# Characterizing Organic Aerosol Oxidation State Using Aerosol Chemical Speciation Monitor and Mass Fragment Concentration Estimation

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## Abstract

Aerosol particles in the atmosphere play an important role in climate, visibility, and human and environmental health. Organic aerosol (OA) is one component of major interest, yet its sources, formation, and evolution are not clearly understood. One approach to understanding OA is the application of the positive matrix factorization (PMF) technique to aerosol chemical speciation monitor (ACSM) data. Through this approach, OA is classified into hydrocarbon-like OA (HOA) and oxygenated OA (OOA). HOA comprise less oxidized species, while OOA comprise more oxidized species. Resolving HOA and OOA provides insights into OA sources and evolution because HOA and OOA loadings correlate with primary and secondary OA, respectively. A simplified adaptation of PMF, applying scaling factors in an algorithm developed from PMF, has been recently developed to estimate HOA and OOA loading from mass fragments at 57 and 44, respectively. These mass fragments are obtained from the ACSM. The data collected from the ACSM at an Aerosol Life Cycle Intensive Observation Period campaign at Brookhaven National Laboratory on Long Island from July 15 to August 15, 2011 was analyzed using this algorithm to evaluate its applicability as a less expensive and more manageable alternative to full PMF analysis. The ACSM data collected on Long Island were also compared to those collected at a rural continental site in the Southern Great Plains, allowing consideration of OA formation in relation to location. Air back trajectories were also used to identify possible sources of OA. The application of this algorithm as an alternative to PMF offers a simpler way to gather the additional data needed to improve understanding of OA atmospheric distribution and effects on the climate and environment.

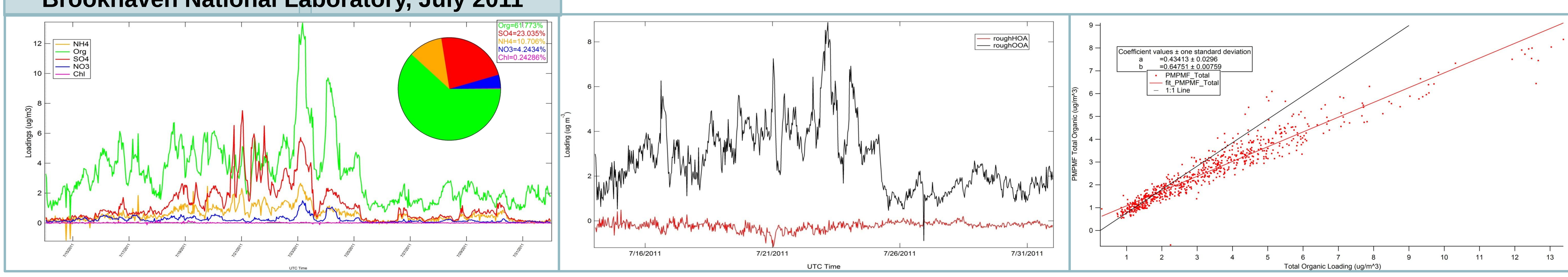
## Introduction

Atmospheric aerosols play a major role in climate, visibility, and human and environmental health. Organic aerosol (OA) is one component of major interest, yet its sources, formation and evolution remain unclear. There is great uncertainty concerning the precursor species and how those species react in the atmosphere. One approach to understanding these processes is deconvolving OA into hydrocarbon-like OA (HOA) and oxygenated OA (OOA), which are closely related to primary and secondary OA, respectively. The positive matrix factorization technique (PMF) resolves mass spectral data from Aerodyne's Aerosol Chemical Speciation Monitor (ACSM) into these component spectra. Scaling factors relating PMF analysis to mass fragment concentrations have been used to develop an algorithm estimating HOA and OOA from m/z fragments 57 and 44, respectively. These mass fragments were chosen because they are characteristic peaks in the component spectra and do not appear to a large extent in other spectra. The estimated loading of OOA and HOA can be compared among data from different locations and times to understand the formation and properties of OA.

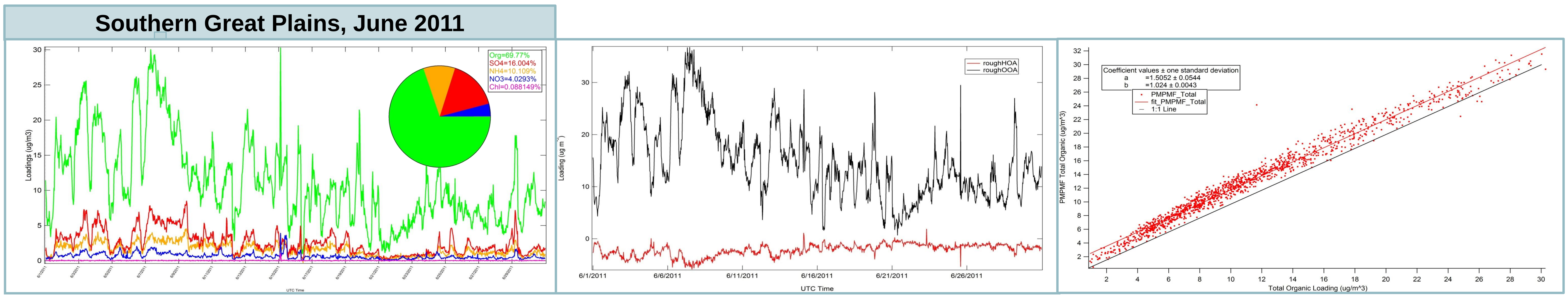
## Methods

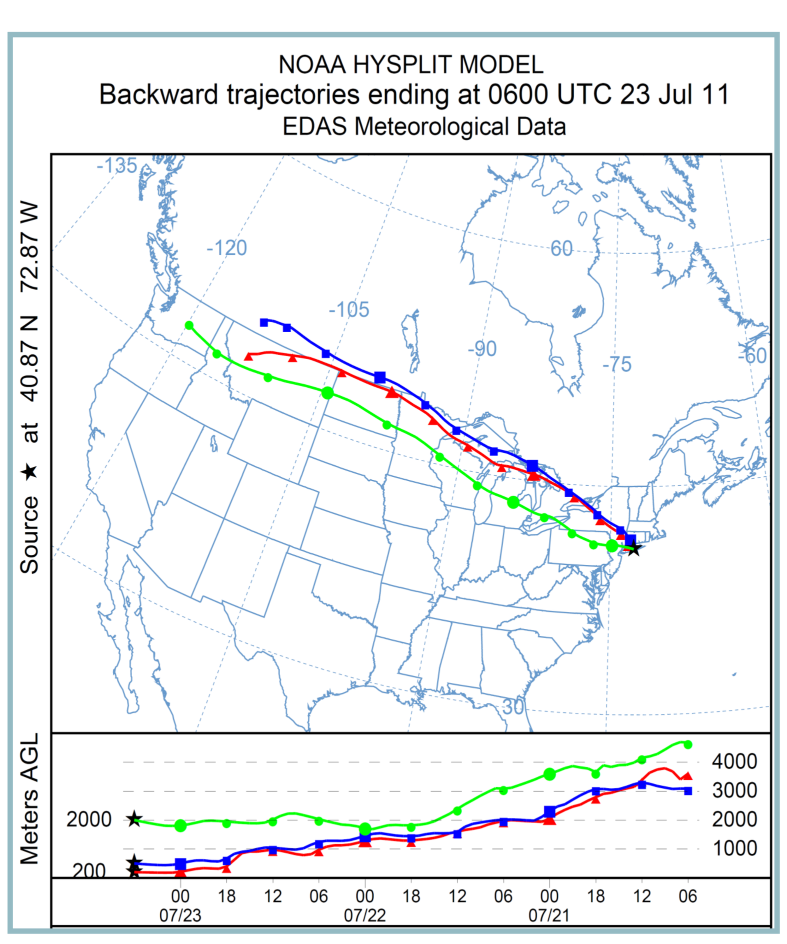
- Two datasets were analyzed: Atmospheric Radiation Measurement Southern Great Plains (SGP) site, June 2011
  Intensive Observation Period at Brookhaven National Laboratory (BNL), July 2011
- ACSM collected data in 30 min time averaged samples.
- ACSM monitors the following aerosol species: $NO_3$, $SO_4$, $NH_4$, Cl, and Total Organics.
- Aerosol mass concentration was determined from mass peak signal intensities.
- OA was deconvolved into OOA and HOA component spectra using a simplified algorithm based on PMF (PMPMF):
  $$HOA \sim 13.4*(C_{57}-0.1*C_{44})$$
  $$OOA \sim 6.6*C_{44}.$$
- Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPLIT) calculated air mass histories.

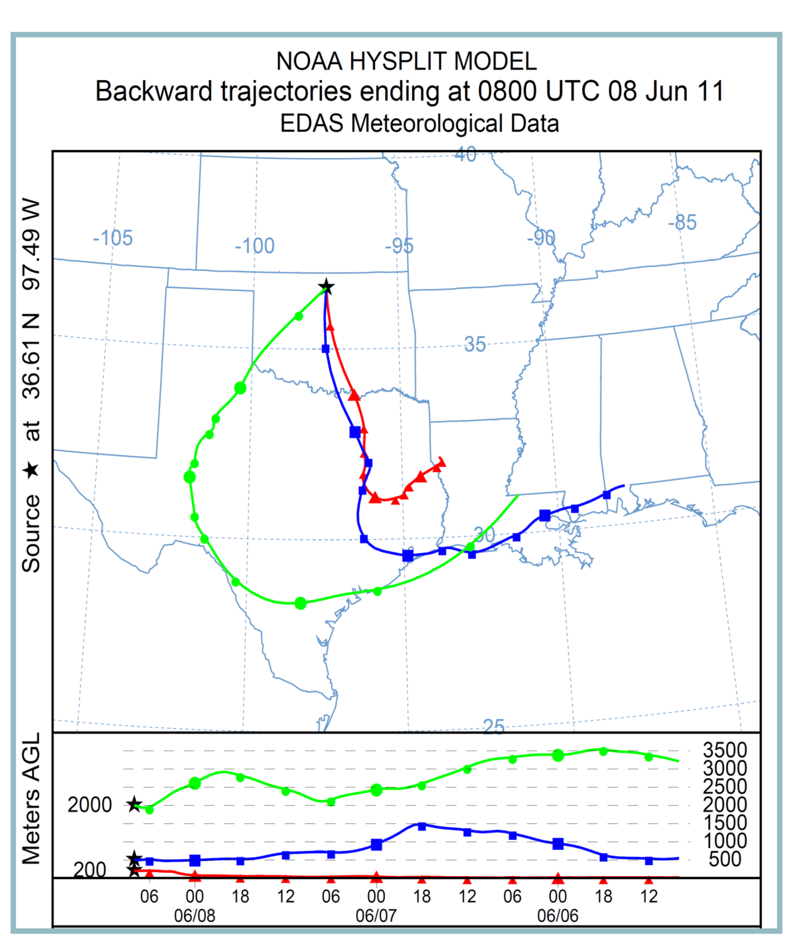
## Brookhaven National Laboratory, July 2011




## Southern Great Plains, June 2011




## Results

- Aerosol loadings are generally higher for SGP than BNL.
- OA dominates aerosol loading for both locations.
- PMPMF analysis suggests OA is predominately OOA. This is substantiated by the triangle plot of f44 vs f43: the clusters of values higher in the triangle represent more oxidized species.
- To evaluate PMPMF estimation of HOA and OOA, the sum of estimated HOA and OOA was compared to total observed OA. At SGP, OA was overrepresented . At BNL, OA was predicted at only approximately 60% of total OA loading. These relationships are represented by the slope of the fit line.

## Discussion

- The large OOA component estimated by PMPMF at both locations suggests that OA are aged, and secondary OA dominates.
- HYSPLIT results show that higher loadings generally correspond to air masses that have traveled across urban centers while lower loadings have traveled over rural areas.
- Negative HOA predicted by PMPMF suggests possible errors with the algorithm's scaling factors; particularly, the contribution of OOA to mz57 may be overestimated. This scaling factor may needs to be reevaluated.
- PMPMF estimation appears to represent the SGP data more accurately than the BNL data. This might suggest that these particular generalized scaling factors are better suited for regions of higher OA loading. The large difference in fit between PMPMF and total OA at the two different locations suggests a need to adjust the scaling factors according to location because of the difficulty of making generalizations about OA , especially when the HOA/OOA distinction is relative, not absolute.
- PMPMF scaling factors generated from primarily urban datasets known to include HOA may not be applicable to rural locations where OOA dominates.

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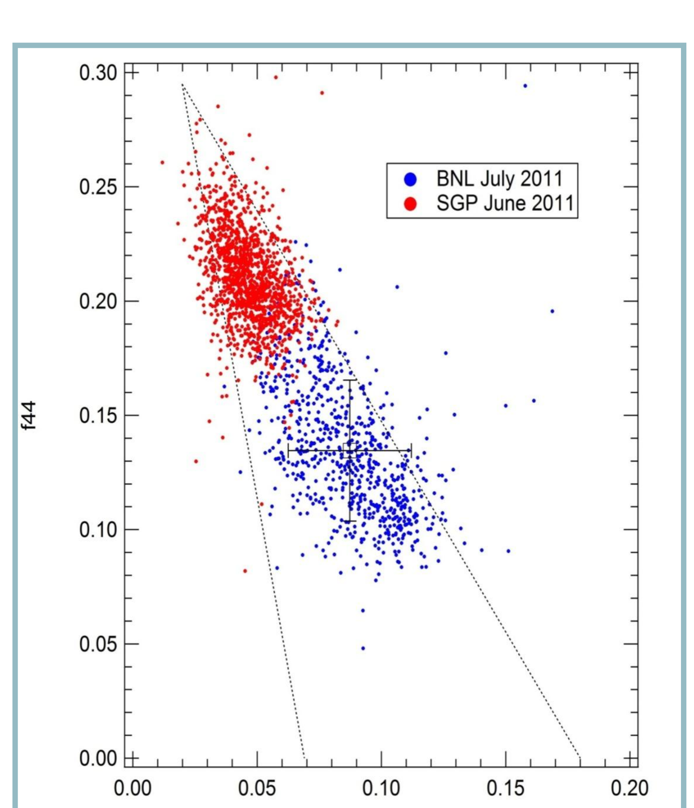


## Conclusion

- PMPMF analysis offers a cursory understanding of OOA and HOA contributions to OA, showing the dominance of OOA at BNL and SGP.
- PMF analysis of these datasets should be conducted to determine PMPMF scaling factors. These scaling factors may be compared against the generalized parameters to understand variance between more urban and rural locations as well as among two more rural locations.
- More rural datasets should be analyzed and utilized to develop PMPMF scaling factors for comparison with those derived from urban datasets. This may demonstrate a need to develop sets of scaling factors that are location specific.
- OA loading may be compared tracer components of primary and secondary OA, possibly CO and $SO_4^{2-}$, respectively. This comparison would offer insight into relationship of OOA and HOA with more or less aged aerosols, aiding in understanding of OA evolution and formation.
- ACSM results could be compared against results from a co-located aerosol mass spectrometer (AMS) at BNL to gain confidence in this less expensive and less labor-intensive instrument as an alternative to AMS. The ACSM has potential to be deployed at large number of locations to increase data sets and thus understanding of OA sources, formation, and evolution.

## References

ACSM image taken from Aerodyne Research, Inc., http://www.aerodyne.com/products/aerosol-chemical-speciation-monitor.
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