Direct atmospheric evidence for the irreversible formation of aqueous secondary organic aerosol (aqSOA)

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Overview and Objective

Recent evidence indicates that the uptake of water-soluble organic gases (WSOC) into atmospheric waters – likely represents an important pathway for secondary organic aerosol (SOA) formation. This aqueous SOA (aqSOA) can help in explaining the current underprediction of SOA concentrations by many state-of-the-art models.

Fundamental aspects of aqSOA formation remain uncertain or unknown including uncertainties in the relative contributions of reversible and irreversible uptake processes.

The purpose of this study was to investigate the reversible/irreversible nature of aqSOA using direct atmospheric observations.

Effect of Temperature on WSOC$_g$ and WSOC$_p$

![Figure 1 Schematic of aqSOA formation in aerosol water.](image)

A central component of this study was an analysis of the behavior of particulate water-soluble organic carbon (WSOC$_g$) under conditions of aerosol drying (liquid water evaporation).

Experimental Setup

1. CO analyzer
2. OCEC analyzer
3. Data acquisition
4. PILS
5. TOC analyzer
6. Mist Chamber
7. 3-way valve
8. Ambient channel
9. Dry channel

![Figure 2 Experimental set-up placed in an enclosure on the rooftop.](image)

Environmental Enclosure

- PILS (carbon denuder)
- WSOC$_g$ ambient channel
- WSOC$_p$ channel
- Dryer
- 3-way valve
- Mist Chamber
- Data Acquisition
- PILS (carbon denuder)
- Distribution valve
- WSOC$_g$ channel
- WSOC$_p$ channel
- TOC Analyzer

![Figure 3 Schematic of experimental set-up. A WSOC$_g$ - WSOC$_p$ cycle was completed every 14 min.](image)

Evidence for Nighttime aqSOA Formation

![Figure 4 Average diurnal profiles of ∆WSOC$_g$/ΔCO (a) and ∆WSOC$_p$/ΔCO (c). Boxplots of daytime ∆WSOC$_g$/ΔCO (b) and daytime ∆WSOC$_g$/ΔCO (d) as a function of temperature. WSOC in both the gas- (WSOC$_g$) and particle (WSOC$_p$) phases increased exponentially during the day with the increase in temperature, highlighting the effect of photochemistry on SOA production.](image)

Assessing Reversibility of aqSOA Partitioning

![Figure 5 Scatter plots of WSOC$_{aqSOA}$ Versus WSOC$_p$ for daytime (a) and nighttime (b); and linear regression results using least squares regression analysis.](image)

![Figure 6 Scatter plots of WSOC$_{aqSOA}$ Versus WSOC$_p$ for daytime (a) and nighttime (b); and linear regression results using least squares regression analysis.](image)

![Figure 7 Median daytime and nighttime values of the WSOC$_{aqSOA}$/WSOC$_p$ ratio as a function of ambient RH. The WSOC$_{aqSOA}$/WSOC$_p$ ratio was unity - within experimental error - across all ambient conditions encountered during the study. No statistical difference between WSOC$_g$ and WSOC$_p$ was observed as a function of RH.](image)

Conclusions and Future Work

- SOA formation was observed primarily due to two pathways: 1) daytime photochemical SOA production, and 2) nighttime aqSOA production.
- SOA formed through the uptake of WSOC$_g$ into aerosol liquid water under dark conditions remained in the particle phase upon the evaporation of aerosol water, i.e. the observed aqSOA was formed irreversibly.
- Methods used in this study will be deployed across multiple seasons to characterize a wider range in meteorology, source influences and aerosol composition.
- A range of drying times will be investigated outside of the 7-s used in this experimental setup.

Acknowledgments

This work was supported by the National Science Foundation through award 1464458.

References