ATMOSPHERIC SCIENCE

The fuel of atmospheric chemistry: Toward a complete description of reactive organic carbon

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The Earth's atmosphere contains a multitude of emitted (primary) and chemically formed (secondary) gases and particles that degrade air quality and modulate the climate. Reactive organic carbon (ROC) species are the fuel of the chemistry of the atmosphere, dominating short-lived emissions, reactivity, and the secondary production of key species such as ozone, particulate matter, and carbon dioxide. Despite the central importance of ROC, the diversity and complexity of this class of species has been a longstanding obstacle to developing a comprehensive understanding of how the composition of our atmosphere, and the associated environmental implications, will evolve. Here, we characterize the role of ROC in atmospheric chemistry and the challenges inherent in measuring and modeling ROC, and highlight recent progress toward achieving mass closure for the complete description of atmospheric ROC.

INTRODUCTION

Gases and particles, present in minute abundances within the atmosphere, have massive environmental impacts. These agents can be deleterious to the air that we breathe and modulate the radiative balance of the planet. The premature deaths of over 8 million people each year are attributed to exposure to outdoor air pollution (*1*). The injection of particles and light-absorbing gases into the atmosphere from anthropogenic sources is the trigger for climate change (*2*). These include not only chemically inert greenhouse gases such as CO_2 and N_2O but also a wide range of short-lived reactive species. These short-lived emitted (primary) species evolve rapidly in the atmosphere and form secondary species such as ozone (O_3), particulate matter (PM), and carbon dioxide (CO_2). These three species are central to atmospheric chemistry; all three affect the climate, and the first two are key ingredients of ground-level smog. Figure 1 shows the major primary reactive gases that serve as precursors to these secondary products; they include a host of inorganic compounds, as well as organic carbon in the form of methane (a greenhouse gas with an atmospheric lifetime of ~10 years) and reactive organic carbon (ROC). We define ROC as all atmospheric organic species excluding methane; this includes volatile organic compounds (VOCs) and other lower-volatility organics such as particulate organic carbon. As shown in Fig. 1(a), ROC is the single largest contributor to total reactive emissions.

ROC is generated by a multiplicity of sources: from wildfires, to vehicles, to broadleaf trees. Once emitted into the atmosphere, specifically the troposphere (which contains ~90% of the atmosphere), most primary species undergo oxidation. The atmosphere is sometimes described as a "low temperature flame" (*3*, *4*), characterized by the radical-initiated oxidation of molecular species and the formation of products and by-products. Because ROC dominates total oxidation [represented by reactivity in Fig. 1(b)], it serves as the fuel of this flame, controlling total oxidant levels and hence the concentrations of all other reactive atmospheric species. Moreover, it is a major (and often dominant) contributor to the production of ozone, PM, and carbon dioxide [Fig. 1(c)] and, as such, influences both climate and human health. ROC is therefore central to the overall chemistry of the atmosphere, and specifically to the formation of atmospheric species that affect our environment and the people who live in it.

CONFRONTING COMPLEXITY

While Fig. 1 highlights the importance of ROC to atmospheric composition and chemistry, the budget, fate, and impacts of ROC are based on best estimates from models and remain highly uncertain. This uncertainty ultimately derives from the immense complexity underlying atmospheric organic chemistry. Whereas the other emitted compounds in Fig. 1 are single molecular species, ROC represents an enormous class of molecules, consisting of (at least) hundreds of thousands of individual chemical species (*5*). Each of these are subject to a complex array of atmospheric oxidation processes, reacting and transforming as they are lofted through the atmosphere. Figure 2 illustrates this atmospheric chemical processing. After emission, primary ROC reacts with strong photooxidants (e.g., OH, O_3, or NO_3); lifetimes of individual species can vary from seconds to months. The subsequent chemistry, which generally proceeds via organic peroxy radical (RO_2) intermediates, can form ozone (through reactions involving RO_2 and nitrogen oxides), and CO_2 (by complete oxidation of the carbon), as well as secondary ROC species. Secondary ROC tends to be highly complex, as the oxidation of a single organic precursor can form thousands of products [and possibly more (*6*)]; these can include compounds that retain the carbon skeleton of the parent, with oxygen-containing functional groups added, as well as smaller fragmentation products, formed by cleavage of carbon-carbon bonds. Some will have low enough volatility to partition into the condensed phase, leading to the formation of organic PM. Secondary ROC species can be removed from the atmosphere via physical deposition, or they can undergo further oxidation, continuing the cycle and forming a new set of secondary products. This chemical complexity of ROC—arising from the diversity of emitted molecules and the surfeit of multigenerational oxidation products—represents a fundamental obstacle to understanding the ROC life cycle and hence for predicting the formation of key secondary pollutants such as O_3 and PM.

Traditionally, the atmospheric chemistry community has confronted this complexity by attempting to understand individual components of ROC, or "slices of the whole." Considerable effort has been expended to understand individual oxidation steps in the laboratory,

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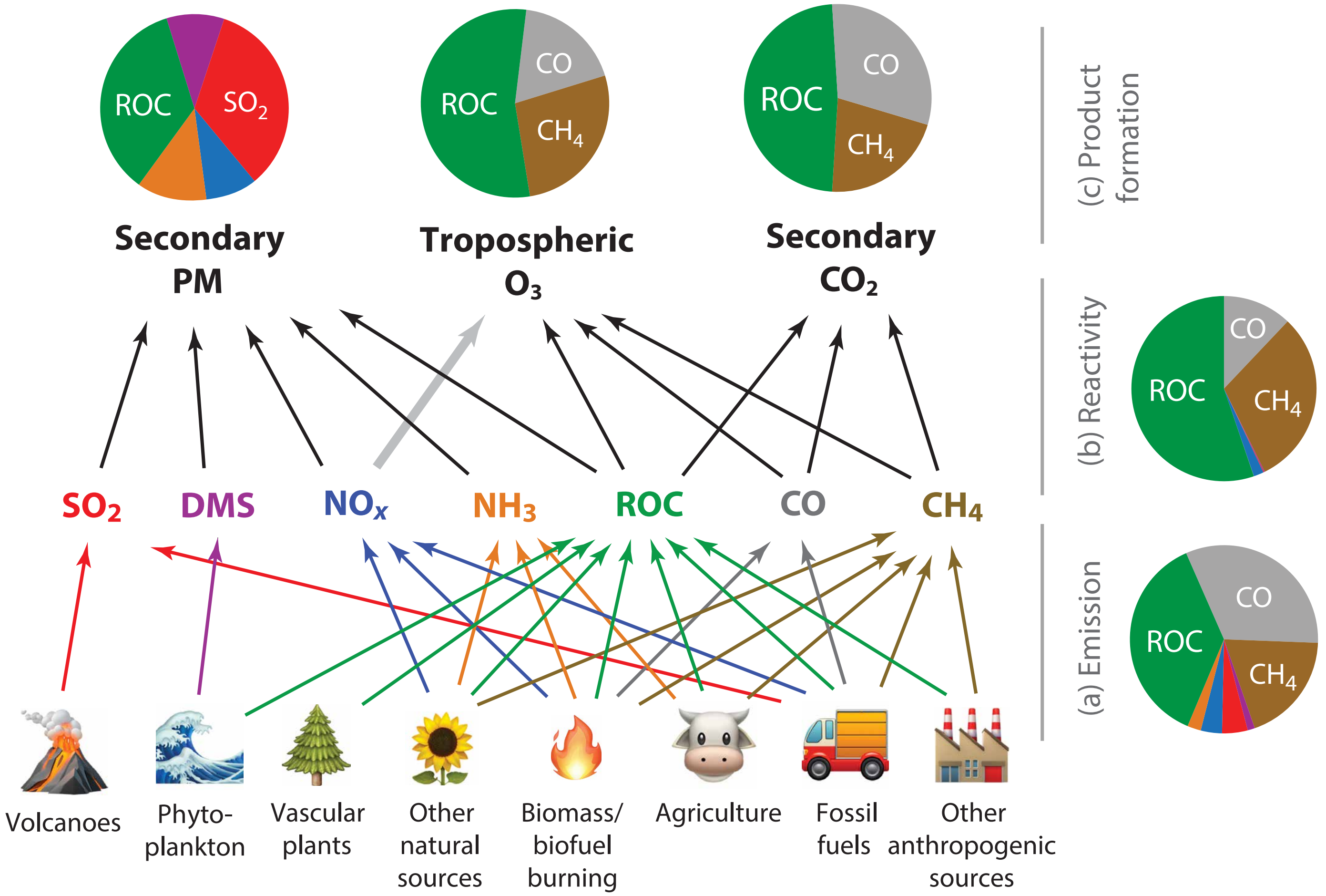

Fig. 1. The sources of key reactive emissions into the atmosphere that lead to secondary products of interest for air quality and climate. Bottom: Emission sectors generate a range of reactive chemical species: sulfur dioxide (SO_2), dimethyl sulfide (DMS), nitrogen oxides (NO_x), ammonia (NH_3), reactive organic carbon (ROC), carbon monoxide (CO), and methane (CH_4). (Given that DMS is a major contributor to the sulfur budget, but a minor component of the ROC budget, we treat it separately here.) Relative global emissions of each are shown on the right (a). Middle (b): The relative contribution of each component to total atmospheric oxidation, estimated from OH reactivity. Top (c): Relative contribution of each species to the global atmospheric burden of secondary $PM_{2.5}$, tropospheric O_3, and secondary CO_2. The gray arrow denotes that tropospheric ozone production is catalyzed by NO_x. Note that the secondary CO_2 source shown here is equivalent to ~10% of the global CO_2 emissions from fossil fuels. In all cases—emissions, oxidation, and formation of secondary species—ROC (shown in green throughout) is a major, if not dominant, contributor, highlighting its central importance in tropospheric chemistry. See the Supplementary Materials for a detailed description of methods and sources (*31*, *58*, *68*, *69*) used to estimate these values.

or the sources and sinks of key organic compounds [e.g., formaldehyde (*7*), a hazardous air pollutant]. But while piecing together the budget of ROC from individual species can provide an overview of measured ROC concentrations, such an approach risks omitting unknown or unmeasured compounds, and even entire classes of compounds. As an example of this, low-volatility gas-phase organics [semivolatile/intermediate-volatility organic compounds (S/IVOCs)], which are easily lost to instrument surfaces and so are inherently challenging to detect, were only recently identified as a major class of ROC compounds, present in both urban and rural environments (*8*–*10*). Moreover, this piecewise approach to describing ROC risks neglecting important interactions between different ROC species (*11*).

The study of organic PM, one of most active areas of research in atmospheric chemistry today, has traditionally followed this narrow "slice of the whole" approach. Organic aerosol (OA) makes up a substantial, sometimes dominant, fraction of fine PM ($PM_{2.5}$, particles less than 2.5 μm in diameter) worldwide (Fig. 1C) (*12*). These particles thus play a central role both in the health effects of air pollution and in climate. Early studies assumed that organic particles were either directly emitted from combustion sources or rapidly produced from the oxidation of a small handful of gas-phase hydrocarbons (monoterpenes from vascular plants, aromatics from fossil fuel use), and that, once formed, these particles were chemically inert. As such, organic PM was studied and described as standalone species, with relatively little interaction with other ROC species. However, over a decade ago, measurements revealed that such simple descriptions vastly underestimated organic PM loadings, indicating substantial gaps in our understanding of their sources and chemistry (*13*–*15*). In the intervening years, it has become clear that the amount and properties of OA are controlled by a much wider range of chemical processes: aerosol can be formed, in both the gas and aqueous phase, from many more gas-phase precursors (*16*–*21*), which are not always measured or identified; they may evolve chemically via dynamic partitioning with the gas phase (*8*, *22*) and oligomerization reactions (*23*, *24*);

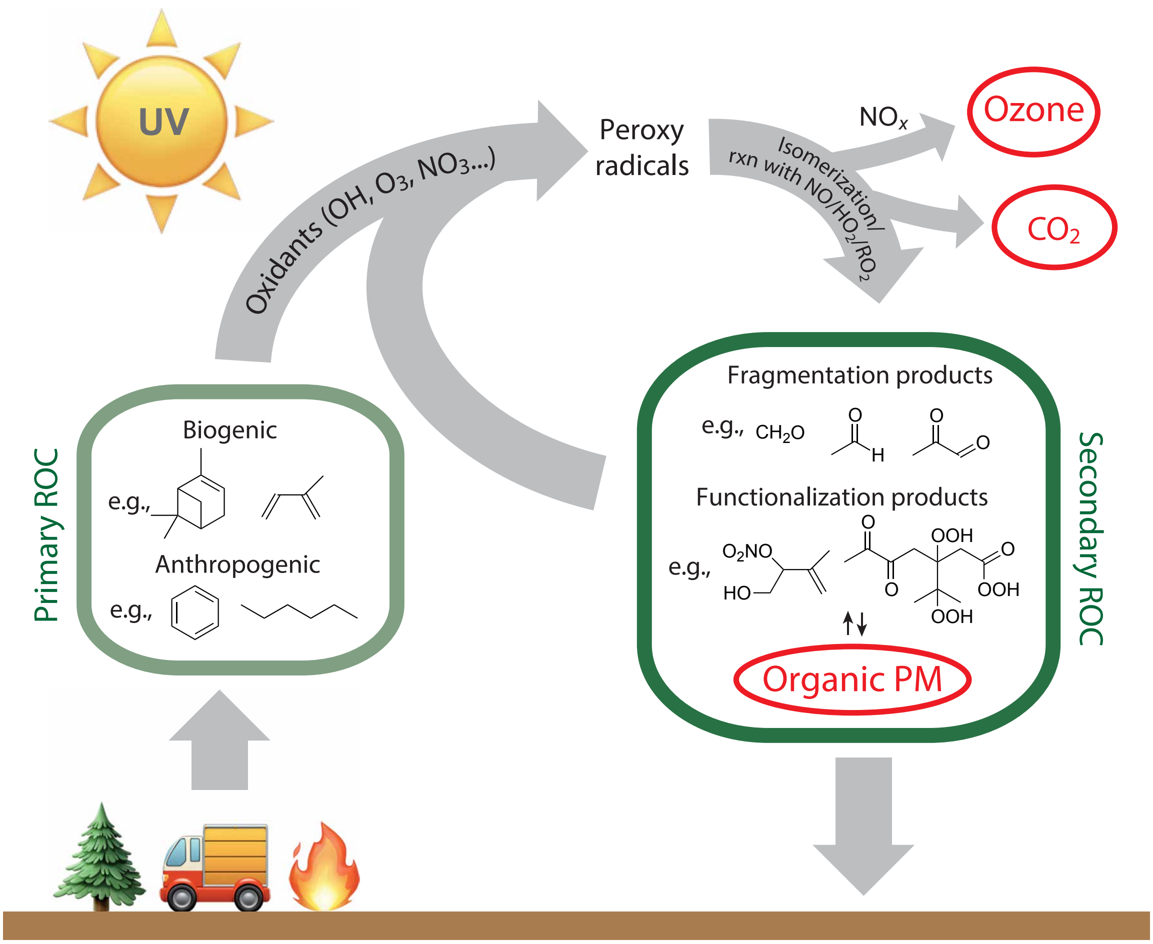

Fig. 2. Simplified atmospheric life cycle of ROC. ROC is emitted into the atmosphere from both biogenic and anthropogenic sources, typically as complex mixtures of reduced molecules. Atmospheric oxidation leads to the formation of a large number of secondary ROC species (some of which keep the carbon skeleton intact; others break it apart). This increase in chemical complexity is likely magnified as oxidation continues over multiple generations.

and once formed or emitted, they undergo atmospheric oxidative "aging" (*8*, *22*, *25*, *26*), which can affect the composition of the OA and may even release organic carbon back to the gas phase (*27*, *28*). This close complex coupling between atmospheric PM and the gas phase, and the related failure of state-of-the-art models to reproduce the observed magnitude and variability of OA [e.g., (*29*–*31*)], highlights how attempting to understand only some fraction of organic species in isolation is inherently inadequate.

TRACKING TOTAL CARBON

A more holistic perspective on the life cycle of ROC in the atmosphere, in which all species are examined in total, is therefore needed (*32*). Such a holistic approach treats the atmospheric organic mixture as a single system and is not limited to just a handful of compounds or some fraction of the whole (e.g., only organic particles). Such a holistic approach was first used to show that known gas-phase precursors could not explain observed OA levels measured downwind of cities in the eastern United States (*14*). A subsequent effort to sum up and contrast ROC concentrations across North America highlighted that the effectiveness of this "total carbon" approach relies critically on mass closure—the need to measure or model all organic carbon in the air (*32*). This total carbon approach enables comprehensive descriptions of the complex system while minimizing any assumptions made about the amount or behavior of any "missing" (unmeasured or unmodeled) carbon. However, the simplicity of mass closure is belied by three longstanding challenges: (i) making comprehensive measurements of ROC, (ii) developing an accompanying understanding of how these species evolve and interconvert, and (iii) including so many species and reactions into already-complex three-dimensional (3D) models. Nonetheless, the last several years have seen substantial progress in addressing all three; this progress and future opportunities for describing and studying atmospheric carbon holistically are highlighted below.

Measurement challenges

The ability to measure all ROC in the atmosphere represents a longstanding analytical obstacle. Measurements of atmospheric composition have evolved rapidly over the past two decades (*33*), enabling the measurement of an ever-increasing fraction of ROC using online (real-time or near–real-time) analytical techniques (Fig. 3). VOCs present in the gas phase (e.g., small hydrocarbons and simple oxygenates) have been measured routinely for decades, first from samples that were analyzed offline (e.g., in the laboratory some time after sample

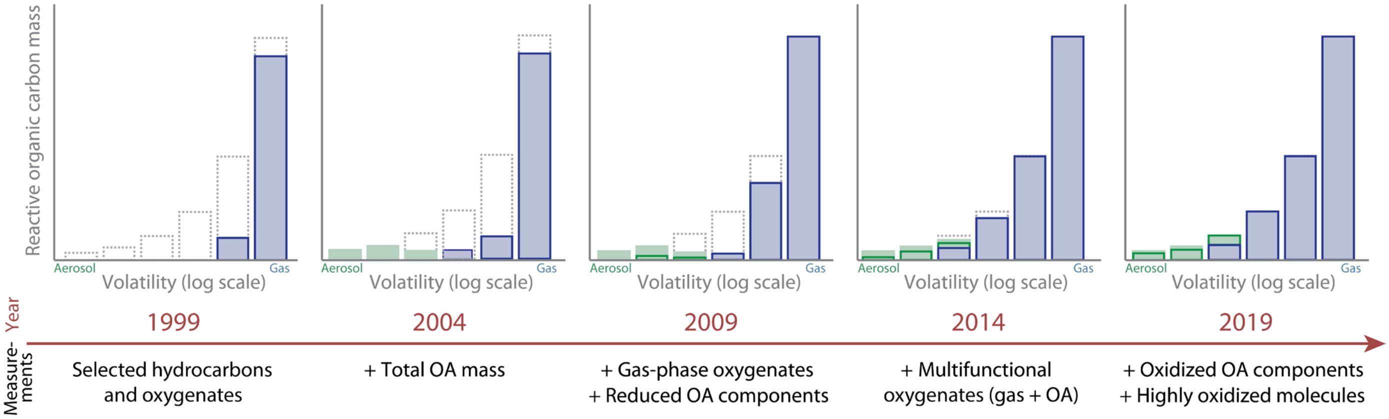

Fig. 3. Illustrative timeline of the advances in the online (real-time or near–real-time) measurement of ambient ROC mass over the last decades. Colored bars are qualitative estimates of measurable carbon (aerosol in green, gases in blue) as a function of volatility; dashed lines denote the amount of ROC in each bin that is measurable using current (2019) instrumentation. Solid outlines indicate the fraction of carbon that is measured as individual species rather than as unresolved mixtures. Dates correspond to the approximate timing that a given measurement approach was adopted for measuring atmospheric ROC. The major developments in analytical techniques depicted in this timeline (*9*, *34*–*36*, *70*–*83*) are given in the Supplementary Materials; see (*33*) for a comprehensive review of modern analytical approaches.

collection) and then with the development of online mass spectrometry techniques. Such online techniques generally do not provide as much chemical structural information as offline ones, but they have the advantage of high time resolution, which is important for understanding the evolving chemical and physical processes that affect ROC composition and concentration on short time scales. Similarly, organic particles (low-volatility species) were originally collected on filters and analyzed offline in the laboratory. Here, too, online mass spectrometry has revolutionized our ability to routinely measure OA concentrations in the atmosphere. These online techniques have been deployed on a range of platforms (from stationary ground-based sites to long-range aircraft), enabling surveys of the concentration of OA and VOCs across a range of environments globally. The greater challenge for ROC measurements has been characterizing the species that are found not purely in the gas phase or the condensed phase but rather can transfer between the two. Such species tend to have large carbon skeletons and/or multiple functional groups; these include S/IVOCs, with volatilities between VOCs and most OA components (in the middle of the volatility range in Fig. 3) (*8*), as well as exceedingly low volatility, highly oxidized species that can be formed in the gas phase but will quickly be lost to any available surface (at the low end of the volatility range) (*34*). Because these species tend to be present in very low concentrations and are easily lost to surfaces, their measurement has long been a challenge. Only in recent years have instruments that can rapidly, routinely measure such low-volatility oxidized species become readily available (*34*–*36*).

The availability of such instruments has opened up the possibility for more complete descriptions of atmospheric ROC than has been possible previously. As an example, the co-location of several such instruments enabled a recent comprehensive survey of ROC at a single location (a forested site in the United States) (*9*). Much of the ROC was present as routinely measured volatile species; however, S/IVOCs, along with previously unmeasured or unreported oxygenates, were shown to contribute almost a third of the reactive carbon (*9*). However, there exist no similarly comprehensive measurements of ROC in other environments (e.g., polluted urban regions or remote areas). Likewise, a total carbon approach can identify contributions from previously unrecognized emissions sources; for example, measurements of a wide range of VOCs enabled the recent identification of volatile chemical products, such as cleaning agents and personal care products, as major components of urban organic emissions in California (*37*). We thus have much to learn about the relative importance of different compound classes and sources in different regions of the world. It is clear that a suite of instruments is currently required to measure all the constituents of ROC; however, the cost and effort associated with the deployment of such instrumentation is not trivial.

Further, any assessment of our understanding of the ROC budget requires comparing such comprehensive ROC measurements with measured ensemble properties of the mixture of the whole. For example, the presence of substantial "missing ROC" has long been inferred from studies of ambient reactivity (*38*, *39*): Measurements of total OH reactivity (how fast OH, the predominant oxidant in the atmosphere, will react away in a given air mass) generally exceed the summed reactivities of measured species, often by a substantial amount (*40*, *41*). Other ensemble measurements that can provide tests of our understanding of key properties of ROC mixtures include NO_3 reactivity (*42*), O_3 reactivity (*43*), ozone production rate (*44*), and OA production potential (*45*). Still, true carbon closure cannot be demonstrated without a measurement of "total ROC" (*32*). Such a measurement is challenging due to the high atmospheric concentrations of other carbon-containing species, namely, CO_2, CO, and CH_4. Instruments for making total ROC measurements involve the pre-separation or measurement of these species followed by the conversion of all ROC to methane or CO_2 (*46*–*48*). However, these approaches have relatively low precision and have been deployed in only a handful of cases, providing limited insight into carbon closure. Continued development and deployment of such total ROC measurements are urgently needed.

Laboratory challenges

Mass closure is also central to laboratory studies of the chemical transformations of organic compounds, because measured reaction product distributions can only be considered "complete" if the amount of carbon in the products equals that in the species originally reacted. However, many laboratory studies focus instead only on the rates of degradation of the parent compound and/or the formation of some key products of interest. While this approach affords insight into the fate of individual species, it precludes a full understanding of the chemistry of the system as a whole. Detailed kinetic mechanisms such as the master chemical mechanism (*49*) rely on our knowledge of individual elementary reactions and are thus vulnerable to incomplete characterization of product formation in the laboratory. Similarly, laboratory studies of OA chemistry have traditionally focused on the particle phase only—the yields and composition of PM formed from a given reaction—with relatively little consideration of the gas-phase products. However, it has been suggested that gas-phase S/IVOCs may form OA over longer time scales (*8*) or be lost to chamber walls (*50*); in either case, this would mean that OA formation in the laboratory would be lower than that in the atmosphere, but this is difficult to verify without direct measurements of other products (including S/IVOCs) along with the OA.

As described above, recent advances in online analytical techniques have made it possible to examine the evolution of far more reactive carbon than was possible previously, thereby providing much-needed constraints on OA formation and the interconversion of ROC species. The development of techniques for the real-time measurements of VOCs first enabled the characterization of most (but generally not all) of the product carbon from complex OA-forming reactions (*51*, *52*). In a more recent laboratory study of the oxidation of α-pinene (a monoterpene emitted from coniferous trees), mass closure was demonstrated after a few generations of oxidation, using an array of instruments measuring the full range of possible products (VOCs, S/IVOCs, and OA) (*53*). It was shown that a substantial fraction of the product carbon was in the form of small gas-phase organics (e.g., acetone and acetic acid) and carbon monoxide as well as OA (*53*). Such measurements connecting particle-phase and gas-phase chemistry can provide information not only on the formation and evolution of OA but also on downstream effects on the gas-phase chemistry of the atmosphere (for example, the generation of ozone or the cycling of radicals). However, that study covered the oxidation of only a single compound, under a limited range of reaction conditions. The product distributions of the oxidation of many other ROC species (both biogenic and anthropogenic), under the full range of conditions found in the atmosphere, remain to be explored, as does our current ability to achieve carbon closure for these chemical systems.

Modeling challenges

One expects mass closure to be a trivial issue for models, and yet chemical mechanisms are not typically designed with this principle in mind. Most chemical mechanisms within 3D models (*54*–*57*) are reductions of explicit schemes, which are themselves based on laboratory studies; as discussed above, these traditionally focus on the formation of some, but not all, products. Thus, the formation of minor products is often not tracked within 3D models, with the implicit assumption that these small organics will ultimately form CO_2. Such chemical mechanisms themselves are often designed to retain chemical functionality, but not mass. Last, for computational tractability, chemical mechanisms in 3D models typically lump species (e.g., all alkanes with four or more carbon atoms), leading to some ambiguity in carbon number and molecular weight and imperfectly balanced chemical reactions.

The first global budget of ROC was recently constructed from a 3D chemical transport model on the basis of a chemical mechanism with enforced carbon closure (*58*). This model was used to explore the fate of ROC in the atmosphere, suggesting that the chemical loss of ROC (ultimately oxidizing to CO_2) is larger than the physical sink through wet and dry processes. While this budget provides a much-needed strawman for conceptualizing the ROC life cycle, it considered only 165 ROC species, with imperfect understanding of their transformations. Further work is needed to develop more detailed descriptions of organic chemistry in 3D models and to evaluate these schemes. While many aspects of oxidation chemistry are well studied in the laboratory, and thus well represented in modern oxidation schemes, substantial gaps remain, for example, in our understanding of the oxidation of monoterpenes in the atmosphere (*59*–*62*). Achieving carbon closure in laboratory experiments, as described above, also provides a strong basis for updating explicit chemical mechanisms (*49*, *63*, *64*). Recent laboratory studies using state-of-the-art instrumentation to measure full product distributions have enabled the development of improved, detailed mechanisms for the oxidation of isoprene, a terpenoid species emitted in large quantities from deciduous plants (*65*, *66*). The similar translation of newly measured product distributions for a wider range of ROC species to improve chemical mechanisms, both detailed mechanisms and simpler ones more suitable for 3D models, is critically needed. In addition, with increasing computational capacity comes opportunities to add more chemical detail to grossly simplified chemical mechanisms. For example, the recent inclusion of a much more explicit description of organic oxidation chemistry in the troposphere, with over 600 organic species, within a global model was found to consume less than twice the computational processor usage of the standard chemistry (*67*). The successful deployment of growing computational resources is predicated on the development of comprehensive schemes for chemical and physical transformations of atmospheric species, as well as the breadth of field measurements to test the skill of resulting 3D model simulations. The assessment of the generality of new 3D model schemes relies implicitly on globally distributed observations of ROC mass and reactivity (*41*, *58*). The degree to which chemical complexity in ROC needs to be described in these models to achieve simulations with predictive fidelity is a key question for the evolution of both air quality and chemistry-climate modeling.

LOOKING FORWARD

ROC dominates emissions of short-lived species in the atmosphere, the ensuing atmospheric oxidation processes, and the formation of secondary pollutants. However, the complexity of this class of compounds has stymied progress in describing the chemistry and impacts of ROC. Thus, mass closure in the field, in the laboratory, and in models is a necessary condition for understanding the role of ROC in the atmosphere. At the same time, it is not sufficient: While we argue here for a holistic perspective, which has been largely absent in this field of study, this must be complemented by detailed chemical understanding. This requires further advances in analytical measurements, particularly ones that can combine detailed structural analysis with high time resolution. In addition, to fully capitalize on new analytical capabilities, it is critical that new methods to analyze, interpret, and share complex datasets be developed. Moreover, progress requires a concerted effort to translate experimental results to the modeling sphere, as well as coordination among measurement communities (laboratory and field) to ensure the best use of resources to comprehensively characterize ROC under the full range of conditions found in the atmosphere.

Analytical and computational advances over the last decade have enabled substantial progress in characterizing the suite of organics that constitute ROC and understanding the formation and transformation of these compounds. This sea change has also created the opportunity for the atmospheric chemistry community to apply the lens of mass closure to guide the future development and deployment of models and measurements. A comprehensive understanding of the total mass (and interconversion) of organic species in the atmosphere is central to tackling the ultimate goal of atmospheric chemistry: to predict key pollutants, their environmental impacts, and how they will respond to global change.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/6/eaay8967/DC1
Section S1. Methodology for estimating values in Fig. 1
Section S2. Methodology for estimating values in Fig. 3
Table S1. Global annual emissions total shown in Fig. 1(a).
Table S2. Global annual mean estimated tropospheric OH reactivity shown in Fig. 1(b).
Table S3. Global annual mean burden of secondary PM shown in Fig. 1(c).
Table S4. Contribution to tropospheric ozone burden shown in Fig. 1(c).
Table S5. Sources of secondary CO_2 production shown in Fig. 1(c).

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