Reactive Organic Carbon Emissions from Volatile Chemical Products

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Volatile Chemical Products (VCPs) emit VOCs

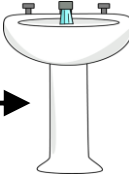**Broad category of non-point sources.**

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

Chemical product emissions are becoming more important:

Khare and Gentner *ACP* 2018
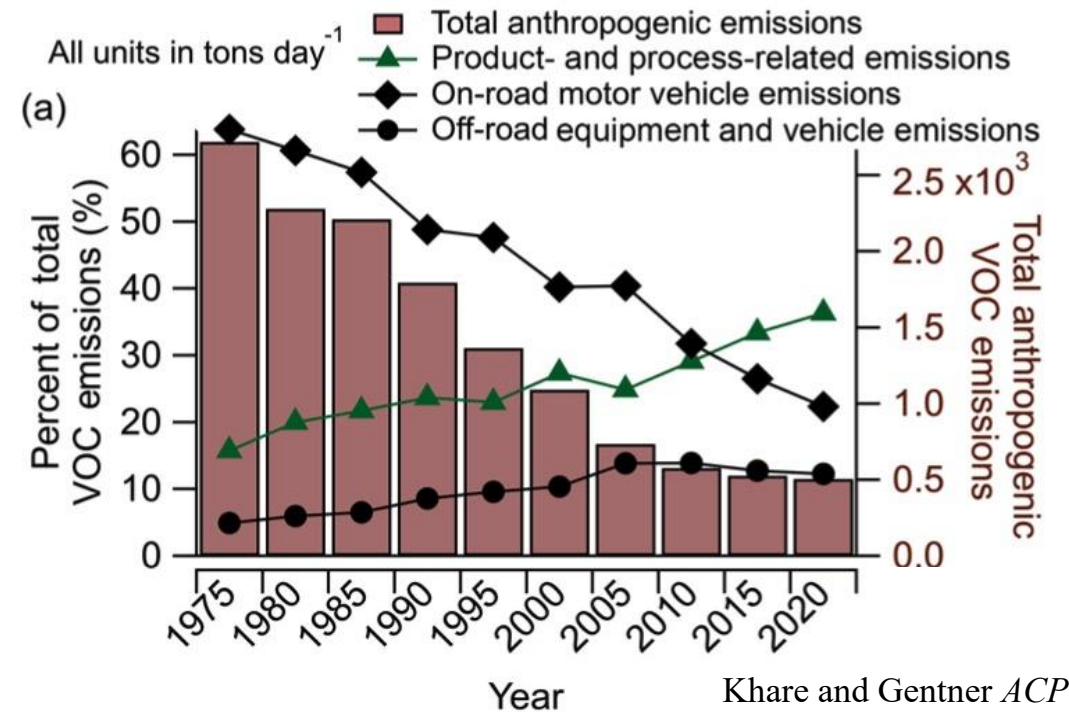
Research suggests NEI may be nationally low biased by a factor of 2-3.

Introducing VCPy

- 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:

Water	Inorganics *(e.g. talc, metal oxides)*	Organics
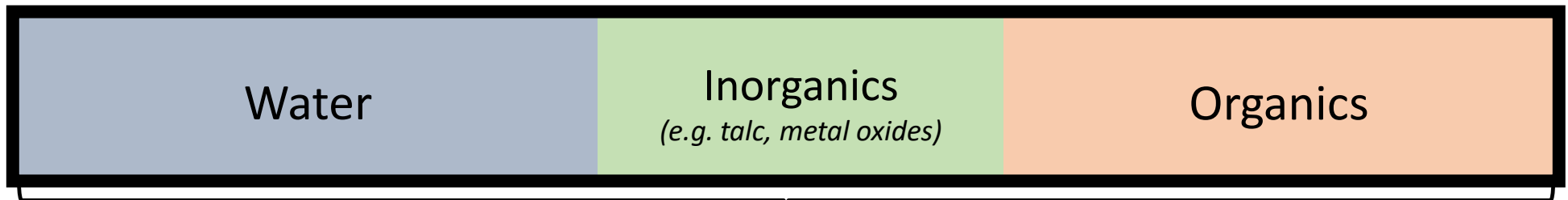
1st Order Product Composition

Organic Composition

Increasing Volatility

VCPy Framework

Sector: Volatile Chemical Products (VCPs)

Product Use Categories (PUCs)

sub-Product Use Categories (sub-PUCs)

Cleaning Products	Personal Care Products	Adhesives & Sealants

sub-PUCs are composites of products featuring similar use timescales and utility.

Coatings	Printing Inks	Pesticides

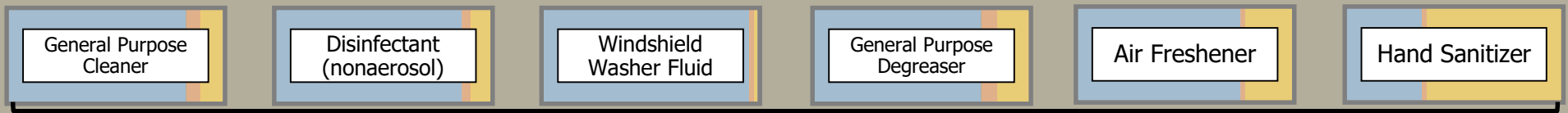| Dry Cleaning	Oil & Gas Solvent Use	Miscellaneous

Sector: Volatile Chemical Products (VCPs)

Key: Water | Inorganics | Organics

PUC: Cleaning Products

sub-PUC: General Cleaners ← User Assigns Use Timescale to sub-PUC

- General Purpose Cleaner
- Disinfectant (nonaerosol)
- Windshield Washer Fluid
- General Purpose Degreaser
- Air Freshener
- Hand Sanitizer

Generate sub-PUC Composite: **1st Order Product Composition**
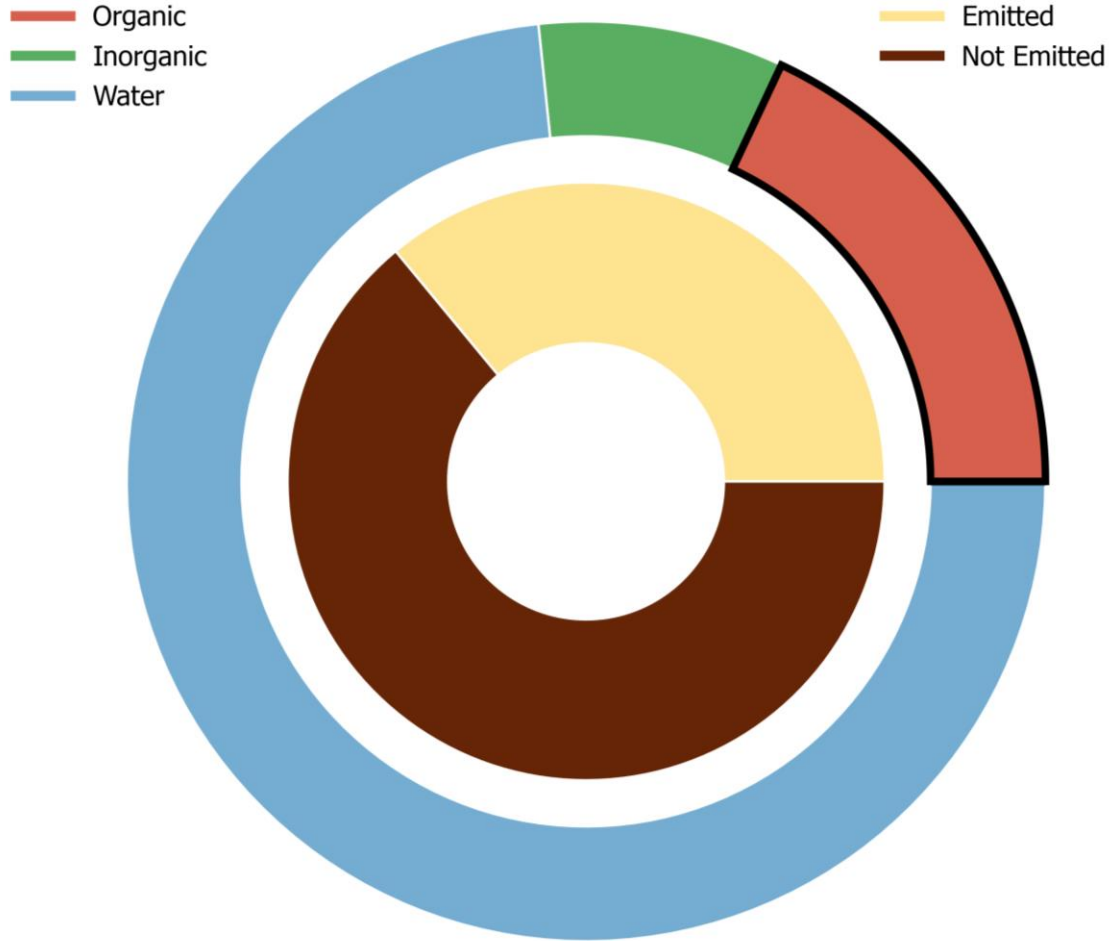
Calculate National sub-PUC Usage:
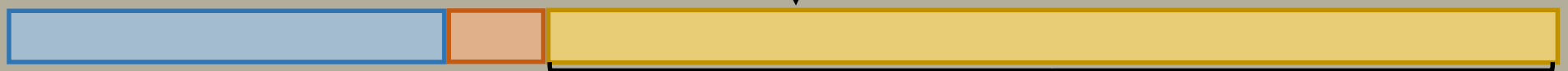
Organic Composition

Calculate Characteristic **Evaporation Timescale**

If Evaporation Timescale < Use Timescale → Compound is Emitted

Product Composition/Emissions Interface **Emissions**

Cleaning Products: General Cleaners

Legend:
- Organic
- Inorganic
- Water
- Emitted
- Not Emitted

Outer Circle: 1st Order Product Composition
Inner Circle: Fate of Organic Components

Chemical Name	HAP?	log(C*)	Emissions [kg person^{-1}year^{-1}]	% of Emissions
Ethanol	FALSE	8.00	0.44	23.80
Acetone	FALSE	8.91	0.21	11.16
Fragrances	FALSE	7.00	0.18	9.82
Ethylene Glycol Monobutyl Ether	FALSE	6.82	0.12	6.60
Isobutane	FALSE	9.83	0.10	5.19
Isopropyl Alcohol	FALSE	7.95	0.09	4.78
Propane	FALSE	9.98	0.07	3.78

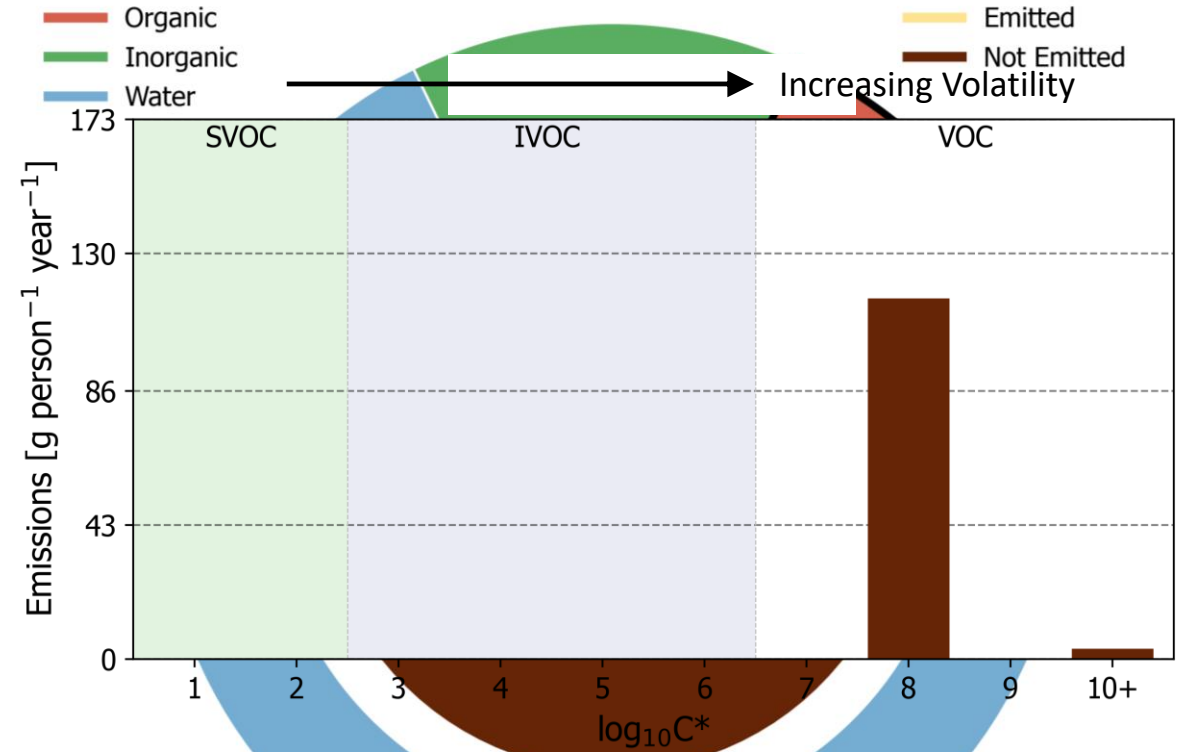Each compound is individually considered.

Total Emissions: 1.85 kg person^{-1} year^{-1}

Impact of Use Timescale Assumptions

General Cleaners: Days
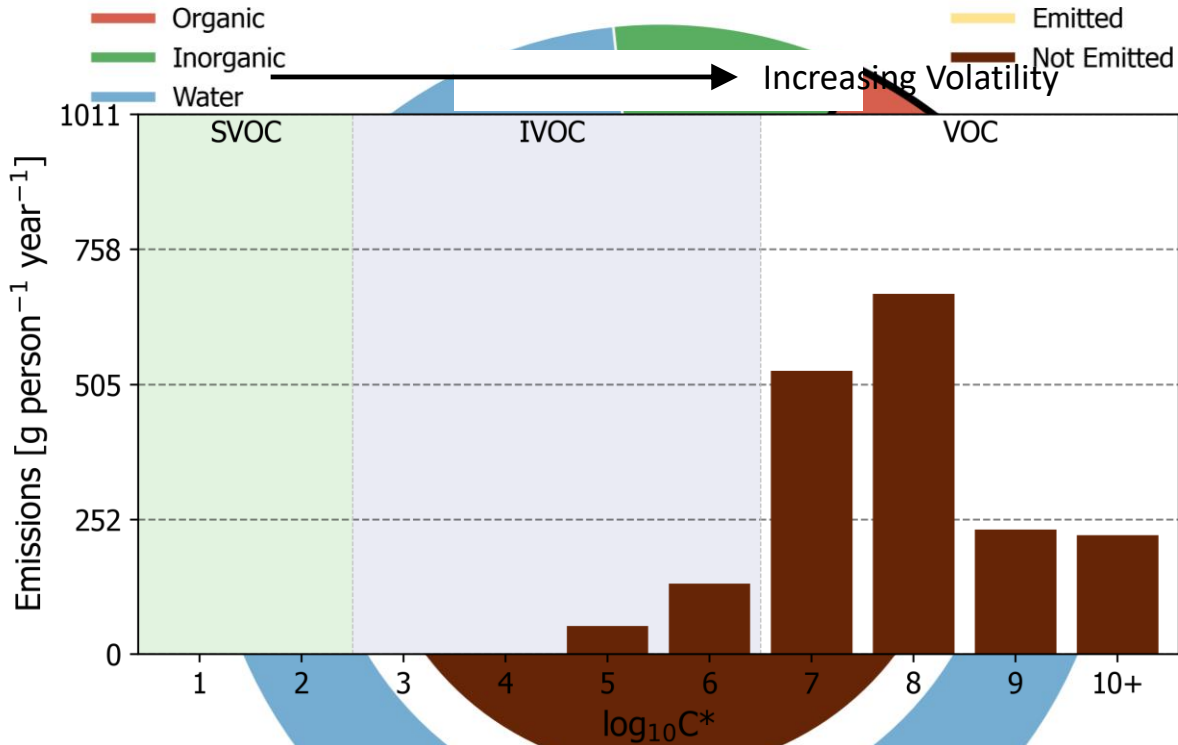
Detergents & Soaps: Minutes

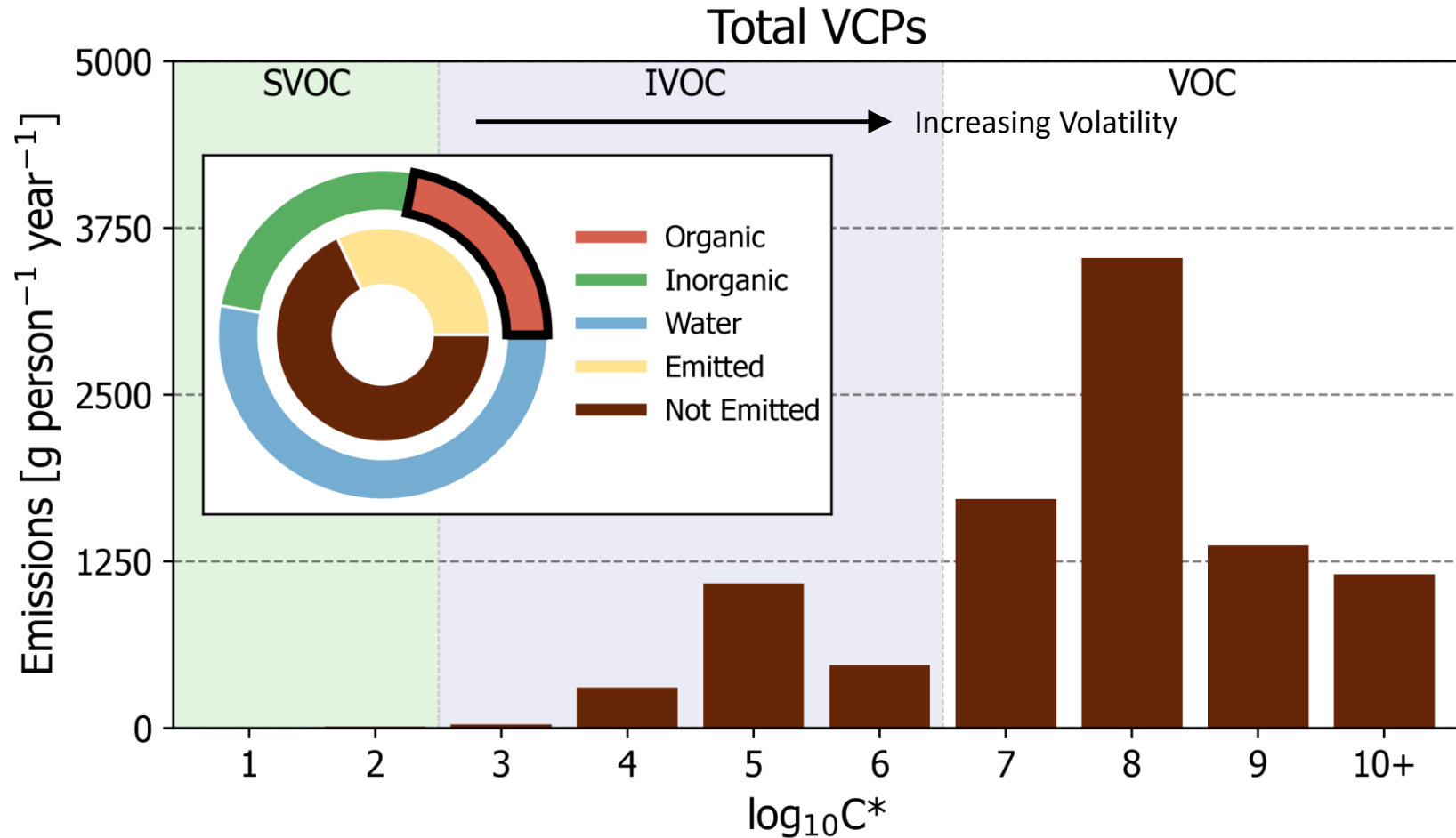Only highly volatile organics are emitted from detergents and soaps.

Outer Circle: 1st Order Product Composition

Note: different scale on y-axis of plots.

Inner Circle: Fate of Organic Components

VCP Sector Emissions

- National, per-capita organic emissions from VCPs are 9.7 kg person^{-1} year^{-1}.

- 20% of organic emissions from VCPs are IVOCs: SOA precursors.

- Nationally, VCPy VOC emissions are consistent with the NEI.

- County-level and categorical estimates can differ substantially from NEI values.
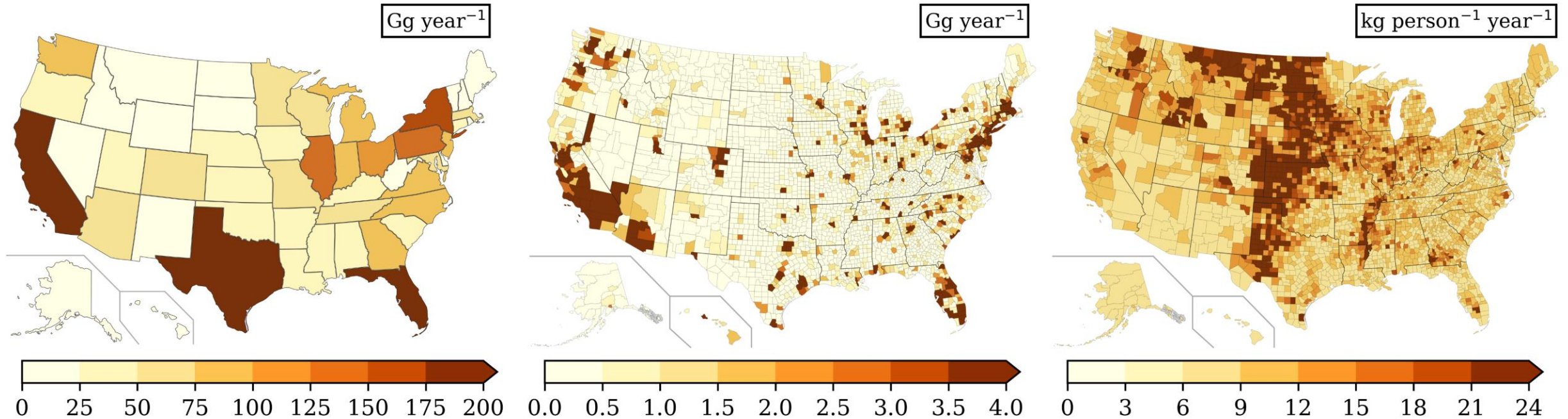
Testing Uncertainty of Inputs

- Emission factor uncertainty related to:
  - Product usage
  - Organic content
  - Use timescale
  - Evaporation timescale

- Sector-wide uncertainty at 95% confidence: ± 1.5 kg person^{-1} year^{-1}.

- Cleaning Products, Personal Care Products, and Paints & Coatings are most uncertain.
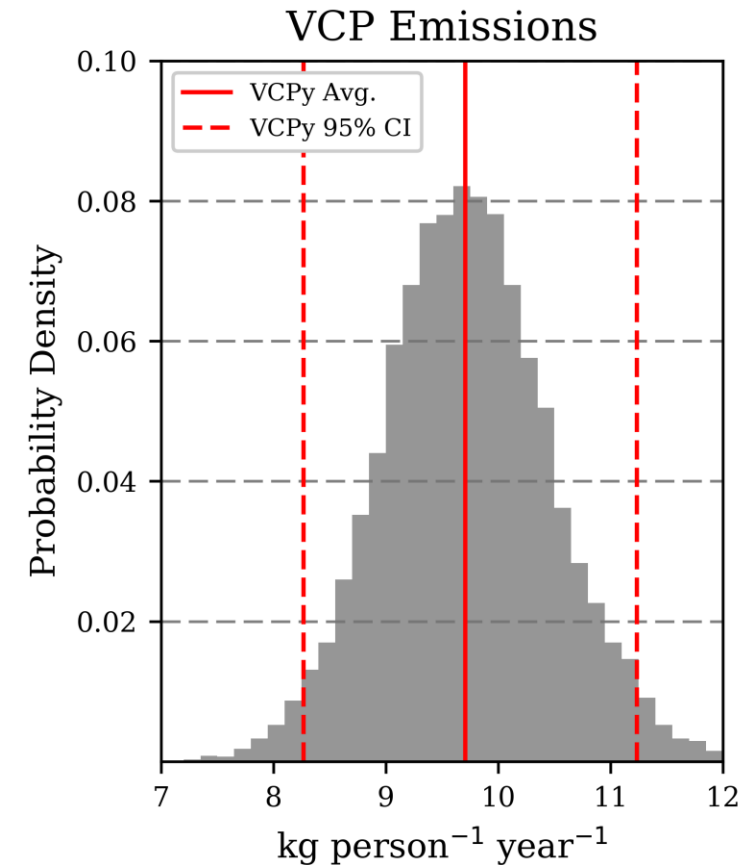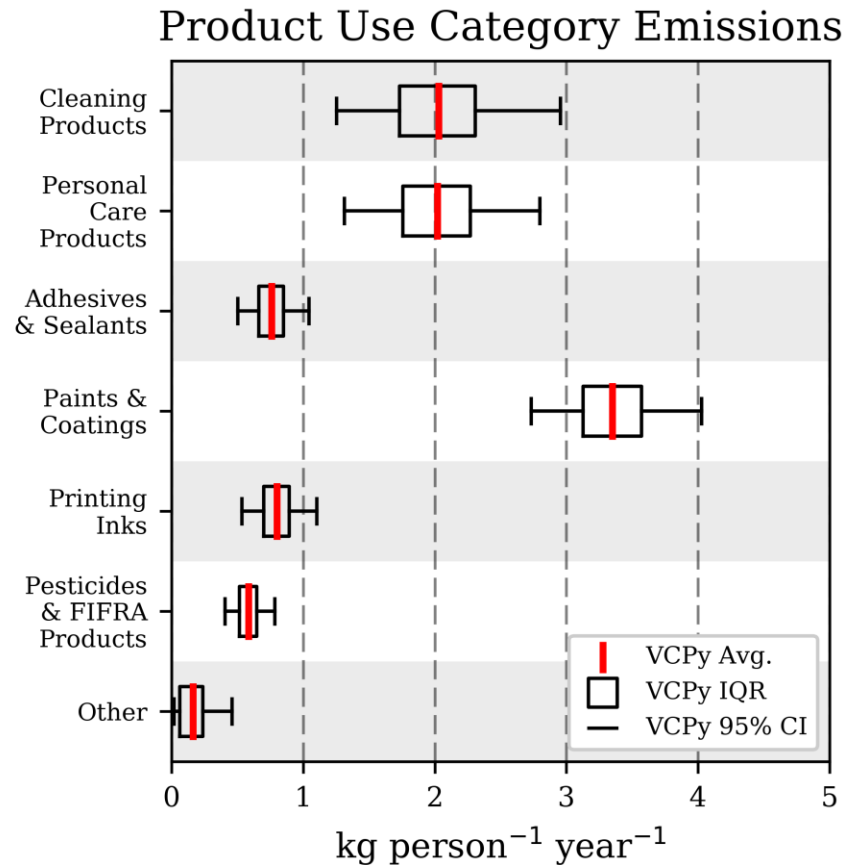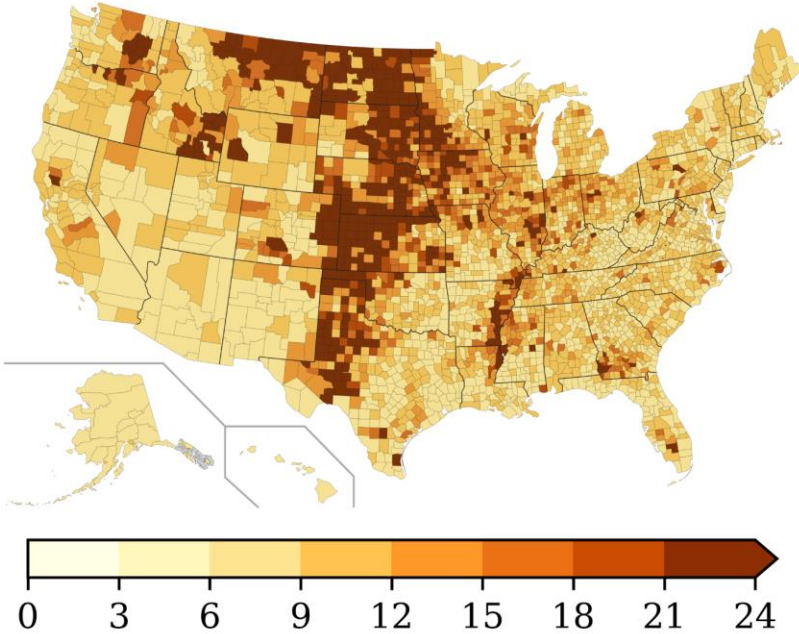
Spatial Allocation of VCP Emissions

Most sub-PUCs are allocated on a per-capita basis. Others (e.g. printing inks, industrial coatings) are allocated based on employment statistics from the U.S. Census Bureau's County Business Patterns Datasets. Two are unique, agricultural pesticides and O&G solvents.
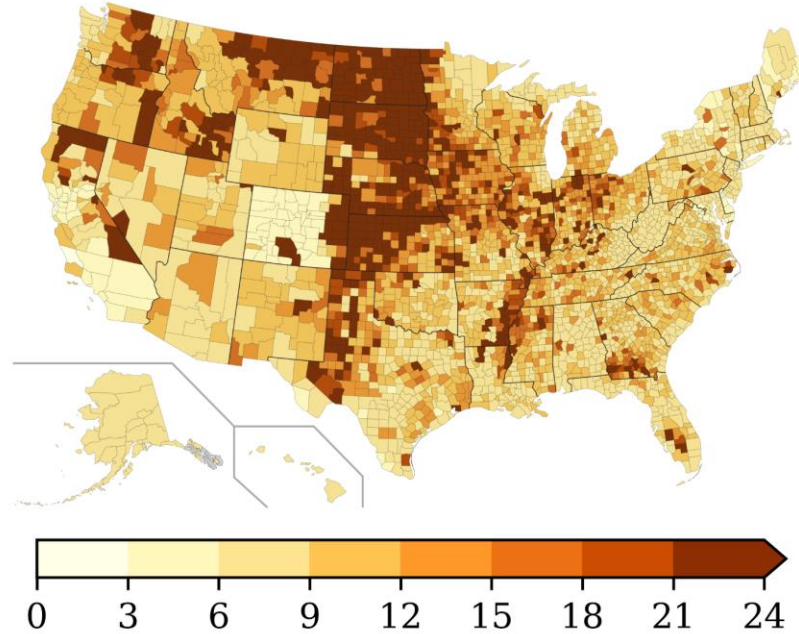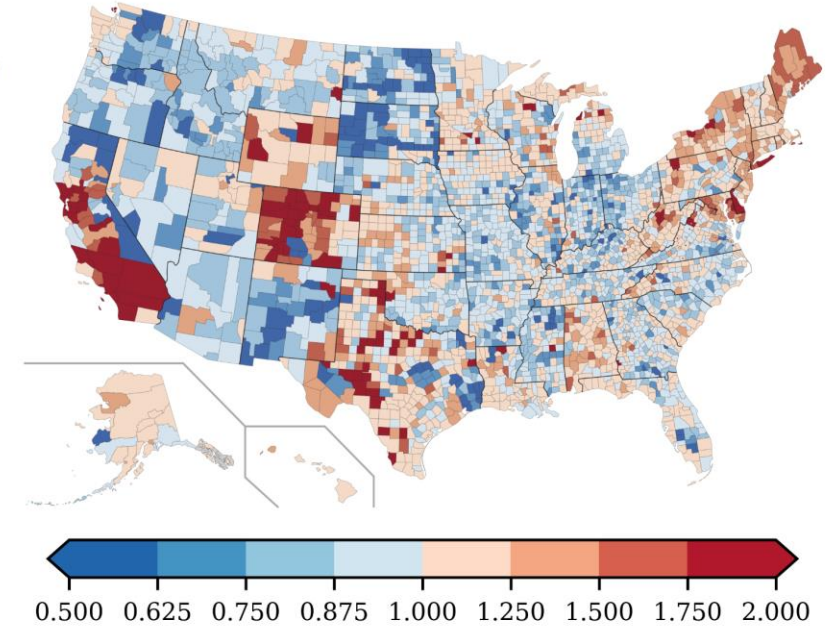
Comparison to 2017 NEI

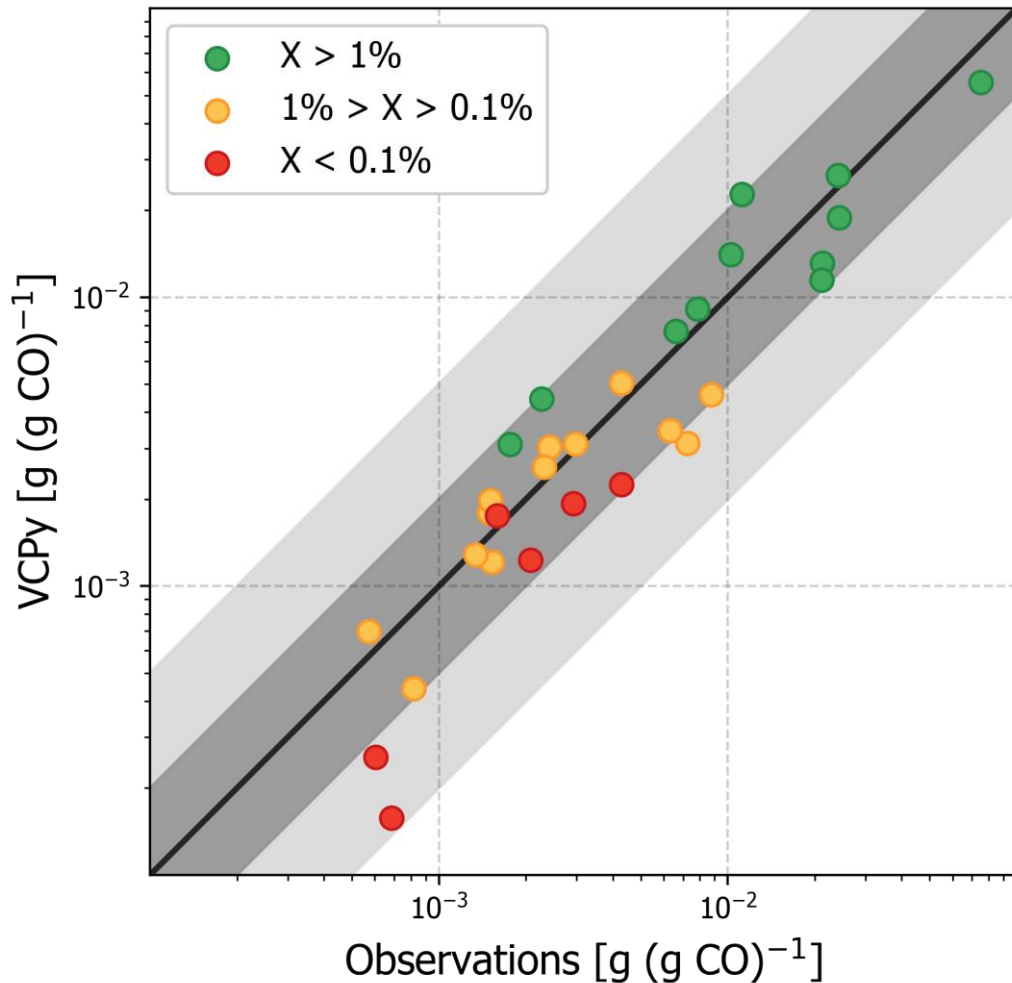VCPy [kg person^{-1} year^{-1}]   2017 NEI [kg person^{-1} year^{-1}]   VCPy / 2017 NEI Ratio

- When compared to the 2017 NEI, ~70% of all counties are $\pm$ 30%.
- When compared to the 2017 NEI, the States with the largest emissions increases were Delaware, California, and Colorado, and the States with the largest emissions decreases were North Dakota and South Dakota.

VCPy Evaluation

- Inventory was evaluated using previously published emission ratios for Los Angeles (CalNex).

- Predicted per-capita VCP emissions in Los Angeles County are 8.42 kg person^{-1} year^{-1} and consist of the 250+ organic compounds.

- Emission ratios available for 30 species, including some of the most abundantly emitted (e.g. ethanol, acetone, isopropyl alcohol, toluene).

- The observed emission ratio sum for all 30 compounds was 0.259 g (g CO)$^{-1}$ and the inventory estimate is 0.226 g (g CO)$^{-1}$, indicating a 13% low bias.

Conclusions

1. VCPy provides new, transparent method to estimate emissions considering:
   a) Product usage
   b) Product composition
   c) Use timescale of product
   d) Characteristic evaporation timescale of product components.

2. National total organic emissions from VCPs are 9.7 kg person^{-1} year^{-1}.
   a) Sector-wide uncertainty at 95% confidence: 8.3 – 11.2 kg person^{-1} year^{-1}.
   b) National VOC emissions from VCPs are 8.2 kg person^{-1} year^{-1}.
   c) Nationally, this is broadly consistent with the US EPA's 2017 NEI; County-level and categorical estimates can differ substantially.

3. An evaluation using published emission ratios indicates high fidelity in the VCPy inventory.

Thank you – any questions?

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