Hands-on Training for Zero-Dimensional (0-D) Photochemical Box Modeling

Final Report

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Prepared for the Texas Commission on Environmental Quality (TCEQ)

Ayse Bozlaker, Project Manager

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James Flynn, University of Houston

Rob Griffin, Rice University

Fangzhou Guo, Rice University

Executive Summary

In January 2020 the TCEQ issued a PGA to the University of Houston (UH), with Rice University (RU) as a sub recipient, to conduct an in person training session for the staff of the TCEQ on the use and application of the NASA Langley Research Center (LaRC) zero-dimensional photochemical box model. This model has been used for many years by the airborne science research community as well as by UH to analyze photochemistry processes using ambient measurements, including for work funded by the TCEQ. The results from this model can be used to help understand the processes for the formation and destruction of O_3 and NO_X as well as contributions of VOCs to the overall VOC reactivity. This information can also allow the user to calculate NO_X:VOC sensitivity parameters and may be able to support decisions related to potential pollution control strategies.

The initial training was scheduled to take place in Austin in April 2020, however due to the COVID-19 situation an extension was granted and the training was ultimately conducted online via Microsoft Teams.

The LaRC model is a simple constrained steady state photochemical box model with 80 species, 36 photolysis rates, and 251 chemical reactions. The chemical mechanism is based on a modified version of the Lurmann (1986) scheme. Like other box models this model does not include emission sources or advection and simply works off of observations.

Output data include total O_3 formation, destruction, and net production rates and their constituent reactions, as well as values for all chemical species, photolysis rates, and selected chemical reaction rates. A second file is also written which contains all 251 reaction rates.

On September 14, 2020 a virtual workshop on the use and application of the LaRC and TUV model was conducted via Microsoft Teams. The workshop was led by Ayse Bozlaker with James Flynn (UH, Research Associate Professor) and Fangzhou Guo (RU, PhD candidate, advisor Rob Griffin). The workshop addressed the following topics:

1) Introduction of LaRC model, it's history, mechanism, comparison to other models, and applications for air quality.
2) Step-by-step instructions for the preparation of an input file, including using measured jNO_2, the TUV model, and TCEQ solar radiation data
3) Use of the LaRC model, the impact of optional constraints, and troubleshooting tips and techniques
4) Example code used by UH and RU to analyze the LaRC model results
5) Overview of data products that can be generated using LaRC results that may help the TCEQ gain additional understanding of the photochemistry regimes within Texas.

In total twenty TCEQ staff attended the workshop. Although the presentation and hands-on training portion likely would have been better in person as originally intended, it went quite well. There were many more participants than expected. UH and RU were able to provide useful instruction on the use and application of the models and will remain available for support beyond the conclusion of the project. If the TCEQ desires to more fully constrain the model it would be beneficial for selected sites to measure key constraints such as HCHO, particularly if the model results suggest that HCHO plays a large role in O_3 production. Measurements of jNO_2 would also be quite useful and simplify the file preparation and reduce uncertainty.

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1. Introduction

In January 2020 the TCEQ issued a PGA to the University of Houston (UH), with Rice University (RU) as a sub recipient, to conduct an in person training session for the staff of the TCEQ on the use and application of the NASA Langley Research Center (LaRC) zero-dimensional photochemical box model. This model has been used for many years by the airborne science research community as well as by UH to analyze photochemistry processes using ambient measurements, including for work funded by the TCEQ. The results from this model can be used to help understand the processes for the formation and destruction of O_3 and NO_X as well as contributions of VOCs to the overall VOC reactivity. This information can also allow the user to calculate NO_X:VOC sensitivity parameters and may be able to support decisions related to potential pollution control strategies.

The initial training was scheduled to take place in Austin in April 2020, however due to the COVID-19 situation an extension was granted and the training was ultimately conducted online via Microsoft TEAMS.

2. Methods

2.1. LaRC Zero Dimensional Photochemical Box Model

The LaRC model is a simple constrained steady state photochemical box model with 80 species, 36 photolysis rates, and 251 chemical reactions. The chemical mechanism is based on a modified version of the Lurmann (1986) scheme. Like other box models this model does not include emission sources or advection and simply works off of observations.

Key inputs for this model include O_3, CO, H_2O, and either NO or NO_2. Additional constraints such as HCHO, HONO, HNO3, and PAN are also available. The model can be operated in several different modes, however for the purposes of this training with a focus on O_3 processes and NO_X:VOC sensitivities, the Time Dependent mode was selected with Instantaneous values as the output. In this mode the model will run the input values through a diurnal cycle and compare selected key species such as O_3 and NO or NO_2 to the initial values. When these values are within 0.5 or 1% of the initial input the model will write the resulting values to the output files and continue to the next line. If convergence is not met then additional diurnal cycles will be run until the convergence criteria are met. The maximum number of "days" is a user input and nominally 400 days are selected to ensure a high likelihood of reaching convergence.

Output data include total O_3 formation, destruction, and net production rates and their constituent reactions, as well as values for all chemical species, photolysis rates, and selected chemical reaction rates. A second file is also written which contains all 251 reaction rates.

This model is a research model and was designed for use on various NASA airborne research projects. As a result the input file is structured to take specific file structures from airborne campaigns. While many of the channels are not required by the model and are simply either discarded or passed through to the output file, UH and RU typically populate these columns with missing data flags such as -9999. Other values such as H_2 and CH_4 can use constant values. Additional settings for various photolysis options (JVS) and VOC fill flags were described in the training discussion and presentation and are included in the example data files.

Photolysis rates are a key aspect of any photochemical model. Since the LaRC is based on observational data it is strongly desirable to include actual observations of at least the NO_2 photolysis rate, jNO_2. A filter radiometer is typically deployed with most UH intensive measurement campaigns in order to provide this data, however typically only zenith measurements are conducted (downwelling photons). In order to estimate the nadir (upwelling) measurement the Tropospheric Ultraviolet and Visible (TUV) model from the National Center for Atmospheric Research (NCAR) is used.

2.2. Tropospheric Ultraviolet and Visible Radiative Transfer Model

The TUV radiative transfer model can be used to estimate clear-sky photolysis rates and allows the user to adjust a variety of parameters for position, surface albedo, atmospheric and aerosol conditions, as well as date and time and wavelength ranges. For the purposes of this training the mode which is optimized for photochemistry is selected and the dowelling and upwelling components are turned either on or off as appropriate to allow the user to generate the proper photolysis rates for the LaRC model.

In the situation described above where zenith jNO_2 measurements were made the TUV model would be run for jNO_2 twice, once with the direct sun and diffuse downwelling components on and the diffuse upwelling component turned off, and once with diffuse upwelling turned on and the other two components turned off. This will simulate the measurements if both a zenith and nadir jNO_2 sensor was deployed. By applying the solar zenith dependent ratio of the modeled nadir to zenith jNO_2 to ambient measurements of zenith jNO_2 the nadir jNO_2 component can be estimated for the LaRC model input file.

In the event jNO_2 was not measured it may be possible to substitute other solar radiation measurements as a proxy, however this approach will introduce additional errors as the spectrum and overall shape of the profile are likely to impact the results. If this approach is taken it is recommended to select a clear sky day and compare the measured solar radiation data to modeled zenith jNO_2. Once this solar zenith angle dependent ratio is determined for a given site it can then be applied to solar radiation measurements for days impacted by clouds. The nadir component can then be estimated using a similar method as described above when using a jNO_2 filter radiometer.

It is important that clear sky modeled jNO_2 is not mixed with ambient measurements as misleading results may occur. Ambient photochemical concentrations, and therefore the measurements, are directly controlled by photolysis rates, particularly jNO_2. Mixing ambient NO_2 and O_3 measurements with modeled jNO_2 rates would result in erroneous partitioning of O_3 vs NO_2 and NO_2 vs NO. To avoid these errors, the TUV model or a similar method should be used to estimate actual jNO_2. If a user wishes to use clear-sky modeled jNO_2 values with the LaRC model and ambient measurements they should contact James Flynn at UH (jhflynn@uh.edu) for more information. Sensitivity tests such as this can aid in estimating the impact of clouds and aerosols on O_3 production.

3. Results

On September 14, 2020 a virtual workshop on the use and application of the LaRC and TUV model was conducted via Microsoft Teams. The workshop was led by Ayse Bozlaker with James Flynn (UH, Research Associate Professor) and Fangzhou Guo (RU, PhD candidate, advisor Rob Griffin). The workshop addressed the following topics:

6) Introduction of LaRC model, it's history, mechanism, comparison to other models, and applications for air quality.
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8) Use of the LaRC model, the impact of optional constraints, and troubleshooting tips and techniques
9) Example code used by UH and RU to analyze the LaRC model results
10) Overview of data products that can be generated using LaRC results that may help the TCEQ gain additional understanding of the photochemistry regimes within Texas.

In total twenty TCEQ staff attended the workshop. The participant list is listed below.

<u>Attendees:</u>

1) Barry Exum
2) Bob Gifford
3) Bryce Kuchan
4) Cara Scalpone
5) Chola Regmi
6) Chuhua Tian
7) David Westenbarger
8) Fernando Mercado
9) Jocelyn Mellberg
10) Jonathan Steets
11) Kasey Savanich
12) Kayla Petersen
13) Pujarini Maiti
14) Raj Nadkarni
15) Robert Ramirez
16) Thuy Phi
17) Timothy Janke
18) Xiao Yu
19) Zhaohua Fang
20) Ayse Bozlaker (Project Manager)

4. Conclusion and Recommendations for Future Work

The workshop was well attended and many questions were asked by the attendees. Although the presentation and hands-on training portion likely would have been better in person as originally intended, it went quite well. There were many more participants than expected. UH and RU were able to provide useful instruction on the use and application of the models and will remain available for support beyond the conclusion of the project.

It is recommended that the TCEQ staff interested in using the LaRC and/or TUV model practice its use in the coming months with new data sets. The preparation of the input file is one of the more challenging aspects of the model. Since most, if not all, of the TCEQ sites do not measure any of the optional constraints it should be reasonable that the sites can be reasonably compared relative to each other or for changes over time. If the TCEQ desires to more fully constrain the model it would be beneficial for selected sites to measure key constraints such as HCHO, particularly if the model results suggest that HCHO plays a large role in O_3 production. Measurements of jNO_2 would also be quite useful and simplify the file preparation and reduce uncertainty.

5. References

Chen, S., Ren, X., Mao J., Chen, Z., Brune, W. H., Lefer, B., Rappenglück, B., Flynn J., Olson, J., Crawford, J. H. (2010) A comparison of chemical mechanisms based on TRAMP–2006 field data, Atmos. Environ., 44, 4116–4125.

Crawford, J., Davis, D., Olson, J., Chen, G., Liu, S., Gregory, G., Barrick, J., Sachse, G., Sandholm, S., Heikes, B., Singh, H., Blake, D. (1999) Assessment of upper tropospheric HO_X sources over the tropical Pacific based on NASA GTE/PEM data: Net effect on HO_X and other photochemical parameters, J. Geophys. Res., 104, 16255–16273.

Kleinman, L. I., Daum, P. H., Imre, D., Lee, Y.-N., Nunnermacker, L. J., Springston, S. R., Weinstein-Lloyd, J., Rudolph, J. (2005), A comparative study of ozone production in five U.S. metropolitan areas, J. Geophys. Res., 110, D02301.

Lurmann, F. W., Lloyd, A. C., *&* Atkinson, R. *(*1986*).* A chemical mechanism for use in long-range transport/acid deposition computer modeling. Journal of Geophysical Research, 91*(*D10*)*, 10,905–10,936. https://doi.org/10.1029/JD091iD10p109

Madronich, S. (1993) The atmosphere and UV-B radiation at ground level. Environmental UV Photobiology, Plenum Press, 1–39.

Mazzuca, G. M., Ren, X., Loughner, C. P., Estes, M., Crawford, J. H., Pickering, K. E., Weinheimer, A. J., Dickerson, R. R. (2016) Ozone production and its sensitivity to NO_X and VOCs: results from the DISCOVER-AQ field experiment, Houston 2013. Atmospheric Chemistry and Physics, 16(22), 14, 463–474.

Olson, J. R., Crawford, J. H., Chen, G., Brune, W. H., Faloona, I. C., Tan, D., Harder, H., Martinez, M. (2006) A reevaluation of airborne HO_X observations from NASA field campaigns, Journal of Geophysical Research-Atmospheres, 111(D10), 12.

Pacsi, A. P., Kimura, Y., McGaughey, G., McDonald-Buller, E. C., Allen, D. T. (2015) Regional Ozone Impacts of Increased Natural Gas Use in the Texas Power Sector and Development in the Eagle Ford Shale, Environ. Sci. Technol., 49, 3966–3973.

Roest, G. and Schade, G. (2017) Quantifying alkane emissions in the Eagle Ford Shale using boundary layer enhancement. Atmos. Chem. Phys. 17, 11163–11176.

Schroeder, J. R., et al. (2017), New insights into the column CH2O/NO2 ratio as an indicator of near-surface ozone sensitivity, J. Geophys. Res. Atmos., 122, 8885–8907, doi:10.1002/2017JD026781

6. Appendix A

Training materials and the workshop presentation for this project can be access by TCEQ using the following link:

https://hoth.geosc.uh.edu:5001/sharing/mHyx85V64

Videos of the training session can be found at the links below when accessed from within the TCEQ network.

https://web.microsoftstream.com/video/357f1ec6-f4fe-4ba1-88b8-beeeda20a52d
https://web.microsoftstream.com/video/64f0b940-1ae0-4313-a073-a393cea44fd4