

Simulation of Secondary Organic Research Needs

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During the *Workshop on Future Air Quality Model Development*, a diverse group of scientists came together to discuss research needs to improve modeling of secondary organic aerosol. This article outlines the principal research needs and recommendations raised during those discussions.

The organic fraction of fine particulate matter ($PM_{2.5}$) can comprise a large fraction of total concentrations of PM across the United States.¹ Typically, organic aerosol (OA) or organic particulate matter (OPM) has been viewed as primary and secondary in nature, referring to material that is directly emitted to the atmosphere or PM that forms through atmospheric processing. The conceptual framework for secondary organic aerosol (SOA) for many years was based on the oxidation of volatile

organic compounds (VOCs) to form less-volatile products that would partition onto the existing particles.^{2,3} Parent VOCs considered large enough to form condensable oxidation products were typically those with eight or more carbon molecules, such as toluene, xylene, monoterpenes, and sesquiterpenes. Similarly, the conceptual framework for primary organic aerosols (POA) was based on the premise that these particles participated in SOA formation process by providing a preexisting



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medium for condensation of new organic mass as per gas-particle partitioning theory.^{4,5} OA models were developed with these gas-phase oxidation mechanisms and representations of gas-particle partitioning. However, when introduced into larger air quality modeling frameworks, the models were unable to simulate organic mass, sometimes falling short by an order of magnitude or more.⁶ Although errors or omissions in emissions inventories may account for part of this discrepancy, the results of several experimental and field studies showed that the conceptual framework for ambient OPM was incomplete.

Recent research has shown that the processes that affect OPM levels are not simply separated into the original categorizations of relatively unreactive POA and oxidation-partitioning-based SOA formation. Even the “traditional” definitions of POA and SOA are being revisited as we discover that organic particles can age in the atmosphere to form products that volatilize back to the gas phase.⁷ These products, formerly considered as POA, can also participate in atmospheric chemistry and perhaps find their way back to the particle phase. The volatility basis set, which represents all organic mass by its volatility distribution—from high volatility gases to low volatility OPM—is an example of one conceptual framework that can improve our representation of these processes in an air quality model.⁸ We realize that between the spectrum of VOC and the lowest volatility POA there is an assortment of intermediate-volatility and semi-volatile organic compounds (IVOC and SVOC, respectively) that require characterization in chemical emissions and in chemical reaction mechanisms. Low-carbon-number and simpler

VOC, such as isoprene, glyoxal and acetylene, are now recognized to form SOA and the properties of condensed-phase particles, such as acidity and liquid water content, can influence the rate or amount of aerosol formed.⁹⁻¹² Atmospheric conditions, such as nitrogen oxides (NO_x) levels, can also determine the total amount of aerosol formed from different sources of VOC or POA.¹³

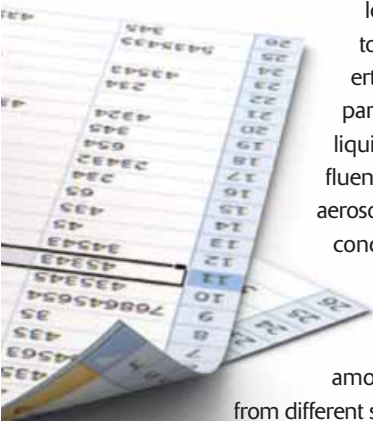
Developing organic aerosol models that accurately simulate the properties of emissions, competing chemical mechanisms, and the impact of atmospheric conditions will be essential to the continued improvement of regional air quality modeling.

Research Needs and Recommendations

Improve treatment (emissions, characterization, and chemistry) of the unresolved complex mixture (UCM) and biogenic species (isoprene, sesquiterpenes)

Historically SOA models have focused on a relatively small number of high flux precursor species, such as single-ring aromatics and monoterpenes. Recent research has identified several potentially important new classes of precursors that are poorly represented in inventories and SOA models. First, a significant component of the emissions from many combustion systems cannot be speciated using traditional analytical techniques and therefore is referred to as UCM. This material is thought to be composed of branched and cyclic compounds that are C10 and higher and are present in the particle and gas phases. This material is typically not included (or misrepresented) in inventories and models because it has not been chemically speciated. For example, SVOC and IVOC may be completely absent from an inventory, thereby precluding any model's ability to properly simulate SOA levels. It is important to understand the chemical character and emissions rates of the UCM from major sources and to elucidate the atmospheric fate of these compounds.

In addition, accurate simulation of biogenic emissions and their processing in the atmosphere—in particular, isoprene and sesquiterpenes—continues to be a critical area of research to improve the ability of models to properly estimate biogenic OPM levels. For isoprene SOA, the main uncertainty is adequately representing the mechanisms of formation and the parameters that affect overall OPM levels, although emissions can also be improved. The key uncertainty with respect to modeling sesquiterpene SOA lies in accurately representing the emissions rates. The regional air quality models need top-of-canopy biogenic emission estimates; leaf/branch enclosure measurements are not as useful for regional modeling applications.



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Develop, evaluate, and condense mechanisms for secondary organic aerosol production

One goal associated with SOA model development is to describe the SOA formation process in as much detail as possible; that is, to embody within the model all our basic understanding of the SOA formation and aging process. A parallel goal is to develop a computationally efficient module that can be included in three-dimensional atmospheric chemical transport models. While the explicit model meets, in principle, the first goal, such a model is computationally infeasible as a component of an atmospheric model. At present, the SOA modules embedded in three-dimensional atmospheric models are of the empirical type. Smog chamber experiments are needed for elucidating the mechanisms, composition, and yield of SOA, and the next generation of SOA models will be built to predict the measureable properties from these chamber experiments. In addition, three-dimensional grid models need parameterizations of tailpipe, fire, and other combustion emissions in which the near-source dilution, evaporation, rapid oxidation, and recondensation has already been accounted for. Overall, the challenge is to balance the need for process detail and chemical fidelity with the need for computational feasibility.

Conduct experiments across the entire range of atmospheric conditions and at longer time scales (multigenerational chemistry)

SOA models are beginning to implement multigenerational chemistry schemes. However, relatively little is known about the oxidation chemistry (e.g., fragmentation vs. functionalization) and atmospheric fate (e.g., deposition vs. chemical loss) of higher molecular weight oxygenated species. The characterization of wet and dry deposition rates of semi-volatile SOA precursors is one research area that can drastically impact model outputs.¹⁴ Therefore, existing multigenerational SOA models are highly uncertain. In addition, implementing multigenerational models requires explicit tracking of all likely SOA precursors, including those formed from oxidation reactions.

Ambient organic aerosol is often much more oxidized than that produced by typical smog chamber experiments, which have been historically used as the basis for SOA models. The recommendation here is to push the envelope of laboratory experiments by extending them to longer timescales and lower organic aerosol concentrations, so as to be more representative of the levels and residence times characteristic of the atmosphere. Longer-time scale data is an especially critical need because models are beginning to implement multigenerational chemistry schemes for SOA that are very poorly constrained with observational data. In addition, experiments should strive to use a variety of atmospherically relevant

seed particles (e.g., diesel soot, wood smoke particles, dust, and sea salt). There is also a need to investigate SOA formation under different NO_x (and, specifically, NO) regimes; as well as the importance of performing experiments under high relative humidity conditions. Another important unknown is the extent to which particle-phase reactions and parameters such as acidity, NO_x levels, and relative humidity influence the SOA formation process. Experimental protocols need to be developed to allow evaluation of the presence and importance of particle-phase chemistry.

Develop new modules incorporating physics and chemistry from new experimental work

There is a need to develop new approaches for modeling SOA, because the comparison between approaches is likely to yield important insights needed to improve the simulation of aerosol formation, aging, and deposition. Such approaches should incorporate physics and chemistry from new experimental work.

Aerosol mass spectrometer (AMS) measurements of organic aerosols, now becoming a routine component of chamber experiments, can help enable derivation of a number of key SOA properties; these include the atomic O:C and H:C ratios, from which one can infer the overall oxidation state of the aerosol. The volatility of SOA is not generally measured as a routine component of chamber experiments, although the volatility of the organic mixture is a key determinant of SOA formation. Current aerosol models tend to overestimate the volatility of ambient organic material. A next-generation model should be capable of representing the processes by which more-volatile material is converted in the atmosphere to less-volatile material. The model should, in some manner, relate the aerosol volatility to its molecular properties. Simple models based on volatility and oxidation state^{15,16} or on carbon number and polarity¹⁷ are in early stages of development and other approaches will undoubtedly emerge in the coming years.

It is important to note that the relationship between oxidation state and volatility is not unique; that is, molecular mixtures with the same overall oxidation state do not necessarily exhibit the same overall volatility. A model might be better suited to express the range of volatility associated with a range of oxidation states. The challenge is to build sufficient chemical reality into the model to adequately constrain the volatility/oxidation state relationship.

Other important research priorities include the integration of work on the aqueous-phase processing of organic gases in order to develop a consistent modeling framework.

(The companion article on heterogeneous chemistry discusses in more detail the role of aqueous-phase processing as a key research area, see page 45.)

Evaluate model results using the richer data obtained from new measurements

There is a need to evaluate model results against richer data than can be obtained from routine monitoring networks. Such rigorous evaluations would compare model results against nonroutine measurements of carbon mass and total organic PM mass, the C14 isotope, molecular markers of POA and SOA, organic O:C ratios, water soluble organic carbon, OPM volatility, and receptor model results. To make these comparisons, it will be important to introduce the ability in models to track sources, chemical composition, and physical properties of the organic aerosol. Such detailed comparisons will help us understand what aspects of organic aerosol models need improvement to reproduce accurately atmospheric concentrations of total OPM.¹⁸

Conclusion

Overall, the modeling of organic aerosol has improved in recent years relative to a decade ago. In general, current regional air quality models tend to represent roughly one half of the mass concentration of organic PM in the atmosphere.¹⁹ Although this is a tremendous improvement from the order of magnitude discrepancies noted earlier, there are still improvements needed to represent observed spatial and temporal patterns of organic PM levels, as well as bring overall OPM mass concentrations in line with observations. Accurately representing the mechanisms for formation and the controlling parameters will also raise confidence in the ability of models to predict changes in air quality (specifically with respect to total PM concentrations) that will result from proposed emission control programs. The recommendations listed herein should be considered as important steps to meet the objective of improved regional air quality models. **em**

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- It will also be important to understand the expectations of what level of model performance is achieved when comparing grid-volume average concentration to point measurements. To better attenuate our expectations, investigations of the spatial variability of pollutants in different regions (e.g., urban, rural, and remote) with different terrain features and climatology will be necessary. Furthermore, when such comparisons are made, it is important to also focus on uncertainties in transport and mixing and the ability of the model to reflect boundary layer phenomena, as discussed in a companion article in this series, to identify the main obstacles to model performance. Finally, the objective of air quality models is to reproduce the chemical composition—and responses to emissions changes—observed in the real atmosphere with minimal bias and low error; the relevant statistics and numerical goals for model performance are important topics for broader discussion within the air quality management community.
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