

# Regional Air Quality Model

by Naresh Kumar

**Naresh Kumar, Ph.D.**, is a senior program manager in the Environment division at Electric Power Research Institute (EPRI), Palo Alto, CA. E-mail: nkumar@epri.com.

This special feature section contains a brief summary of the *Workshop on Future Air Quality Model Development Needs*, which was held September 2011 in Arlington, VA, to develop a framework to guide future research in air quality model development. The workshop brought together researchers from academia, government and private institutions, industry, and other stakeholders to brainstorm on various model development needs. The workshop's recommendations for future research are described in detail in the next four articles.

Regional air quality models (RAQMs) are the primary tools used by regulators, states, industry, and other agencies for a variety of applications, including the development of regulations, design of air quality control strategies and implementation plans, and short-term operational air quality forecasting. They have gone through extensive scientific and computational improvements in the past two decades, as their use has expanded over time. The

major RAQMs used in the United States (and in many parts of the world) are the Community Multiscale Air Quality (CMAQ) model,<sup>1</sup> the Comprehensive Air Quality Model with Extensions (CAMx),<sup>2,3</sup> and the Weather Research and Forecasting/Chemistry (WRF/Chem) model.<sup>4</sup>

Most states rely on either the CAMx or the CMAQ model to develop State Implementation Plans (SIPs) for



# Development Needs

developing control strategies to meet attainment for National Ambient Air Quality Standards (NAAQS) for ozone and particulate matter (PM) and to meet the Regional Haze Rule progress goals. The U.S. Environmental Protection Agency (EPA) also uses these two models for federal rulemakings. For example, EPA recently used the CAMx to model the impact of individual states to ozone and fine PM concentrations in the downwind states,<sup>5</sup> and used the CMAQ model for developing the Mercury and Air Toxics Standards (MATS) rulemaking.<sup>6</sup> RAQMs have also been used for new applications ranging from health studies<sup>7</sup> to integration with global-scale models for climate studies.<sup>8</sup>

The chemical and physical processes in RAQMs are represented by state-of-the-art modules that have gone through continuous improvements over the years. However, there are still many processes that are represented poorly or need to be improved. A workshop, entitled the *Workshop on Future Air Quality Model Development Needs*, was held on September 12 and 13, 2011, in Arlington, VA, to develop a framework to guide future research in air quality model development. The workshop was attended by 79 participants from the United States, Canada, and Europe. The two main objectives of the workshop were to (1) identify research gaps in air quality process representations and (2) develop a research agenda for future model development. A full description of the workshop can be found in a report by the Electric Power Research Institute (EPRI).<sup>9</sup>

To facilitate the discussions, the workshop was organized around four key topics:

**① Homogeneous chemistry**

- ② Multi-phase chemistry (including inorganic and organic aqueous-phase chemistry)**
- ③ Organic PM: Formation and aging of secondary organic aerosol**
- ④ Meteorological processes affecting air quality**

Spanning two full days, the first day of the workshop was devoted to plenary sessions, where two invited speakers per workshop topic gave their viewpoints on the state of the science, identified knowledge gaps, and provided recommendations for future research. Presentations from the speakers are available online at [http://events.awma.org/epri\\_proceedings/proceedings.html](http://events.awma.org/epri_proceedings/proceedings.html).

During the second day, attendees were divided into four breakout sessions by topic, in which they further expanded the discussions to identify a future research agenda for each topic. The groups were also charged with prioritizing the research ideas. The workshop recommendations for future research are categorized into the same four topics listed above and are described in detail in the next four articles in this issue. All the recommendations were considered high priority and are listed in no particular order in those articles. However, within each topic, recommendations that were considered “new directions” (i.e., issues that presently are receiving insufficient attention) and where research activity is needed in particular, were identified. We hope that these recommendations can serve as guidelines for researchers, as well as research agencies, as they consider future work related to RAQM development. **em**

## References

1. Byun, D.; Schere, K.L. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system; *Appl. Mech. Rev.* **2006**, *59*, 51-77.
2. Morris, R.E.; Yarwood, G.; Emery, C.; Wilson, G. Recent Advances in CAMx Air Quality Modeling. In *Proceedings of the A&WMA 94th Annual Conference & Exhibition, Orlando, FL, USA, June 2001*.
3. Morris, R.E.; Yarwood, G.; Emery, C.A.; Wilson, G. Recent Advances in Photochemical Air Quality Modeling Using the CAMx Model: Current Update and Ozone Modeling of Point Source Impacts. In *Proceedings of the A&WMA 95th Annual Conference & Exhibition, Baltimore, MD, USA, June 2002*.
4. Grell, G.A.; Peckham, S.E.; Schmitz, R.; McKeen, S.A.; Frost, G.; Skamarock, W.C.; Eder, B. Fully coupled “online” chemistry within the WRF model; *Atmos. Environ.* **2005**, *39*, 6957-6975.
5. *Regulatory Impact Analysis for the Federal Implementation Plans to Reduce Interstate Transport of Fine Particulate Matter and Ozone in 27 States; Correction of SIP Approvals for 22 States; Docket ID No. EPA-HQ-OAR-2009-0491*; U.S. Environmental Protection Agency, 2011.
6. *Regulatory Impact Analysis for the Final Mercury and Air Toxics Standards; EPA-452/R-11-011*; U.S. Environmental Protection Agency, 2011.
7. Isakov, V.; Jawad S.; Touma J.S.; Burke, J.; Lobdell, D.T.; Palma, T.; Rosenbaum, A.; Özkanak, H. Combining Regional- and Local-Scale Air Quality Models with Exposure Models for Use in Environmental Health Studies; *J. Air & Waste Manage. Assoc.* **2009**, *59*, 461-472.
8. Zhang, Y.; Pan, Y.; Wen, X.-Y.; Dong, X.-Y.; Karamchandani, P.; Streets, D.G.; Skamarock, W.C.; Grell, G.A. Simulating Climate-Air Quality Interactions Using Global-through-Urban WRF/Chem. In *Proceedings of the 11th Conference on Atmospheric Chemistry/the 89th AMS Annual Meeting, Phoenix, AZ, USA, January 2009*.
9. EPRI and A&WMA Workshop on Future Air Quality Model Development Needs: A Summary Report; EPRI, Palo Alto, CA, 2012.

**ACKNOWLEDGMENTS:**  
The workshop was sponsored/supported by the following organizations:

EPRI  
A&WMA  
American Meteorological Society  
American Petroleum Institute  
EPA  
Lakes International  
TRC

Their support is greatly appreciated.

The author would also like to thank all of the speakers who provided keynote presentations at the workshop and all of the participants who contributed to the discussions during the breakout sessions.



# Gas-Phase Chemistry in Air Quality Models Research Needs and Recommendations

by Gookyoung Heo  
and Greg Yarwood

**Gookyoung Heo** is a chemical mechanism developer in the College of Engineering, Center for Environmental Research and Technology, at the University of California, Riverside.

**Greg Yarwood** is a principal at ENVIRON International Corporation working on air quality research and planning.  
E-mail:  
gyarwood@environcorp.com.

Based on discussions at the *Workshop on Future Air Quality Model Development Needs*, this article identifies and offers recommendations on where developments are needed to address both traditional and new gas-phase chemical mechanism applications.



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 ( $\text{SO}_2$ ), and nitrogen oxides ( $\text{NO}_x$ ).<sup>1</sup> The main chemical drivers are photolysis by sunlight and reactive species with unpaired electrons (radicals) such as hydroxyl ( $\text{OH}$ ), nitrate ( $\text{NO}_3^-$ ), and ozone ( $\text{O}_3$ ). Mechanism applications have expanded from urban  $\text{O}_3$  to include regional/global  $\text{O}_3$ , other oxidants, sulfate/nitrate aerosol, acid deposition, secondary organic aerosol (SOA), and hazardous air pollutants (HAPs). New issues continue to arise such as winter  $\text{O}_3$  formation occurring in freezing conditions.<sup>2</sup> 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<sup>1,3</sup> are needed to obtain reliable kinetic and mechanistic reaction parameters to describe atmospheric reactions, particularly under low- $\text{NO}_x$  conditions. For example, radical formation from biogenic emissions of isoprene under low- $\text{NO}_x$  conditions is not well understood, despite many efforts and is important because isoprene emissions are large and widespread.<sup>4</sup> When direct  $\text{NO}_x$  emissions are small, secondary sources such as  $\text{NO}_x$  recycled from organic nitrogen compounds (e.g., peroxyacetyl nitrates

[PANs], isoprene nitrates, alkyl nitrates, and nitrophenols) can become important and need to be better characterized. Low- $\text{NO}_x$  conditions will become more prevalent as  $\text{NO}_x$  emissions continue to be reduced. Halogen chemistry<sup>5</sup> influences both mercury chemistry and oxidant formation/destruction (e.g., when nitril chloride [ $\text{CINO}_2$ ]<sup>6</sup> is formed and then photolyzed or when bromine [ $\text{Br}$ ] or iodine [ $\text{I}$ ] atoms react with  $\text{O}_3$ ) 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  $\text{NO}_2$  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<sup>7</sup> and radical isomerization<sup>8,4</sup> for isoprene and mechanisms for ring-fragmentation and ring-retaining products for aromatics.<sup>9</sup> Understanding the chemistry that leads to high  $\text{O}_3$  concentrations on cold winter days (e.g., in Wyoming and Utah) is an urgent issue for complying with  $\text{O}_3$  air quality standards. Current chemical mechanisms may not



REGISTER NOW!

## AEROSOL AND ATMOSPHERIC OPTICS VISIBILITY & AIR POLLUTION

SEPTEMBER 24-28, 2012 • WHITEFISH, MT

This international conference will provide a technical forum on advances in the scientific understanding of the effects of aerosol on urban, regional, continental and global scale haze and radiation balance. Four professional courses, designed to provide both a technical foundation and a timely refresher, will be offered on-site prior to the conference. There is also a photo contest planned, as well as a mid-conference field trip to the Glacier National Park Class I area.

Sponsorship and exhibit opportunities are available

**CONFERENCE LOCATION**  
Grouse Mountain Lodge  
+1-406-892-6722  
Hotel Rate: \$145

**HOTEL CUTOFF/  
REGISTRATION DEADLINE**  
August 20, 2012  
<http://visibility.awma.org>



REGISTER NOW!

## VAPOR INTRUSION

OCTOBER 3-4, 2012 • DENVER, CO

Join the Air & Waste Management Association (A&WMA) and internationally-recognized scientists, engineers, regulators, communications experts and attorneys to discuss the latest developments and innovations in regulatory policy, sampling, analysis and remediation of VI.

Sponsorship opportunities are available

**CONFERENCE LOCATION**  
Grand Hyatt Denver  
+1-888-421-1442  
Hotel Rate: \$199

**HOTEL CUTOFF/  
REGISTRATION DEADLINE**  
September 5, 2012  
<http://vapor.awma.org>

implement known temperature effects (e.g., products of alkoxy radicals, yields of alkyl nitrates)<sup>10</sup> that could be important for understanding winter vs. summer O<sub>3</sub>. 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.<sup>11</sup> 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.<sup>12</sup> Changes in fuel and energy production (e.g., biomass combustion, biofuel production, oil and gas production using non-traditional 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<sub>2</sub>) capture.<sup>13</sup>

### 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<sub>2</sub>, NO<sub>3</sub>, semi-volatile organic compounds)<sup>14</sup> and aqueous phase (e.g., glyoxal, and other multi-functional organic compounds).<sup>15,16</sup> Important radical-generating heterogeneous processes (e.g., nitrous acid [HONO] formation<sup>17</sup>) seem to be missing from current mechanisms/models. Expanding mechanisms to explicitly represent marker compounds that fingerprint emission sources 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.<sup>1,3</sup> 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 aqueous 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<sup>14</sup> and aqueous chemistry.<sup>15,16</sup> Continued development and integration of research-scale mechanisms, such as Master Chemical Mechanism (MCM),<sup>18</sup> Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A),<sup>19</sup> and Chemical Aqueous Phase Radical Mechanism (CAPRAM)<sup>15</sup> 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. em

### **References**

- Dodge, M.C. Chemical oxidant mechanisms for air quality modeling: critical review; *Atmos. Environ.* **2000**, *34*, 2103-2130.
- Schnell, R.C.; Oltmans, S.J.; Neely, R.R.; Endres, M.S.; Molenar, J.V.; White, A.B. Rapid photochemical production of ozone at high concentrations in a rural site during winter; *Nat. Geosci.* **2009**, *2*, 120-122.
- Carter, W.P.L.; Cocker, D.R.; Fitz, D.R.; Malkina, I.L.; Bumiller, K.; Sauer, C.G.; Pisano, J.T.; Bufalino, C.; Song, C. A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation; *Atmos. Environ.* **2005**, *39*, 7768-7788.
- Taraborrelli, D.; Lawrence, M.G.; Crowley, J.N.; Dillon, T.J.; Gromov, S.; Groß, C.B.M.; Vereecken, L.; Lelieveld, J. Hydroxyl radical buffered by isoprene oxidation over tropical forests; *Nat. Geosci.* **2012**, *5*, 190-193.
- Platt, U.; Henniger, G. The role of halogen species in the troposphere; *Chemosphere* **2003**, *52*, 325-338.
- Osthoff, H.D.; Roberts, J.M.; Ravishankara, A.R.; Williams, E.J.; Lerner, B.M.; Sommariva, R.; Bates, T.S.; Coffman, D.; Quinn, P.K.; Dibb, J.E.; Stark, H.; Burkholder, J.B.; Talukdar, R.K.; Meagher, J.; Fehsenfeld, F.C.; Brown, S.S. High levels of nitril chloride in the polluted subtropical marine boundary layer; *Nat. Geosci.* **2008**, *1*, 324-328.
- Paulot, F.; Crouse, J.D.; Kjaergaard, H.G.; Kürten, A.; St. Clair, J.M.; Seinfeld, J.H.; Wennberg, P.O. Unexpected epoxide formation in the gas-phase photooxidation of isoprene; *Science* **2009**, *325*, 730-733.
- Peeters, J.; Nguyen, T.L.; Vereecken, L. HO<sub>x</sub> radical regeneration in the oxidation of isoprene; *Phys. Chem. Chem. Phys.* **2009**, *11*, 5935-5939.
- For example, see: Birdsall, A.W.; Elrod, M.J. Comprehensive NO-dependent study of the products of the oxidation of atmospherically relevant aromatic compounds; *J. Phys. Chem. A* **2011**, *115*, 5397-5407; Arey, J.; Obermeyer, G.; Aschmann, S.M.; Chattopadhyay, S.; Cusick, R.D.; Atkinson, R. Dicarbonyl products of the OH radical-initiated reaction of a series of aromatic hydrocarbons; *Environ. Sci. Technol.* **2009**, *43*, 683-689.
- Carter, W.P.L.; Seinfeld, J.H. Winter ozone formation and VOC incremental reactivities in the Upper Green River Basin of Wyoming; *Atmos. Environ.* **2012**, *50*, 255-266.
- Jaffe, D.A.; Wigder, N.L. Ozone production from wildfires: A critical review; *Atmos. Environ.* **2012**, *51*, 1-10.
- Heo, G.; Kimura, Y.; McDonald-Buller, E.; Carter, W.P.L.; Yarwood, G.; Allen, D.T. Modeling alkene chemistry using condensed mechanisms for conditions relevant to southeast Texas, USA; *Atmos. Environ.* **2010**, *44*, 5365-5374; Heo, G.; McDonald-Buller, E.; Carter, W.P.L.; Yarwood, G.; Whitten, G.Z.; Allen, D.T. Modeling ozone formation from alkene reactions using the Carbon Bond chemical mechanism; *Atmos. Environ.* **2012**, *59*, 141-150; doi:10.1016/j.atmosenv.2012.05.042, in press.
- Ge, X.; Wexler, A.S.; Clegg, S.L. Atmospheric amines - Part I. A review; *Atmos. Environ.* **2011**, *45*, 524-546.
- Kroll, J.H.; Seinfeld, J.H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere; *Atmos. Environ.* **2008**, *42*, 3593-3624.
- Hermann, H.; Tilgner, A.; Barzaghi, P.; Majid, Z.; Gligorovski, S.; Poulin, L.; Monod, A. Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0; *Atmos. Environ.* **2005**, *39*, 4351-4363.
- Ervens, B.; Turpin, B.J.; Weber, R.J. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies; *Atmos. Chem. Phys.* **2011**, *11*, 11069-11102.
- Wong, K.W.; Tsai, C.; Lefer, B.; Haman, C.; Grossberg, N.; Brune, W.H.; Ren, X.; Luke, W.; Stutz, J. Daytime HONO vertical gradients during SHARP 2009 in Houston, TX; *Atmos. Chem. Phys.* **2012**, *12*, 635-652.
- Saunders, S.M.; Jenkin, M.E.; Derwent, R.G.; Pilling, M.J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds; *Atmos. Chem. Phys.* **2003**, *3*, 161-180.
- Aumont, B.; Szopa, S.; Madronich, S. Modelling the evolution of organic carbon during its gas-phase tropospheric oxidation: Development of an explicit model based on a self generating approach; *Atmos. Chem. Phys.* **2005**, *5*, 2497-2517.

### **ACKNOWLEDGMENT:**

The authors thank Ronald Cohen and Dick Derwent for addressing the homogeneous-phase chemistry session at the workshop and many workshop participants for contributing to the discussion and providing the basis for this article.



# Accounting for Heterogeneous-Phase Chemistry in Air Quality Models Research Needs and Applications

Below is a list of recommendations to address some of the largest uncertainties, as identified at the *Workshop on Future Air Quality Model Development Needs*. By identifying those aspects of heterogeneous chemistry with the greatest potential to affect air quality modeling predictions, we can better focus resources to improve the treatment of heterogeneous chemistry and its role in atmospheric photochemistry.

by Deborah Luecken  
and Rohit Mathur

**Deborah Luecken** is an atmospheric chemistry modeler and **Rohit Mathur** is a senior science advisor, both with the Atmospheric Modeling and Analysis Division at the U.S. Environmental Protection Agency, Research Triangle Park, NC. E-mail: luecken.deborah@epa.gov.



Understanding the extent to which heterogeneous chemical reactions affect the burden and distribution of atmospheric pollutants is important because heterogeneous surfaces are ubiquitous throughout our environment. They include materials such as aerosol particles, clouds and fog, snow, dust particles, building surfaces, snow packs, and even vegetated surfaces such as grass and leaves.

While heterogeneous surfaces have long been known to be important reaction matrices for atmospheric chemistry,<sup>1,2</sup> emerging laboratory, field, and computational studies continue to demonstrate additional routes for atmospheric chemical reactions on heterogeneous surfaces. From a regulatory perspective, heterogeneous chemistry has the potential to affect several criteria pollutants, including ozone ( $O_3$ ), nitrogen dioxide ( $NO_2$ ), and fine particulate matter ( $PM_{2.5}$ ), as well as the formation of acidic and toxic air pollutants.

While there is evidence that heterogeneous reactions occur, how much do they impact the chemical composition of the atmosphere, and where are the greatest impacts likely to be seen? This is difficult to answer because large uncertainties exist not only in characterizing the

area and characteristics (e.g., size, age, composition, etc.) of reaction surfaces, but also the kinetics of surface reactions. The experimental set-up for measuring heterogeneous chemistry is challenging due to the need to introduce and characterize surface properties, as well as gas-phase and wall chemistry. The wide variety of surface types also adds to the difficulty—building exteriors are very different than water droplets, for example. These surfaces may also be temporally variable; clouds are one example of an ephemeral medium.

For regulatory air quality model (AQM) applications, we need to know how uncertainties and inaccuracies in describing heterogeneous chemical reactions might affect predictions of harmful air pollutants.

## Recommendations to Address Multi-Phase Chemistry Uncertainties

### Quantify the magnitude and uncertainties of aqueous-phase chemistry impacts on secondary organic aerosol (SOA), oxidants, and hazardous air pollutants (HAPs)

The atmospheric aqueous phase—clouds, fog, snow, water layers on particles and other surfaces—provides

many routes for chemical reaction. While more detail in describing chemistry is generally better from a scientific standpoint, complex schemes can dramatically slow down model simulations. AQMs require a careful balance between complexity and computational efficiency. How much detail is needed in aqueous chemistry for models to accurately predict air pollutant concentrations? We recommend using existing knowledge to develop upper bounds of the potential effect of aqueous reactions, including speculative pathways, on model predictions. These upper bound calculations would test the importance of aqueous chemical pathways on sulfate, O<sub>3</sub>, and SOA production, provide guidance on whether the inclusion of such detailed pathways in AQMs is warranted, and help identify additional, major aqueous-phase organic SOA precursors and pathways.

#### **Improve descriptions of heterogeneous dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) hydrolysis pathways**

Heterogeneous reactions of N<sub>2</sub>O<sub>5</sub> with water provide a sink for NO<sub>2</sub>, producing nitric acid (HNO<sub>3</sub>), and impacting O<sub>3</sub> and PM formation. The physical parameters governing this reaction, including the reaction probability ( $\gamma$ ), are uncertain.<sup>3</sup> The importance of this heterogeneous pathway relative to the homogeneous hydrolysis reaction also needs to be quantified. We recommend synthesizing and extending current studies to harmonize heterogeneous and homogeneous pathways and develop a “best estimate” for use in AQMs.

#### **Determine the effect of nitryl chloride (ClNO<sub>2</sub>) formation on criteria pollutants**

When N<sub>2</sub>O<sub>5</sub> reacts heterogeneously with aqueous chloride instead of water, the resulting ClNO<sub>2</sub> provides an alternate pathway which can recycle NO<sub>2</sub> rather than terminate it as HNO<sub>3</sub>.<sup>4</sup> Although this reaction was thought to be important near coastlines, recent measurements indicate that it could also be significant far inland.<sup>5,6</sup> There is uncertainty in the ClNO<sub>2</sub> yield, the emissions of chlorine compounds, and in the potential affect on O<sub>3</sub> and PM<sub>2.5</sub> over regional scales.

#### **Bound the effects of nitrous acid (HONO) formation from urban, soil, and possibly canopy surfaces on O<sub>3</sub>, PM<sub>2.5</sub>, and other species**

HONO is a powerful source of hydroxyl radicals that initiate photochemistry, but HONO concentrations are generally underestimated by AQMs. Heterogeneous, daytime sources of HONO from soils, building surfaces, and vegetated canopies<sup>7-10</sup> have been proposed to account for this “missing” HONO. How much do model predictions of O<sub>3</sub>, PM<sub>2.5</sub>, and other regulated air pollutants depend on accurately reproducing heterogeneous sources of HONO? We recommend extending modeling studies<sup>11</sup>

where surface sources of HONO chemistry are tuned to fit observations of HONO, and examining the effect on O<sub>3</sub> predictions.

#### **Evaluate the importance of snow and ice chemistry for O<sub>3</sub>, PM<sub>2.5</sub> and HAP formation**

The potential role of snow and ice surfaces in photochemically generating reactive trace gases has been recognized.<sup>12</sup> The impact of these reactive gases on modifying concentrations of radicals is another area of much uncertainty. There are ongoing field studies, particularly in the Western United States,<sup>13</sup> through which we hope to learn more about the role of frozen surfaces in O<sub>3</sub> formation. We recommend that the community support and monitor these studies, and use the results to determine whether to invest more intensive resources.

#### **Assess the importance of chemistry on dust particles for regional pollutant concentrations**

Mineral dust is predicted to perturb the nitrogen, sulfur, and photochemical oxidant cycles,<sup>14</sup> but these effects are highly dependent on properties of the surface, such as previous photochemical processing, and number of activated sites. It is unclear how much the uncertainty in our treatment of reaction on dust surfaces might contribute to model error compared to other components in the AQMs. A simple upper bounding study would help modelers determine how much effort should be invested in detailed descriptions of dust chemistry.

#### **Recommendations for Modeling Heterogeneous Chemistry**

##### **Examine whether AQMs appropriately solve chemistry in all phases**

Current models employ operator splitting, whereby the gas and aqueous chemistry are solved separately. The inclusion of heterogeneous reactions necessitates the consideration of feedbacks between chemistry occurring in various phases and surfaces. Consequently, the traditional approach of operator or time splitting employed in most atmospheric chemistry model formulations may need to be revisited. Alternate approaches, wherein homogeneous and heterogeneous chemistry is solved simultaneously, should be considered.

##### **New Direction: Use detailed aqueous schemes to create condensed descriptions for regional models**

While highly detailed aqueous chemical schemes, such as CAPRAM,<sup>15</sup> are important for fully understanding aqueous chemistry, the use of such detail may be computationally prohibitive for most model applications. To account for aqueous chemistry in large-scale routine

simulations, it will be necessary to derive and comprehensively evaluate condensed schemes that strike a balance between representation of reactant compounds and computational efficiency.

### **Improve gas-phase predictions and evaluations of species that participate in heterogeneous chemistry**

Even if we fully understood heterogeneous chemistry, it would be impossible to model correctly if the gas-phase precursors, on which they depend, are not accurately predicted. It is unclear how well current AQMs predict concentrations of noncriteria pollutants and individual volatile organic compounds<sup>16,17</sup> because these are rarely evaluated and not routinely measured.<sup>18</sup> We recommend greater emphasis on accurately describing the concentrations of pollutants in the gas phase, which are key participants in heterogeneous-phase chemistry. This would include measuring concentrations and evaluating model predictions of compounds, such as carbonyls, organic acids, acid anhydrides, organic nitrates, hydroxyl, and nitrate radical.

### **Reduce uncertainties in meteorological parameters that affect heterogeneous chemistry**

The accurate representation of heterogeneous reactions also depends on several meteorological parameters and processes, especially relative humidity, aerosol liquid water, and cloud microphysics. Consequently, assessments of the relative importance of heterogeneous chemistry

through modeling experiments must be conducted in the context of uncertainties in representation of these key meteorological processes and variables.

### **Conclusion**

Numerous heterogeneous reactions occur in the atmosphere, with the potential to perturb gas-phase photochemistry and contribute to secondary organic and inorganic aerosol formation. How important is it to represent heterogeneous chemistry in a detailed manner for the purposes which AQMs are applied now and in the near future and with respect to uncertainties in other processes? There are many gaps in our understanding of aqueous and surface chemistry. If detailed representation does matter, we need to identify which species/matrices are the most important and focus future research in those areas. We need to know whether addressing deficiencies in our current treatment of heterogeneous chemistry in AQMs will make a large difference in predictions of those species of greatest interest for regulatory and research purposes.



Several recommendations listed above describe "bounding studies" using existing knowledge to determine upper limits of the effects of heterogeneous pathways on overall AQM concentration predictions. By identifying those processes that have the greatest potential to change predictions of regulated pollutants, we can focus research efforts where they might have the largest impact on improving human and ecosystem health. em

### **References**

1. Molina, M.J.; Molina, L.T.; Kolb, C.E. Gas-phase and heterogeneous chemical kinetics of the troposphere and stratosphere; *Ann. Rev. Phys. Chem.* **1996**, *47* (1), 327-367.
2. Ravishankara, A.R. Heterogeneous and Multiphase Chemistry in the Troposphere; *Science* **1997**, *276* (5315), 1058-1065.
3. Chang, W.L.; Bhawe, P.V.; Brown, S.S.; Riemer, N.; Stutz, J.; Dabdub, D. Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N<sub>2</sub>O<sub>5</sub>: A Review; *Aer. Sci. Technol.* **2011**, *45* (6), 665-695.
4. Finlayson-Pitts, B.J.; Ezell, M.J.; Pitts, J.N. Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub>; *Nature* **1989**, *337*, (6204) 241-244.
5. Mielke, L.H.; Furgeson, A.; Osthoff, H.D. Observation of ClNO<sub>2</sub> in a Mid-Continental Urban Environment; *Environ. Sci. Technol.* **2011**, *45* (20), 8889-8896.
6. Thornton, J.A.; Kercher, J.P.; Riedel, T.P.; Wagner, N.L.; Cozic, J.; Holloway, J.S.; Dubé, W.P.; Wolfe, G.M.; Quinn, P.K.; Middlebrook, A.M.; Alexander, B.; Brown, S.S. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry; *Nature* **2010**, *464* (7286), 271-274.
7. Zhou, X.; Civerolo, K.; Dai, H.; Huang, G.; Schwab, J.; Demerjian, K. Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York State; *J. Geophys. Res.* **2002**, *107*, 4590; doi:10.1029/2001JD001539.
8. Ammar, R.; Monge, M.E.; George, C.; D'Anna, B. Photoenhanced NO<sub>2</sub> Loss on Simulated Urban Grime; *ChemPhysChem* **2010**, *11* (18), 3956-3961.
9. Stemmler, K.; Ammann, M.; Donders, C.; Kleffmann, J.; George, C. Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid; *Nature* **2006**, *440* (7081), 195-198.
10. Kleffmann, J. Daytime Sources of Nitrous Acid (HONO) in the Atmospheric Boundary Layer; *ChemPhysChem* **2007**, *8* (8), 1137-1144.
11. Elshorbagy, Y.F.; Steil, B.; Brühl, C.; Lelieveld, J. Impact of HONO on global atmospheric chemistry calculated with an empirical parameterization in the EMAC model; *Atmos. Chem. Phys. Discuss.* **2012**, *12* (5), 12885-12934.
12. Grannas, A.; Jones, A.E.; Dibb, J.; Ammann, M.; Anastasio, C.; Beine, H.; Bergin, M.; Bottenheim, J.; Boxe, C.; Carver, G. An overview of snow photochemistry: evidence, mechanisms and impacts; *Atmos. Chem. Phys.* **2007**, *7* (16), 4329-4373.
13. For example, Uintah Basin Winter Ozone Study. See <http://www.esrl.noaa.gov/csd/groups/csd7/measurements/2012ubwos/>.
14. Usher, C.R.; Michel, A.E.; Grassian, V.H. Reactions on Mineral Dust; *Chem. Rev.* **2003**, *103* (12), 4883-4940.
15. Tilgner, A.; Herrmann, H. Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM. *Atmos. Environ.* **2010**, *44* (40), 5415-5422.
16. Stavrakou, T.; Müller, J.F.; De Smedt, I.; Van Roozendael, M.; Kanakidou, M.; Vrekoussis, M.; Wittrock, F.; Richter, A.; Burrows, J.P. The continental source of glyoxal estimated by the synergistic use of spaceborne measurements and inverse modelling; *Atmos. Chem. Phys.* **2009**, *9*, 8431-8446.
17. Doraiswamy, P.; Hogrefe, C.; Hao, W.; Henry, R.F.; Civerolo, K.; Ku, J.-Y.; Sistla, G.; Schwab, J.J.; Demerjian, K.L. A diagnostic comparison of measured and model-predicted speciated VOC concentrations; *Atmos. Environ.* **2009**, *43* (36), 5759-5770.
18. Steiner, A.L.; Cohen, R.C.; Harley, R.A.; Tonse, S.; Millet, D.B.; Schade, G.W.; Goldstein, A.H. VOC reactivity in central California: comparing an air quality model to ground-based measurements; *Atmos. Chem. Phys.* **2008**, *8* (2), 351-368.

### **ACKNOWLEDGMENT:**

The authors gratefully acknowledge Barbara Turpin and Hartmut Herrmann, who provided keynote presentations at the *Workshop on Future Air Quality Model Development Needs*, and the workshop participants who contributed to the identification of issues and recommendations.

### **DISCLAIMER:**

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here. It has been subjected to agency's administrative review and approved for publication.

# Simulation of Secondary Organic Research Needs

by Eladio M. Knipping  
and Donald Dabdub

**Eladio M. Knipping** is a senior technical manager at the Electric Power Research Institute, Washington, DC.

**Donald Dabdub** is a professor of mechanical and aerospace engineering at the University of California, Irvine. E-mail: eknippin@epri.com; ddabdub@uci.edu.

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 ( $\text{PM}_{2.5}$ ) can comprise a large fraction of total concentrations of PM across the United States.<sup>1</sup> 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.<sup>2,3</sup> 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

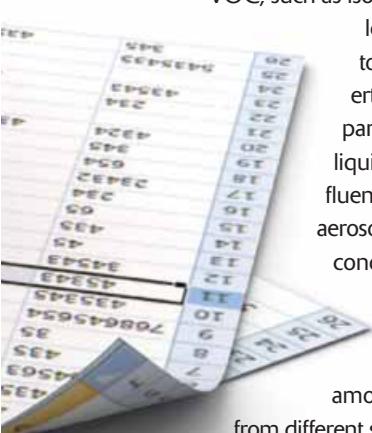


# Aerosols in Regional Air Quality Models

medium for condensation of new organic mass as per gas-particle partitioning theory.<sup>4,5</sup> 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.<sup>6</sup> 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.<sup>7</sup> 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.<sup>8</sup> 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.<sup>9-12</sup> Atmospheric conditions, such as nitrogen oxides ( $\text{NO}_x$ ) levels, can also determine the total amount of aerosol formed from different sources of VOC or POA.<sup>13</sup>



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 mis-represented) 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.

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.

### **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 measurable 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.<sup>14</sup> 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<sub>x</sub> (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<sub>x</sub> 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<sup>15,16</sup> or on carbon number and polarity<sup>17</sup> 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.<sup>18</sup>

### 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.<sup>19</sup> 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

### References and End Notes

- Ng, N.L.; Canagaratna, M.R.; Zhang, Q.; Jimenez, J.L.; Tian, J.; Ulbrich, I.M.; Kroll, J.H.; Docherty, K.S.; Chhabra, P.S.; Bahreini, R.; Murphy, S.M.; Seinfeld, J.H.; Hildebrandt, L.; Donahue, N.M.; DeCarlo, P.F.; Lanz, V.A.; Prevot, A.S.H.; Dinar, E.; Rudich, Y.; Worsnop, D.R. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry; *Atmos. Chem. Phys.* **2010**, *10*, 4625-4641.
- Pun, B.K.; Wu, S.Y.; Seigneur, C.; Seinfeld, J.H.; Griffin, R.J.; Pandis, S.N. Uncertainties in modeling secondary organic aerosols: Three-dimensional modeling studies in Nashville/Western Tennessee; *Environ. Sci. Technol.* **2003**, *37*, 3647-3661.
- Although nucleation of organic vapors to form new particles was and continued to be an area of vibrant research, most air quality models did not, and still do not, explicitly simulate formation of new organic particles.
- Odum, J.R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R.C.; Seinfeld, J.H. Gas/particle partitioning and secondary organic aerosol yields; *Environ. Sci. Technol.* **1996**, *30*, 2580-2585.
- Pankow, J.F. An absorption-model of gas-particle partitioning of organic-compounds in the atmosphere; *Atmos. Environ.* **1994**, *28*, 185-188.
- Volkamer, R.; Jimenez, J.L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L.T.; Worsnop, D.R.; Molina, M.J. Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected; *Geophys. Res. Letts.* **2006**, *33*, L17811; doi:10.1029/2006GL026899.
- Pandis, S.N.; Donahue, N.M.; Robinson, A.L. Atmospheric organic particulate matter: Primary or secondary?; *Geochim. Cosmochim. Acta* **2009**, *73*, A990.
- Robinson, A.L.; Donahue, N.M.; Shrivastava, M.K.; Weitkamp, E.A.; Sage, A.M.; Grieshop, A.P.; Lane, T.E.; Pierce, J.R.; Pandis, S.N. Rethinking organic aerosols: Semivolatile emissions and photochemical aging; *Science* **2007**, *315*, 1259-1262.
- Zhang, Y.; Huang, J.-P.; Henze, D.K.; Seinfeld, J.H. Role of isoprene in secondary organic aerosol formation on a regional scale; *J. Geophys. Res.* **2007**, *112*, D20207; doi:10.1029/2007JD008675.
- Chan, M.N.; Surratt, J.D.; Claeys, M.; Edgerton, E.S.; Tanner, R.L.; Shaw, S.L.; Zheng, M.; Knipping, E.M.; Eddingsaas, N.C.; Wennberg, P.O.; Seinfeld, J.H. Characterization and Quantification of Isoprene-Derived Epoxides in Ambient Aerosol in the Southeastern United States; *Environ. Sci. Technol.* **2010**, *44*, 4590-4595.
- Ervens, B.; Volkamer, R. Glyoxal processing by aerosol multiphase chemistry: Towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles; *Atmos. Chem. Phys.* **2010**, *10*, 8219-8244.
- Volkamer, R.; Zieman, P.J.; Molina, M.J. Secondary Organic Aerosol Formation from Acetylene ( $C_2H_2$ ): Seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase; *Atmos. Chem. Phys.* **2009**, *9*, 1907-1928.
- Pye, H.O.; Chan, A.W.H.; Barkley, M.P.; Seinfeld, J.H. Global modeling of organic aerosol: The importance of reactive nitrogen ( $NO_x$  and  $NO_3^-$ ); *Atmos. Chem. Phys.* **2010**, *10*, 11261-11276.
- Karl, T.; Harley, P.; Emmons, L.; Thornton, B.; Guenther, A.; Basu, C.; Turnipseed, A.; Jardine, K. Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation; *Science* **2010**, *330*, 816-819.
- Kroll, J.H.; Donahue, N.M.; Jimenez, J.L.; Kessler, S.H.; Canagaratna, M.R.; Wilson, K.R.; Altieri, K.E.; Mazzoleni, L.R.; Wozniak, A.S.; Bluhm, H.; Mysak, E.R.; Smith, J.D.; Kolb, C.E.; Worsnop, D.R. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol; *Nat. Chem.* **2011**, *3*, 133-139.
- Donahue, N.M.; Epstein, S.A.; Pandis, S.N.; Robinson, A.L. A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics; *Atmos. Chem. Phys.* **2011**, *11*, 3303-3318.
- Pankow, J.F.; Barsanti, K.C. The carbon number-polarity grid: A means to manage the complexity of the mix of organic compounds when modeling atmospheric organic particulate matter; *Atmos. Environ.* **2009**, *43*, 2829-2835.
- 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.
- Carlton, A.G.; Bhave, P.V.; Napelenok, S.L.; Edney, E.D.; Sarwar, G.; Pinder, R.W.; Pouliot, G.A.; Houyoux, M. Model Representation of Secondary Organic Aerosol in CMAQv4.7; *Environ. Sci. Technol.* **2010**, *44*, 8553-8560.

### ACKNOWLEDGMENT:

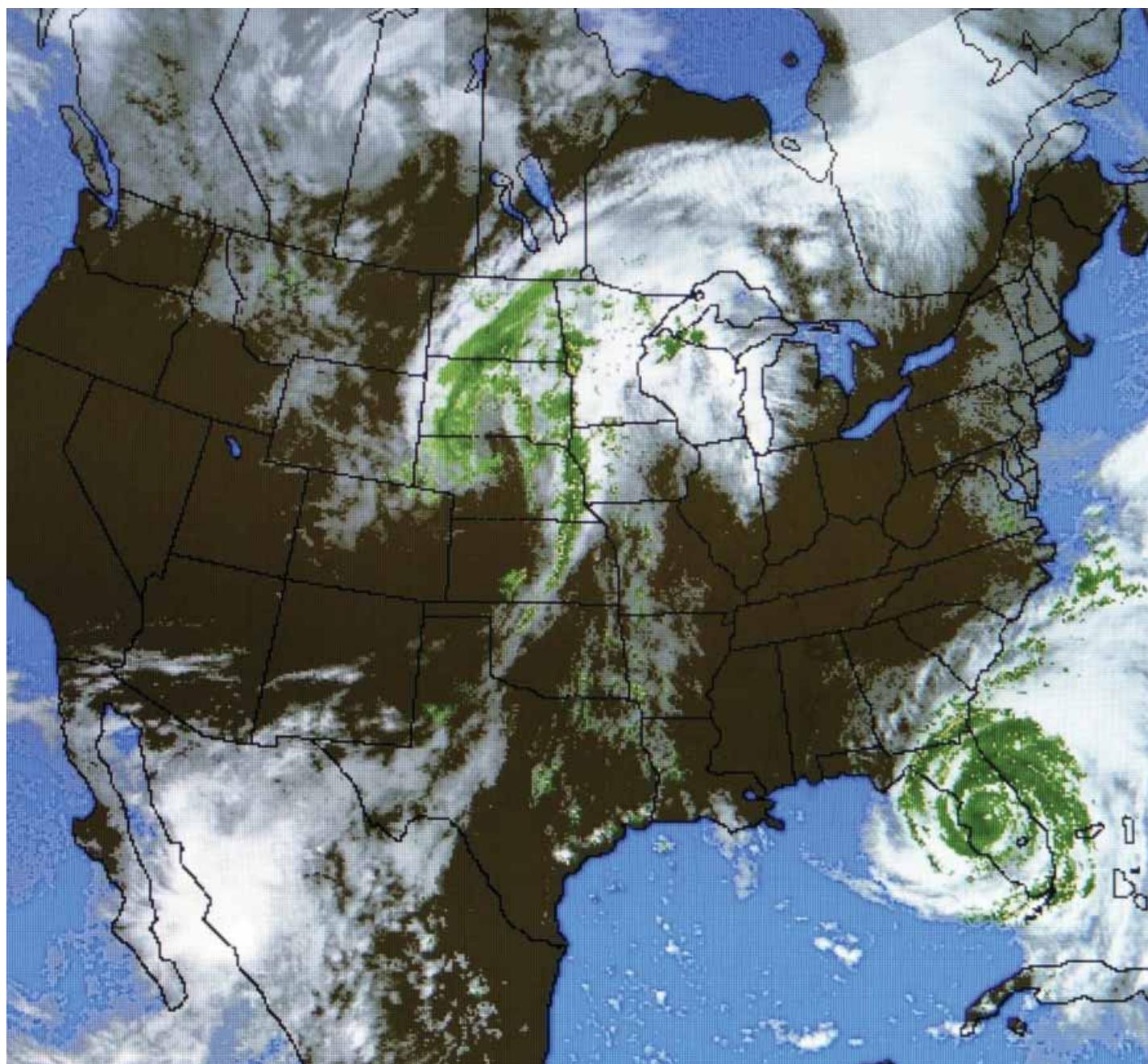
The authors thank Prakash Bhave and Allen Robinson for addressing the secondary organic aerosol session at the workshop and John Seinfeld for his plenary presentation on the topic, as well as many workshop participants for contributing to the discussion and providing the basis for this article.



# Meteorological Processes Affecting Air Quality

## Research and Model Development Needs

The recommendations for further research and development outlined in this article were distilled from the discussions at the *Workshop on Future Air Quality Model Development Needs* and the two invited presentations on "meteorological processes affecting air quality."<sup>1,2</sup> While these recommendations are not exhaustive, they are the product of focused discussions by a group of air quality and meteorology modelers with considerable experience and knowledge.



Meteorology modeling is an important component of air quality modeling systems that defines the physical and dynamical environment for atmospheric chemistry. The meteorology models used for air quality applications are based on numerical weather prediction models that were developed over the past several decades primarily for forecasting the weather. While many of the same characteristics and processes are important for both weather forecasting and for air quality modeling, there are particular meteorological conditions, such as stagnant high pressure systems and convergence zones associated with occluded fronts, which are especially conducive to air pollution episodes, but are of lesser interest to weather forecasters.<sup>3</sup> Furthermore, there is general recognition that many of the greatest uncertainties in air quality modeling systems stem from uncertainties in the dynamical and thermodynamic processes simulated by meteorological models.<sup>4</sup>

There are many meteorological processes affecting air quality. Radiation and cloud cover have direct effects on photolysis rates for photochemistry and are the primary input to the surface energy budget. Surface heating drives the sensible and latent heat fluxes that influence near-surface air temperature and humidity and drive the diurnal evolution of the planetary boundary layer (PBL), which controls the mixing depth for air pollutant dispersion. The three-dimensional wind fields are responsible for advection of trace gases and aerosols. Even small errors in wind speed and direction can result in large displacements of urban and industrial pollutant plumes. In addition to their interactions with radiation, clouds also contribute to aqueous chemistry processes, wet scavenging and deposition, and aerosol processing.

Meteorology also controls surface fluxes of important chemicals, both upward from the surface as emissions of biogenic volatile organic compounds from vegetation and windblown dust and pollen and to the surface as dry deposition. Some chemicals, such as ammonia and mercury, are now being modeled as bi-directional fluxes, where they emit or deposit according to the concentration gradient across the air-surface interface. All of these surface processes are strongly influenced by near-surface atmospheric turbulence, which is controlled by static stability, wind shear, and surface roughness.<sup>5</sup> Vegetation also has important influences on surface exchange processes by direct uptake and/or emissions of pollutants,

by contributing to evaporative moisture fluxes through transpiration, and through greater surface roughness that enhances all surface fluxes.

### **Meteorological Processes Affecting Air Quality: What Are the Gaps?**

Inaccurate model representation of any of the processes mentioned above can lead to errors in air quality modeling results. Thus, it is worthwhile to identify some of the most serious gaps in the ability of meteorological models to adequately represent these processes. Because clouds directly affect so many chemical and physical processes, errors in cloud extent and characteristics propagate to errors in chemical concentrations and depositions. Model analysis studies using synoptic typing have constantly shown much poorer performance for types characterized by cloudiness.<sup>6</sup> Also, a common problem for air quality modelers, particularly forecasters, is whether or not afternoon shallow convection occurs, which can significantly reduce peak afternoon concentrations of ozone and other oxidants, but increase heterogeneous cloud oxidation of important aerosol precursors. Observations of the radiative, oxidative, and turbulent mixing characteristics of shallow cumulus, and their proper treatment within regional transport models, are key gaps in air quality modeling.

Surface level concentrations are very sensitive to the timing of morning and evening transitions in surface fluxes and PBL mixing, which coincide with high emissions during morning and evening rush hours. Hence, accurate modeling of these transitions, which is closely related to land surface processes, is essential for accurate diurnal concentration simulations. Since the highest emission rates are in more developed areas, surface parameterizations that account for the characteristics of urban and suburban developments can improve surface fluxes, near-surface stability, and PBL mixing during these critical transition periods. Considerations such as the heat capacity of built and impervious surfaces, reduced effective albedo due to radiation trapping in street canyons, and high roughness lengths of building canopies can be important for modeling pollutant dispersion at high to medium grid resolutions (1–12 km). While urban schemes have been added to meteorology models such as the Weather Research and Forecasting (WRF) model,<sup>7</sup> they are limited to the grid cells that are predominantly urban land use and are therefore applied mainly to high-resolution urban modeling studies.<sup>8</sup> Thus,

**by Jonathan Pleim and Stuart McKeen**

**Jonathan Pleim, Ph.D.**, is head of the Atmospheric Model Development Branch of the U.S. Environmental Protection Agency's Atmospheric Modeling and Analysis Division. **Stuart McKeen, Ph.D.**, is a research scientist with the Cooperative Institute for Research in Environmental Sciences (CIRES) at University of Colorado and the Chemical Sciences Division in the Earth System Research Laboratory (ESRL) of the National Oceanic and Atmospheric Administration (NOAA). E-mail: pleim.jon@epa.gov; stuart.a.mckeен@noaa.gov.

the effects of development should be routinely incorporated in meteorology and air quality models applied at regional, mesoscale, and local scales.

Other gaps include stable boundary layer and nocturnal low level jets which control long range transport;<sup>9</sup> accurate vegetation distribution, type, and phenology, which are needed for surface fluxes of heat, moisture, and chemistry in all seasons; and chemical fog and cloud deposition in complex terrain (occult deposition). Also, models have difficulty representing flow separation and isolation of stable cold pools, which trap pollutants for extended periods leading to high concentrations. Such cold pool pollution events are common in the western United States predominantly in the winter.<sup>10</sup>

## **Recommendations**

### **Improve data assimilation, including new data sources for wind, temperature, water vapor, clouds, and chemistry**

Meteorological modeling for air pollution applications has long relied on four-dimensional data assimilation (FDDA) for retrospective simulations for research and regulatory planning and assessment. A variety of techniques, such as grid analysis nudging, spectral nudging, and observation nudging are available in meteorological modeling systems like the WRF model. A well-designed FDDA strategy incorporating a variety of measurement data and using techniques most appropriate for the scale and objectives of the modeling study can maintain the accuracy of the simulation over unlimited durations.<sup>11</sup> However, recent studies have shown that grid analysis nudging in the lowest model layers, even when limited to only wind nudging, results in greater errors throughout the PBL than restricting FDDA to layers above the PBL.<sup>12</sup> A critical need is to augment the twice-daily radiosonde observations with spatially denser and more frequent vertical profile data from radar wind profilers, velocity azimuth display (VAD) profiles from the National Weather Service's Doppler radar network, and commercial aircraft measurements (ACARS). Additional observations of clouds, moisture, and surface temperature can be derived from satellite retrievals and used for FDDA. Assimilation of chemical data from satellites, aircraft, and surface networks also needs to be developed.

### **Improve model physics for PBL, shallow convective clouds, land surface models (LSM)/surface fluxes, deep convection, and precipitation**

Since certain aspects of physical processes in meteorological models are more important for air quality applications than for weather forecasting, the needed improvements are likely to come from the air quality modeling community. For example, while PBL processes are important to weather forecast modeling (WFM), the diurnal evolution

of turbulent mixing and PBL depth are much more important for chemical transport modeling (CTM). In particular, the rate of morning PBL growth controls entrainment from aloft and influences the photochemical regime. Similarly, shallow convective clouds are more important for CTM than WFM because they influence photolysis, PBL venting, and aqueous chemistry. Land surface modeling in meteorology and air quality models should be harmonized and further developed to represent heat fluxes (latent and sensible heat fluxes) and chemical fluxes (dry deposition, bi-directional exchange, and biogenic emissions) with maximum consistency using common datasets (e.g., land-use and vegetation indexes) and common parameterizations.

### **Improve modeling of removal processes**

Wet and dry removal processes are the predominant atmospheric loss terms for aerosols, and important gas-phase species that are soluble, highly oxidized, or otherwise assimilated at the earth's surface. Within mass budget estimates and as a source to many ecosystem model applications, reducing uncertainties in the absolute magnitude and physical representation of wet and dry removal processes is often a critical need. Ammonia is a prime example where the bi-directionality of surface fluxes requires adequate estimation of the deposition terms.<sup>13</sup> Although a mature physical understanding exists for the processes determining the dry deposition of particulate matter (PM) and its constituents, routine regional or continental scale observations do not currently exist, and the set of available observations is limited by the land-use categories sampled and by large variability within the reported measurements.<sup>14</sup>

By contrast, a reasonable North American surface network exists for wet deposition analysis of a few important PM anions and cations, but current model formulations are unable to account for important laboratory and field observations such as the PM size-dependence of rainwater scavenging coefficients. Physical parameterizations of gas-phase and PM constituent scavenging by snow and rain, and the transformations occurring during hydrometeor evaporation/sublimation are essentially unconstrained due to the lack of observations and measurements. Support for observations, laboratory measurements, and the development of physical parameterizations related to wet and dry deposition are certainly needed, but typically overlooked within the air quality model community.

### **Develop better coupled or integrated meteorological and chemistry models**

Coupled (or in-line) meteorological and chemistry models have been available for more than a decade and are valuable research tools used to study interactions between the chemistry-aerosol-cloud-radiation-climate

#### **ACKNOWLEDGMENT:**

The authors thank Jerome Fast and Leiming Zhang for their presentations at the workshop on meteorology affecting air quality and the workshop participants.

#### **DISCLAIMER:**

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here. It has been subjected to agency's administrative review and is approved for publication.

systems. The indirect feedback effects of aerosol on cloud properties and precipitation are estimated to be one of the largest unknowns related to anthropogenic climate forcing, and the meteorological impact of extreme aerosol events (e.g., dust outbreaks and forest fires) has been shown to be significant in recent on-line model applications.<sup>15</sup> Thus, continued research into the coupling between aerosols and radiation, aerosol and clouds, and clouds and radiation, deserves resources and support. This should also include the application of advanced computational architectures, modeling frameworks, and numerical infrastructure in support of these computationally demanding calculations. Aside from aerosol feedback studies, air quality applications are increasingly requiring high spatial and temporal resolution, and often the only means of incorporating the effects of model-resolved turbulence is via tight temporal coupling between transport variables from the meteorology with the aerosol and chemistry constituents. Again, support for large, coupled models with documented numerical integrity that are available to both regulatory and research communities is essential for near- and long-term advancements in air quality modeling.

#### New Direction: Adapt air quality modeling to more flexible grid structures and coordinates

As domestic emissions are reduced and global emissions continue to increase, particularly in Asia, the chemical lateral boundary conditions (LBC) used for limited-area

modeling are becoming increasingly important fractions of modeled concentrations and deposition.<sup>16</sup> Currently, most modeling studies extract LBCs from global model simulations, which in principle is a distinct advancement over the previous practice of using constant LBCs. However, in practice, inconsistencies in chemical mechanisms and speciation and large discontinuities in grid resolution contribute to significant errors. A promising new direction is the development of global icosahedral chemistry/meteorology models with grid refinement. Such models can represent the spatial continuum from global to local scales with chemical and dynamical consistency and seamless resolution refinement. One challenge of such multi-scale modeling, however, is the need to develop “scale-aware” physics, particularly for convective cloud parameterizations.



#### Conclusions

The recommendations resulting from this workshop have primarily focused on the application of air quality modeling systems, which include meteorology models, for retrospective analysis and decision support for air quality regulators. Modeling systems developed for air quality forecasting have many of the same issues and gaps, but also present their own unique challenges. For example, reliance on data assimilation for reducing model error is limited to the initialization stage of forecast model runs. Thus, realistic physics and accurate input data are even more critical for air quality forecast systems.<sup>17</sup> em

#### References and End Notes

- Fast, J. Meteorological Processes Affecting Air Quality: Clouds. Presented at *The Workshop on Future Air Quality Model Development Needs, September 12-13, 2012, Arlington, VA*.
- Zhang, L. Dry and Wet Removal Processes in Air Quality Models—Status, Gaps, and Needs. Presented at *The Workshop on Future Air Quality Model Development Needs, September 12-13, 2012, Arlington, VA*.
- Seaman, N.L. Meteorological modeling for air-quality assessments; *Atmos. Environ.* **2000**, *34*, 2231-2259.
- Vautard, R.; Moran, M.D.; Solazzo, E.; Gilliam, R.C.; Matthias, V.; Bianconi, R.; Chemel, C.; Ferreira, J.; Geyer, B.; Hansen, A.B.; Jericevic, A.; Prank, M.; Segers, A.; Silver, J.D.; Werhahn, J.; Wolke, R.; Rao, S.T.; Galmarini, S. Evaluation of the meteorological forcing used for the Air Quality Model Evaluation International Initiative (AQMEII) air quality simulations; *Atmos. Environ.* **2012**, *53*, 15-37.
- Pleim, J.E.; Ran, L. Surface Flux Modeling for Air Quality Applications; *Atmosphere* **2011**, *2*, 271-302.
- Appel, K.W.; Gilliland, A.B.; Sarwar, G.; Gilliam, R.C. Evaluation of the Community Multiscale Air Quality (CMAQ) model version 4.5: Sensitivities impacting model performance: Part I—Ozone; *Atmos. Environ.* **2007**, *41*, 9603-9615.
- Chen, F. et al. The integrated WRF/urban modeling system: development, evaluation, and applications to urban environmental problems; *International J. of Climatol.* **2011**, *31*, 273-288.
- Chen, F.; Miao, S.; Tewari, M.; Bao, J.-W.; Kusaka, H. A numerical study of interactions between surface forcing and sea breeze circulations and their effects on stagnation in the greater Houston area; *J. Geophys. Res.* **2011**, *116*, D12105; doi:10.1029/2010JD015533.
- Godowitch, J.M.; Gilliam, R.C.; Rao, S.T. Diagnostic evaluation of ozone production and horizontal transport in a regional photochemical air quality modeling system; *Atmos. Environ.* **2011**, *45*, 3977-3987.
- Silcox, J.D.; Kelly, K.E.; Crosman, E.T.; Whiteman, C.D.; Allen, B.L. Wintertime PM2.5 concentrations during persistent, multi-day cold-air pools in a mountain valley; *Atmos. Environ.* **2012**, *46*, 17-24.
- Otte, T.L. The Impact of Nudging in the Meteorological Model for Retrospective Air Quality Simulations. Part I: Evaluation against National Observation Networks; *J. Appl. Meteor. Climatol.* **2008**, *47*, 1853-1867.
- Gilliam, R.C.; Godowitch, J.M.; Rao, S.T. Improving the horizontal transport in the lower troposphere with four dimensional data assimilation; *Atmos. Environ.* **2012**, *53*, 186-201.
- Zhang, L.; Wright, L.P.; Asman, W.A.H. Bi-directional air-surface exchange of atmospheric ammonia—A review of measurements and a development of a big-leaf model for applications in regional-scale air-quality models; *J. Geophys. Res.* **2010**, *115*, D20310.
- Pryor, S.C.; Gallagher, M.; Sievering, H.; Larsen, S.; Barthelmie, R.J.; Birsan, F.; Nemitz, E.; Rinne, J.; Kulmala, M.; Grönholm, T.; et al. A review of measurement and modelling tools for quantifying particle atmosphere-surface exchange; *Tellus* **2008**, *60B*, 42-75.
- Wong, D.C.; Pleim, J.; Mathur, R.; Binkowski, F.; Otte, T.; Gilliam, R.; Pouliot, G.; Xiu, A.; Young, J. O.; and Kang, D. WRF-CMAQ two-way coupled system with aerosol feedback: software development and preliminary results; *Geosci. Model Dev.* **2012**, *5*, 299-312.
- Zhang, L.; Jacob, D.J.; Boersma, K.F.; Jaffe, D.A.; Olson, J.R.; Bowman, K.W.; Worden, J.R.; Thompson, A.M.; Avery, M.A.; Cohen, R.C.; Dibb, J.E.; Flock, F.M.; Fuellberg, H.E.; Huey, L.G.; McMillan, W.W.; Singh, H.B.; Weinheimer, A.J. Transpacific transport of ozone pollution and the effect of recent Asian emission increases on air quality in North America: an integrated analysis using satellite, aircraft, ozonesonde, and surface observations; *Atmos. Chem. Phys.* **2008**, *8*, 6117-6136.
- Daubbert, W.; Carroll, M.A.; Baumgardner, D.; Carmichael, G.; Cohen, R.; Dye, T.; Ellis, J.; Grell, G.; Grimmond, S.; Hanna, S.; Irwin, J.; Lamb, B.; Madronich, S.; McQueen, J.; Meagher, J.; Odman, T.; Pleim, J.; Schmid, H.P.; Westphal, D.L. Meteorological Research Needs for Improved Air Quality Forecasting: Report of the 11th Prospectus Development Team of the U.S. Weather Research Program; *Bull. Am. Meteorol. Soc.* **2004**, *85*, 563-586.