CRC Report No. A-136

COMPARING OZONE PRODUCTION EFFICIENCY (OPE) OF CHEMICAL MECHANISMS USING CHEMICAL PROCESS ANALYSIS (CPA)

Final Report

May 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.

Comparing Ozone Production Efficiency (OPE) of Chemical Mechanisms Using Chemical Process Analysis (CPA)

CRC A-136

Final Report

RAMBOLL

Prepared for:

Coordinating Research Council, Inc.

1 Concourse Parkway, Suite 800

Atlanta, GA 30328

Prepared by:

Ramboll Americas Engineering Solutions, Inc.

7250 Redwood Blvd., Suite 105

Novato, California, 94945

www.ramboll.com

May 2025

EXECUTIVE SUMMARY

Three-dimensional Chemical Transport Models (CTMs) are one of the tools used by regulatory agencies for air quality planning and emissions control strategies. Chemical mechanisms are critical to CTMs and describe the formation of secondary pollutants, such as ozone (O_3) and particulate matter <2.5 μm ($PM_{2.5}$), through chemical reactions of oxidants, organic compounds, and other precursors such as nitrogen oxides (NO_X). Mechanism intercomparison, especially using metrics which reduce sensitivity to modeling scenarios, is important for interpreting results and assessing uncertainties. In this study, we investigate Ozone Production Efficiency (OPE) as a comparison metric under conditions where ozone production is limited by the availability of NO_X. OPE is the net number of O_3 molecules produced per NO_X molecule lost (Kleinman et al., 2002) and is a key descriptor of NO_X-limited O_3 formation.

The main objectives of this study were to:

- Compute OPE in box model simulations using four widely used chemical mechanisms and compare differences in OPE and O_3 between mechanisms
- Analyze the response of modeled OPE and O_3 to varying anthropogenic emissions
- Review available OPE measurements and compare model results to appropriate data.

We used the Comprehensive Air Quality Model with Extensions (CAMx), configured as a 2-box model, to compute OPE for three Texas locations, Houston-Galveston-Brazoria (HGB), Dallas-Fort Worth (DFW), and San Antonio (SAN). Each model scenario represents typical high-ozone summertime conditions for the locations and input data were developed from 3D CAMx simulations from the Texas Commission on Environmental Quality's (TCEQ) 2019 modeling platform. The CAMx 2-box model scenarios were run using four chemical mechanisms: Carbon Bond version 6 revision 5 (CB6r5; Yarwood et al., 2020), Carbon Bond version 7 revision 1 (CB7r1; Yarwood et al., 2021), Statewide Air Pollution Research Center 2007 (SAPRC07; Carter, 2010); and Regional Atmospheric Chemistry Mechanism version 2 (RACM2; Goliff et al., 2013). We developed new methods to compute OPE in CAMx using chemical process analysis (OPE-CPA) as the ratio of net O_3 production, $Pn(O_3)$, to net NO_Z production, $Pn(NO_Z)$, where NO_Z is the sum of NO_X oxidation products, including nitric acid (HNO_3), peroxyacyl nitrates (PANs), and organic nitrates (ONs).

Our results show that OPE-CPA can be used successfully to compare mechanisms under NO_X-limited conditions. Comparison of OPE-CPA, along with concentrations of important species such as O_3, nitrogen species, and oxidants, provide a better understanding of how O_3 formation varies between mechanisms, which can support the validity of air quality planning. The four mechanisms considered in this work show a similar response of both OPE-CPA and O_3 to varying anthropogenic emissions of volatile organic compounds (VOCs) and NO_X. OPE-CPA generally

increases with increasing VOC and decreases with increasing NO_X. O_3 response surfaces for all mechanisms show that the base emissions simulations for 2019 are in a NO_X-limited regime and the location of the 'ridgeline', which separates NO_X-limited from VOC-limited conditions, is in a similar location with all mechanisms. There are differences between the mechanisms, however. RACM2 consistently produces the largest OPE-CPA, O_3, and OH, which is due partially to a slower OH + NO_2 reaction rate constant. HNO_3 is the dominant NO_Z species in all mechanisms, highlighting the importance of the OH + NO_2 reaction in NO_Z net production, and consequently OPE, for all mechanisms. Uncertainty in the OH + NO_2 reaction rate is therefore especially important to resolve due to its strong influence on O_3 and OPE. OPE-CPA differences between mechanisms are also greatest at high VOC/NO_X ratios, indicating the differences in the treatment of NO_X recycling between mechanisms may be important under these conditions.

We also reviewed available OPE measurements and provide a comprehensive overview of the methods used to calculate OPE from measurements. We determined that aircraft measurements downwind of Houston which estimate OPE from the slope of a linear regression of O_3 and NO_Z concentrations (OPE-plot) are most comparable to our modeled OPE-CPA. Surface measurements are considered unsuitable for comparison due to uncertainties introduced by deposition, especially of NO_Z. OPE-CPA from the HGB simulations was interpolated from the base model year (2019) to measurement years (2000, 2006, 2013) using emissions trends in Harris County. OPE-CPA is generally consistent with OPE-plot, but direct comparison is difficult due to differences in how deposition impacts the two OPE metrics, and uncertainties in how VOC speciation changed over the time period considered. There are no suitable measurements available near Dallas-Fort Worth or San Antonio. Results from the DFW and SAN simulations are therefore provided for comparison to the HGB simulation but are not compared to measurements.

A significant finding of this work is that OPE-CPA for all mechanisms responds nonlinearly to NO_X and increases at low NO_X even though O_3 production decreases. Using OPE to predict ozone response to NO_X emissions reductions is therefore an oversimplification that will tend to overstate ozone reductions. The nonlinear response of OPE-CPA to NO_X also conflicts conceptually with OPE-plot, which is derived from a linear relationship over varying NO_X input. Additional measurement and modeling studies are needed to better understand these findings. Aircraft based OPE measurements downwind of previously studied locations would be useful to test mechanism response to emission reductions, and speciated VOC measurements would help characterize the reactivity of emissions. Applying CPA-OPE in 3D simulations is also feasible and complementary with other methods used to probe 3D model simulations, such as sensitivity analysis. 3D simulations of urban plumes using a fine horizontal grid resolution could investigate why measured OPE is often stable within a plume even when subject to varying NO_X

emissions. Comparison of OPE-CPA and OPE-plot along pseudo aircraft transects in the same simulated plume would help us better understand if the two provide similar estimates of OPE.

References

Carter, W.P.L.: Development of the SAPRC-07 chemical mechanism. Atmospheric Environment, 44 (40), pp. 5324-5335, 2010b.

Goliff, W. S., Stockwell, W. R., and Lawson, C. V.: The regional atmospheric chemistry mechanism, version 2., Atmospheric Environment, 68, pp. 174-185, https://doi.org/10.1016/j.atmosenv.2012.11.038, 2013.

Kleinman, L. I., Daum, P. H., Lee, Y-N, Nunnermacker, L. J., Springston, S. R., Weinstein-Lloyd, J., and Rudolph, J.: Ozone production efficiency in an urban area, J. Geophys. Res. 107 (D23), 4733, doi.org/10.1029/2002JD002529, 1-12, 2002.

Yarwood, G., Shi, Y., Beardsley, R., 2020. Impact of CB6r5 Mechanism Changes on Air Pollutant Modeling in Texas. Report prepared for Texas Commission on Environmental Quality, July 30 2020. https://web.archive.org/web/20210529064250/https://www.tceq.texas.gov/assets/public/implementation/air/am/contracts/reports/pm/5822011221014-20200730-Ramboll-CB6r5MechanismChanges.pdf

Yarwood, G., Shi, Y., Beardsley, R., 2021. Develop CB7 Chemical Mechanism for CAMx Ozone Modeling. Report prepared for Texas Commission on Environmental Quality, June 30 2021. https://web.archive.org/web/20220119125447/https:/www.tceq.texas.gov/downloads/air-quality/research/reports/photochemical/5822121802020-20210630-ramboll-cb7.pdf