Chemical Characterization of Water Soluble Organic Aerosol in Contrasting Rural and Urban Environments in the Southeastern United States

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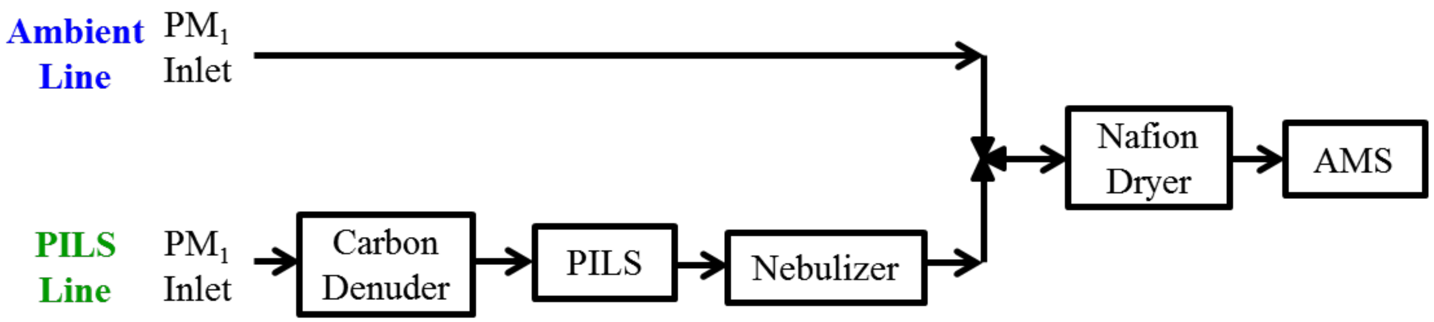
Introduction

- Water-soluble organic matter (WSOM) is an important component of atmospheric PM
  - alter the hygroscopicity and surface tension of particles
  - chemical composition and sources of WSOM are poorly understood

- Water-solubility of organic aerosols from different sources is different
  - possible to understand the sources of atmospheric OA from the perspective of water-solubility

Method: Novel PILS-AMS System

Xu et al., ES&T, 2017



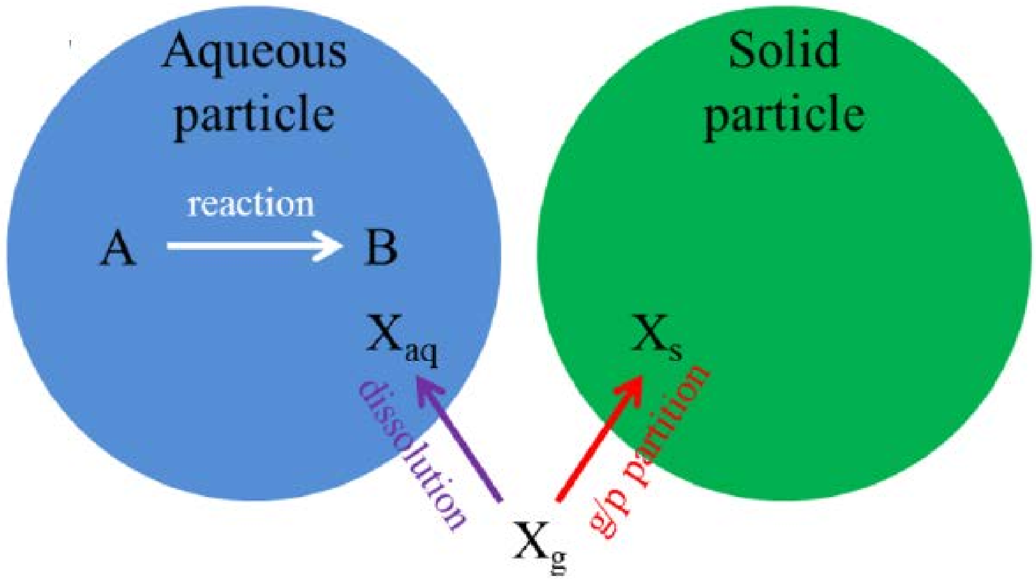
- Online collection and quantification of water-soluble OA and total ambient OA with one instrument

- The AMS alternated sampling between ambient line and PILS line every 30 min.

SOAS: Rural site in Centreville, AL (June 1- July 15, 2013)
Post-SOAS: Urban site in Atlanta, GA (August, 2013)

Note: Species Collected by PILS

Xu et al., ES&T, 2017



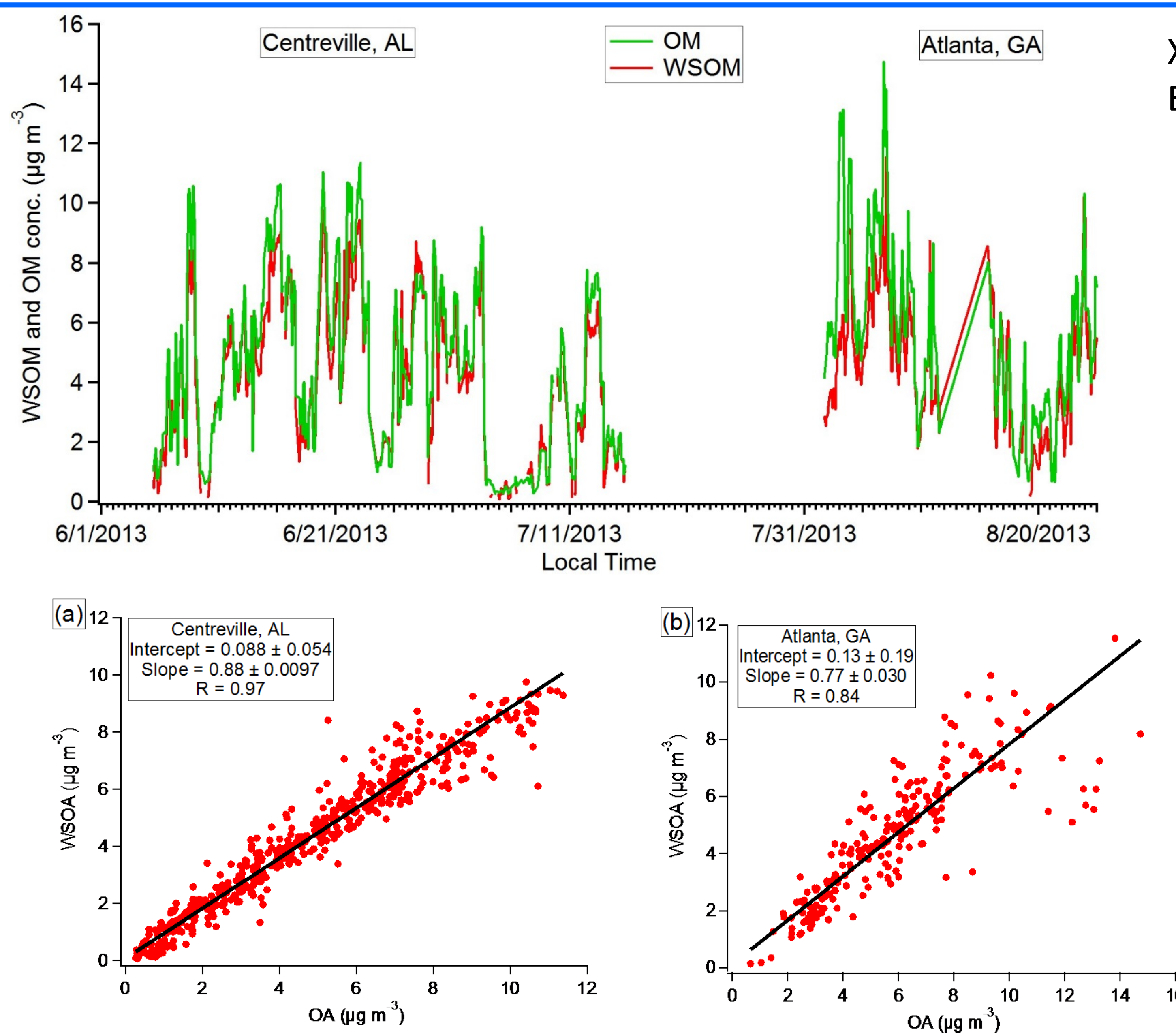
Species measured by PILS: B, Xaq, and Xs

NOT THE SAME AS

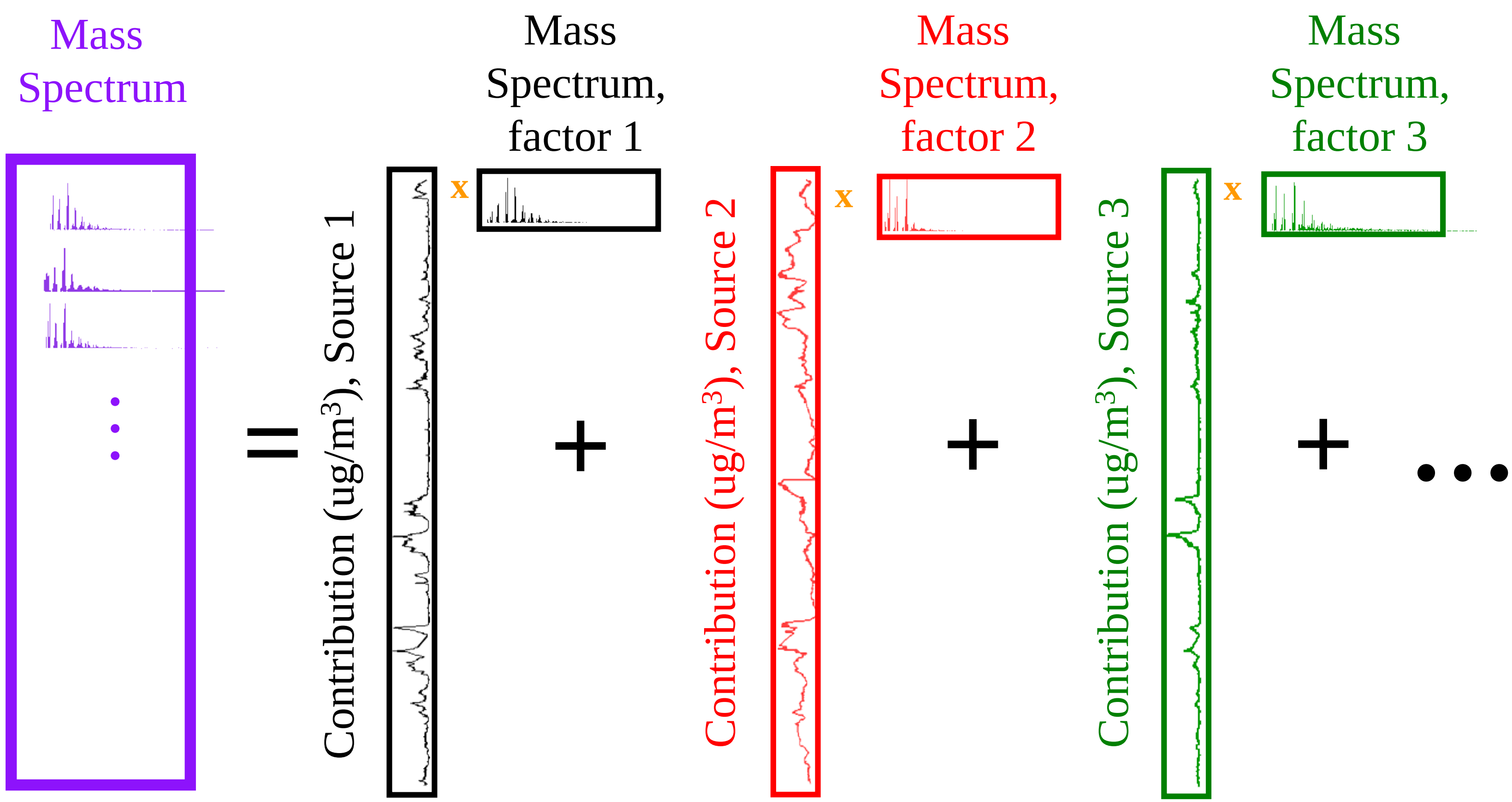
Species formed through aqueous-phase reactions (i.e., B) or
Species already in the ambient aqueous aerosols (i.e., B and Xaq)

Water-solubility of Organic Aerosols

Xu et al., ES&T, 2017



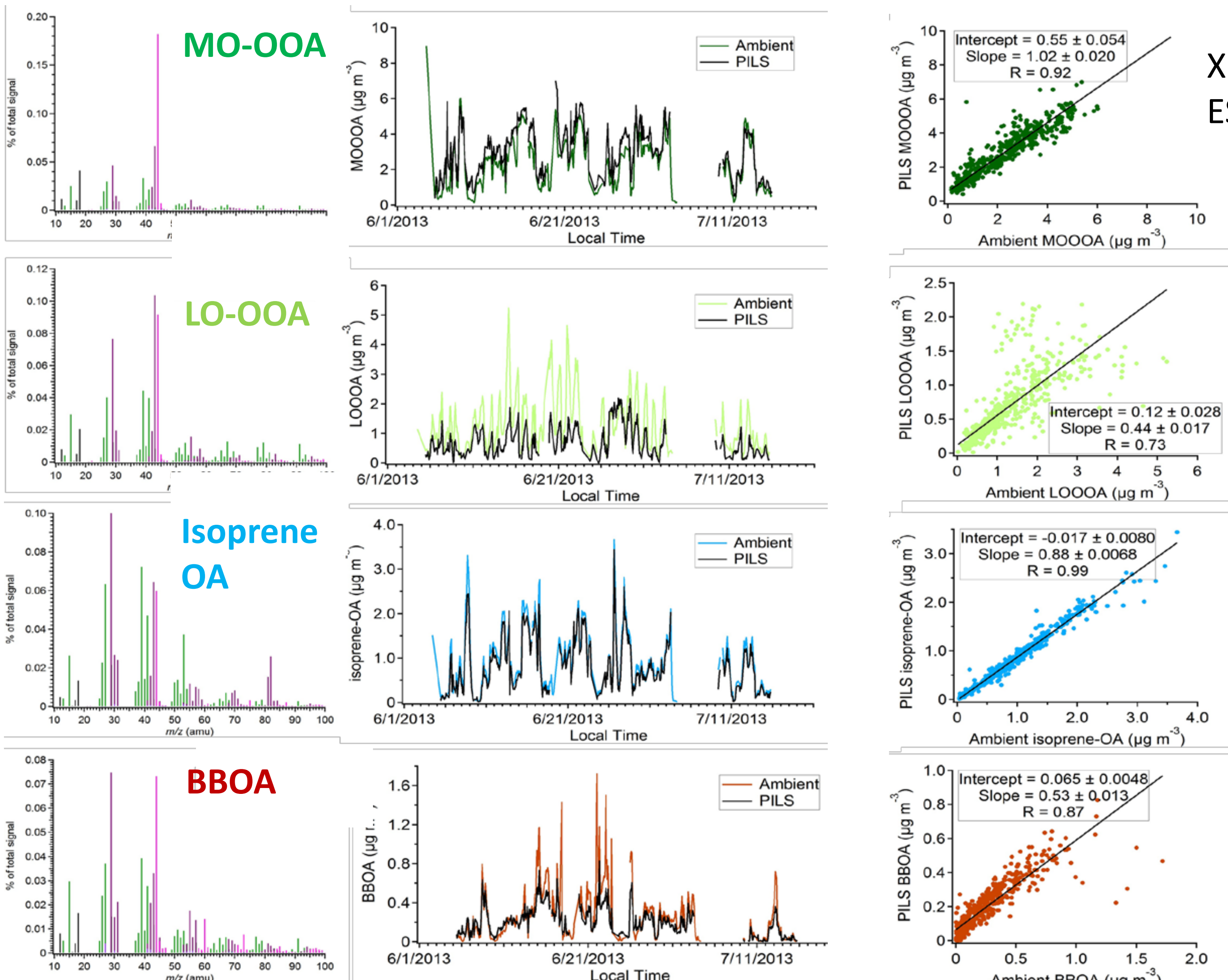
Positive Matrix Factorization (PMF) analysis



PMF is a bilinear mixing model in which a dataset matrix is assumed to be comprised of the linear combination of factors with constant profiles that have varying contributions across the dataset.

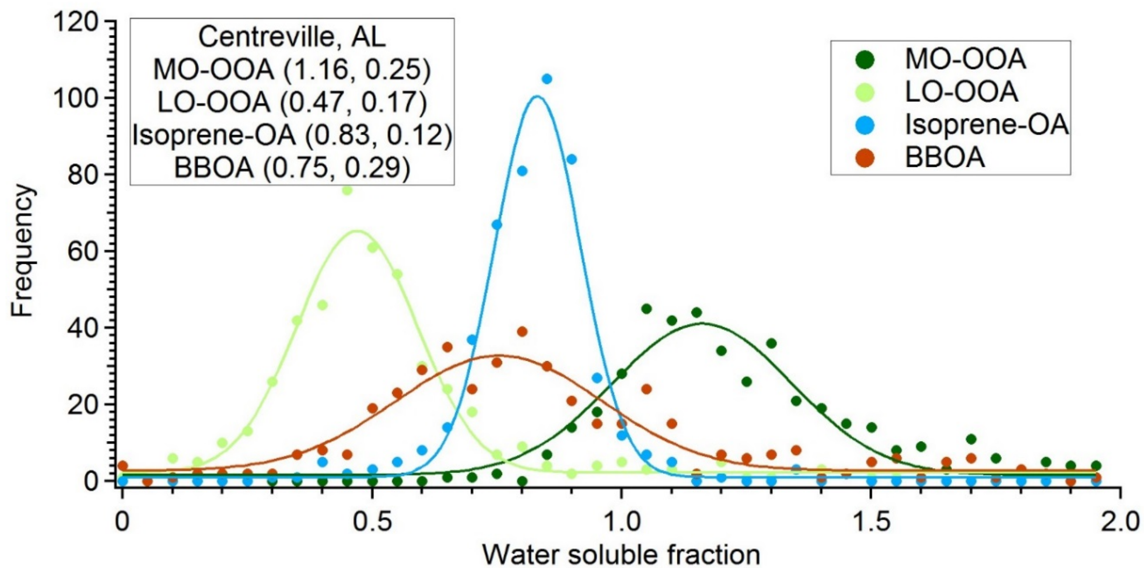
Ulbrich et al. 2009 ACP

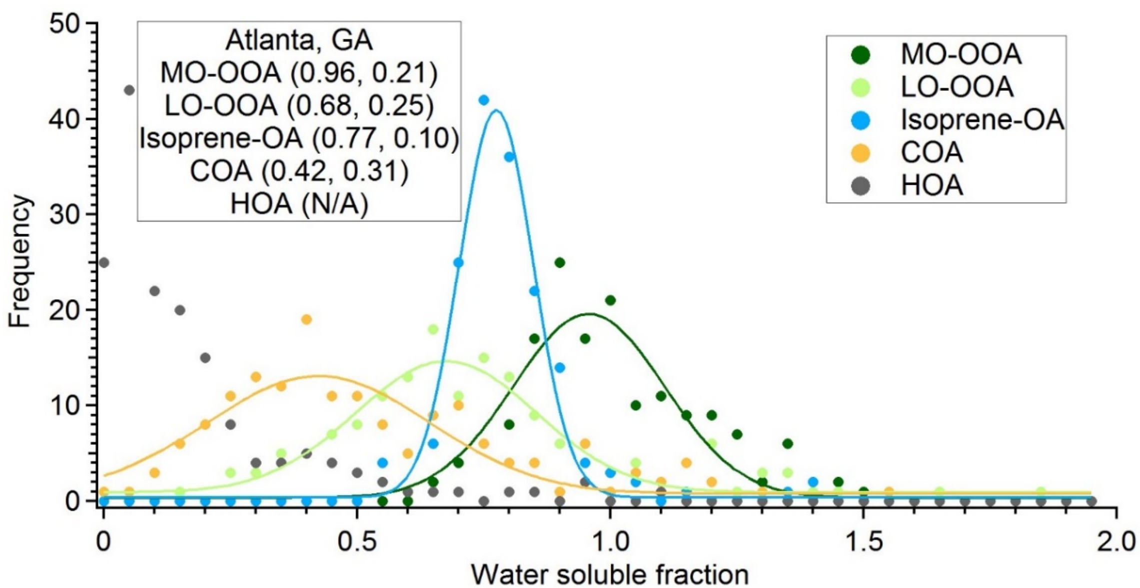
Water-Solubility of OA Factors



Xu et al., ES&T, 2017

Water-Solubility of OA Factors

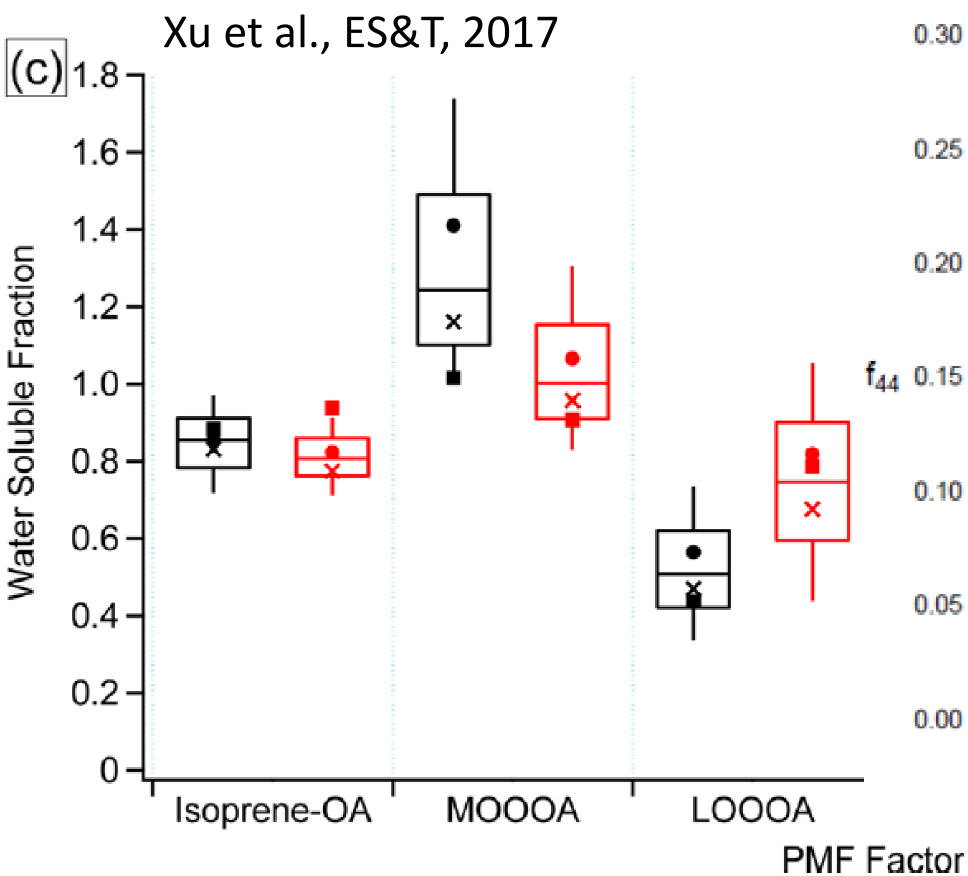


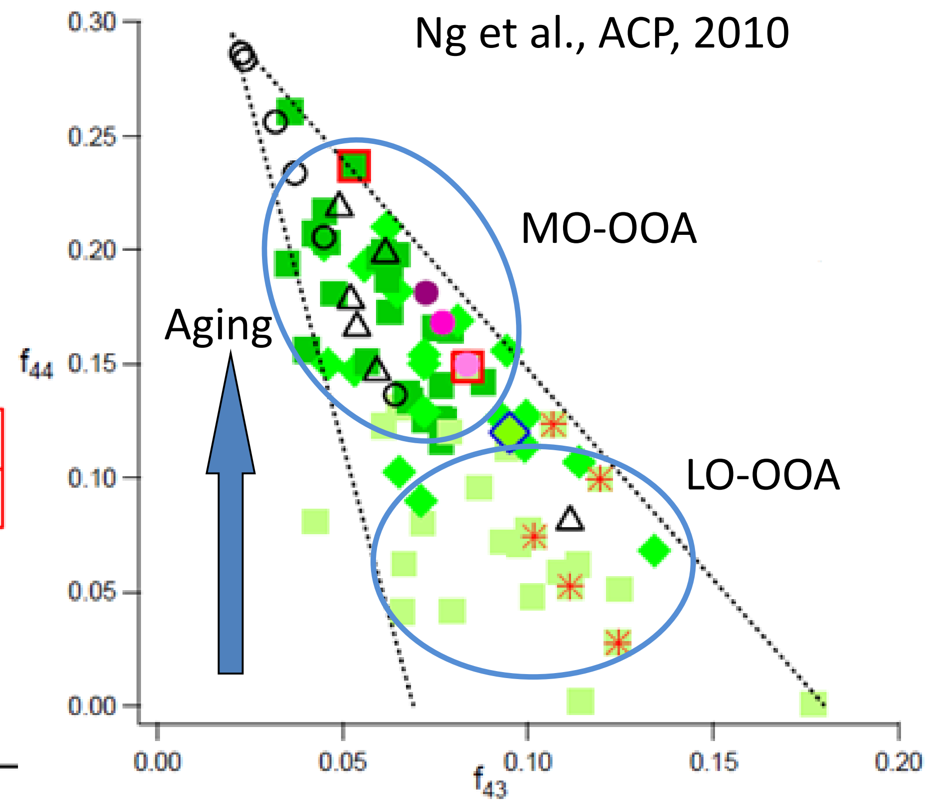


- Isoprene-OA is water soluble.
  → Aqueous-phase reaction.
- MOOOA is water soluble.
  → Highly oxidized species.
- 40-80% of LOOOA is water soluble
  → Contribution from organic nitrates (largely water-insoluble).
- Half of BBOA is water soluble.
- COA and HOA are largely water insoluble.

Xu et al., ES&T, 2017

Water-Solubility of OA Factors

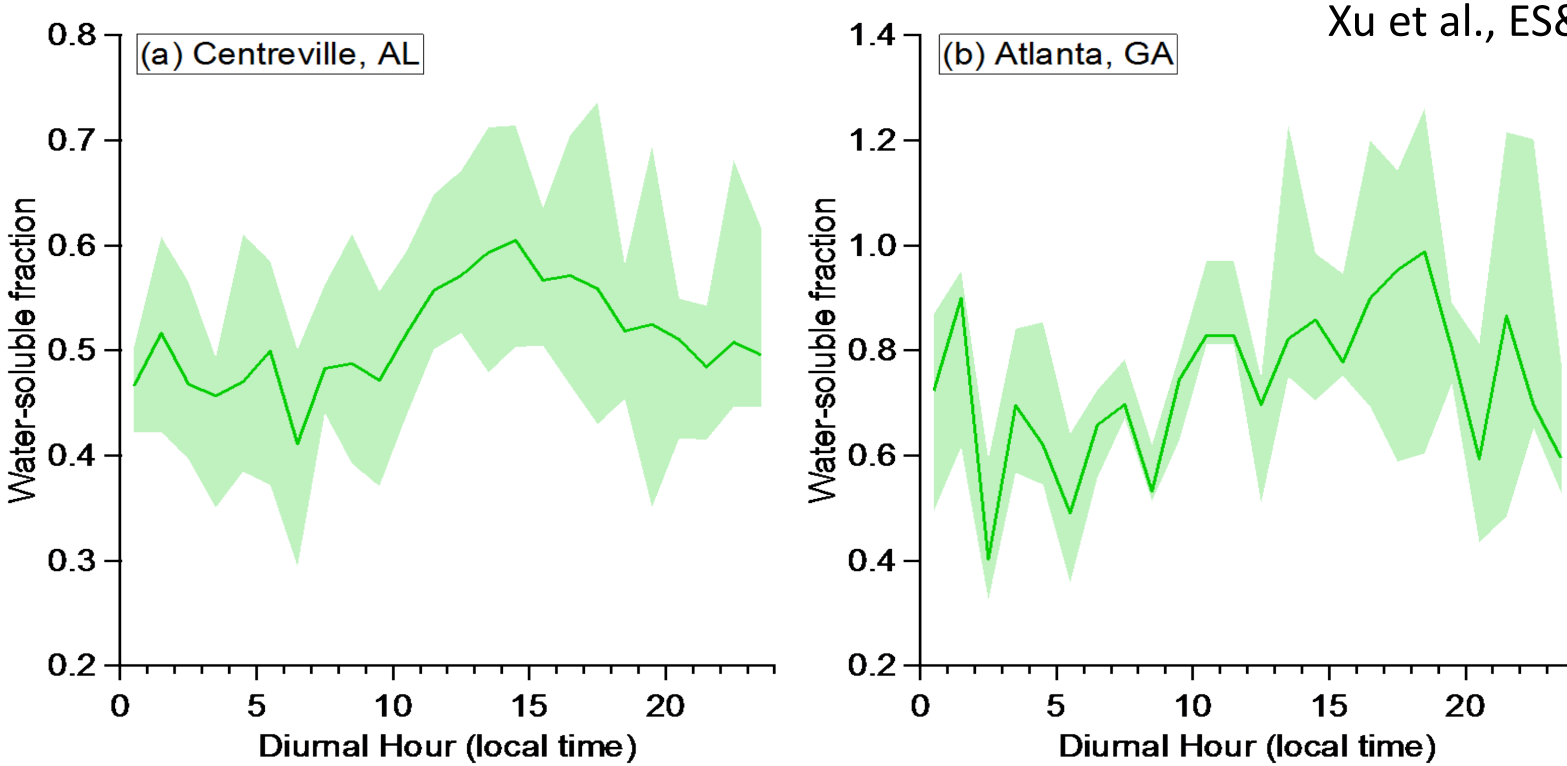




- Solubility of MO-OOA > LO-OOA; aerosols become more oxidized and hygroscopic with atmospheric aging
- MO-OOA: wide distribution suggests a variety of sources

Diurnal Trends of LO-OOA Water-Solubility

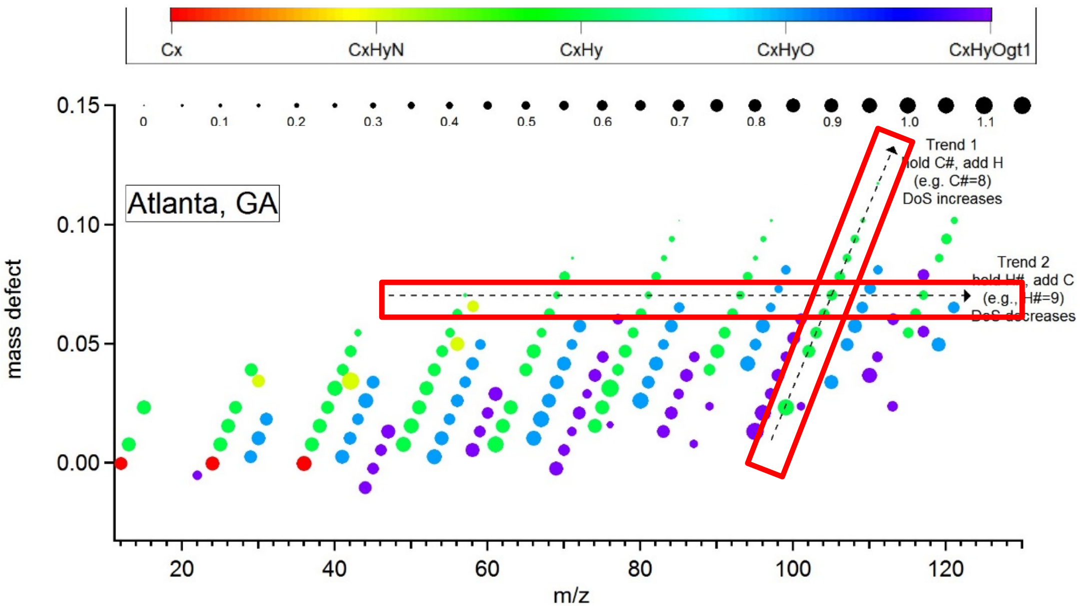
Xu et al., ES&T, 2017

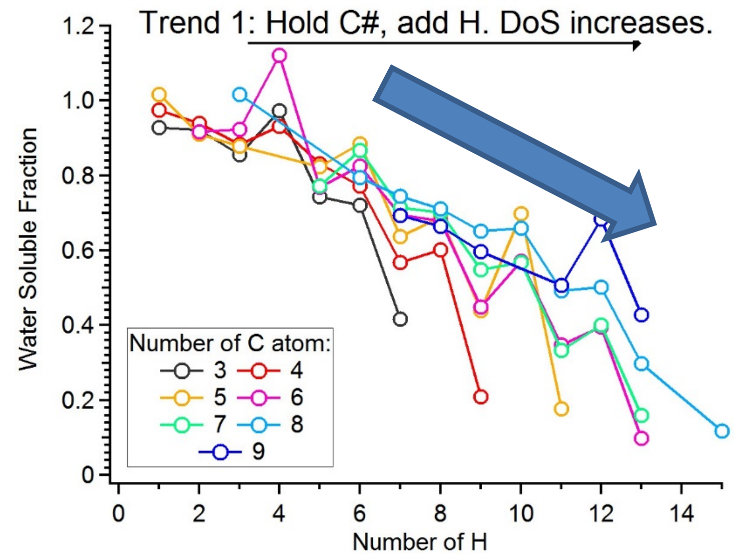


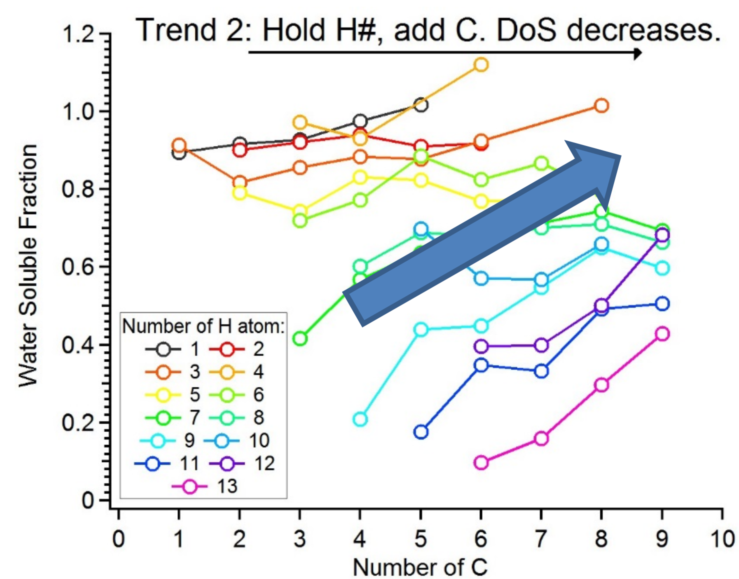
- Organic nitrates from monoterpene + NO_3 contributes to LO-OOA
- Organic nitrates fairly water insoluble (e.g., Suda et al., 2014; Pye et al., 2016)

- Smaller fraction of LO-OOA is water-soluble at night than in the day, which is consistent with more abundant organic nitrates at night.

Water-Solubility of AMS Ions





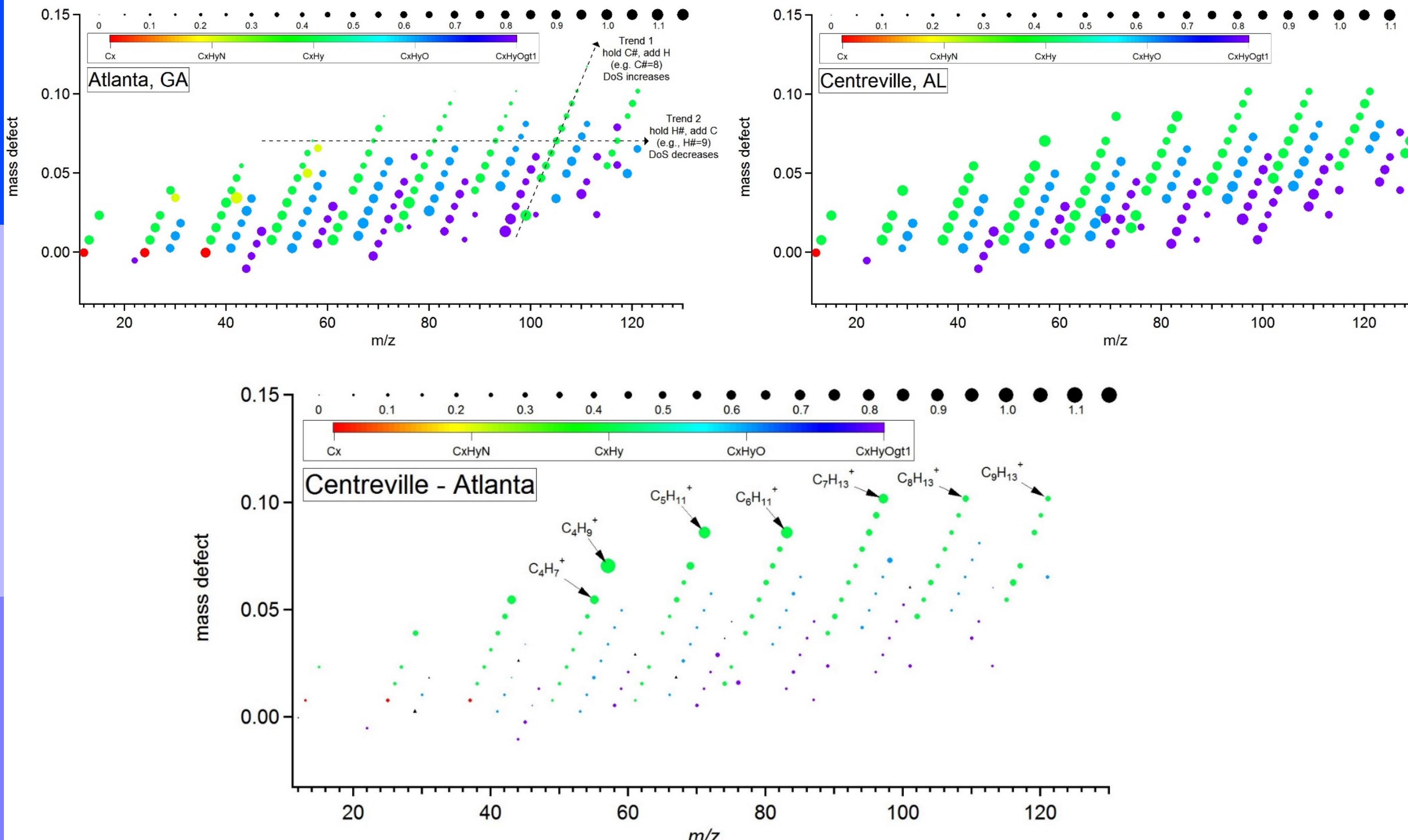


Higher degree of saturation of the $C_xH_y^+$ ions
→ Lower water solubility

Xu et al., ES&T, 2017

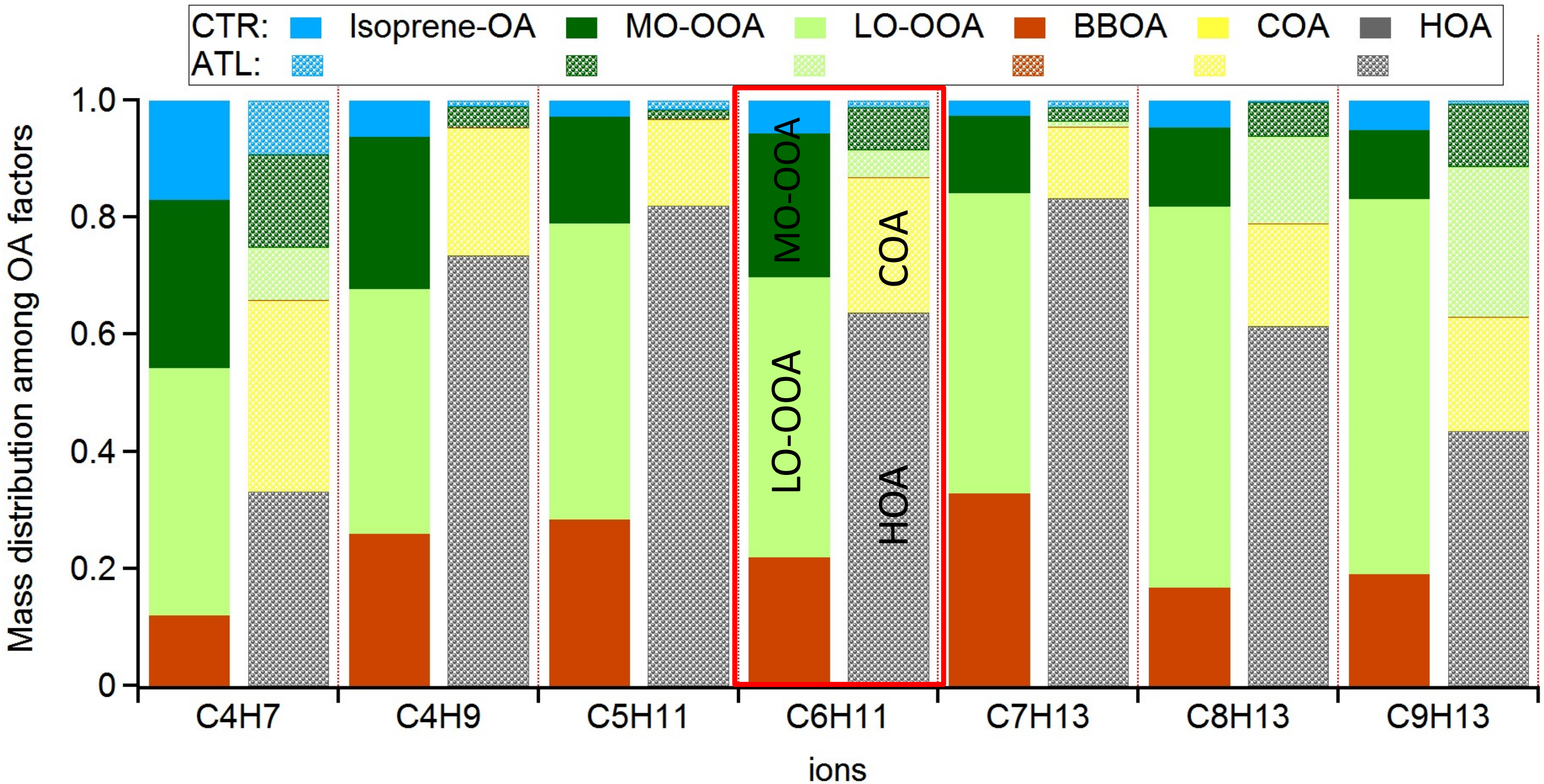
Water-Solubility of AMS Ions

Xu et al., ES&T, 2017



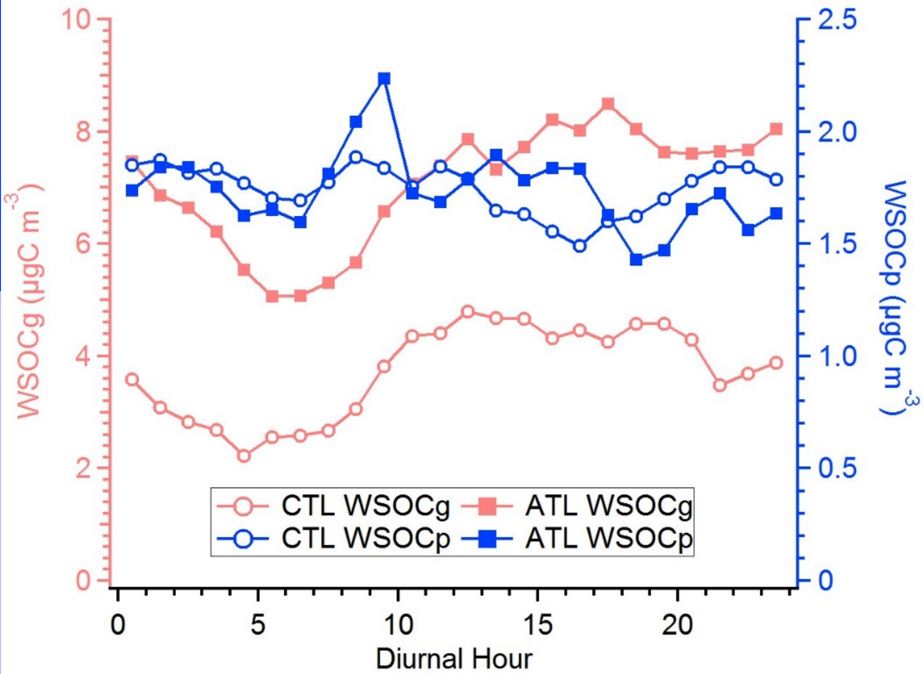
- The water-solubility of $C_xH_y^+$ ions with higher degree of saturation (i.e., $C_4H_7^+$, $C_4H_9^+$, $C_5H_{11}^+$, $C_6H_{11}^+$, $C_7H_{13}^+$, $C_8H_{13}^+$, and $C_9H_{13}^+$) is substantially larger in CTR than ATL.

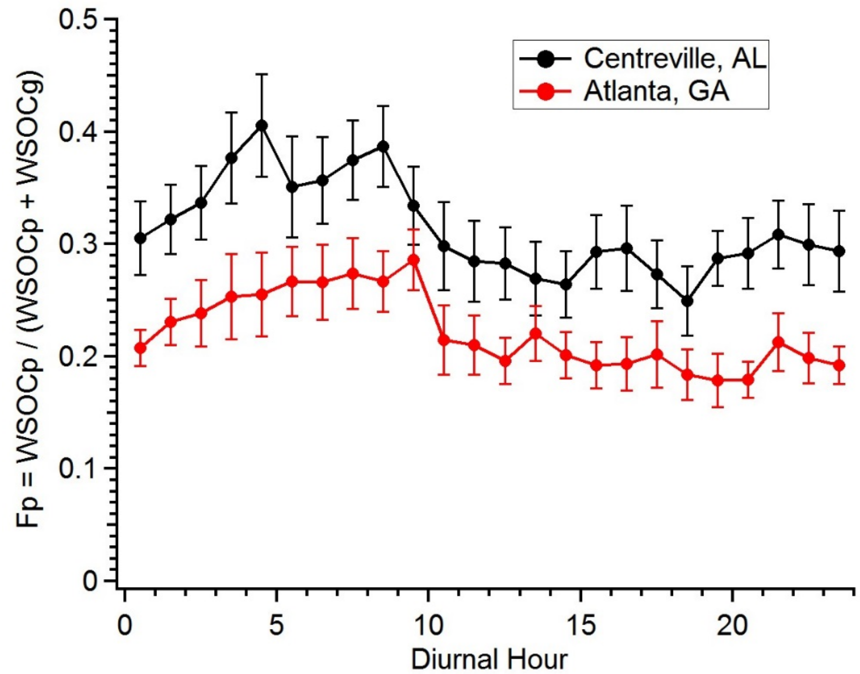
Water-Solubility of AMS Ions



- These $C_xH_y^+$ ions have different sources at the two sites.
- Atlanta: HOA and COA → long-chain alkanes from vehicle emissions or fatty acids from cooking.
- Centreville: MO-OOA and LO-OOA → secondary production from monoterpenes and sesquiterpenes etc.

WSOC Gas/Particle Partitioning





- The $WSOC_g$ concentration is two and four times higher than that of $WSOC_p$.
- $WSOC_g$ peaks in the afternoon. $WSOC_p$ is relatively constant.

- F_p is lower in Atlanta than Centreville. This is likely because of higher concentrations of small organic acids and carbonyls in Atlanta, which arise from the fragmentation during the oxidation of VOCs under high-NO_x conditions

Implications for Offline AMS Analysis of Filter Samples

- Water soluble extracts; source apportionment of WSOM extrapolated to ambient OA using a recovery ratio
- Accuracy of ambient OA source apportionment depends on the recovery ratio of the water-solubility of OA factors
- Things to keep in mind / Uncertainties; More work needed
  - Recovery ratio is a surrogate for, but not identical to, water-solubility
  - Water-solubility of OA factors varies with time and location; recovery ratio derived from one study may not be applicable to another study at a different site
  - Challenges in estimating ambient concentration of HOA or OA from any sources with low water-solubility

Xu et al., ES&T, 2017

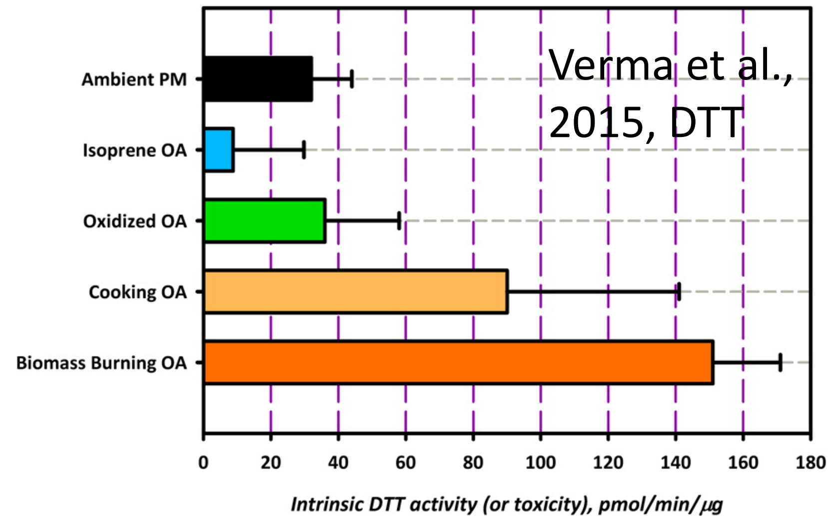
Conclusions

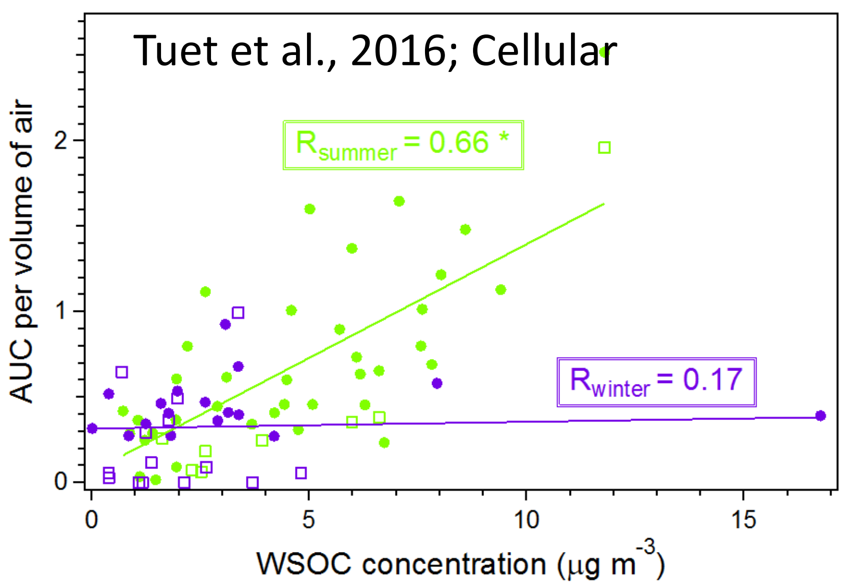
Approximately 88% and 77% of OA are water-soluble in rural Centreville and urban Atlanta, respectively.

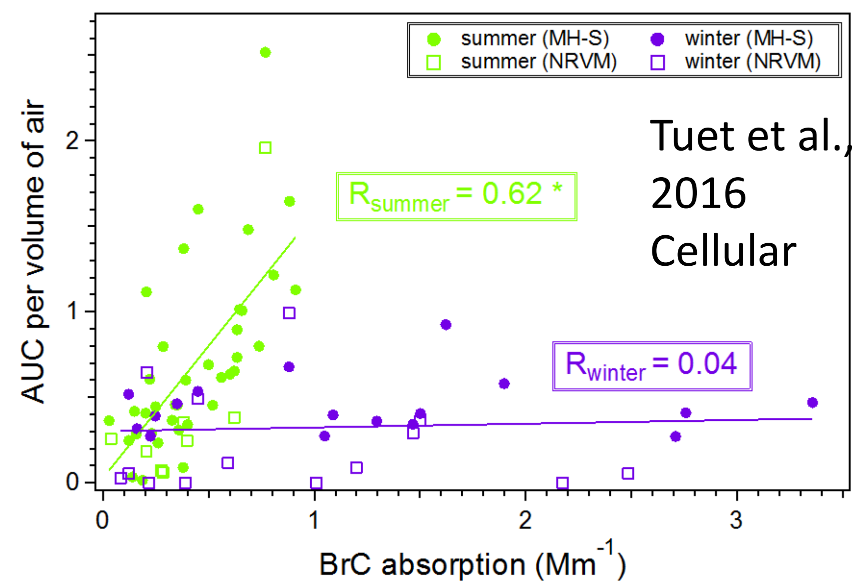
PMF factor	Water-solubility	Interpretation
Isoprene-OA	>80%	represents OA formed through the aqueous-phase reaction of isoprene epoxydiols
MO-OOA	~100%	represents highly oxidized compounds
LO-OOA	47-68%	includes contributions from organic nitrates
BBOA and COA	a wide range	diverse burning conditions and cooking activities
HOA	~0%	primary emissions from combustions

Health Effects of Aerosols

- DTT Assay (chemical assay, oxidative potential)
- Macrophage assay (cellular assay, reaction oxygen species, ROS, generation)
- Linking aerosol composition to health effects

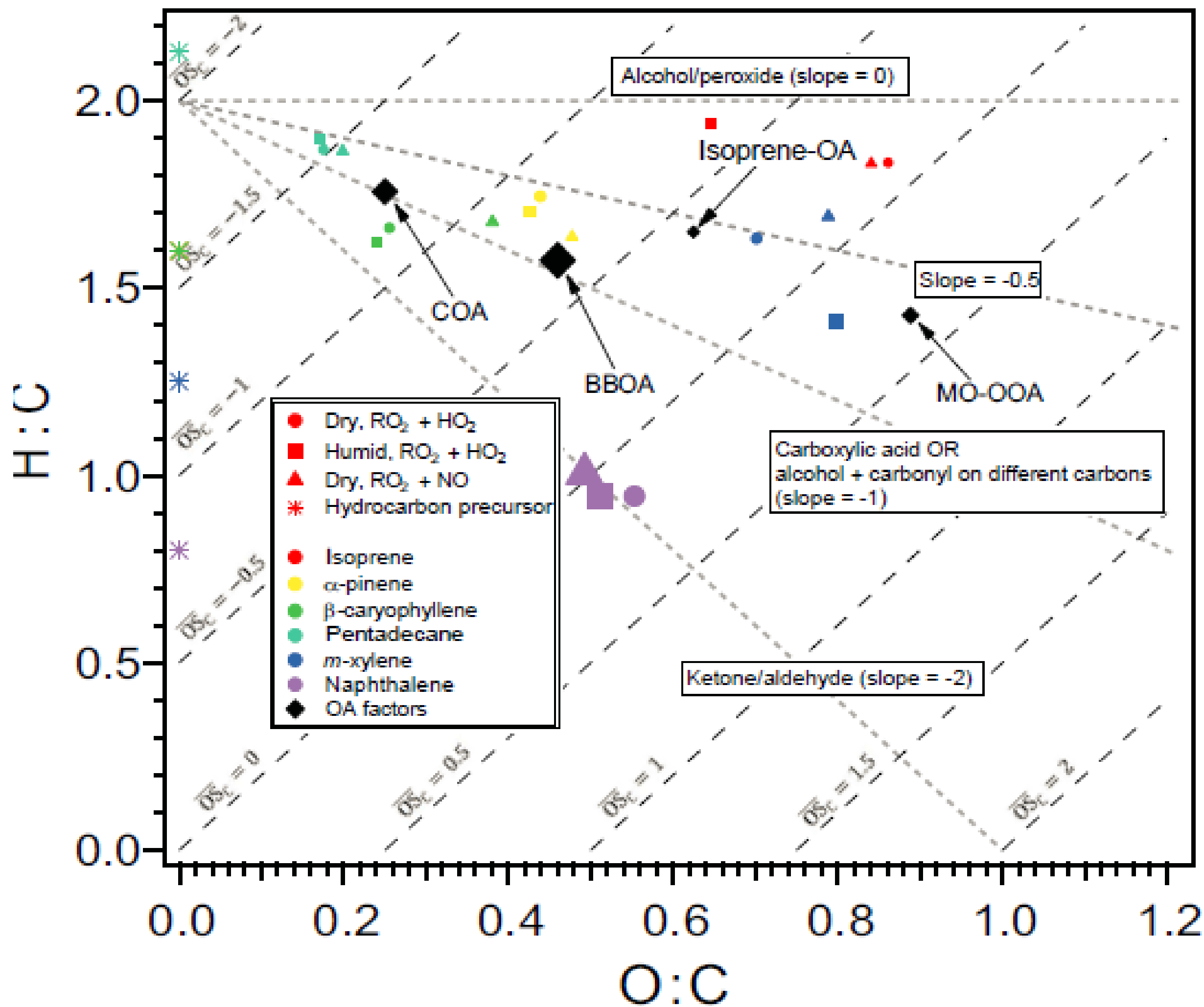




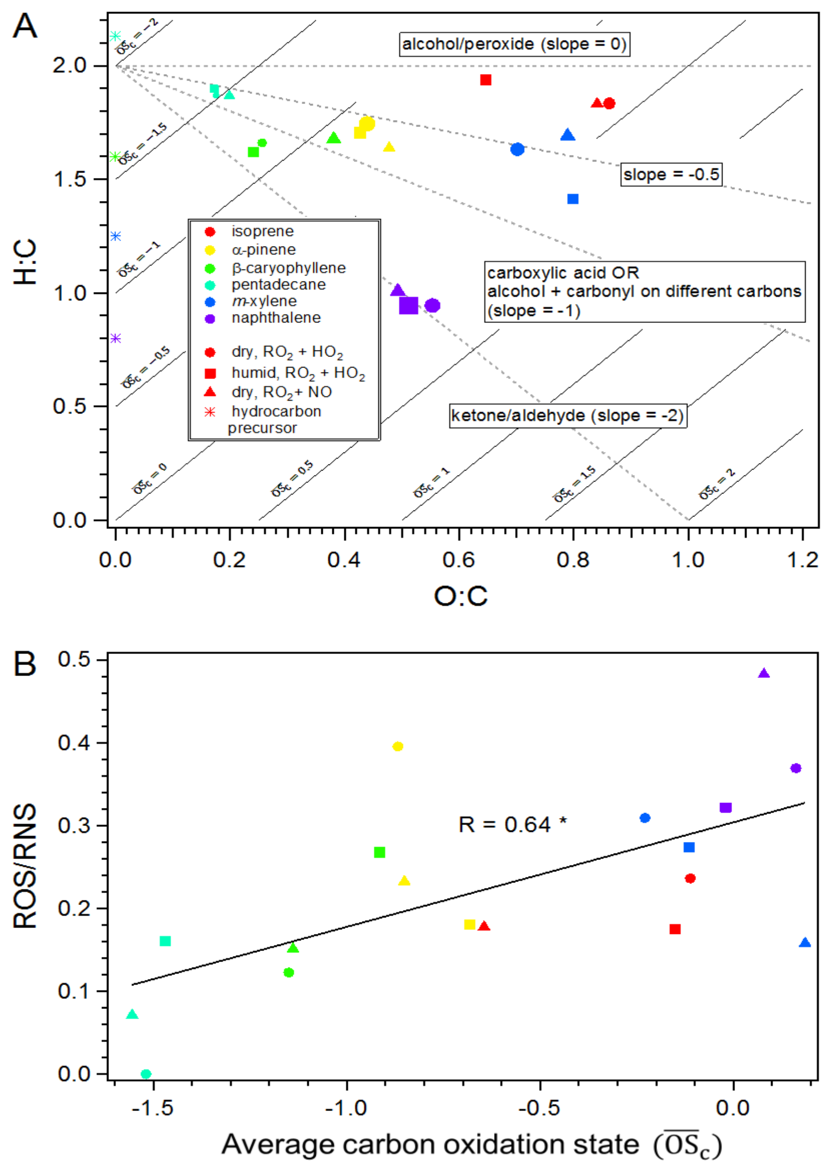


DTT Activity of Different Types of SOA (Chamber Data)

Size of data point = DTT activity, see details in Tuet et al., ACP, 2017



Cellular ROS of Different Types of SOA (Chamber Data)



Size of data point = cellular reactive oxygen species (ROS), see details in Tuet et al., ACPD, 2017

References

Water Soluble Organics:

See Supplementary Information of publications for PMF details
Users responsibility!

Xu, L., Guo, H., Weber, R. J., and Ng, N. L.: Chemical Characterization of Water-Soluble Organic Aerosol in Contrasting Rural and Urban Environments in the Southeastern United States, *Environ. Sci. Technol.*, 51, 78-88, 2017.

Aerosol Health Effects:

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