Development of Future Atmospheric Chemical Mechanisms for Photochemical Modeling

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Air Pollution Kills!

For decades, pollution and its harmful effects on people's health, the environment, and the planet have been neglected both by Governments and the international development agenda. Yet, pollution is the largest environmental cause of disease and death in the world today, responsible for an estimated 9 million premature deaths.

- The Lancet Commission on pollution and health

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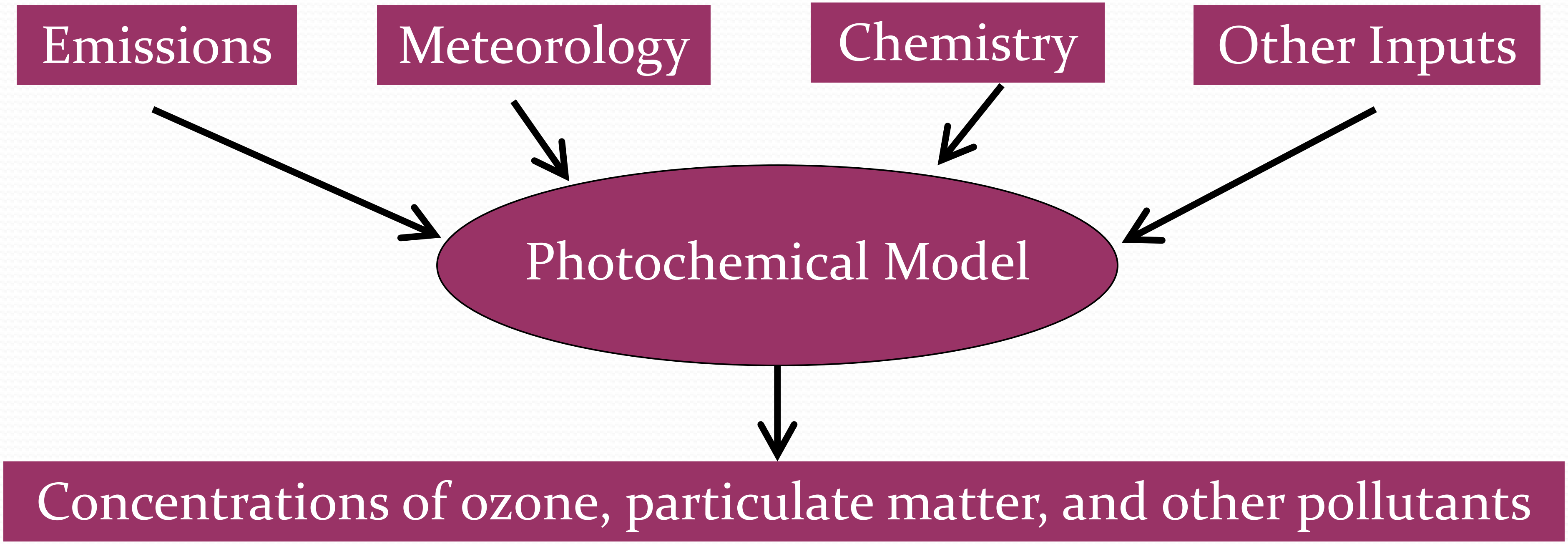
Photochemical Modeling



Models are mathematical representations of our best current knowledge of atmospheric processes

Atmospheric Chemical Mechanisms

- Master Chemical Mechanism (http://mcm.leeds.ac.uk/MCM/)
  - Near-explicit reference benchmark
  - Too big for routine regulatory applications
- SAPRC (http://www.cert.ucr.edu/~carter/)
  - SAPRC07
    - Condensed and routinely used in regulatory applications
  - SAPRC16
    - More explicit and in peer-review
- RACM2 (http://www.cert.ucr.edu/~carter/Mechanism_Conference/12%20B%20Stockwell.pdf)
- Carbon Bond 06 (https://www.tceq.texas.gov/assets/public/implementation/air/am/committees/pmt_set/20101014/20101014-GregYarwood-CB6.pdf)

Major Improvements in SAPRC16

- Updated Aromatics (SAPRC11)
- Complete update to the base mechanism.
- More model species added to support toxics and SOA.
- Mechanism generation system completely updated. New peroxy isomerization and other reactions that change low NOx organic products and radical cycling.
- Less approximate peroxy lumping method implemented.

History of SAPRC Peer-Reviews

- **SAPRC90**: Gery, M.W. (1991), Review of the SAPRC-90 mechanism. Final Report to California Air Resources Board, Contract No. A132-055. (www.arb.ca.gov/research/apr/past/a132-055.pdf)
- **SAPRC99**: Stockwell, W.R. (1999), Review of the updated maximum incremental reactivity scale of Dr. William Carter. Final Report to California Air Resources Board. Contract No. 98-401. (www.arb.ca.gov/research/apr/past/98-401.pdf)
- **SAPRC07**: http://www.arb.ca.gov/research/reactivity/rsac-mtgsum-09.pdf. Also described in four peer-reviewed publications. Reviewers: Robert Harley (UC Berkeley), William Stockwell (Howard University), Merched Azzi (CSIRO), and Richard Derwent (rdscientific)
- **SAPRC11**: Minor update not peer reviewed

Peer-Review of SAPRC16

- As with SAPRC99 and SAPRC07, SAPRC16 underwent an in-depth systematic peer-review
  - Merched Azzi, CISRO, Australia
  - Richard Derwent, rdscientific, UK
  - John Seinfeld, Caltech
  - William Stockwell, Howard University (now at DRI/UTEP)
  - Michael Kleeman, UC Davis, PI
- Partial findings were presented at the UC Davis Atmospheric Chemical Mechanism Conference in December 2016
- Final reports, publication, and mechanism files will be available very soon

Future Chemical Mechanisms

Kaduwela, A., Luecken, D., Carter, W., Derwent, R., 2015. New Directions: Atmospheric chemical mechanisms for the future. Atmospheric Environment, 122, 609-610.

- Focus is mostly on gas phase but applicable to PM
- Argues that current mechanisms are not designed to handle lowering standards and new scientific understanding of exposure
- Stresses that future chemical mechanisms should be robust, transparent, and free of scientific challenge
- Proposes four discernable stages of mechanism development
- Highlights coordinated support/funding needed for this endeavor

Stage 1: Assembling Information

- All that is known and is accepted by the atmospheric community
- Formation and reactions of O_3 , $PM_{2.5}$, air toxics and other important chemical constituents
- Essential components
  - IUPAC (Ammann et al., 2013)
  - NASA (Sander et al., 2011)
  - other published literature reviews
  - existing smog chamber, laboratory, and field experiments
  - estimation methods (e.g., structure-reactivity relationships)
  - quantum chemistry
- Needs to be an ongoing streamlined process that continually tracks new research in atmospheric chemistry
- Make the results openly available to all

Stage 2: Mechanism Compilation

- Compounds and processes that need to be represented in air quality models, together with their linkages through radical and stable intermediates, are determined and represented in computer-readable formats
- Ideally this description should be as complete and as detailed as possible
- MCM, GECKO, and SAPRC may provide examples of starting points for reference mechanisms
- Should reveal gaps where our experimental and theoretical knowledge is insufficient

Stage 3: Mechanism Evaluation

- Protocols on how to compare the predictions of the mechanism against experimental data
- Evaluation at all the steps in mechanism development, both for subsets of the mechanism for individual species and for the entire integrated mechanism.
- Evaluation data needed for a wide range of environmental conditions,
  - smog chamber experiments
  - laboratory/field investigations

Stage 4: Mechanism Reduction

- Systematic condensation of a detailed, integrated mechanism down to computational constraints of the air quality models.
- Research studies may be best served by moderately detailed mechanisms.
- Regulatory modeling may require more reduced chemical mechanisms so that many alternative scenarios may be examined.
- Fundamental predictive capability of the mechanism and the accuracy of model predictions should be preserved during condensation.

UCD/CIT CTM 3D predictions for High O_3 events (US)

City and Simulation date for 3D predictions of High O_3 events

City/Area	Dates Simulated
North East (NYC and Philadelphia), US	Aug. 29 – Sep. 01, 2010
San Joaquin Valley, CA	Aug. 24 – Aug. 27, 2010
South Coast Air Basin, CA	Sep. 23 – Sep. 26, 2010
Baltimore, MD	Aug. 8 – Aug. 11, 2010
Houston, TX	Oct. 4 – Oct. 8, 2010
Atlanta, GA	Mar. 30 – Apr. 2, 2010

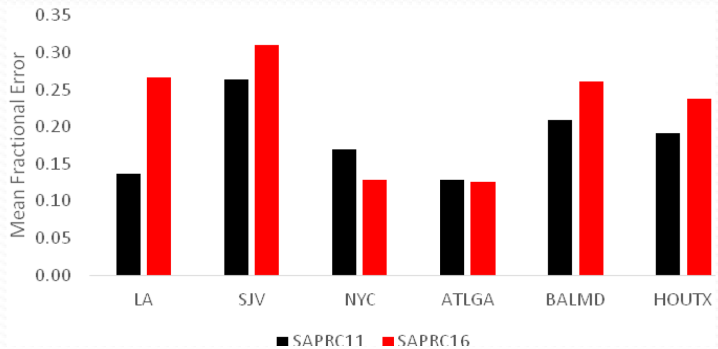
Predicted values compared to measured 1hr O3 concentration:

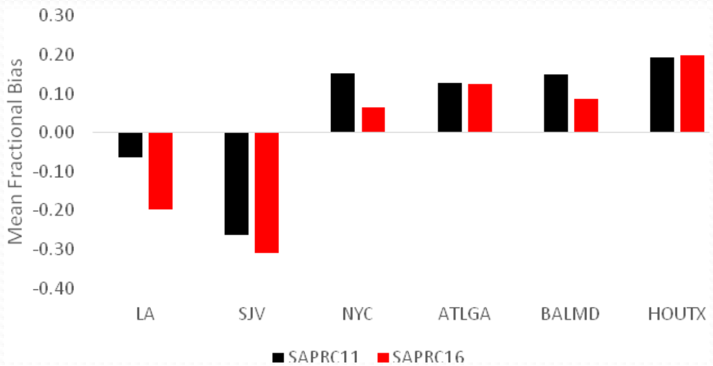
Mean Fractional Bias:

$$\frac{2}{N}\sum_{i=1}^{N}\frac{(Pred_{x,t}^{i}-Obs_{x,t}^{i})}{(Pred_{x,t}^{i}+Obs_{x,t}^{i})} \quad \text{Eq. 1.1}$$

Mean Fractional Error:

$$\frac{2}{N}\sum_{i=1}^{N}\frac{|Pred_{x,t}^{i}-Obs_{x,t}^{i}|}{(Pred_{x,t}^{i}+Obs_{x,t}^{i})} \quad \text{Eq. 1.2}$$

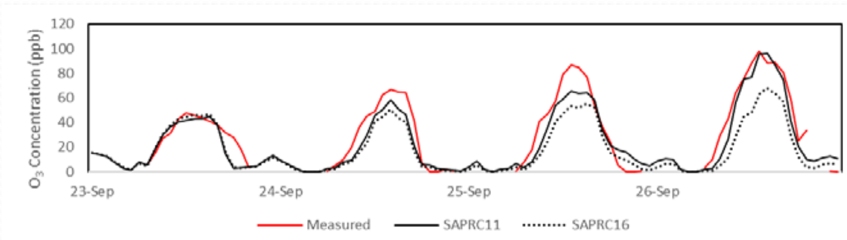




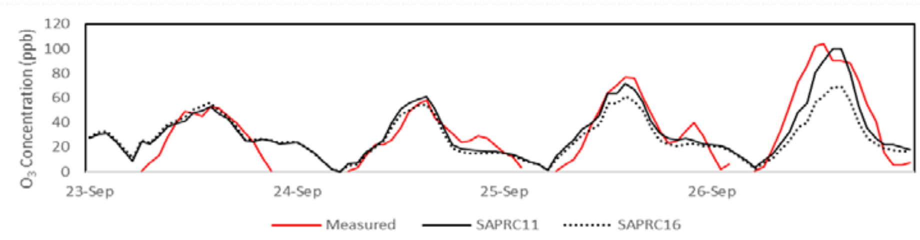
Mean Fractional Error for SAPRC11 and SAPRC16 vs measured 1-hour O3 (ppb) concentrations

UCD/CIT CTM 3D analysis predictions for High O_3 events (Los Angeles)

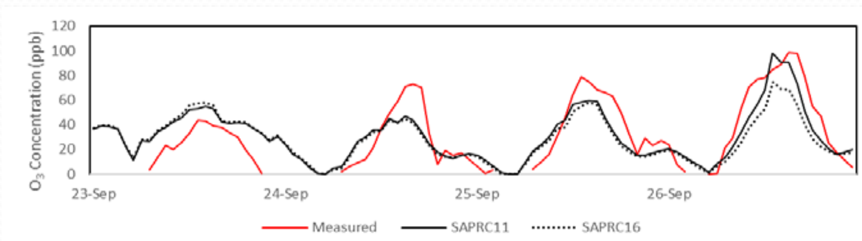
Site A. North Main St. / Downtown LA



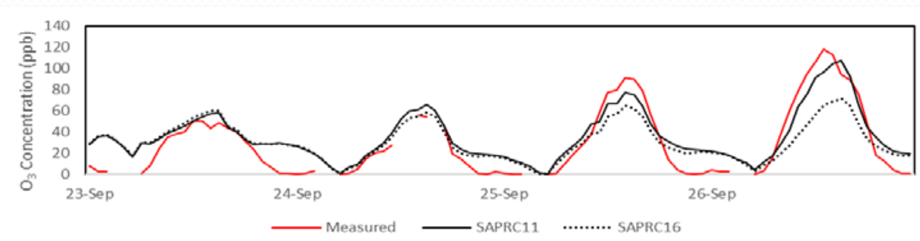
Site B. Long Beach



Site C. West Anaheim

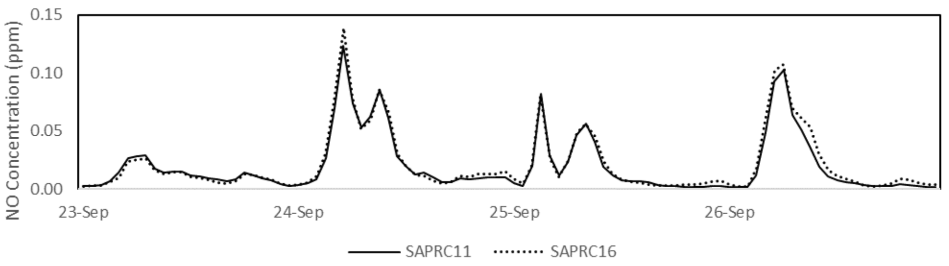


Site D. La Habra

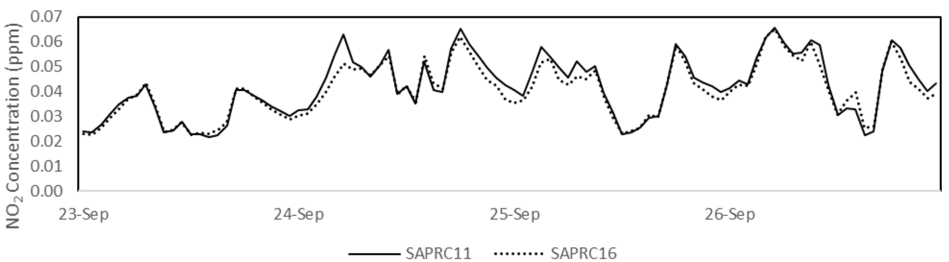


Time series of 1-hr Ozone prediction (SAPRC11 black, SAPRC16 dashed) against measurements (red) for all four sites in SOCAB.

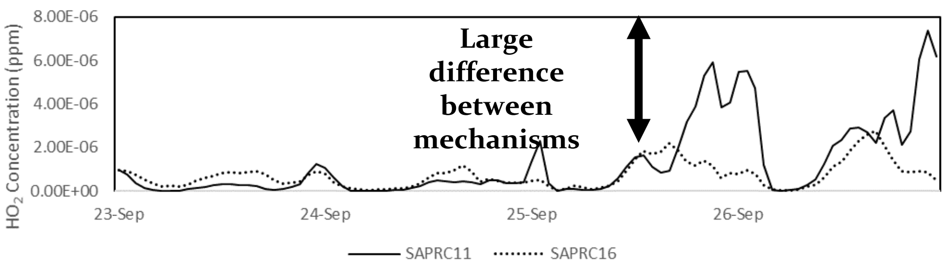
UCD/CIT CTM 3D analysis predictions for High O_3 events (LA North Main site)



Predicted NO Concentration
Similar between SAPRC11 and SAPRC16



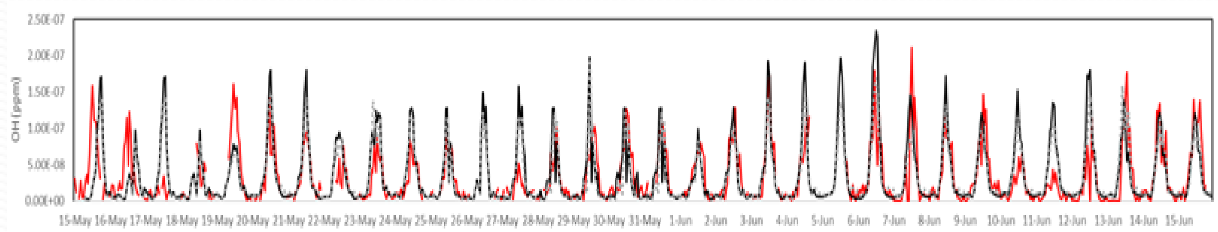
Predicted NO_2 Concentration
Similar between SAPRC11 and SAPRC16



Predicted HO_2 Concentration
SAPRC16 very low simulation of HO2 radical concentration. *Need to quantify model predictions with measurements*

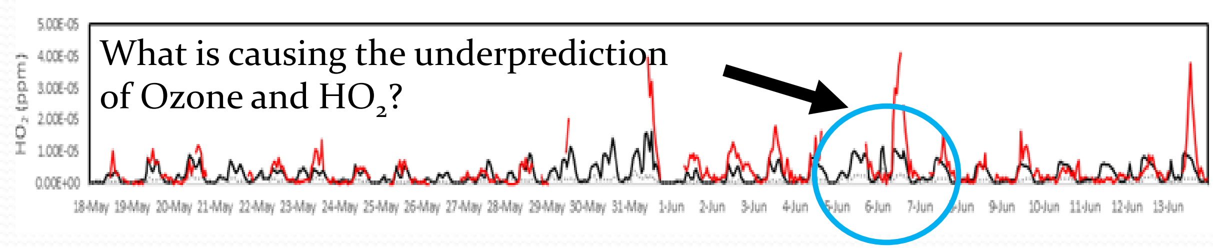
UCD/CIT CTM 3D analysis predictions for CalNex Field Campaign

OH	MFB	MFE
SAPRC11	0.0267	0.591
SAPRC16	-0.005	0.601



Time series of average 1-hr OH prediction (SAPRC11 black, SAPRC16 dashed) against measurements (red) at CalNex

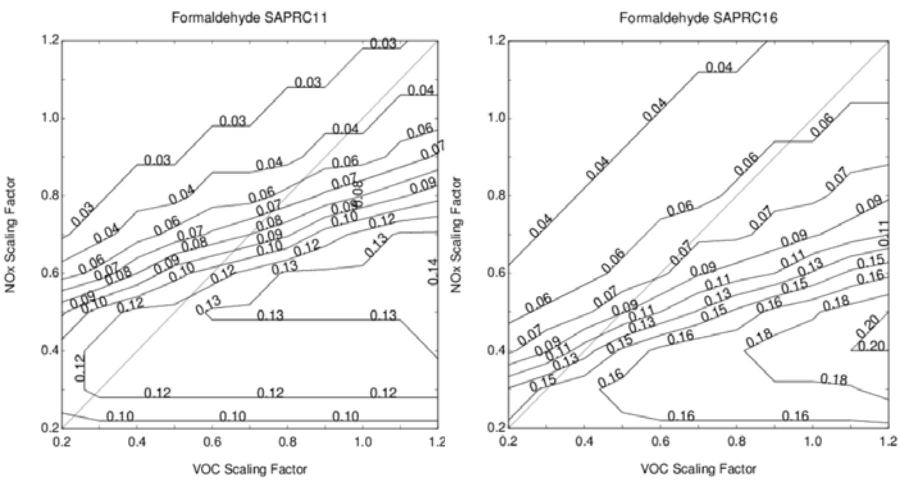
HO_2	MFB	MFE
SAPRC11	-0.261	0.723
SAPRC16	-0.893	1.129

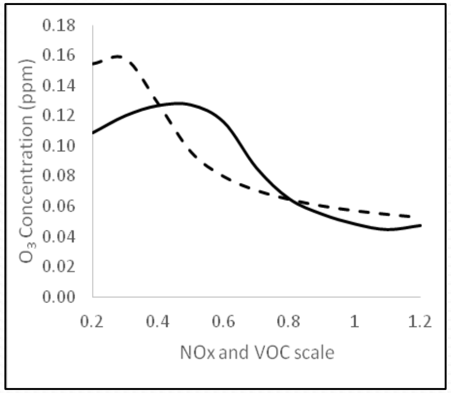


Time series of average 1-hr HO2 prediction(SAPRC11 black, SAPRC16 dashed) against measurements (red) at CalNex

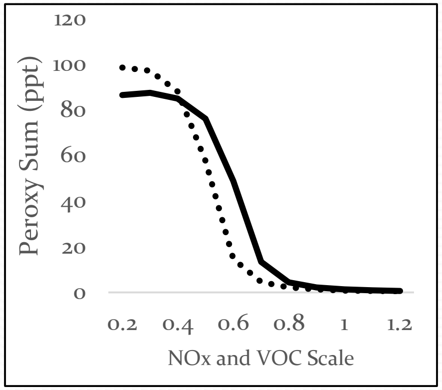
Box Model analysis for Formaldehyde (HCHO)

Initial concentrations [HCHO] = 20 ppb and [NOx] = 80 ppb with scaling factor 0.2 – 1.2





O_3 concentrations (ppm) along the "equal scaling" transect (SAPRC11 – black, SAPRC16 –dashed line)



Sum of peroxy species concentrations (ppt) (SAPRC11 – black, SAPRC16 –dashed line)

- Ozone formation predicted from SAPRC16 peaks at lower initial condition NOx concentrations and then quenched
- SAPRC16 peroxy-radical concentrations also peak at lower NOx concentrations in comparison to the SAPRC11 peroxy-radical concentrations
- This trend is similar for other species : acetaldehyde, ethane, ethene and ALK3

Conclusions:

- Gas phase is not fully understood yet (not done!). So, please keep on working.
- Should we coalesce around one detailed mechanism and, if yes, which one?
- Do we need a more streamlined process of feeding new information into the detailed mechanism(s)?
- SAPRC16 needs a bit more work before it can be used in regulatory applications.
- We really appreciate community help/input on taking atmospheric chemistry form the lab to regulators!

Thank you and any questions?

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