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March 16, 2020 from 3:00-4:00 pm ET

Implications of Volatile Chemical Products (VCPs) on Ozone and Particulate Matter in Urban Atmospheres

Webinar Slides: Will be posted on the web with a recording of the Webinar

To Ask a Question: Type in the "Questions" box located in right navigation bar on your screen.

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Presenter

Havala O.T. Pye, Ph.D. (Pye.Havala@epa.gov)

Havala is a research scientist in the EPA's Office of Research and Development. Her work focuses on computational methods to understand fine particles and other airborne pollutants that can impact human health and climate change. Specifically, she leads work on the representation of fine particles and organic species in the Community Multiscale Air Quality modeling system allowing for improved quantification of air pollution impacts in regulatory analysis. Havala holds a Ph.D. in chemical engineering with a minor in environmental science and engineering from the California Institute of Technology.

Current and ongoing work at EPA seeks to understand the magnitude of emissions from VCPs as well as the chemical reactions that result in criteria pollutant formation. This webinar will cover how the contribution of VCPs to ozone and fine particle pollution was constrained using models and measurements with a focus on southern California.

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Acknowledgements

Students and Postdocs at EPA:
Momei Qin, Karl Seltzer, Lauren Koval, Quanyang Lu, Elyse Pennington

EPA collaborators:
Ben Murphy, Kristin Isaacs, Tesh Rao, Madeleine Strum

NOAA Collaborators:
Brian McDonald, Stuart McKeen

Carnegie Mellon University:
Allen Robinson

General Dynamics Information Technology Contributors:
Christos Efstathiou, Chris Allen

nature sustainability

ARTICLES

https://doi.org/10.1038/s41893-020-00614-1

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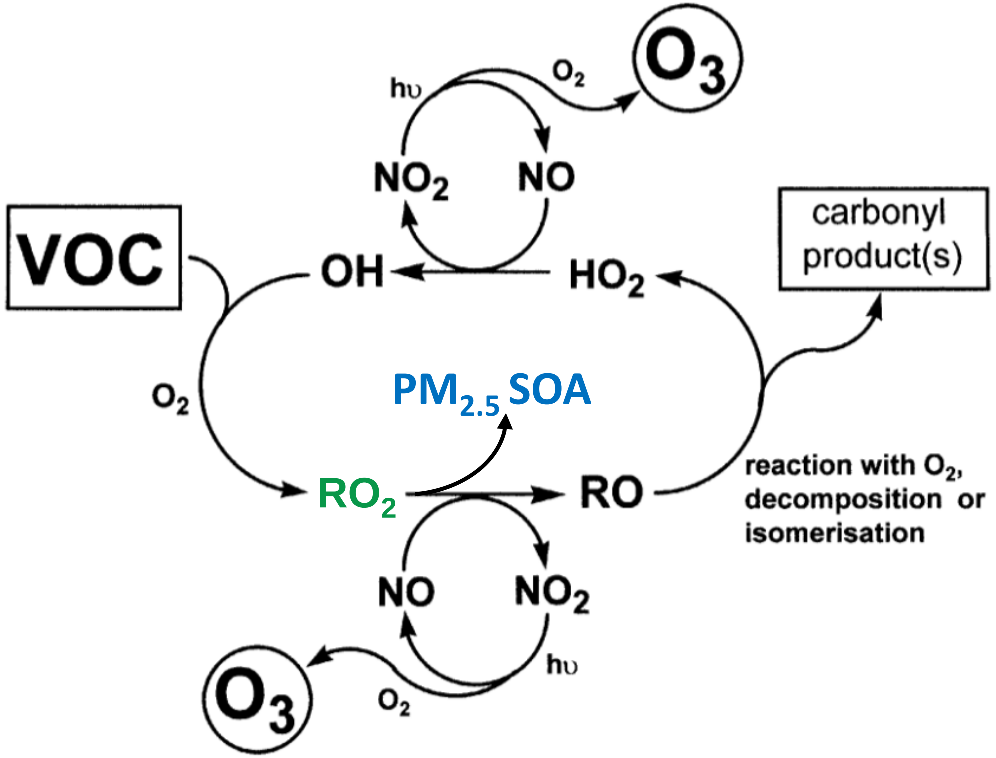
Criteria pollutant impacts of volatile chemical products informed by near-field modelling

Momei Qin[1,2] ✉, Benjamin N. Murphy[3], Kristin K. Isaacs[3], Brian C. McDonald[4], Quanyang Lu[5,6], Stuart A. McKeen[4,7], Lauren Koval[8], Allen L. Robinson[5,6], Christos Efstathiou[9], Chris Allen[9] and Havala O. T. Pye[3] ✉

Read access available at:
https://rdcu.be/b76hV

VOCs lead to criteria pollutant formation

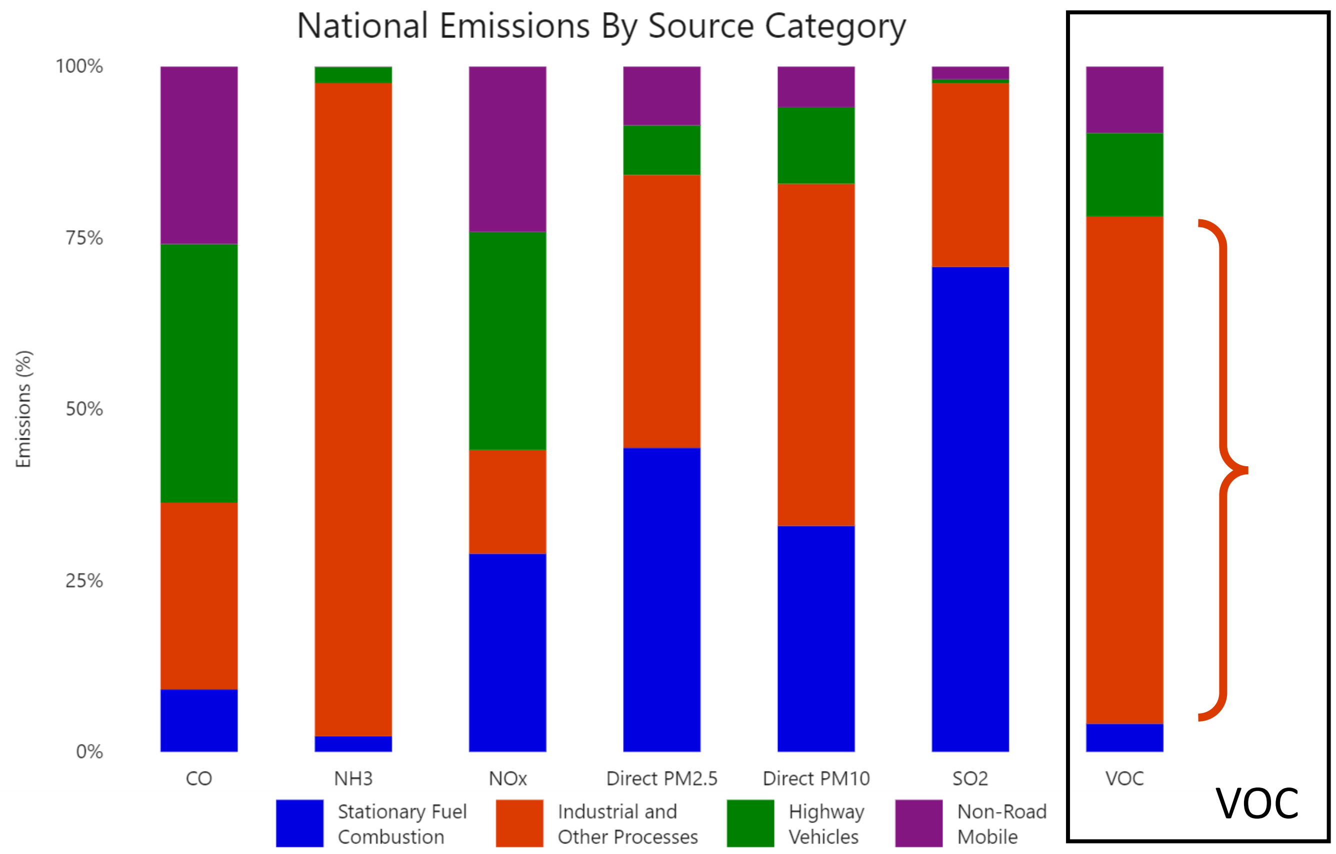


Jenkin and Hayman *AE* 1999 with modification

VOCs react in the atmosphere to form radicals and low-volatility (or highly water-soluble) products.

- Radicals (RO_2) go on to catalyze O_3 formation.
- Low-volatility (high-solubility) oxidation products condense to form the secondary organic aerosol (SOA) component of $PM_{2.5}$.

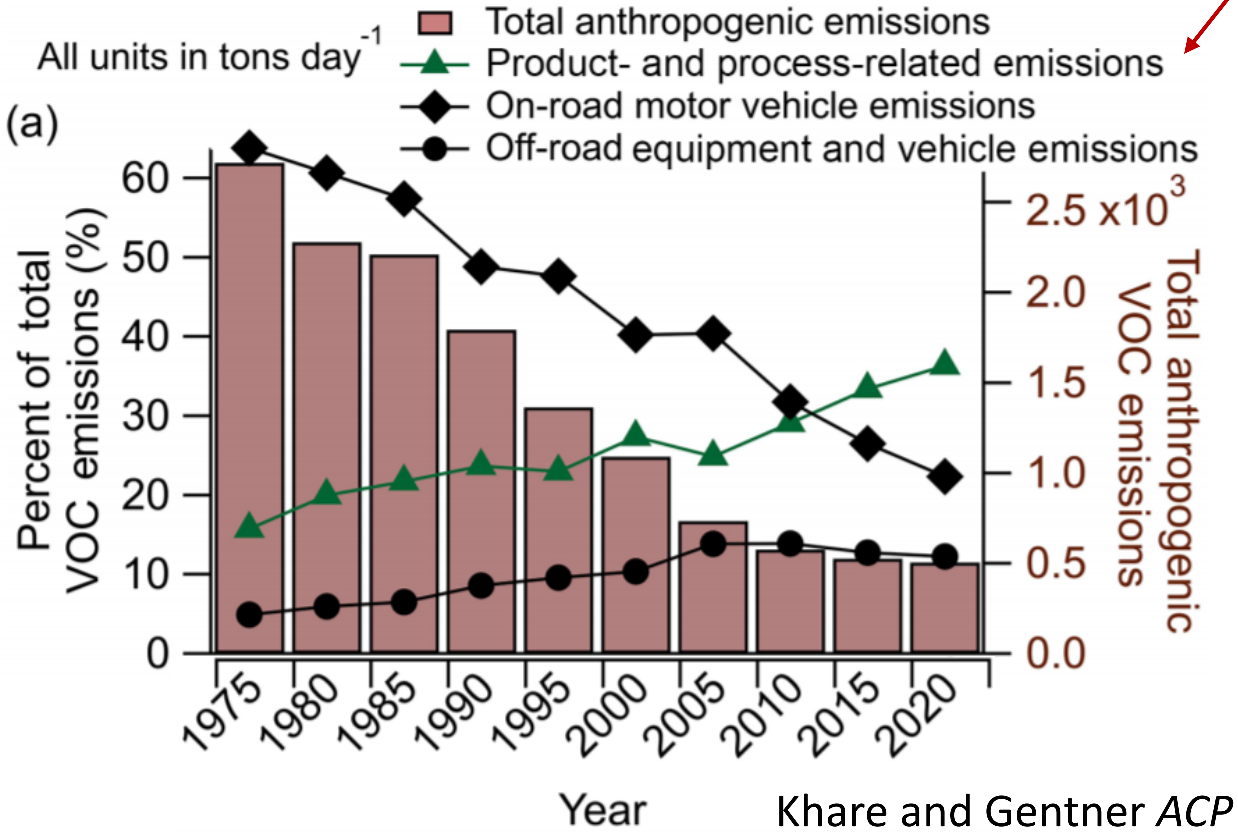
VOC emissions dominated by sources other than vehicles and power plants



2017 EPA National Emissions Inventory
https://gispub.epa.gov/air/trendsreport/2020/#sources

The relative importance of product and process VOCs is growing

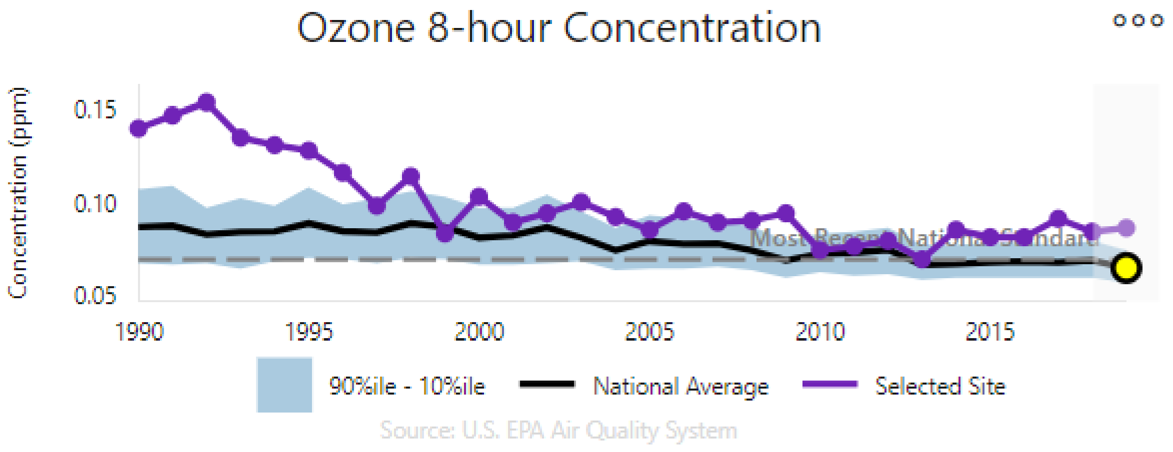
South Coast Air Basin (Los Angeles) Emissions:

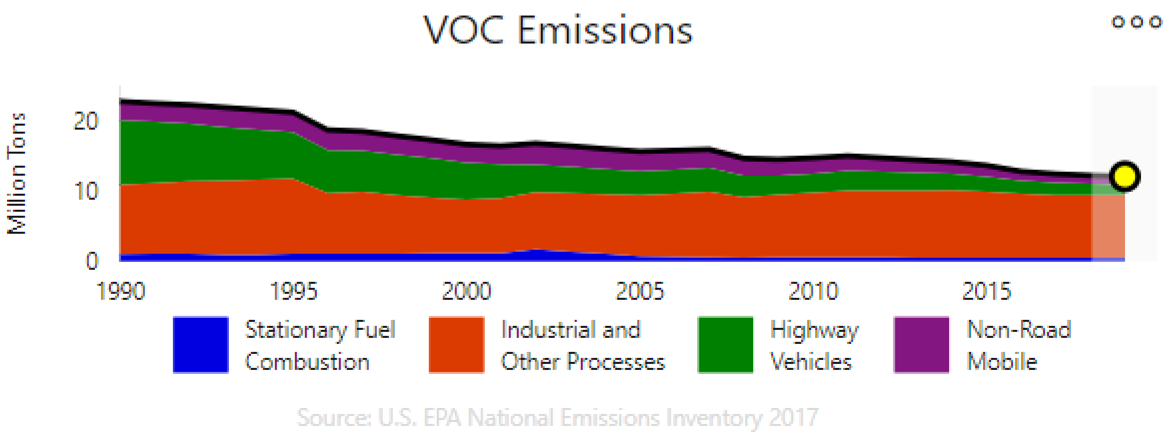


Khare and Gentner *ACP* 2018

Ozone trends indicate lack of recent changes

Pasadena, CA



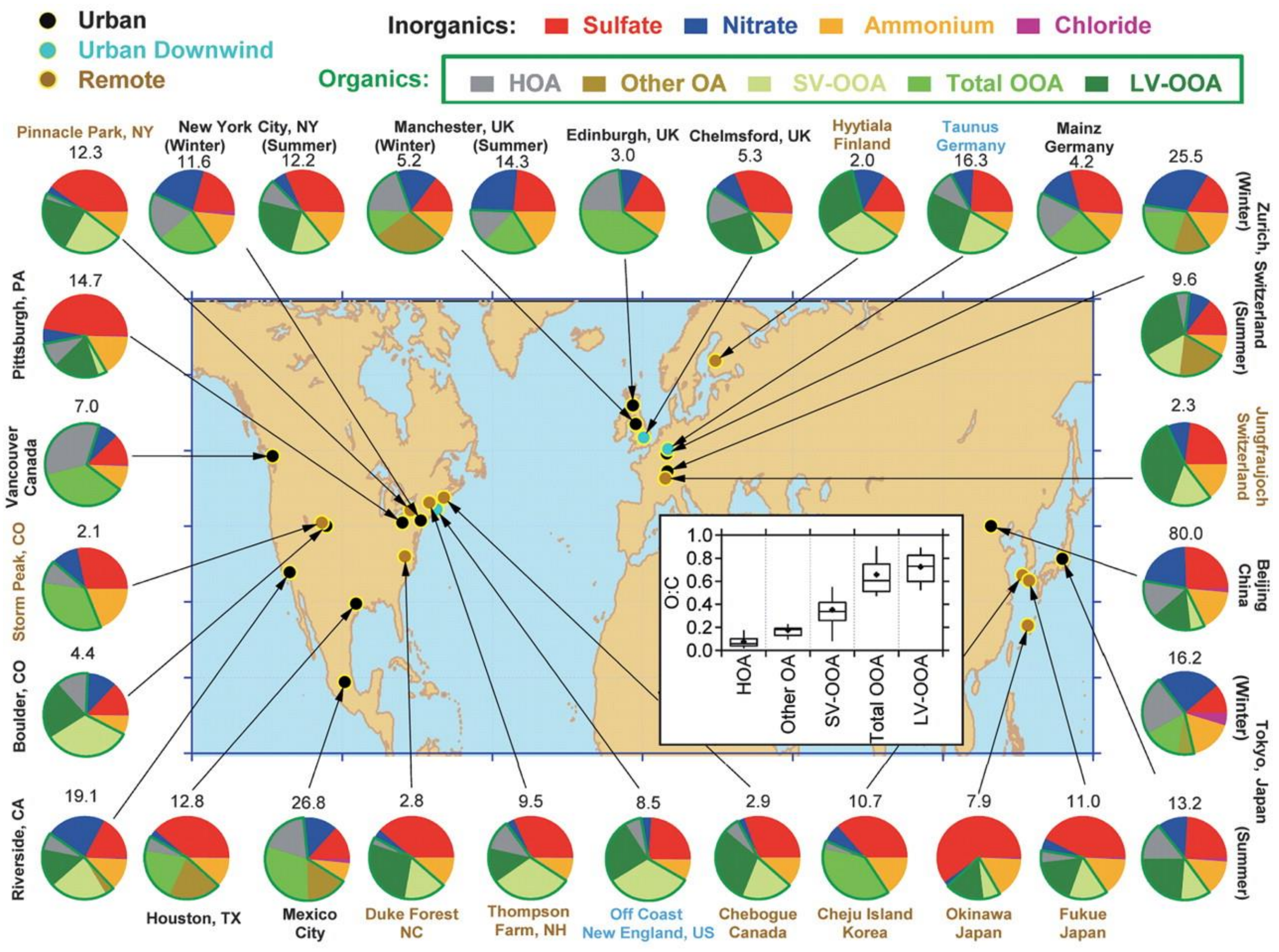


EPA Annual Air Trends Report 2020

https://gispub.epa.gov/air/trendsreport/2020/#naaqs_trends

SOA is major fine particle component

Jimenez et al. *Science* 2009



OOA (SV-OOA, Total OOA, or LV-OOA)=SOA

- SOA dominates over primary organic aerosol (Zhang et al. *GRL* 2007; Robinson et al. *Science* 2007; Jimenez et al. *Science* 2009).
- SOA variability is associated with 3.5× greater per capita county-level cardiorespiratory mortality than total $PM_{2.5}$ (Pye et al. *in review*).

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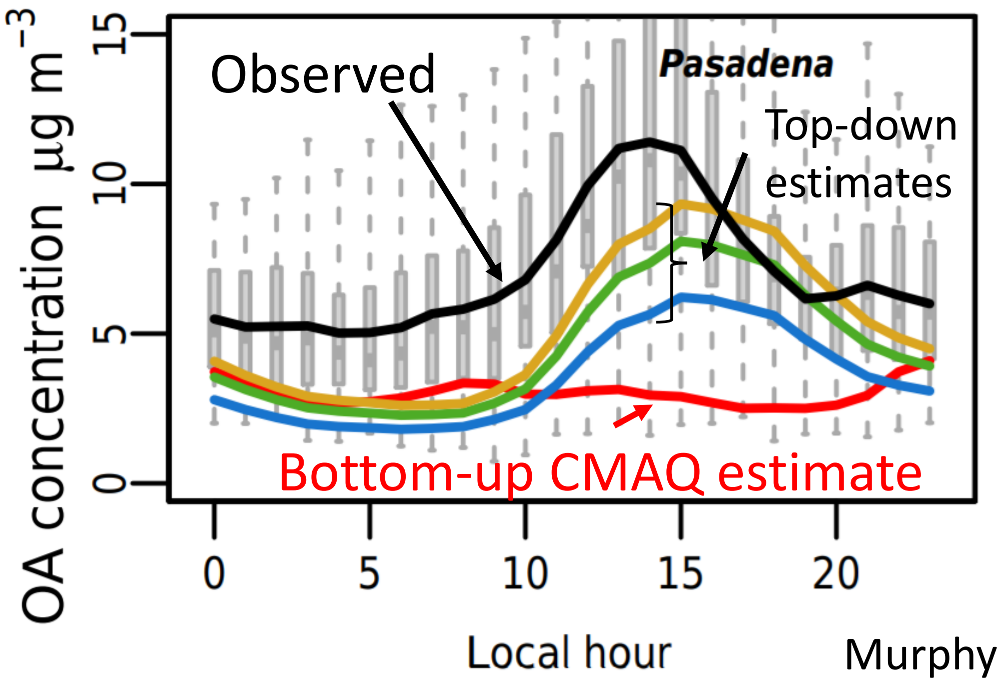
Anthropogenic SOA can be difficult to predict



Murphy et al. *ACP* 2017

CMAQ requires empirical top-down SOA representation to reproduce OA in Pasadena, CA.

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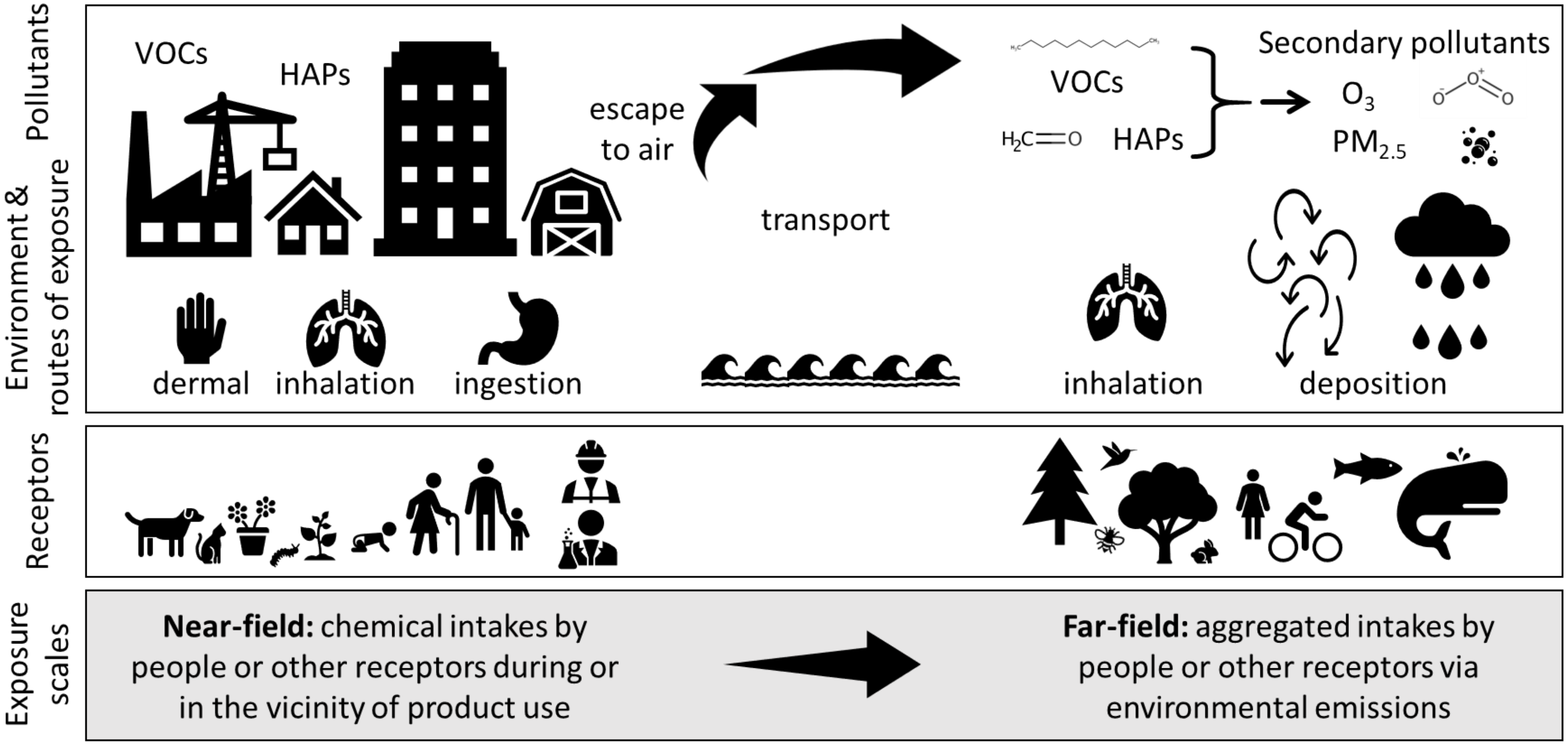
Volatile chemical products (VCPs) emit VOCs

VCPs include:

- Cleaning products
- Personal care products
- Adhesives and sealants
- Paints and coatings
- Printing inks
- Pesticides
- Dry cleaning
- Oil and gas solvents
- Lighter fluid fuels
- Other products

VOCs cause both near and far-field exposure



Objectives

1. Understand emissions
    - Estimate magnitude of VOC emissions from VCPs.
    - Identify role for near-field exposure models (SHEDS).

2. Estimate air quality impacts
    - Predict SOA and ozone.
    - Infer VCP VOC emissions based on observational constraints (top-down).

Emissions per capita are a useful diagnostic

Emissions (Gg yr^{-1} or similar)

$$\mathbf{E} = \sum_i \boldsymbol{EF_i} \times \boldsymbol{A_i}$$

Emission Factor (kg $person^{-1}$ yr^{-1})

Activity (population)

$$\boldsymbol{EF_i} = \boldsymbol{S_i} \times \boldsymbol{\gamma_i}$$

"Solvent" usage from products (kg $person^{-1}$ yr^{-1})

Volatilization factor (fraction)

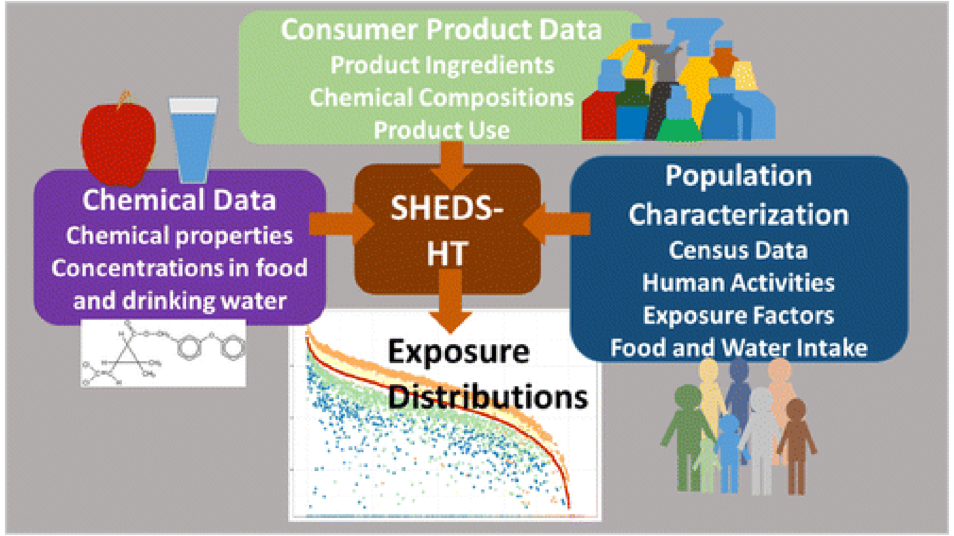
i = product use categories (personal care, pesticides, coatings, etc).

"Solvent" broadly defined as organic compounds in products.

Multiple emissions methods were examined

- Multiple inventory methods:
  - EPA National Emissions Inventory (NEI) (2011 state submitted or EPA fallback method)
  - NEI (CA) (California Air Resources Board/local submission to 2011 NEI)
  - EPA Solvent Tool v1.7 (2014 NEI method)
  - EPA Stochastic Human Exposure and Dose Simulation Model for High-Throughput (SHEDS-HT, Isaacs et al. *ES&T* 2014)
  - McDonald et al. *Science* 2018
- Converted all methods to a population-based emission factor (EF).

SHEDS-HT synthesizes consumer product usage

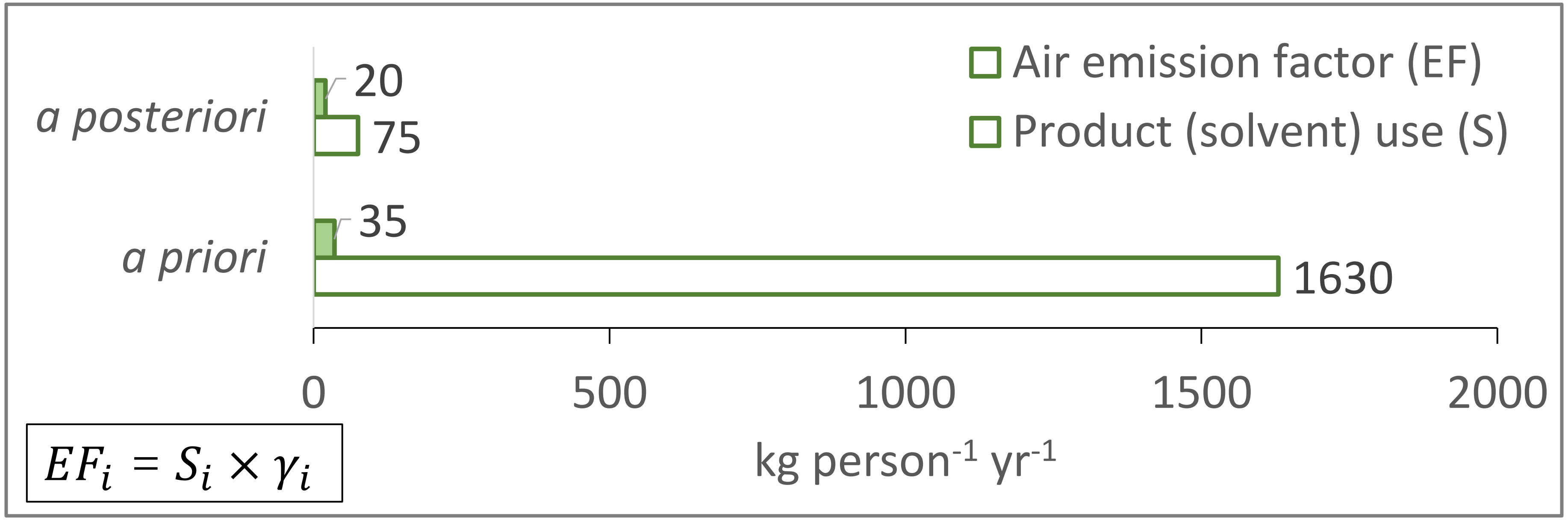


(Isaacs et al. *ES&T* 2014)

- Developed for chemical safety research.
- Provides conservative near-field exposure to individual chemicals for a population (e.g., 10,000 people).
- Informed by consumer product use patterns: habits and practices.
- ★ Conservative product market share assumptions for individual chemicals (100% chemical prevalence).
- ★ Conservative volatilization assumptions (e.g., dermally applied products do not volatilize).

★ Requires revision to reconcile near-field with far-field (ambient air) information.

SHEDS estimate: 20 kg person^{-1} yr^{-1} air emission



Critical adjustments resulting in *a posteriori*:

- More mass-conservative market-share assumptions for products (S_i reduced).
- Parameterized volatilization (effective γ_i increased from 2% to 26%)→post-use near-field inhalation now more competitive with dermal and ingestion exposure.

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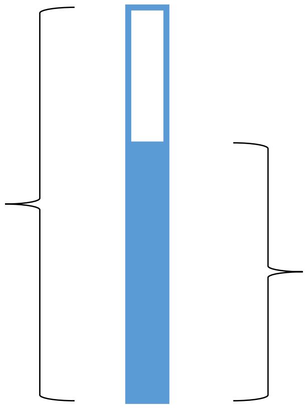
Usage and emissions are connected

Product solvent usage, S_i

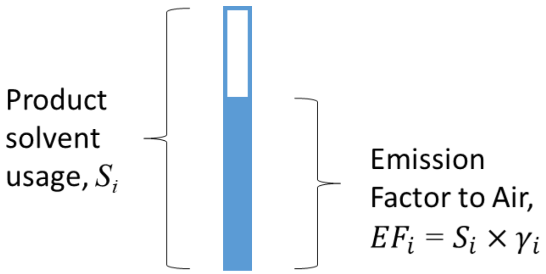


Emission Factor to Air, $EF_i = S_i \times \gamma_i$

$$\boldsymbol{EF_i = S_i \times \gamma_i}$$

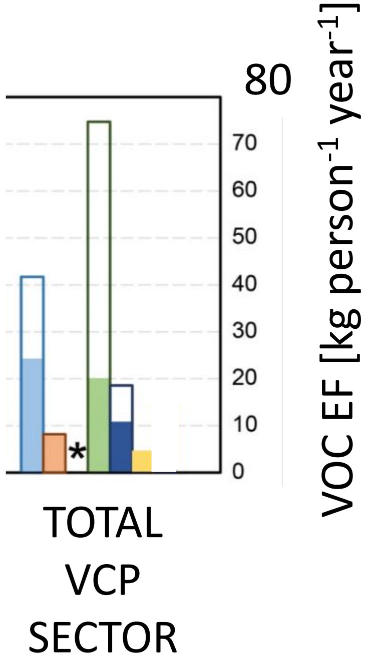
Emissions are constrained by the total amount of “solvent” usage.

Product solvent usage varies by method



Emission estimation methods:

McDonald
2011 NEI
Solvent Tool
SHEDS-HT
McDonald (CA)
2011 NEI (CA)



- NEI does not require solvent usage to be reported (only VOC emissions).
- Solvent Tool contains emission factors by sub-sector (no value for total sector shown).
- SHEDS and McDonald et al. show high product solvent usage.

*Indicates EF not available; Total on right axis

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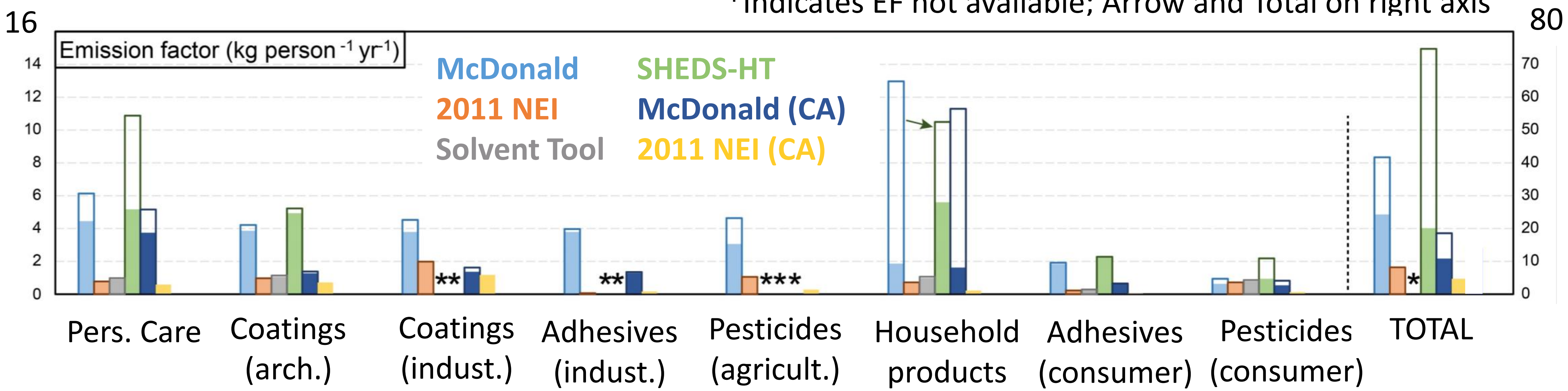
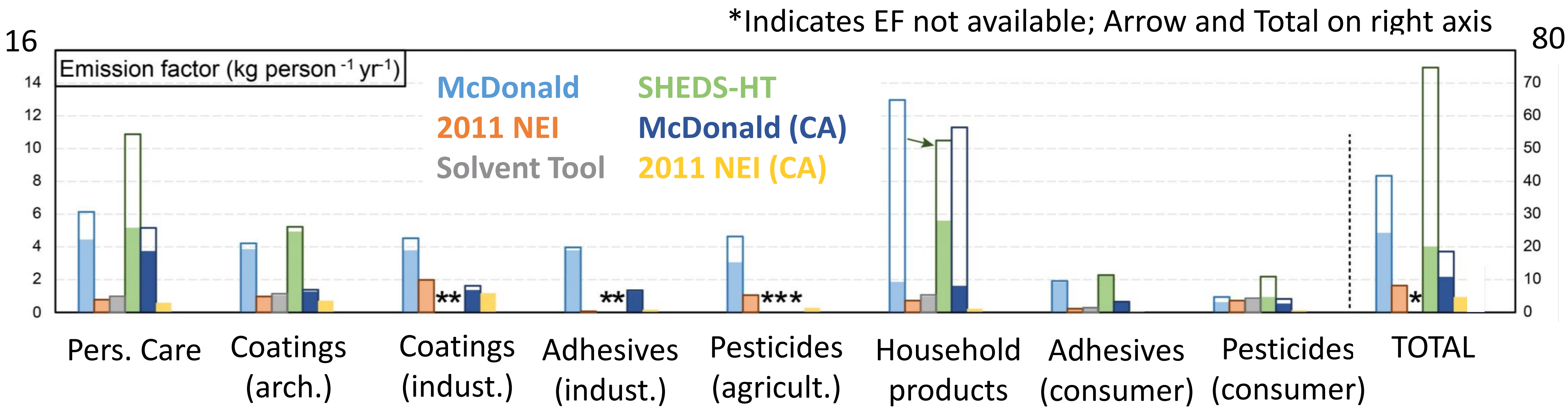
Lower solvent usage explains lower NEI emissions

*Indicates EF not available; Arrow and Total on right axis



- NEI (CA): S_i not shown (CARB considers $\gamma_i \neq 1$)
- NEI (2011)/Solvent Tool (2014 NEI) Methodology
  - No fate and transport (volatilization) adjustment (γ_i = 1)
  - Low emissions driven by low solvent usage estimates

Fate and transport can play a significant role



Fraction volatilized varies by method:

γ_i = 58% for McDonald et al.

γ_i = 27% for SHEDS

γ_i = 100% for NEI

Lessons learned about emissions

Models, like SHEDS, allow us to connect product usage and volatilization to near-field inhalation exposure.

NEI methods represented in the Solvent Tool indicate much lower "solvent" usage than other methods and that lower usage explains why NEI/Solvent Tool emissions are lowest.

The fraction volatilized is an important modulator of emissions and varies by about 2x between methods.

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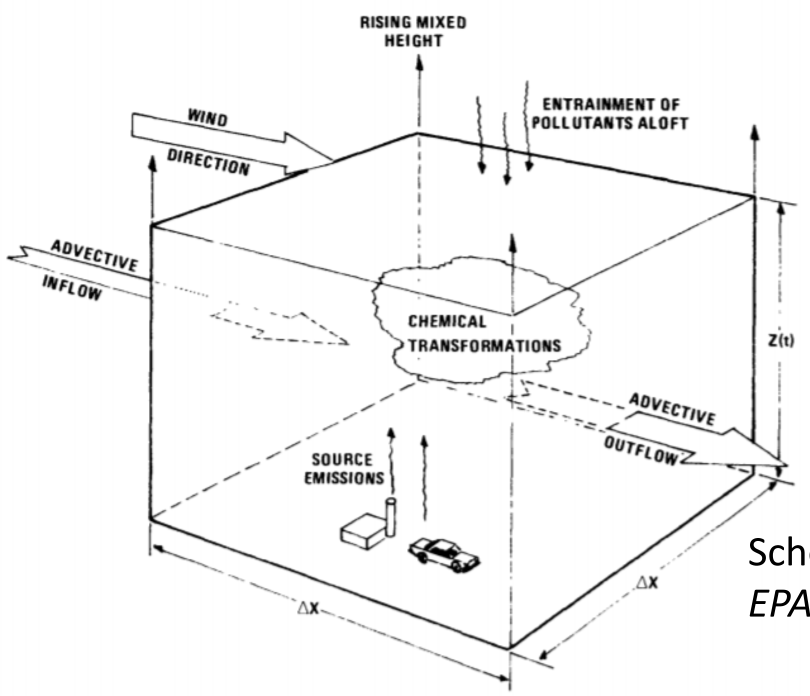
Objective 2: Estimating air quality impacts with CMAQ



Schere and Demerjian, *EPA Report*, 1984

- Base Model: Community Multiscale Air Quality (CMAQ) model version 5.3 (www.epa.gov/cmaq)
- State-of-the-science combustion emissions and resulting SOA (Lu et al. *ACP* 2020)

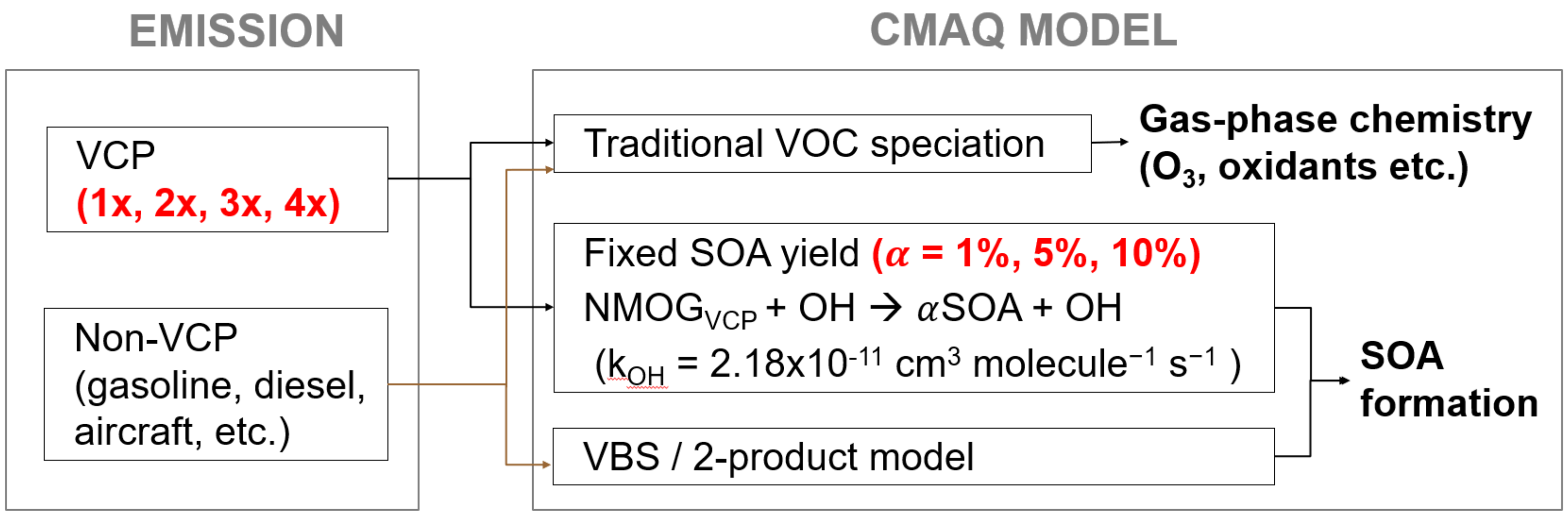
Field data from Pasadena, California

CMAQ modeling domain

Aerosol samplers at Caltech (image: PSI)

- CalNex campaign from May 15 to June 15, 2010

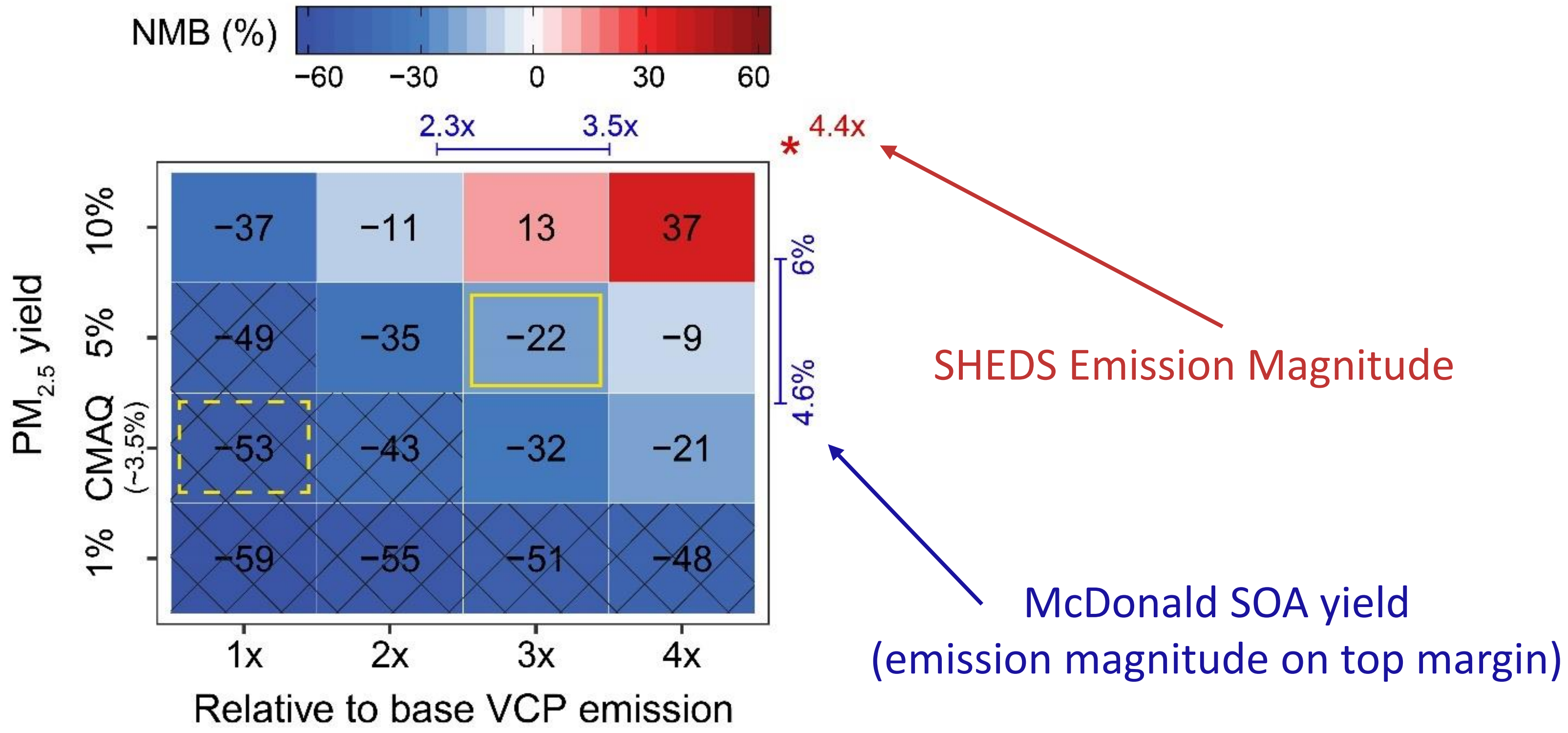
Emissions and SOA yields perturbed in simulations



CMAQ Sensitivity Simulations

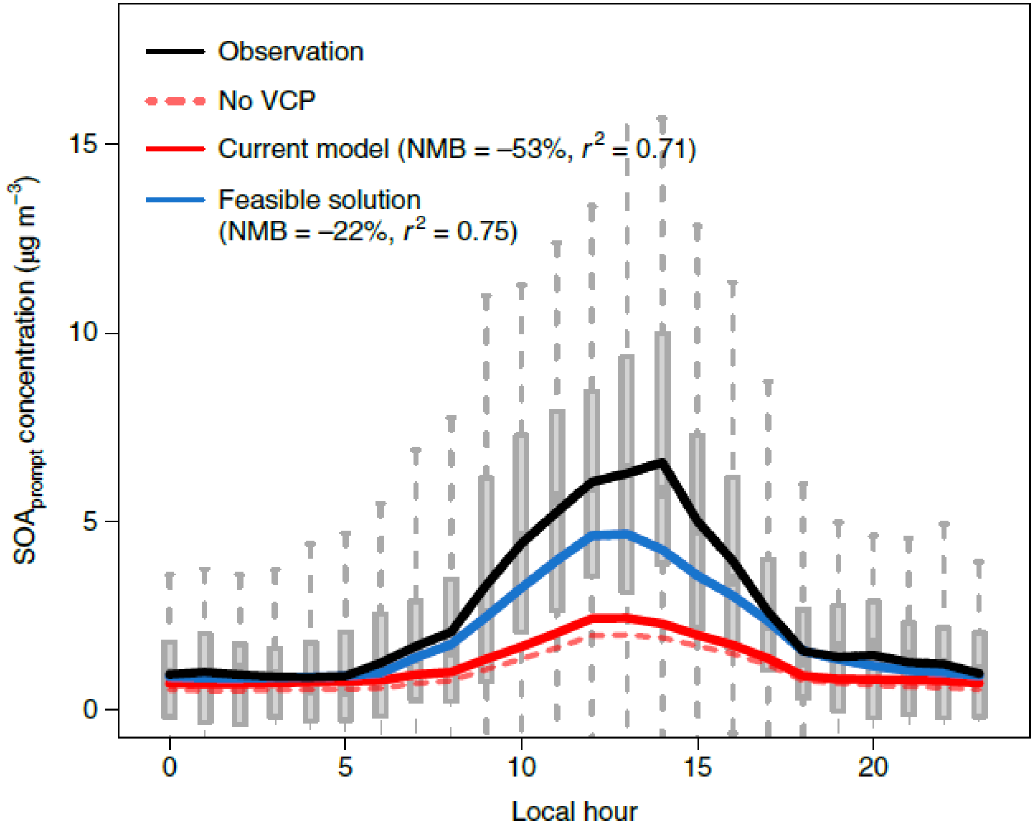
- Imposed VCP VOC emission magnitudes: 1× (base), 2×, 3×, 4×
- Imposed VCP SOA yields: 1%, 5%, 10% by mass

SOA evaluation suggests higher emissions and yield



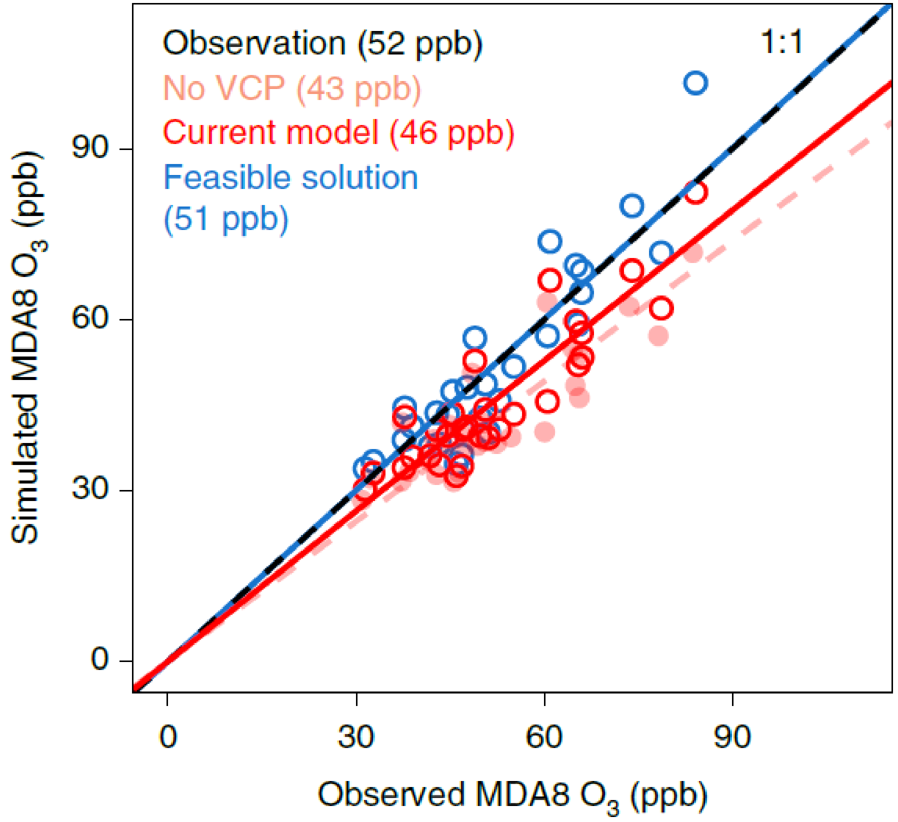
Daytime increase requires high yield (5-10%).

VCPs are responsible for ~41% of the prompt SOA



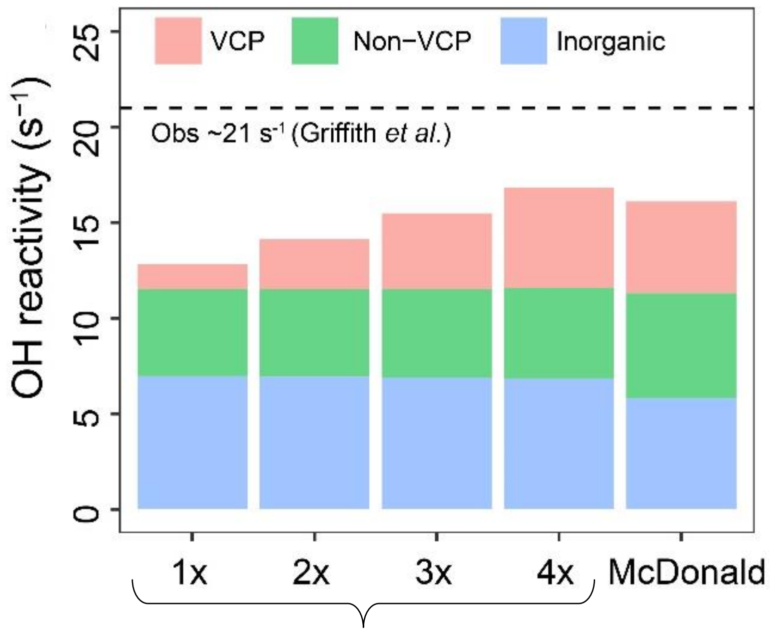
With 3x NEI (CA) and 5% SOA yield, predicted VCP SOA is 1.1 ± 0.3 $\mu g\ m^{-3}$.

3× VCP emissions eliminates ozone bias



VCPs responsible for ~17% of maximum daily 8-hr average O_3 (MDA8) at Pasadena (9 ± 2 ppb VCP contribution) with 3x emissions.

OH reactivity improved with higher VCP emissions



CMAQ Predictions as a Function of Emissions

- OH reactivity is indication of ambient VOC burden (and speciation).
- CMAQ still missing some reactivity
  - Observed OH Reactivity (Griffith et al. *JGR* 2016): 21 s^{-1}
  - Base CMAQ OH Reactivity: 13 s^{-1}
  - Feasible Solution CMAQ OH Reactivity: 16 s^{-1}

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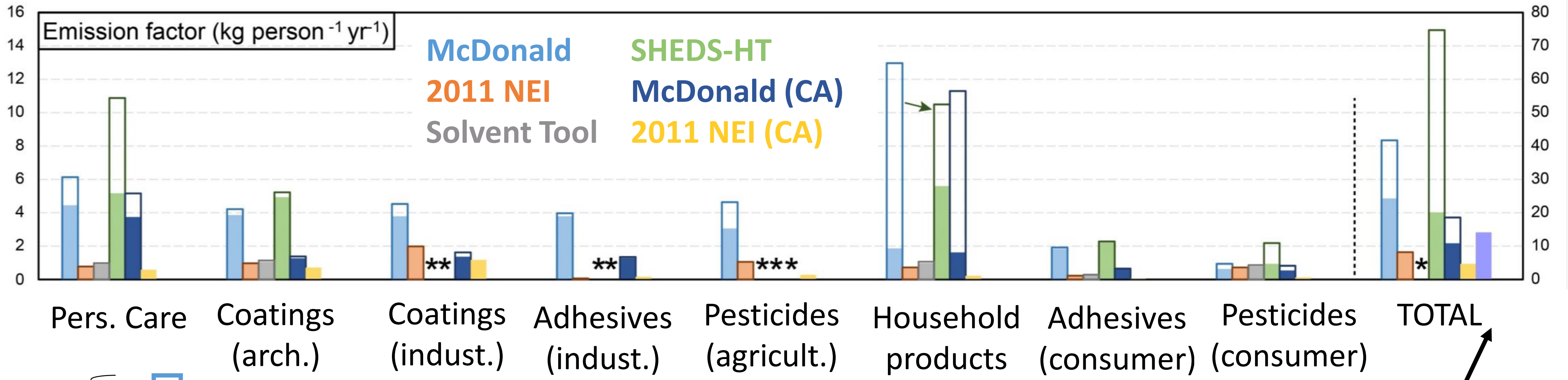
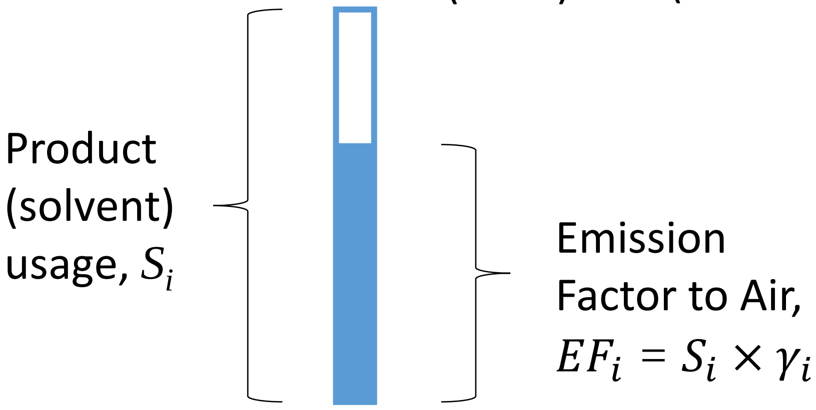
Ambient air evaluation constrains emissions from VCPs

*Indicates EF not available; Arrow and Total on right axis





Top-down constraints imposed by ambient air measurements suggest 14 kg person^{-1} yr^{-1} emissions to air (**CMAQ solution**).

(CMAQ does not constrain product usage, S_i)

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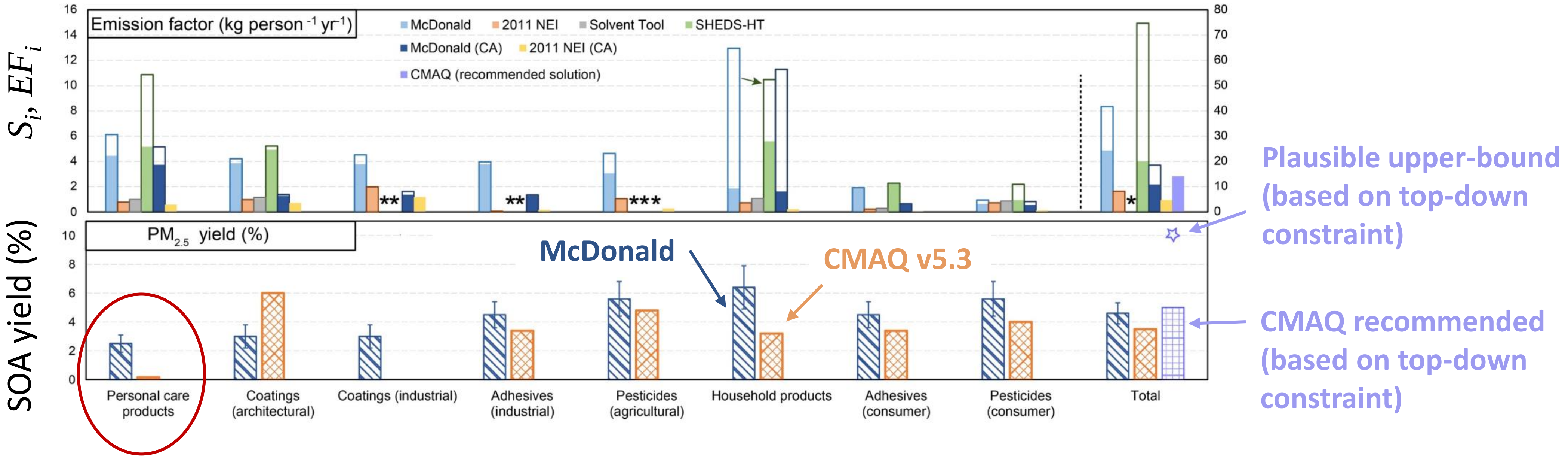
Lack of SOA in CMAQ due to emissions and/or yields

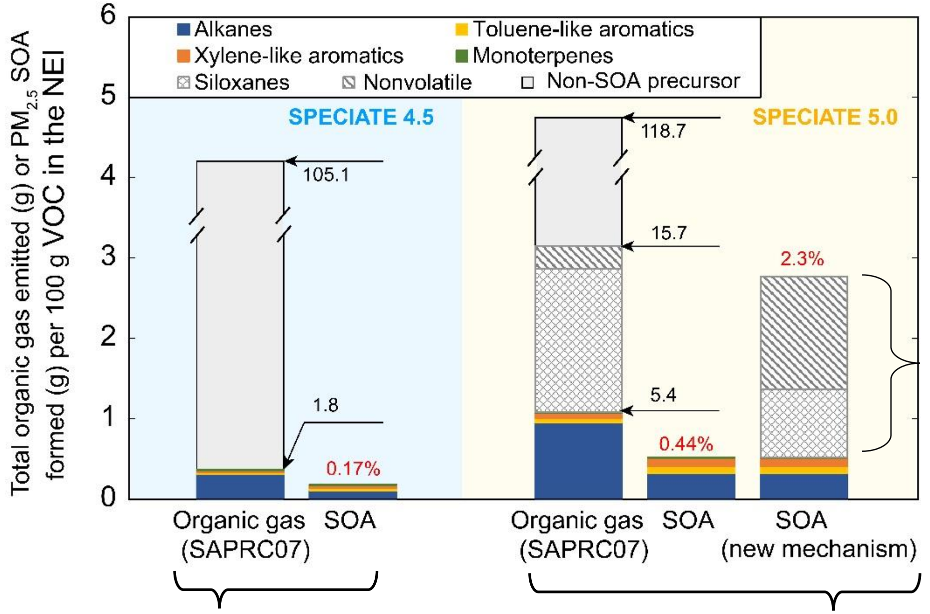
(depending on sector)



- Pesticide and adhesive <u>emission</u> underestimates drive $PM_{2.5}$ emission underestimates (115 Gg yr^{-1} underestimate).
- Personal care <u>emission</u> underestimates, combined with low $PM_{2.5}$ <u>yields</u> in CMAQ, drive SOA underestimates for that sector (35 Gg yr^{-1}).

How do we get higher SOA yields in CMAQ?

Emissions and SOA formation for personal care sector



The majority of the SOA comes from mass that is discarded from CMAQ mechanism species

Current Operations
CMAQv5.3+SPECIATE 4.5
0.17% SOA yield

Possible updates with existing information
2.3% SOA yield

- Biggest issue: Model mechanisms and lack of suitable SOA precursors.

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In summary

- Near-field inhalation of VOCs from product usage may be more important and competitive with dermal exposure than previously predicted.
- Multiple inventory methods and top-down constraints suggest VCP usage results in higher air emissions of VOCs than previously estimated by the California component of the NEI.
- For summer Los Angeles, CMAQ indicates VCPs may be responsible for:
    - ~41% of the prompt SOA (1.1 ± 0.3 $\mu g\ m^{-3}$)
    - ~17% of maximum daily 8-hr average O_3 (9 ± 2 ppb)

Ongoing work

- New methods leveraging product usage and composition information are planned for the 2020 NEI VCP/solvent sector (Seltzer et al. *ACPD* 2020).
- Robust bottom-up SOA prediction algorithms with consideration of intermediate to semivolatile species from VCPs are in development for future versions of CMAQ (Pennington et al. *in prep*).

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New methods are planned for emissions

https://doi.org/10.5194/acp-2020-1111

Abstract | Discussion | Metrics

09 Nov 2020

Review status: a revised version of this preprint was accepted for the journal ACP and is expected to appear here in due course.

Reactive Organic Carbon Emissions from Volatile Chemical Products

Karl M. Seltzer[1], Elyse Pennington[2,3], Venkatesh Rao[4], Benjamin N. Murphy[5], Madeleine Strum[4], Kristin K. Isaacs[5], and Havala O. T. Pye[5]

[1]Oak Ridge Institute for Science and Education Postdoctoral Fellow in the Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC 27711
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Short summary

Volatile chemical products (VCPs) are an increasingly important source of anthropogenic reactive...
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Seltzer et al. preprint available at: https://acp.copernicus.org/preprints/acp-2020-1111/

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VCPy: A new framework to model organic emissions from VCPs

Name derived from Volatile Chemical Products and Python

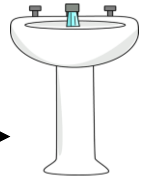
The magnitude and speciation of emissions is directly related to:

i. The mass of chemical products used.

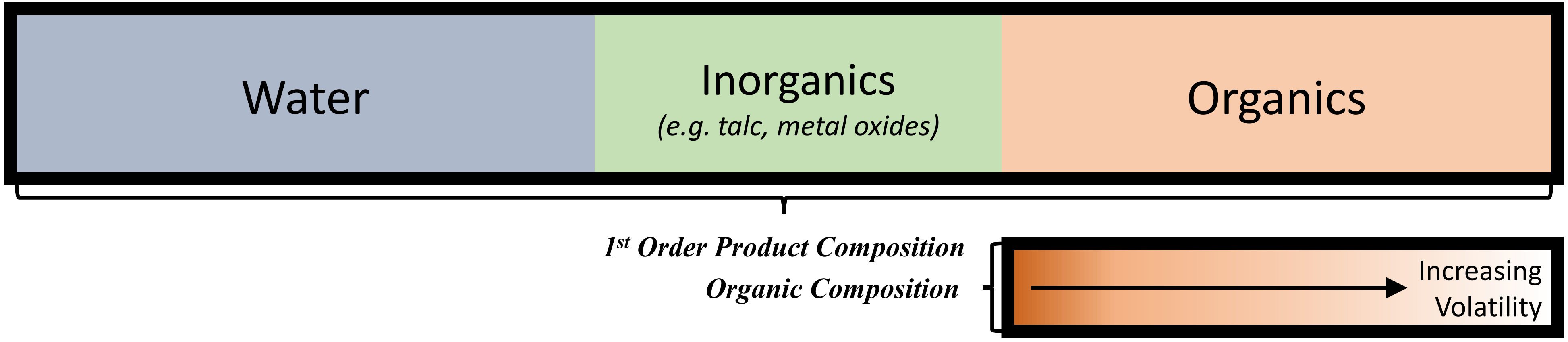
ii. The composition of these products.

iii. The physiochemical properties of their constituents that govern volatilization (evaporation timescale).

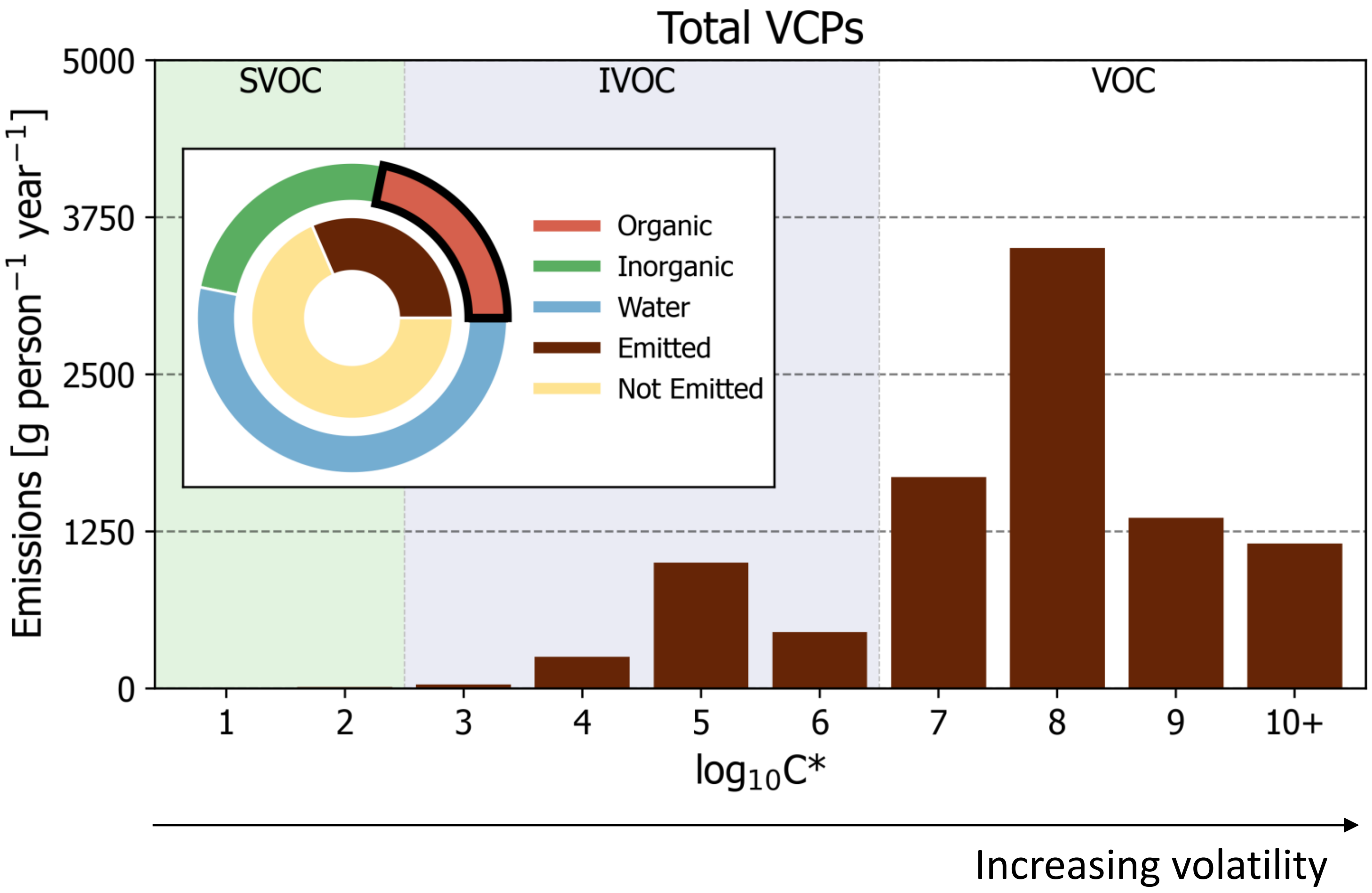
iv. The timescale available for these constituents to evaporate (use timescale).



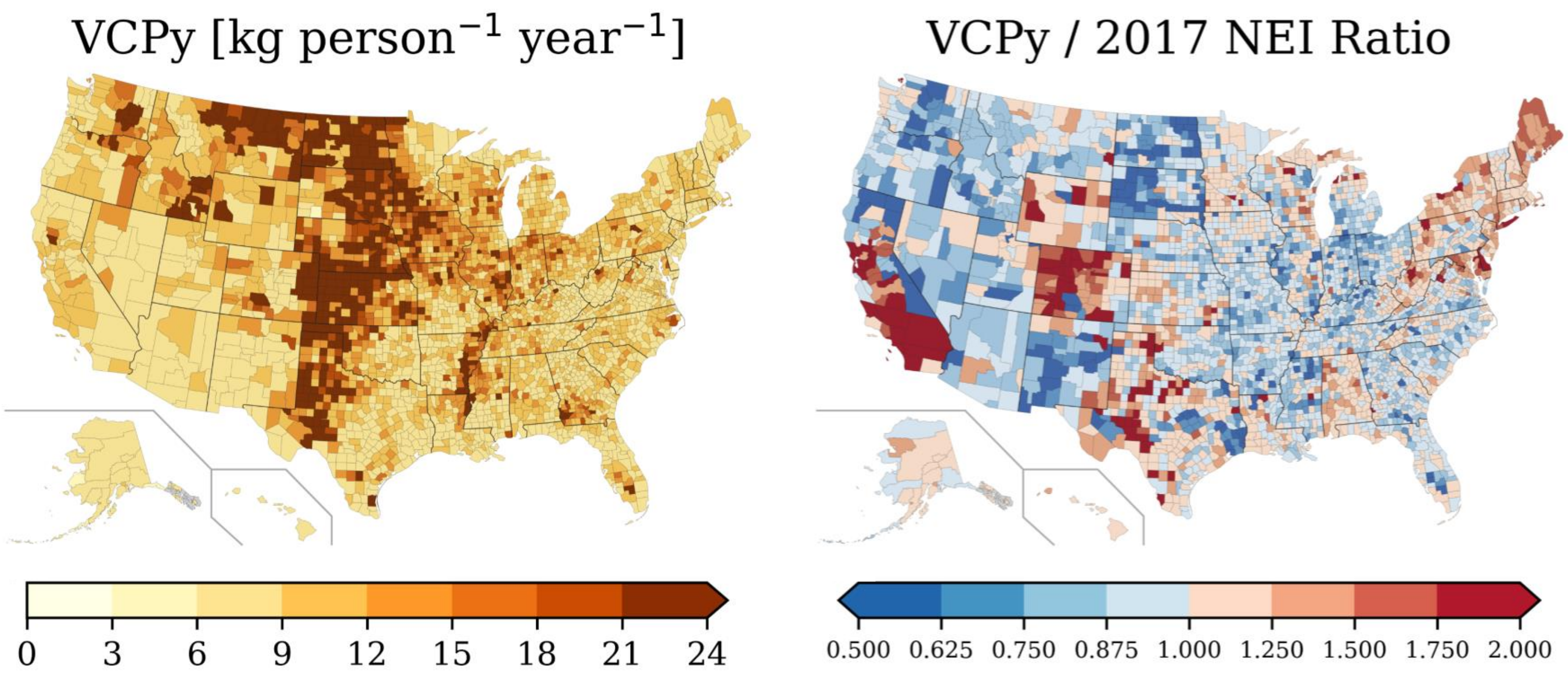
Illustrative Chemical Product:



National emissions from VCPs: 9.5 kg $person^{-1}$ $year^{-1}$



County-level differences in emissions predicted



When compared to the 2017 NEI:

- ~80% of all counties are ± 30%.
- States with the largest emissions increases were DE, CA, and CO.
- States with the largest emissions decreases were ND and SD.

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In summary

- Near-field inhalation of VOCs from product usage may be more important and competitive with dermal exposure than previously predicted.
- Multiple inventory methods and top-down constraints suggest VCP usage results in higher air emissions of VOCs than previously estimated by the California component of the NEI.
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Ongoing work

- New methods leveraging product usage and composition information (Seltzer et al. *ACPD* 2020).
- Robust bottom-up SOA prediction algorithms for CMAQ (Pennington et al. *in prep*).

nature sustainability ARTICLES
https://doi.org/10.1038/s41893-020-00614-1
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Criteria pollutant impacts of volatile chemical products informed by near-field modelling

Momei Qin[1,2], Benjamin N. Murphy[3], Kristin K. Isaacs[3], Brian C. McDonald[4], Quanyang Lu[5,6], Stuart A. McKeen[4,7], Lauren Koval[8], Allen L. Robinson[5,6], Christos Efstathiou[9], Chris Allen[9] and Havala O. T. Pye[3]

https://rdcu.be/b76hV

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https://acp.copernicus.org/preprints/acp-2020-1111/

Questions?

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