

The Future of Atmospheric Chemical Mechanism Development: A Training and A Panel Discussion of Possible Forward Paths

Instructions

This document answers the questions posed by attendees at “The Future of Atmospheric Chemical Mechanism Development Training and Panel Discussion.” In many questions there is discussion amongst the panelists. The ACM Panelists now invite you to join in the discussion, contribute your ideas and follow up questions. A version of this document is permanently available on the UC Davis Air Quality Research Center ACM Conference Website here. The document below is available for you to comment on yourself.

1. When placing a comment, please list it as follows:
 - What is the weather today?
 - Joe Johnson: It’s raining Bend, Oregon!
 - Sally Smith: @Joe Johnson - I’m sorry to hear that. It’s sunny in Pasadena, California!
 - Chris Charleston: @Joe Johnson - I am too! The forecast in Houston, Texas says sun for the next four days.
2. After placing a comment, please add your name and email address to the [Commenter list](#) so that participants can reach out if they would like to follow up with you further.
3. You can reach out to any of the [Panelists](#) if you would like to follow up with them directly.

If you have not yet watched the training, you should do so before providing comment.

[Watch the training on demand >>](#)

If you have not yet watched the panel discussion, you should do so before providing comment.

[Watch the panel discussion on demand >>](#)

Topics

MCM: [pg.7](#)

SAPRC: [pg.10](#)

RACM2/GACM: [pg.11](#)

CB: [pg.14](#)

EPA-OAQPS: Discussed in Panel

CARB: Discussed in Panel

General Audience Questions & Panelist Answers

- **How developed mechanisms using machine learning can be used in CTMs?** - Anonymous
 - [Carter](#): My understanding is that the machine can learn how to predict what a detailed mechanism would predict, based on analyzing data provided from model simulations using the mechanism.
 - [Rickard](#): I am hoping that new ML techniques can be applied in the systematic reduction of auto generated “explicit” mechanisms so they can be used in CTMs. Some recent interesting examples of how ML techniques have been applied to look at model bias using observations (Atmos. Chem. Phys., 20, 8063–8082, 2020), and in the solving of the atmospheric chemistry in

a CTM (does emulating the numerically stiff differential equations speed up the model? - Geosci. Model Dev., 12, 1209–1225, 2019)

- **What is the degree of sensitivity to temperature change in current mechanisms?** - Arash Yeganeh
 - Carter: Probably the effect of temperature on emissions is more important in practice than effects on reaction rates. Note that temperature change due to climate change is small compared to normal temperature variability that models already need to handle. Modern mechanisms, explicitly the more explicit ones, should have the most important temperature dependent parameters in them, though some lumped mechanisms may not represent how temperature affects product yields.
 - Yarwood: Representing temperature and pressure effects should consider some branching ratios (e.g., organic nitrate yields) as well as rate constants.
 - Rickard: Again, on this point, T & p dependencies of photolysis cross-sections and quantum yields also need to be adequately represented in models.
- **I wonder if the panelists could comment on the utility of multiple evaluations for chemical kinetics? It seems like the choice that modelers take between IUPAC or JPL (or whatever) leads to a source of error in the model output. Is it useful to have two evaluations? Why not three or five?** - Alex Archibald
 - Yarwood: Panel evaluations of kinetic and photolytic data are highly valuable to atmospheric modeling. Maintaining several evaluations is preferable from my perspective.
- **Should we be taking the NOAA weather modelling approach and evaluating many models to create a central trend with bands of uncertainty?** - Amy Heinder
 - Yarwood: There is work that investigates utility of CTM ensembles, for example “Model evaluation and ensemble modelling of surface-level ozone in Europe and North America in the context of AQMEII” <https://www.sciencedirect.com/science/article/abs/pii/S1352231012000064>
- **I think it is much easier to test sensitivity for say o3 or PM to kinetic/branching ratios in an existing mechanism. Much harder to test for completeness. What is the strategy for this?** - Paul Wennberg.
 - Carter: comparing mechanisms using different assumptions or approaches about uncertain mechanisms can provide some information about that, but this is difficult in practice, and may not deal with the “group think” issue.
 - Yarwood: Discrepancies between mechanism predictions and detailed ambient measurements could point to gaps in the mechanism formulation. Understanding the level of uncertainty in existing mechanisms will be helpful for assessing when such discrepancies need to be investigated.
 - Automatic generation of chemical mechanisms allows us to evaluate the sensitivities of the mechanism construction protocol(s), which should point to priority areas of where the measurements/theory are most critically needed.
- **Many of the speakers mentioned performance metrics. Does there exist a consensus on the most important and useful quantities to get 'right' beyond absolute concentrations (e.g. chemical ratios, production efficiencies, etc.)? I assume this hypothetical list would be informed by the importance of particular pathways but also by the existence of reliable measurements to evaluate performance. Of course this is useful to compare these widely used mechanisms to**

each other, but also for us users who would like to add some new particular chemistry and check to make sure we haven't messed up the most important things. - Ben Murphy

○

- **Is it possible miscategorized or missing emissions are more important than chemistry?** - Arash Yeganeh
 - Carter: I would think that errors in emissions could be more important than errors in the chemistry. It doesn't matter if you get the chemistry right if you don't know what is there.
- **What is the role of the general community in developing these mechanisms? Should mechanisms facilitate user modification (e.g. split out precursors, add products) or should mechanisms be viewed as a complete set of reactions that require a "top-down" protocol for modification?** - Havala Pye
 - Carter: Certainly mechanism developers should provide the files for their mechanisms in such a way that others can modify them for their research, as done with MCM. But the results would be a different mechanism. Information on details of how the mechanism was developed and the assumptions used should be available for the community to comment on. Mechanism generation systems should be available online and document their estimation methods or assignments used so users use it to derive mechanisms for compounds of interest to them and provide feedback if the system gives predictions they think are incorrect.
- **Bill Stockwell's presentation mentioned about creating a more diverse community to contribute to better mechanism and model development. Can anyone from the panel comment on how this goal can be accomplished in the current scientific community?** - Emily Saunders
 - Stockwell: More opportunities for young scientists in this area need to be supported. Some preference should be given to the young scientists needed to create a diverse community. Older scientists need to mentor a broader range of young scientists too.
 - Thanks to William Stockwell for highlighting this important issue facing science and society.
- **ECMWF have been doing ensemble forecasts because of the inherent uncertainty of models for the last decade or so** - Alex Archibald
 - *(The ensemble approach was discussed during the live meeting)*
 - Carter: Ensemble methods may be appropriate for meteorological models because of their large sensitivities to seemingly random factors and how they are dealt with in the model. But using ensembles of chemical mechanisms will not work as well because (1) there are not that many different state-of-the-science mechanisms available, and often the same or very similar assumptions are made about important uncertainties in mechanism details. A better approach is to do sensitivity analysis with different assumptions about uncertain parameters. Considerations involving such sensitivity analyses were discussed during the meeting.
 - Yarwood: Ensembles can be useful and I hope to see more work in this direction with CTMs. For example, Dunker et al., (<https://pubs.acs.org/doi/abs/10.1021/acs.est.9b07543>) use an ensemble of mechanisms to quantify how uncertainty in one mechanism (CB6r4) influences uncertainty in CTM predictions and compare it to other sources of uncertainty. Also, "Model evaluation and ensemble modelling of surface-level ozone in Europe and North America in the context of AQMEII" <https://www.sciencedirect.com/science/article/abs/pii/S1352231012000064>

- **Is it possible to develop a single efficient mechanism to account for the important chemistry across the varied environments/chemical regimes that are important for national/hemispheric/global modeling?**
 - **Do we have necessary lab and field data to test and QA mechanisms for these various environments?**
 - Carter: We do not, but we may have enough information to come up with estimates needed to provide a mechanism that is better than what we are using now.
 - Rickard: I agree with Bill here. An all encompassing chemical mechanism that can be used for ozone and SOA prediction is a long way off, if possible at all. However, the development of a hierarchical range of (adaptive) bespoke mechanisms is a near field objective that is possible. Machine Learning may also play an important role here in the future.
 - **Do we think these mechanisms are reliable for predicting chemistry out to a future year with potentially different chemistry and meteorological conditions? Does COVID provide a natural experiment with which to test the fidelity of these mechanisms in a lower NOx environment?**
 - Carter: I don't think the chemical composition or temperature range in the foreseeable future will be so different from current conditions to make detailed mechanisms that are considered appropriate for today to not work in the future. This may be more of a problem with highly condensed mechanisms where lumped reactions, and their effects on temperature, are based on assumptions about speciation of emissions. The need for basic kinetic and mechanistic research is the same for better mechanisms for the future as it is for better mechanisms for today.
 - Yarwood: In my view, COVID is likely to teach us more about the quality of our emission inventories than our chemical mechanisms.
 - Rickard: If we really wanted to use the "COVID shutdown experiment" to evaluate our mechanisms, then we need/needed the right coverage of long-term observations, especially VOCs - which brings us to the point of "are we really measuring the important VOCs in the field?". For example, in London, only 13 of the top 20 observed VOCs are routinely measured (<https://doi.org/10.1098/rsta.2019.0328>). Need speciated measurements of what is actually important, including IVOCs. Sources of SOA are also not well understood (and it is not clear COVID shutdown had that much effect on PM concentrations anyway...).
- **How should model improvement resources be allocated between chemistry updates versus other model processes or inputs? How do uncertainties in chemical mechanisms compare to other uncertainties in model parameters and inputs (i.e. emissions and meteorology)?**
 - Carter: Uncertainties in emissions and meteorology will affect model predictions much more than uncertainties in the mechanism. But this may not necessarily be the case when it comes to assessing control strategies if effects are examined in a relative sense. In any case, reducing uncertainties in mechanisms is still needed to increase confidence in model predictions of relative changes.
- **What should mechanism developers do when mechanisms with a reaction scheme that is indicted by accepted data and theories gives predictions that are inconsistent with what appears to be well characterized data, but when a different scheme fits the data well under different conditions?**

- Carter: The priority should be predictive capability for mechanisms to be used in regulatory models, but the developer needs to make the model users and the scientific community aware of the problem and encourage research to resolve the issue. Those using the mechanism to analyze their laboratory data or their mechanistic should be aware of the discrepancy and consider what implications their new data may have on the issue.
 - Rickard: These detailed master chemical mechanisms can be seen as representing our “state of the science” understanding of atmospheric chemistry, and provides an important link between the laboratory and the modellers. However, it should be made clear where our current understanding is lacking or uncertain, something that the modellers and the laboratory scientists need to take into account.
- **Is it acceptable to use a mechanism for regulatory applications that is consistent with accepted science but known to give incorrect predictions of results of reasonably well characterized experiments?**
 - Carter: See response above.
 - **Do you think that having additional chemical detail in the mechanism, even if some of the estimates behind that detail are highly uncertain, will tend to reduce or increase uncertainties in predictions of species included in less detailed mechanisms?**
 - Carter: Even condensed mechanisms must be derived based on an assessment of the actual chemistry that is occurring, so it’s hard to see how ignoring the detail would give better results. Of course, the detail may not be needed and could be omitted from the final mechanism if it is shown not to be relevant or necessary for the predictions of interest. But if you don’t know the detail, how will you know it is not needed, or that your assumed manually-derived mechanism is consistent with available data and theories?
 - **Do you believe it is satisfactory for models to continue to use parameterized SOA mechanisms whose only inputs from the gas-phase are the amounts the model species that have reacted?**
 - Carter: I don’t think regulatory modelers have much choice now, given the fact that current parameterized SOA models being used are at least traceable to chamber data, and SOA predictions of detailed mechanisms such as MCM or Gecko have large uncertainties and not shown to be consistent with available data. However, the applicability of available SOA chamber data to ambient conditions is highly uncertain, nor are the data sufficient to cover the wide variety of conditions. Ultimately we will need SOA models based more on the actual chemistry, or at least based closer on chemical considerations that extrapolations from chamber to ambient conditions may be less uncertain.
 - Yarwood: Compact SOA schemes for 3D models already use more information than the amount of precursor reacted: they consider NO/HO₂ influence on SOA-yield as well as photolytic SOA destruction, for example. Improving performance of SOA schemes in 3D models will depend on improving both emission estimates and chemistry with coordinated and balanced effort.
 - Rickard: Taking a step further back, I don’t think we adequately know the actual sources of SOA (certainly under urban conditions) at a fundamental level yet...
 - **Do you believe it is possible to get more reliable SOA predictions if the SOA model used yields of various product model species as input, rather than amounts of primary emissions that react, if there are chamber data or other means to obtain volatility and SOA yield parameters for these species?**

- Carter: I would think this would be the next step in moving from parameterized SOA models linked to primary emissions to SOA models based on considerations of chemistry, and how chemical conditions affect SOA yields. Presently the parameterized models have to assume that SOA yields depend only how much the precursor has reacted, which we know is not the case for many types compounds.
- **Do operational mechanisms need to combine oxidant with SOA chemistry in a single mechanism? What considerations are important?**
 - Simon: For regulatory applications I believe it is important to have mechanisms that simulate both oxidant and SOA chemistry. For instance if an agency is evaluating the overall air quality impacts of a regulation that impacts NO_x emissions, the effects of that regulation will be evaluated both on PM (SOA + SIA) and ozone levels and potentially on toxic pollutants as well whose phase/fate/lifetime could be impacted both by oxidant and SOA chemistry. Furthermore, past studies have shown that oxidant levels have a substantial impact on SOA formation (e.g. Carlton et al. *Environ. Sci. Technol.* 2010, 44, 9, 3376–3380 <https://doi.org/10.1021/es903506b> and others) so I am not sure that the two processes can be credibly separated.
 - Yarwood: Separating the oxidant and SOA schemes is a type of operator splitting - and we use operator splitting throughout 3D models. Operator splitting is effective unless there is strong 2-way coupling between processes that operates at timescale comparable to the process splitting.
- **Do we have adequate methods for mechanism condensation?**
 - Carter: We have adequate methods for lower levels of condensation by combining reactions and removing steady-state intermediates, but this may not be enough to get the smaller mechanisms modelers are used to. Lumping products greatly condenses the mechanism and is easy to do, though it is not as easy to determine which lumpings are best for any application. Methods are not adequate to determine the optimum condensation for any given application.
 - Yarwood: Developing improved condensation methods should be a priority so that condensed mechanisms can benefit from advances in computerized mechanism generation.
 - Rickard: I am also hoping that members of the science, engineering and mathematics communities can help us in the effort to provide novel solutions to condensation, and ML could have an important role to play here.
- **Can we estimate uncertainties in mechanism parameters (i.e., rate constants and stoichiometric coefficients) that can feed into global uncertainty analysis of mechanisms and models?**
 - Stockwell: This has been done, but it would be great to do this for updated mechanisms. Here are three references that may provide some guidance:
 - Russell, A., J.B. Milford, M.S. Bergin, S. McBride, L. McNair, Y. Yang, W.R. Stockwell and B. Croes, Urban Ozone Control and Atmospheric Reactivity of Organic Gases, *Science*, 269, 491-495, 1995.
 - Yang Y-J., W.R. Stockwell and J.B. Milford, Effect of Chemical Product Yield Uncertainties on Reactivities of VOCs and Emissions from Reformulated Gasolines and Methanol Fuels, *Environ. Sci. Technol.*, 30, 1392-1397, 1996.
 - Gao, D., W.R. Stockwell and J.B. Milford, Global Uncertainty Analysis of a Regional Scale Gas-Phase Chemical Mechanism, *J. Geophys. Res.*, 101, 9107-9119, 1996.
 - Carter: You need to be careful to consider which parameters are independent and which are not when assessing effects of parameter uncertainties. But this doesn't deal with effects of "unknown unknowns", which can't really be systematically assessed.
 - Yarwood: Coming up with uncertainty estimates, even rough estimates, is useful and possible.

- **Evaluation of model and mechanism performance – what are the appropriate metrics to use? (ozone is not good enough anymore!!). How can ML be used to aid in testing and evaluation?**
 - Carter: The appropriate metrics depend on what you are using the model for but, more importantly, on the data available and their associated analytical and characterization uncertainties. Evaluation data need to have less uncertainty than what is being evaluated.
 - Carter: It's not clear to me how machine learning could be useful to evaluate assumptions about the chemistry. What will the machine be learning from? I can see how ML may be helpful for SAR developments in cases where estimates are based on large data sets, but actually there are not that many SAR cases where this may be possible because input data are not all that extensive. It's potential utility as a reduction tool has no relevance for evaluating chemical accuracy.
- **New producers on satellite data (from Andrew Rickard) - satellite measurements are now available for isoprene and HCHO - useful for chemical mechanism evaluation? (Satellite isoprene retrievals constrain emissions and atmospheric oxidation)**
<https://doi.org/10.1038/s41586-020-2664-3>
 - Carter: I would think their main utility would be evaluating emissions estimates. HCHO data may test secondary chemistry, but the HCHO precursor and primary HCHO emissions are too uncertain to test the chemistry used in mechanisms.
 - Simon: Another innovative way to use satellite data was demonstrated by Laughner and Cohen (Science 08 Nov 2019: Vol. 366, Issue 6466, pp. 723-727 DOI: 10.1126/science.aax6832) who used spatial gradients in satellite NO₂ near cities to estimate NO₂ atmospheric lifetime. Perhaps box models could be used to see whether the satellite inferred NO₂ lifetimes match expected lifetimes given various chemical mechanism assumptions. This type of analysis would be most useful in areas with extensive ground measurements of NO₂ and speciated VOCs to constrain concentrations and/or emissions in a box model.
 - Yarwood: Satellite data are certainly useful but don't yet tightly constrain chemical mechanisms. Surely this situation will improve.

MCM - Andrew Rickard

- **Is autoxidation (RO₂ H-shift) part of the MCM protocol? Didn't see it on the diagram.**
 - RO₂ H-shift chemistry is included in MCMv3.3.1 for certain isoprene RO₂ species (see Atmos. Chem. Phys., 15, 11433–11459, 2015 and Atmos. Chem. Phys., 19, 7691–7717, 2019 for discussion)
 - In the latest SAR paper on RO₂ chemistry (Atmos. Chem. Phys., 19, 7691–7717, 2019), a number of RO₂ H-shift isomerisation reactions are discussed and defined as important under certain conditions. However, it is noted that “information is lacking and further studies would be beneficial for unimolecular isomerization reactions, further systematic studies are required for the rates of 1;*n*-H-shift reactions from C-H and O-H bonds in different chemical environments, and for the effect of ring size and substituents on ring-closure reactions, to build upon recently reported data for these reaction classes”.
 - This important area is subject of ongoing work, with improved instrumentation now available to give us new information on branching ratio and kinetics
 - Some studies are already being carried out with MCM chemistry as a base mechanism (including presentations at this conference (Weber et al.) - MCM as the backbone (see also comment below)

- Autoxidation has been added to the CRI-HOM mechanism, an add-on to CRI v2.2 (*EVENTMOBI response*)
- **Would there be plans to extend to the particle phase?** - Shantanu Jathar
 - MCM and MCM/GECKO-A are primarily gas-phase mechanisms designed to look at photochemical ozone formation
 - However, they are sufficiently detailed enough to investigate SOA formation when incorporate into an appropriate aerosol model
 - Updates and developments to the MCM isoprene scheme in MCMv3.3.1 were designed with improved representation of channels important for SOA formation (see *Atmos. Chem. Phys.*, 15, 11433–11459, 2015)
 - Therefore, the MCM is useful basis to start with respect to gas-phase precursors for SOA formation, and has been used in many studies of aerosol formation and composition
 - New updates to the mechanism protocols, especially RO₂ chemistry, will enviably improve the formation for aerosol precursors.
 - Autogeneration of mechanisms using the GECKO-A system will enable us to evaluate the sensitivity of mechanism “trimming” of branching ratios, commonly applied in the reduction of mechanisms, with respect to SOA formation (fragmentation vs. carbon chain retention/oxidation)
- **Would there be plans to extend this larger framework mechanism (i.e., MCM/GECKO) to the particle phase?**- Shantanu Jathar
 - The GECKO-A platform can partition low volatile species to the condensed phase and has been used to look at aerosol formation processes.
 - With incorporating the new updated protocols into MCM/GECKO-A we can certainly look into more detail on the evaluation and sensitivity to SOA formation (see comments above).
- **Could you explain again differences in number of species that you mentioned on two different slides 6900 vs 201, and number of reactions 17500 vs 605, was the latter for isoprene mechanism only?** - Beata Czader
 - Indeed, the latter was for the isoprene chemistry update
 - Slide 6 are for complete MCM versions, Slide 9 for the isoprene chemistry only
- **Has the parametrization of photolysis rates been changed in the new MCM/GECKO framework?** - Roberto Sommariva
 - Yes, the databases of cross-sections and quantum yields have been updated, with some SAR estimations looked at, based on the sparse observational datasets available, especially for QYs.
 - The new updates have been coded into TUV (<https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model>) for photolysis rate calculations under a range of conditions.
 - Sasha Madronich will discuss aspects of the CS updates in one of the Fundamental of Oxidation Chemistry sessions
- **How close are you to coming up for a reduction protocol to get Gecko output into MCM? Are you close enough to tell us what will it look like?**
 - Preliminary testing has been carried out
 - Ozone formation is still the primary criterion if we are to reduce the standard version of MCM/GECKO-A to the size of the MCM (c.f. 10,000 reactions):
 - Reduction by elimination (removal of non-volatile/water soluble species)

- Reduction by elimination (removal of lower pathways (< 5% (sensitivity)))
 - Reductions by substitution (lumping of structural isomers)
 - Reduction of RO₂ classes
 - Evaluations have been carried out with target metrics for MCM/GECKO-A (carbon/nitrogen budgets, SOA formation, reactivity, Ox production/tendencies, ...)
 - However, we are reaching a glass ceiling with these reductions, with further reductions leading to a loss of information
 - Need more help from other science, engineering and mathematics communities, as discussed
 - This is where Machine Learning techniques could potentially help out enormously
 - Can currently provide(large) mechanisms for a subset of core species...
- **Are you familiar with the work done on the Island of Hawaii during the major eruption a few years ago? They found that volcanic ash and gasses chemically reacted with the atmosphere and that reaction was affected by the meteorology in a very profound way. Will your work look into weather interaction, e.g., mixing?** - Amy Heidner
 - The MCM is a detailed gas-phase chemistry mechanism, which when incorporate into an appropriate atmospheric model that also takes into account meteorology and transport, as well as aerosol phase, aqueous phase and heterogenous chemistry, can provide a powerful tool with which to investigate the effects of volcanic eruptions on air quality and climate.
- **It have been known that the decay of several aromatic hydrocarbons are underpredicted in MCM. Thus, OH radical is added to mechanisms. Do you have any plan to improve aromatic HC oxidation mechanisms.** - Myoseon Jang
 - Rickard: There are still several issues with aromatic chemistry in all chemical mechanisms, notably the under prediction of (early) OH levels coupled to a general over prediction of ozone profiles in chamber experiments (as also discussed by Bill Carter and Greg Yarwood below).
 - Rickard: There is an ongoing community effort look further at the fundamental gas-phase chemistry of aromatics, both in the laboratory (new instrumentation) and theoretically, as well as new chamber experiments being carried out so that chamber wall effects are taken into account more effectively.
 - Carter: underrediction of OH levels in aromatic-NO_x chamber experiments is a consistent problem with SAPRC mechanisms that has not improved with the latest updates. I think it is also a problem with RADM/RACM and CB mechanisms as well, which have similar representations of aromatic chemistry.
 - Yarwood: We seem to lack complete mechanistic explanations for high OH production from aromatics.
- **Could you please say something about HOM modeling? Is autooxidation the only pathway to lead to HOMs?** - Mohammed Jaoui
 - There is active work being carried out looking at incorporating HOMs chemistry into the MCM and the CRI mechanisms (e.g see talk by Weber et al.,) – see also comments above
 - It is clear that HOMs chemistry is important for a range of atmospherically relevant emissions (i.e. monoterpenes and aromatics)
 - HOMs formation can occur rapidly via accretion reactions to form large dimer species though RO₂ + R'O₂ = ROOR' reactions.
 - Again, this is discussed, along with autooxidation in the latest RO₂ SAR paper (Atmos. Chem. Phys., 19, 7691–7717, 2019).

- More kinetic and mechanistic information is needed before a reliable SAR can be developed, but it is clear that there is much research being carried out in this area, with new instrumentation providing detailed data.
- **Do you believe that MCM, either current or updated, can give reliable SOA predictions?**
 - See discussions above...
 - MCM and MCM/GECKO-A are primarily gas-phase mechanisms designed to look at photochemical ozone formation
 - However, they are sufficiently detailed enough to investigate SOA formation in an appropriate model
 - The MCM is useful basis to start with respect to gas-phase precursors for SOA formation, and has been used in many studies on gas-phase and aerosol composition
 - Updates and developments to the MCM isoprene scheme in MCMv3.3.1 were designed with improved representation of channels important for SOA formation
 - New updates to the mechanism protocols, especially RO₂ chemistry, will enviably improve the formation for aerosol precursors.
 - With incorporating the new updated protocols into MCM/GECKO-A we can certainly look into more detail of the evaluation and sensitivity to SOA formation
- **What is the priority for improving SOA predictions in the MCM update? Do you expect the SOA predictions to be much more reliable after MCM is updated?**
 - Again, see previous discussions
 - Addition of HOMs formation chemistry is a priority
 - Autogeneration will enable us to look at the sensitivity of the protocol for ozone formation vs. SOA formation (see discussions above). Ultimately, we will be able to develop bespoke mechanisms, depending on applications, with varying complexity, as appropriate.
- **Do you expect the SOA predictions to be much more reliable after MCM is updated?**
 - MCM/GECKO-A provides a good basis with which to start to look at the precursors to SOA formation and chemistry
 - Updates to new protocol should improve the prediction of these gas-phase precursors
 - Autogeneration will help with sensitivity analysis and the assessment of areas of uncertainty
- **Andrew, what type of observations are needed for evaluating the machine learning techniques?**
- Brian McDonald
 - Rickard: This point comes back to what metrics do we need to evaluate and constrain the models? Having discussed this interesting point with my York colleague Mat Evans, he suggests that a different question would be to ask “what if you could create a ML version of atmospheric chemistry from observations?”. You could then incorporate this observationally derived chemistry into a model. At the moment that would appear difficult but not impossible. Mat suggests that from an observational perspective, observations of species which have high degrees of node (chemical connectivity) within the atmospheric chemistry network ‘graph’ would be the most useful to constrain the chemistry scheme..

SAPRC - Bill Carter

- **Does it make sense to support an intermodel evaluation (i.e., SAPRC vs GECKO vs MCM vs others) to better quantify differences as well as uncertainties?** - Shantanu Jathar

- Definitely, and we are planning to do this as part of our EPA mechanism development program that we are in collaboration with NCAR and the Gecko developers.
- **What happened to SAPRC-16?**
 - *This was discussed during the meeting.*
 - SAPRC-16 is a preliminary version of SAPRC-18. The main difference is that SAPRC-18 has updates made to some estimates in the mechanism generation system, resulting in differences mainly for lumped model species representing products. The mistake with SAPRC-16 as used by Venecek et al (2016) was that the files and MechGen databases used to derive it were not archived before they were subsequently updated, so SAPRC-16 can't be regenerated. Therefore, it is no longer recommended for models.
- **Is SAPRC-18 now in its final form?**
 - *This was discussed during the meeting.*
 - SAPRC-18 has been "frozen" and the files and Mechgen databases it uses have been archived so it can be re-generated and its details examined. The plan is not to update it further, but needs for updates to the estimation methods may become apparent when the documentation is prepared. The decision on whether to apply the updates to this version or create a new version will depend on how many groups are using SAPRC-18 at the time.
- **What do you recommend be updated or modified first for the next version of your mechanisms?**
 - *This was discussed during the meeting.*
 - The first priority is documenting the estimation methods, and in some cases improving fits to chamber data, which may require some estimates and assignments, and therefore the mechanism, be updated. The next priority is developing more reduced versions of the mechanisms, which may be based on SAPRC-18 as it is or on an updated version.
- **As emissions are necessarily changing/have changed over the past decades and into the next, how will SAPRC adapt to changing emissions ratios (VOC/NOx) and the changing reactive mix of VOCs (e.g. "unusual" consumer products becoming more important at the indoor/outdoor continuum)**
 - I don't think the chemical composition or temperature range in the foreseeable future will be so different from current conditions to make detailed mechanisms that are considered appropriate for today to not work in the future. This may be more of a problem with highly condensed mechanisms where lumped reactions, and their effects on temperature, are based on assumptions about speciation of emissions. The need for basic kinetic and mechanistic research is the same for better mechanisms for the future as it is for better mechanisms for today.

RACM2/GACM - William Stockwell & Wendy Goliff & Rosa Fitzgerald

- **Now a day, the one of concerns is the impact of the chamber wall on model parameters. Do you think that the rate constant or the evaluation were biased due to the inheritance of the chamber artifacts?** - Myoseon Jang
 - Stockwell: Chamber artifacts have been a problem. However, aromatic schemes have become more and more based on laboratory measurements so there is less fitting (although there is some) involved in producing the mechanisms. Hopefully we will become less dependent on fitting while still using chamber and field data for evaluating mechanisms.
- **Regarding the uncertainty issue, doesn't the required complexity of the mechanism depend on the species or parameter that is being modeled. Simpler mechanisms have low uncertainties for**

some species (say NO_x), but more complex mechanisms might be required for other species (say OH). What do you think? - Christopher Cantrell

- Stockwell: I agree that the required complexity of a mechanism depends on what is being simulated and the purpose of the simulations. VOC-ozone reactivity requires a much more detailed mechanism for the VOC being evaluated than one for many general air quality modeling applications. SOA modeling seems to require more detailed mechanisms too.
- **How can machine learning based reactions be implemented into CTMs? Do not we need reactions and etc. for use in CTMs? How much help will we get from these methods?**
 - Stockwell: No. I believe it is important to explore new methods. Chemical modules in CTMs consist of many ordinary differential equations and a solver for numerical stiff systems. It should be possible to construct other methods. My hope is that it will become possible to use the available kinetic data base but with a minimum of making up reactions that are not known. This may help reduce noise in simulations.
 - Carter: I think Bill Stockwell is referring to machine learning as a way to derive efficient algorithms for implementing mechanisms into CTMs that will give the same (or close enough) answers as using differential equations derived from actual chemical mechanisms. Otherwise, what would the machine be learning from? Chamber data are insufficient to derive complete mechanisms without considering chemistry, and ambient data have too much uncertainty that is not related to chemistry.
 - Stockwell: That is close, but I don't believe that we really need to write detailed chemical mechanisms with millions of reactions. I do believe in using the full chemical database. In meteorology, models solve equations to simulate windflow, temperature, pressure changes, etc. During the last 40 years data assimilation methods are used to build "attractors" that nudge the simulations toward more accurate solutions. Although "nudging" has been superseded by more advanced techniques I suspect we can do something similar to construct chemical modules. The chemical module would consist of a core mechanism that would be "nudged" by parameterizations derived from AI, data mining and other advanced forms of information science and the extended chemical database.
- **How would RACM deal with situations like Beijing? i.e. extreme diurnal profiles of NO (very high in the morning, then O₃ transported in scavenges most of the NO (converting to NO₂) in the afternoon? This has significant effects on switching from RO₂ + NO to RO₂ + HO₂/ RO₂ isomerisations... - Andrew Rickard**
 - Stockwell: RACM1 and RACM2 has an extensive and rather explicit treatment of RO₂ + NO, RO₂ + HO₂, RO₂ + CH₃O₂, RO₂ + RCO₃ and RO₂ + NO₃ where RO₂ represents an RO₂ generated from each VOC included in the mechanism. We did sensitivity tests that indicated that given the concentrations of HO₂, CH₃O₂ and RCO₃ and NO₃ found these were important while the RO₂ + R'O₂ were not. RACM1 and RACM2 have been used extensively in China with some success.
 - Carter: These considerations are applicable to any urban area. I don't see how Beijing would be that different than cities in the U.S. or Europe in terms of the best type of mechanism to use.
 - Stockwell: I note that Bill Carter has adopted an approach similar to the RACM1 and RACM2 for his most recent version of SAPRC.

- **Is the motivation for having GACM vs RACM as separate to speed up the model by only having the most relevant species for the given conditions? Or, is it more about the challenging of spanning chemical regimes with condensed reactions for a given set of species?**
 - Stockwell: The original goal was to develop GACM for the U.S. EPA's global-hemispherical model to provide boundary to the CMAQ regional model running with RACM2. It was hoped that having two related mechanisms would make it easier to translate between the global and regional models. Now we are developing a separate chemical mechanism, RACM2-H (RACM2 with halogens) that may be used in CMAQ and it will be more detailed than RACM2.
- **I think the discussion on uncertainty in mechanisms is very interesting. I for one and interested in this type of work. But how large is the uncertainty from mechanisms versus the uncertainty in (i) transport (ii) numerics (iii) emissions? It seems to me that this is still an open question.**
 - Stockwell: On the uncertainty of emissions I completely agree. Although a lot of work has been done on emissions there is much to do. Chemistry is one area where almost we know what we don't know. I feel more confident with transport and numerics.
 - Carter: Uncertainty in transport, meteorology, and (maybe, but hopefully not) numerics is a major consideration when evaluating mechanisms using ambient data, and limits its utility for evaluating the chemistry almost as much as uncertainties in emissions, and may even have larger effects on model predictions in some cases.
 - Stockwell: In some past studies, measured chemical ratios have been compared with simulated ratios to help reduce the influence of transport and meteorology on the evaluations.
 - Stockwell: Numerics remains a concern. Eulerian modelers may make tradeoffs between speed and numerical accuracy. The transition between day and night places stress on numerical schemes and sometimes modelers settle for less accurate solutions for radicals (for example) to be sure the numerical solver does not fail.
- **I noticed the RO₂+NO reaction rate constant is 4.0e-12 in RACM2, which is much smaller than some literatures (9~10e-12). Could you please comment on this difference? - Zhaofeng Tan**
 - Stockwell: I will need to get back with you on that one.
- **You mention the importance of observations. How far we need to go in this direction (chamber and/or real world data)? Mainly for machine learning ... - Mohammed Jaoui**
 - Stockwell: Much field data is collected but far too little is analyzed. It would be great if more would be made publicly available and that agencies would fund more data analysis. There is always room for more chamber data but it needs to become more accessible to everyone, especially those who need to use it to evaluate chemical mechanisms.
- **In current mechanisms, how much focus is on interactions between different chemistries such as SOA, O₃, and inorganics?**
 - Stockwell: It's critical to have inorganic chemistry to model ozone so the air quality mechanisms include this. To simulate ozone many of the precursors for SOA are included in the gas-phase mechanisms. However, for SOA simulations it would be good to include higher molecular weight VOC.
- **Are your mechanisms designed for use in SOA predictions?**
 - Stockwell: I would not use the word designed, but RADM2 includes a range of aromatic compounds and treats alkanes by species that are grouped by reactivity but represent a range of molecular weights. We have used RACM2 to examine the production of SOA from

anthropogenic sources but given that measurements of SOA can not distinguish anthropogenic SOA from biogenic SOA we could not evaluate our results.

- **What do you recommend be updated or modified first for the next version of your mechanisms?**
 - *This was discussed during the presentation*
 - Stockwell: The next major goal is to complete adding halogen chemistry (chlorine, bromine and iodine) to create the RACM-2H mechanism. When that is completed we may consider a general updating and / or new approaches to the development of chemical modules that we mentioned today.
- **How can predictions using a mechanism for a compound that is derived by analogy from a simpler surrogate species have less uncertainty than those derived using a mechanism generation system, even if many of the estimates in that system are highly uncertain, and the mechanisms perform equally well in simulating the available data?**
 - Stockwell: It's not a question of differences between estimates from analogy or a mechanism generation system. Reactions estimated by both may well have the same degree of uncertainty. The question is how close an estimated reaction is to laboratory measurements. Mechanism generation systems may well allow a very large (too large?) a number of reactions to be generated that are far from the laboratory database.
 - Carter: At least the details provided by a mechanism generation systems can show how the final mechanism is related to the estimates, and can provide information on the extent to which the estimates behind the final mechanism disagree with available data.
 - Stockwell: This can be done manually too.

CB - Greg Yarwood

- **Do you anticipate new versions of CB will come out soon, or are in the pipeline?**
 - CB development history and plans is covered in my slides.
- **I am curious about the prediction of the decay of aromatic species. The reaction rate of each aromatic HC with OH radicals can be different. If lumping species are used, can we differentiate the different oxidation rate of aromatic species?** - Myoseon Jang
 - Lumping necessarily removes specificity. Some of the remaining uncertainties in aromatics chemistry probably need to be worked out with explicit mechanisms before insights can be transferred to condensed mechanisms.
- **Are there any satellite data comparisons of isoprene emissions vs the inventories yet over the states?** - Andrew Rickard
 - Current satellite data (e.g., for formaldehyde and isoprene) don't sufficiently constrain isoprene emission estimates to the level of accuracy that we need for atmospheric models.
- **Is there any appetite for including the uncertainty in model forecasts/simulations? For example, using the 10% uncertain as an error that is sampled randomly during the run. So rather than deterministic output we have a probabilistic output?**
 - Hopefully, providing information about uncertainty in model results will lead to more informed decision making.

- **If the uncertainty analysis were applied to look at OH rather than ozone, would a similar list of top-contributing reactions fall out, or are there others that would matter more?** - Kelvin Bates
 - Considering that OH has short lifetime compared to O₃, I would expect removal reactions to rank more highly for OH than they do for O₃.
- **Bill & Greg, have you seen this? Impact of uncertainties in inorganic chemical rate constants on tropospheric composition and ozone radiative forcing**
<https://acp.copernicus.org/articles/17/14333/2017/> - Andrew Rickard
 - Thanks for pointing out this work to everyone. Good to see others looking into effects of mechanism uncertainty.
- **Do you see a role for mechanism generation in developing or updating the CB mechanisms in the future?**
 - Certainly. Improved mechanism condensation methods are needed to take advantage of computer generated mechanisms. Ideally, new condensation methods will be able to condense from an explicit mechanism (i.e., composed of elementary reactions) to any type of condensed mechanism formulation.

Panelists

[Heather Simon, Office of Air Quality Planning & Standards, US EPA](#)

simon.heather@epa.gov

[Jeremy Avise, Branch Chief, Modeling and Meteorology Branch, California Air Resources Board](#)

jeremy.avise@arb.ca.gov

[Andrew Rickard, Associate Professor, National Centre for Atmospheric Science](#)

andrew.rickard@york.ac.uk

[Bill Carter, Research Chemist, UC Riverside](#)

william.carter@ucr.edu

[William Stockwell, Professor, University of Texas at El Paso](#)

william.r.stockwell@gmail.com

[Rosa Fitzgerald, Professor & UTEP Representative, NOAA](#)

rfitzgerald@utep.edu

[Wendy Goliff, Assistant Research Engineer, UC Riverside](#)

dr_weh@yahoo.com

[Greg Yarwood, Principal, Ramboll](#)

gyarwood@ramboll.com

[Rahul Zaveri, Senior Scientist, Atmospheric Sciences & Global Change Division, Pacific Northwest National Laboratory](#)

Rahul.Zaveri@pnnl.gov

[Ajith Kaduwela, Senior Scientist - California Air Resources Board/University of California at Davis](#)

ajith.kaduwela@arb.ca.gov

Commenters

First Name	Last Name	Organization	Email

