# CRC Report No. A-132

# OZONE FORMATION AND ITS SENSITIVITY TO NOX AND VOCS FROM VOLATILE CHEMICAL PRODUCT, MOBILE SOURCE, AND BIOGENIC EMISSIONS IN URBAN CENTERS

## Executive Summary

**February 2025**

**COORDINATING RESEARCH COUNCIL, INC.**
**1 CONCOURSE PARKWAY • SUITE 800 • ATLANTA, GA 30328**

**The Coordinating Research Council, Inc. (CRC) is a non-profit corporation supported by the petroleum and automotive equipment industries with participation from other industries, companies, and governmental bodies on research programs of mutual interest. CRC operates through the committees made up of technical experts from industry and government who voluntarily participate. The five main areas of research within CRC are: air pollution (atmospheric and engineering studies); aviation fuels, lubricants, and equipment performance; heavy-duty vehicle fuels, lubricants, and equipment performance (e.g., diesel trucks); light-duty vehicle fuels, lubricants, and equipment performance (e.g., passenger cars); and sustainable mobility (e.g., decarbonization). CRC's function is to provide the mechanism for joint research conducted by industries that will help in determining the optimum combination of products. CRC's work is limited to research that is mutually beneficial to the industries involved. The final results of the research conducted by, or under the auspices of, CRC are available to the public.**

**Executive Summary: Ozone Formation and its Sensitivity to NOx and VOCs from Volatile Chemical Product, Mobile Source, and Biogenic Emissions in Urban Centers**

Long-term reductions in emissions of volatile organic compounds (VOCs) from motor vehicles and other major point sources in U.S. cities (Warneke et al., 2012) have resulted in an anthropogenic VOC mixture dominated by emissions from understudied, non-traditional sources that include volatile chemical products (VCPs), which includes personal care products, cleaning agents, coatings, adhesives, and inks (Gkatzelis et al., 2021; Coggon et al., 2021; McDonald et al., 2018) and cooking activities. While the anthropogenic emissions of VCPs and cooking account for an important fraction of the urban VOC budget, their impacts on atmospheric chemistry are not well understood, but likely contribute to the formation of ground-level ozone ($O_3$) and aerosols.

**Objective:**

The objective of this research is to attribute ozone formation to source-specific sectors, including mobile sources, VCPs, cooking VOCs, and biogenics, in a modern U.S. urban atmosphere. We used an emissions inventory-based Lagrangian box model, informed by source apportionment, that includes updates to cooking VOC emissions and chemistry. An additional focus was on ozone sensitivity to changing $NO_x$ and inventory VOC mixtures. Finally, we investigated the spatial distribution of biogenics and evaluated inventory-measurement biogenic VOC agreement using field observations in Pasadena.

**Key summary of findings:**

1. Box model configuration and evaluation

A Lagrangian box model using the Framework for 0-D Atmospheric Modeling (F0AM) (Wolfe et al., 2016) was developed to simulate the evolution of emissions, chemistry, and dilution of pollutants as they are transported across the LA Basin to Pasadena and Redlands, CA. A FLEXPART particle dispersion model was used to calculate backward-trajectory coordinates that move with the wind at 15-minute intervals arriving hourly at each receptor site. FLEXPART was coupled with Weather Research and Forecasting v4.2.2 (WRF) numerical weather prediction model (FLEXPART-WRF) to obtain ancillary information (photolysis rates, planetary boundary layer height, temperature, and pressure) used to constrain the model along each trajectory path. The corresponding spatially-gridded emissions from FIVE-VCP-NEI17NRT and BEISv3.14 inventories are mixed into the defined box volume at each coordinate and are photochemically processed, transported, and diluted. The model accurately reproduced the variability and magnitude of $O_3$, $NO_x$, and speciated VOCs from 7 August – 7 September 2021 in Pasadena, CA, with a normalized mean bias (NMB) for $O_3$ of -0.001 and an $R^2$ of 0.77. The model-measurement agreement for all VOCs including VCP and cooking VOCs show that the model adequately represents the important emissions and chemical reactions that influence $O_3$ formation.

2. MDA8 $O_3$ contributions and sensitivities

VOC sensitivity analyses to determine $O_3$ response in Pasadena, CA, showed the total anthropogenic VOC (AVOC) contribution at daily maximum 8-hour average (MDA8) $O_3$ was 13 ppb and the AVOC MDA8 $O_3$ distribution indicates the VOCs from VCP sectors account for 45%, fossil fuels for 29% and cooking for 26% of the anthropogenic $O_3$. The biogenic VOCs (BVOC) contribution to $O_3$ in Pasadena was ~9.4 ppb, approximately 42% of the total VOC MDA8 $O_3$ (AVOC+BVOC) attribution. The AVOC $O_3$ magnitude and distribution determined in Redlands is consistent with Pasadena, but the relative contributions in other cities likely vary with population density, restaurant density, VCP usage, and transportation. Modeled $O_3$ sensitivities to $NO_x$ suggest that the urban core of Los Angeles, including along the typical transport pathway to Pasadena, is primarily $NO_x$–saturated, but sits near the transitional point during peak production, requiring only a 10-20% reduction in $NO_x$ to transition. Further downwind to the east, Redlands is $NO_x$–limited. Ozone is also sensitive to the total VOC emissions prescribed by anthropogenic inventories: when using VOC emissions as they are represented by the NEI, Pasadena is more $NO_x$–saturated and nearly a 40% decrease in $NO_x$ would be needed to transition to $NO_x$–limited chemistry. This demonstrates that accurate anthropogenic and biogenic VOC representation in inventories and models is critical to inform regulation decisions.

3. Distribution of urban biogenic VOCs

The biogenic VOC emissions contribute significantly to $O_3$ production in the LA Basin as demonstrated by the box model sensitivity analysis. Ground site measurements show that isoprene emitting vegetation is important especially in Pasadena and measurements on the mobile laboratory show that the spatial distribution of biogenic VOCs compares well to what is expected from TROPOMI gross primary production. But model-measurement comparisons using a WRF-Chem 3D model shows that isoprene and its oxidation products methacrolein (MACR) and methyl vinyl ketone (MVK) are underestimated in Pasadena, and as a result modeled $O_3$ in the LA Basin might underestimate the biogenic contribution.

**Publications from this work:**

Stockwell, C. E., Coggon, M. M., Schwantes, R. H., Harkins, C., Verreyken, B., Lyu, C., Zhu, Q., Xu, L., Gilman, J. B., Lamplugh, A., Peischl, J., Robinson, M. A., Veres, P. R., Li, M., Rollins, A. W., Zuraski, K., Baidar, S., Liu, S., Kuwayama, T., Brown, S. S., McDonald, B. C., and Warneke, C.: Urban ozone formation and sensitivities to volatile chemical products, cooking emissions, and NOx across the Los Angeles Basin, EGUsphere, 2024, 1-24, 10.5194/egusphere-2024-1899, 2024

**References**

Coggon, M. M., Gkatzelis, G. I., McDonald, B. C., Gilman, J. B., Schwantes, R. H., Abuhassan, N., Aikin, K. C., Arend, M. F., Berkoff, T. A., Brown, S. S., Campos, T. L., Dickerson, R. R., Gronoff, G., Hurley, J. F., Isaacman-VanWertz, G., Koss, A. R., Li, M., McKeen, S. A., Moshary, F., Peischl, J., Pospisilova, V., Ren, X. R., Wilson, A., Wu, Y. H., Trainer, M., and Warneke, C.: Volatile chemical product emissions enhance ozone and modulate urban chemistry, Proceedings

of the National Academy of Sciences of the United States of America, 118, 10.1073/pnas.2026653118, 2021.
Gkatzelis, G. I., Coggon, M. M., McDonald, B. C., Peischl, J., Gilman, J. B., Aikin, K. C., Robinson, M. A., Canonaco, F., Prevot, A. S. H., Trainer, M., and Warneke, C.: Observations Confirm that Volatile Chemical Products Are a Major Source of Petrochemical Emissions in US Cities, Environ. Sci. Technol., 55, 4332-4343, 10.1021/acs.est.0c05471, 2021.
McDonald, B. C., de Gouw, J. A., Gilman, J. B., Jathar, S. H., Akherati, A., Cappa, C. D., Jimenez, J. L., Lee-Taylor, J., Hayes, P. L., McKeen, S. A., Cui, Y. Y., Kim, S. W., Gentner, D. R., Isaacman-VanWertz, G., Goldstein, A. H., Harley, R. A., Frost, G. J., Roberts, J. M., Ryerson, T. B., and Trainer, M.: Volatile chemical products emerging as largest petrochemical source of urban organic emissions, Science, 359, 760-764, 10.1126/science.aaq0524, 2018.
Warneke, C., de Gouw, J. A., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E., Blake, D., Trainer, M., and Parrish, D. D.: Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions, Journal of Geophysical Research: Atmospheres, 117, https://doi.org/10.1029/2012JD017899, 2012.
Wolfe, G. M., Marvin, M. R., Roberts, S. J., Travis, K. R., and Liao, J.: The Framework for 0-D Atmospheric Modeling (F0AM) v3.1, Geosci. Model Dev., 9, 3309-3319, 10.5194/gmd-9-3309-2016, 2016.