Characterizing the impact of volatile chemical products (VCPs) and cooking on air quality in major US cities

Matt Coggon
NOAA Chemical Sciences Laboratory

Georgios Gkatzelis
Becky Schwantes
Jessica Gilman
Karl Seltzer
Steve Brown
Carsten Warneke
Brian McDonald
Chelsea Stockwell
Lu Xu
Jeff Peischl
Qindan Zhu
The Past...

Los Angeles Civic Center

January 1948

The Transition...

Warneke et al. (JGR 2012)

The Present...

McDonald et al. (Science 2018)

Solvent emissions from Volatile Chemical Products (VCPs) now as important as fossil fuel emissions
1. VCP emissions represented by the 2011 National Emissions Inventory (NEI) are $\sim$ 3-4 times lower than those estimated using a personal exposure model (SHEDS) or the McDonald inventory.

2. With higher VCP emissions, simulated ozone increases, and better agrees with measured MDA8 $O_3$. 

"Impact of VCP emissions on ozone formation in LA (Qin et al., 2020)"
Study Motivation

Impact of VCP emissions on ozone formation in LA (Qin et al., 2020)

Simulated MDA8 $O_3$ (ppb)

Observed MDA8 $O_3$ (ppb)

Research Needs:

1. **Emissions**: Need better observational constraints on VCP emissions to determine impact on urban ozone formation.

2. **Chemistry**: How does the chemistry of major VCP components impact our understanding of urban atmospheric composition
NY-ICE, LISTOS, and SUNVEx

NY-ICE / LISTOS - 2018

U.S. Population Density

NY-ICE
LISTOS

NYC

Las Vegas

Denver

Chicago

LA

SUNVEx

VOC measurements to determine emissions

Modeling to determine impacts

Key reference:
Coggon et al. (2021), PNAS
Results – Improved Constraints on VCP emissions

Fossil Fuels Only

VOC/CO Obs. (g/kg)

VOC/CO Inventory (g/kg)

- toluene
- benzene
- ethanol
- acetone
- C9+C10 alkane
- mek

Bias = -73 ± 7%

$R^2 = 0.44$
Results – Improved Constraints on VCP emissions

Key Takeaways

1. VCPs are needed in order to explain observed VOC ratios of alkanes, oxygenates, and higher aromatics
Key Takeaways

1. VCPs are needed in order to explain observed VOC ratios of alkanes, oxygenates, and higher aromatics
2. Specific VCP tracers provide better constraints on emissions inventories

Learn more!
Gkatzelis et al. (2021). Identifying volatile chemical product tracers in U.S. cities, ES&T
Evaluate Ozone Pollution Sources Using Models

3D Chemical Transport Model (WRF-Chem)

Purpose: Quantitatively Evaluate Ozone Pollution in NYC

0-D Lagrangian Box Model

Emissions + Chemistry

Purpose: Identify Largest Ozone Precursors
Evaluate Ozone Pollution Sources Using Models

3D Chemical Transport Model (WRF-Chem)

1. **Effect of Emissions**: Conducted sensitivity analyses of emissions to quantify VCP contribution to ozone.

2. **Effects of Chemistry**: Conducted sensitivity analyses of chemical mechanisms used to represent oxygenated VCP chemistry:

![Chemical Mechanism Diagram]

Many thanks to the EPA STAR program for supporting our mechanism development!
WRF-Chem modeling during a heatwave event in NYC generally captures the spatial and temporal patterns of ozone formation as measured by routine ozone monitors (circles).
Results – VCPs Needed to Explain Ozone

Ozone during heatwave, July 2, 2018

WRF-Chem modeling during a heatwave event in NYC generally captures the spatial and temporal patterns of ozone formation as measured by routine ozone monitors (circles).

NEXT: Evaluate WRF-Chem simulations of ozone produced at ozone maximum under different scenarios:

- Biogenics + $\text{NO}_x$
- Biogenics + Fossil Fuels + $\text{NO}_x$
- Biogenics + Fossil Fuels + VCPs + $\text{NO}_x$
Results – VCPs Needed to Explain Ozone

Ozone during heatwave, July 2, 2018

VOC sensitivity analyses at ozone maximum

8-h O₃ (ppb)

+20 ppb

Max 8-h Ozone (ppb)

Obs.

Key Takeaways

Biogenic VOCs reacted alongside NOₓ to elevate ozone beyond the NAAQS

Ma x
Fossil fuel emissions increase ozone within the NYC plume, and contribute \( \approx 8 \) ppb of ozone to the ozone max.
**Results – VCPs Needed to Explain Ozone**

Ozone during heatwave, July 2, 2018

VOC sensitivity analyses at ozone maximum

**Key Takeaways**

*VCP emissions further enhance exceedance with an additional 11 ppb of ozone*
Results – VCPs Needed to Explain Ozone

Ozone during heatwave, July 2, 2018

VOC sensitivity analyses at ozone maximum

Key Takeaways

The exchange to oxygenate chemistry has a modest effect on ozone simulations.
Results – VCP chemistry plays a role in PAN formation

Simulated PAN columns

VOC sensitivity analyses at PAN maximum

Key Takeaways

1. VCPs emissions play an important role in simulated PAN production.

2. oVCP chemistry plays an important role in model simulations of key atmospheric constituents

20% increase
McDonald et al. (2018) Inventory in LA

- McDonald Inventory could not explain observations of aldehydes in CalNex dataset.
• McDonald Inventory could not explain observations of aldehydes in CalNex dataset.

• Cooking emissions\(^1\) and skin ozonolysis\(^2\) are a potential source of aldehydes to the atmosphere:

\begin{center}
\textit{Cooking profile from olive oils (Klein et al. 2016)}
\end{center}

\(^1\)Klein et al. (2016), ES&T; \(^2\)Wang et al. (2022), ES&T
Something’s Cooking in Las Vegas

Molecular tracers, such as nonanal and octanal, enhanced in regions with high restaurant density.
Something’s Cooking in Las Vegas

**Potential Impact**

- Per capita emissions $\sim 7-12$ g person$^{-1}$ d$^{-1}$
- Daytime OH Reactivity: $1.3 – 1.5$ s$^{-1}$
- More to come in Qindan Zhu’s talk on Friday, Dec. 9!

Cooking emissions are rich in saturated and unsaturated aldehydes.
Implications

1. New measurements of VCP tracers provide improved constraints on the bottom-up emission inventory first described by McDonald et al. (2018). These measurements support that VCPs are a significant source of carbon in major cities.

2. VCPs account for ~ 50% of the ozone produced from anthropogenic VOCs.

3. Model sensitivity analyses show that oVCP chemistry impacts model simulations of key atmospheric constituents, such as peroxy acyl nitrates, which has implications on downwind ozone formation.

4. Other sources require further investigation, including cooking emissions.

Funding Acknowledgement: EPA Star Grant 84001001. This work has no been formally reviewed by EPA, and the views expressed in this document are solely those of the authors and do not necessarily reflect those of the EPA.