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Multiphase Atmospheric Chemistry in Liquid Water: Impacts and Controllability of Organic Aerosol

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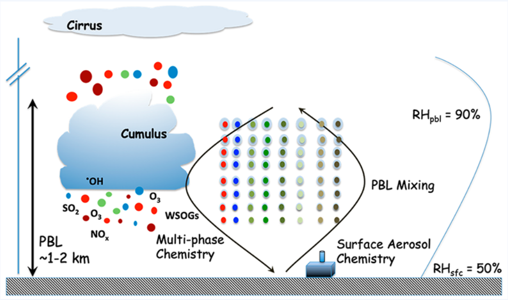

CONSPECTUS: Liquid water is a dominant and critical tropospheric constituent. Over polluted land masses low level cumulus clouds interact with boundary layer aerosol. The planetary boundary layer (PBL) is the lowest atmospheric layer and is directly influenced by Earth's surface. Water−aerosol interactions are critical to processes that govern the fate and transport of trace species in the Earth system and their impacts on air quality, radiative forcing, and regional hydrological cycling. In the PBL, air parcels rise adiabatically from the surface, and anthropogenically influenced hygroscopic aerosols take up water and serve as cloud condensation nuclei (CCN) to form clouds. Water-soluble gases partition to liquid water in wet aerosols and cloud droplets and undergo aqueous-phase photochemistry. Most cloud droplets evaporate, and low volatility material formed during aqueous phase chemistry remains in the condensed phase and adds to aerosol mass. The resulting cloud-processed aerosol has different physicochemical properties compared to the original CCN. Organic species that undergo multiphase chemistry in atmospheric liquid water transform gases to highly concentrated, nonideal ionic aqueous solutions and form secondary organic aerosol (SOA). In recent years, SOA formation modulated by atmospheric waters has received considerable interest.

Key uncertainties are related to the chemical nature of hygroscopic aerosols that become CCN and their interaction with organic species. Gas-to-droplet or gas-to-aqueous aerosol partitioning of organic compounds is affected by the intrinsic chemical properties of the organic species in addition to the pre-existing condensed phase. Environmentally relevant conditions for atmospheric aerosol are nonideal. Salt identity and concentration, in addition to aerosol phase state, can dramatically affect organic gas miscibility for many compounds, in particular when ionic strength and salt molality are outside the bounds of limiting laws. For example, Henry's law and Debye−Hückel theory are valid only for dilute aqueous systems uncharacteristic of real atmospheric conditions. Chemical theory is incomplete, and at ambient conditions, this chemistry plays a determining role in total aerosol mass and particle size, controlling factors for air quality and climate-relevant aerosol properties.

Accurate predictive skill to understand the impacts of societal choices and policies on air quality and climate requires that models contain correct chemical mechanisms and appropriate feedbacks. Globally, SOA is a dominant contributor to the atmospheric organic aerosol burden, and most mass can be traced back to precursor gas-phase volatile organic compounds (VOCs) emitted from the biosphere. However, organic aerosol concentrations in the Amazon Rainforest, the largest emitter of biogenic VOCs, are generally lower than in U.S. national parks. The Interagency Monitoring of Protected Visual Environments (IMPROVE) air quality network, with sites located predominantly in national parks, provides the longest continuous record of organic aerosol measurements in the U.S. Analysis of IMPROVE data provides a useful chemical climatology of changing air resources in response to environmental rules and shifting economic trends. IMPROVE data provides an excellent test bed for case studies to assess model skill to accurately predict changes in organic aerosol concentrations in the context of a changing climate.

KEY REFERENCES

- Carlton, A. G.; et al. Synthesis of the Southeast Atmosphere Studies: Investigating Fundamental Atmospheric Chemistry Questions. *Bull. Am. Meteorol. Soc.* **2018**, *99*, 547−567.[1] *Synthesis of intensive surface and aircraft field campaigns during the summer of 2013 to*

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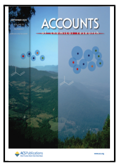

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investigate, in part, atmosphere–biosphere interactions that modulate ambient pollutant concentrations through mechanisms not yet adequately captured in atmospheric models.

- Carlton, A. G.; Pye, H. O. T.; Baker, K. R.; Hennigan, C. J. Additional Benefits of Federal Air-Quality Rules: Model Estimates of Controllable Biogenic Secondary Organic Aerosol. *Environ. Sci. Technol.* **2018**, *52*, 9254–9265.[2] *Revisits the question, "to what extent is biogenic secondary organic aerosol controllable?" with more explicit and field-evaluated organic chemistry in aerosol liquid water that showed ancillary benefits of Federal* NO_x *and* SO_2 *rules that concurrently reduce organic fine particle mass.*
- Carlton, A. G.; Turpin, B. J. Particle Partitioning Potential of Organic Compounds Is Highest in the Eastern US and Driven by Anthropogenic Water. *Atmos. Chem. Phys.* **2013**, *13*, 10203–10214.[3] *CMAQ modeling study and thought experiment that showed SOA formation in the Eastern U.S. due to chemistry in aerosol liquid water is substantial and facilitated in humid locations by anthropogenic NOx and SOx emissions.*
- Carlton, A. G.; Pinder, R. W.; Bhave, P. V.; Pouliot, G. A. To What Extent Can Biogenic SOA Be Controlled? *Environ. Sci. Technol.* **2010**, *44*, 3376–3380.[4] *First quantitative estimate of the anthropogenic enhancement of biogenic secondary organic aerosol over the contiguous United States using EPA's CMAQ model that found at least half of biogenic SOA in the Eastern U.S. is controllable.*

■ MULTIPHASE TROPOSPHERIC CHEMISTRY: BIOSPHERE-ATMOSPHERE INTERACTIONS AND REACTIVE CARBON

Atmospheric fine particulate matter with an aerodynamic diameter (assumes unit density) that is roughly 2.5 μm or smaller ($PM_{2.5}$) is associated with a variety of adverse health end points even at daily concentrations below World Health Organization (WHO) guidelines, and small increases induce substantial economic costs for society.[5] Anthropogenic emissions at the surface form hygroscopic fine aerosols that alter climate-scale cloud radiative properties,[6] affect mesoscale convective systems, and change precipitation patterns.[7] The majority of atmospheric fine aerosol, or $PM_{2.5}$, forms in the atmosphere from precursor gases. It is chemically complex and contains mixtures of inorganic and organic material including aerosol liquid water (ALW)[8] and exhibits variable phase and mixing states.[9] The organic fraction is ubiquitous and often abundant.

Gas-phase oxidation of volatile organic compounds (VOCs) produces semivolatile or water-soluble compounds that can create new particles or partition to a pre-existing aerosol matrix to form secondary organic aerosol (SOA) through semivolatile partitioning and multiphase chemistry involving ALW.[10,11] Globally, SOA is a dominant contributor to aerosol mass, and the majority of precursor VOCs that form SOA derive from the biosphere. Traditionally SOA is described as "biogenic" or "anthropogenic" based on the source of the VOC precursor. While emissions of biogenic VOCs are natural, subsequent formation of aerosol usually is not, and this naming convention can falsely imply that biogenic SOA is a natural part of background air. "Biogenic" SOA mass concentrations can be largely reduced through control of emissions from human activity[4] even in pristine environments such as the Amazon Rainforest.[12] For example, anthropogenic emissions alter radical budgets, change oxidation pathways, and increase aerosol hygroscopicity to facilitate SOA formation through multiphase chemistry in both summer[3] and winter.[13] When ALW pathways are considered in atmospheric models, estimates of biogenic SOA controllability across the United States increase and anthropogenic source sector importance changes.[2]

Atmospheric organic gases are more likely to encounter high ionic strength ALW as an available partitioning medium than particulate organic carbon under most ambient conditions in humid locations.[3,8] Inorganic salts promote ALW, which can serve as a medium to partition polar, water-soluble gas phase organic species to the condensed phase, facilitating aqueous SOA formation (aqSOA). In continental locations, ALW is driven by particulate ammonium sulfate and ammonium nitrate,[3,14] derived from anthropogenic emissions of the precursor gases, NH_3, SO_2, and NO_x. Modeling and field experiments suggest that organic chemistry in ALW is a dominant SOA formation pathway in the eastern U.S.[1−3,15−18] and imparts a determining impact in western arid regions of the U.S. as well.[19] An aqSOA mechanism makes it possible for sulfate and nitrate containing particles to grow in organic mass under conditions of elevated relative humidity (RH). Inorganic salts can react directly to form S- and N-containing species[20,21] or alter the partitioning and volatility of organic compounds at atmospherically relevant conditions.[17,22] In response to environmental regulations, emissions of SO_2 and NO_x have dramatically reduced over the past decades, as have mass concentrations of the corresponding hygroscopic inorganic salts, sulfate and nitrate, and ALW.[23,24] Decadal reductions in particulate total organic carbon (TOC) are also noted with links to ALW-influenced chemistry.[19,23,25,26] Air quality modeling over the contiguous United States (CONUS) that includes aqSOA is able to qualitatively reproduce geospatial and temporal trends in particulate organic carbon in response to changing energy sector SO_2 and NO_x emissions.[2,24−26] This represents improvement over simulations that do not include aqSOA (e.g., ref 27) though other factors, such as concurrent decreases in POA emissions, are also proposed as an explanation for the connection between inorganic and organic aerosol components.[28]

Low-level cumulus clouds interact with boundary layer SOA, which can contribute to cloud condensation nuclei (CCN) and form droplets that modulate aerosol physicochemical properties.[29] Clouds are primary drivers of Earth's albedo and vertical transport in the troposphere. Partitioning of water-soluble gases to cloud droplets and the subsequent oxidative chemistry in liquid water transfer species from the polluted boundary layer and generate particle mass aloft, such as sulfate and water-soluble organic carbon ($WSOC_p$),[30] including organosulfur compounds[20] and brown carbon.[31] While the fundamental chemistry is the same, the fate, long-range transport, air quality, and radiative influences of aloft SOA are dramatically different from near-surface mass. Radiative impacts in the free troposphere are substantial, in particular when located above clouds where aerosols scatter and absorb both incoming solar radiation and diffuse back scatter from clouds. Aerosol–cloud interactions remain highly uncertain in models, and accurate prediction remains elusive across scales, in part because the controlling chemical mechanisms that govern interaction among inorganic and organic species are not well characterized.

Despite the abundance, importance, and decades of study, understanding of SOA chemistry remains incomplete, and application of formation processes in most routinely applied atmospheric models is simplified. Critical open questions

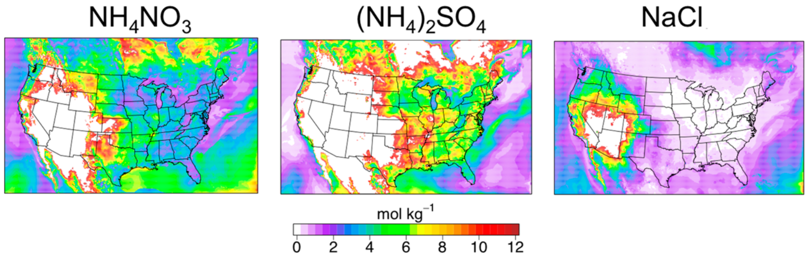

Figure 1. June 2013 average molality ([salt]/[ALW]) for three common atmospheric salts. Sulfate mass concentrations are highest in the eastern U.S.; however, molality is highest in the arid west where [ALW] is low. NOTE: light purple is negligible molality; bright white areas are molality >12.

regarding the chemistry of organic compounds in highly concentrated inorganic salt solutions persist, impairing quantitative estimation of the fate and transport of SOA and its subsequent impacts. Unless models accurately employ the underlying fundamental chemical mechanisms and their feedbacks, misrepresentation of the anthropogenic perturbations on air quality and climate arise.[32] This hinders development of effective strategies to safeguard human health and the environment.

INORGANIC SALTS AND HIGH IONIC STRENGTH PARTITIONING OF ORGANIC COMPOUNDS

The U.S. EPA's Community Multiscale Air Quality (CMAQ) model predicts summertime aerosol molality of three individual salts, ammonium nitrate, ammonium sulfate, and sodium chloride, in ALW over the CONUS to be >1 mol kg^{-1} in nearly all locations (Figure 1). Observational estimates at surface locations in the Eastern U.S. as part of the IMPROVE air quality network are consistent with CMAQ predictions (Figure 2). Despite reduction in sulfate mass in the Eastern U.S. during the last 15 years, aerosol acidity is not reduced.[33,34] Sulfate molality in particulate matter is estimated to be >3 mol kg^{-1} in all seasons and rising due to decreasing ALW mass concentrations. Increasing temperatures cause an associated reduction in relative humidity; however the Eastern U.S. is sufficiently humid that sulfate mass tends to be more limiting for ALW formation than gas-phase water vapor mixing ratios. Ammonium nitrate is more volatile, and molality is higher in winter than summer.

The presence of inorganic salts can alter the effective partitioning coefficient (Henry's law constant, K_H) by more than an order of magnitude, depending on the organic species, salt identity, and concentration.[36] Henry's law and Debye–Hückel theory are valid only for dilute aqueous systems (ionic strength, $z < 1$, and electrolyte concentration, $<10^{-3}$ mol L^{-1}, respectively). Most extensions to these formulations and estimates of activity coefficients to describe uptake are empirical in nature, and extrapolation does not properly apply to the highly concentrated salt solutions (Figure 1) typical of atmospheric aerosol. There are large uncertainties in the effective solubility, and thus gas-to-particle partitioning, of many organic gases. Inorganic salts can shift the partitioning equilibrium of organics in favor of the condensed or vapor phase, which can enhance or inhibit aqSOA formation ("salting in" and "salting out", respectively). For example, salts enhance particle-phase partitioning of glyoxal (salting in) and reduce the particle phase partitioning of methylglyoxal and butenedial (salting out).[37−39] Implementation of salt-based Setschenow coefficients for K_H from these experiments in CMAQ for glyoxal and methylglyoxal dramatically impact partitioning and thus the

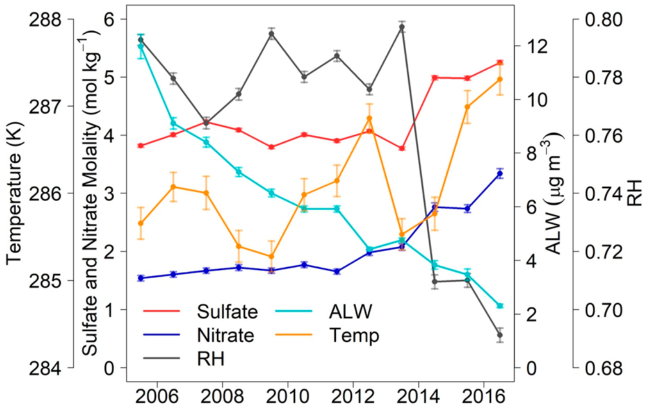

Figure 2. Salt molality (salt/[ALW]), ALW mass concentrations, relative humidity (RH), and temperature for IMPROVE sites in the eastern U.S. in 2005−2016. Whiskers represent standard error in the distribution of measurements. ALW is estimated using the thermodynamic model ISORROPIA[35] with inputs of IMPROVE inorganic aerosol measurements and meteorology from the North American Reanalysis data product of NOAA's National Centers for Environmental Information.

subsequent fate and transport of reactive carbon.[17] For example, particle phase glyoxal increases by a factor of 3, with corresponding decreases in the gas phase mixing ratio. Model results underscore the importance of accounting for the salting effect in predicting the magnitude, spatial distribution, and ultimately the fate of reactive carbon. Further, the most common and best predictors of dissolved organic carbon (DOC) in ecological studies of wet deposition find that inorganic salt concentrations are the most common significant predictors of DOC concentrations in precipitation (i.e., aqueous droplets) across ecosystems.[40] Detailed chemical analysis of continental and marine precipitation suggests DOC in rainwater predominantly derives from the same atmospherically processed organic species found in aqSOA.[41,42]

Thousands of individual organic gases are present in the atmosphere, and aqueous aerosols are highly concentrated electrolyte solutions. While K_H values have been measured for a diverse array of atmospheric organic gases, the gas–aqueous partitioning behavior under high ionic strength conditions has only been studied experimentally for a much smaller group of polar organic compounds.[43] Computational approaches based on structure–activity relationships can be used to predict K_H; however, theoretical predictions of K_H systematically worsen as molecules become more oxygenated and thus more water-soluble. In a series of laboratory experiments, Kampf et al.[38] estimate Setschenow coefficients for glyoxal uptake by ammonium sulfate particles. Initial fast uptake of glyoxal was followed by a slower increase in effective Henry's Law constants over several hours. Deviation from predicted Setschenow salting coefficients occurred at an ammonium sulfate concentration of 12 mol kg^{-1} or ionic strength of 36 mol kg^{-1}.[44] These electrolyte concentrations are typical of predicted atmospheric aerosol values over the CONUS (Figure 1). The transition in uptake rates suggests kinetic limitations above a threshold value that may be due to phase separation or the formation of glassy aerosol.

A polar solvent such as water favors the partitioning of polar organic compounds, and water can act as a plasticizer. The glass transition temperature of organic material is heavily influenced by the oxygen/carbon (O/C) ratio,[45] and the salting effect is most dramatic for the most water-soluble organic species, which generally have polar moieties and higher O/C ratios. Phase state can impart kinetic limitations to affect aerosol hygroscopic growth, CCN, and ice nucleating particle (INP) activation.[46] Some organic substances tend to form semisolid or amorphous solid (glassy) phases as humidity decreases or induce liquid–liquid phase separation (LLPS) in mixed organic/inorganic particles. The salting effects on LLPS have been studied more extensively than salting impacts on effective Henry's Law partitioning to ALW for atmospheric systems.[43] Yet, testing of theoretical, laboratory, and modeling experiments that identify interactions among inorganic and organic species and their impacts on partitioning remains to be evaluated in field samples.

LIQUID WATER AND THE CHANGING NATURE OF ORGANIC AEROSOL

Chemical regimes for ozone production change over spatial and temporal scales. For example, ozone production in urban airsheds versus rural ones is vastly different, and regimes change over time in response to environmental rules, such as the U.S. EPA's "NOx SIP Call". The overall photochemistry that oxidizes gas-phase organic species to produce ozone, also produces organic precursors for SOA. This suggests that the chemical nature of SOA also changes spatially and temporally and is consistent with routine network measurements of total organic carbon (TOC). Organic aerosol collected at IMPROVE sites often contains highly oxidized functional groups, such as alcohols, carboxylic acids, and organosulfur moieties that contribute noncarbonaceous organic mass. The ratio of functionalized organic matter-to-organic carbon (OM/OC) measured at surface sites across the U.S. in the IMPROVE network is lowest in urban locations in winter and highest in rural areas in summer.[47] OM/OC ratios are increasing across the CONUS at rates that vary by location,[47] and aqSOA generally has higher oxygen-to-carbon (O/C) ratios.[48] While reduction in mass concentrations of TOC are noted for the CONUS, in particular in the east,[23,25,26,28] organic aerosol mass concentrations do not decline at the same rate. Across the CONUS, TOC mass concentrations decrease at IMPROVE sites at a rate of −3.4% yr^{-1}. When site- and time-dependent OM/OC ratios[19] are applied to TOC measurements, total organic matter (TOM) decreases −2.4% yr^{-1} (Figure 3).

Thermal optical techniques, such as the "OC/EC" (organic carbon/elemental carbon) measurements at sites in the IMPROVE network classify TOC by thermal volatility. The IMPROVE temperature protocol defines four OC volatility fractions, OC1 (most volatile), OC2, OC3, and OC4 (least volatile), at temperatures ranging from 140 to 580 °C, the temperature ramp applied routinely since 2005. Organic species tend to pyrolyze above 300 °C, and pyrolysis is monitored and corrected via transmittance. Charred or pyrolyzed carbon (PC) mass is also a reported fraction. Thermal separation provides some insight but not precise chemical detail. Since 2005, the overall decrease in TOC is driven primarily by OC2 (organic carbon that volatilizes at 280 °C) and PC.[19] The change in contribution of different thermal fractions to total TOC suggests change in the volatility and viscosity[49] of organic aerosol. Both OC2 and PC may be linked to multiphase chemistry of biogenically derived isoprene oxidation products in ALW. Water-soluble organic carbon, which includes aqSOA, is particularly susceptible to pyrolysis during analysis.[50] Carboxylic acids, which are formed during aqueous-phase chemistry of isoprene oxidation products,[51,52] are observed as part of OC2.[53] The largest absolute mass decreases in OC2 and PC occur in humid eastern locations of the U.S. where isoprene emissions and ALW concentrations are high.[19] When the atmospheric model GEOS-Chem is applied to the CONUS from 2005 to 2015 and includes aqSOA, the predicted model species "ISOAAQ", which represents isoprene oxidation products that form via liquid water chemistry, correlates significantly with IMPROVE-measured OC2.[19]

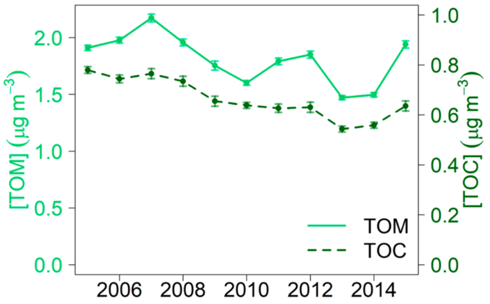

Figure 3. Decadal trend in TOM and TOC at IMPROVE monitoring sites across the CONUS for 2005−2015 (corresponding to consistent thermal protocols and hardware). Decadal decrease in [TOC] is −3.4% yr^{-1} and [TOM] is −2.4% yr^{-1}. Whiskers represent standard error in the distribution of measurements.

In a given year, the largest seasonal increase in mass concentrations of TOC occurs during the transition from spring into summer in two separate and contrasting areas of the CONUS, IMPROVE's "East Coast" (humid) and "Southern California" (arid)[25] (Figure 4) regions. The change in fractional contribution by volatility bins is also largest during this seasonal transition. The pattern is observed and more pronounced when noncarbonaceous mass is considered, which indicates a greater presence of functionalized organic matter during summer. There are large uncertainties in chemical assessment of organic carbon volatility measurements; however existing data sets provide a useful index. Further, while the assessment here focuses on the CONUS, ALW-mediated chemistry is demonstrated to play an important role in other regions of the globe, such as the Po Valley of Italy[14] and the North China Plain.[54]

CONNECTING PHYSICAL AND CHEMICAL AEROSOL MEASUREMENTS THROUGH LIQUID WATER

Consideration of multiphase chemistry that includes ALW provides a plausible explanation to reconcile physical and chemical aerosol measurements across platforms. Satellites record substantial summertime enhancement of aerosol optical depth (AOD), an index of the atmospheric aerosol burden, in the southeast U.S. However, surface $PM_{2.5}$ mass measurements

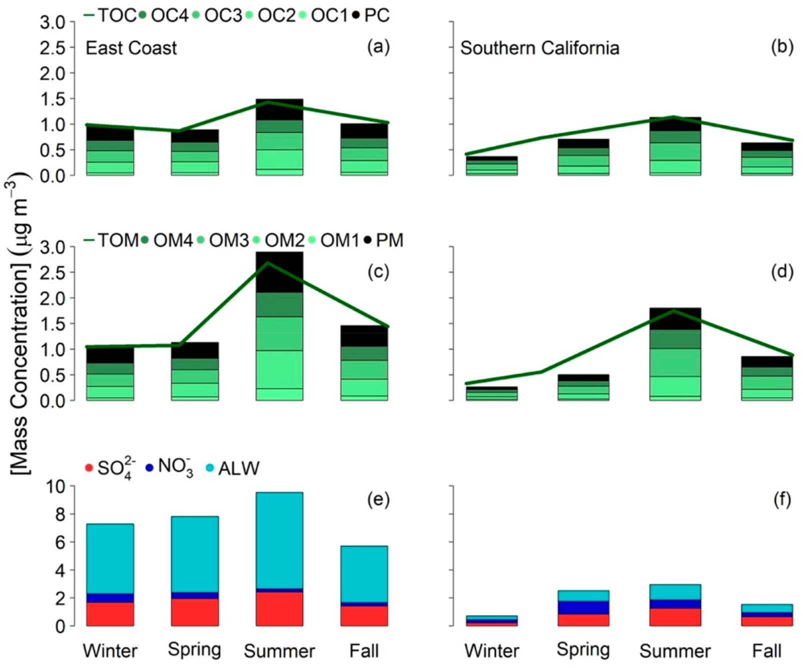

Figure 4. Seasonal patterns in organic aerosol thermal fractions, sulfate, nitrate, and ALW for two IMPROVE chemical climatology regions, "Southern California" (left) and "East Coast" (right), in 2016, a typical year in the record. Summertime enhancement in noncarbonaceous organic mass [TOM] is more pronounced than for organic carbon mass concentrations [TOC].

in the area do not exhibit seasonality.[55,56] Interestingly, ALW estimated from surface-based measurements of particle chemical composition demonstrate a similar pattern to satellite observations. ALW effectively scatters radiation in the visible part of the spectrum where satellite measurements are made. Satellites observe aerosol *in situ* and unperturbed from ambient conditions,[57] and remotely sensed aerosol radiative properties are strongly affected by ALW. Filter-based $PM_{2.5}$ measurements lose water[57] and aqSOA[58] mass relative to ambient conditions during transport and equilibration to laboratory conditions. On average, over the CONUS the strongest satellite AOD is observed over the east,[59,60] where ALW mass concentrations are highest. In the southeast U.S., optical particle extinction estimates to quantitatively describe visibility at IMPROVE sites that include contribution from ALW are positively associated with AOD measurements from the CALIPSO satellite and surface instruments.[60,61] Decadal trends in the southeast of particle inorganic chemical constituents that control ALW are positively associated with changes in surface visibility and can be linked to climate-relevant particle radiative properties that impact regional climate.[62−64] Particle size is the dominant factor that determines aerosol scattering, and chemical composition, in partiuclar speciation that promotes increased water uptake, has a determining effect on size.

Preliminary analysis of colocated physical and chemical aerosol measurements provides a plausible mechanism to connect ALW to satellite AOD. NASA's ground-based AErosol RObotic NETwork (AERONET)[65] station colocated with an IMPROVE network monitoring site in Bondville, IL, provides observations of aerosol size distributions and chemical composition. AERONET measures AOD and Ångström exponents (α) at wavelengths λ = 440 and 870 nm. In eq 1, τ is the optical depth at a given wavelength (λ). Ångström exponents are inversely proportional to size for the fine mode particles[66] measured at IMPROVE sites.

$$\frac{\tau_\lambda}{\tau_{\lambda_1}} = \left(\frac{\lambda}{\lambda_1}\right)^{-\alpha} \qquad (1)$$

Cloud flags from Aqua and Terra satellites' Moderate Resolution Imaging Spectroradiometer (MODIS) are paired in space and time for the site at Bondville, IL,[67] from January 2010 to August 2014. Surface estimates of ALW and measurements of α are binned as "cloudy" or "clear sky" based on the MODIS cloud flags. ALW mass concentrations are significantly higher on cloudy days than clear sky ones, and Ångström exponents are significantly smaller (Figure 5). This is consistent with cloudy conditions being favored by increased abundance of hygroscopic aerosols that efficiently take up water and can serve as CCN and are physically larger than aerosol on clear sky days when there is less ALW. Note that in Figure 5 we present quality assured, but not cloud-screened, data from the AERONET Level 1 data product (https://aeronet.gsfc.nasa.gov/).[68]

There are large uncertainties in this preliminary analysis. The presence of organic compounds can affect water uptake. Detailed thermodynamic modeling in the southeast U.S. at the Great Smoky Mountains demonstrated that *in situ* ALW measurements at ambient conditions differed from thermodynamic estimates calculated from inorganic species only (e.g., the method employed here). Discrepancies were positively associated with the organic mass fraction.[69] During the Southern Oxidant and Aerosol Study (SOAS)[1] at certain times of day (~7−11 AM) when the organic fraction (not mass) was highest, aerosol volume grew to larger than ambient values when the aerosol was dried to remove ALW and then rehumidified back up to ambient RH.[18] There are large uncertainties, but this is suggestive that drying aerosol also removes semivolatile organic species that affect water uptake under certain conditions. This also suggests that particle growth factors commonly calculated from dried aerosol rehumidified to instrument-defined, and not ambient, RH values may not accurately describe ALW-related

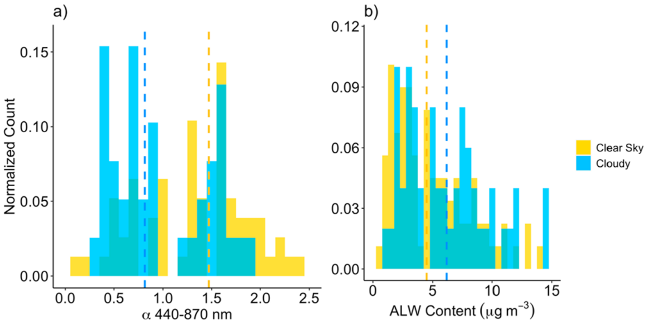

Figure 5. Ångström exponent and ALW at a colocated IMPROVE and AERONET station in Bondville, IL, from January 2010 to August 2014 binned by MODIS' cloud flag categories. Fine mode particle diameter is inversely proportional to Ångström exponent values. This analysis suggests that boundary layer aerosol contains more ALW and is physically larger during cloudy time periods compared to clear sky conditions.

extinction *at ambient* conditions when applied in models. Additional cases must be evaluated. Analysis of long-term data derived from diverse platforms and instrumentation and interaction among atmospheric chemists and physicists is imperative to resolve long-standing model inadequacies, such as aerosol−cloud interactions.

■ CONCLUSION AND OUTLOOK

Important problems of broad global significance will not be solved in isolation. Aerosol−cloud interactions in models remain a dominant uncertainty in projections of future climate. Models useful to protect human health and environment require chemical and physical fidelity. The atmosphere is connected globally, and the governing principles behind atmospheric processes are consistent across scales and fields of study.

Current critical open questions, areas, and tools to improve understanding of atmospheric multiphase chemistry involving tropospheric water include the following:

1. Lack of direct measurements to test model predictions of aqSOA are a key deficiency.
2. What are the underlying fundamental chemical mechanisms that control organic compound partitioning to high inorganic salt molality solutions?
3. How does organic chemistry in high molality salt solutions affect the fate and transport of reactive species? This Account focuses on carbon; however organic matter contains other species such as reactive nitrogen with largely uncertain budgets.
4. What is the relative importance of aqSOA in dilute (clouds) versus concentrated aqueous aerosols?
5. Holistic assessment of aerosol measurements is possible with the plethora of publicly available, yet underutilized chemical and physical atmospheric data from existing routine networks. How can that work be encouraged across research communities?
6. Application of sophisticated statistical approaches such as machine learning techniques may elucidate organic chemical composition more precisely from routine network data.

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Notes

The authors declare no competing financial interest.

Biographies

Annmarie Carlton is a Professor of Chemistry at UC, Irvine. She received B.S. (1995) and M.S. (1999, Bioenvironmental Engineering) degrees and a Ph.D. (2006, environmental science) all from Rutgers University. Her research interests are focused on chemistry in atmospheric water. Prior to academia, Dr. Carlton worked as an environmental engineer for Region 2 of the U.S. EPA in New York, NY, and as a CMAQ model developer in the Office of Research and Development of the U.S. EPA in Research Triangle Park, NC. Prior to joining the faculty at UC-Irvine, Dr. Carlton started her tenure-track faculty career at Rutgers University.

Amy Christiansen is a Postdoctoral Research Associate in the Department of Chemistry and Biochemistry at University of Montana. She received a B.A. (2015, Chemistry and Environmental Studies) from Gustavus Adolphus College and Ph.D. (2020) from the University of California, Irvine. Dr. Christiansen studies interactions between water and chemical components of aerosols and clouds and model development to improve representation and understanding of aerosol and trace gas spatial distribution, temporal trends, and radiative impacts.

Madison Flesch is a Ph.D. candidate in chemistry at UC, Irvine. She received a B.S. (2018, chemistry) from University of Northern Iowa, Ms. Flesch studies how aerosols are different on cloudy versus clear sky days and how those aerosol−cloud interactions may affect their physicochemical properties.

Chris Hennigan is an Associate Professor in the Department of Chemical, Biochemical and Environmental Engineering at the University of Maryland, Baltimore County (UMBC). His research interests include secondary aerosol formation, atmospheric multiphase chemistry, and particle acidity. He received a B.S. degree (2001, Chemistry) from the University of Florida and Ph.D. degree (2008, Environmental Engineering) from the Georgia Institute of Technology. After a postdoctoral appointment (2008−2012, Center for Atmospheric Particle Studies) at Carnegie Mellon University, he began his tenure-track position at UMBC. Before attending graduate school, he worked as an Analytical Chemist for the Department of Energy at the Savannah River Site (2001−2003).

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■ REFERENCES

(1) Carlton, A. G.; de Gouw, J.; Jimenez, J. L.; Ambrose, J. L.; Attwood, A. R.; Brown, S.; Baker, K. R.; Brock, C.; Cohen, R. C.; Edgerton, S.; Farkas, C. M.; Farmer, D.; Goldstein, A. H.; Gratz, L.; Guenther, A.; Hunt, S.; Jaeglé, L.; Jaffe, D. A.; Mak, J.; McClure, C.; Nenes, A.; Nguyen, T. K.; Pierce, J. R.; de Sa, S.; Selin, N. E.; Shah, V.; Shaw, S.; Shepson, P. B.; Song, S.; Stutz, J.; Surratt, J. D.; Turpin, B. J.; Warneke, C.; Washenfelder, R. A.; Wennberg, P. O.; Zhou, X. Synthesis of the Southeast Atmosphere Studies: Investigating Fundamental Atmospheric Chemistry Questions. *Bull. Am. Meteorol. Soc.* **2018**, *99*, 547−567.

(2) Carlton, A. G.; Pye, H. O. T.; Baker, K. R.; Hennigan, C. J. Additional Benefits of Federal Air-Quality Rules: Model Estimates of Controllable Biogenic Secondary Organic Aerosol. *Environ. Sci. Technol.* **2018**, *52*, 9254−9265.

(3) Carlton, A. G.; Turpin, B. J. Particle Partitioning Potential of Organic Compounds Is Highest in the Eastern US and Driven by Anthropogenic Water. *Atmos. Chem. Phys.* **2013**, *13*, 10203−10214.

(4) Carlton, A. G.; Pinder, R. W.; Bhave, P. V.; Pouliot, G. A. To What Extent Can Biogenic SOA Be Controlled? *Environ. Sci. Technol.* **2010**, *44*, 3376−3380.

(5) Wei, Y.; Wang, Y.; Di, Q.; Choirat, C.; Wang, Y.; Koutrakis, P.; Zanobetti, A.; Dominici, F.; Schwartz, J. D. Short Term Exposure to Fine Particulate Matter and Hospital Admission Risks and Costs in the Medicare Population: Time Stratified, Case Crossover Study. *BMJ.* **2019**, *367*, l6258.

(6) Diamond, M. S.; Director, H. M.; Eastman, R.; Possner, A.; Wood, R. Substantial Cloud Brightening From Shipping in Subtropical Low Clouds. *AGU Adv.* **2020**, *1*, No. e2019AV000111.

(7) Kawecki, S.; Steiner, A. L. The Influence of Aerosol Hygroscopicity on Precipitation Intensity During a Mesoscale Convective Event. *J. Geophys. Res.-Atmospheres* **2018**, *123*, 424−442.

(8) Nguyen, T. K. V.; Zhang, Q.; Jimenez, J. L.; Pike, M.; Carlton, A. G. Liquid Water: Ubiquitous Contributor to Aerosol Mass. *Environ. Sci. Technol. Lett.* **2016**, *3*, 257−263.

(9) Riemer, N.; Ault, A. P.; West, M.; Craig, R. L.; Curtis, J. H. Aerosol Mixing State: Measurements, Modeling, and Impacts. *Rev. Geophys.* **2019**, *57*, 187−249.

(10) Shrivastava, M.; Cappa, C. D.; Fan, J.; Goldstein, A. H.; Guenther, A. B.; Jimenez, J. L.; Kuang, C.; Laskin, A.; Martin, S. T.; Ng, N. L.; Petaja, T.; Pierce, J. R.; Rasch, P. J.; Roldin, P.; Seinfeld, J. H.; Shilling, J.; Smith, J. N.; Thornton, J. A.; Volkamer, R.; Wang, J.; Worsnop, D. R.; Zaveri, R. A.; Zelenyuk, A.; Zhang, Q. Recent Advances in Understanding Secondary Organic Aerosol: Implications for Global Climate Forcing. *Rev. Geophys.* **2017**, *55*, 509−559.

(11) McNeill, V. F. Aqueous Organic Chemistry in the Atmosphere: Sources and Chemical Processing of Organic Aerosols. *Environ. Sci. Technol.* **2015**, *49*, 1237−1244.

(12) Shrivastava, M.; Andreae, M. O.; Artaxo, P.; Barbosa, H. M. J.; Berg, L. K.; Brito, J.; Ching, J.; Easter, R. C.; Fan, J.; Fast, J. D.; Feng, Z.; Fuentes, J. D.; Glasius, M.; Goldstein, A. H.; Alves, E. G.; Gomes, H.; Gu, D.; Guenther, A.; Jathar, S. H.; Kim, S.; Liu, Y.; Lou, S.; Martin, S. T.; McNeill, V. F.; Medeiros, A.; de Sa, S. S.; Shilling, J. E.; Springston, S. R.; Souza, R. a. F.; Thornton, J. A.; Isaacman-VanWertz, G.; Yee, L. D.; Ynoue, R.; Zaveri, R. A.; Zelenyuk, A.; Zhao, C. Urban Pollution Greatly Enhances Formation of Natural Aerosols over the Amazon Rainforest. *Nat. Commun.* **2019**, *10*, 1046.

(13) Haskins, J. D.; Lopez-Hilfiker, F. D.; Lee, B. H.; Shah, V.; Wolfe, G. M.; DiGangi, J.; Fibiger, D.; McDuffie, E. E.; Veres, P.; Schroder, J. C.; Campuzano-Jost, P.; Day, D. A.; Jimenez, J. L.; Weinheimer, A.; Sparks, T.; Cohen, R. C.; Campos, T.; Sullivan, A.; Guo, H.; Weber, R.; Dibb, J.; Green, J.; Fiddler, M.; Bililign, S.; Jaegle, L.; Brown, S. S.; Thornton, J. A. Anthropogenic Control Over Wintertime Oxidation of Atmospheric Pollutants. *Geophys. Res. Lett.* **2019**, *46*, 14826−14835.

(14) Hodas, N.; Sullivan, A. P.; Skog, K.; Keutsch, F. N.; Collett, J. L.; Decesari, S.; Facchini, M. C.; Carlton, A. G.; Laaksonen, A.; Turpin, B. J. Aerosol Liquid Water Driven by Anthropogenic Nitrate: Implications for Lifetimes of Water-Soluble Organic Gases and Potential for Secondary Organic Aerosol Formation. *Environ. Sci. Technol.* **2014**, *48*, 11127−11136.

(15) Budisulistiorini, S. H.; Nenes, A.; Carlton, A. G.; Surratt, J. D.; McNeill, V. F.; Pye, H. O. T. Simulating Aqueous-Phase Isoprene-Epoxydiol (IEPOX) Secondary Organic Aerosol Production During the 2013 Southern Oxidant and Aerosol Study (SOAS). *Environ. Sci. Technol.* **2017**, *51*, 5026−5034.

(16) Pye, H. O. T.; Murphy, B. N.; Xu, L.; Ng, N. L.; Carlton, A. G.; Guo, H.; Weber, R.; Vasilakos, P.; Appel, K. W.; Budisulistiorini, S. H.; Surratt, J. D.; Nenes, A.; Hu, W.; Jimenez, J. L.; Isaacman-VanWertz, G.; Misztal, P. K.; Goldstein, A. H. On the Implications of Aerosol Liquid Water and Phase Separation for Organic Aerosol Mass. *Atmos. Chem. Phys.* **2017**, *17*, 343−369.

(17) Sareen, N.; Waxman, E. M.; Turpin, B. J.; Volkamer, R.; Carlton, A. G. Potential of Aerosol Liquid Water to Facilitate Organic Aerosol Formation: Assessing Knowledge Gaps about Precursors and Partitioning. *Environ. Sci. Technol.* **2017**, *51* (6), 3327−3335.

(18) Nguyen, T. K. V.; Petters, M. D.; Suda, S. R.; Guo, H.; Weber, R. J.; Carlton, A. G. Trends in Particle-Phase Liquid Water during the Southern Oxidant and Aerosol Study. *Atmos. Chem. Phys.* **2014**, *14*, 10911−10930.

(19) Christiansen, A. E.; Carlton, A. G.; Porter, W. C. The Changing Nature of Organic Carbon over the United States. *Environ. Sci. Technol.* **2020**, DOI: 10.1021/acs.est.0c02225.

(20) Pratt, K. A.; Fiddler, M. N.; Shepson, P. B.; Carlton, A. G.; Surratt, J. D. Organosulfates in Cloud Water above the Ozarks' Isoprene Source Region. *Atmos. Environ.* **2013**, *77*, 231−238.

(21) Lee, B. H.; Mohr, C.; Lopez-Hilfiker, F. D.; Lutz, A.; Hallquist, M.; Lee, L.; Romer, P.; Cohen, R. C.; Iyer, S.; Kurten, T.; Hu, W.; Day, D. A.; Campuzano-Jost, P.; Jimenez, J. L.; Xu, L.; Ng, N. L.; Guo, H.; Weber, R. J.; Wild, R. J.; Brown, S. S.; Koss, A.; de Gouw, J.; Olson, K.; Goldstein, A. H.; Seco, R.; Kim, S.; McAvey, K.; Shepson, P. B.; Starn, T.; Baumann, K.; Edgerton, E. S.; Liu, J.; Shilling, J. E.; Miller, D. O.; Brune, W.; Schobesberger, S.; D'Ambro, E. L.; Thornton, J. A. Highly Functionalized Organic Nitrates in the Southeast United States: Contribution to Secondary Organic Aerosol and Reactive Nitrogen Budgets. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 1516−1521.

(22) Hakkinen, S. A. K.; McNeill, V. F.; Riipinen, I. Effect of Inorganic Salts on the Volatility of Organic Acids. *Environ. Sci. Technol.* **2014**, *48*, 13718−13726.

(23) Nguyen, T. K. V.; Capps, S. L.; Carlton, A. G. Decreasing Aerosol Water Is Consistent with OC Trends in the Southeast U.S. *Environ. Sci. Technol.* **2015**, *49*, 7843−7850.

(24) Hand, J. L.; Schichtel, B. A.; Malm, W. C.; Pitchford, M. L. Particulate Sulfate Ion Concentration and SO2 Emission Trends in the United States from the Early 1990s through 2010. *Atmos. Chem. Phys.* **2012**, *12*, 10353−10365.

(25) Malm, W. C.; Schichtel, B. A.; Hand, J. L.; Collett, J. L. Concurrent Temporal and Spatial Trends in Sulfate and Organic Mass Concentrations Measured in the IMPROVE Monitoring Program. *J. Geophys. Res.-Atmospheres* **2017**, *122*, 10462−10476.

(26) Marais, E. A.; Jacob, D. J.; Turner, J. R.; Mickley, L. J. Evidence of 1991−2013 Decrease of Biogenic Secondary Organic Aerosol in Response to SO 2 Emission Controls. *Environ. Res. Lett.* **2017**, *12*, 054018.

(27) Carlton, A. G.; Bhave, P. V.; Napelenok, S. L.; Edney, E. O.; 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.

(28) Ridley, D. A.; Heald, C. L.; Ridley, K. J.; Kroll, J. H. Causes and Consequences of Decreasing Atmospheric Organic Aerosol in the United States. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 290−295.

(29) Ervens, B. Modeling the Processing of Aerosol and Trace Gases in Clouds and Fogs. *Chem. Rev.* **2015**, *115*, 4157−4198.

(30) Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Seitzinger, S. P.; Mathur, R.; Roselle, S. J.; Weber, R. J. CMAQ Model Performance Enhanced When In-Cloud Secondary Organic Aerosol Is Included: Comparisons of Organic Carbon Predictions with Measurements. *Environ. Sci. Technol.* **2008**, *42*, 8798−8802.

(31) Zhang, Y.; Forrister, H.; Liu, J.; Dibb, J.; Anderson, B.; Schwarz, J. P.; Perring, A. E.; Jimenez, J. L.; Campuzano-Jost, P.; Wang, Y.; Nenes, A.; Weber, R. J. Top-of-Atmosphere Radiative Forcing Affected by Brown Carbon in the Upper Troposphere. *Nat. Geosci.* **2017**, *10*, 486−489.

(32) Mao, J.; Carlton, A.; Cohen, R. C.; Brune, W. H.; Brown, S. S.; Wolfe, G. M.; Jimenez, J. L.; Pye, H. O. T.; Lee Ng, N.; Xu, L.; McNeill, V. F.; Tsigaridis, K.; McDonald, B. C.; Warneke, C.; Guenther, A.; Alvarado, M. J.; de Gouw, J.; Mickley, L. J.; Leibensperger, E. M.; Mathur, R.; Nolte, C. G.; Portmann, R. W.; Unger, N.; Tosca, M.; Horowitz, L. W. Southeast Atmosphere Studies: Learning from Model-Observation Syntheses. *Atmos. Chem. Phys.* **2018**, *18*, 2615−2651.

(33) Weber, R. J.; Guo, H.; Russell, A. G.; Nenes, A. High Aerosol Acidity despite Declining Atmospheric Sulfate Concentrations over the Past 15 Years. *Nat. Geosci.* **2016**, *9*, 282−285.

(34) Guo, H.; Xu, L.; Bougiatioti, A.; Cerully, K. M.; Capps, S. L.; Hite, J. R., Jr; Carlton, A. G.; Lee, S.-H.; Bergin, M. H.; Ng, N. L.; Nenes, A.; Weber, R. J. Fine-Particle Water and PH in the Southeastern United States. *Atmos. Chem. Phys.* **2015**, *15*, 5211−5228.

(35) Fountoukis, C.; Nenes, A. ISORROPIA II: A Computationally Efficient Thermodynamic Equilibrium Model for $K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O$ Aerosols. *Atmos. Chem. Phys.* **2007**, *7*, 4639−4659.

(36) Wang, C.; Lei, Y. D.; Endo, S.; Wania, F. Measuring and Modeling the Salting-out Effect in Ammonium Sulfate Solutions. *Environ. Sci. Technol.* **2014**, *48*, 13238−13245.

(37) Waxman, E. M.; Elm, J.; Kurtén, T.; Mikkelsen, K. V.; Ziemann, P. J.; Volkamer, R. Glyoxal and Methylglyoxal Setschenow Salting Constants in Sulfate, Nitrate, and Chloride Solutions: Measurements and Gibbs Energies. *Environ. Sci. Technol.* **2015**, *49*, 11500−11508.

(38) Kampf, C. J.; Waxman, E. M.; Slowik, J. G.; Dommen, J.; Pfaffenberger, L.; Praplan, A. P.; Prévôt, A. S. H.; Baltensperger, U.; Hoffmann, T.; Volkamer, R. Effective Henry's Law Partitioning and the Salting Constant of Glyoxal in Aerosols Containing Sulfate. *Environ. Sci. Technol.* **2013**, *47*, 4236−4244.

(39) Birdsall, A. W.; Hensley, J. C.; Kotowitz, P. S.; Huisman, A. J.; Keutsch, F. N. Single-Particle Experiments Measuring Humidity and Inorganic Salt Effects on Gas-Particle Partitioning of Butenedial. *Atmos. Chem. Phys.* **2019**, *19*, 14195−14209.

(40) Iavorivska, L.; Boyer, E. W.; Grimm, J. W. Wet Atmospheric Deposition of Organic Carbon: An Underreported Source of Carbon to Watersheds in the Northeastern United States. *J. Geophys. Res.-Atmospheres* **2017**, *122*, 3104−3115.

(41) Altieri, K. E.; Hastings, M. G.; Peters, A. J.; Sigman, D. M. Molecular Characterization of Water Soluble Organic Nitrogen in Marine Rainwater by Ultra-High Resolution Electrospray Ionization Mass Spectrometry. *Atmos. Chem. Phys.* **2012**, *12*, 3557−3571.

(42) Altieri, K. E.; Turpin, B. J.; Seitzinger, S. P. Composition of Dissolved Organic Nitrogen in Continental Precipitation Investigated by Ultra-High Resolution FT-ICR Mass Spectrometry. *Environ. Sci. Technol.* **2009**, *43*, 6950−6955.

(43) Sander, R. Compilation of Henry's Law Constants (Version 4.0) for Water as Solvent. *Atmos. Chem. Phys.* **2015**, *15*, 4399−4981.

(44) Koop, T.; Bookhold, J.; Shiraiwa, M.; Poeschl, U. Glass Transition and Phase State of Organic Compounds: Dependency on Molecular Properties and Implications for Secondary Organic Aerosols in the Atmosphere. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19238−19255.

(45) Shiraiwa, M.; Li, Y.; Tsimpidi, A. P.; Karydis, V. A.; Berkemeier, T.; Pandis, S. N.; Lelieveld, J.; Koop, T.; Pöschl, U. Global Distribution of Particle Phase State in Atmospheric Secondary Organic Aerosols. *Nat. Commun.* **2017**, *8*, 15002.

(46) Berkemeier, T.; Shiraiwa, M.; Poeschl, U.; Koop, T. Competition between Water Uptake and Ice Nucleation by Glassy Organic Aerosol Particles. *Atmos. Chem. Phys.* **2014**, *14*, 12513−12531.

(47) Malm, W. C.; Schichtel, B. A.; Hand, J. L.; Prenni, A. J. Implications of Organic Mass to Carbon Ratios Increasing Over Time in the Rural United States. *J. Geophys. Res.: Atmos.* **2020**, *125*, e2019JD031480.

(48) 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.

(49) Champion, W. M.; Rothfuss, N. E.; Petters, M. D.; Grieshop, A. P. Volatility and Viscosity Are Correlated in Terpene Secondary Organic Aerosol Formed in a Flow Reactor. *Environ. Sci. Technol. Lett.* **2019**, *6*, 513−519.

(50) Khan, B.; Hays, M. D.; Geron, C.; Jetter, J. Differences in the OC/EC Ratios That Characterize Ambient and Source Aerosols Due to Thermal-Optical Analysis. *Aerosol Sci. Technol.* **2012**, *46*, 127−137.

(51) Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Seitzinger, S.; Reff, A.; Lim, H.-J.; Ervens, B. Atmospheric Oxalic Acid and SOA Production from Glyoxal: Results of Aqueous Photooxidation Experiments. *Atmos. Environ.* **2007**, *41*, 7588−7602.

(52) Tan, Y.; Carlton, A. G.; Seitzinger, S. P.; Turpin, B. J. SOA from Methylglyoxal in Clouds and Wet Aerosols: Measurement and Prediction of Key Products. *Atmos. Environ.* **2010**, *44*, 5218−5226.

(53) Aswini, A. R.; Hegde, P.; Nair, P. R.; Aryasree, S. Seasonal Changes in Carbonaceous Aerosols over a Tropical Coastal Location in Response to Meteorological Processes. *Sci. Total Environ.* **2019**, *656*, 1261−1279.

(54) Wu, Z.; Wang, Y.; Tan, T.; Zhu, Y.; Li, M.; Shang, D.; Wang, H.; Lu, K.; Guo, S.; Zeng, L.; Zhang, Y. Aerosol Liquid Water Driven by Anthropogenic Inorganic Salts: Implying Its Key Role in Haze Formation over the North China Plain. *Environ. Sci. Technol. Lett.* **2018**, *5*, 160−166.

(55) Ford, B.; Heald, C. L. Aerosol Loading in the Southeastern United States: Reconciling Surface and Satellite Observations. *Atmos. Chem. Phys.* **2013**, *13*, 9269−9283.

(56) Kim, P. S.; Jacob, D. J.; Fisher, J. A.; Travis, K.; Yu, K.; Zhu, L.; Yantosca, R. M.; Sulprizio, M. P.; Jimenez, J. L.; Campuzano-Jost, P.; Froyd, K. D.; Liao, J.; Hair, J. W.; Fenn, M. A.; Butler, C. F.; Wagner, N. L.; Gordon, T. D.; Welti, A.; Wennberg, P. O.; Crounse, J. D.; St Clair, J. M.; Teng, A. P.; Millet, D. B.; Schwarz, J. P.; Markovic, M. Z.; Perring, A. E. Sources, Seasonality, and Trends of Southeast US Aerosol: An Integrated Analysis of Surface, Aircraft, and Satellite Observations with the GEOS-Chem Chemical Transport Model. *Atmos. Chem. Phys.* **2015**, *15*, 10411−10433.

(57) Babila, J. E.; Carlton, A. G.; Hennigan, C. J.; Ghate, V. P. On Aerosol Liquid Water and Sulfate Associations: The Potential for Fine Particulate Matter Biases. *Atmosphere* **2020**, *11*, 194.

(58) El-Sayed, M. M. H.; Amenumey, D.; Hennigan, C. J. Drying-Induced Evaporation of Secondary Organic Aerosol during Summer. *Environ. Sci. Technol.* **2016**, *50*, 3626−3633.

(59) Li, S.; Garay, M. J.; Chen, L.; Rees, E.; Liu, Y. Comparison of GEOS-Chem Aerosol Optical Depth with AERONET and MISR Data over the Contiguous United States. *J. Geophys. Res. Atmospheres* **2013**, *118*, 11228−11241.

(60) Christiansen, A. E.; Ghate, V. P.; Carlton, A. G. Aerosol Optical Thickness: Organic Composition, Associated Particle Water, and Aloft Extinction. *ACS Earth Space Chem.* **2019**, *3*, 403−412.

(61) Nguyen, T. K. V.; Ghate, V. P.; Carlton, A. G. Reconciling Satellite Aerosol Optical Thickness and Surface Fine Particle Mass through Aerosol Liquid Water. *Geophys. Res. Lett.* **2016**, *43*, 11903−11912.

(62) Attwood, A. R.; Washenfelder, R. A.; Brock, C. A.; Hu, W.; Baumann, K.; Campuzano-Jost, P.; Day, D. A.; Edgerton, E. S.; Murphy, D. M.; Palm, B. B.; McComiskey, A.; Wagner, N. L.; de Sa, S. S.; Ortega, A.; Martin, S. T.; Jimenez, J. L.; Brown, S. S. Trends in Sulfate and Organic Aerosol Mass in the Southeast U.S.: Impact on Aerosol Optical Depth and Radiative Forcing. *Geophys. Res. Lett.* **2014**, *41*, 7701−7709.

(63) Leibensperger, E. M.; Mickley, L. J.; Jacob, D. J.; Chen, W.-T.; Seinfeld, J. H.; Nenes, A.; Adams, P. J.; Streets, D. G.; Kumar, N.; Rind, D. Climatic Effects of 1950−2050 Changes in US Anthropogenic Aerosols - Part 1: Aerosol Trends and Radiative Forcing. *Atmos. Chem. Phys.* **2012**, *12*, 3333−3348.

(64) Li, C.; Martin, R. V. Decadal Changes in Seasonal Variation of Atmospheric Haze over the Eastern United States: Connections with Anthropogenic Emissions and Implications for Aerosol Composition. *Environ. Sci. Technol. Lett.* **2018**, *5*, 413−418.

(65) Holben, B. N.; Eck, T. F.; Slutsker, I.; Tanre, D.; Buis, J. P.; Setzer, A.; Vermote, E.; Reagan, J. A.; Kaufman, Y. J.; Nakajima, T.; Lavenu, F.; Jankowiak, I.; Smirnov, A. AERONET - A Federated Instrument Network and Data Archive for Aerosol Characterization. *Remote Sens. Environ.* **1998**, *66*, 1−16.

(66) Schuster, G. L.; Dubovik, O.; Holben, B. N. Angstrom Exponent and Bimodal Aerosol Size Distributions. *J. Geophys. Res.* **2006**, *111* (D7), D07207.

(67) Christiansen, A. E.; Carlton, A. G.; Henderson, B. H. Differences in Fine Particle Chemical Composition on Clear and Cloudy Days. *Atmospheric Chem. Phys. Discuss.* **2020**, 1−26.

(68) Aerosol Robotic Network (AERONET) Homepage https://aeronet.gsfc.nasa.gov/ (accessed March, 2020).

(69) Dick, W. D.; Saxena, P.; McMurry, P. H. Estimation of Water Uptake by Organic Compounds in Submicron Aerosols Measured during the Southeastern Aerosol and Visibility Study. *J. Geophys. Res.-Atmospheres* **2000**, *105*, 1471−1479.