

Policy Summary

- U. S. Approach – models used to find best ways to meet standards. Accuracy is important because models are used to decide on controls, which are expensive
 - Focus on pollutants with health-based standards
 - Mechanisms are important to predictions of secondary pollutants
 - Mechanism verification (to extent possible) important because bad models can lead to bad policy choices
- European approach – pollutant reductions are negotiated politically
 - Focus on *reductions* not *standards* (?)
 - Models apparently does not play a central role in determining strategies
 - “Integrated assessment” modeling used for cost-benefit analysis – apparently to aid political process

U.S. Regulatory Modeling Issues

- U. S. had the choice between BACT “doing the best we can” and setting standards “we can do better” and chose the latter
- Both California and EPA are increasingly interested in need to represent different pollutants at once (“one atmosphere”) (“multi-pollutant framework”)
- New standards require reduced uncertainties, place increased demands on mechanisms
- Big focus in EPA is on PM – concern that this is taking resources away from O₃ model research. But O₃ still problem
 - Many areas of California do not meet O₃ standards Use of reactivity-based regulations highly mechanism dependent
 - Texas (not discussed) is still more concerned with meeting ozone standards. Unique, mechanism-related modeling issues

General Mechanism Issues

- Mechanisms function as archive, explanatory vehicle, and for communication as well as for prediction
- Ideally mechanisms can serve as link between laboratory studies and models (objective for many detailed mechanisms)
- Issue of compensating errors is important in model evaluation (e.g., bad emissions mask model errors; bad chamber effects model masks mechanism errors)
 - Dangerous to change model inputs based on model performance
- Evaluation is not “validation”. Cannot *validate* a model – can only show if it is giving bad predictions
- A high level of detail in a mechanism does not mean that it can give accurate predictions. Estimates can be wrong. Things can be missing. Evaluation may be inadequate
- “Models are always more simple than the real world”

General mechanism issues (cont'd)

- Current mechanisms give different O₃ predictions in regional models
 - Differences seem to be greatest in urban areas, where VOC control is more of an issue (relatively small geographical extent doesn't mean that these areas are not important)
 - Houston seems to be a particularly mechanism-sensitive area
 - Good news (?) mechanisms seem to be trending closer as they are updated
 - But could all the new mechanisms be making the same mistakes? Based on same body of knowledge
 - Models seem to be giving similar predictions of effects of VOC and NO_x controls (except in Texas and Chicago?)

General modeling issues

- Need more error analysis in model evaluation and mechanism research. Can guide research
 - But what about uncertainty in what's missing (or bad formulation or parameterization)?
- Solvents are >50% of anthropogenic VOCs and contain many compounds that are not adequately tracked in lumped models
- Need to process emissions consistently when comparing mechanisms

Current Gas-Phase Mechanisms

MCM

- Objective is to represent the state of the art and be a “benchmark” organic mechanism
- “Near Explicit” mechanism for both emitted VOCs and oxidation products (but less important pathways not included)
- Manually generated using a standard protocol and semi-empirical estimation methods
- Widely used in Europe for research (and some policy) applications, becoming more widely used in the US
- Presently not fully peer-reviewed, but working to address this with an advisory panel
- Aromatics mechanism performs poorly simulating chamber data and needs work

Current Gas-Phase Mechanisms

SAPRC

- Objective is to represent the state of the art and give accurate predictions of effects of reactions of many different compounds
 - Performance in evaluation against chamber data is equal or greater than consistency with lab data
- Formulation similar in many ways to MCM with respect to initial reactions, but reactions of secondary products lumped
- *Mechanism generation system* important in development. Same objective and general approach as MCM, but automated
- Aromatics mechanism formulation and performance unsatisfactory. Being updated but still problems
- Updated version available early next year

Current Gas-Phase Mechanisms

Other Self-Generated mechanisms

- Computer programs needed to handle fully explicit mechanisms
- Automated systems can produce huge mechanisms, especially if products are also generated
- Reduction approaches (or lumping) needed for self-generated mechanisms can be used in practical applications

RACM mechanisms

- Moderately condensed mechanism, recently updated. Updates caused changes in radical predictions, but not indicator ratios
- Aromatics mechanism improved
- Used extensively in Europe as alternative to MCM

Current Gas-Phase Mechanisms

CB Mechanisms

- High computational efficiency. Favored in many applications for that reason
- Recently updated. Objective to replace CB4 for use in regulatory models where CB4 used
- Adding radical recycling important
- Aromatics mechanism needs to be improved

GRS “mechanism”

- Not really a mechanism – a parameterization to predict O₃ as function of VOC and NO_x levels for screening purposes
- Adjusted to fit chamber dat. Complexity added to improve performance

Gas and Condensed Phase Mechanisms

Several such mechanisms (or mechanism pairs) in development:
e.g., CACM/MCMPO, LM-ART, Donahue's work, Kamens' work

- Primary objective is PM predictions. Gas phase mechanism joined with partitioning model with condensed phase model
- Varying levels of detail. Gas mechanisms need to be expanded to support PM predictions
- Improvements needed. Potentially important uncertainties
 - Oligimerization, polymerization a "huge issue"
 - Heterogeneous sources of HONO (Important to O₃ models)
 - N₂O₅ + H₂O (also important to O₃ models)
 - Partitioning of volatile compounds such as glyoxal
 - nucleation

Gas and Condensed Phase Mechanisms (cont'd)

- Separation between volatile and nonvolatile organics may be arbitrary – actually a continuous difference in VP
- Need to represent chemical “processing” of organics over multiple days.
 - When does chemistry make vapor pressures go UP, not down?
- Radiative characteristics of aerosol affected by chemical composition
- How well do PM mechanisms perform in atmosphere, which is much more complex than chambers?

Aqueous Phase Mechanisms

- Aqueous phase chemistry looks even more complex than gas-phase.
 - Many of same processes, plus additional ones
- Probably wider variety of organics, especially after “processing”
- CAPRAM looks like aqueous analogue to MCM
- Can be incorporated into models, but condensation needed for efficient implementation
- Are automatic generation approaches potentially useful?

Mechanism Evaluation and Chamber Data Base

- Modeling chamber data necessary to evaluate predictive capabilities of mechanism
 - Knowledge insufficient to rely on mechanisms a-priori
- But chamber data have uncertainties
 - Chamber effects
 - Modelers need to be aware of measurement uncertainties and biases
- Available chamber data base
 - European chambers – emphasis on chemistry studies and comprehensive chemical characterizations
- UCR, UNC, TVA chamber database
 - Emphasis has been on mechanism evaluation for predictions of O₃

Mechanism Evaluation and Chamber Data Base

- UCR chamber database designed for evaluating mechanisms for reactivity predictions.
- Data need to be made available so mechanism developers can use it. Not easy to model chamber data
 - Most mechanisms not adequately evaluated
 - Now: MCM focuses on European chambers, SAPRC focuses on UCR chambers,
 - Eurochamp program: Eventually make chamber data to others? That would aid use of this important database
 - UCR chambers: Need to make evaluated data for large numbers of runs since 1995. Not adequately used by some mechanisms

Mechanism Evaluation and Chamber Data Base

- Utility of chambers for instrument comparison needs to be exploited more
 - Value to field projects
 - Provide highly advanced measurements for at least some mechanism evaluation experiments
- Care must be taken when using chamber data to evaluate condensed mechanisms
- Current chamber database not adequate for evaluating mechanisms for secondary products.
 - Even effects reactivity in 1-day simulations (e.g., MIR)
 - Important uncertainty. Most mechanisms lump products more than reactants.

Mechanism Evaluation and Chamber Data Base

- HONO source in chambers
 - Limits low NO_x evaluations, causes variability
 - Need to understand it. Does this operate in the atmosphere?
- Chambers can be used to test indicatory ratios and other uses of models besides just absolute predictions
- “Data to Knowledge” methods
 - Systematic methods to use multiple data sources, considering uncertainty has been applied to other (simpler?) chemical systems.
 - Is it practical to do this in atmospheric chemistry? PM chemistry?
- Data base development needed.

New Chemistry Results Having Mechanism Implications

- Different products formed in oxidations of n-alkanes than currently assumed.
 - This MAY cause higher incremental reactivities of alkanes
 - Current chamber database not adequate to test this aspect of the mechanism (wrt O₃ reactivity)
- Mechanisms for aromatic ring-retaining products appear to be different than assumed in current models
 - Cresol, nitrophenol reactions important in predictions of aromatic impacts, especially in NO_x-limited conditions
 - HONO from nitrophenols may have a large effect (?)
- Quantum chemistry
 - Application problems in some cases

New Chemistry Results Having Mechanism Implications

- Quantum chemistry
 - Applied to isoprene case
 - Seems to fail in RO₂+NO case, uncertain in RO₂+NO₂
 - Utility for the pressing problems in mechanism development –e.g. aromatics, PM, needs to be demonstrated
 - Potential to support estimation methods – work needed here

Implementation and Application Issues

- Sensitivity analysis methods
 - DDM vs Adjoint methods
 - Being applied to 3-D models
- Process analysis methods
 - Useful to understand why mechanisms act as they do, and understand mechanism differences
 - Potentially useful for communicating model issues to policymakers
- Photochemical mechanism reduction
 - Examples given, but improved systematic methods needed

- Computer implementation
 - It is feasible to use very large mechanisms in 3-D models, but not practical for some applications (forecasting, annual average calculations, considering many control strategies, etc)
 - Various algorithms exist, but accuracy may suffer if you are not careful
 - Need *flexible* mechanism implementation methods
- Source apportionment
 - Modified and “tagged” mechanisms can play a role for this
 - Only as accurate as model in first place

Next Steps

- Data Base and Evaluation Collaborations?
- Next Meeting?