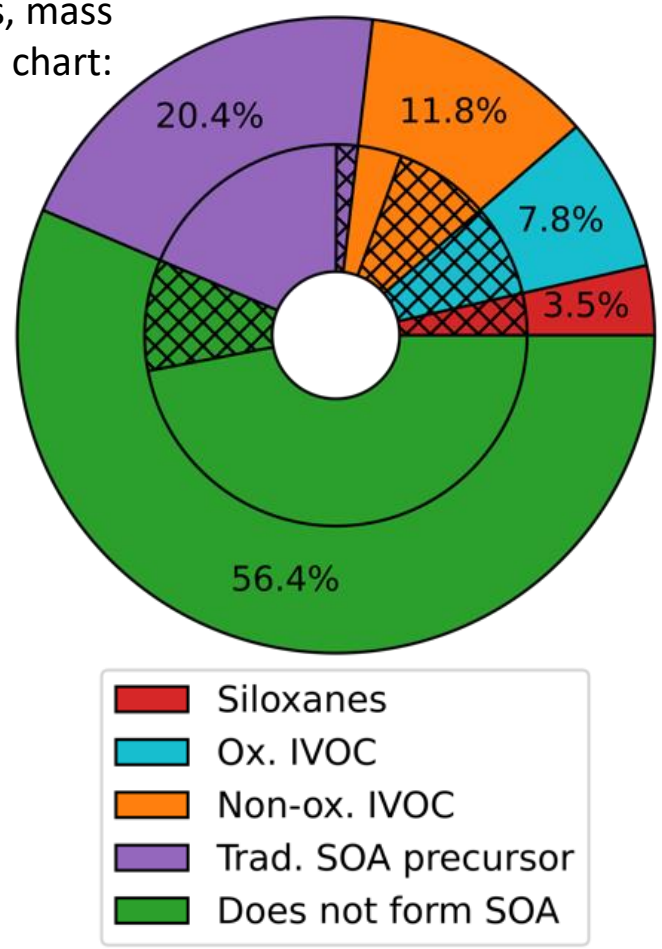
Chemical Treatment of VCP Emissions

- VCP emissions are chemically complex and feature considerable variability in reactivity/SOA potential.
- Here, we adopt the methods of Lu et al. (ACP) and Pennington et al. (ACPD).
  - Treatment of non-oxygenated IVOCs and subsequent aging (Lu et al., *ACP 2020*).
  - Treatment of oxygenated IVOCs and siloxanes (Pennington et al., *ACPD 2021*).



Minimize Mass Loss in Emissions Processing

~400 species, mass weighted, in pie chart:



Pennington et al., *ACPD 2021*

- Required revisiting mapping of explicit compounds to model species.
- Outer circle: Mass allocation of emissions following updated mapping.
- Inner circle: All hatched portions of pie chart are currently mapped to NROG, NVOL, or IVOC. These species do not participate in CMAQ model chemistry. ~30% of VCP mass, most of which are IVOCs and SOA precursors, are effectively ignored.

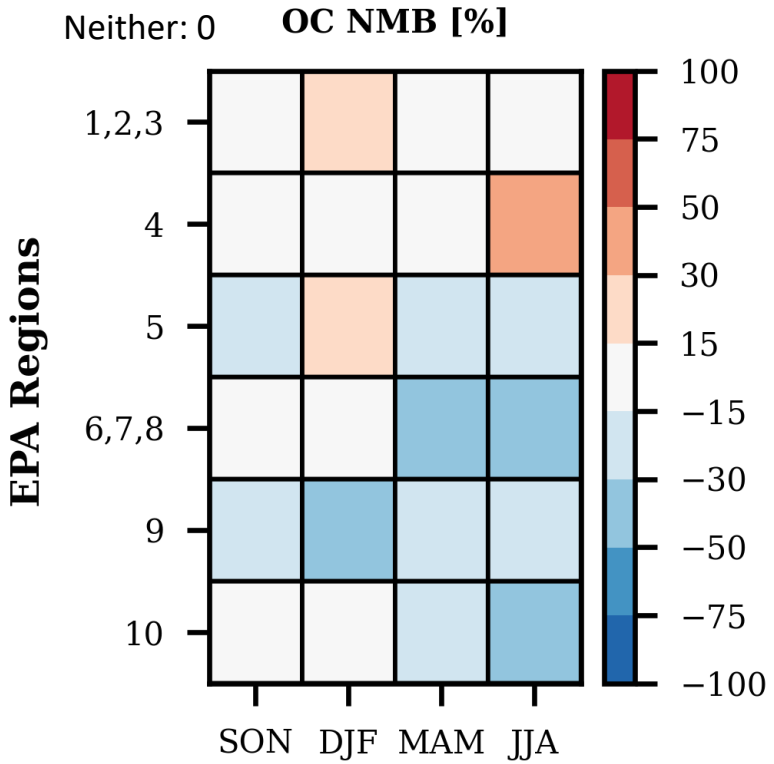
EPA United States Environmental Protection Agency

Air Quality Modeling

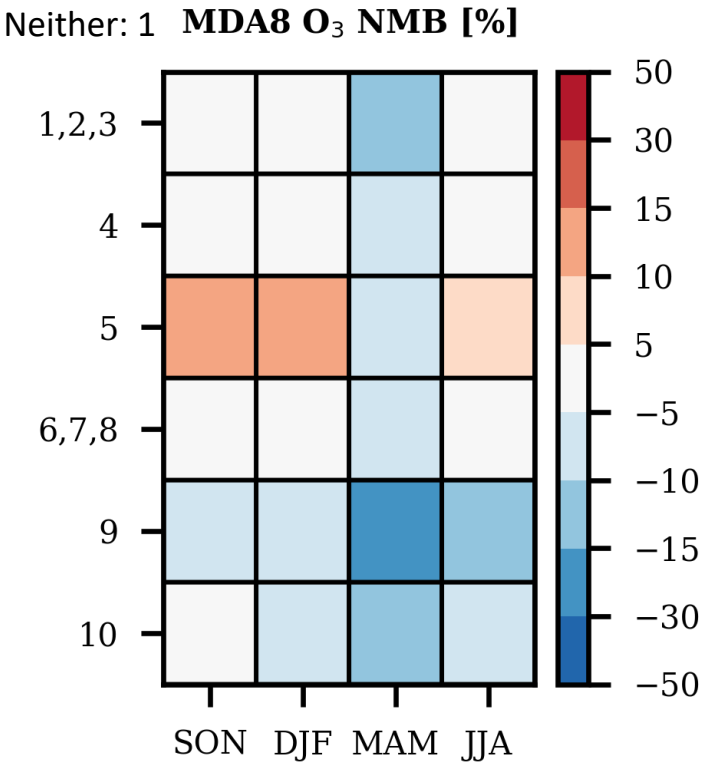
- A full-year 2016 simulation using CMAQv5.3.2 at 12-km resolution (12US1 domain).
- CB6r3_AE7_aq chemical mechanism, non-VCP anthropogenic emissions from the 2016v1 modeling platform, and VCPy derived emissions for 2016.
- All sources featured semi-volatile POA, mobile emissions featured state-of-science IVOC treatment (Lu et al. 2020), and pcSOA (i.e., an empirical representation of potential SOA) was not included.
- Model performance was compared to the top 33rd percentile ("goal") or the top 67th percentile ("criteria") of past evaluation applications (Emery et al., *JA&WMA 2017*).

Modeling Performance

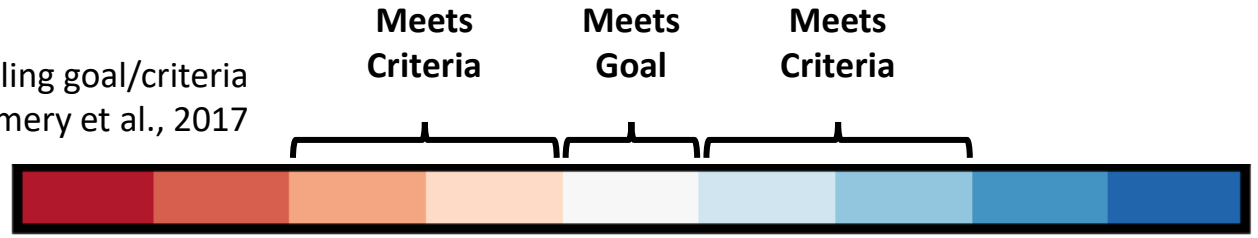
Goal: 10
Criteria: 14
Neither: 0



Goal: 10
Criteria: 13
Neither: 1



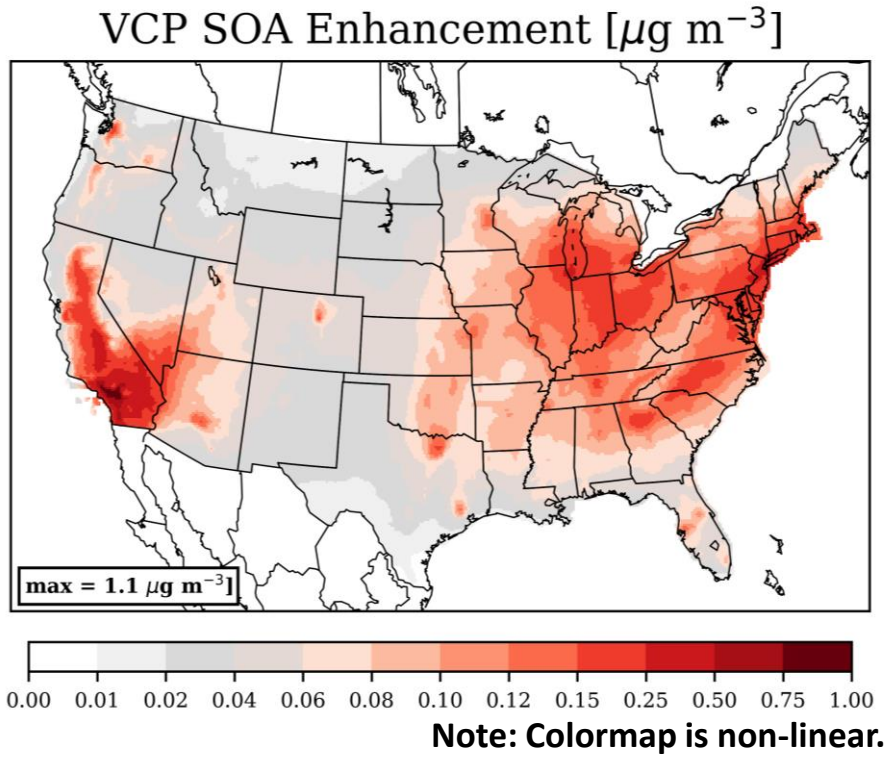
Modeling goal/criteria specified in Emery et al., 2017



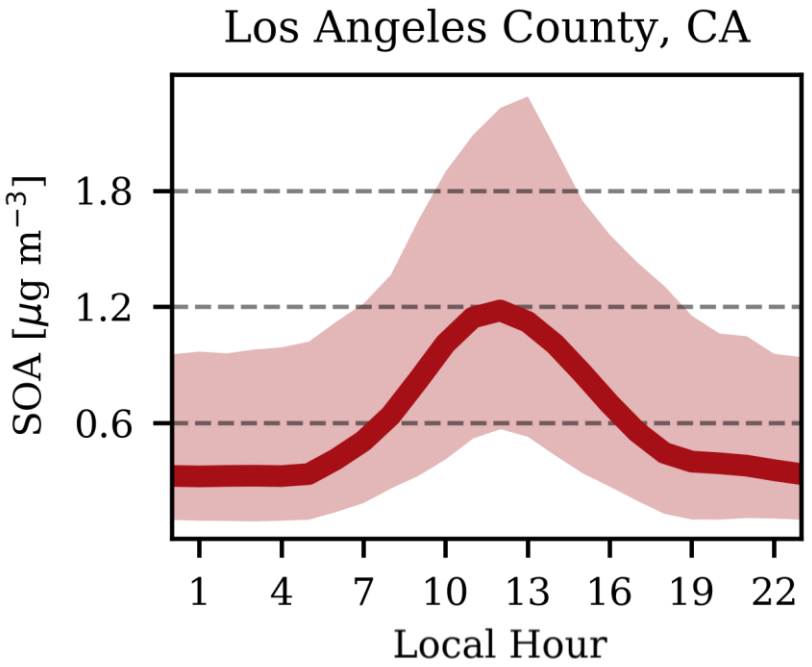
- Almost always met "goal" or "criteria": comparatively good model performance.
- While generally low by ~12%, OC meets "criteria" (< ±50%) bias in all aggregations and is often < ±15% biased (meets "goal").
- Broadly, maximum daily 8-hr average (MDA8) O_3 is almost always within ±15% of observations and is often within ±5%.

Seltzer et al., *in review.*

VCP Enhancements of Summer SOA



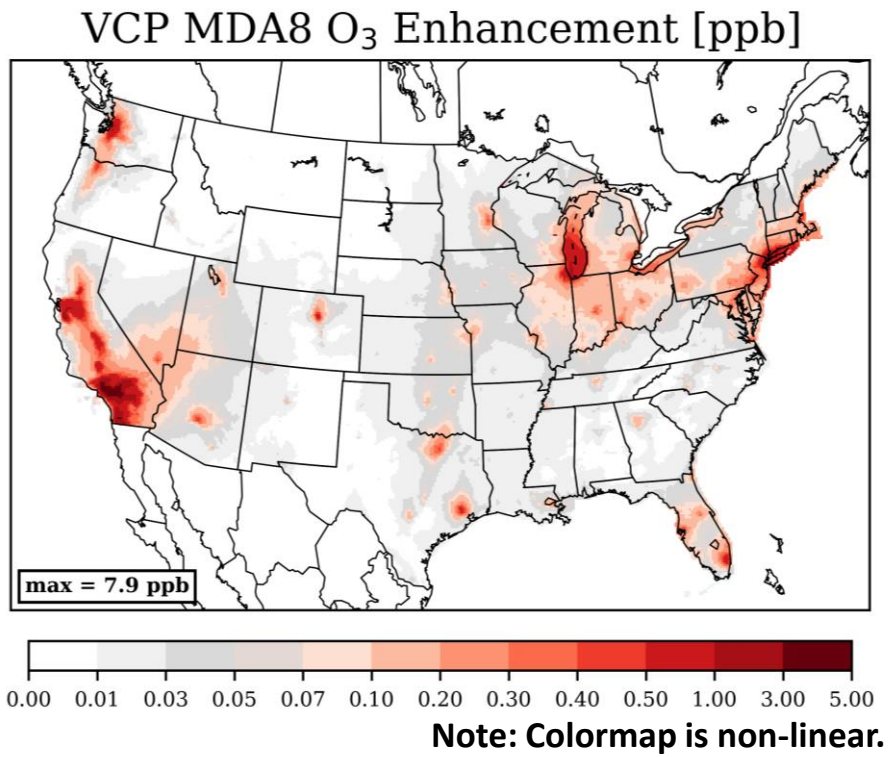
Note: Colormap is non-linear.



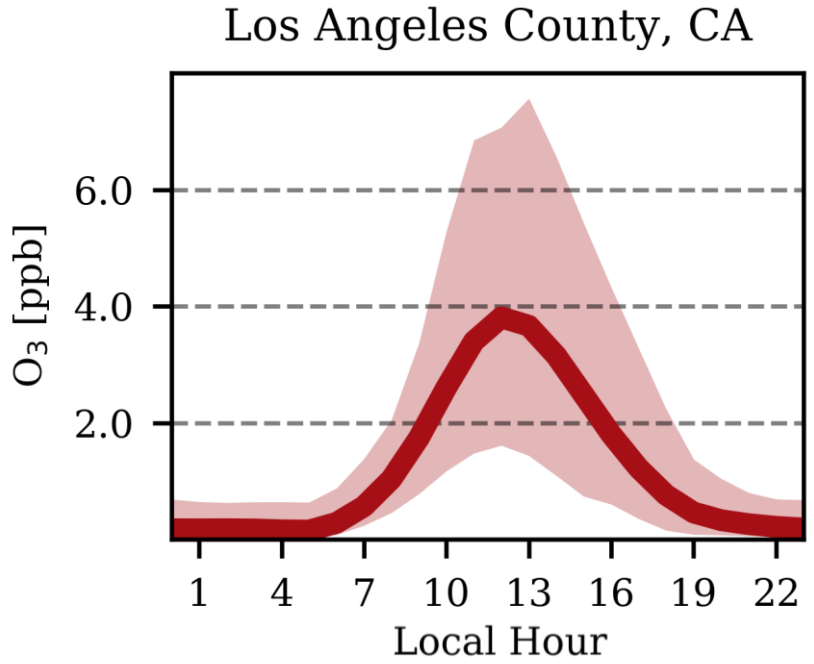
- Seasonal, 24-hour averages:
  - Southern California: 0.5-0.9 µg m^{-3}
  - New York City: 0.3-0.4 µg m^{-3}
- Enhancements can fluctuate from day-to-day.
  - Population weighted average VCP enhancement of SOA at each hour of the day (line) and the hourly enhancement for 95% of all days (shading).

Seltzer et al., *in review.*

VCP Enhancements of Summer MDA8 Ozone



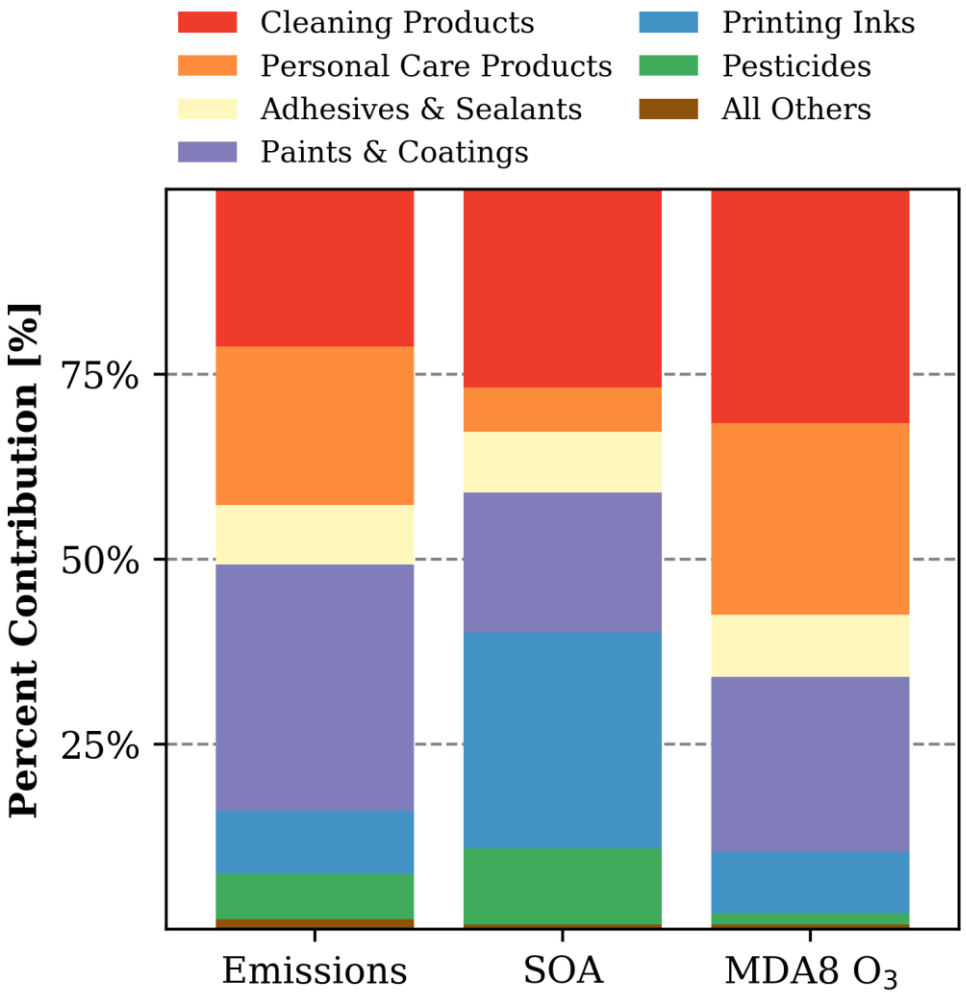
Note: Colormap is non-linear.



- Seasonal, MDA8 averages:
  - Southern California: 1.7-5.8 ppb
  - New York City: 0.9-1.7 ppb
- Enhancements can fluctuate from day-to-day.
  - Population weighted average VCP enhancement of SOA at each hour of the day (line) and the hourly enhancement for 95% of all days (shading).

Seltzer et al., *in review.*

Product Use Category Contributions



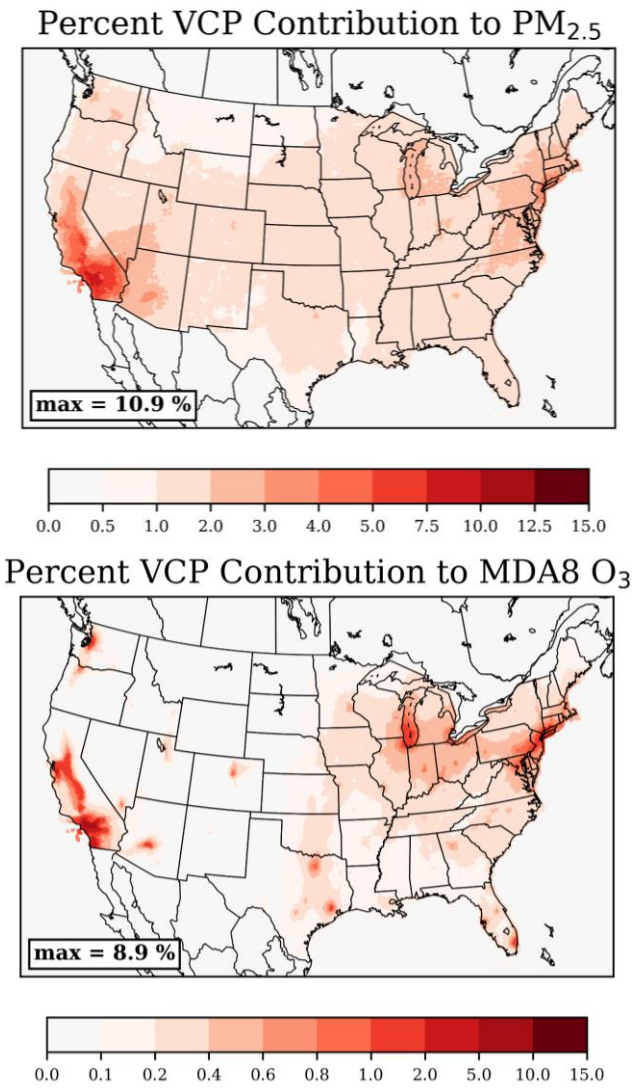
- Emission contributions are diverse in magnitude and can regionally vary (e.g., pesticides).
- Paints & Coatings are the largest emissions category, by mass, followed by Personal Care Products and Cleaning Products.
- SOA contributions are dominated by Printing Inks, Cleaning Products, and Paints & Coatings.
- Summertime MDA8 O_3 contributions are proportional to emissions → Paints & Coatings, Personal Care Products, and Cleaning Products make up ~76% of emissions and ~81% of the summertime MDA8 O_3 enhancements.

Seltzer et al., *in review.*

Conclusions

- VCPy estimates that the national total organic emissions from VCPs are 9.5 kg person^{-1} year^{-1}.
- VCP contributions to criteria pollutants are highest in California. Sizable influences in other urban regions, including NYC.
- VCP contributions to county-level annual SOA and MDA8 O_3 reach 0.55 µg m^{-3} (15 – 30% of total) and 3 ppb (2 – 6% of total), respectively.

Annual:



Note: Colormap is non-linear. Seltzer et al., *in review.*

Contact:

pye.havala@epa.gov
seltzer.karl@epa.gov