Gas-phase chemical mechanisms have been used in air quality models for more than three decades to simulate oxidant formation and the atmospheric reactions of organic compounds, sulfur dioxide (SO$_2$), and nitrogen oxides (NO$_x$). The main chemical drivers are photolysis by sunlight and reactive species with unpaired electrons (radicals) such as hydroxyl (OH), nitrate (NO$_3$), and ozone (O$_3$). Mechanism applications have expanded from urban O$_3$ to include regional/global O$_3$, other oxidants, sulfate/nitrate aerosol, acid deposition, secondary organic aerosol (SOA), and hazardous air pollutants (HAPs). New issues continue to arise such as winter O$_3$ formation occurring in freezing conditions. Accurate chemical mechanisms are critical to ensuring that air quality planning activities achieve their goals.

**Recommendations**

**Collect Data to Better Understand Gas-Phase Chemistry**

Basic laboratory data and environmental chamber data are needed to obtain reliable kinetic and mechanistic reaction parameters to describe atmospheric reactions, particularly under low-NO$_x$ conditions. For example, radical formation from biogenic emissions of isoprene under low-NO$_x$ conditions is not well understood, despite many efforts and is important because isoprene emissions are large and widespread. When direct NO$_x$ emissions are small, secondary sources such as NO$_x$ recycled from organic nitrogen compounds (e.g., peroxyacyl nitrates [PANs], isoprene nitrates, alkyl nitrates, and nitrophenols) can become important and need to be better characterized. Low-NO$_x$ conditions will become more prevalent as NO$_x$ emissions continue to be reduced. Halogen chemistry influences both mercury chemistry and oxidant formation/destruction (e.g., when nitryl chloride [ClNO$_2$] is formed and then photolyzed or when bromine [Br] or iodine [I] atoms react with O$_3$) and this halogen chemistry is neither fully understood nor robustly accounted for in many chemical mechanisms. Field studies gathering detailed atmospheric chemical measurements and satellite data (e.g., satellite NO$_2$ data) can clarify aspects of gas-phase chemistry that should be studied in depth in laboratories and environmental chambers.

**Implement New Chemistry into Chemical Mechanisms**

Condensed chemical mechanisms used in air quality modeling need to be continually updated with new knowledge. Oxidation mechanisms for isoprene, aromatics, and their major products can be improved using available information. Potential improvements include radical generation via epoxide formation and radical isomerization for isoprene and mechanisms for ring-fragmentation and ring-retaining products for aromatics. Understanding the chemistry that leads to high O$_3$ concentrations on cold winter days (e.g., in Wyoming and Utah) is an urgent issue for complying with O$_3$ air quality standards. Current chemical mechanisms may not
implement known temperature effects (e.g., products of alkoxy radicals, yields of alkyl nitrates)\textsuperscript{10} that could be important for understanding winter vs. summer $O_3$. Condensed mechanisms may need expanding to better describe the influence of compounds with large emissions such as benzene, acetylene, and propane.

**Improve and Implement Mechanisms to Better Represent Certain Emission Categories**

Improved chemical knowledge and/or mechanisms may be needed to address new or emerging emissions and conditions where a few source types or reactive compounds dominate. Wildfire emissions influence air quality in many regions, and the production of oxidants and SOA in fire plumes is not well understood.\textsuperscript{11} Highly reactive industrial emissions (e.g., alkenes) strongly influence air quality in many regions (e.g., Southeast Texas) and can be better described by condensed mechanisms that are tailored for the conditions.\textsuperscript{12} Changes in fuel and energy production (e.g., biomass combustion, biofuel production, oil and gas production using nontraditional techniques) may alter the composition of emissions and call for mechanism improvements. The chemistry of amines needs to be included in mechanisms to assess the potential atmospheric impacts of using amines for carbon dioxide ($CO_2$) capture.\textsuperscript{13}

**Continue Expanding Condensed Mechanisms Beyond Oxidants**

Chemical mechanisms need to be continuously updated and expanded to meet new needs and maintain their usefulness, accuracy, and compatibility with current scientific data. Mechanisms must provide accurate predictions of species that influence SOA formation in the gas phase (e.g., $OH$, $NO$, $HO_2$, $NO_3$, semi-volatile organic compounds)\textsuperscript{14} and aqueous phase (e.g., glyoxal, and other multi-functional organic compounds).\textsuperscript{15,16} Important radical-generating heterogeneous processes (e.g., nitrous acid [HONO] formation\textsuperscript{17}) seem to be missing from current mechanisms/models. Expanding mechanisms to explicitly represent marker compounds that fingerprint emission source emissions would enable emission inventory evaluation using air quality models.

**Evaluate Chemical Mechanisms Before Implementing in Air Quality Models**

Chemical mechanisms are difficult to evaluate within air quality models because they are confounded with other model components and inputs (e.g., emissions). Environmental chamber data produced under atmospherically-relevant chemical conditions (e.g., reactant concentrations) and under well controlled and well characterized environmental conditions (e.g., light conditions) are essential
for mechanism evaluation. Detailed ambient data (e.g., with measured radical concentrations and/or oxidant production rates) can also be useful in evaluating individual elements of a chemical mechanism. Using data from multiple field campaigns is recommended whenever possible so that evaluation can be done under a wide range of chemical conditions.

Use Multiple Chemical Mechanisms and Evaluate Sensitivity in Real-World Applications

Selecting a single chemical mechanism for air quality modeling is difficult to justify in light of the difficulties in formulating and evaluating mechanisms mentioned above. Good mechanism performance in simulating ambient conditions is no guarantee of accuracy because of possible errors (sometimes, compensating errors) in the various model components. Therefore, sensitivity testing with using multiple chemical mechanisms is recommended to gauge whether conclusions and policy decisions are robust across the range of current understanding.

New Direction: Work Toward Chemical Mechanisms that Unify Oxidant, SOA, and Heterogeneous Chemistry

Developing unified chemical mechanisms for modeling oxidants, SOA formation, and aequoreous reactions is a significant challenge that needs to be met. Progress can be made by explicitly representing (in the gas-phase chemistry) species that are important to modeling SOA formation and aging processes and aqueous chemistry. Continued development and integration of research-scale mechanisms, such as Master Chemical Mechanism (MCM), Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A), and Chemical Aqueous Phase Radical Mechanism (CAPRAM) is recommended. Mechanism evaluation is just as important for detailed mechanisms as for condensed mechanisms because incorporating more detail does not guarantee improved model results.

Conclusion

Improving areas of high uncertainty in chemical mechanisms is critical to ensuring that policy decisions are accurate and robust. Therefore, we recommend obtaining new laboratory, chamber, and field data to better understand gas-phase chemistry; implementing new findings into chemical mechanisms in air quality models; continuously improving and evaluating chemical mechanisms; using multiple chemical mechanisms to assess reliability of policy decisions; and developing chemical mechanisms unifying oxidant, secondary organic aerosol, and heterogeneous chemistry.

References


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