Advances in the quantitation of atmospheric organosulfates

Elizabeth A. Stone
University of Iowa
betsy-stone@uiowa.edu

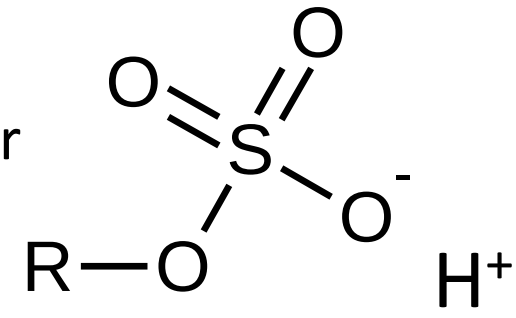
Advances in the quantitation of atmospheric organosulfates

- Authentic standard development
- Optimization of detection by mass spectrometry
- Improvements in liquid chromatographic resolution
- Results from complementary measurements of organic species

Organosulfates (a.k.a. sulfate esters)

Goals: Characterize the molecular composition and abundance of organosulfates in the atmosphere, to better understand their sources and role in climate forcing.

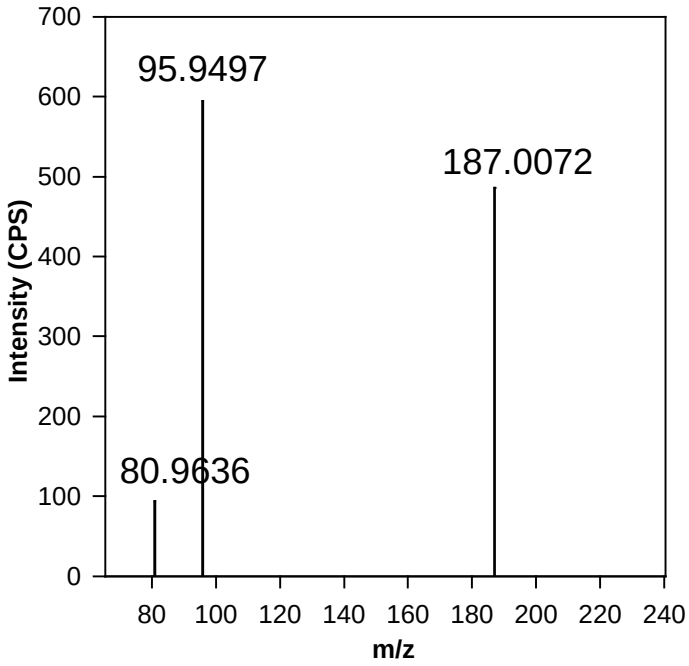
- Organic molecules with a sulfate moiety
- Small molecules to high-MW organic matter
- Strong acids ($pK_a < -2$), ∴ anionic
  - Non-volatile
  - Readily detected by ESI mass spectrometry



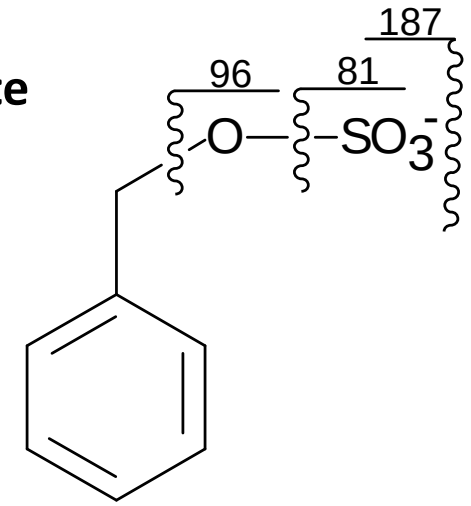
The Southern Oxidant and Aerosol Study

- Centreville, AL (CTR) Ground Site
- June 1 – July 15, 2013
- Day (08:00-19:00) and night (20:00-07:00)
- Chemical measurements *(completed or planned)*
  - Elemental and organic carbon
  - Inorganic ions
  - Organic species by GCMS
  - Organosulfates by LCMS

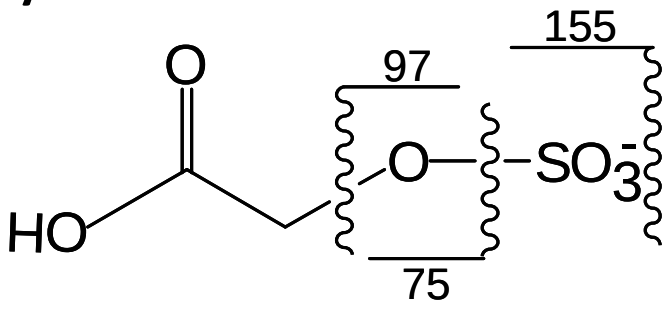
Tandem mass spectrometry

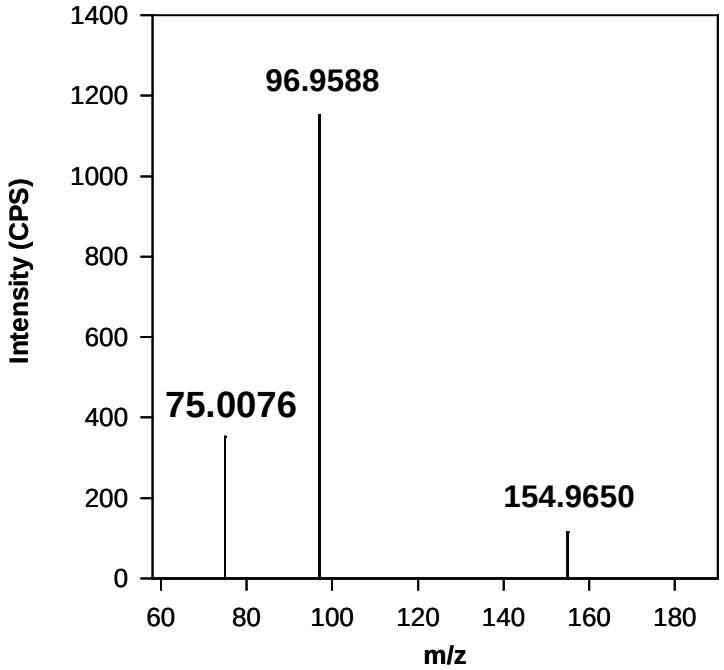


Benzyl sulfate



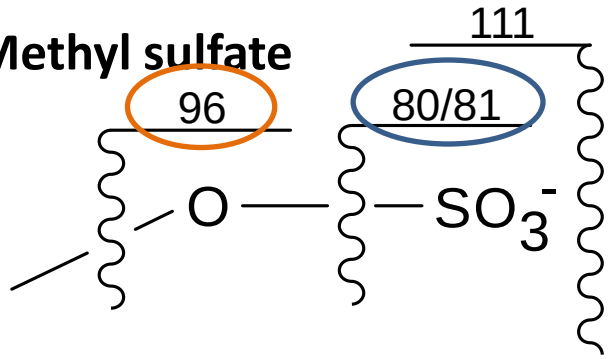
Hydroxyacetone sulfate



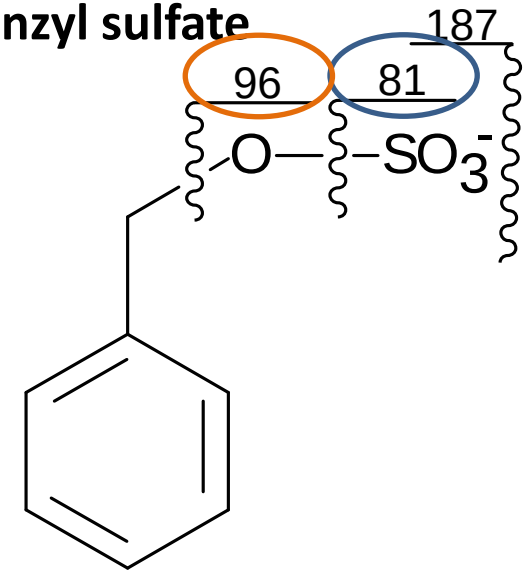


ESI Fragmentation of organosulfates

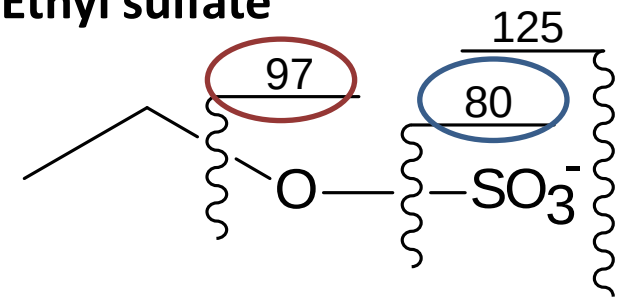
Methyl sulfate



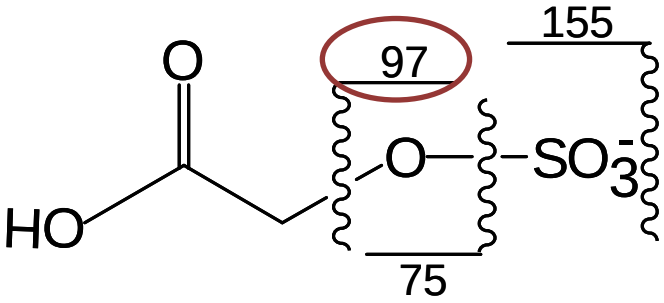
Benzyl sulfate



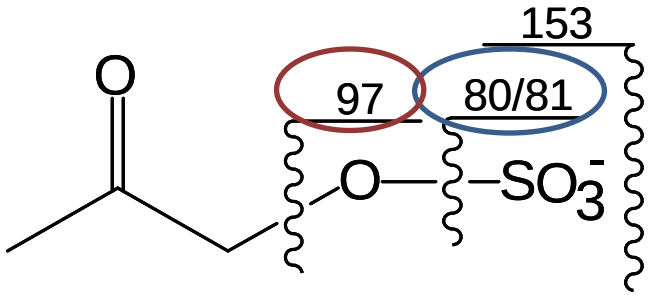
Ethyl sulfate



Glycolic acid sulfate



Hydroxyacetone sulfate

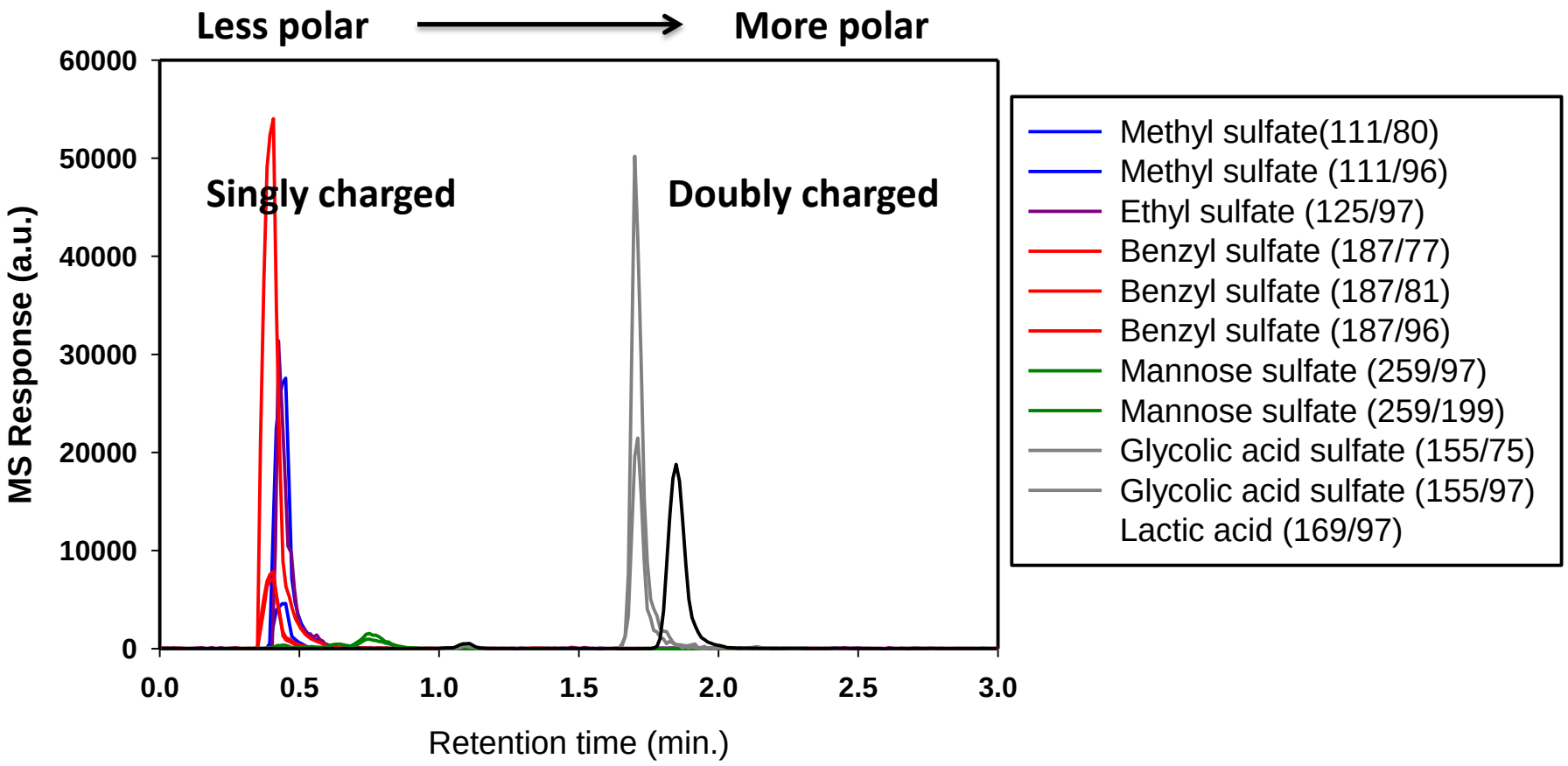


ESI Fragmentation of organosulfates

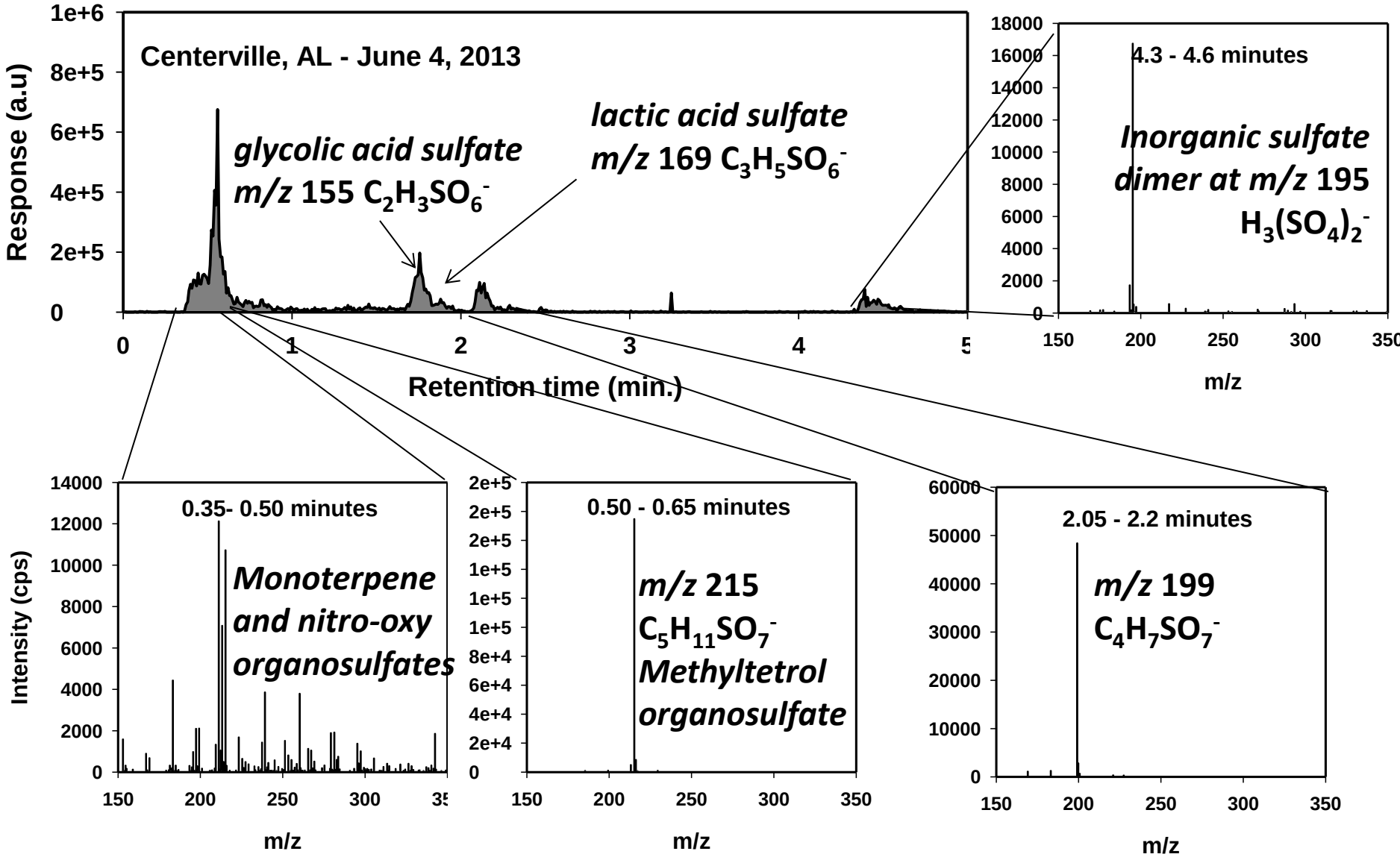
Organo-sulfate	Collision Energy (V)	Molecular ion (m/z)		Error (mDa)	Fragment ions (m/z)		Error (mDa)
Methyl sulfate	20	$CH_3SO_4^-$	110.9753	0.1	79.9571	$SO_3^{-\cdot}$	0.3
					80.9649	HSO_3^-	0.3
					95.9499	$SO_4^{-\cdot}$	-1.8
Ethyl sulfate	10	$C_2H_5SO_4^-$	124.9912	0.3	79.9558	$SO_3^{-\cdot}$	-1.0
					96.9598	HSO_4^-	0.2
Benzyl sulfate	15	$C_7H_7SO_4^-$	187.0072	0.7	80.9636	HSO_3	-1.0
					95.9497	$SO_4^{-\cdot}$	-2.0
Hydroxy-acetone sulfate	15	$C_3H_5SO_5^-$	152.9836	-2.2	79.9533	$SO_3^{-\cdot}$	-3.5
					80.9609	HSO_3^-	-3.7
					96.9564	HSO_4^-	-3.2
Glycolic acid sulfate	10	$C_2H_3SO_6^-$	154.9650	0.0	75.0076	$C_2H_3O_3^-$	-0.6
					96.9588	HSO_4^-	-0.8

Separation Development

A variation of normal phase chromatography
- Ionic, polar, and van der Waals interactions



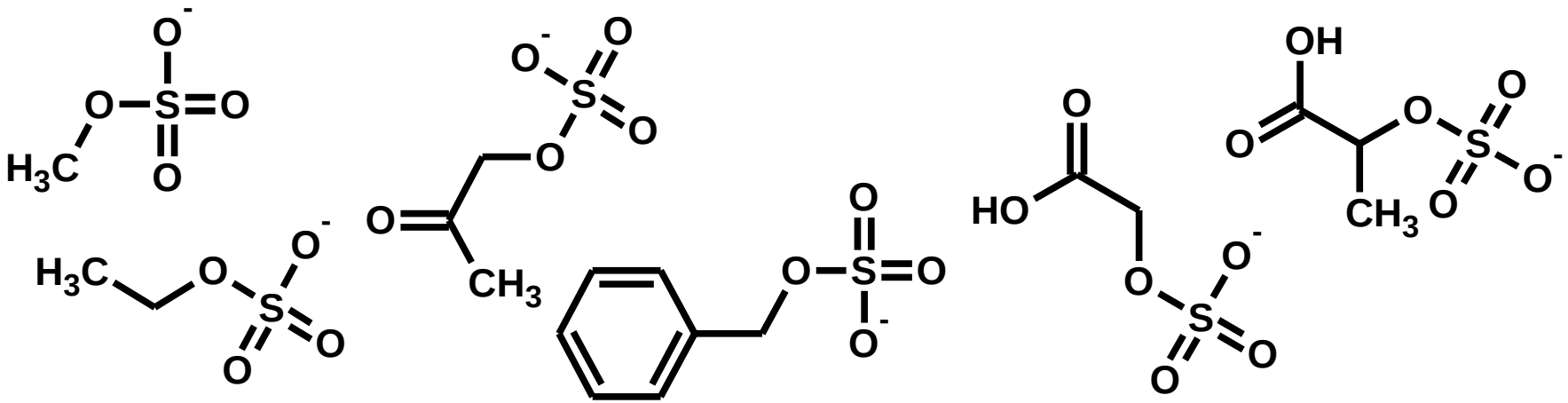
Qualitative analysis – precursor to m/z 97



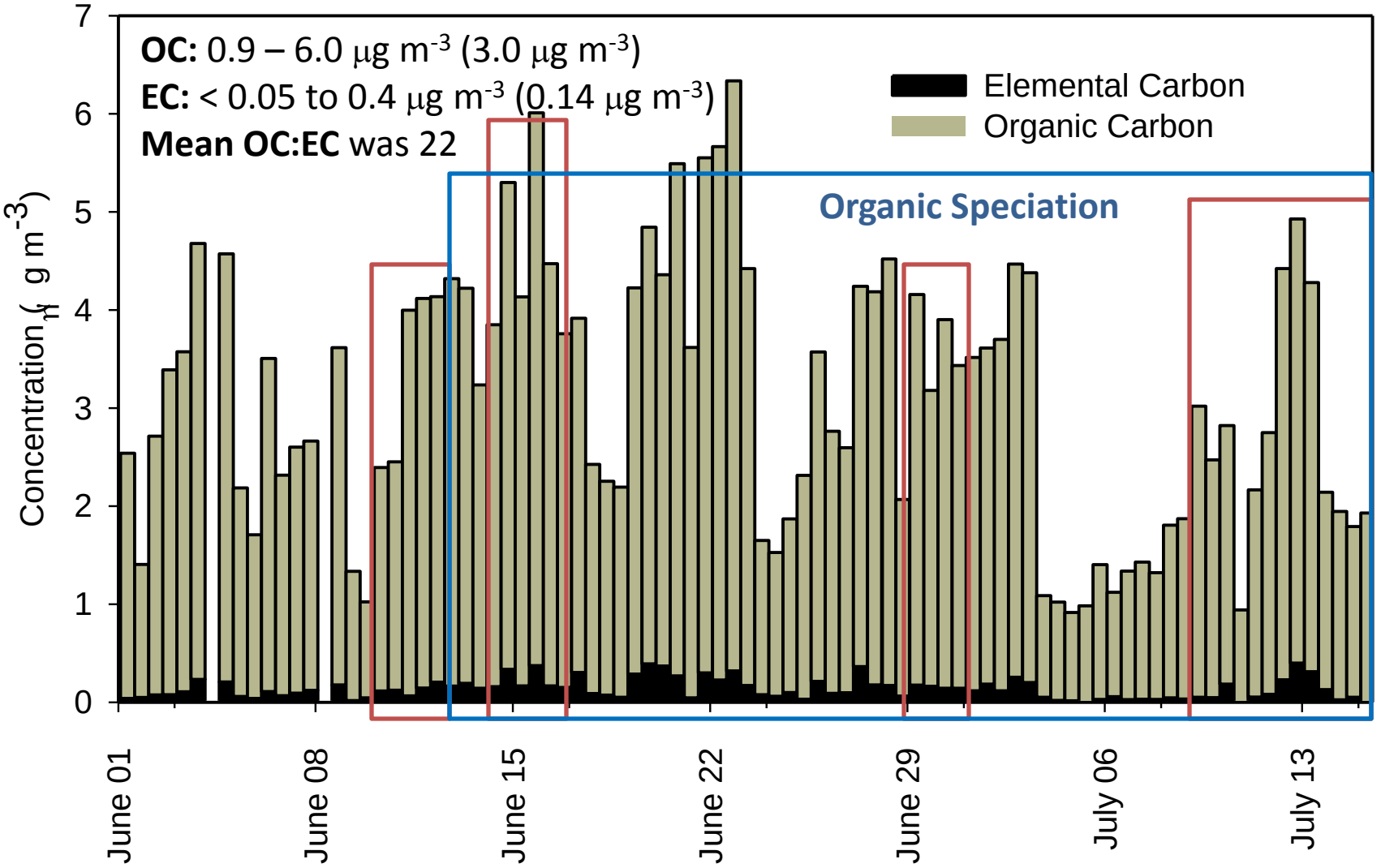
Quantitation of Organosulfates

UPLC-MS/MS Method - Figures of Merit (in ppb)

Organosulfate	Linear Range	R^2	Detection Limit	Limit of Quantification
Methyl sulfate	0.5 - 500	0.996	0.04	0.12
Ethyl sulfate	0.5 - 200	0.996	0.03	0.11
Hydroxy acetone sulfate	0.5 - 400	0.995	0.05	0.16
Benzyl sulfate	0.5 - 300	0.997	0.03	0.09
Glycolic acid sulfate	0.5 - 300	0.997	0.33	1.1
Lactic acid sulfate	0.5 - 50	0.999	0.09	0.3



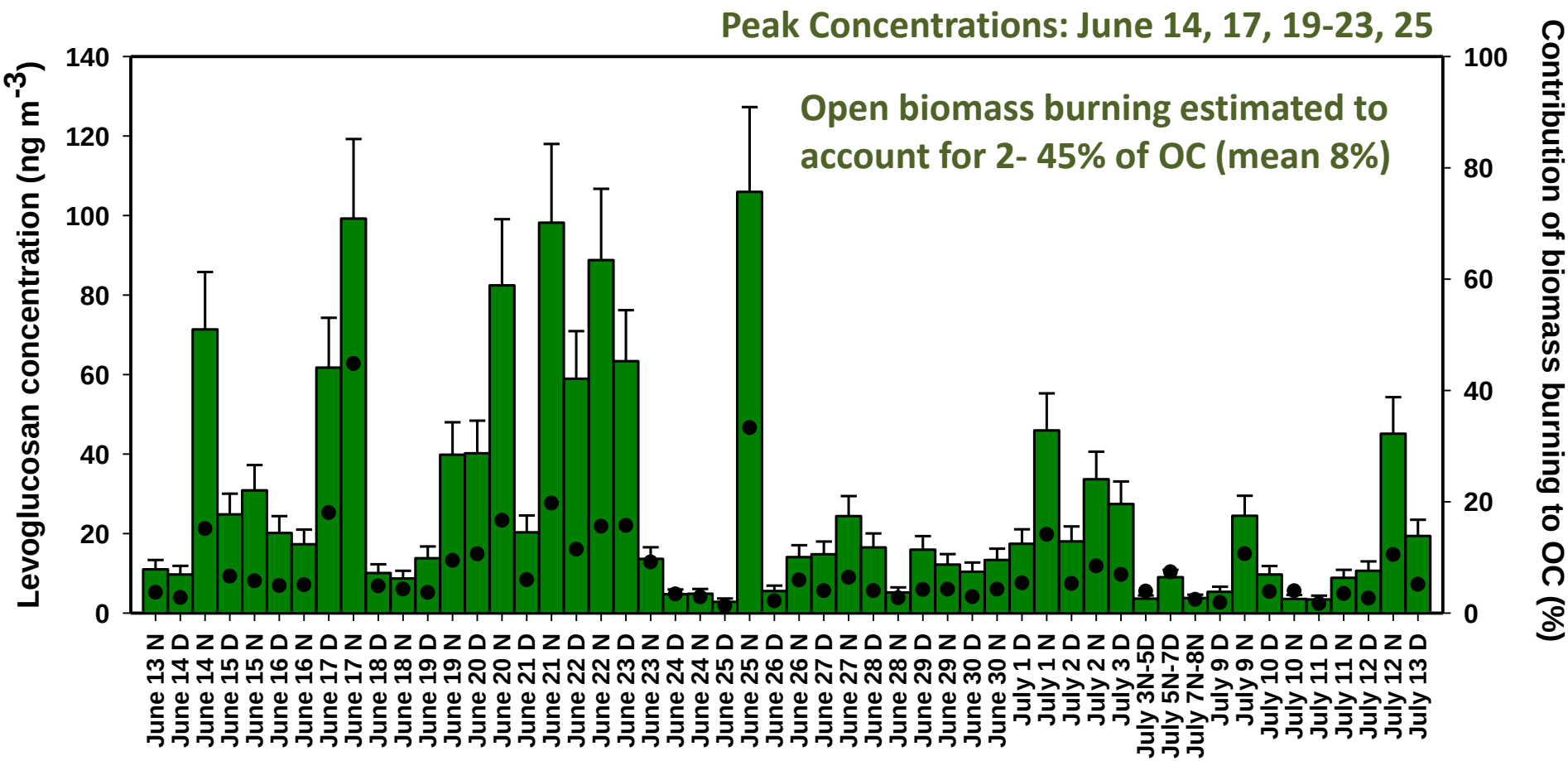
Organic and Elemental Carbon



Biomass Burning in during SAS

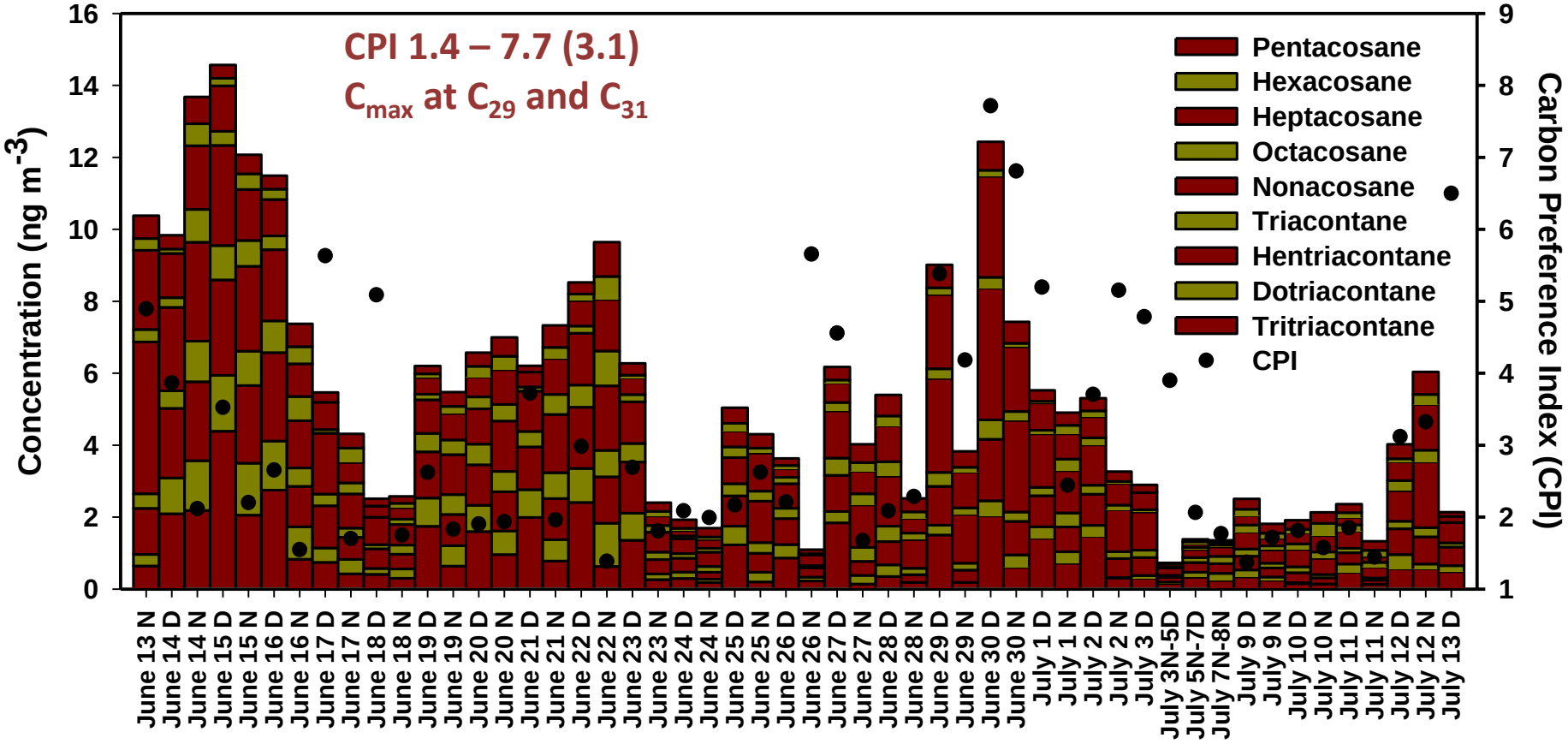
Agricultural fires in the Mississippi delta region on July 9, 2013 ***(photo by Joost de Gouw)***

Biomass Burning at Centreville

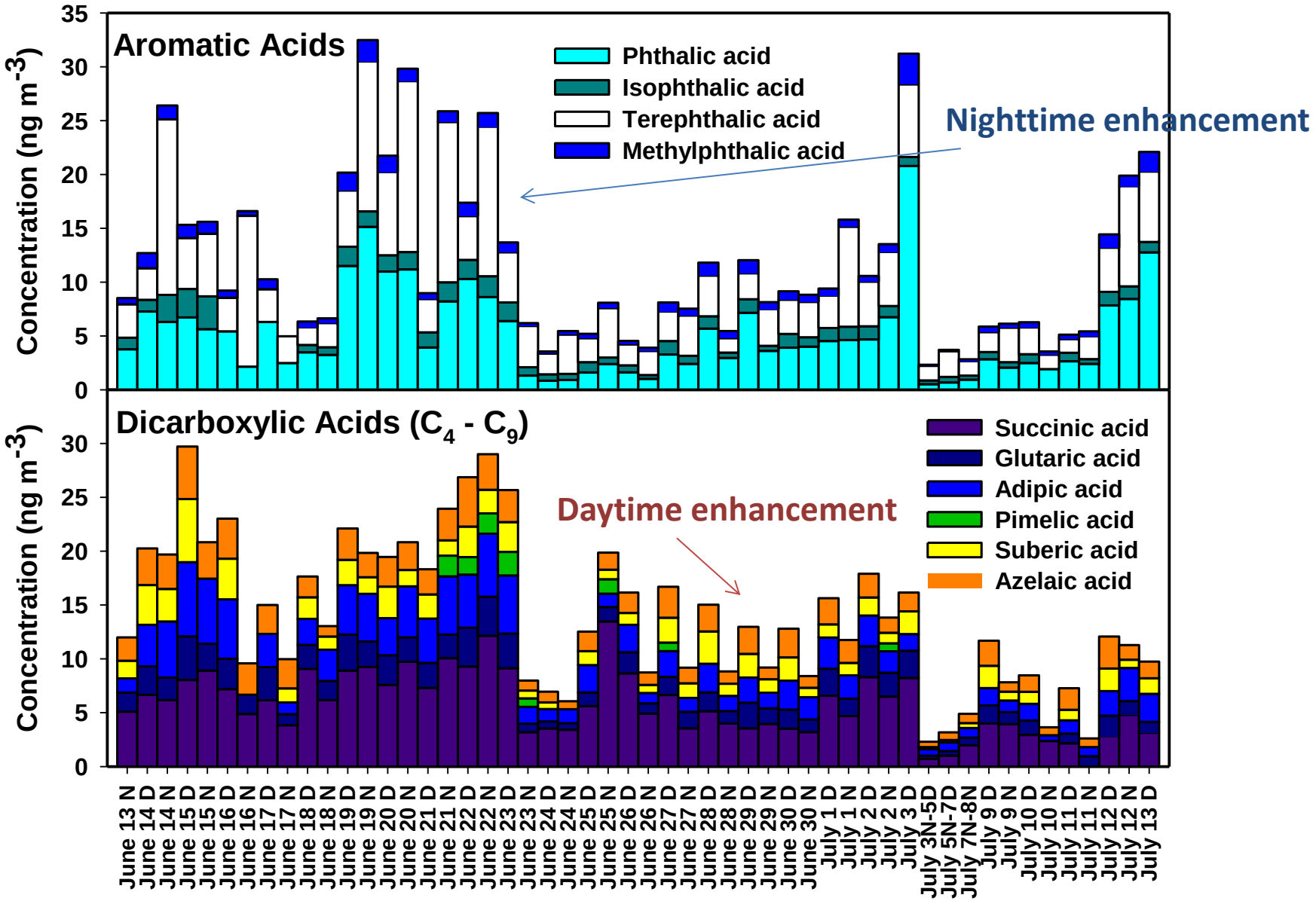


Primary biogenic organic aerosol

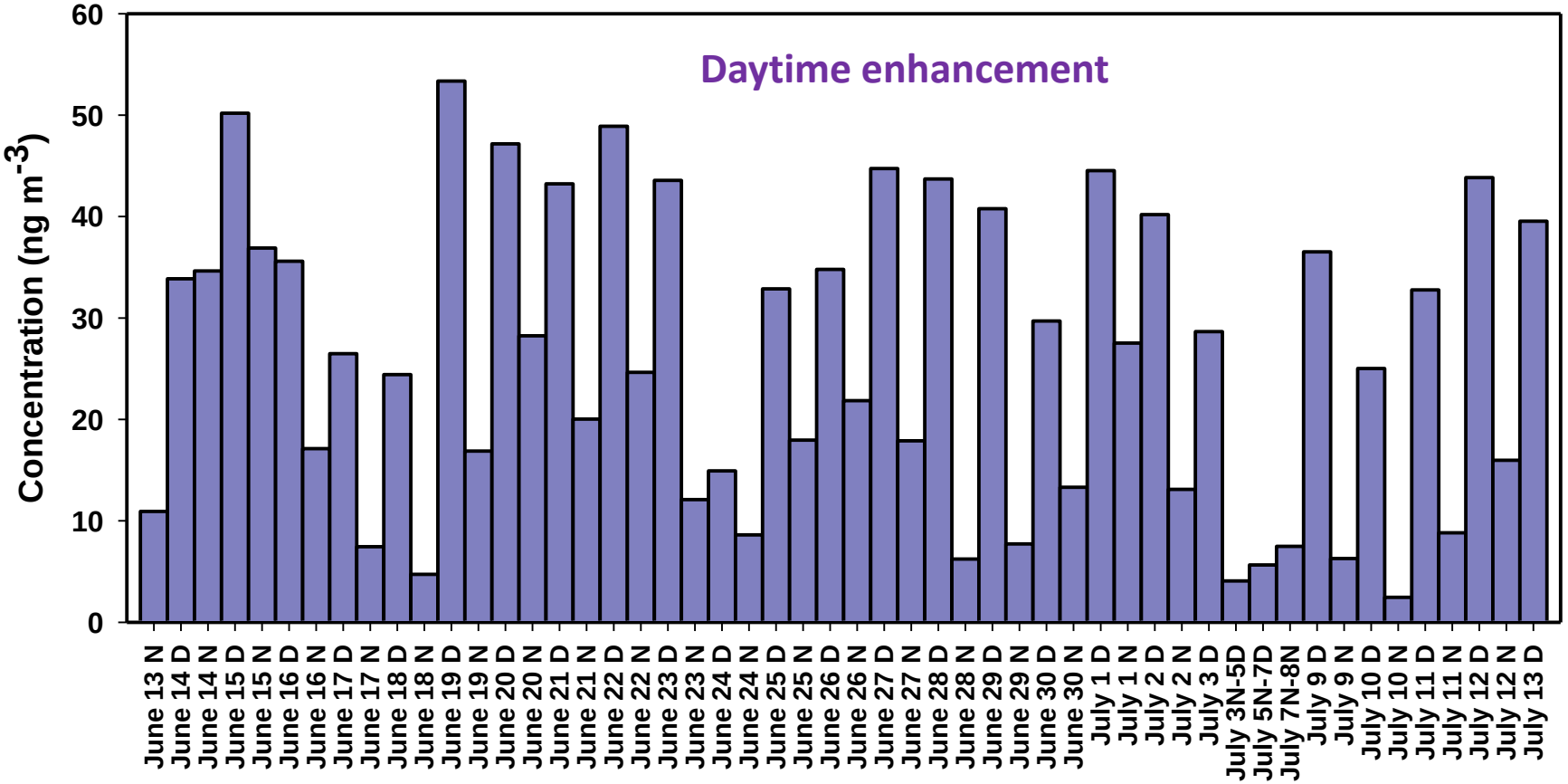
$$CPI = \frac{\sum C_{27,29,31,33}}{\sum C_{26,28,30,32}}$$



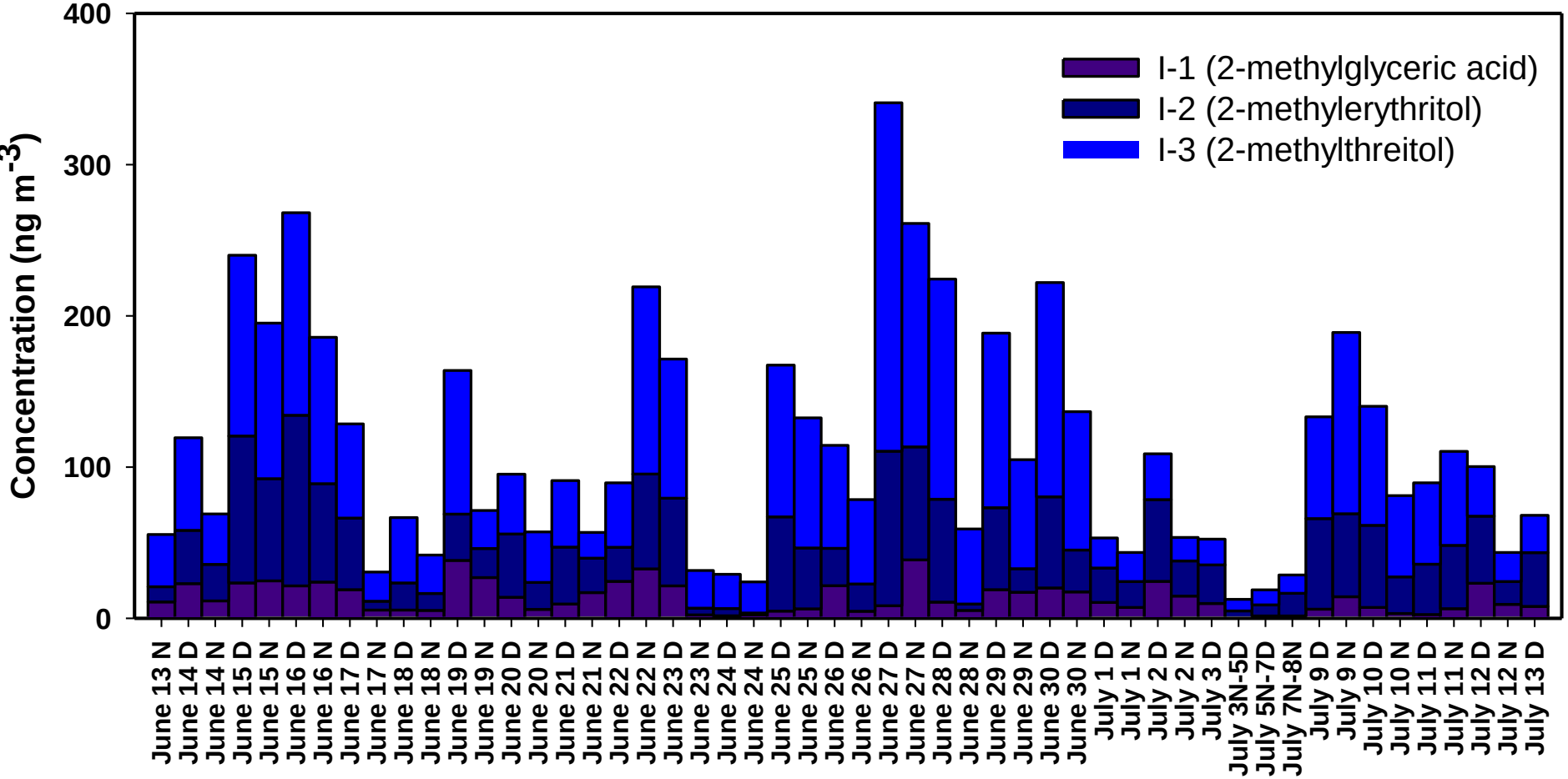
Diurnal trends in carboxylic acids



Pinonic acid – a tracer for monoterpene SOA



Isoprene SOA tracers



Work in progress…

- Additional organosulfate standard development
  - Based on qualitative results from SOAS
  - Analytical method development and physical characterization
- Complete complementary measurements - diurnal variation
- Measurement inter-comparison
- Source apportionment modeling of $PM_{2.5}$ and OC
  - Primary v. secondary, natural v. anthropogenic

Acknowledgements

Stone Research Group

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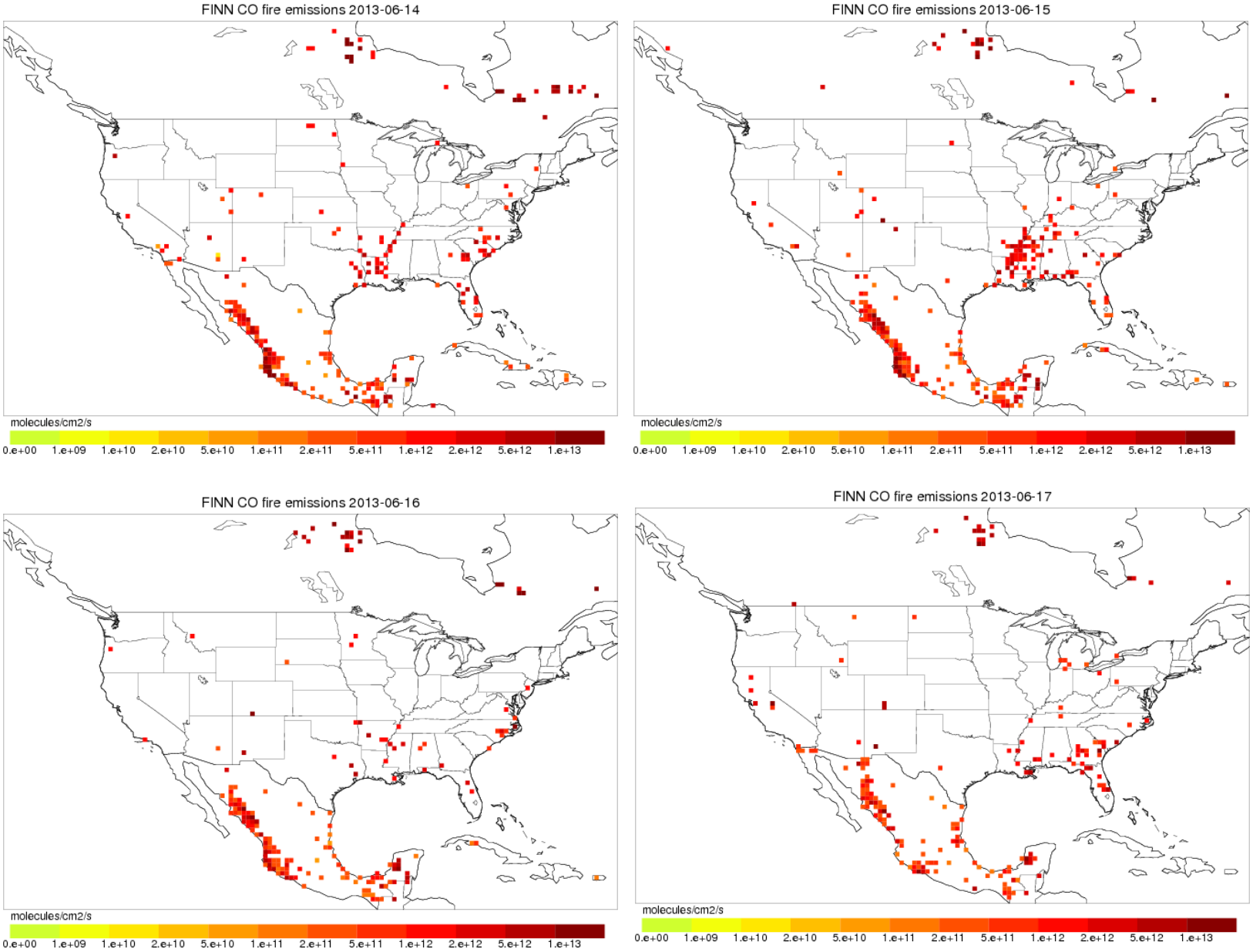
Near-real-time fire emissions from the Fire Inventory of NCAR (FINN), based on MODIS Rapid Response fire counts (FIRMS).



http://www.acd.ucar.edu/acresp/forecast/fire-emissions.shtml