Atmospheric Chemistry Mechanisms: Current State and Future Needs

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Environmental Issue

An accurate characterization of atmospheric chemistry, the chemical mechanism, is essential for reliably predicting the response of air pollutants to emissions changes, spatial and temporal concentrations, and pollutant deposition. We believe that gas, aqueous, and aerosol chemistry in air quality models should be treated in an integrated, multi-phase, multi-pollutant manner (National Research Council, 2004).

In the past five years, our requirements for air quality modeling have also changed: the new National Ambient Air Quality Standards (NAAQS) for ozone and fine particulate matter ($PM_{2.5}$) have shifted our focus from urban-scale ozone episodes (~7 days) to regional/continental-scale simulations over longer time periods (decadal). In addition, our chemical mechanisms must adapt quickly to address emerging issues of high importance, such as impacts of biofuels and nanotechnolgy.

Research Objectives

- Ensure that CMAQ and other models that EPA uses for regulatory and research purposes have scientifically credible, up-to-date chemical representations, and are appropriate for the application.
- Improve interactions between gas-, aqueous-, and particle-phase chemistries.
- Develop techniques and strategies to efficiently expand current mechanisms to predict the chemistry of atmospheric pollutants that may become important in the future.

Modeling Approach

We are moving beyond ozone and primary/inorganic particulate matter to expand the scope of the traditional atmospheric chemistry mechanisms. New gas-phase chemical mechanisms now create explicit and condensed species needed by the secondary organic aerosol and aqueous chemical modules, and explicit description of Hazardous Air Pollutants (HAPs).
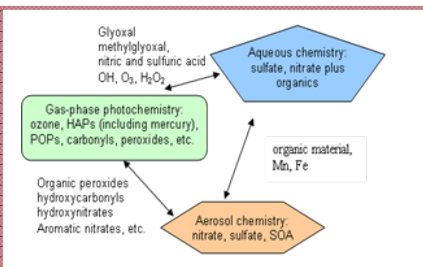

Figure 1. Current efforts to represent interactions between gas, aqueous, and aerosol chemistry in CMAQ

We continually seek to improve all chemical mechanisms in CMAQ, working closely with internal and external chemists, so that the mechanisms are consistent with recent measurements and theory. When we determine that a new reaction or product might be important, we assess the credibility of the research and robustness of the science, and prioritize it for inclusion in the mechanisms. We test new and modified mechanisms against laboratory observations in controlled smog chambers, as well as against measurements within the boundary layer, and in the free troposphere, where long-range transport is important. We are continually noting new research in the field and identifying discoveries that could significantly impact model predictions. We develop tools to aid implementation of new and modified mechanisms to respond quickly to new chemistry and emerging, future issues.

Results and Discussion

Figures 2 through 7 show some examples of results of our efforts to improve the chemical mechanisms in CMAQ have resulted in more complete and up-to-date descriptions of important chemical pathways that influence concentrations of criteria pollutants such as ozone and $PM_{2.5}$, as well as HAPs chemistry.
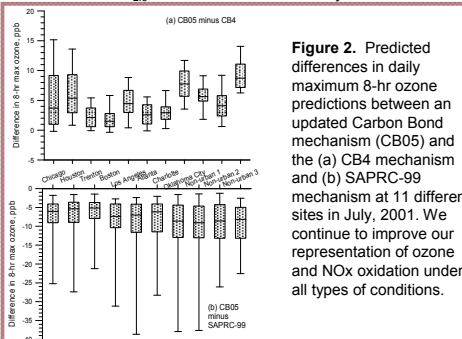

Figure 2. Predicted differences in daily maximum 8-hr ozone predictions between an updated Carbon Bond mechanism (CB05) and the (a) CB4 mechanism and (b) SAPRC-99 mechanism at 11 different sites in July, 2001. We continue to improve our representation of ozone and NOx oxidation under all types of conditions.
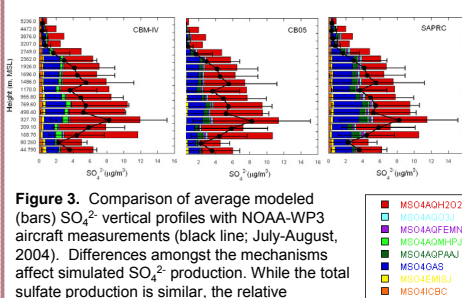

Figure 3. Comparison of average modeled (bars) SO_4^{2-} vertical profiles with NOAA-WP3 aircraft measurements (black line; July-August, 2004). Differences amongst the mechanisms affect simulated SO_4^{2-} production. While the total sulfate production is similar, the relative contribution of gas and aqueous pathways (right box) is different among mechanisms.
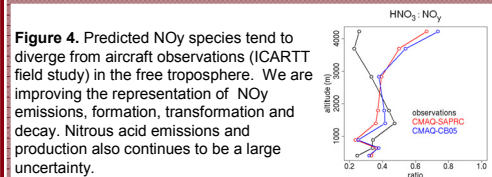

Figure 4. Predicted NOy species tend to diverge from aircraft observations (ICARTT field study) in the free troposphere. We are improving the representation of NOy emissions, formation, transformation and decay. Nitrous acid emissions and production also continues to be a large uncertainty.
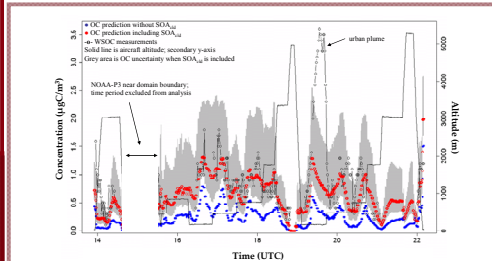

Figure 5. CMAQ organic carbon predictions that include cloud-produced SOA agree better with water soluble organic carbon measurements made during ICARTT (Carlton et al., 2008). Including these processes can potentially account for some missing SOA.
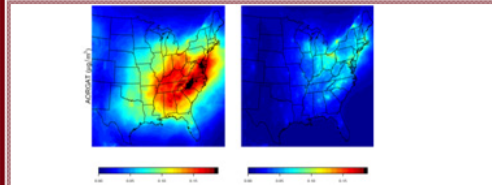

Figure 6. Monthly-average predicted SOA from aromatics, August 2006. Competition between NO and HO_2 reactions of aromatic peroxy radicals increases SOA from aromatics by a factor of 3 (left side) over previous representation. Future efforts will include a more mechanistic production of nonvolatile and semi-volatile species.
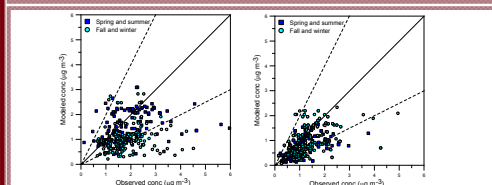

Figure 7. Comparison of predicted concentrations of HAPs against limited observations for acetaldehyde (left) and benzene (right) for 2001, by season grouping. Inconsistent emissions reporting and infrequent observations can contribute to uncertainties in the concentration estimates of some important HAPs.

Conclusions

Atmospheric chemistry in CMAQ has evolved in the last 5 years from a single-pollutant focus to an integrated, multi-pollutant approach. Since 2003, we have updated the chemical mechanisms, leading to improvements in the inorganic gas phase reactions, aromatic reactions forming semivolatile products, aqueous chemistry, secondary aerosol formation, and interactions with the gas phase have helped reduce the uncertainty related to atmospheric chemistry in CMAQ predictions. We have expanded our evaluations beyond surface level, which has helped us to identify areas for future improvement.

Future Directions

Because atmospheric chemistry impacts every component of CMAQ, our future efforts in chemical mechanisms will rely on expertise in gas, aqueous, and aerosol chemistry. We will continue to enhance our representation of aqueous and SOA chemistry, and improve gas-aerosol-aqueous linkages. We will also work to modify the mechanisms to be consistent with the latest science and include new information.

Some areas that we will focus on improving include 1) reactive nitrogen photolysis, partitioning and reaction, 2) description of aromatic reaction products, 3) evaluation of radical predictions, and 4) description of heterogeneous chemistry. We continue to refine and expand HAPs chemistry to include species such as polynuclear aromatic hydrocarbons and other pollutants that pose large risks to human and ecosystem health.

Impact

Our chemical mechanism improvements within CMAQ have been used by EPA during the past 5 years to predict the potential benefits of a number of different national programs such as the Clean Air Interstate Rule (CAIR), the Clean Air Visibility Rule (CAVR), the NOx SIP call and the ozone NAAQS RIA (Regulatory Impact Assessment). We provided new mechanisms to the scientific community, including regulators and scientists throughout the world. The criteria/HAPs version of CMAQ underlies EPA/OAQPS' 2002 Multipollutant platform, which is being used for upcoming rules to examine potential co-benefits of regulatory actions such as the Renewable Fuels Standard Act (RFS2) and for calculation of residual risk, addressing Section 112 of the Clean Air Act.

Contributors/Collaborators

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