Off-line UPLC/ESI-HR-Q-TOFMS Analyses of SOA Heterogeneous-Reaction Products in $PM_{2.5}$ Collected from the CalNex-Pasadena Ground Site

Ying-Hsuan Lin [1], John H. Offenberg [2], Xiaolu Zhang [3], Rodney J. Weber [3], Tadeusz E. Kleindienst [2], Jason D. Surratt [1]

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

[1] *Departments of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, NC, USA*
[2] *U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, NC, USA*
[3] *School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA*

Introduction

Secondary organic aerosol (SOA) arising from the oxidation and multi-generational chemical transformation of biogenic and anthropogenic emissions substantially contribute to the ambient PM2.5 mass (Hallquist et al., 2009). Recently, heterogeneous chemistry has been realized to be important to SOA formation based on mass spectrometric evidence from both laboratory-generated and ambient SOA samples. Specifically, heterogeneous-reaction products, such as organosulfates (Surratt et al., 2007; Surratt et al., 2008), have been demonstrated to contribute to SOA formation by reactive uptake of certain oxidation products onto pre-existing aerosol surfaces, acid-catalyzed particle-phase reactions, and in-cloud reactions in the atmosphere.

In the present work, SOA constituents are chemically characterized by using advanced off-line mass spectrometry approaches, with specific focus on identifying biogenic isoprene- and monoterpene-derived organosulfates and nitrated organosulfates. This work aimed to provide temporal information of these known tracer species to better understand what conditions lead to their formation.

Experimental

I. Filter Sampling

- PM2.5 samples collected on 8×10 quartz filters with high volume samplers at flow rates approximate 1 m^3/min.
- 23-hr time integrated filter samples collected daily throughout the campaign.
- Intensive sampling with fine time resolution (i.e., 3- to 6-hr) performed additionally on selected days, including 4 weekends and 5 weekdays.

II. Extractions

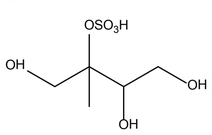
- Filters extracted with methanol by sonication
- Blown dry under a gentle stream of $N_{2(g)}$
- Reconstituted with a 50:50 (v/v) solvent mixture of methanol and water containing 0.1% acetic acid (LC/MS mobile phase)

III. Ultra Performance Liquid Chromatography/ Electrospray Ionization High Resolution Quadrupole Time-of-Flight Mass Spectrometry (UPLC/ESI-HR-Q-TOFMS)

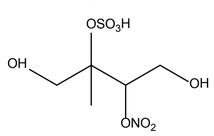
- Agilent 6500 Series Accurate-Mass Q-TOF LC/MS
- Column: Waters ACQUITY UPLC HSS T3 (2.1×100mm,1.8 μm)
- Mobile phase : water + 0.1% acetic acid (A)
  methanol+ 0.1% acetic acid (B)
- Gradient elution in 12 minutes
- Mass range: m/z 63 to 1000
- Mass resolution: ~9,000

Representative Tracer Compounds Detected in this Study

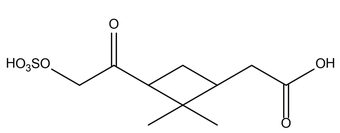
Isoprene-derived organosulfate



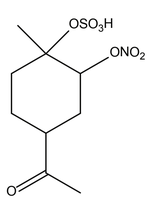
Isoprene-derived nitrated organosulfate



Monoterpene (α-pinene, β-pinene) -derived organosulfate

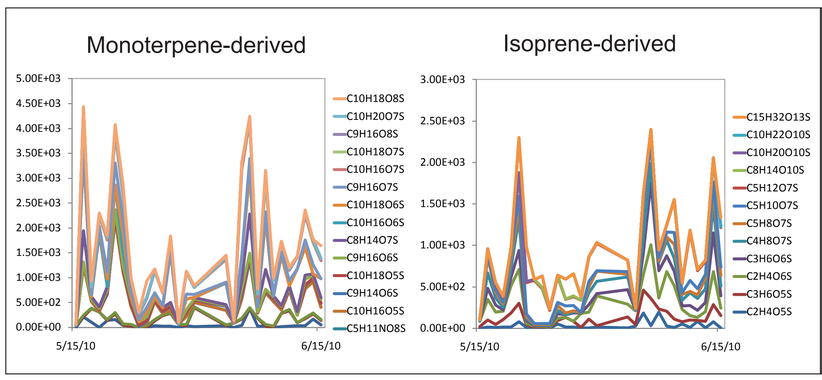


Monoterpene (limonene)-derived nitrated organosulfate

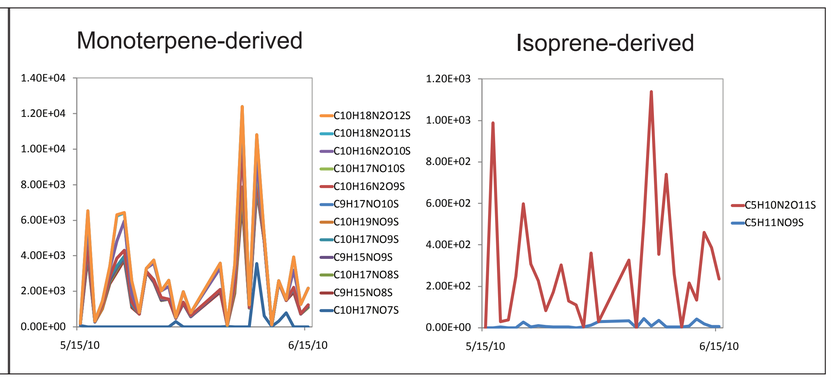


Temporal Profile of Observed Organosulfates and Nitrated Organosulfates During the Campaign (05/15/10-06/15/10)

- Organosulfates



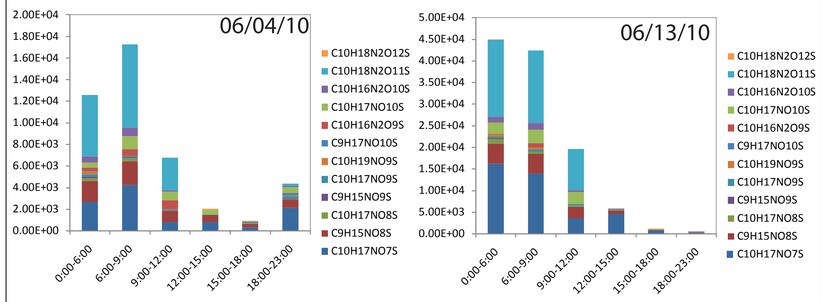
- Nitrated Organosulfates



- Abundance is expressed with peak areas normalized by sampling volume (peak area/ m^3)
- Temporal variation of known organosulfates agree with OC measurements on most high aerosol loading days during the campaign.

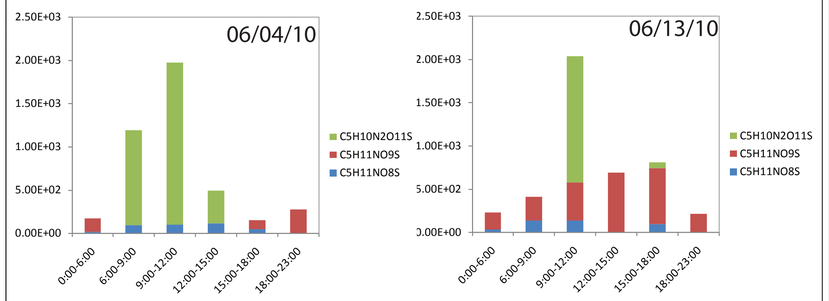
Diurnal Variation of Organosulfates and Nitrated Organosulfates on 06/04/10 (weekday) and 06/13/10 (weekend)

- Nitrated organosulfates derived from monoterpenes

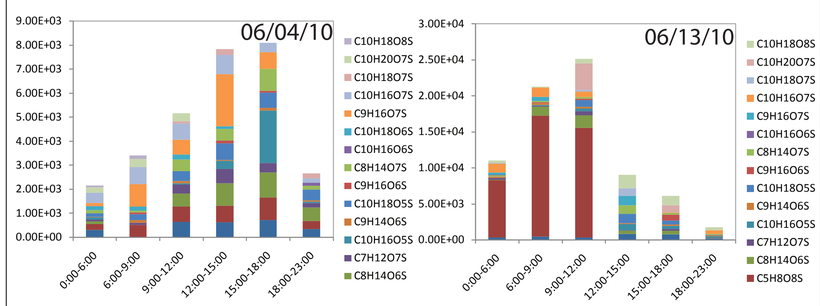


Monoterpenes-derived nitrated organosulfates have high concentrations at night (0:00-6:00) and in the early morning (6:00-9:00) on both intensive sampling days. The level of trhese compounds decreased during the day.

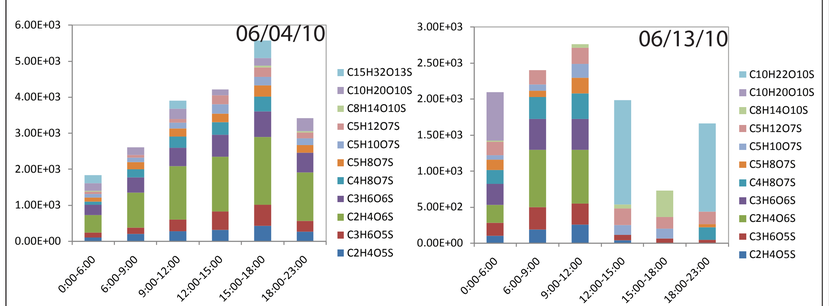
- Nitrated organosulfates derived from isoprene



- Organosulfates derived from monoterpenes



- Organosulfates derived from isoprene



Summary

1. Organosulfates and nitrated organosulfates are observed on 23-hr time-integrated filters on most days.

2. Time-resoluted intensive samples provide evidence for the role of nighttime nitrate radical (NO_3) initiated chemistry of monoterpenes. Enhanced night-time and early morning concentrations of monoterpene-derived nitrated organosulfates could also be due to a more shallow boundary layer.

Future Work

1. Quantify organosulfates and nitrated organosulfates with authentic or surrogate standards to estimate their mass concentrations and contributions to OM in ambient $PM_{2.5}$.

2. Correlate our data with other available complementary chemical and meteorological measurements to investigate favorable conditions for the formation of these compounds.

Acknowledgements

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Reference

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