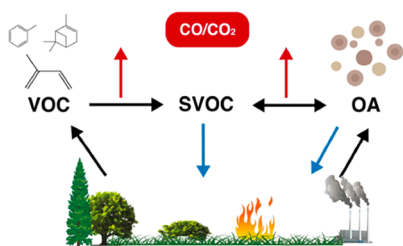


Recent Discoveries and Future Challenges in Atmospheric Organic Chemistry

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Earth's atmosphere contains a multitude of organic compounds, which differ by orders of magnitude regarding fundamental properties such as volatility, reactivity, and propensity to form cloud droplets, affecting their impact on global climate and human health. Despite recent major research efforts and advances, there are still substantial gaps in understanding of atmospheric organic chemistry, hampering efforts to understand, model, and mitigate environmental problems such as aerosol formation in both polluted urban and more pristine regions. The analytical toolbox available for chemists to study atmospheric organic components has expanded considerably during the past decade, opening new windows into speciation, time resolution and detection of reactive and semivolatile compounds at low concentrations. This has provided unprecedented opportunities, but also unveiled new scientific challenges. Specific groundbreaking examples include the role of epoxides in aerosol formation especially from isoprene, the importance of highly oxidized, reactive organics in air-surface processes (whether atmosphere–biosphere exchange or aerosols), as well as the extent of interactions of anthropogenic and biogenic emissions and the resulting impact on atmospheric organic chemistry.

■ WHAT HAS BEEN LEARNED ABOUT THE SOURCES AND PROPERTIES OF ORGANIC COMPOUNDS IN THE ATMOSPHERE DURING THE PAST DECADE?

Organic compounds are emitted to the atmosphere directly from natural sources, especially vegetation, and from combustion of fossil fuels or biomass (see Figure 1). Globally, about 1000 Tg of volatile organic compounds (VOC, with vapor pressure $>10^{-5}$ atm) are naturally emitted each year from plants, primarily terrestrial, as isoprene (2-methyl-1,3-butadiene, about 50%), monoterpenes ($C_{10}H_{16}$, 15%) and sesquiterpenes ($C_{15}H_{24}$, 3%),¹ but also as nonisoprenoid, oxidized VOC, for example, about 10% as methanol.¹ Anthropogenic combustion and use of fossil fuels (including leakage during production and transport) emits approximately 127 Tg y^{-1} (range 98–158 Tg y^{-1}).² Additional emissions come from wild fires and domestic heating and cooking with biomass fuels.

Plants emit VOC during growth and decay as a response to environmental conditions, especially light, temperature, and phenology, and in response to stress, such as lack of water, high temperatures, and presence of herbivores or pathogens.³ The emissions dominantly occur directly from leaves and needles, in addition to woody parts, roots and decaying plant matter in the soil, where microbes degrade organic material, releasing VOC such as stored monoterpenes and degradation products such as methanol and acetone.⁴

When Went in 1960 first suggested that emissions of VOC from vegetation could influence atmospheric chemical processes and form secondary organic aerosols (SOA),⁵ he would probably not have guessed after more than 50 years that a large fraction of the field of atmospheric chemistry would today be focused on understanding the role of these chemicals, or that there would remain such incomplete knowledge and understanding of this system. There has been tremendous progress, but also the constant identification of new unknowns, providing new impetus for research.

In the 1980s models of biogenic VOC emission were initially built on leaf or branch level measurements of emission factors for individual plants and then scaled up to the landscape or region. Starting in the 1990s, flux measurements began to be made at the ecosystem scale, integrating over all plants, soil, etc., and then compared to models.^{1a,6} Especially during the past decade, the use of remote sensing of formaldehyde, whose dominant source is isoprene oxidation, has enabled inversion models to estimate isoprene flux at regional and global scales, allowing verification of the emission inventory.⁷ Furthermore, measurements of biogenic VOC fluxes from aircraft have provided a new perspective and ability to test models at the landscape or regional scale.⁸ A major finding from these studies is that models can make accurate estimates of biogenic VOC emissions, when the landcover databases driving the model are accurate. While these models have begun to be tested extensively in the past decade for isoprene emissions, little has been done to validate them for other biogenic VOC.

Atmospheric lifetime, impact, and fate of an organic compound depend on its properties, of which volatility is one of the most decisive. Volatility is assumed to govern the partitioning between gas and particle phase, and consequently the atmospheric lifetime of the compound. Since lifetime in the gas phase depends on reactivity and availability of radical oxidants and sun light, while lifetimes in the particle phase are assumed to be longer, due to lower formation or uptake rates of oxidants, shielding effects of neighboring compounds, and slow

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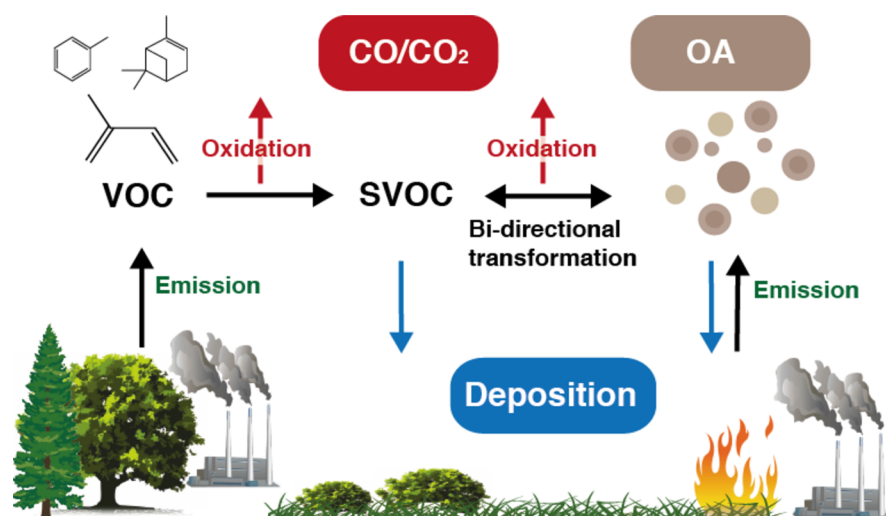


Figure 1. Major processes in atmospheric organic chemistry. The fate of organic compounds in the atmosphere can be seen as competition between complete oxidation to CO_2 (fragmentation), functionalization also contributing to organic aerosols (OA), and deposition.

diffusion rates. Organic compounds with lower vapor pressures ($<10^{-11}$ atm) are found in aerosol particles, whereas semi-volatile compounds (vapor pressures in the range 10^{-5} – 10^{-11} atm) can exchange between gas and particle phase, primarily depending on temperature and pressure.

Within the past decade it has become increasingly clear that SOA particles are not just liquids but can be highly viscous or have glass-like properties,⁹ affecting reactivity, evaporation and diffusion time scales.¹⁰ This is especially pronounced at low relative humidity,¹¹ at which many previous chamber studies were carried out to avoid, for example, condensation on chamber surfaces. Re-evaporation of organic compounds can occur during hours or days, which is much longer than the order of minutes as calculated from evaporation kinetics.^{9b} The high, tar-like, viscosity of SOA also contributes to the challenges encountered in measurements of equilibrium vapor pressures of low-volatility compounds, where differences of several orders of magnitude have been observed in, for example, widely studied dicarboxylic acids.¹²

Organic aerosols (OA) can be emitted directly as e.g. biological aerosol particles (pollen, fungi spores, bacteria¹³) or from combustion sources, but a major fraction of atmospheric OA have a secondary origin from oxidation of VOC followed by condensation of low-volatility products, uptake in acidic aerosol particles, or aqueous phase chemical transformations.¹⁴ Chamber studies in the 1990s and beginning of 2000s contributed to fundamental understanding of SOA formation from monoterpenes, including aerosol yields and chemical composition.¹⁵ Formation of SOA from isoprene was considered negligible until the discovery in 2004 of 2-methyltetrols (from heterogeneous isoprene reactions) in aerosol samples from the Amazon forest,¹⁶ initiating laboratory studies to elucidate SOA yields and composition.¹⁷

As much as 50–85% of the total OA can be SOA, though the contribution varies greatly in time and space with respect to proximity of sources, and there are currently significant differences between different models and estimation approaches.^{14a,18} Quantitative estimates of SOA are within a range of 20–380 Tg y^{-1} for most studies,¹⁹ with estimates of 140 Tg y^{-1} for total SOA^{18a} or 150 Tg y^{-1} for biogenic SOA (BSOA).^{14a} For comparison, a recent intercomparison of global models showed median emissions of primary OA of 56 (34–144) Tg y^{-1}

and formation of 51 (16–121) Tg SOA y^{-1} calculated by the subset of models with the most complex parametrization of SOA processes, while the four models accounting for multiphase chemistry found a significant contribution of up to 50% of total SOA formation at least regionally from this previously under-recognized source.^{18b} In contrast to these models which generally suggest BSOA to be the dominant source, Shrivastava et al.²⁰ suggested that biomass burning is the largest global source of SOA (71%), with BSOA the second largest source (22%), and fossil fuel SOA being of minor importance (6% of SOA).

General agreement now exists that SOA is a major contributor to the global OA budget, but lack of understanding of relevant emissions, transformation processes and fate still hamper our efforts to accurately estimate air quality and climate effects of atmospheric aerosols.

■ HOW HAS UNDERSTANDING OF TRANSFORMATIONS AND FATE OF ATMOSPHERIC ORGANICS CHANGED DURING THE PAST DECADE?

The fate of atmospheric organic compounds is a competition between three overall pathways, as previously suggested by Goldstein and Galbally:²¹ Complete oxidation to CO_2 (fragmentation), functionalization to form products of lower volatility contributing to SOA, and wet or dry deposition (illustrated in Figure 1). Of these processes we especially lack quantitative understanding of the amount of SOA produced, and the magnitude of deposition. Furthermore, we lack understanding of how these fates vary as a function of the diverse organic compounds with different properties such as volatility, water solubility, and hygroscopicity. Here we will describe these processes and some of the remaining uncertainties.

VOC are transformed in the atmosphere by photolysis and oxidation; hydroxyl radicals during daytime, nitrate radicals during night, and ozone throughout day and night.²² In addition, ocean-derived chlorine and bromine species can become important oxidants in marine and arctic areas under certain conditions.²³ Reactions with Criegee intermediates (carbonyl oxides) have also received renewed attention,²⁴

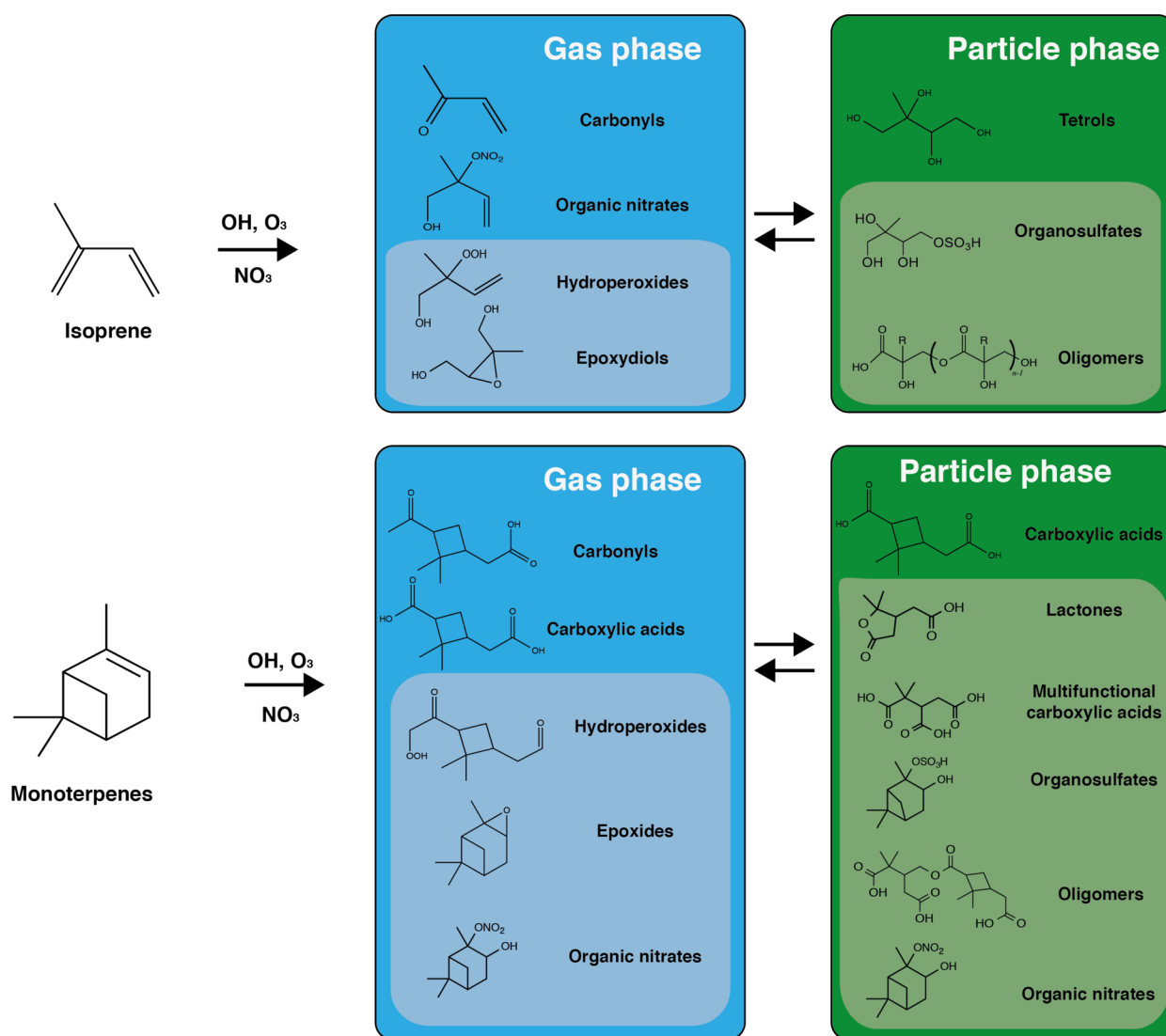


Figure 2. Oxidation products of isoprene and monoterpenes in the gas phase and particle phase. Shaded areas show oxidation products, where major progress in understanding has been achieved during the past decade.

though their importance on a global scale remains to be accurately understood.

Oxidation of VOC initially forms a wide range of alkyl, alkoxy, and peroxy radicals followed by stable products such as carbonyl compounds, alcohols and carboxylic acids. These are either fragmentation or functionalization pathways, of which fragmentation leads to more volatile products and finally carbon dioxide, whereas functionalization pathways produce a complex array of lower volatility compounds which can condense to form SOA.²⁵ Recently, both gas and particle phase autoxidation reactions have been discovered, involving inter- and intramolecular hydrogen abstraction by peroxy radicals, which can quickly form extremely low volatility products found in aerosols.²⁶

A large body of work has been carried out to characterize stable VOC oxidation products in gas and particle phases, and the importance of intermediate, reactive products such as epoxides and hydroperoxides has been revealed especially during the past decade. Figure 2 presents an overview of some major, recent advances in understanding speciation of secondary atmospheric organics. These include organosulfates of isoprene and α -pinene,²⁷ oligomers of isoprene and α -

pinene,^{17b,e,28} as well as lactones, multifunctional carboxylic acids, and organic nitrates of α -pinene.²⁹

The presence of organic hydroperoxides in the atmosphere was first shown in 1991,³⁰ but the formation and occurrence of hydroperoxides, as well as epoxides, were until recently only studied in a few papers, partly due to lack of adequate instrumentation.³¹ Now the role of reactive intermediates such as hydroxy hydroperoxides, peroxy hemiacetals and epoxides in atmospheric reactions is increasingly recognized as a mechanism for efficient uptake of volatile products in aerosols, and has thus been identified as an important missing link in our understanding of atmospheric organic chemistry and processes.³² Upon oxidation by OH at low NO_x conditions, isoprene can form a hydroxy hydroperoxide, which is further oxidized by OH to isoprene epoxydiol, IEPOX, that readily reacts at aerosol surfaces to form SOA.^{32a,33} Other reactive intermediates of isoprene (e.g., methacrylic acid epoxide) are involved in SOA formation in urban areas with higher NO_x concentrations.³⁴ Identification of these reaction pathways and detailed chemical speciation has turned out to be decisive in understanding of aerosol formation from isoprene.

Anthropogenic pollutants affect transformation of biogenic VOCs and formation of SOA through several mechanisms;³⁵ The presence of NO_x affects the fate of peroxy radical species in gas phase reactions, and oxidation of sulfur dioxide leads to sulfate aerosols, which influence aerosol processes by changing both acidity and water content affecting reaction pathways and particle viscosity, as well as increasing the particle surface available for condensation of semivolatile organic compounds.

Formation of organosulfates from reactive uptake of semivolatile organics especially in acidic aerosol particles has been observed for isoprene, monoterpenes, green leaf unsaturated aldehydes, and PAHs.^{27,36} The process poses an interesting coupling of aerosol formation from biogenic VOC and sulfate aerosols, which are typically of anthropogenic origin. This coupling, providing a regional cooling in southeastern U.S., was first suggested based on a combination of satellite data and ground-based measurements³⁷ and seems to be especially important for understanding aerosol formation from isoprene.³⁸ This has been further elucidated in recent major measurement efforts during the Southern Oxidants and Aerosol Study (SOAS). These investigations also point toward the importance of atmospheric water and heterogeneous reactions for the high levels of aerosols observed in this region during summer.³⁹

Oligomers in aerosols were first observed in laboratory studies of SOA formation more than a decade ago,⁴⁰ and have also been detected in atmospheric aerosols, though often at considerably lower numbers of species and levels.^{28,41} Fast, gas-phase oligomerization reactions would contribute to explain nucleation and SOA formation, especially in laboratory studies without seed aerosol and in regions of high biogenic emissions such as the boreal forest during spring. Dimers and oligomers of monoterpene oxidation products may form within seconds after the start of reactions and can be observed before monomers in aerosol particles, indicating a key role in SOA formation and initial particle growth.⁴² Observations of extremely low volatility organic compounds (ELVOC) indicate that gas-phase oligomerization can indeed happen both in chambers and in areas with high concentrations of precursors such as the boreal forest,⁴³ but the global implications are still to be elucidated.

Oligomerization reactions can also occur during aging of aerosols, which increase particle viscosity and consequently reduce the rate of diffusion and evaporation processes.^{9b} An example is particle phase oligomerization of hemiacetals from oxidation of pentadecane by OH.⁴⁴ Some oligomers in α -pinene SOA decrease in concentration during aging by OH, due to fragmentation reactions, whereas others with higher O/C ratios form as products of functionalization pathways.⁴⁵ In contrast, some specific dimers of α -pinene oxidation products have been observed to be relatively stable during chamber experiments.⁴⁶

Organic aerosols are removed from the atmosphere by wet and dry deposition, of which a recent model intercomparison suggests that wet deposition dominates (85%).^{18b} Wet deposition is influenced by the hygroscopicity of aerosol constituents affecting their propensity to grow by condensation of water vapor to form cloud condensation nuclei (CCN), which may then either evaporate again or deposit.⁴⁷ Despite ongoing research efforts on hygroscopicity and related properties, our lack of detailed understanding results in large uncertainties in quantitative estimates.

There is new and growing scientific understanding of the deposition processes of semivolatile VOC and the significance to the SOA budget. Hodzic et al.⁴⁸ found that the Henry's law constants of condensable organics are orders of magnitude larger than previously realized, which increases estimates of wet deposition of semivolatile VOC considerably. Wet deposition of VOC may thus be an important removal pathway, which also reduces the amount of precursors for SOA. Furthermore, Park et al.⁴⁹ observed active atmosphere-ecosystem exchange in an orange orchard of as many as 162 VOCs with greater deposition fluxes for oxygenated hydrocarbons, typically oxidation products, than the pure hydrocarbons.⁴⁹ This is corroborated by Nguyen et al.,⁵⁰ who found that dry deposition is an important sink for small, oxygenated VOC in a temperate, mixed forest. Especially water-soluble compounds, such as hydroperoxides and epoxydiols (IEPOX), are efficiently deposited due to low surface-resistance. Furthermore, these compounds are highly reactive, leading to formation of products with lower volatility, that will not evaporate once deposited.

The study of Park et al.⁴⁹ also highlights the importance of measurements of a wide range of compounds. Most previous investigations have only quantified exchange of typically less than 10 compounds, that may make up only about 1/4 of the total emission of carbon from some ecosystems and account for almost none of the total VOC deposition.⁴⁹

The relative importance of the pathways for fate of VOC—fragmentation, functionalization, and deposition—was recently modeled by Shrivastava et al. using an updated version of the Community Atmosphere Model (CAM), where SOA is treated as basically nonvolatile (based on previous work^{9b,51}), and fragmentation and deposition schemes were also updated to reflect recent findings.²⁰ They find that dry and wet deposition of SVOC contribute to 60–75% of loss of SOA and condensable vapors, whereas wet deposition of SOA is responsible for most of the remaining loss. The results of Karl et al.⁵² and Nguyen et al.⁵⁰ suggest that dry removal of oxygenated VOCs might be underestimated in these calculations. Overall the updated model shows very good agreement between model results and ground-based, airborne as well as satellite measurements, suggesting that our understanding of atmospheric organic chemistry budget is improving.

Goldstein and Galbally²¹ pointed out the importance of unknown atmospheric organic compounds and the lack of understanding of deposition processes, which would greatly affect the SOA budget. Recent research efforts, as outlined above, have certainly improved the scientific knowledge of both the complexity of atmospheric organics and their deposition, but it seems that we have only just begun to understand these processes and quantitatively estimate their implications for the budget of organic compounds in the atmosphere.

■ WHAT ARE THE MEASUREMENT CHALLENGES TODAY?

Measurement challenges in atmospheric organic chemistry today focus in two primary directions: speciation and time resolution. Regarding speciation there are several subgroups of challenges: Reactive species, oligomers, accurate molecular identification, and quantification. Rapid advancements are occurring in instrumentation for investigation of atmospheric chemical composition, both by necessity and due to application of advances in related fields, in particular mass spectrometry, with improved resolving capacity, and a broadening array of

ionization approaches. This has enabled instrumentation with high time resolution or high mass resolution, but seldom both. Here we will highlight some recent advances in techniques for measurement of atmospheric organics as well as remaining measurement challenges, while more detailed reviews of instruments and methods for atmospheric measurements are found elsewhere.⁵³

New types of chemical ionization mass spectrometers (CIMS) enable measurements of organic trace gases through ionization with reactive ions such as H_3O^+ , NO_3^- , CF_3O^- , or acetate,^{53a} to provide data with high time resolution of relatively stable compounds of atmospheric relevance such as carbonyls and carboxylic acids, but also of reactive, short-lived species such as hydroperoxides and multifunctional nitrates.⁵⁰ These new measurement capabilities have provided information on previously overlooked processes in the atmosphere and in chamber studies. One example is the loss of reactive, semivolatile species on the walls of Teflon chambers often used for laboratory studies of atmospheric reactions and processes.⁵⁴ Another example is atmosphere-ecosystem exchange of reactive VOCs, as mentioned earlier.^{49,50} It is a challenge to achieve molecular identification from the complex mass spectra obtained without chromatographic separation, especially when applying quadrupole MS with unit-mass resolution. Therefore, time-of-flight mass spectrometers (TOF-MS) have been widely adapted in the atmospheric chemistry community for such analyses. However, even higher mass resolution than is typically achieved by current field deployable TOF-MS instruments would be desirable for differentiating SVOCs and particle phase species. Another challenge is the need for fundamental studies of ionization mechanisms and efficiencies of target compounds as well as possible interferences such as relative humidity, in order to achieve more accurate identifications and quantification.

Techniques for analysis of gas phase compounds have been expanded to include aerosols after thermal desorption to evaporate organic particle constituents. Separation of gas and particle phase organics also enables important information on gas-particle distribution with high time-resolution on the order of minutes to hours. The Thermal Desorption Aerosol Gas Chromatograph (TAG) system is an example of such an instrument, where in the most recent configuration either particles or particles and SVOC are collected, then thermally desorbed, derivatized (by silylation), and separated by GC before electron ionization (EI) and detection by MS.⁵⁵ This version of the instrument enables quantitative analysis of alkanolic acids, polyols, diacids, sugars, and multifunctional compounds with hourly time resolution. The advantage of EI is the extensive fragmentation, providing information on molecular composition and structure, though at the cost of information on the molecular ion. Another related instrument is the multiorifice volatilization impactor (MOVI) coupled to TOF/CIMS.⁵⁶ Since CIMS is a soft ionization technique, it provides the molecular mass of an ion, but typically not fragmentation to identify isomers or additional, unknown compounds.

Measurements of aerosol composition in a variety of environments with time resolution of minutes or half hour have become increasingly available through deployment of the aerosol mass spectrometer (AMS)^{25a} commercially available from Aerodyne. The instrument relies on EI for ionization, which results in complex mass spectra that are resolved using positive matrix factorization into factors with different

characteristics (such as hydrocarbon-like OA and oxygenated OA).^{25a,57} On-going work is focused on identification of fragment ions that can be related to specific molecular tracers, such as m/z 60 from levoglucosan and m/z 82 from isoprene SOA.⁵⁸ Due to both the complexity of the fragment mass spectra and the complexity of atmospheric organic aerosols it is critical to be cautious of potential interferences from related compounds or due to environmental conditions.

Increasing availability of higher-resolution mass spectrometers has supported molecular identification in both online and off-line analyses. For online analyses of both gas phase and particle phase compounds, the availability of small TOF-MS analyzers with a resolution of typically a few thousand has improved identification and speciation considerably. Off-line analyses have the possibility to achieve much higher resolution as provided by larger TOF-MS instruments (typical resolution up to 40 000). A recent example is particle-into-liquid sampling followed by ultrahigh performance liquid chromatography coupled with electrospray ionization and quadrupole-TOF-MS (PILS-UPLC/ESI-Q-TOF-MS) enabling time-resolved molecular analysis of ~58–72% of α -pinene SOA mass.^{46c,59}

There is still a lack of understanding of the chemistry of oligomers in atmospheric aerosols including specific types and strengths of bonds, effects on aerosol properties, and persistence, which hampers our ability to understand and accurately model organic aerosols in the atmosphere. Part of this is due to the complexity in accurate identification and quantification of oligomer chemistry.

Determination of elemental composition of thousands of individual compounds in aerosols is achieved by instruments such as Orbitrap MS and FT-ICR-MS (Fourier transform ion cyclotron resonance MS) with resolution on the order of 1 000 000 or more,^{41,53a,60} and yet we must realize that there are a large number of other compounds either not extracted, transferred through the instrument, ionized and/or detected. There remains a strong need to target high-resolution MS studies toward improving process level understanding of atmospheric organic chemistry and to further develop techniques with high time resolution for identification and quantification of compounds that are presently not detected or less studied.

A major measurement challenge today is to develop accurate techniques to identify and quantify the particle phase products from condensation of ELVOC, which are probably highly multifunctional hydroperoxides.⁴³ This is challenging because such compounds are highly reactive, making it difficult to measure them without inducing reactions on, for example, instrument surfaces that change their molecular structure. Other groups of important reactive compounds that should be prominent but are difficult to measure include organonitrates, especially multifunctional ones. Quantification of the sum of organonitrates without speciation is a useful strategy which has enabled progress in understanding of their formation and chemistry,⁶¹ but in situ measurement techniques for speciated compounds are still needed. Furthermore, organosulfates can only be observed by a subset of analytical techniques, namely electrospray-MS (ESI-MS), while they fragment in the EI source of AMS or GC-MS, pointing out the strength of instrument diversity and the need for in situ measurement techniques of speciated organosulfates.

Many reactive, semivolatile species may have been overlooked in chamber studies of SOA formation due to adsorption on the widely used Teflon chamber walls.⁶² In an experiment

where semivolatile reaction products are produced, condensation to form SOA should thus be viewed as a competition between condensation on particles and on the walls of the chamber, and the ratio will affect observed SOA yields.^{62b} This effect could be even more critical for the most reactive species, and is also affected by relative humidity of the air.

It is thus crucial to keep investigating the interferences and artifact formation of all measurement techniques and to understand the limitations of each method. Recent work elucidating fast conversion of hydroperoxides from isoprene oxidation to carbonyl compounds within commonly used analytical instrumentation⁶³ demonstrates the importance of such efforts.

At some point the atmospheric scientist must ask: How much more do we need to be able to measure? Our answer is that we need to measure enough to quantitatively understand the fate of organic carbon, and to identify the important chemical and physical processes determining its fate. We also need to understand the detailed chemistry well enough to enable accurate extension of processes into models to test a broader understanding beyond the localized measurements. Embracing the complexity of atmospheric organic compounds is central in advancement of understanding in the field of atmospheric chemistry, as first suggested by Worton et al.⁶⁴ This is well illustrated by some of the cases presented above: Exchange of reactive organics between ecosystems and the atmosphere affecting the global SOA budget, formation of organosulfates linking biogenic and anthropogenic emissions in SOA formation, formation and fate of LVOCs contributing to SOA.

■ WHAT FURTHER RESEARCH IS NEEDED TO UNDERSTAND ATMOSPHERIC ORGANIC CHEMISTRY?

Building on recent advances in scientific understanding of atmospheric organic chemistry, future research directions should cover fundamental photochemical processes, improved chemical speciation, deposition, reactive carbon and nitrogen budget closure, and temporal and spatial diversity in chemical regimes. This knowledge should be applied to the specific societal challenges related to climate change and human health impacts of air pollution, and sustainable responses including land use changes, urban development and development of new energy systems. In turn, societal responses will have important feedbacks on atmospheric chemistry, which our community must strive to understand and predict.

Photochemical oxidation of even small organic compounds can lead to formation of tens to hundreds of first generation products, which will then undergo further oxidation and transformation. Thus, atmospheric chemists will probably never be able to identify all oxidation products of all VOC in the atmosphere. However, we must strive to achieve speciation to understand the complexity of trace compounds to a degree that is detailed enough to enable process level understanding of atmospheric organic chemistry.

Recent research has shed light on the importance of short-lived, reactive species such as hydroperoxides, ELVOCs and organic nitrates, for atmospheric processes. New and improved instrumentation is urgently needed to enable accurate speciation and quantification of these compounds in both gas and particle phase, to close present gaps in the scientific knowledge of photochemical fate, surface exchange processes, and aerosol formation and growth. Such studies will also

improve identification of previously encountered experimental or measurement artifacts that can bias understanding of atmospheric organic chemistry. For the most important species, more than one technique is desirable, and authentic quantitative standards are critical yet often currently unavailable.

There is also a need to obtain better understanding of atmospheric organic chemistry at the interfaces from micro to macro scale. These include gas-particle interfaces, as well as interfaces between the atmosphere and the biosphere, cryosphere and hydrosphere. Aqueous phase processes as well as interactions between inorganic and organic components of aerosols require further investigation as they will likely reveal previously unrecognized processes.

There is an extreme scarcity of quantitative, comprehensive investigations of dry and wet deposition for a comprehensive range of organic compounds. Such measurements have previously been hampered by lack of adequate instrumentation, but there is a growing opportunity to use newly developed fast response instrumentation for detailed investigations of atmosphere–surface exchange processes, which are poorly understood at present.

Vertical profiles of atmospheric trace compounds and processes should also be further investigated. Previously vertical profiling has mainly been achieved using towers (up to only a hundred meters), aircrafts, and even a zeppelin in the European PEGASOS project, but most of these modes of instrument transport are very expensive and infrequent. Availability of vertical measurements may be expanded in the future with development of, for example, smaller less expensive drones carrying sensors or samplers for chemical measurements.

A critical goal for atmospheric organic chemists is to work toward closing the atmospheric organic carbon budget. Previous studies have found that the gap between measurements and carbon closure increases with distance from sources, presumably due to further oxidation of emissions to secondary products not detected by available measurement techniques.⁶⁵ As further development and deployment of a broader suite of instrumentation to measure oxidized organics occurs, we should strive to understand how carbon accounting improves.

Vast areas of the globe remain unexplored from the perspective of atmospheric organic chemistry. This includes measuring emissions of especially BVOC, aerosol chemical composition and studies of atmospheric photochemical processes to determine prevalent oxidant and oxidation routes, and atmosphere–surface exchange processes. Such investigations are important since understudied or unstudied environmental systems can differ in unexpected ways. Examples include the importance of sea-ice and halogen chemistry for photochemical oxidation in the polar troposphere, which was not recognized before measurements showed surprising depletion in tropospheric ozone concentrations at polar sunrise in the Arctic,⁶⁶ initiating further studies of this phenomenon. Major research efforts should also be directed toward studying the effects of global changes in distribution of anthropogenic emissions on atmospheric chemistry. During the coming decades, emissions of anthropogenic nitrogen oxides, sulfur dioxide, and VOCs are expected to be continually reduced in North America and Europe, while increased emissions are expected in for example, Asia. Projected changes in climate will impact global ecosystem distributions and BVOC emission rates. These changes will influence, for example, ozone levels and SOA formation on both regional and global scales.⁶⁷

Projected changes in climate will also lead to global environmental changes through societal responses including land use changes, urban development and new energy systems. The associated consequences on atmospheric chemistry and processes must be investigated. The vulnerable Arctic environment is under special threat, since it has experienced warming at twice the rate of the global average¹⁹ and future increased anthropogenic emissions from activities such as shipping, mining and petroleum exploration are likely. The impact of the increased emissions cannot be understood and estimated without more detailed knowledge of sources and physical-chemical processes affecting atmospheric organic chemistry in the region.

Despite major advances in our understanding of atmospheric organic chemistry during the past decade, major scientific challenges still remain to be investigated.

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