Organic nitrogen in aerosols at a forest site in southern Appalachia

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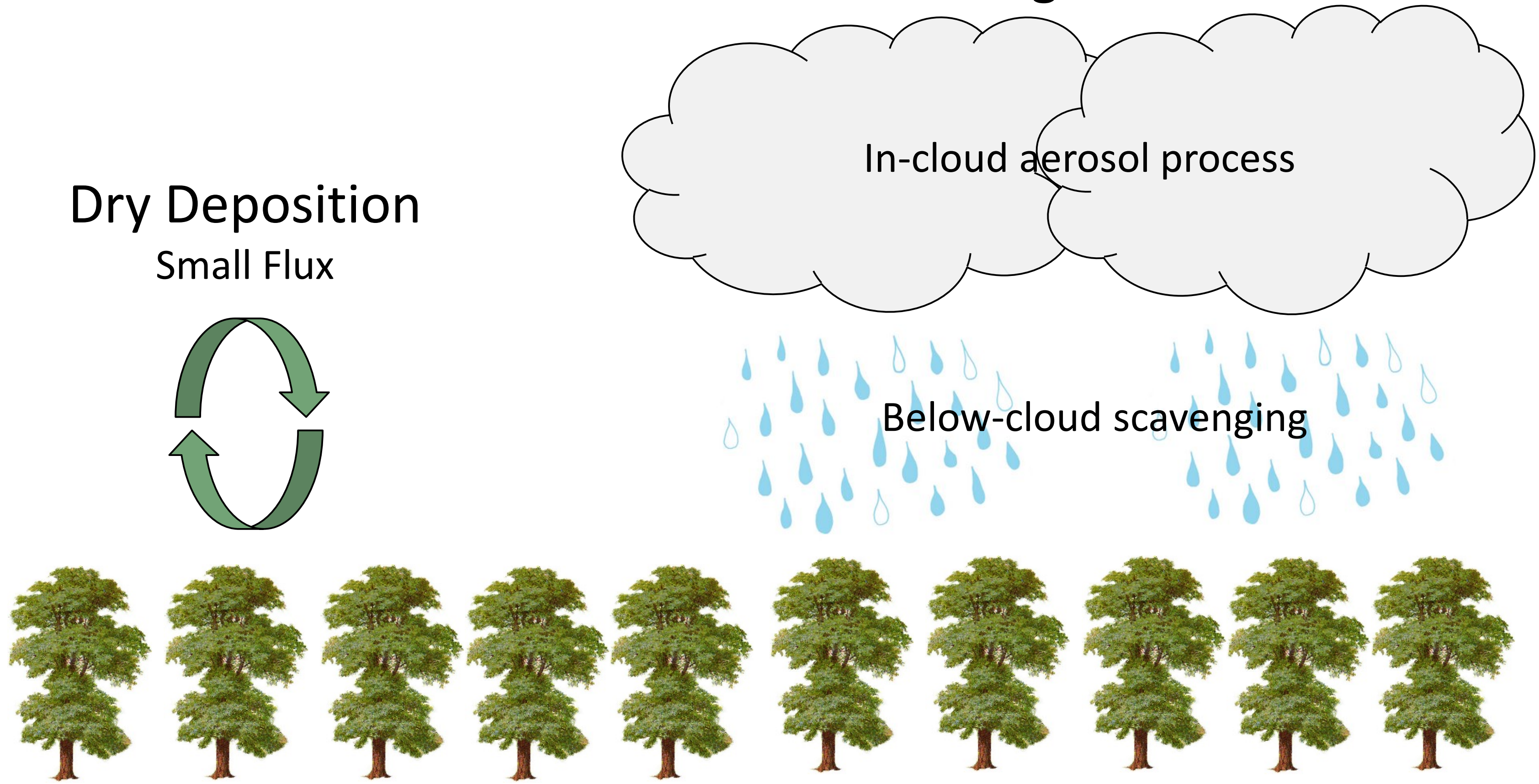
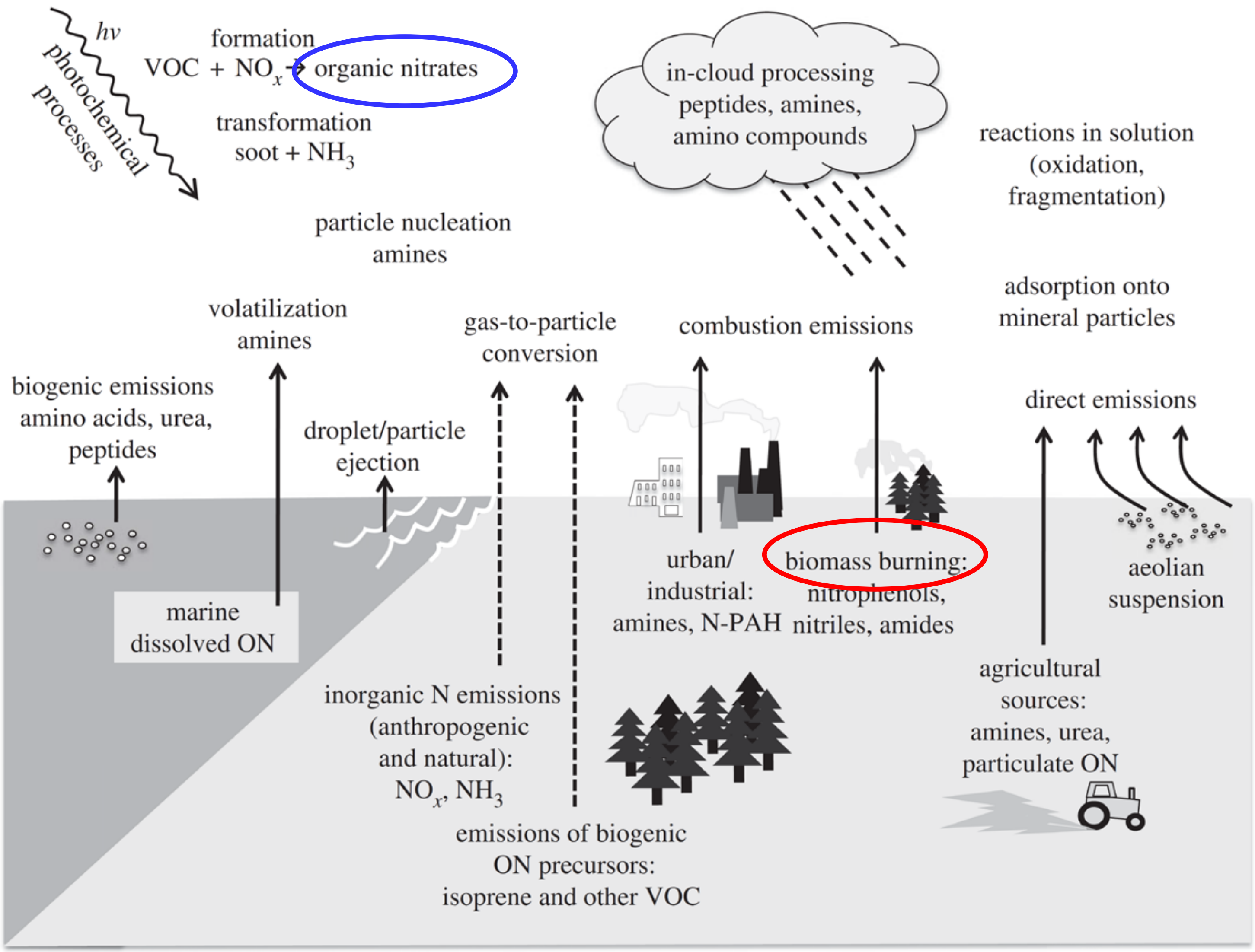
Motivation

- ON is the least understood component of atmospheric N
  - *New particle formation*
  - *Aerosol characteristics*
  - *Atmospheric N deposition*

Wet Deposition
Large Flux



Sources of atmospheric organic N



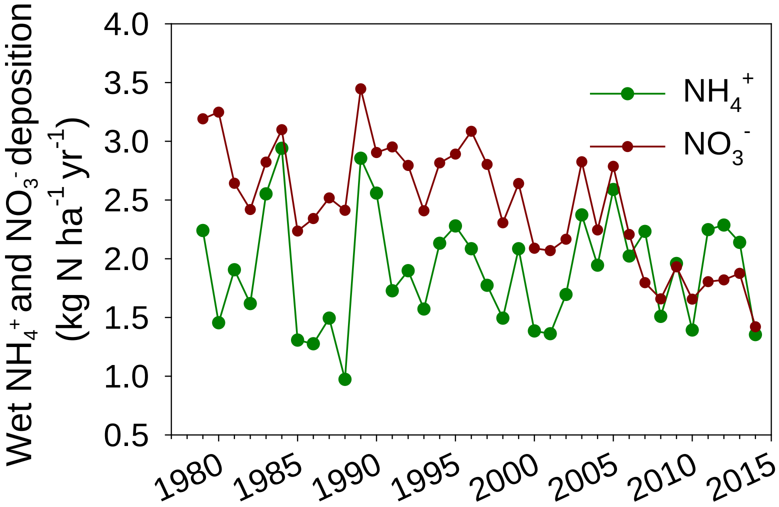
From: Jickells, T.; Baker, A. R.; Cape, J. N.; Cornell, S. E.; Nemitz, E. The Cycling of Organic Nitrogen through the Atmosphere. *Phil. Trans. R. Soc. B.* 2013, *368*, doi:10.1098/rstb.2013.0115.

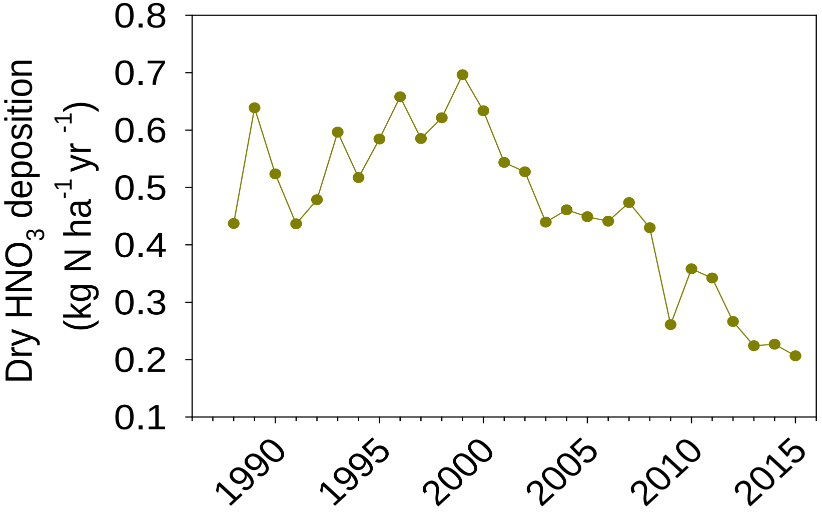
Study objectives

- Characterize the contribution of water soluble organic N (WSON) to water soluble total N (WSTN) in $PM_{2.5}$
- Focus on the role of organic N in sulfur-containing secondary organic aerosols (SOA) and aerosols associated with biomass burning
- Target four groups of compounds for speciation:
  - nitro-aromatics associated with biomass burning
  - organosulfates and nitrooxy-organosulfates
    - *produced from biogenic SOA precursors interacting with anthropogenic pollutants*
  - terpenoic acids formed from monoterpene oxidation
    - *characterize extent of aerosol aging*
  - organic molecular markers
    - *characterize extent of aerosol aging and influence of biomass burning signature*

Site

- Remote forest site in southwestern NC
- U.S. Forest Service
  - Coweeta Hydrologic Laboratory
- LTER site
- CASTNET
- NADP
- AMoN





Data from National Atmospheric Deposition Program and U.S. EPA Clean Air Status and Trends Network

Sampling and analytical methods

24-hour high-volume $PM_{2.5}$ sample (Tisch) on quartz filter

$$WSON = WSTN - NH_4^+ - NO_3^- - NO_2^-$$

WSTN: Combustion/ Chemiluminescence

NH_4^+, NO_3^-, NO_2^-: Ion Chromatography

Isoprene SOA markers
Monoterpene tracers
Levoglucosan

Gas Chromatography/ Mass Spectrometry

GC-MS

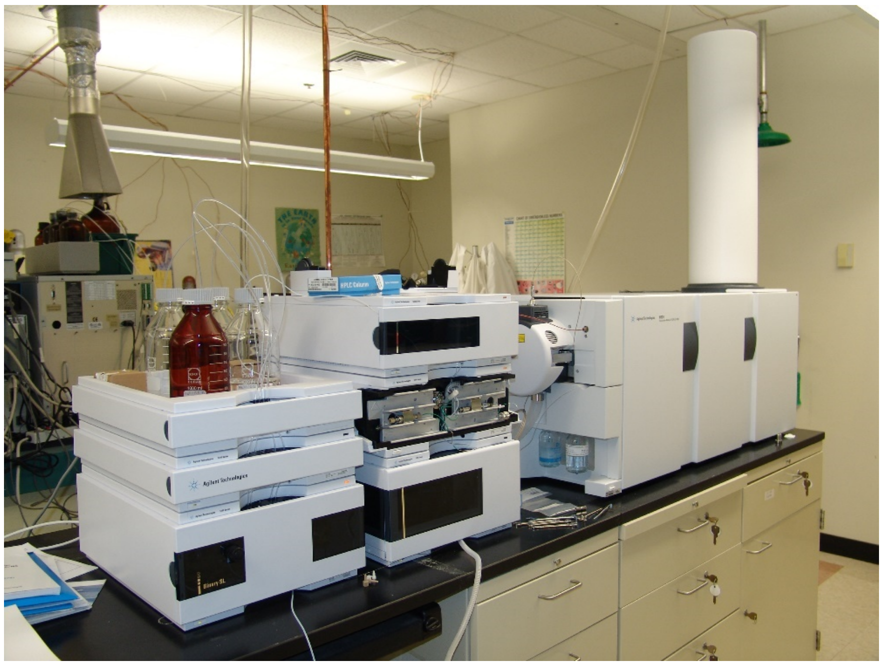
Organosulfates
Nitro-aromatics
Terpenoic acids

High Performance Liquid Chromatography/ Quadrupole Time of Flight/ Mass Spectrometry

HPLC-QTOF-MS

Sampling and analytical methods

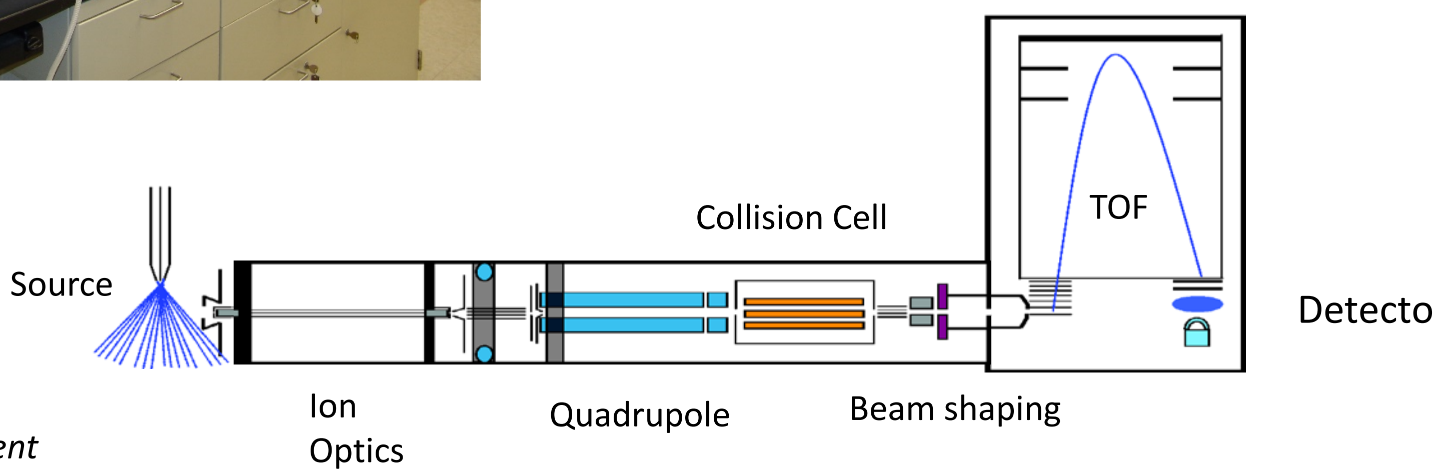
- HPLC-QTOF-MS



- The Quadrupole is used to scan across a preset *m/z* or *m/z* range and select an ion of interest.

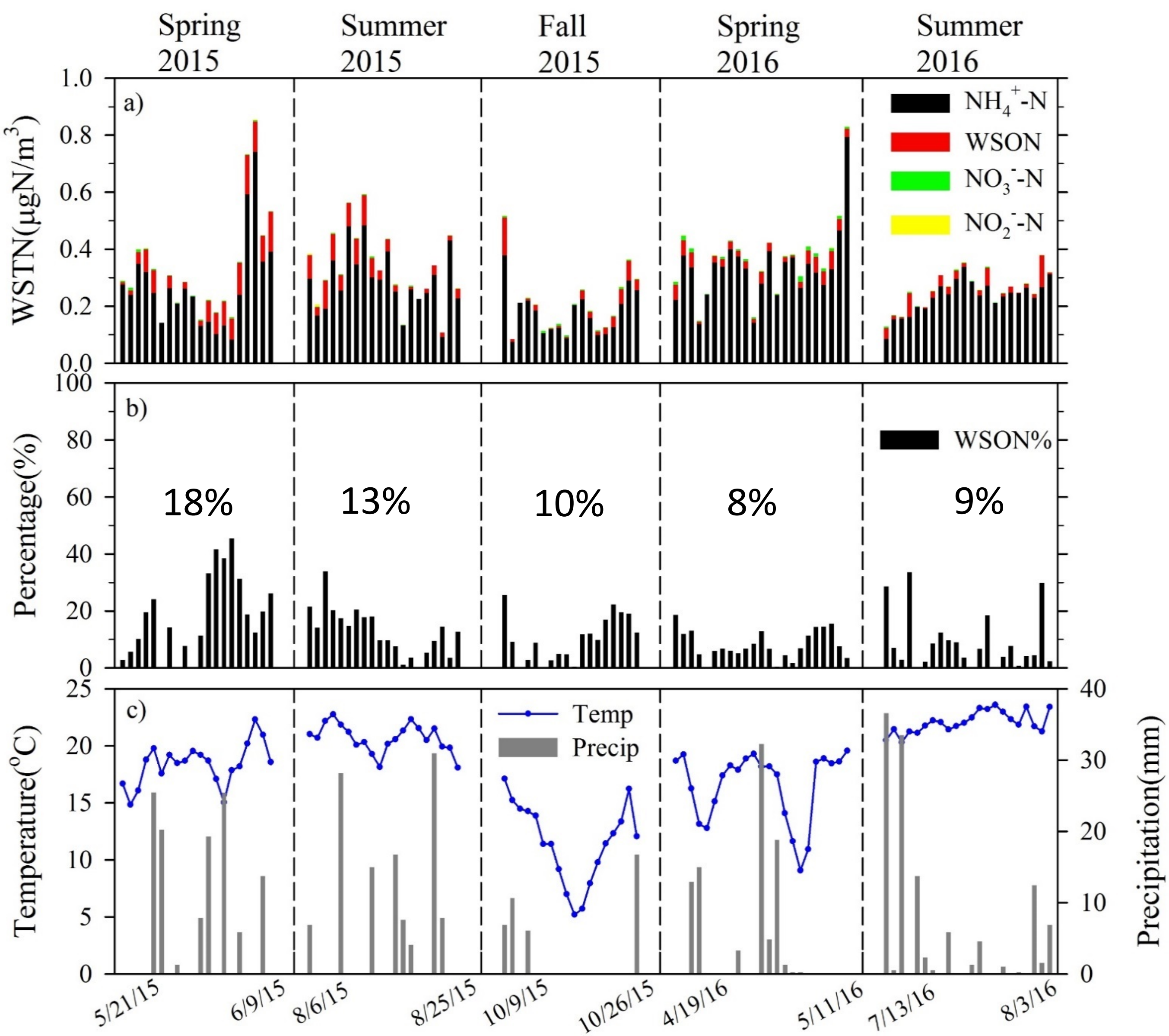
- The Collision Cell focuses and transmits the ions while introducing a collision gas into the flight path of the selected ion.

- The Time-of-Flight (TOF) serves to analyze the fragment ions generated in the Collision Cell.



Schematic courtesy of Agilent

Results – Bulk WSON



- WSON is 12% of WSTN on average.
- Values > 40% observed in spring 2015
  - Associated with low PM concentrations
  - TOC > 90% WSOC during this period
- Average aerosol ON contribution to WSTN similar to precipitation (11% WSON)
- Weak but significant correlations between WSON and NH_4^+ and WSOC

Bulk WSON

- Comparison to other work

			Average WSON (ng N/m^3)	% WSTN
Forest	Coweeta, NC	This work	40	12
Forest	RMNP (2009)	Benedict, 2012	80	21
Forest	RMNP (2010)	Benedict, 2012	30	14
Forest	GTNP	Benedict, 2012	70	29
Forest	Duke Forest, NC	Lin et al., 2010	160	33
Urban	Davis, CA	Zang et al., 2002	260	20
Coastal	Lewes, DE	Russell et al., 2003	60	3
Coastal	Miami, FL	Zamora et al., 2011	30	5
Coastal	Tampa, FL	Calderon et al., 2007	90	10

Organosulfates and nitro-aromatics

Organosulfates	Chemical Formula	MW
Isoprene SOA	$C_2H_4O_5S$	140.1
	$C_3H_6O_5S$	154.1
	$C_2H_4O_6S$	156.1
	$C_5H_{10}O_6S$	198.2
	$C_3H_6O_6S$	170.1
	$C_4H_8O_7S$	200.2
	$C_5H_{12}O_7S$	216.2
	$C_5H_8O_7S$	212.2
	$C_5H_{10}O_7S$	214.2
	$C_5H_{11}NO_9S$	261

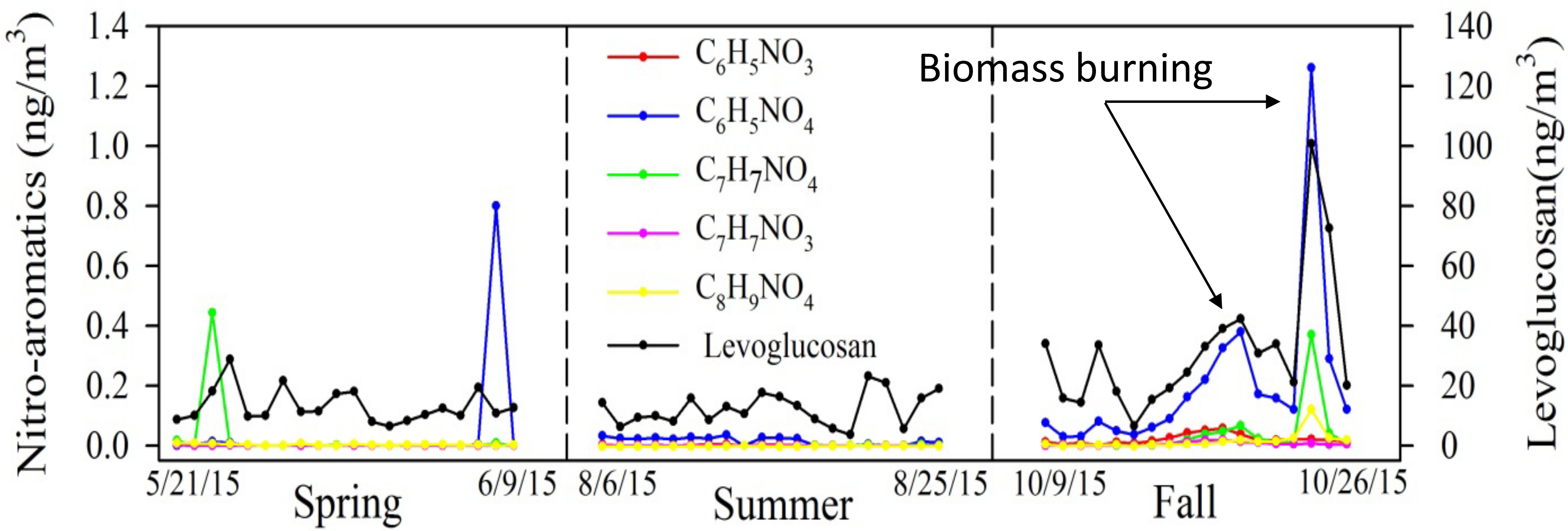
Organosulfates	Chemical Formula	MW
Monoterpene SOA	$C_{10}H_{18}O_5S$	250.3
	$C_{10}H_{16}O_7S$	280.3
	$C_7H_{12}O_7S$	240
	$C_{10}H_{18}O_7S$	282.1
	$C_{10}H_{17}NO_7S$	295.3
	$C_{10}H_{17}NO_8S$	311.1
	$C_{10}H_{17}NO_9S$	327.1
	$C_{10}H_{15}NO_9S$	325
	$C_{10}H_{17}NO_{10}S$	343.1
Other SOA	$C_5H_{10}O_8S$	230.2

Nitrooxy-organosulfates indicated in red.

Nitro-aromatics	Chemical Formula	MW
Nitrophenol	$C_6H_5NO_3$	139.1
Nitrocatechol	$C_6H_5NO_4$	155.1
Methyl nitro catechol	$C_7H_7NO_4$	169.1
Methyl nitro phenol	$C_7H_7NO_3$	153.1
Dimethyl nitro catechol	$C_8H_9NO_4$	183.2

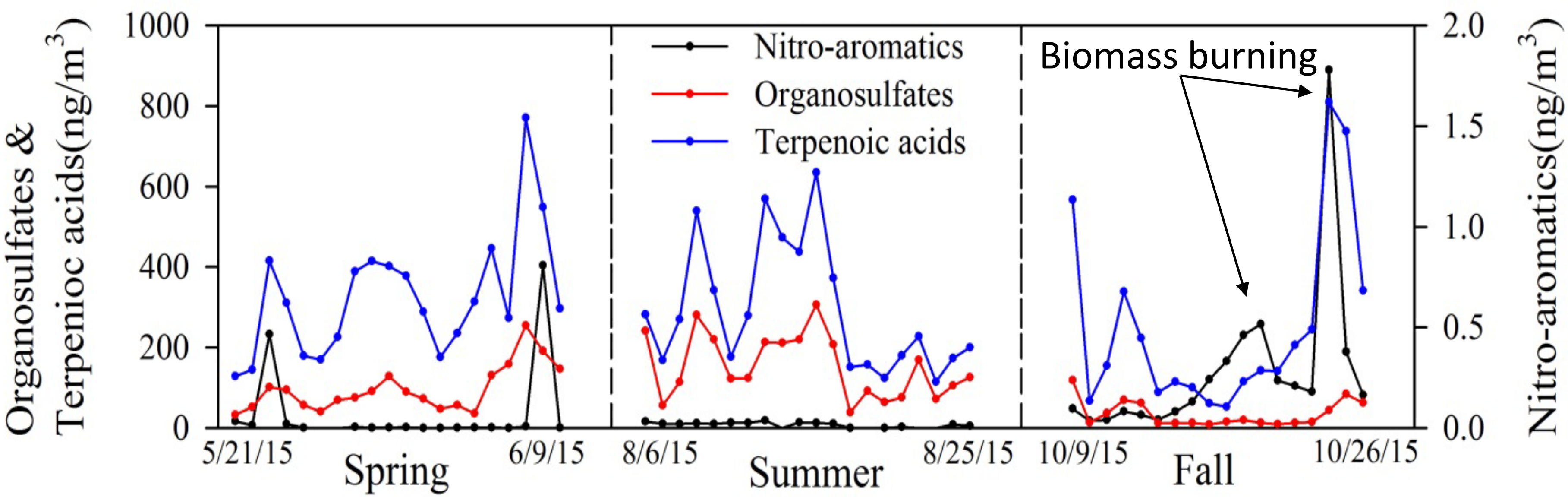
Negative mode electrospray ionization

Nitro-aromatics



- Strong correlation with levoglucosan and terpenoic acids in fall
- During biomass burning events on 10/20 and 10/24, nitro-aromatics contributed 2.7 and 0.3% of WSON, respectively.
- These events did not correspond to elevated concentrations of bulk WSON
    - Correlation with specific terpenoic acids suggest aged plumes

Organosulfates



- Organosulfates account for 3.9 and 1.0 % w/w of OM mass (OC*2), respectively, during summer and fall

- m/z 215, 2-methyltetrol derived, is most abundant compound
  - isoprene derived epoxydiols (IEPOX) under low NOx conditions

- Nitrooxy-organosulfate concentrations (summed) range from 0.05 to 1.8 ng N/m^3
  - Account for 2.5% of WSON, on average, and up to 7% during summer.
  - Night-time formation

Conclusions

- Concentrations of bulk WSON similar to other non-urban sites
- Highest contributions (> 40%) of WSON to WSTN were associated with relatively clean conditions and high (>80%) soluble fraction of organic carbon
- Identified nitro-aromatic and nitrooxy-organosulfate compounds accounted for a small fraction of WSON in $PM_{2.5}$, on average, ranging from ~ 1% in spring to ~ 4% in fall
    - as much as 28% of WSON in individual samples
- Similar to other studies, the majority of ON was unspeciated.
    - Amino acids, urea, alkyl amines
- Observed biomass burning events reflected aged plumes containing relatively low concentrations of levoglucosan. These air masses did not contain elevated concentrations of WSON.
    - Proximity to fire important

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