

# Embracing Complexity: Deciphering Origins and Transformations of Atmospheric Organics through Speciated Measurements

David R. Worton,<sup>†,‡,\*</sup> Drew R. Gentner,<sup>§</sup> Gabriel Isaacman,<sup>†</sup> and Allen H. Goldstein<sup>†,§</sup>

<sup>†</sup>Department of Environmental Science, Policy and Management, University of California, Berkeley, California 94720, United States

<sup>‡</sup>Aerosol Dynamics Inc., Berkeley, California 94710, United States

<sup>§</sup>Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720, United States



Atmospheric aerosols have received substantial attention in recent years as air pollution mitigation strategies have focused on minimizing their detrimental impacts on air quality and human health. A substantial fraction of fine mode aerosols are organic and the majority are formed in the atmosphere through oxidation processes. Organic compounds are emitted to the atmosphere from a variety of natural and man-made sources. As a result, the atmosphere contains thousands of individual organic species whose complexity increases exponentially with carbon number and degree of oxidation associated with atmospheric reactions.<sup>1,2</sup>

Research on bulk properties of organic aerosol has led to important advancements and considerable progress has recently been made with modeling efforts. However, current atmospheric models still cannot adequately represent organic aerosols; they are able to reproduce the mass but not the spatial distribution, and a low level of confidence remains in the identification of important precursors and formation pathways. The inability to accurately model organic aerosol suggests insufficient understanding about the sources and oxidation mechanisms of organic compounds in the atmosphere. Parameterizations that capture the complexity of precursor compounds, their oxidation products and the key atmospheric reactions remain critical for improving the representation of organic aerosols in models.

Speciated measurements are a necessary complement to bulk chemical analyses because they can provide a detailed characterization of oxidation products that constrains potential oxidation pathways and crucial information for apportioning organic carbon from an often convoluted mixture of primary

and secondary sources. Detailed descriptions of current measurement techniques can be found in recent reviews;<sup>3,4</sup> here we focus on what we believe are the most important contemporary challenges. It is our view that the major factors limiting a more comprehensive understanding of speciated organics relate to difficulties in the collection and identification of the broad range of organic compounds in the atmosphere.

There has been significant progress probing the chemical complexity of atmospheric organics through offline analyses of time-integrated samples using a variety of analytical techniques.<sup>3</sup> However, the atmosphere is highly dynamic and measurements with high temporal resolution are necessary to adequately observe variations in chemical composition caused by changes in sources or atmospheric reactions. This can be achieved in two ways, either by collecting frequent short duration samples for offline analysis or by making in situ (i.e., online) measurements. Online measurements are advantageous as they avoid potential chemical artifacts related to sample collection and storage and are often easier to implement for achieving high time resolution data. Nevertheless, some methods cannot feasibly be conducted in the field environment and remain valuable offline analytical tools.

Current gas and particle-phase instrumentation has focused on measuring organic compounds in the volatility range of hydrocarbons containing less than 10 or more than 25 carbon atoms largely because the compounds in between are problematic to measure. However, these species need to be better characterized as they are thought to be important organic aerosol precursors. Many current collection methods for offline analyses of these compounds, such as filters or adsorbent tubes, are prone to positive and negative artifacts that can be difficult to adequately quantify. Therefore, developing novel collection systems that quantitatively capture these challenging compounds while maintaining the ability to distinguish between their gas and particle phase fractions is critically important and substantial innovative research is required.

Speciated measurements of atmospheric organics have commonly utilized gas chromatography because it is relatively simple, reliable and provides accurate quantification. However, due to absorptive losses in chromatography columns, it cannot quantify highly oxygenated compounds without derivitization, where problematic functional groups are chemically altered making them readily measurable.<sup>3</sup> Liquid chromatography is more suited to the analysis of oxygenates but has substantial

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quantitative limitations due to the structurally dependent response of electrospray ionization. Recently, chemical ionization mass spectrometry techniques have opened up major new windows into observations of oxidation products and reactive intermediates. However, without some separation capability they have limitations and usually only target specific classes of molecules that are often not applicable to a broad range of organics. When used in conjunction with more explicit separation techniques these methods would provide vital information on reaction pathways through the characterization of short-lived or highly reactive intermediate compounds.

Quadrupole mass spectrometers have most commonly been used for measuring speciated organics because these detectors are a good compromise between sensitivity, reliability, and size while providing the advantages of mass spectral information. However, low sensitivity when operated in full scan mode and limited mass resolution restricts the range of compounds that can be observed and quantified. Time of flight mass spectrometry has advanced dramatically in the past decade and now compact, reliable and portable instruments are available. Time of flight mass spectrometry offers several advantages over quadrupole detectors: the ability to collect all mass fragments simultaneously, fast data acquisition rates and high mass resolution. Fast data acquisition rates permit the use of comprehensive two-dimensional chromatography, which can separate a larger number of compounds than traditional one-dimensional chromatography. High mass resolution can be particularly powerful when used with “soft” ionization techniques for obtaining molecular formulas. This method is very useful for identifying unknown compounds or for deconvoluting complex mixtures of structurally similar hydrocarbons such as petrochemical based precursor compounds.<sup>5</sup> However, the range of organic compounds in the atmosphere far exceeds the number of compounds included in published mass spectral libraries, especially for oxidation products, many of which may be uniquely created in the atmosphere. Understanding the mechanisms of atmospheric oxidation will continue to be hindered until a larger fraction of precursor compounds and their multigenerational oxidation products are characterized and included in these libraries.

While substantial progress has been made on both measurement and modeling fronts in the past decade, future efforts must pay significant attention to the information concealed within the complexity of atmospheric organics. Our viewpoint is that speciated organic measurements hold the key to quantitatively constraining source contributions and dramatically advancing the understanding and parametrization of atmospheric oxidation mechanisms. We believe improvements in speciated organic measurement capabilities will ultimately lead to better representation of organic aerosols in models with implications for pollution mitigation strategies.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone: 510-643-6449 ; fax: 510-643-5098; e-mail: dworton@berkeley.edu.

### Notes

The authors declare no competing financial interest.

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