Technical Report

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Title: Characterizing Organic Aerosol Processes and Climatically Relevant Properties via Advanced and Integrated Analyses of Aerosol Mass Spectrometry Datasets from DOE Campaigns and ACRF Measurements
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Aerosol particles significantly influence the radiative budget of the Earth's atmosphere through scattering and absorption of radiation (i.e., direct effect) and modulating the formation and properties of clouds (i.e., indirect effect). A quantitative understanding of these effects is critical to energy policies which rely on model projections of future climate for different emission scenarios. But predictions by current climate models are still highly uncertain, and direct radiative forcing of aerosols and aerosol-cloud interaction are one of the largest sources of uncertainty.

The properties and climatic impacts of aerosol particles are intrinsically linked to their chemical composition. Organic aerosols (OA), which account for ~ 10 - 90% of fine aerosol mass globally, are a key determinant of the radiative properties of aerosols. A thorough understanding of the concentration, composition, properties, and lifecycle processes of atmospheric OA is therefore crucial for quantification of aerosol effects and improving the fidelity and predictive capability of models. However, due to the complex nature of OA, which comprise thousands of compounds with vastly different properties including oxidation degree, volatility, and hygroscopicity, the sources and chemical evolution processes of atmospheric OA remain poorly characterized. This knowledge gap is reflected in the substantial prediction biases in aerosol models, especially in regard to secondary OA (SOA). SOA is globally a major component of ambient submicrometer aerosols, often showing concentration levels comparable to or higher than those of sulfate – a well-known secondary inorganic aerosol species. But most models underestimate the relative importance of SOA and model simulated SOA concentrations in urban and regional polluted atmosphere can be biased low by a factor of ~10. Furthermore, studies found that even models incorporating newly identified mechanisms cannot predict accurately the volatility and oxidation degree of SOA despite improvements in predictions of SOA mass concentrations.

Field studies play crucial roles in elucidating the properties, sources, formation, and aging processes of aerosol-phase organics and improving model representation of the complex atmospheric OA system. This is because development and improvement of aerosol models require phenomenological descriptions derived from field observations and because model representation must be evaluated against ambient measurements. In this regard, advanced analysis efforts are necessary for deducing and synthesizing the rich measurement data provided by state-of-the-art aerosol instruments such as aerosol mass spectrometers (AMS). AMS field data is massive and multidimensional, thus requires advanced analyses to fully exploit the rich

information contents. Focused analyses of selected AMS dataset have proven effective in distilling fundamental information about OA properties and elucidating lifecycle processes. Advanced multivariate analyses of the AMS data can also simplify the enormously complex atmospheric OA system into lumped descriptions of a limited number of components that may be related to distinct sources, physicochemical properties, and atmospheric processes. For example, a broad overview of the chemistry, variability, and evolution characteristics of aerosol in Northern Hemisphere has emerged as the results of performing positive matrix factorization (PMF) analyses to dozens of AMS datasets.

In this project, we performed advanced and integrated analyses of multiple DOE AMS datasets acquired from intensive field campaigns and long-term routine measurement programs. Our goals are to improve a process-level understanding of the lifecycle processes of OA in the Earth's atmosphere and to bridge between observations and models via synthesizing and translating the results and insights generated from this research into data products and formulations that may be directly used to inform, improve, and evaluate regional and global models.

Our work has successfully met the main objectives of the project, as summarized below for each of the 3 focus areas:

Focus Area #1: *Perform systematic and advanced analyses of the HR-AMS data from two DOE intensive campaigns, i.e., CARES and BNL-IOP, to gain detailed, quantitative understanding of the characteristics, sources, secondary formation, evolution, and radiative properties of organic aerosols under different atmospheric and aerosol regimes (e.g., urban, biogenic, marine etc) and to generate data products for informing and evaluating aerosol process models.*

We have performed detailed analyses of the high resolution time-of-flight AMS (HR-AMS) data and associated aerosol, gas phase, and meteorological data acquired from two DOE sponsored intensive field campaigns – the CARES (Carbonaceous Aerosols and Radiative Effects Study. Campaign period: June 2-28, 2010; Location: Sacramento Valley Air Basin, Northern California) and the ALC-IOP (Aerosol Lifecycle Intensive Observation Period. Campaign period: June – August, 2011; Location: Brookhaven National Laboratory at Long Island, New York). Our results demonstrate that both SOA formation and new particle growth are significantly enhanced when anthropogenic emissions interact with biogenic precursors. In addition, we have collaborated with other ASR scientists (mainly from PNNL and BNL) on studying aerosol hygroscopic properties and CCN activities. The findings from these works provide new insights into aerosol chemistry and microphysics in urban downwind areas, contributing to a better understanding of aerosol lifecycle processes and the climatic effect. Following are a list of 11 published papers and 1 submitted manuscript that reported findings from this project:

1. Setyan, A. et al. (2012) Submicron aerosols influenced by mixed biogenic and anthropogenic emissions: high-resolution aerosol mass spectrometry results from CARES, Atmos. Chem. & Phys., 12, 8131-8156
2. Zaveri, R. et al. (2012), Overview of the 2010 Carbonaceous Aerosols and Radiative Effects Study (CARES), Atmos. Chem. and Phys., 12, 7647-7687.

3. Sedlacek, A. et al. (2012) Determination of and evidence for non-core-shell structure of particles containing black carbon using the SP2, Geophys. Res. Lett., 39(L06802)
4. Vladutescu, D. et al. (2013) Aerosol transport and source attribution using sunphotometer, models and in situ chemical composition measurements, IEEE Transaction on Geoscience and Remote Sensing 1-9, 10.1109/tgrs.2012.2227489
5. Shilling, J. et al. (2013) Enhanced SOA formation from mixed anthropogenic and biogenic emissions during the CARES campaign, Atmos. Chem. and Phys., 13, 2091-2113
6. Mei, F. et al. (2013) CCN activity of organic aerosols observed downwind of urban emissions during CARES, Atmos. Chem. Phys., 13, 12155-12169.
7. Setyan, A. et al. (2014) Chemistry of new particle growth in mixed urban and biogenic emissions: Insights from CARES, Atmos. Chem. Phys., 14, 6477-6494.
8. Fast, J. D. et al. (2014) Modeling regional aerosol and aerosol precursor variability over California and its sensitivity to emissions and long-range transport during the 2010 CalNex and CARES campaigns, Atmos. Chem. Phys., 14, 10013-10060.
9. Atkinson, D. B. et al. (2015) Aerosol optical hygroscopicity measurements during the 2010 CARES campaign, Atmos. Chem. Phys. 15, 4045-4061
10. O'Brien et al. (2015) Chemical imaging of ambient aerosol particles: Observational constraints on mixing state parameterization, Journal of Geophysical Research – Atmospheres, 10.1002/2015JD023480.
11. Lupascu, A. et al. (2015) Modeling particle nucleation and growth over northern California during the 2010 CARES campaign, *Atmos. Chem. Phys.,* 15, 12283-12313, 10.5194/acp-15-12283-2015,
12. Kleinman, L. et al. (2016) What do Correlations tell us about Anthropogenic – Biogenic Interactions and SOA Formation in the Sacramento Plume during CARES? *Atmospheric Chemistry & Physics*, 16, 1729 – 1746, 10.5194/acp-16-1729-2016
13. Zhou, S. et al. (2016) Influences of upwind emission sources and atmospheric processing on aerosol chemistry and properties at a rural location in the Northeastern US. *J. Geophys. Res. Atmos.*, 121, 6049 – 6065, 10.1002/2015JD024568.
14. M. Gyawali et al. (2016) Evolution of multispectral aerosol absorption properties in a biogenically-influenced urban environment during the CARES campaign, *Aerosol Science and Technology* (submitted)

Focus Area #2: 1) *Develop and improve multivariate factor analysis techniques, especially Positive Matrix Factorization (PMF), for AMS data analysis and analyze aerosol chemistry data generated by the Aerosol Chemical Speciation Monitor (ACSM) systems deployed at the ARM Climate Research Facility sites for improved understanding of aerosol's roles in radiative forcing.*

Evaluation and development of aerosol process modules require data products generated from field observations. In addition to AMS, which have been frequently used in intensive DOE field campaigns for characterizing aerosol composition and elucidating aerosol sources and processes, three ACSMs have been used at ARM long-term measurement sites (e.g., Southern Great Plains) and a mobile facility. The ACSM is a mini version of the AMS developed for

continuous, low maintenance operation. The typical time resolution of AMS measurements is 2 - 5 min at fixed-sites and 30 s or less on mobile-platforms (e.g., aircraft), while the time resolution of ACSM is generally 30 min. As part of this project, we developed a value-added product (VAP) for deriving OA components from the ACSM mass spectral data – OACOMP. This VAP tool implements a rolling window analysis that performs PMF on long-term ACSM data in user-defined intervals and determines the concentrations of distinct OA factors as well as their uncertainties while allowing factors to vary overtime. The code is currently running operationally within the Data Management Facility of ARM and the data products are available on the ARM archive. In addition, we have performed a detailed analysis of 19 months of ACSM data from the ARM Southern Great Plains (SGP) site and interpreted the results together with backtrajectories and emission sources in order to determine the contributions of different sources to aerosol chemistry at SGP. We have published two papers that report the development of OAcomp VAP and the analysis of ACSM data (Article #16 and #21).

In parallel to developing VAP and analyzing SGP long term ACSM data, we have worked on developing and optimizing factor analysis of AMS to better deconvolve and determine atmospheric OA sources and transformation processes. The PI of this project wrote a review article on PMF methodology and the results from various field campaigns (Article #15). In addition, we published four other papers on methods that significantly improve factor analysis of the AMS data, one each on 3D factorization using PMF (Article #18), applying PMF on combined organic and inorganic mass spectral matrices (Article #19), rapid factor analysis of AMS data (Article #17), improving quantification of the fraction contribution of organic signal at m/z = 44 and O/C via proper gas phase CO_2 subtraction (Article #20), and a thorough evaluation of the technical issues with AMS/ACSM quantification (Article #21).

15. Zhang Q. et al. (2011) Understanding Atmospheric Organic Aerosol via Factor Analysis of Aerosol Mass Spectrometry: A Review, Anal. & Bioanal. Chem., 401, 3045-3067.
16. Ng, N. L. et al. (2011) An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, Aerosol Sci. & Technol. 45, 770-784.
17. Ng, N. L. et al. (2011), Development of Real-Time Methods for the Estimation of Organic Components for AMS Data, Environ. Sci. & Technol., 45(3), 910-916
18. Ulbrich, I. et al. (2012), Three-dimensional factorization of size-resolved organic aerosol mass spectra from Mexico City. Atmos. Meas. Tech., 5, 195-224.
19. Sun, Y. L. et al. (2012) Factor Analysis of Combined Organic and Inorganic Aerosol Mass Spectra from New York City, Atmos. Chem. & Phys., 12, 8537-8551.
20. Collier, S., and Zhang, Q. (2013) Gas-phase CO_2 subtraction for improved measurements of the organic aerosol mass concentration and oxidation degree by aerosol mass spectrometer, Environ. Sci. & Technol., 47, 14324–14331.
21. Parworth, C. (2014) Long-term measurements of submicrometer aerosol chemistry at the ARM Southern Great Plains (SGP) site using an Aerosol Chemical Speciation Monitor (ACSM), Atmospheric Environment, 106, 43–55, doi:10.1016/j.atmosenv.2015.01.060.
22. Jimenez, J. L. et al. (2016) Comment on "The effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer", *Aerosol Sci. Tech.*, 10.1080/02786826.2016.1205728.

Focus Area #3: *Synthesize the results and insights generated from this research for integration with other worldwide AMS data and increase our collaborations with modelers.*

The focus area includes two main tasks: A) further develop a global database of aerosol mass spectrometry and integrate DOE data and the analysis results generated from Focus Areas 1&2 with other AMS and ACSM observations supplied by collaborators and other members of the AMS community; B) Increase our collaborations with modelers on using the global AMS data products for improved treatment of aerosol processes and representation of aerosol climatology in global aerosol models.

We have performed integrated analyses to a large number of AMS field data to reach a broad overview on OA sources, processes, and interactions in various environments worldwide. Our field data analysis efforts were complemented by laboratory studies to better elucidate how specific precursor compounds may affect SOA formation in the atmosphere. In addition, we have continued to expend an online database of worldwide aerosol measurement data acquired with AMS and ACSM (https://sites.google.com/site/amsglobaldatabase/). The website is continuously expanding with new datasets and currently contains ~ 100 aerosol datasets acquired from various atmospheric environments via different platforms. Each dataset has its own webpage with information about the field campaign and contains data including: mass concentration time series, mass spectra, tracer ions, elemental ratios, size distributions, and factor analysis results. The dataset in its entirety provides an encompassing overview of the current understanding of PM sources and evolution processes around the globe. These datasets can be used to increase our understanding of OA and are useful for evaluating aerosol models, as well as comparing concentrations and other PM properties across different locations. All this information have allowed us to improve understanding of the properties and effects of OA in the Earth's atmosphere on a process level and to translate the results and insights generated from field measurements into data products and formulations that may be directly used to inform, improve, and evaluate models. We have collaborated with modelers on using our AMS data and have coauthored the following 11 papers.

23. Spracklen, D. V. et al. (2011), Aerosol Mass Spectrometer Constraint on the Global Secondary Organic Aerosol Budget, Atmos. Chem. and Phys. 11, 12109-12136
24. Ervens, B., et al. (2011) CCN predictions using simplified assumptions of organic aerosol composition and mixing state: a synthesis from six different locations, Atmos. Chem. Phys., 10, 4795-4807.
25. Hodas, N. (2012) Variability in the fraction of ambient fine particulate matter found indoors and observed heterogeneity in health effect estimates, *Journal of Exposure Science and Environmental Epidemiology*, doi:10.1038/jes.2012.34
26. C. Knote (2014) Simulation of semi-explicit mechanisms of SOA formation from glyoxal in aerosol in a 3-D model, *Atmospheric Chemistry and Physics,* 14, 6213-6239, 10.5194/acp-14-6213-2014,
27. Philip S. et al. (2014) Spatially and seasonally resolved estimate of the ration of organic matter to organic carbon, Atmos. Environ., 87, 34-40.
28. Tsigaridis, K. et al. (2014) The AeroCom evaluation and intercomparison of organic aerosol in global models, Atmos. Chem. Phys., 14, 10845-10895.

29. Chen, Q. et al. (2015) Elemental composition of organic aerosol: The gap between ambient and laboratory measurements, *Geophys. Res. Lett.*, 42, 10.1002/2015GL063693S
30. Shrivastava, M. et al (2015) Global transformation and fate of SOA: Implications of low volatility SOA and gas-phase fragmentation reactions, *J. Geophys. Res.*, 120, 10.1002/2014JD022563
31. Shrivastava, M. (2016) Sensitivity Analysis of simulated SOA loadings using a Variance-Based Statistical Approach, *Journal of Advances in Modeling Earth Systems (JAMES),* 8, doi:10.1002/2015MS000554.
32. Nguyen, T. (2016) Liquid water: ubiquitous contributor to aerosol mass. *Environ. Sci. and Technol. Letter*, 10.1021/acs.estlett.6b00167.
33. Reddington, C. L. et al. (2017) The Global Aerosol Synthesis and Science Project (GASSP): Measurements and modelling to reduce uncertainty, *Bulletin of the American Meteorological Society* (in press; http://journals.ametsoc.org/doi/abs/10.1175/BAMS-D-15-00317.1)

Other Project Information Sources:

Project URL:

https://sites.google.com/site/amsglobaldatabase/

http://cires.colorado.edu/jimenez-group/wiki/index.php/PMF-AMS_Analysis_Guide

Related URL at institution:

http://etox.ucdavis.edu/directory/faculty/zhang-qi/

http://cires.colorado.edu/jimenez

http://cires.colorado.edu/jimenez-group/wiki/index.php/Field_Data_Analysis_Guide

http://cires.colorado.edu/jimenez-group/AMSsd/

http://cires.colorado.edu/jimenez/ams-papers.html

http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/

http://cires.colorado.edu/jimenez-group/wiki/index.php/High_Resolution_ToF-AMS_Analysis_Guide