Atmospheric System Research

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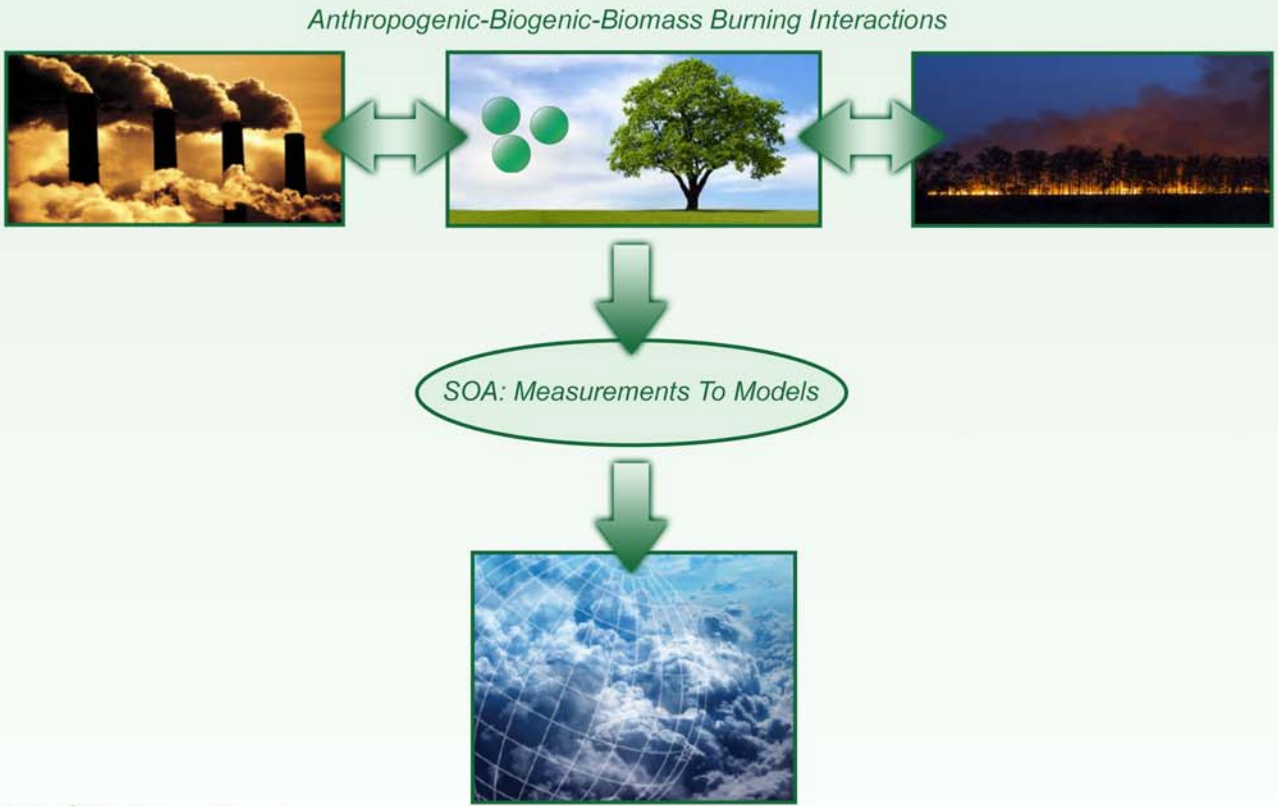
New Strategies for Addressing Anthropogenic-Biogenic Interactions of SOA in Climate Models



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New Strategies for Addressing Anthropogenic-Biogenic Interactions of SOA in Climate Models

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Executive Summary

The uncertainties in representing aerosols and their effect on climate forcing are much larger than the well-constrained positive forcing due to the increase of carbon dioxide concentration. Secondary organic aerosol (SOA) is often the dominant component of fine and ultrafine particulate matter throughout the globe. Volatile organic compounds (VOCs) emitted from combustion activities such as fossil fuel and biomass burning, and also naturally from terrestrial vegetation and the marine biosphere, are oxidized in the atmosphere to form lower volatility organic vapors. These oxidized organic vapors play a fundamental role in setting number size distribution of atmospheric particles by potentially participating in the nucleation of new particles and driving their subsequent growth from ~1 nm, representing molecular clusters, to the larger sizes that influence radiation and clouds. Our understanding of changes in aerosol climate effects from preindustrial to present-day is therefore strongly tied to our ability to represent the impacts of VOC oxidation on aerosol particle formation and growth.

A number of studies over the past 5 years, many of which were funded by U.S. Department of Energy (DOE) Atmospheric System Research (ASR), produced groundbreaking fundamental insights about processes governing SOA particles; however, several of these processes are yet to be included in atmospheric models. In order to identify the most critical recently discovered processes that could make a large impact on the radiative effects of SOA and to discuss future development needs, a DOE ASR-sponsored workshop titled “New Strategies for Addressing Anthropogenic-Biogenic Interactions of Organic Aerosols in Climate Models” was held at PNNL on June 8 and 9, 2015. This workshop also fostered collaborative strategies designed to develop and implement new measurement-based modeling paradigms for SOA particles that enable rapid progress in addressing some of the major questions related to the radiative effects of SOA. The workshop covered the following seven themes based on the latest advances in our understanding of the processes governing the SOA life cycle:

1. Acidity, sulfate, and water effects on isoprene SOA formation

2. Role of low-volatility and extremely low-volatility organics on new particle formation, number concentration of cloud condensation nuclei (CCN), SOA loadings, and lifetimes

3. Role of SOA viscosity/phase on SOA growth and CCN activity

4. Anthropogenic emissions interacting with biogenic SOA

5. Importance of biomass burning for SOA

6. Mechanistic insights from laboratory studies of SOA formation pathways

7. Modeling approaches to represent interactions between aerosols and clouds.

These themes all have crosscutting contributions to current modeling uncertainties that can be broadly classified as relating to the SOA burden and lifetime and to mechanisms of particle growth to sizes relevant for both CCN and the scattering and absorption of radiation.

The workshop participants recognized that recent measurement-based findings indicate a need for substantial changes in process-level representations of SOA particles in climate models. Under each of

the seven workshop themes, the report describes those critical missing processes that workshop participants identified for parameterization in atmospheric SOA models in the near term based on recent measurement-based insights. Some of these processes include:

- Gas-phase chemical reactions associated with isoprene epoxydiol (IEPOX) formation, and an IEPOX-driven isoprene-SOA source that depends on particle-phase reactions
- Reactions producing low-volatility and extremely low-volatility organics (LVOC and ELVOC) and their dependence on anthropogenic species, such as NO_x
- Diffusion-controlled SOA growth kinetics
- Process-based understanding of anthropogenic-biogenic interactions, such as the dependence of SOA on NO_x regimes
- SOA formation due to aging of organics emitted from biomass burning
- SOA hygroscopic behavior in subsaturated and supersaturated conditions.

All of these processes impact particle formation and growth and consequently the global CCN budget, but are mostly neglected by global climate models. Findings from recent DOE Atmospheric Radiation Measurement (ARM) Climate Research Facility campaigns (e.g., Carbonaceous Aerosols and Radiative Effects Study [CARES], Green Ocean Amazon [GoAmazon], and Biogenic Aerosol Effects on Clouds and Climate [BAECC]) and laboratory studies should be exploited more effectively to constrain parameters used to describe these processes. The workshop report also suggests future research directions in terms of using integrated model-measurements approaches that could solve outstanding issues related to the uncertainties in the radiative effects of SOA for each theme. Several fruitful directions were discussed, including:

- Reducing the uncertainty in key parameters that govern IEPOX uptake kinetics
- Improving understanding of the evolution of viscosity and volatility distribution of ambient organics as a function of source-type, combustion conditions, and their atmospheric multigenerational aging
- Investigating LVOC and ELVOC formation through newly discovered pathways as gas-phase autoxidation and particle-phase accretion/oligomerization
- Deriving SOA yields and volatility distributions using physically realistic aging parameterizations that include both functionalization and fragmentation reactions, diffusion-controlled SOA growth kinetics, and also including processes, such as wall losses of condensable organic vapors
- Investigating additional process-level anthropogenic-biogenic interaction pathways, e.g., interactions between SOA and polycyclic aromatic hydrocarbons (PAHs)
- Quantifying the effects of SOA on ice nuclei and their resulting feedbacks on clouds

- Investigating the effects of grid spacing and subgrid-scale processes on SOA formation as well as the effects of cloud and aqueous phase aerosol chemistry

- Using field and laboratory measurements coupled with satellite products to evaluate the ability of climate models to predict SOA formation in regions affected by strong emissions sources such as biomass burning.

Focused and collaborative chamber and field experiments combined with further evaluation and development of our modeling tools could be conducted. In these collaborative studies, several research groups could come together to address the key questions related to the radiative effects of SOA as outlined in this study. Participants also agreed that one significant effort in the next 5 years must be aimed at the development and implementation of simplified mechanisms that faithfully represent the mechanistic understanding of SOA developed to date. This will also increase confidence in century-timescale climate simulations focused on understanding present-day, preindustrial, and future climate changes.

The findings of this workshop report formed the basis of a new review article on SOA that was recently published in *Reviews of Geophysics* (Shrivastava et al. 2017).

Acknowledgement

The workshop organizers Manish Shrivastava and Joel Thornton thank all the scientists, listed in Appendix B of this report, who actively participated in the workshop discussions and/or provided their valuable feedback and comments during the preparation of this report. We appreciate the speakers (Jiwen Fan, Steven Ghan, Allen Goldstein, Alex Guenther, Tuukka Petäjä, Jeff Pierce, Pontus Roldin, Siegfried Schobesberger, John Shilling, Manish Shrivastava, James Smith, Rahul Zaveri, Alla Zelenyuk, Joel Thornton, Jian Wang) who gave talks to stimulate the discussions about the cutting-edge, emerging findings in the SOA field, and those who served as facilitators (Alex Guenther, Jeffrey Pierce, Philip Rasch, John Shilling, Manish Shrivastava, James Smith, Rahul Zaveri, Alla Zelenyuk, Joel Thornton) for the different themes during the workshop. We especially thank John Seinfeld, Douglas Worsnop, and Christopher Cappa for providing useful feedbacks during this activity. We are also thankful to Jerome Fast, Ian Kraucunas, and Charlette Geffen for providing their support during this important activity, and to Emily Davis, Alyssa Cummings, and Kathy Westcott for workshop logistics. Finally, we thank Ashley Williamson for critical feedbacks during the inception and execution of the workshop.

Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research program
BAECC	Biogenic Aerosols-Effects on Clouds and Climate
BBOP	Biomass Burning Observation Project
BVOC	biogenic volatile organic compound
CARES	Carbonaceous Aerosols and Radiative Effects Study
CCN	cloud condensation nuclei
DOE	U.S. Department of Energy
ELVOC	extremely low-volatility organic compound
FIGAERO	Filter Inlet for Gases and Aerosols
GoAmazon	Green Ocean Amazon
HO_2	hydroperoxyl radical, also known as the perhydroxyl radical
HR-ToF-CIMS	High-Resolution, Time-of-Flight Chemical Ionization Mass Spectrometer
IEPOX	isoprene epoxydiols
IN	ice nuclei
IVOC	intermediate volatility organic compound
LASIC	Layered Atlantic Smoke Interactions with Clouds
LVOC	low-volatility organic compound
MEGAN	Model of Emissions of Gases and Aerosols from Nature
NO	nitric oxide
NVSOA	non-volatile secondary organic aerosol
OA	organic aerosol
OH	hydroxyl radical
PAH	polycyclic aromatic hydrocarbon
PNNL	Pacific Northwest National Laboratory
POA	primary organic aerosol
RH	relative humidity
RO_2	peroxy radical
SGP	Southern Great Plains
SOA	secondary organic aerosol
SVOC	semi-volatile organic compound
VOC	volatile organic compound
VFR	volume fraction remaining
WRF-Chem	Weather Research and Forecasting Model coupled with Chemistry

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1.0 Introduction

Aerosol forcing constitutes one of the largest uncertainties affecting our ability to project future climate change (Stevens and Feingold 2009; Stocker et al. 2013). Organic aerosol (OA) is a major component of submicron-size atmospheric aerosols throughout the globe (Zhang et al. 2007) and originates from both anthropogenic and natural processes. OA includes directly emitted primary organic aerosol (POA), and secondary organic aerosol (SOA) formed in the atmosphere by chemical reactions of organic gases emitted from a variety of sources such as fossil-fuel consumption, biomass burning, and natural vegetation. It is becoming clear that there are important interactions between natural sources of SOA and anthropogenic pollution. For example, many studies indicate that present-day anthropogenic pollution has most likely increased the amount of biogenic SOA (e.g., Shilling et al. 2013; Spracklen et al. 2011). Anthropogenic emissions such as NO_x also affect the CCN number grown by biogenic SOA through the formation of low-volatility organics (Ehn et al. 2014; Jokinen et al. 2015). In addition, land-use changes in the present day compared to preindustrial times have also affected biogenic VOC emissions. All these processes have made large potential impacts on the radiative effects of SOA in the present day compared to preindustrial times. Due to these non-linear interactions between human and natural systems, there could be even larger variations in regional forcing of SOA compared to the global average. Climate models mostly ignore such interactions (e.g., Carslaw et al. 2013), and therefore likely miss potentially important changes in direct and indirect aerosol effects due to anthropogenic activities.

A key need is to determine how the interactions between natural biogenic emissions and anthropogenic pollutants such as SO_2, NO_x, sulfate, nitrate, and ammonia quantitatively affect predictions of direct and indirect aerosol radiative forcing. Addressing this question requires a better fundamental understanding of: 1) the relevant physical and chemical processes that affect SOA formation and its atmospheric burden and lifetimes, and 2) the impact of biogenic SOA on the growth of aerosol particles to sizes that efficiently scatter solar radiation and act as cloud condensation nuclei. A major goal for the aerosol community should be to improve regional and global earth system model treatments of SOA using measurement-based fundamental insights for more accurate estimates of the magnitude of aerosol and cloud radiative effects.

Over the past 5 years, several studies, many of which were funded by the U.S. Department of Energy (DOE) Atmospheric System Research (ASR), produced groundbreaking fundamental insights about the formation and atmospheric evolution of SOA particles and the interactions between anthropogenic and natural biogenic emissions, as discussed in this report. However, these insights are not yet incorporated in most current-generation climate models. In view of this discrepancy, a DOE ASR-sponsored workshop titled "New Strategies for Addressing Anthropogenic-Biogenic Interactions of Organic Aerosols in Climate Models" was held at DOE's Pacific Northwest National Laboratory (PNNL) on June 8 and 9, 2015.

The main objectives of the workshop were twofold: 1) identify, through facilitated discussions, recently discovered SOA life cycle processes of high potential impact that are missing in climate models, and 2) define crosscutting collaborative strategies to develop and implement these new measurement-based paradigms in climate models. The ultimate goal is to develop a strategy for making more rapid progress in solving some of the major questions related to aerosol radiative effects, e.g., 1) How can we obtain a more quantitative understanding of anthropogenic-biogenic interactions affecting SOA formation based on process-level insights? and 2) What is the impact of new measurement-based findings on the radiative effects of SOA?

These goals align with the missions of the DOE ASR program, which aims towards “improving fundamental process-level understanding of aerosols and their interactions with clouds and radiation in order to reduce the uncertainty in regional and global climate simulations.” The workshop covered the following main themes based on the latest advances in our understanding of the processes governing the SOA life cycle:

1. Acidity, sulfate, and water effects on isoprene SOA formation
2. Role of low-volatility and extremely low-volatility organics on new particle formation, number concentrations of cloud condensation nuclei (CCN), SOA loadings, and lifetimes
3. Role of SOA viscosity/phase on SOA growth and CCN activity
4. Anthropogenic emissions interacting with biogenic SOA
5. Importance of biomass burning for SOA
6. Mechanistic insights from laboratory studies of SOA formation pathways
7. Modeling approaches to represent interactions between aerosols and clouds.

The workshop participants recognized that many of the latest process-level insights under these themes have not yet been transferred to climate models, and remedying this deficiency might make large impacts on climate model predictions of SOA radiative effects. This report focuses on what has been learned in the last 5 years, based on results from the latest laboratory and field campaigns supported by DOE and other agencies. Participants discussed how this new information could be added to models at multiple scales, from simple box models to regional and global climate models, and noted an immediate need to evaluate the sensitivities of SOA radiative effects predicted by climate models to these missing processes. In some cases, the climate modeling community will have to change some decades-old model parameterizations, and continue to use more measurements to constrain the parameterized processes. Participants also recognized that since the processes governing SOA are complex, it would benefit the aerosol modeling community if we were to identify the most critical interactions governing SOA, and then develop “minimal representations” that include those interactions for driving longer-timescale climate simulations to understand their impacts on climate forcing.

2.0 Summary of SOA Themes

2.1 Acidity, Sulfate, and Water Affecting Isoprene SOA

Isoprene is the most abundantly emitted biogenic VOC on a global basis, but was thought to be an insignificant source of SOA up to ~2008. However, several studies suggest that isoprene SOA yields are significant, but that they vary depending on both the photochemical interactions of radical intermediates with anthropogenic species such as NO_x (Xu et al. 2015a; Xu et al. 2014), and on particle-phase reactions involving liquid water, sulfate, and ammonia (Eddingsaas et al. 2010; Gaston et al. 2014). For example, recent evidence from both field measurements and chamber studies indicates that IEPOX is formed under low nitric oxide (NO) conditions due to reactions of isoprene with OH radicals, and this IEPOX species reacts in ambient particles to form organosulfates, 2-methyltetrols, and oligomers thereof, which can contribute significantly to ambient SOA due to either their low volatility or high solubility (Paulot et al.

2009; Surratt et al. 2010; Surratt et al. 2008; Surratt et al. 2007). This multi-phase chemistry of IEPOX SOA is schematically illustrated in Figure 1. So-called IEPOX SOA from isoprene has been found to account for 15-30% of total OA in some places, such as the southeastern United States during the summer (Xu et al. 2015a).

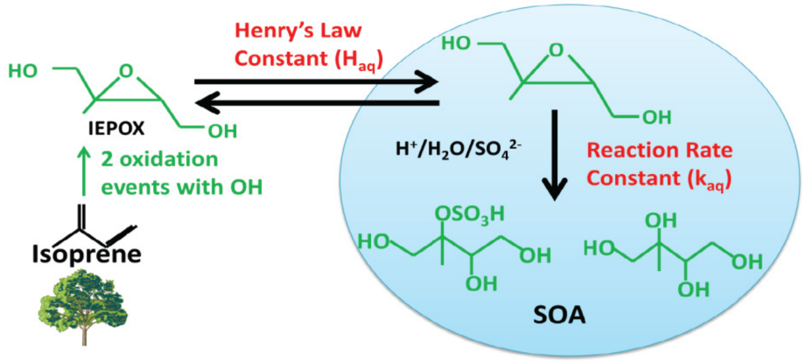

Figure 1. Multi-phase chemistry of IEPOX resulting in SOA formation under low NO_x conditions. Only a few of the IEPOX-derived SOA components are shown for simplicity.

2.1.1 Advances

2.1.1.1 Sulfate Effects

In the past few years, the community has constrained the reactive uptake of gas-phase IEPOX on aqueous acidified inorganic aerosols with uncertainties of ~10% (Eddingsaas et al. 2010; Gaston et al. 2014). In addition, recent field measurements have consistently shown that IEPOX SOA is highly correlated with sulfate aerosols (e.g., Xu et al. 2015a). Carslaw et al. (2013) suggested that natural emissions affect the uncertainty in the aerosol indirect effects by affecting the background aerosol state. Anthropogenic SO_2 and sulfate emissions have maximized and begun to decrease across North America and Europe, and the sulfate burden is expected to decrease further in the future. The interactions between sulfate and isoprene SOA suggest that biogenic SOA, which in some cases has been considered to be a natural, nearly invariant, component of background aerosol (Carslaw et al. 2013), could instead also vary as a function of anthropogenic sulfate, thereby altering our understanding of the changes in aerosol abundance that have occurred since preindustrial times.

2.1.1.2 IEPOX SOA Yield

Recent laboratory work has determined that the IEPOX SOA mass yield from the reactive uptake of IEPOX may be <15% (Riedel et al. 2015). This work combined constraints on the reactive uptake rate of IEPOX (Eddingsaas et al. 2010; Gaston et al. 2014) with the observed mass growth of aerosol particles. While needing further confirmation, such information is crucial for implementing this process into models. In addition, Gaston et al. (2014) showed that the presence of organic coatings could suppress reactive uptake of IEPOX on acidified seeds. This observation points to a possible self-limiting pathway in the formation of IEPOX SOA, wherein, as more IEPOX SOA forms, further uptake of IEPOX is hindered by the growth of an organic coating.

2.1.1.3 SOA Lifetime Effects due to Oligomers

Continuing advances in online chemical characterization of SOA particles and associated gas-phase organics have provided unprecedented insights about gas-particle partitioning and other processes governing the properties and lifetime of SOA. For example, measurements using the dual-cell, semi-volatile thermal desorption aerosol gas chromatograph (SV-TAG, described in Isaacman et al. [2014]) during the Green Ocean Amazon, GoAmazon 2014/5 field campaign, showed that a major fraction of methyl-tetrols (a part of IEPOX SOA) reside in the particle phase, contrary to their expected semi-volatile nature (Isaacman et al. 2015). In addition, both laboratory and field measurements using the Filter Inlet for Gases and Aerosols (FIGAERO) coupled to a high-resolution, time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) instrument have shown that both tetrols and triols/furan diols (comprising IEPOX SOA) thermally desorb from aerosol particles at orders-of-magnitude-lower volatilities than their pure-component saturation vapor concentrations (Lopez-Hilfiker et al. 2015a). Thus, IEPOX SOA appears to be mostly low-volatility material, even though the measured components constituting IEPOX SOA (such as triols and tetrols) are semi-volatile. The most plausible explanation for this behavior is that these particle-phase IEPOX SOA components are in the form of oligomers or organosulfates, which affect their volatility and evaporation characteristics.

2.1.1.4 Isoprene Emission Distributions

Airborne direct flux measurements during the GoAmazon field campaign revealed new insights into the processes controlling the regional and seasonal variations in isoprene emissions. Dry-season emissions were shown to be more than a factor of two higher than in the wet season. Emissions from upland tropical forest landscapes were significantly higher than the isoprene emission rates observed for bottomland forests (Gu et al. 2015). These emissions are not captured in the default Model of Emissions of Gases and Aerosols from Nature (MEGAN) that is widely used for estimating biogenic SOA precursor emissions in atmospheric models such as WRF-Chem (Fast et al. 2014; Knote et al. 2015; Shrivastava et al. 2013a; Shrivastava et al. 2015; Shrivastava et al. 2011; Shrivastava et al. 2013b). Because of the short lifetime of isoprene (~ 1 hour), these spatial and temporal variations, not considered in current models, could lead to large differences in the amount of isoprene available for SOA production at a given location and time.

2.1.2 What Could Go into Climate Models?

Most current climate models do not include an acidity- and particle-phase-dependent, IEPOX-driven SOA source, which could vary regionally and globally, due to variations in emissions of anthropogenic and biogenic precursors. The gas-phase IEPOX production and its dependence on oxidants and NO could be easily implemented in models by using existing simplified gas-phase chemical mechanisms. Similarly, the IEPOX reactive uptake kinetics on inorganic seed particles, and its dependence on aerosol acidity and relative humidity (RH) has been well studied (e.g., Eddingsaas et al. 2010; Gaston et al. 2014). Suitable parameterizations of these uptake processes exist, and can be implemented in atmospheric models with aerosol chemistry. Similarly, new isoprene emission parameterizations are being developed and tested against DOE field measurements such as GoAmazon (e.g., Gu et al. 2015), and can be integrated into climate models. However, there is a need to continuously develop and evaluate biogenic VOC emissions parameterizations at other locations and times to simulate their spatial and temporal heterogeneities and better integrate land-atmosphere interactions within these models.

2.1.3 What Needs More Investigation?

In the real atmosphere, the particle seeds available for IEPOX uptake are not purely inorganic, but are a mixture of several chemical constituents including organics. Gaston et al. (2014) showed that the uptake kinetics of IEPOX decrease with increasing organic mass fraction in the particle-phase. The effects of organic coatings on reducing the reactive uptake of IEPOX on sulfate aerosols needs to be further investigated to refine the estimates of the IEPOX uptake rate. Such an understanding is important to establish how IEPOX SOA formation may vary between preindustrial times, the present day, and the future as sulfate emissions vary. At present, robust upper limits on the IEPOX SOA formation rate can be calculated, given inputs of aerosol surface area and inorganic composition. However, there is a limited understanding of IEPOX SOA formation in mixed organic-inorganic particles such as inorganics coated with SOA particles. Furthermore, the effects of temperature and relative humidity on IEPOX SOA formation and properties need to be investigated. For example, increasing RH increases the water content of particles, and thus decreases particle acidity and potentially changes IEPOX solubility. Gaston et al (2014) found only a small (factor of 2) effect of RH on the IEPOX reactive uptake efficiency between 30 and 70% RH. Reactive uptake was relatively enhanced at low RH, and the enhancement could be explained by the increased kinetics at higher acidity. All else being constant, RH could further impact the competition between sulfate and water as nucleophiles, and thus the distribution of products. Thus, sulfate, water, and acidity have convoluted interactions. While a robust mechanistic understanding of their competing roles on IEPOX SOA formation is developing, an expanded set of laboratory measurements at RH higher than 70% could improve model parameterizations.

Useful insights on IEPOX uptake and SOA formation could also be obtained by looking at the kinetics of size-distribution evolution. The relative rates between gas-phase mass transfer and particle-surface reactive uptake kinetics govern the evolution of particle size-distributions. If reactive uptake kinetics are faster, the size evolution will be surface-area controlled, whereas a slower reactive uptake means that the size evolution is limited by H^* and is volume controlled. If the uptake process is surface-area controlled, the size distribution will narrow to a greater extent during growth than if the uptake is volume controlled. Recent studies of IEPOX uptake kinetics on laboratory-generated inorganic aerosols and macroscopic solution (Eddingsaas et al. 2010; Gaston et al. 2014) suggest a volume-controlled process for typical atmospheric aerosol particles. Reactive uptake kinetics are also critical for understanding IEPOX lifetimes and transport, which could significantly affect regional variations of SOA loadings in the atmosphere. While these mechanistic processes should continue to be investigated, there should also be a focus on further constraining the IEPOX SOA yields. Recent laboratory and field measurements provide valuable constraints on IEPOX SOA yields, which can in turn be used to evaluate the sensitivity of SOA radiative effects to IEPOX-driven SOA formation in climate models.

To quantify regional- and global-scale impacts of sulfate-mediated isoprene SOA formation pathways, any mechanistic insights incorporated into models should be able to explain measurements from different regions of the world. Thus, we need to use data collected in the Southeast U.S., the Amazon, the boreal forests, etc., to assess factors controlling isoprene SOA such as aerosol phase water, particle acidity, etc.

Any additional controlling parameters identified through such model-measurement comparisons can then be investigated under controlled laboratory conditions.

2.2 Role of Low-Volatility and Extremely Low-Volatility Organics

Volatility is a fundamental property of SOA that governs the formation of new particles and their growth to CCN sizes. For example, extremely low-volatility organics (ELVOCs) with saturation vapor concentrations $C^{*} \leq 10^{-3}$ μg m^{-3} (Ehn et al. 2014) condense to particle surface area and efficiently promote new particle formation and growth, while other semi-volatile organics (C^{*} ranging 1-1000 μg m^{-3}) would condense on particle volume, limited by particle-phase diffusivity (Zaveri et al. 2014), which has important implications for CCN production.

2.2.1 Advances

Recently, several studies suggest that a major fraction of ambient SOA has an effective volatility orders of magnitude lower than that previously assumed, and SOA can be treated as effectively non-volatile—i.e., of such low volatility that it would not evaporate under atmospheric conditions (Cappa and Jimenez 2010; Ehn et al. 2014; Lopez-Hilfiker et al. 2015a; Shrivastava et al. 2013b; Vaden et al. 2011). In addition, other studies have shown that SOA is condensing as if it is non-volatile during the growth of new particles (Pierce et al. 2011; Riipinen et al. 2011), which could be due to either the formation of ELVOCs in the gas-phase phase and subsequent condensation, or particle-phase transport limitations (described in section 2.3), or a combination of the two. The low-volatility organics are essential for the growth of ultrafine particles to CCN sizes in many parts of the atmosphere, and have a large impact on the overall CCN budget (D'Andrea et al. 2013). While the formation of low-volatility organic vapors has generally been attributed to multigenerational successive gas-phase oxidation of VOCs through functionalization reactions (Robinson et al. 2007), recent studies have identified the following new potential pathways:

- A direct gas-phase autoxidation pathway leading to direct formation of ELVOC at significant yields (Ehn et al. 2014; Jokinen et al. 2015).
- Condensation and/or reactive uptake of organic vapors followed by particle-phase accretion reactions (Cappa and Wilson 2011; Lopez-Hilfiker et al. 2015b; Shiraiwa et al. 2013; Ziemann and Atkinson 2012), or organic salt formation (Yli-Juuti et al. 2013).

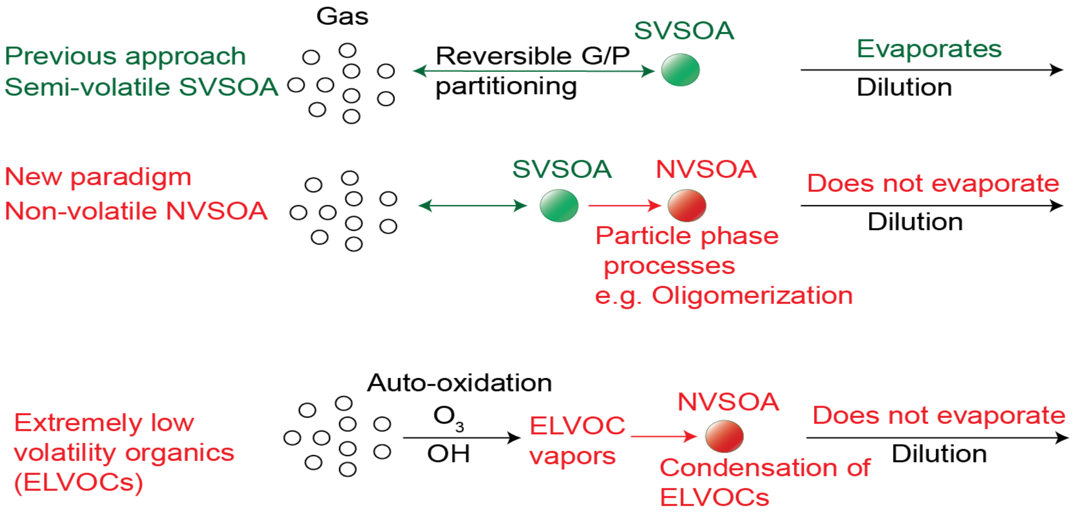

Figure 2. Pathways to formation of low-volatility and extremely low-volatility organics as compared to the default semi-volatile SOA treatment used in most aerosol models.

Each of these pathways likely contributes to the low volatility of SOA (also indicated schematically in Figure 2). Due to its low volatility, this SOA can often be treated as non-volatile SOA (NVSOA) under most atmospherically relevant conditions. The potential importance of both pathways for SOA formation has been established in the past 5 years. The community has made some progress in investigating the role of these pathways on the loadings and spatial distribution of SOA within climate models (Jokinen et al. 2015; Shrivastava et al. 2015; Shrivastava et al. 2013b). For example, a global modeling study compared SOA loadings calculated by the default semi-volatile approach to one in which particle-phase processes lead to the formation of NVSOA as illustrated in Figure 3. The NVSOA approach increased the average lifetime of SOA substantially (by a factor of 3), and also increased the SOA burden by up to a factor of 5, most notably in continental outflow over clean marine environments, as illustrated in Figure 3 (Shrivastava et al. 2015). Since cloud albedo is especially sensitive to aerosols over pristine locations such as the oceans (Carslaw et al. 2013), this increase in SOA burdens could have large implications on cloud albedo and radiative forcing. Another modeling study showed that inclusion of ELVOC increased the number concentration of CCN in pristine areas such as the Amazon (Jokinen et al. 2015). However, a comprehensive treatment of the combined effects of low-volatility organics with C^* ranging 0.01-1 µg m^{-3} (LVOC) and ELVOC due to gas-phase auto-oxidation and particle-phase accretion is still missing in climate models.

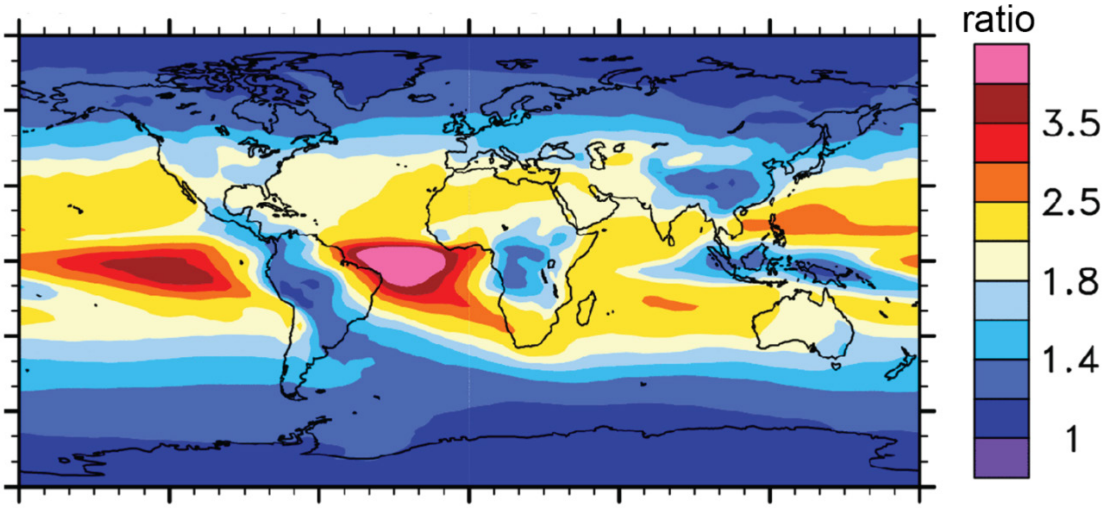

Figure 3. Simulated global annual mean ratio of SOA burdens from the non-volatile to semi-volatile SOA treatment, adapted from Shrivastava et al. (2015).

2.2.2 What Could Go into Models Now?

The effects of the recent measurement-based discoveries of ELVOC and LVOC on SOA loadings, SOA spatial distribution, and CCN number concentrations can be investigated in climate models with a relatively small effort needed to incorporate the basic features. A quantitative understanding of how this treatment affects the radiative effects of SOA is needed. For example, auto-oxidation processes responsible for the formation of ELVOC will depend on NO concentrations (Ehn et al. 2014) as well as VOC emissions and oxidant concentrations; the latter also depend upon NO. Thus, the net effect on ELVOC due to anthropogenic changes in NO_x through fuel combustion or VOC through land-use change is best determined with a fully coupled atmospheric chemistry model. The importance of these anthropogenic feedback processes on ELVOC formation, and the resulting climate forcing, should then be investigated with climate models.

ELVOC formation also depends strongly on the chemical structure of biogenic VOCs and oxidant levels. While biogenic VOCs emitted from boreal forests (mainly comprised of monoterpenes) efficiently produce ELVOCs due to ozonolysis, emissions representative of the tropics (mainly isoprene) produce minor quantities of ELVOCs due to oxidation by hydroxyl radicals (OH) (Jokinen et al. 2015). Additional insights on LVOC and ELVOC yields come from different field campaign measurements such as DOE GoAmazon (isoprene-dominated environments) (Martin et al. 2015) and Biogenic Aerosols-Effects on Clouds and Climate (BAECC) (terpene-dominated) (Petäjä 2013; Petäjä et al. 2015). These findings will need to be integrated in climate models to account for the large expected spatial and temporal (seasonal) heterogeneities in SOA formation and their climate effects.

2.2.3 What Needs To Be Done To Further Constrain the Models?

Part of the challenge in assessing the importance of the formation of ELVOCs and low-volatility SOA stems from the limited understanding of how these pathways depend on precursor identity and concentrations, oxidant identity and concentrations, NO_x levels, concentrations of atmospheric bases (e.g., ammonia and amines), and atmospheric variables such as temperature and relative humidity. For example, it is still not established how gas-phase autoxidation and subsequent ELVOC formation varies as a function of temperature. Similarly, the role of NO_x on ELVOC formation needs to be more carefully assessed given that there may be competition between fragmentation, which can lower ELVOC yields, and formation of organic nitrate functional groups, which can increase SOA yields by substantially lowering volatility. Aerosol water could also play an important role in particle-phase oligomerization and organic salt formation, thereby affecting the volatility of SOA. For example, a recent study showed that aging of SOA particles at high relative humidity reduces the effective volatility of these particles compared to dry conditions (Wilson et al. 2015). Figure 4 illustrates that the effective volatility of SOA particles reduces significantly with time as the particles are left in the dark bag for ~24 hours at elevated RH conditions as compared to fresh SOA formed at very low RH (Wilson et al. 2015). However, some oligomers might be subject to hydrolysis (Hallquist et al. 2009). Such competing effects of water need to be better quantified and mechanistically understood. Particle-phase reactions that drive reactive uptake of organics and contribute to SOA formation need to be investigated under atmospherically relevant conditions. Measurements should investigate formation of low-volatility organics as a function of precursor type, as well as NO_x, oxidant, and base concentrations, and also investigate whether the formation and lifetime of low-volatility organics changes with atmospheric variables such as radiation, temperature, and relative humidity. Climate models need to include the dynamic changes in formation and evolution of low-volatility organics as a function of these variables.

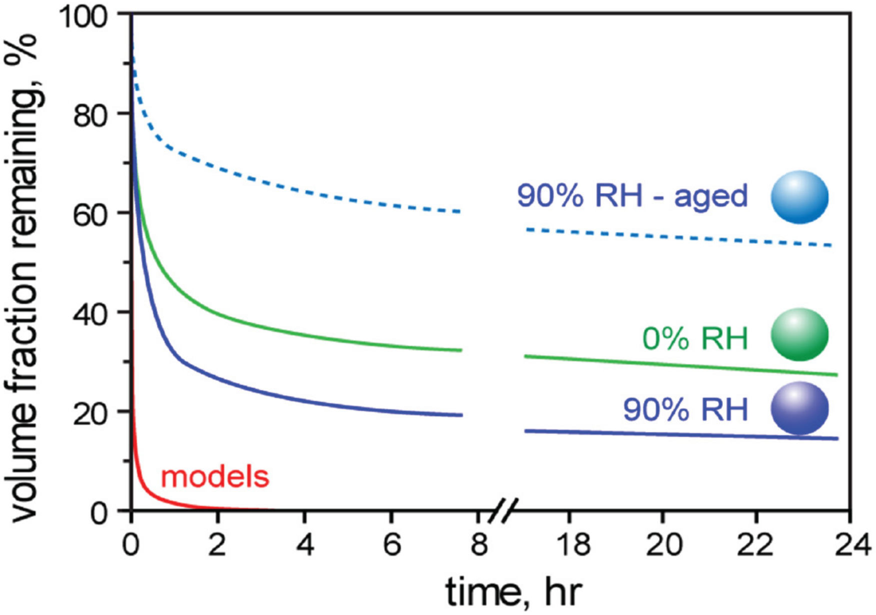

Figure 4. Effects of relative humidity on the room temperature evaporation kinetics of SOA particles, adapted from Wilson et al. (2015).

Another important consideration is how to obtain more accurate estimates of the vapor pressures of highly oxidized multifunctional organics relevant for SOA formation. Current approaches use functional group contribution methods to estimate the vapor pressure of these highly oxidized multifunctional organics, which are uncertain by orders of magnitude. Lumped volatility distributions derived from fitting smog chamber measurements highly depend on the theory used to derive these fits. Better characterization of volatilities of these organic compounds would reduce the uncertainties in quantifying their role in SOA formation.

Speciation of compounds most relevant to biogenic SOA formation has to be improved through measurements. Further, additional or modified source categories need to be added to models based on their relative roles in SOA formation. Current models generally use a very limited number of categories (e.g., isoprene, monoterpenes) with fixed properties, which likely do not capture the variability in SOA formation potential between different biogenic VOCs. Since different biogenic VOCs have very different ELVOC formation potentials depending on their chemical structure and oxidant type—e.g., ozonolysis-pathways for monoterpenes, and oxidation by OH radicals for isoprene (Jokinen et al. 2015)—we need better speciation of these VOCs in inventories as a function of land-use type and representation of their chemistry in models. Current biogenic VOC emission models such as MEGAN have a framework in place for calculating emissions of individual biogenic VOC species, but lack the detailed set of observations needed for parameterizing these emissions. Field measurements of speciated VOCs (e.g., aircraft flux measurements) in different regions are needed to parameterize these emissions as a function of vegetation type and land-use. In addition, since emission spectra of biogenic VOCs such as monoterpenes could vary by species type and with the diversity within trees (Back et al. 2012), detailed ground-based flux and chamber emission studies in different environments would be needed and this variability should be included in atmospheric models.

2.3 Role of Viscosity/Phase on Size Evolution of SOA and CCN

For the past two decades, regional and global climate models have represented SOA particles as well-mixed, liquid-like solutions that continuously maintain equilibrium with the gas phase by mixing and evaporation/ condensation. The atmospheric evolution of these particles has been described by absorptive partitioning theory (Donahue et al. 2006; Pankow 1994), typically with an assumption of "instantaneous equilibrium". This assumption, when applied to the atmosphere or to interpretation of chamber experiments, requires that condensed-phase diffusion is sufficiently fast that equilibrium is achieved on short timescales (< a few minutes). Such a fast diffusion process implies that the particles are well mixed, and are in equilibrium with the gas-phase. However, recent advances in measurements of SOA suggest that under several atmospherically relevant conditions, condensed-phase diffusion processes are much slower than assumed, and this has important implications on the size evolution of SOA and CCN number.

2.3.1 Recent Advances

In sharp contrast to previously used assumptions, recent experimental data indicate that under many conditions SOA particles are not liquid-like solutions, but are highly viscous semi-solids (Abramson et al. 2013; Cappa and Wilson 2011; Kuwata and Martin 2012; Renbaum-Wolff et al. 2013; Vaden et al. 2011; Vaden et al. 2010; Virtanen et al. 2010; Wilson et al. 2015). Viscosity is also found to be a function of relative humidity and SOA precursor type. In general, increasing RH decreases the viscosity of particles (Bateman et al. 2015; Renbaum-Wolff et al. 2013). Thus, viscosity of SOA particles could exhibit a dynamic range in the atmosphere as a function of precursor type and RH conditions. Viscosity and associated particle-phase diffusivity affects the equilibration of semi-volatile organic compound (SVOC) vapors with particles. The uptake of SVOC is particle-phase diffusion-controlled for semi-solids, and volume-controlled for liquid-like particles. Compared to standard models, which assume instantaneous gas-particle equilibrium where partitioning of SVOCs is proportional to pre-existing liquid-like organic mass (through Raoult's law), high viscosity will slow down SOA growth rates for large particles. Zaveri et al. (2014) developed a new SOA modeling framework that takes into account the effect of particle-phase diffusion in viscous particles on the size distribution dynamics. Figure 5, adapted from Zaveri et al.

(2014), illustrates that both bulk particle-phase diffusivity and the volatility of the condensing gas-phase species (C_g^*) have large effects on the evolution of the aerosol number size distribution. Particles with the smallest bulk-diffusivity (and highest viscosity) exhibit the most pronounced narrowing in their size distribution, similar to a reference case that assumes surface-area (gas-kinetic) controlled growth (the “instantaneous reaction” case in Figure 5d), while larger liquid-like bulk diffusivities approach the Raoult’s law partitioning case (volume-controlled growth). For a given bulk-diffusivity, this narrowing in the size distribution is more pronounced as the volatility of the condensing gas decreases. Zaveri et al. (2014) also showed that diffusion time scales increase with particle size, so that smaller particles are able to compete much more effectively to absorb semi-volatile vapors, resulting in enhanced growth of ultrafine particles to optically and CCN-active sizes.

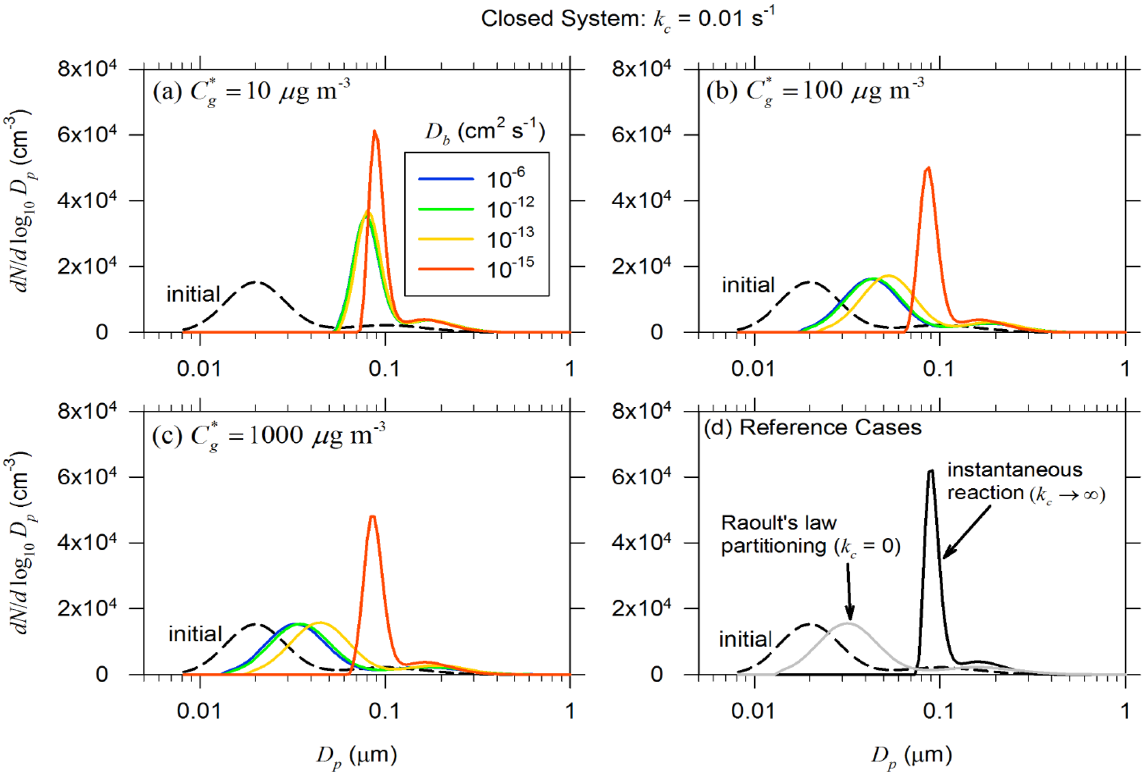

Figure 5. Evolution of aerosol number size distribution showing the initial (dashed line) and final (solid line) size distributions for different bulk particle-phase diffusivities and condensing gas-phase species with three different volatilities from Zaveri et al. (2014).

2.3.2 What Could Go into Models Now?

The effects of high viscosity on inhibiting the uptake of semi-volatile organics on larger particles could have large impacts on the evolution of size distribution of aerosols and production of CCN. On one hand, the increase in mass transfer timescales to larger highly viscous SOA particles increases the availability of semi-volatile organics for growing smaller particles to CCN sizes. On the other hand, the semi-volatile vapors could also react further in the gas-phase to form low-volatility vapors or be lost due to gas-phase fragmentation and depositional scavenging. In addition, different combinations of volatility of SOA precursors and viscosity of SOA (as illustrated in Figure 5) can result in different regimes of the evolution of SOA size distribution. For example, as discussed in section 2.2, the condensation of ELVOC is a particle-surface-area-controlled process. In comparison, the condensation of semi-volatile organics is controlled by both particle-phase diffusion and the volatility of the condensing species. New model parameterizations that explicitly account for the effects of SOA precursor volatility, including ELVOC formation, changes in particle volatility due to accretion reactions, and the diffusion-controlled SOA growth, need to be implemented in models to test their impacts on the global CCN budget. The resulting impacts on the production of climatically active particles and their direct and indirect radiative effects could then be investigated using regional and global climate models.

2.3.3 Future Work to Constrain the Models

Laboratory experiments need to focus on understanding the size evolution of SOA particles and the effects of viscosity and volatility for a range of SOA precursors emitted from different sources, e.g., biogenic, fossil fuel, and biomass burning, over the atmospherically relevant RH and temperature range under different precursor and oxidant regimes. While direct ambient measurements of SOA viscosity are not available and are challenging, several insights could be gained from laboratory measurements in terms of how different atmospherically relevant conditions could affect the viscosity of these particles. These insights could be used to develop new model parameterizations that capture SOA formation and size distribution dynamics accounting for the dynamic changes in SOA viscosity as a function of precursor type, aerosol mixing state, aging, and meteorological variables (temperature and relative humidity). Note that the availability of ELVOCs and semi-volatile organics also depends on several other factors such as emissions, oxidant availability, and their deposition/scavenging. Errors in simulating the availability and relative amounts of these organics (e.g., ELVOCs vs. semi-volatile organics) could partially offset the errors in process-level representations of SOA within earth systems models. Constraining these processes will reduce the offsetting errors in simulating other variables such as emissions, and increase our ability to predict the size evolution of SOA.

2.4 Impacts of Anthropogenic Emissions on Biogenic SOA

The global budget of SOA is highly uncertain and previous global modeling estimates of SOA loadings and their radiative effects differ by up to an order of magnitude (Myhre et al. 2009; Spracklen et al. 2011). A large part of this uncertainty is due to limitations in our understanding of the interplays between anthropogenic, biomass burning, and biogenic emissions and their roles in SOA formation.

Observations of large fractions of modern carbon (indicating a non-fossil-fuel source) in aerosols, even in urban areas, has led to a search for conditions under which anthropogenic emissions enhance biogenic SOA formation, and some studies have included proxy mechanisms for reactions between anthropogenic and biogenic precursors forming SOA (Hodzic and Jimenez 2011; Spracklen et al. 2011). However, these sources of “anthropogenically influenced SOA” do not provide a physical basis to estimate how this influence has changed over time or will change in the future. The workshop recognized that there is a need to start identifying and including specific, recently discovered, process-level interactions between anthropogenic, biogenic, and biomass burning emissions affecting SOA formation, which are not represented in climate models.

2.4.1 Advances

2.4.1.1 Recent Pathways for Anthropogenic-Biogenic Interactions

In previous sections, we highlighted mechanisms by which anthropogenic sulfur emissions might enhance biogenic SOA formation by promoting multiphase chemistry related to isoprene epoxy diols. Importantly, measurements show that anthropogenic emissions may not always enhance biogenic SOA, but may reduce it, or have otherwise non-linear effects due to interactions between NO_x and other radical species. As NO_x and sulfur emissions have been correlated in the past, incorporating such competing effects into models is the only way to fully assess the net outcome on SOA budgets. As illustrated in Figure 6, Xu et al. (2014) found that both the volatility and mass yield of chamber-generated isoprene SOA exhibited a non-linear dependence on NO_x levels. The non-linear behavior in volume fraction remaining (VFR) was interpreted as being possibly the result of an optimum NO_x concentration for facilitating oligomerization (Nguyen et al. 2011). The chemistry of organic peroxy radicals (RO_2) with NO_x could be responsible for this non-linearity in SOA yields. In addition, the composition of oligomers and their volatility could also depend on NO_x conditions (Hallquist et al. 2009; Xu et al. 2014).

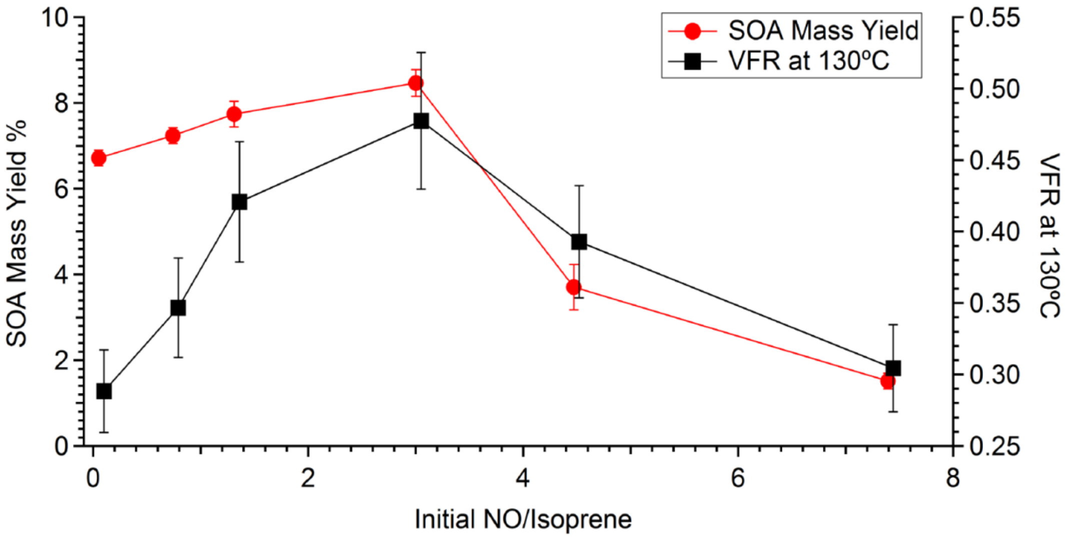

Figure 6. Dependence of SOA mass yield and volume fraction remaining on initial NO/isoprene ratio, adapted from Xu et al. (2014).

The reactions of RO_2 with HO_2 and NO_2 produces mostly lower-volatility products (though thermally labile ones in the case of NO_2), while the RO_2+NO reaction can form higher-volatility products via fragmentation of the resultant RO radical for some precursors (Atkinson 1997; Hatakeyama et al. 1989; Kroll and Seinfeld 2008). The yield and fate of organic nitrates formed during oxidation of monoterpenes and isoprene will alter this simplified picture, and is an area of active research.

Similarly, analyzing data collected during the 2010 DOE Carbonaceous Aerosols and Radiative Effects Study (CARES 2010) field campaign, Shilling et al. (2013) and Setyan et al. (2012) showed that production of OA was enhanced when anthropogenic emissions mixed with biogenic isoprene-rich air, and suggested that NO_x concentrations played a strong role in enhancing isoprene SOA. In addition, Setyan et al. (2012) further showed that mixed anthropogenic and biogenic emissions likely played an important role in the frequent new particle formation events observed during CARES. However, a mechanistic understanding of the interactions between anthropogenic and biogenic emissions was still missing.

Climate forcing depends strongly on how well we understand preindustrial aerosols (Carslaw et al. 2013). A new laboratory chamber study funded by the DOE ASR program (under review) measured isoprene SOA yields of up to 15% (larger than most previous reports) in the absence of pollutants such as NO_x and acidic sulfate particles, a situation that could be thought to represent preindustrial conditions (Liu et al. 2015). Using a global model, the study suggested that isoprene SOA yields may have decreased substantially in the present day due to anthropogenic pollution (such as NO_x) compared to preindustrial times. Similarly, another recent study suggested that previously measured isoprene SOA yields under both low NO_x and high NO_x conditions have been underestimated by factors of three and two, respectively, due to effects of losses of organic vapors to the walls of the smog chamber, discussed further in section 2.5 (Zhang et al. 2014). Again, the global aerosol forcing in the light of these new findings should be included and quantified in models.

A key mechanism that couples biogenic and anthropogenic emissions in SOA production is the oxidation of biogenic volatile organic compounds (BVOC) by the nitrate radical (NO_3), derived from the emissions and oxidation of nitrogen oxides. Not only is the BVOC+NO_3 chemistry an efficient SOA formation mechanism (Boyd et al. 2015; Fry et al. 2014; Griffin et al. 1999) under several monoterpene-dominated environments, but it is also a major pathway for the production of organic nitrates, which are important reservoirs (if not sinks) of atmospheric NO_x. Recent studies have identified an OA subtype (referred to as LO-OOA) that contributes substantially to ambient OA, peaks at night, and correlates well with particulate organic nitrates (Xu et al. 2015a; Xu et al. 2015b) in the southeast USA. These measurements clearly indicate that nitrate radical chemistry can play an important role in SOA formation, but its effects on SOA yields could vary with the structure of the biogenic VOCs, and need to be investigated in models. Moreover, the importance of NO_3 chemistry is likely to vary significantly vertically in the atmosphere, even within the first 1 km, given that the largest impact is at night when vertical mixing is suppressed and isoprene emissions have ceased. Field campaigns that provide vertically resolved observations of nocturnal NO_3-BVOC chemistry are critical for constraining the actual importance of this pathway.

Interestingly, the presence of polycyclic aromatic hydrocarbons (PAHs) during SOA formation was recently shown to drastically reduce SOA evaporation and thus its “effective volatility” (Zelenyuk et al. 2012). The PAH-SOA interactions represent another mechanism whereby anthropogenic PAHs (emitted from a variety of combustion sources including fossil fuels and biomass burning) enhance SOA formation yields, and SOA particles, in turn, shield PAHs from atmospheric chemical degradation. These synergistic PAH-SOA interactions represent another potentially important anthropogenic-biogenic interactions pathway that is not represented in current climate models.

2.4.2 What Can Be Investigated in Models Now?

Climate models need to include the latest mechanistic insights gained from recent measurements. For example, current atmospheric SOA models treat the effects of NO_x at best as a linear combination of SOA formation under two extremes (“low NO_x and “high NO_x” conditions) (Lane et al. 2008; Pye et al. 2010; Shrivastava et al. 2011). Clearly, the recently discovered non-linear effects of NO_x on SOA formation, as described above, are missing and need to be included in these models. Similarly, the recently discovered enhanced isoprene SOA yields under low NO_x conditions, both in the absence of acidic sulfate seeds (e.g., Liu et al. 2015, described above) and the presence of acidic seeds (multiphase chemistry of IEPOX SOA discussed in section 2.1), need to be included. The importance of $BVOC+NO_3$ chemistry as a night-time SOA formation mechanism (Boyd et al. 2015; Fry et al. 2014; Griffin et al. 1999) could also be included, and evaluated with analysis of field measurements that identify the contribution of particulate organic nitrates. Recent DOE field measurements of OA such as during CARES 2010, BAECC 2014, and the GoAmazon 2014/5 campaigns could be used to investigate the importance of NO_x and NO_3 chemistry for SOA. For example, a recent study measured significant contributions of organic nitrates to SOA mass during the BAECC campaign using the FIGAERO HR-ToF-CIMS (Thornton 2015).

2.4.3 What Needs To Be Done in the Future?

We suggest an integrated model/measurements framework for reducing some of the largest uncertainties governing the radiative effects of SOA. For example, multigenerational aging parameterizations and losses of vapors and particles could be included when fitting SOA yield and volatility distributions to chamber data, so that these chamber results could be better extrapolated to longer atmospheric timescales within regional and global models. At the same time, these multigenerational aging parameterizations need to be physically realistic. Since oxidation of organics results in both functionalization and fragmentation reactions (Chacon-Madrid and Donahue 2011; Kroll et al. 2011; Lambe et al. 2012), both these types of reactions need to be included in SOA models. A new study pointed out that fragmentation of SOA precursor VOCs and oxidation products can substantially decrease the amount of SOA formed globally (Shrivastava et al. 2015). However, the functionalization-fragmentation branching ratio is not well constrained and depends on the VOC considered and the relative reaction rates between NO_x, HO_2, and RO_2 radicals (Loza et al. 2014; Xu et al. 2014). Thus, we need to evaluate and constrain the ability of current mechanisms to parameterize the dependence of SOA on radical budgets and VOC precursor. This need in turn requires molecular-level information on the radical intermediates and the closed-shell gas and particle-phase reaction products to elucidate the mechanisms by which gas-phase VOC are oxidized and converted into SOA components.

The atmospheric relevance of mechanistic pathways discovered in the laboratory relating to the interactions between anthropogenic and biogenic emissions should be assessed by analyzing field campaign measurements such as GoAmazon, CARES, and BAECC. The available comprehensive radical and SOA precursor measurements, although rare (e.g., measured at BAECC), could be analyzed to understand the relationships between precursor types, oxidant chemistry, and combustion emissions. Such measurements in Barrow, Alaska or at ARM's Southern Great Plains (SGP) site would also be highly beneficial, when a comprehensive in situ campaign is operated in close connection with aircraft measurements, and connected to active remote-sensing measurements performed at the site.

2.5 Importance of Biomass Burning for SOA

2.5.1 Advances

Biomass burning emissions have large impacts on the OA budget. Measurements in both field and laboratory have reported that a major fraction of non-methane organic compounds emitted from biomass burning emissions could be in the semi-volatile and intermediate volatility (SVOC and IVOC) range, i.e.,

$1 \leq C^{*} \geq 10^{6}$ μg m^{-3} (Yokelson et al. 2013), which are important SOA precursors, and are missing in most atmospheric models. A global modeling study (Shrivastava et al. 2015) found that biomass burning S/IVOC emissions are the largest contributors to OA globally. Figure 7 illustrates that when the multigenerational aging of biomass burning S/IVOC emissions were included as described by Shrivastava et al. (2015), the model agreement with measurements was improved significantly compared to the previous approach. Most aerosol models have treated only the oxidation of certain VOCs as a source of SOA from biomass burning emissions, and neglected the contribution of S/IVOC emissions. However, several studies have indicated the importance of rapid oxidation processes of compounds emitted from biomass burning comprising a broad spectrum of volatility (including S/IVOCs), leading to formation of substantial amounts of SOA (Grieshop et al. 2009; Hennigan et al. 2011; Hennigan et al. 2012; Heringa et al. 2011; Ortega et al. 2013). In addition, several field studies showed evidence of substantial increase of biomass burning aerosol mass and particle number concentrations and also their oxidation state during their atmospheric transport (Akagi et al. 2012; Hobbs et al. 2003; Vakkari et al. 2014; Yokelson et al. 2009)). Evidence from other studies clearly indicates that SOA particle loadings due to oxidation of biomass burning emissions could be higher than POA particle loadings (Lee et al. 2008; Yokelson et al. 2009). Recently, monoterpenes and sesquiterpenes were also detected in biomass burning emissions in both field and laboratory studies (Akagi et al. 2013; Hatch et al. 2015; Stockwell et al. 2015). Their role in SOA formation due to reactions with anthropogenic species (such as NO_x) and oxidants as NO_3 radicals could be of similar importance as biogenic terpenes.

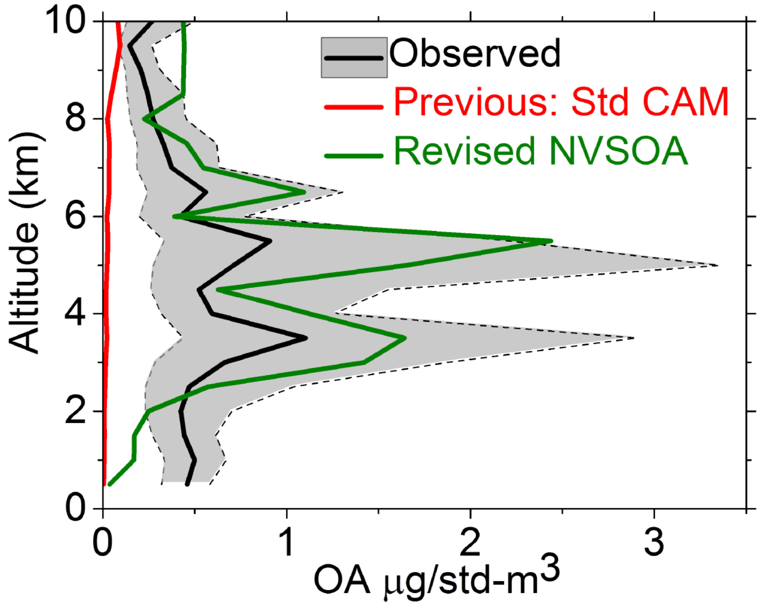

Figure 7. Aircraft-observed and simulated OA vertical profiles adapted from Shrivastava et al. (2015). The revised treatment, which includes multigenerational aging of SIVOCs from biomass burning, shows much better agreement with observations than the previous approach.

2.5.2 What Can Be Investigated in Models Now?

Integrated model-measurement comparisons need to be conducted to provide insights into models' ability to account for the emissions, volatility, and multigenerational aging of SOA precursors from biomass burning (Shrivastava et al. 2015; Shrivastava et al. 2013b). Recently concluded DOE field campaigns, such as BBOP and phase 2 of the GoAmazon 2014/5 field campaign, focused on biomass burning aerosols. These field campaigns, in conjunction with laboratory measurements and satellite products such as aerosol optical depth, could be used to evaluate the model's ability to predict OA in regions affected by biomass burning. These improved constraints could then be used in climate models to evaluate the radiative effects of biomass burning OA.

2.5.3 What Needs To Be Done in the Future?

Since biomass burning emissions and their aging are highly variable in the atmosphere, upcoming DOE ARM field campaigns can enhance our understanding of biomass burning OA in different regions of the world. For example, the Layered Atlantic Smoke Interactions with Clouds (LASIC) campaign is expected to provide understanding of aged carbonaceous aerosols from Southern African biomass burning. The importance of biomass burning aerosols from Southern African emissions and their high-latitude impacts were also highlighted by a recent global modeling study (Shrivastava et al. 2015). Integrated information from the latest and continuing laboratory and biomass burning field measurements and satellite data (both horizontal and vertical) should be used to develop and constrain the emissions, volatility, atmospheric aging, and climate-relevant properties of OA. From this comprehensive investigation, we expect to improve our ability to model and predict the highly variable (in space and time) impacts of biomass burning OA on regional-scale and global-scale aerosol radiative effects.

In addition, global aerosol climate models are too coarse to resolve the early stages of dispersing plumes such as those related to biomass burning sources. The details of plume size and dispersion greatly affect species concentrations and thus the importance of difference chemical mechanisms may change between fresh plumes and disperse plumes. Because the global models cannot capture this plume evolution, parameterizations of sub-grid plumes could be developed to capture the sub-grid chemistry and physics in the plumes that determine the SOA production.

2.6 Mechanistic Insights from Laboratory Studies of SOA Formation

Most of our existing knowledge of the nature of SOA formation has come from laboratory chamber experiments. The laboratory chamber will remain the fundamental vehicle to unravel the detailed chemistry and physics of SOA formation, including dependence on oxidation conditions, relative humidity, temperature, etc. As noted above, recent advances in mass spectrometry applied to chamber SOA have revealed, for example, the crucial role played by ELVOCs in SOA formation. New understanding of gas-phase chemistry, such as the importance of autoxidation, has allowed us to unravel mechanisms of SOA formation that to date were only speculative. Measurements of particle-phase composition of SOA would bring closure of the chemistry from the parent VOC to the SOA itself within reach (Zhang et al. 2015).

While the laboratory chamber will remain the fundamental system for studying SOA formation, chambers are not free of complications. It has long been known that particles diffuse to, and adhere to, the walls of a chamber. Careful measurement of the rate of loss of well-characterized aerosols allows one to bound the effect of wall deposition of SOA-containing particles on the overall estimated yield of SOA. Recently, it has been shown that wall deposition of the oxidized vapors that condense to form SOA can lead to underestimation of SOA yields by as much as a factor of 3 (Zhang et al. 2014). If, indeed, past reported SOA yields were significantly underestimated, this fact alone would reconcile the well-established mismatch between ambient OA measurements and OA levels predicted by atmospheric models based on parameterized chamber SOA yields. Consequently, a major effort is underway to characterize the nature of vapor wall loss in chambers, its dependence on species volatility, oxidation state, etc. and the role that such loss might have played in the parameterization of the SOA yields used in atmospheric models.

Three types of laboratory systems are used to study SOA formation:

1. The traditional chamber operated as a batch reactor
2. The chamber operated as a steady-state, continuous-flow, well-mixed reactor
3. The oxidation flow tube reactor.

Each of these types of systems provides basic data on which SOA formation in models can be parameterized. Little cross-characterization of these systems has been carried out, with respect to detailed mechanisms and predicted levels of SOA formation. Limited experience with focused studies in which a number of research groups converge on a particular laboratory with an array of instrumentation shows the enormous potential benefit of such studies (Nguyen et al. 2014). Such studies, envisioned as a "field experiment" carried out under well-characterized laboratory conditions, could be conducted and used to develop and evaluate the mechanistic insights in our models. These studies will not replace actual field studies, but they provide data subject to a degree of control not possible to achieve in the ambient.

2.7 Modeling Approaches to Represent Interactions between Aerosols and Clouds

The uncertainties in representing the interactions between aerosols and clouds are much larger than the well-constrained positive forcing due to increase of carbon dioxide concentration. In addition to the size distribution, another important property of SOA particles relevant to CCN and clouds is their hygroscopicity, often characterized through the dimensionless parameter κ. The hygroscopicity of SOA is fairly low compared to sulfate and nitrate, which implies that variations in SOA hygroscopicity may have limited influence on the net CCN activity in environments wherein sulfate and nitrate make up a large fraction of the particle volume. However, during preindustrial times, the effects of organic aerosol hygroscopicity on CCN number concentrations and cloud droplets were much larger than in the present day due to much smaller sulfate concentrations (Liu and Wang 2010). Further, the CCN activity of particles smaller than around 150 nm is particularly sensitive to variations in hygroscopicity, and growth of such ultrafine particles is thought to occur in large part due to condensation of organics. Thus, it is important that variations in particle composition are considered as a function of size if the full influence of SOA on clouds is to be quantitatively understood. Similarly, ELVOC formation could have been larger in preindustrial times (due to low NO conditions) compared to the present day, which could have resulted in the stronger impact of organics on aerosol hygroscopicity and CCN concentration during preindustrial times. Also, a quantitative understanding about the role of biomass burning OA in terms of influencing climate forcing is still lacking given the fact that most climate models do not include SOA formation due to aging of S/IVOCs emitted from biomass burning. These studies clearly suggest that the radiative effects of SOA in both the present-day and preindustrial atmosphere could be re-evaluated in a new light, as recent process-level understanding is implemented in models.

A recent finding in the laboratory shows that the water uptake of slightly oxygenated SOA is an adsorption-dominated process under subsaturated conditions, where low solubility inhibits water uptake until the humidity is high enough for dissolution to occur (Pajunoja et al. 2015). The difference in SOA hygroscopic behavior in subsaturated and supersaturated conditions can lead to an effect up to about 30% in the direct aerosol forcing—highlighting the need to implement correct descriptions of these processes in atmospheric models. Obtaining closure across the water saturation point is therefore a critical issue for accurate climate modeling.

As discussed in previous sections, particle-phase water could promote aqueous phase chemistry that results in SOA formation, and a similar process could occur in clouds. While laboratory measurements suggest that aqueous SOA production in clouds could be significant, some DOE/ARM field campaigns showed very little change in OA amounts between cloud droplet residuals and interstitial aerosols (non-activated) (Shrivastava et al. 2013a; Zelenyuk et al. 2010). In contrast, sulfate and nitrate were clearly higher in cloud droplet residuals. A future DOE ARM field campaign could be planned to focus more directly on assessing the impacts of cloud processing on aqueous-phase SOA and SOA precursors.

Other examples of physical processes not well represented by climate models, but likely perturbed by changes in the CCN budget, include suppression of warm rain and reduction in fall velocity of ice particle due to smaller ice sizes. These processes lead to increased cloud cover, cloud-top height, and cloud thickness. Additionally, SOA may affect ice nuclei (IN) formation. Changes in IN concentrations are thought to change ice-phase and mixed-phase microphysical processes and precipitation (Fan et al. 2014). Studies have shown that SOA-coated dust has significantly reduced IN abilities (Mohler et al. 2008). But, glassy SOA can serve as effective heterogeneous IN due to kinetic limitations to water diffusion into SOA particles (Berkemeier et al. 2014). However, no modeling work has considered this pathway relating SOA impacts on clouds through changing IN. Future studies could explore the SOA impacts on IN through their impacts on coating dust and increased IN effectiveness of semi-solid (glassy) SOA. More measurements of IN concentrations together with detailed SOA precursor and SOA composition measurements are needed to improve our understanding on the role of SOA in ice nucleation, both in the laboratory and the field.

An important consideration in development of modeling approaches for aerosol-cloud interactions could be the well-recognized limitations of coarse-grid climate models in simulating cloud-aerosol interactions. As climate models move towards increasingly finer resolutions, it is important to understand how the simulated climate impacts of aerosols varies with grid resolution. It is expected that smaller grid-spacings will better resolve both aerosols and clouds near strong urban sources, although the importance of grid resolution is likely not limited to near urban sources. For example, recent studies (Ma et al. 2014) have shown that grid-spacing affects the long-range transport of aerosols, and cloud susceptibility to aerosol forcing decreases as model horizontal grid spacing decreases (i.e., with increasing spatial resolution). Another recent study investigated effects of inorganic aqueous-phase chemistry within shallow cumulus clouds and found that sulfate increased significantly within non-precipitating, sub-grid-scale shallow clouds (Berg et al. 2015). This study established the importance of including aqueous chemistry related to aerosol-cloud interactions within sub-grid-scale clouds, which are not simulated by most climate models.

While gaining a better understanding of the present-day and preindustrial atmospheres is important, it is also necessary to evaluate how future global warming climate scenarios will influence the radiative effects of SOA and vice-versa. For example, wildfires in the Western U.S. are projected to increase by the 2050s due to global warming, which would likely impact climate through various feedback processes. Ultimately, the improved process-level understanding gained through these activities is expected to improve the abilities of our regional and global climate models to predict the impacts of SOA on climate forcing in the future-day scenarios.

3.0 Conclusion

The seven main themes of this workshop reflect important aspects of the progress made in the understanding of SOA life cycle processes within the last 5 years. Although these themes were not meant to include everything we know about SOA today, this workshop was targeted towards defining strategies and future directions for developing process-based modeling strategies based on the latest state-of-the-art measurements that could make large impacts on our understanding of the radiative effects of SOA. These themes are not independent, since several of them are inherently coupled by the same processes. For example, particle-phase processes such as oligomerization decrease volatility and also increase viscosity of SOA particles. Similarly, understanding the effects of organic aerosols on clouds requires an understanding of their size evolution and hygroscopicity, which are a function of both physical and chemical processes that affect SOA formation. Thus, these themes all have crosscutting contributions to current modeling uncertainties, which can be broadly classified as relating to the SOA burden and lifetime, mechanisms of particle growth to sizes relevant for both CCN, and the scattering and absorption of radiation. Moreover, this report has also suggested that recent measurement-based findings indicate a need for substantial changes in process-level representations of SOA particles in climate models.

For the past two decades, SOA formation has been described using equilibrium gas-particle partitioning and yields inferred from chamber experiments. These yields are static, and do not reflect the dynamic feedbacks between SOA and anthropogenic perturbations that change factors such as atmospheric oxidation mechanisms and aerosol acidity. Transferring the latest insights about SOA formation and properties into climate models remains a major and important task. Ultimately, climate models need to capture enough important features of the chemical and dynamic evolution of SOA as a function of atmospheric variables and anthropogenic perturbations to reasonably predict the spatial and temporal distributions of SOA. For example, the fact that SOA drives the growth of CCN in many regions of the world argues for size-resolved, sectional-type representations of these particles in climate models. Algorithms that simplify the transport of multiple tracers related to the different sizes of aerosols in atmospheric models would therefore be useful. Thus, the workshop participants agreed that one significant effort in the next 5 years should be the development and implementation of simplified mechanisms that faithfully represent the mechanistic understanding of SOA developed to date. Yet before conducting century-timescale climate simulations, we need to make sure that these chemical and physical processes of SOA particles are well represented by the newly developed simplified frameworks. To validate the model sufficiently will require using existing observations as well as new field campaigns in different regions/conditions.

While significant advances in our understanding of SOA formation and properties have occurred, significant gaps remain, and present challenges for accurately modeling the radiative effects of SOA. For example, ELVOC formation, IEPOX chemistry, accurate accounting of the volatility distribution during oxidation, and oligomerization processes are frequently missing in atmospheric models, though a varying degree of understanding of these factors does exist. In some cases, model-ready parameterizations exist, and could be used to assess the sensitivity of SOA distributions to these parameterizations, while other cases likely require more refined fundamental process-level understanding. Therefore, it remains important to continue improving the experimental constraints on as many relevant processes as are likely to go into models, and that both bottom-up and top-down constraints are needed. For example, molecular speciation of gas and particle phases provide bottom-up information on reaction mechanisms and volatility distributions (e.g., Liu et al. 2015; Lopez-Hilfiker et al. 2015a) and the evolution of particle size distributions provide top-down insights on growth mechanisms and particle properties such as diffusion limitations due to highly viscous particles. Importantly, since the volatility distributions used in some modeling parameterizations to define the lumped properties of the SOA precursors are operationally determined from chamber experiments, and depend on assumptions about the dominant SOA formation mechanism, they are in fact "theory-specific volatility distributions". Combining the molecular information of gas- and particle-phase composition with the size distribution dynamics could better constrain both the volatility distribution of SOA precursor organics and the dominant growth mechanisms, with fewer assumptions. In addition, wall losses of gas-phase SOA precursors are a known problem in laboratory chambers, and recent studies have shown that accounting for these losses could be important, especially for lower volatility compounds, and therefore for SOA yields and volatility distribution parameters.

A major unifying goal is to develop a detailed enough understanding of SOA formation and properties to allow for a robust determination of how much anthropogenic emissions and land-use changes have modified organic aerosol size distributions since preindustrial times. The net forcing from anthropogenic activities due to changes in SOA is then more reliably determined, thereby decreasing uncertainties in climate sensitivity to changing greenhouse gas concentrations. The background OA could have been very different in preindustrial times compared to the present. We have identified several process-level mechanisms related to the interactions between anthropogenic and biogenic SOA precursors, and the corresponding impacts on the radiative effects of SOA need to be investigated in three-dimensional chemical transport models. Given that many climate models do not have explicit chemistry linking anthropogenic emissions, biogenic emissions, and SOA formation and properties (Liu et al. 2012; Mann et al. 2012), potential aerosol-centered feedbacks between land-use change, climate change, biosphere productivity, and anthropogenic and biomass-burning emissions are not captured. As such, the workshop participants concluded that there are still potentially significant errors in the spatial and temporal distributions of SOA, and its changes through time (preindustrial, present-day, and future), and thus its direct and indirect climate effects, which need to be address through integrated model-measurement approaches.

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Appendix A
Workshop Agenda

June 8

TIME	TOPIC
8:30 – 9:00 am	Badging U.S. Citizens meet in EMSL Lobby Non U.S. Citizens meet in ETB Lobby
9:00 – 9:30 am	Introduction, workshop objectives and plans Manish Shrivastava, Joel Thornton
9:30 – 10:30 am	Acidity, sulfate and water affecting SOA: Latest findings from measurements, Main uncertainties, Modeling approaches Facilitators: Alex Guenther and Joel Thornton 9:30 – 9:45: Joel Thornton – Isoprene SOA and sulfate/acidity 9:45 – 10:00: Allen Goldstein – Isoprene SOA and sulfate/acidity 10:00 – 10:15: Sally Ng/Manish Shrivastava: Direct effects of sulfate on isoprene SOA in southeast USA, preliminary results on isoprene SOA from GoAmazon field campaign 10:15 – 10:30: Alex Guenther – BVOC Emission Modeling: What are we missing?
10:30 – 10:45 am	Break
10:45 – 11:45 am	Discussions - Topic: What is needed in terms of developing model parameterizations to represent the latest measurements in terms of aqueous phase SOA (e.g. sulfate-isoprene SOA) within regional and global climate models? What is the implication and expected impact of these findings on radiative forcing of SOA?
11:45 – 12:30 pm	Working Lunch – Continued discussions on the effect of aqueous SOA on radiative forcing.
12:30 – 2:00 pm	Role of low volatility organics Facilitators: Jeff Pierce and Jim Smith • 12:30 – 12:45: Jim Smith - Role of low volatility organics on new particle/CCN number • 12:45 – 1:00: Siegfried Schobesberger - Ion cluster formation involving oxidized organics • 1:00 – 1:15: Jeff Pierce - Modeling Role of low volatility organics on CCN • 1:15 – 1:30: Pontus Roldin - Role of low volatility organics on CCN • 1:30 – 1:45: Joel Thornton - Effects of ELVOCs in SOA • 1:45 – 2:00: Manish Shrivastava - Role of low volatility organics on SOA loadings/lifetimes

2:00 – 2:30 pm Break

2:30 – 5:00 pm Discussions: What are the next steps in terms of representing the chemistry of formation of low volatility organics and their effects on SOA loadings and CCN number in climate models? What are the modeling implications related to formation of low volatility organics?

June 9

TIME **TOPIC**

8:30 – 9:30 am Role of viscosity/phase on SOA
Facilitators: Rahul Zaveri and Alla Zelenyuk

- 8:30 – 8:45: Alla Zelenyuk - Role of viscosity/oligomers in SOA
- 8:45 – 9:00: Rahul Zaveri – Role of viscosity on SOA size distribution evolution
- 9:00 – 9:15: Pontus Roldin – Modeling Role of viscosity/oligomers in SOA

9:30 – 10:30 am Discussions: How can findings from these measurements be implemented in climate models? What are implications of viscosity/oligomers on SOA burdens, lifetimes, CCN and radiative forcing?

10:30 – 10:45 am Coffee break

10:45 – 11:30 am Anthropogenic/biomass emissions interacting with biogenic SOA: Short talks
Facilitators: Manish Shrivastava and John Shilling

What are the specific process-level mechanisms related to how anthropogenic emissions interact with biogenic SOA, which are missing in climate models?

- 10:45-11:00 Alla Zelenyuk: Effects of hydrophobic organics on SOA
- 11:00-11:15 John Shilling: Anthropogenic emissions interacting with biogenic SOA
- 11:15-11:30 Manish Shrivastava: Modeling approaches in SOA related to anthropogenic-biogenic interactions and biomass burning

11:30 – 12:00 pm EMSL Tour – Meet Nancy Washton in EMSL Lobby

12:00 – 12:30 pm Working lunch break – Anthropogenic emissions interacting with biogenic SOA

12:30 – 1:30 pm	Discussions: What are next steps forward in terms of implementing these newly-discovered anthropogenic biogenic interactions in climate models? What is missing?
1:30 – 2:30 pm	Short talks on interactions between aerosols and clouds Facilitator: Phil Rasch • 1:30 – 1:45 Steven Ghan: Need to get natural aerosol concentrations for aerosol indirect effects • 1:45 – 2:00 Tuukka Petäjä: Aerosol cloud interactions • 2:00 – 2:15 Jian Wang: SOA, hygroscopicity and CCN • 2:15 – 2:30 Jiwen Fan: Aerosol deep convective-cloud interactions
2:30 – 3:00 pm	Discussions about modeling approaches to represent cloud-aerosol interactions
3:00 – 3:15 pm	Break
3:15 – 4:30 pm	Workshop summary, presentation of next steps and related discussions
4:30 pm	Adjourn

Appendix B
Participants

Christopher Cappa, University of California, Davis
Duli Chand, Pacific Northwest National Laboratory
Jiwen Fan, Pacific Northwest National Laboratory
Jerome Fast, Pacific Northwest National Laboratory
Steven Ghan, Pacific Northwest National Laboratory
Allen Goldstein, University of California, Berkeley
Alex Guenther, Pacific Northwest National Laboratory
Chongai Kuang, Brookhaven National Laboratory
Tuukka Petäjä, University of Helsinki
Jeffrey Pierce, Colorado State University
Philip Rasch, Pacific Northwest National Laboratory
Pontus Roldin, Lund University
John Seinfeld, California Institute of Technology
John Shilling, Pacific Northwest National Laboratory
Manish Shrivastava, Pacific Northwest National Laboratory
Nga Lee (Sally) Ng, Georgia Institute of Technology
Siegfried, Schobesberger, University of Washington
James Smith, University Corporation for Atmospheric Research
Joel Thornton, University of Washington
Jian Wang, Brookhaven National Laboratory
Douglas Worsnop, Aerodyne
Rahul Zaveri, Pacific Northwest National Laboratory
Alla Zelenyuk-Imre, Pacific Northwest National Laboratory
Qi Zhang, University of California, Davis