Sources and Radiative Properties of Organosulfates in the Atmosphere

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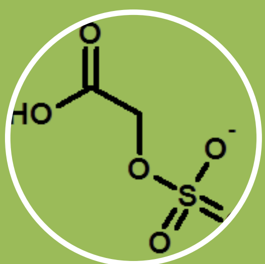
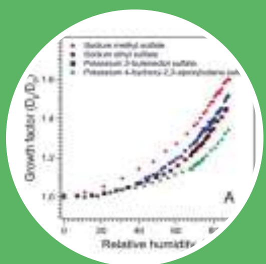
Sources and Radiative Properties of Organosulfates in the Atmosphere

Central research hypotheses:

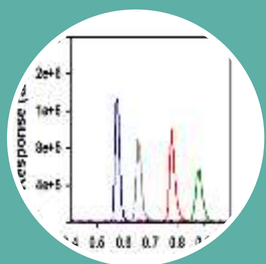
- Anthropogenic emissions impact biogenic SOA formation
- Organosulfates are climate forcing agents



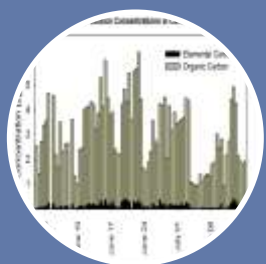
Synthesis



Hygro-scopic growth



Method develop-ment



Chemical analysis of $PM_{2.5}$

Source apportion-ment

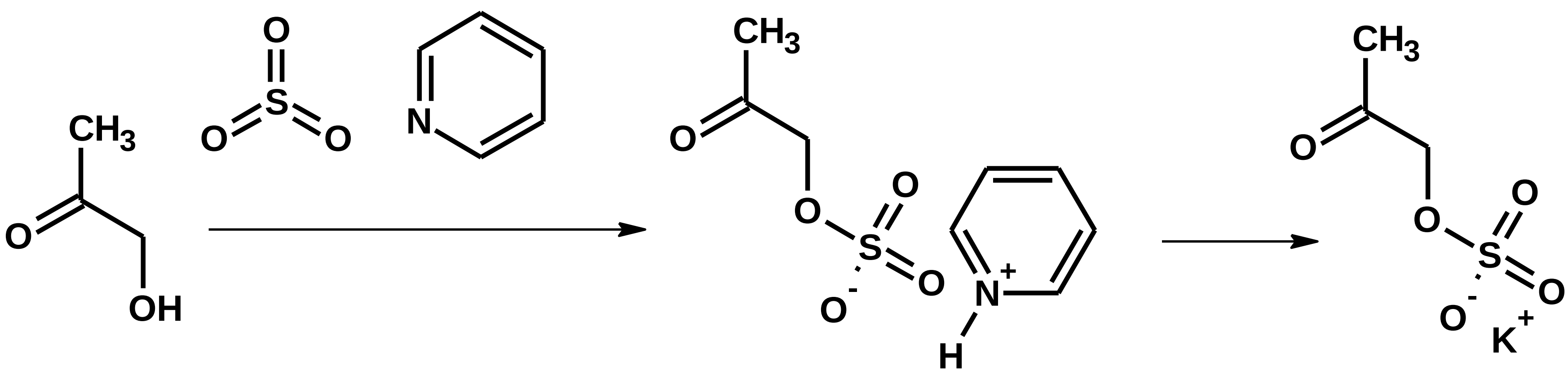
Approach

Synthesis of Organosulfate Standards

1) Reaction of alcohol with pyridine sulfur trioxide complex

(Hoff, et al., *JACS*, 2001)

2) Cation exchange

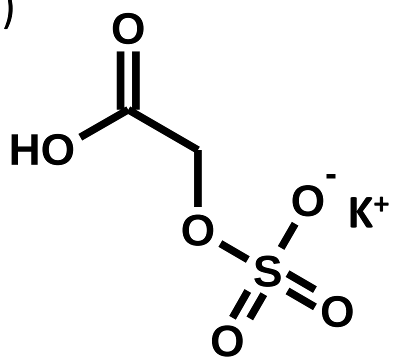


- Potassium salts formed white needles upon recrystallization
- Structure and purity confirmed by ^{13}C NMR, ^{1}H NMR, high-resolution MS, elemental analysis

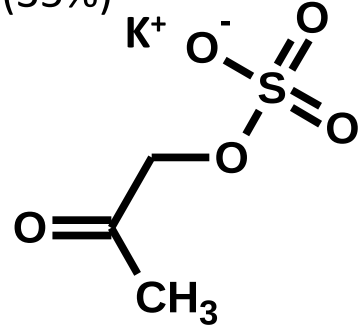
(Hettiyadura, et al., *AMT*, 2015; Estillore et al. *ES&T, in press*)

Organosulfate Standards

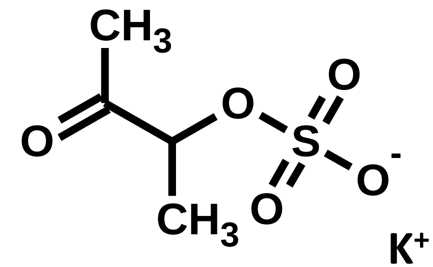
Glycolic acid sulfate
(45%)



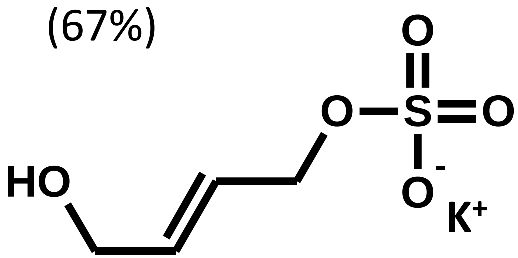
Hydroxyacetone sulfate
(35%)



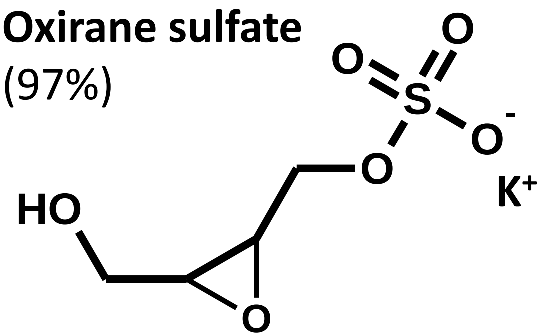
Acetoin sulfate
(65%)



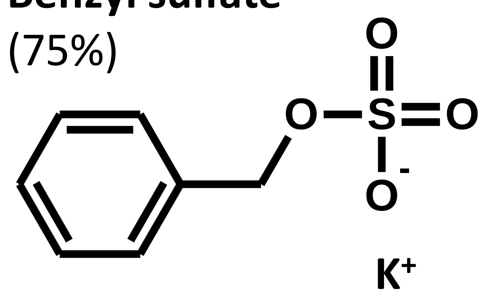
Butenediol sulfate
(67%)



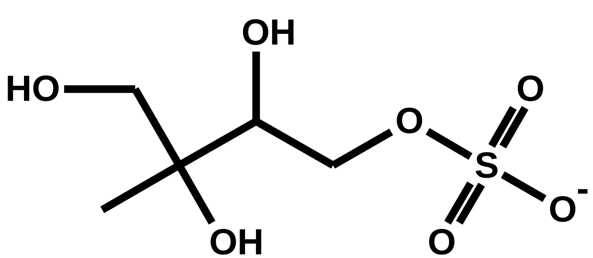
Oxirane sulfate
(97%)



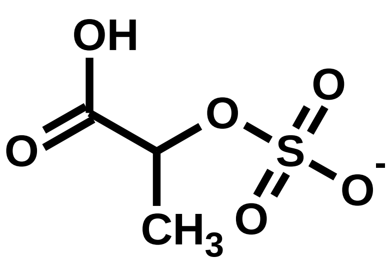
Benzyl sulfate
(75%)



2-Methyltetrol sulfate



Lactic acid sulfate



Commercially available as sodium salts:

- **Methyl sulfate**
- **Ethyl sulfate**
- **Propyl sulfate**

Characterization of climate-relevant properties

“Water uptake and hygroscopic growth of organosulfate aerosol”

Armando Estillore, Anusha Hettiyadura, Zhen Qin, Erin Leckrone, Becky Wombacher, Tim Humphry, Elizabeth Stone, Vicki Grassian

Available online as a just accepted article in Environmental Science & Technology (10.1021/acs.est.5b05014)

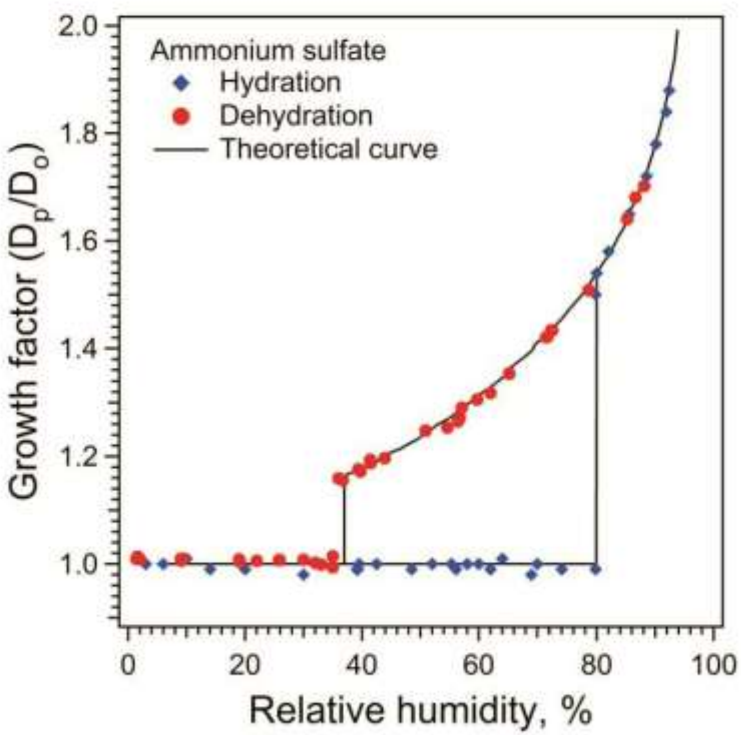
Characterization of climate-relevant properties

Property	Measurement technique	Summary of results
Light absorption	UV-vis spectrophotometry	No absorption
Hygroscopicity	Hygroscopicity-tandem differential mobility analyzer	Continuous water uptake

Model Compounds	Formula
Sodium methyl sulfate	CH_3SO_4Na
Sodium ethyl sulfate	$C_2H_5SO_4Na$
Sodium propyl sulfate	$C_3H_7SO_4Na$
Potassium 2-butenediol sulfate	$C_4H_7SO_5K$
Potassium 4-hydroxy-2,3-epoxybutane sulfate	$C_4H_7SO_6K$
Potassium glycolic acid sulfate	$C_2H_3SO_6K$
Potassium hydroxyacetone sulfate	$C_3H_5SO_5K$
Sodium benzyl sulfate	$C_7H_7SO_4Na$

Ammonium sulfate has distinct phase transitions

Hydration curve for ammonium sulfate

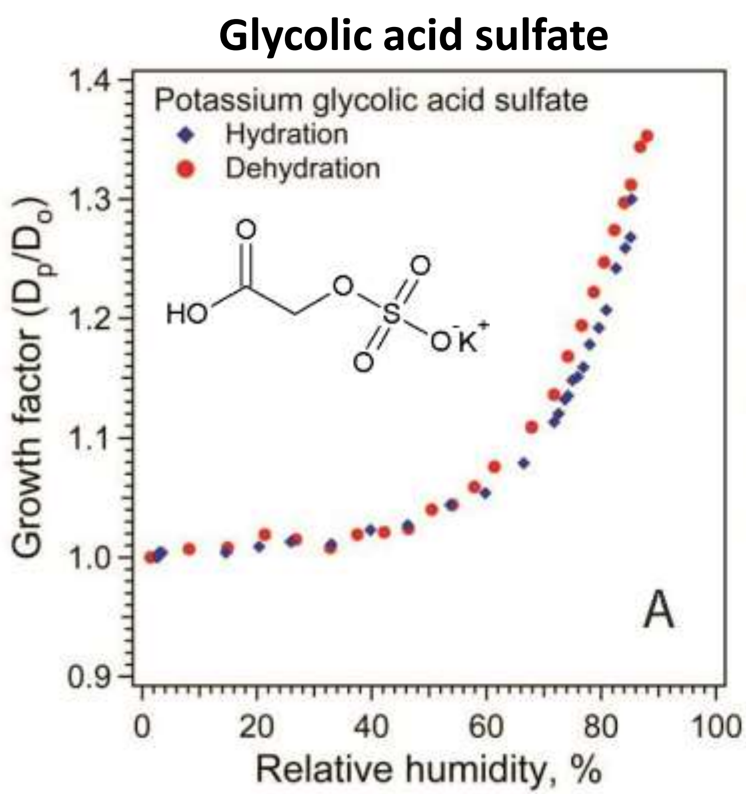


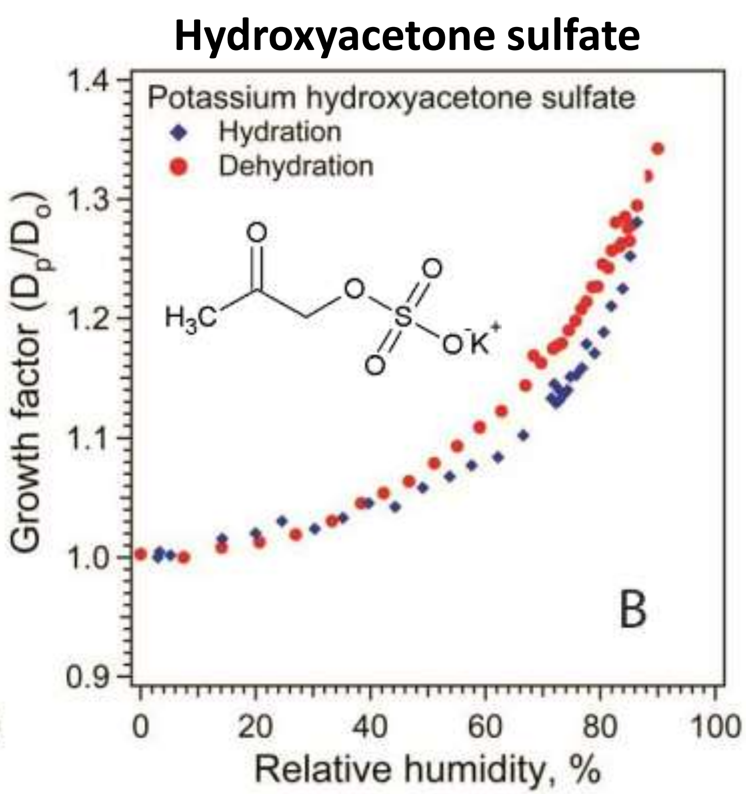
Deliquescence RH 79.9 ± 0.10 %
Efflorescence RH 36.7 ± 1.8%

(Estillore, et al. *ES&T, in press*)

Organosulfates show continuous and reversible uptake of water

Hydration curve for organosulfates





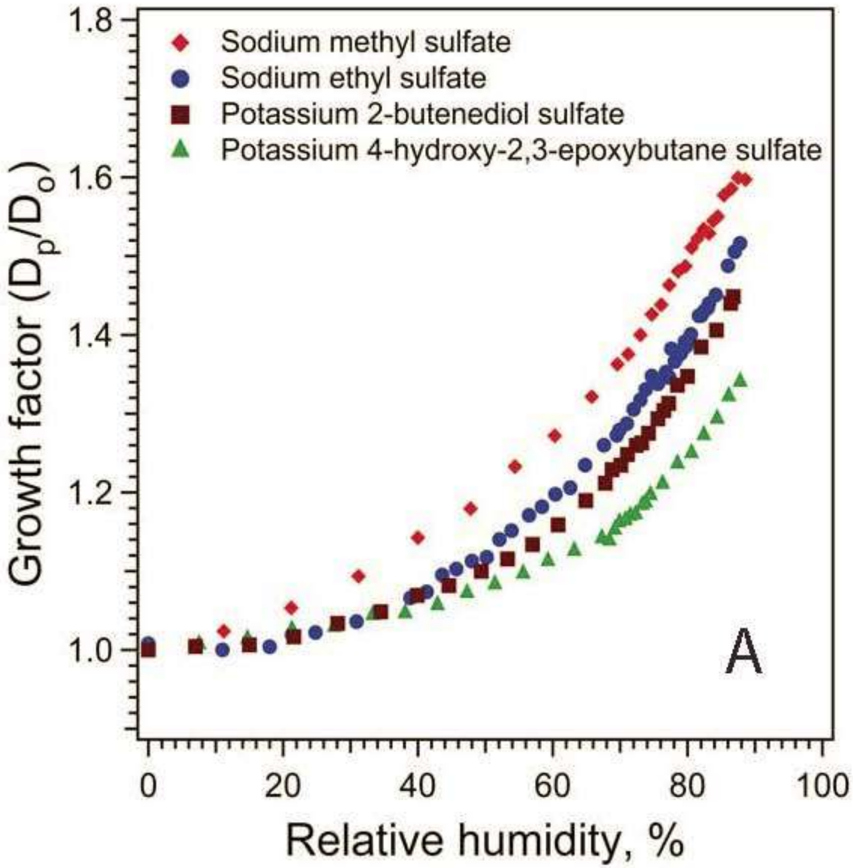
No distinct transitions; continuous growth upon hydration

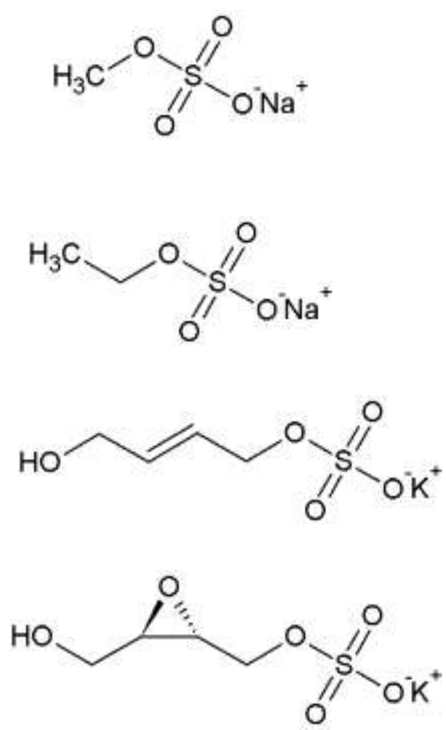
Absorption of water at low RH

(Estillore, et al. *ES&T, in press*)

Organosulfates show continuous and reversible uptake of water

Hydration curve for additional organosulfates





(Estillore, et al. *ES&T, in press*)

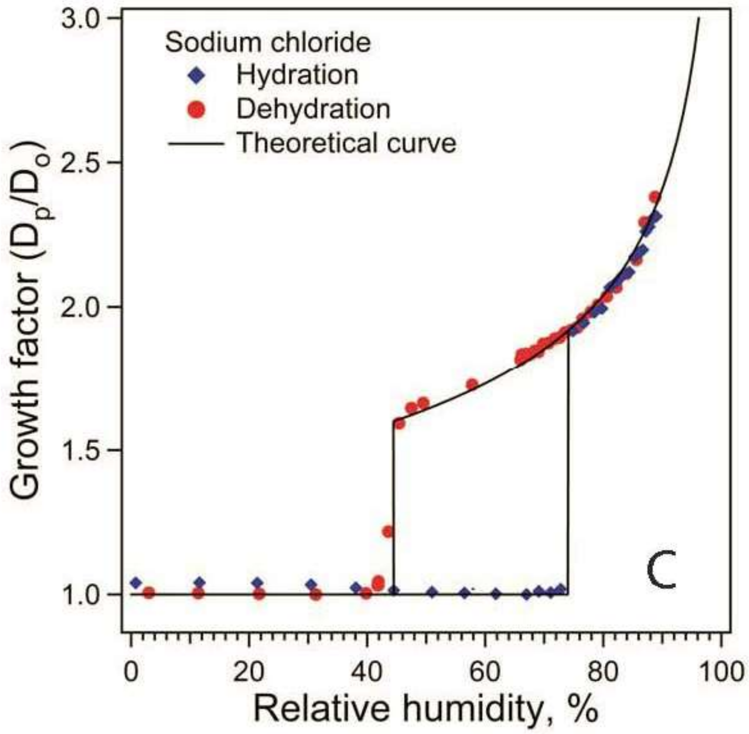
Growth factors of 100 nm particles at 85% RH

Organosulfate	Molecular weight	Growth factor	Reference
Sodium methyl sulfate	111	1.50	Estillore, et al. *in press*
Sodium ethyl sulfate	125	1.45	
Potassium 2-butenediol sulfate	167	1.40	
Potassium 4-hydroxy-2,3-epoxybutane sulfate	183	1.30	
Potassium glycolic acid sulfate	155	1.29	
Potassium hydroxyacetone sulfate	153	1.30	
Limonene-derived organosulfates (OS)	250	1.03	*Hansen et al. ACPD, 2015*
Limonene OS 10% w/w ammonium sulfate	250	1.20	
Limonene OS > 20% w/w ammonium sulfate	250	~ 1.5	

Low molecular weight, alkyl organosulfates have the greatest growth factors

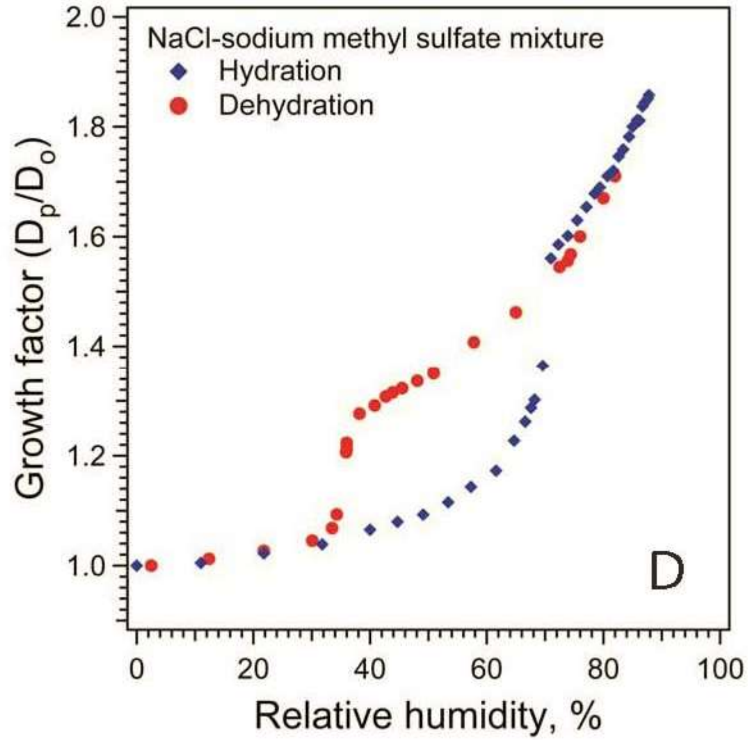
Hygroscopic growth of methyl sulfate and NaCl

Hydration curve for sodium chloride



Deliquescence RH 75.0 ± 0.50 %
Efflorescence RH 44.0 ± 1.0%

Hydration curve for methyl sulfate/NaCl (1:1 wt%)



Deliquescence RH 69.6 ± 1.0 %
Efflorescence RH 36.0 ± 0.5%

(Estillore, et al. *ES&T, in press*)

Conclusions from Hygroscopic Growth Studies

- While ammonium sulfate shows distinct deliquescence and efflorescence points upon hydration and dehydration, organosulfates show continuous water uptake.
  →Organosulfates are hygroscopic even at low relative humidity
  →Thus, they are expected to extend the range of environmental conditions that water is taken up onto aerosol particles

- When mixed with organosulfates, the deliquescence and efflorescence RH of sodium chloride were shifted to lower values
  → Organosulfates modify the hygroscopic properties of inorganic salts

(Estillore, et al. *ES&T, in press*)

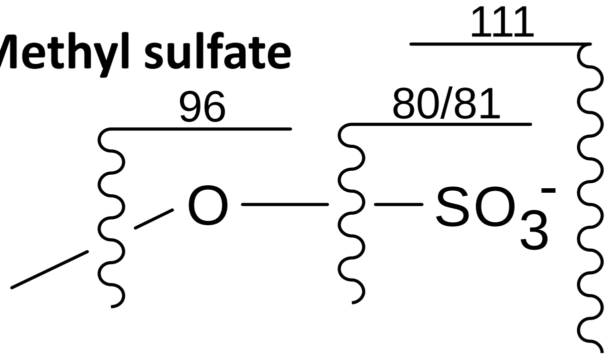
Quantification of Organosulfates in Ambient Aerosol

Develop and validate a method for organosulfate speciation:

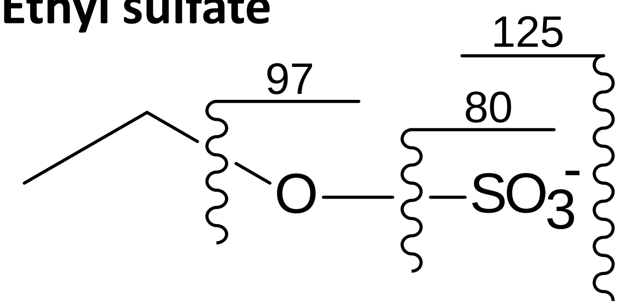
1) ESI-MS/MS optimization
2) LC separation development using HILIC
3) Assess sample preparation protocols
4) Apply to ambient aerosol

ESI Fragmentation of Organosulfates

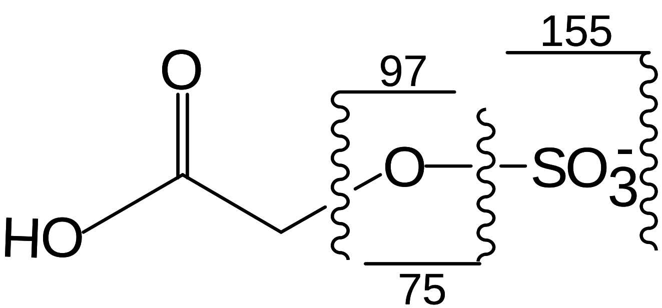
Methyl sulfate



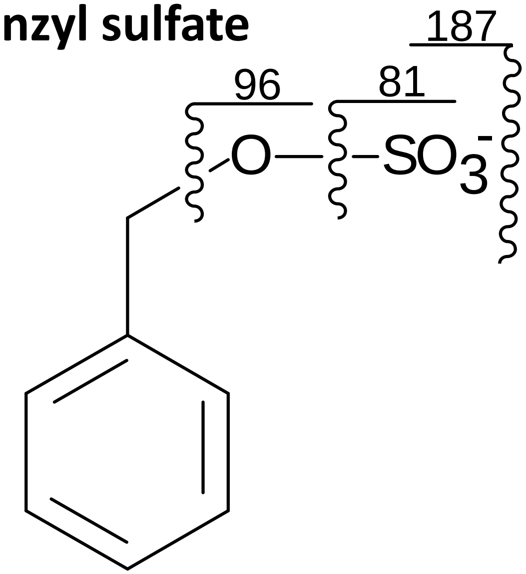
Ethyl sulfate



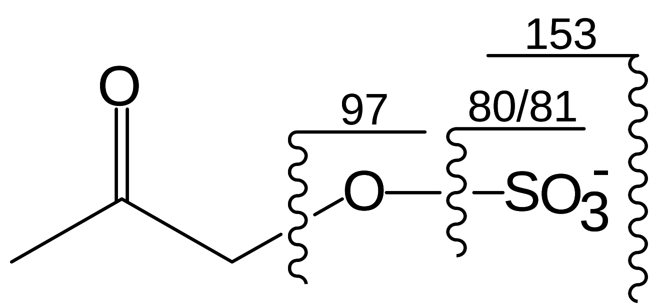
Glycolic acid sulfate



Benzyl sulfate



Hydroxyacetone sulfate



(Hettiyadura, et al. AMT 2015)

Multiple Reaction Monitoring (MRM)

Compound	Precursor ion and m/z		Product ion and m/z		Cone voltage (V)	Collision energy (eV)
Methyl sulfate	$CH_3SO_4^-$	111	$SO_3^{-\cdot}$	80	36	18
			$SO_4^{-\cdot}$	96		14
Ethyl sulfate	$C_2H_5SO_4^-$	125	HSO_4^-	97	26	12
Benzyl sulfate	$C_7H_7SO_4^-$	187	HSO_3^-	81	42	18
			$SO_4^{-\cdot}$	96		20
Hydroxyacetone sulfate	$C_3H_5SO_5^-$	153	$SO_3^{-\cdot}$	80	32	18
			HSO_4^-	97		20
Glycolic acid sulfate	$C_2H_3SO_6^-$	155	$C_2H_3O_3^-$	75	26	18
			HSO_4^-	97		14
Lactic acid sulfate	$C_3H_5SO_6^-$	169	HSO_4^-	97	28	16

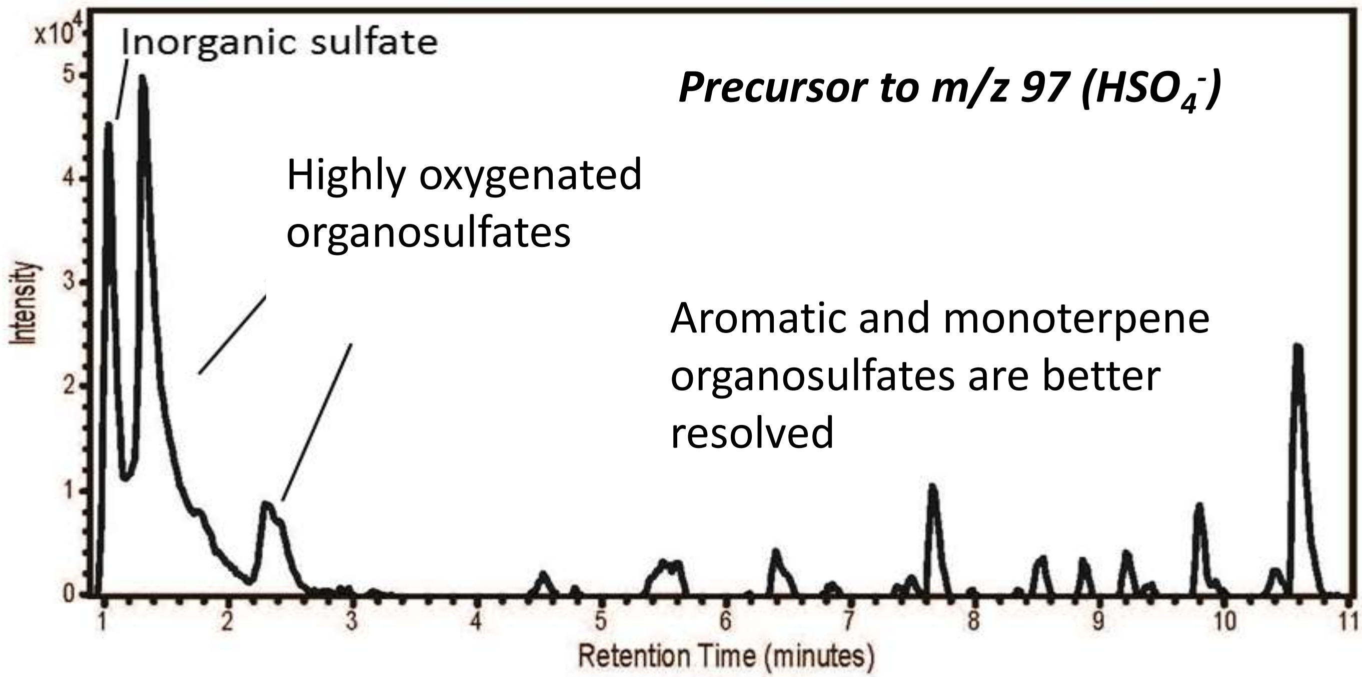
(Hettiyadura, et al. AMT 2015)

Separation of Organosulfates

Objectives:

1) Selective retention of oxygenated organosulfates
2) Separation from the sample matrix

Retention of organosulfates on a reversed-phase (C18) column):



Hydrophilic interaction liquid chromatography (HILIC)

Stationary phase:

Ethylene Bridged Hybrid (BEH) amide column (Waters)

Retains extremely polar compounds (including sugars) and involves ion exchange

Mobile phase:

Acetonitrile (ACN) and water

10 mM ammonium acetate

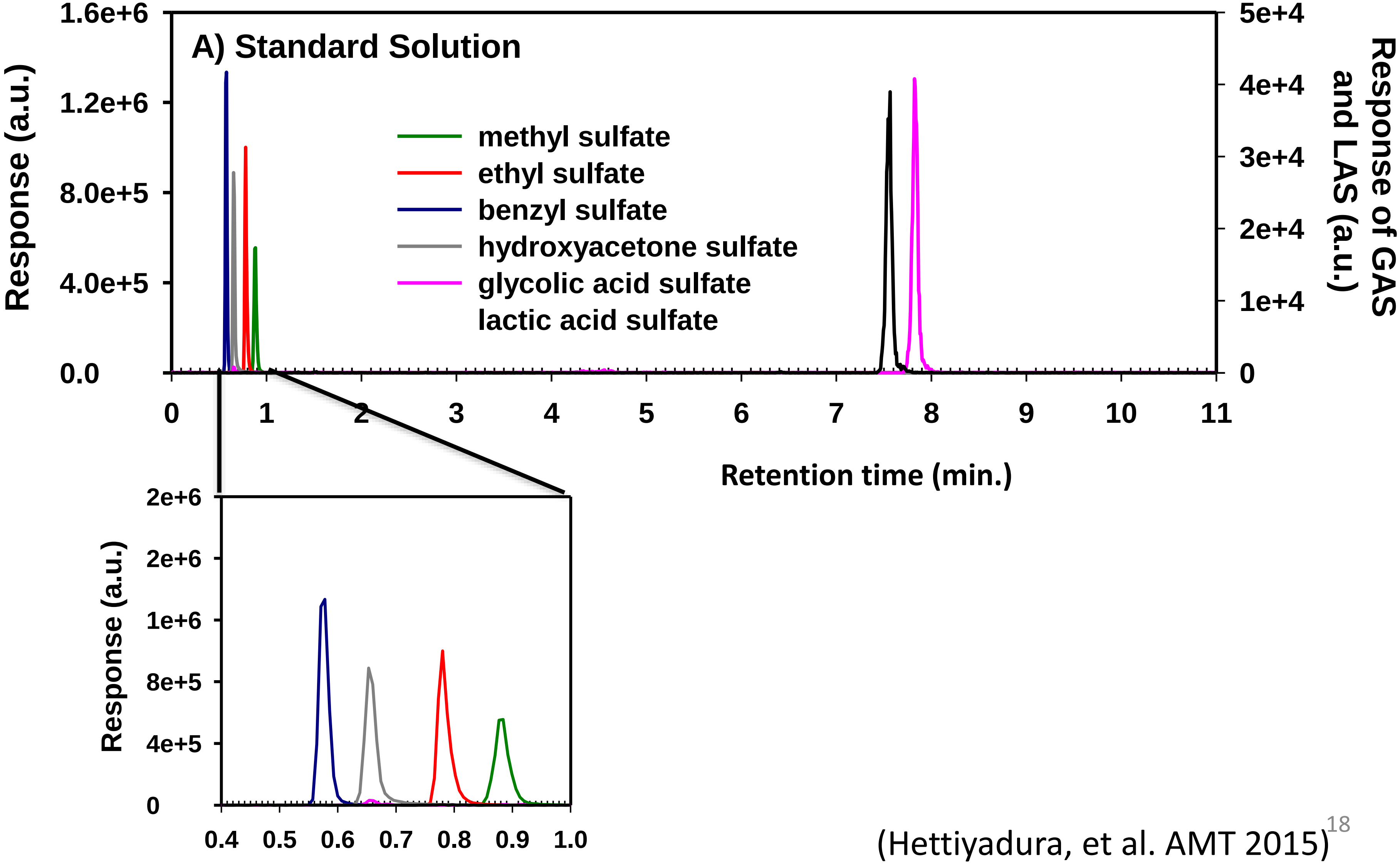
pH 9

Gradient

Time (min.)	H_2O	ACN
0	5	95
2	5	95
4	20	80
11	20	80

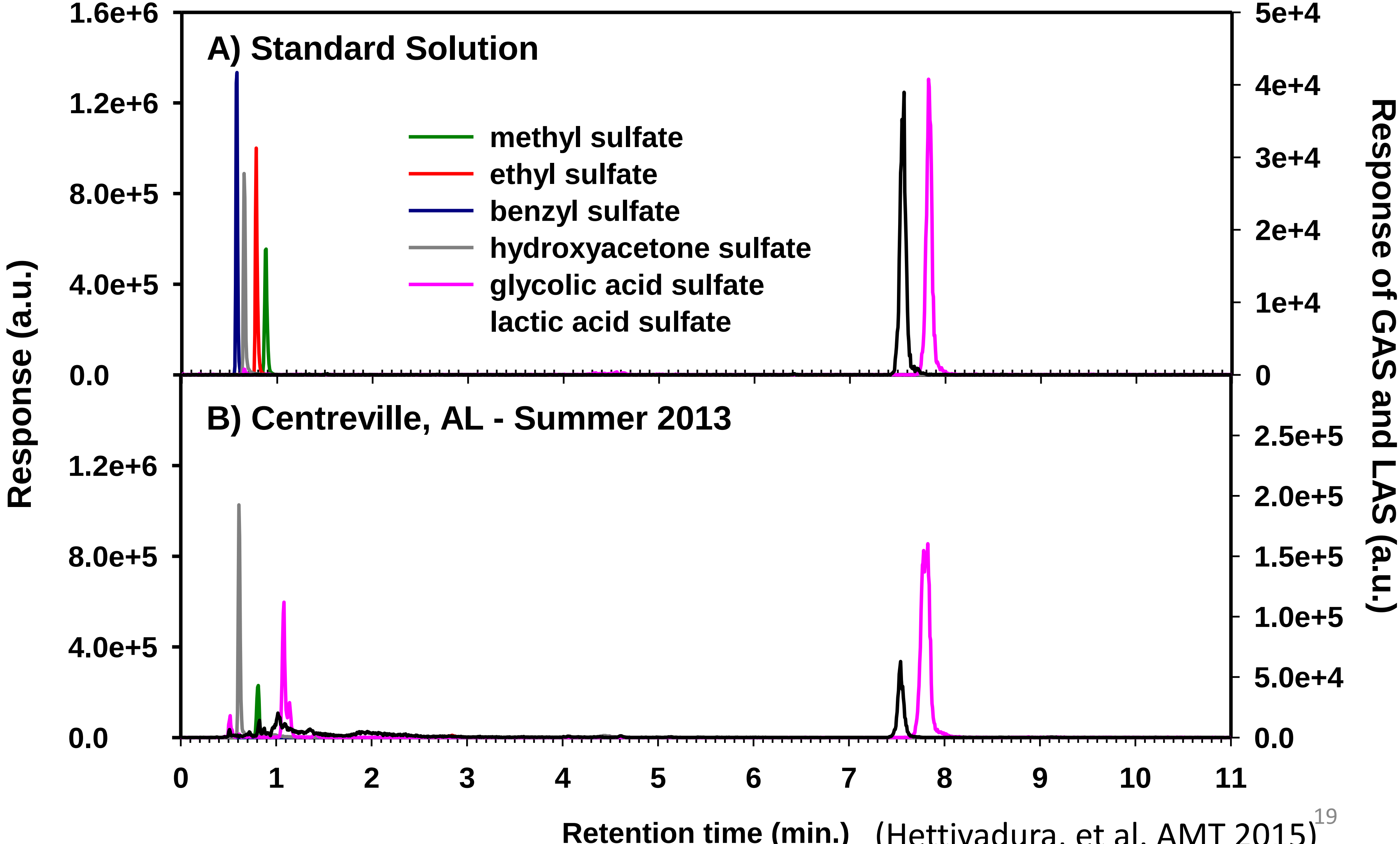
(Hettiyadura, et al. AMT 2015)

HILIC Separation Development



(Hettiyadura, et al. AMT 2015)

HILIC separation of $PM_{2.5}$ from Centreville, AL



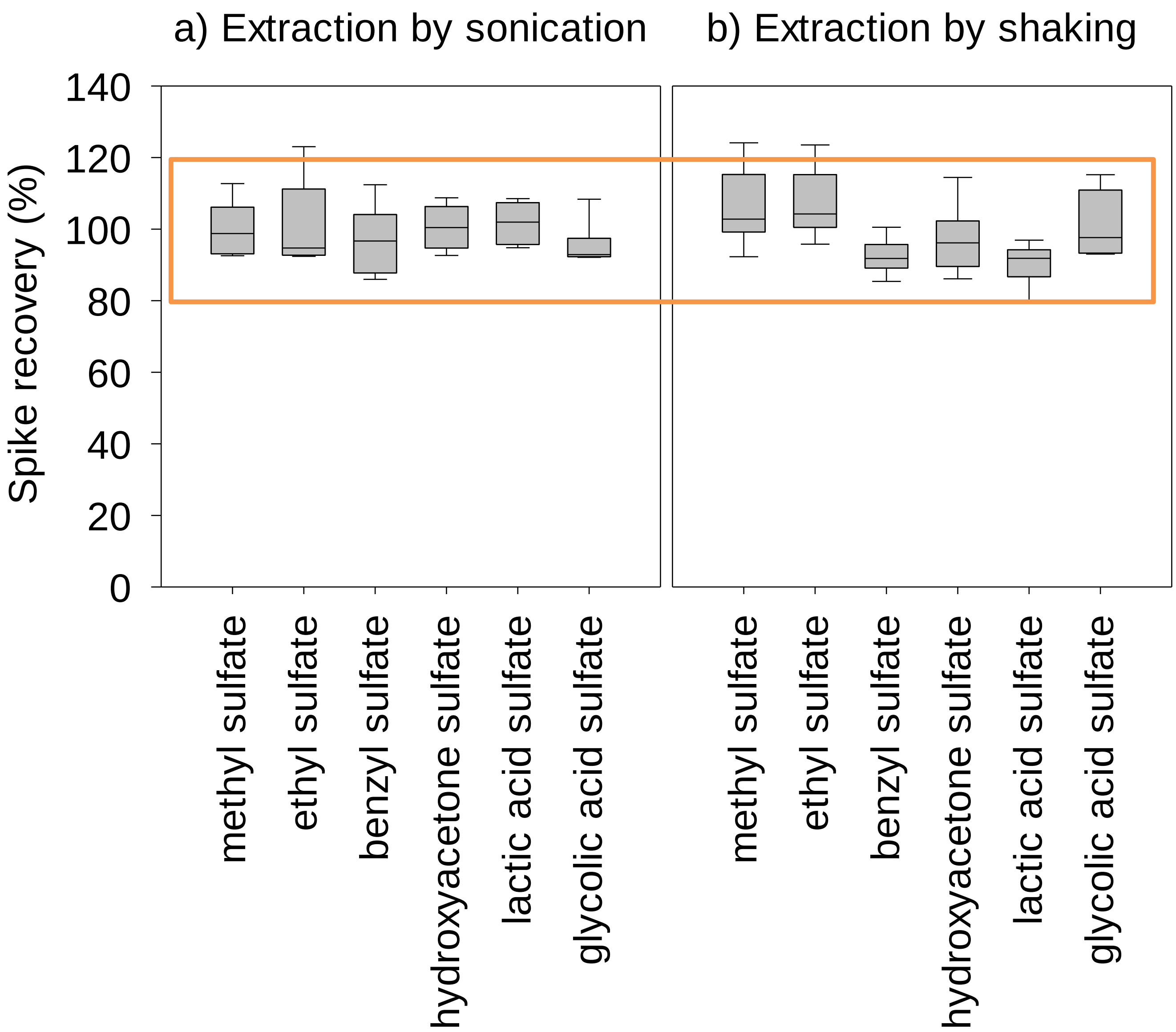
(Hettiyadura, et al. AMT 2015)

UPLC-MS/MS Method Performance

Compound	Retention time (min.)	Linear range (μg L^{-1})	R^2	LOD (μg L^{-1})	LOQ (μg L^{-1})	RSD (%)
methyl sulfate	0.88 ± 0.03	25.0-500.0	0.998	2.6	8.6	2.9
ethyl sulfate	0.78 ± 0.03	25.0-500.0	0.998	3.4	11.2	2.5
benzyl sulfate	0.58 ± 0.02	25.0-300.0	0.995	3.9	13.2	3.0
hydroxyacetone sulfate	0.66 ± 0.02	25.0-300.0	0.996	2.6	8.7	3.0
glycolic acid sulfate	7.84 ± 0.01	25.0-300.0	0.998	1.9	6.3	15.6
lactic acid sulfate	7.57 ± 0.02	25.0-300.0	0.995	3.9	13.0	5.9

(Hettiyadura, et al. AMT 2015)

Sample preparation: to shake or sonicate?



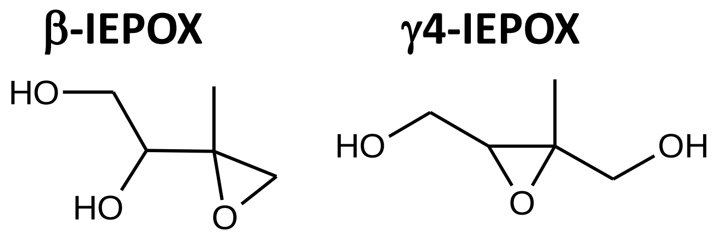
(Hettiyadura, et al. AMT 2015)

Southern Oxidant and Aerosol Study

- Centreville, AL (CTR) Ground Site
- June 1 – July 15, 2013
- Daytime (08:00-19:00) and nighttime (20:00-07:00)
- Chemical measurements
  - Elemental and organic carbon
  - Organic species by GCMS
  - Organosulfates by LCMS
- Source apportionment of $PM_{2.5}$ and organic carbon

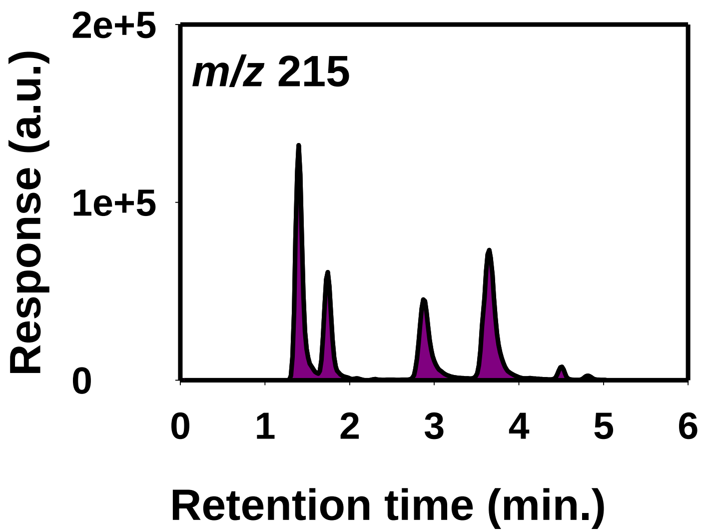
Methyltetrol sulfates (m/z 215)

Low-NO_x isoprene oxidation products:



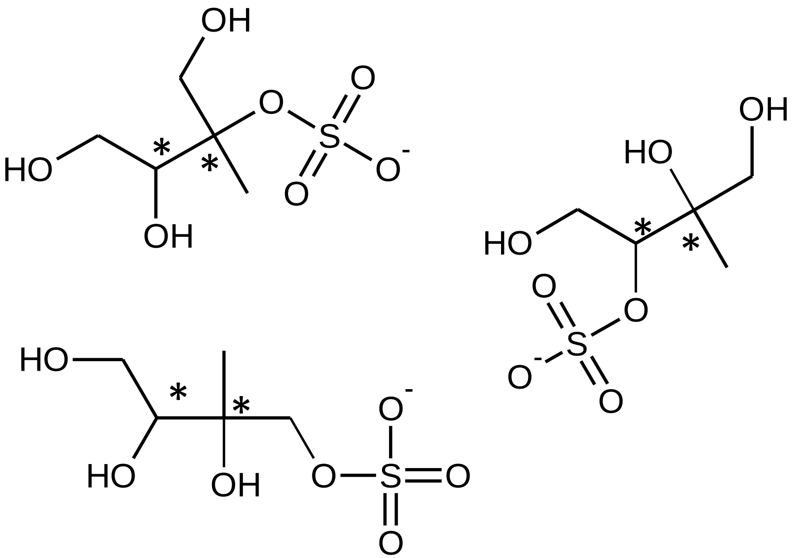
(Paulot et al., *Science,* 2009)

HILIC resolves 6 IEPOX-sulfate isomers



IEPOX-sulfates form by acid catalyzed ring opening of IEPOX with sulfate

(Surratt et al., *PNAS,* 2010)



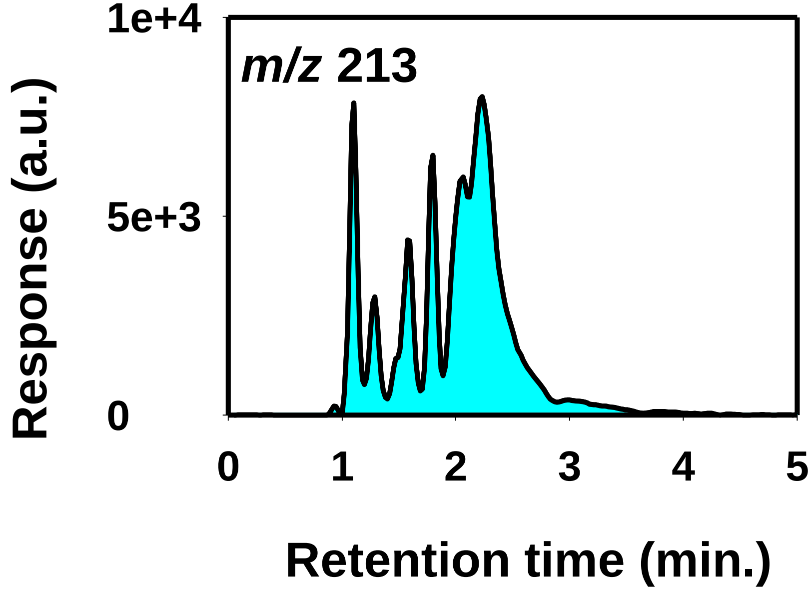
Regioselectivity: 3° > 1° > 2°
Chiral centers

(Hettiyadura, et al., *AMT*, 2015)

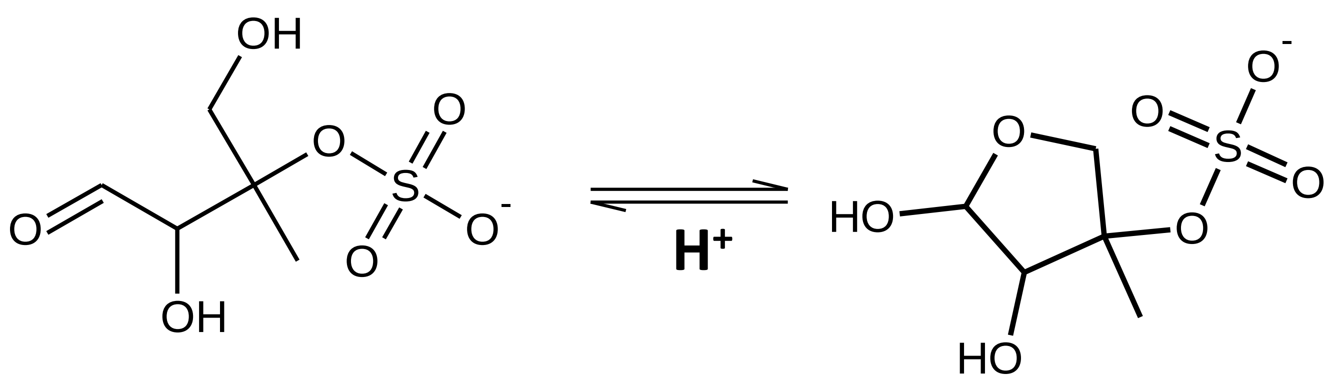
Other biogenic organosulfates (*m/z* 213)

High resolution extracted ion chromatogram

$C_5H_9O_7S^-$

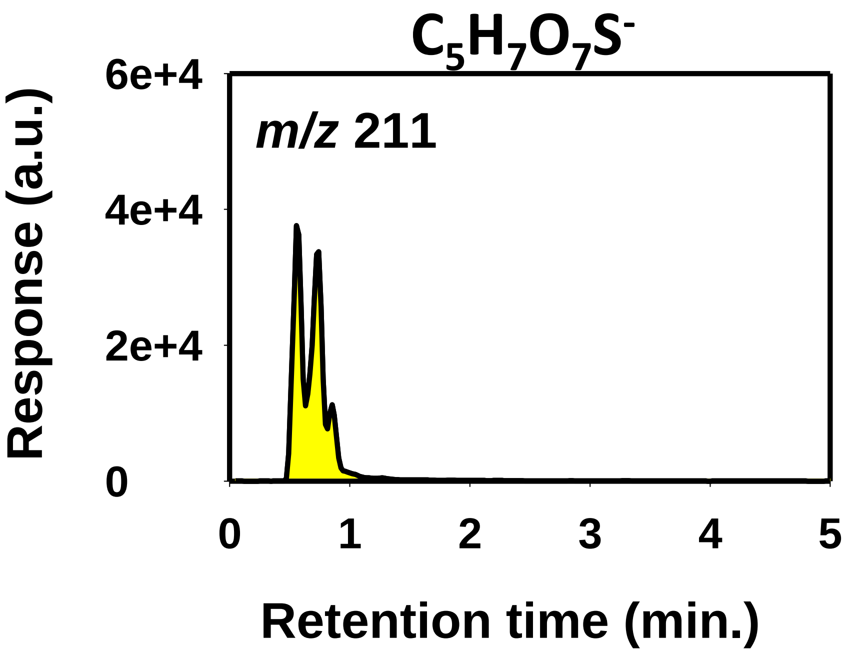


- Forms in chamber experiments of isoprene (Surratt et al. *JPCA,* 2008) and potentially other VOC (Gómez-Gónzalez et al. 2008; Shalamzari et al. *ES&T,* 2014)
- Short retention times suggest keto- and hydroxy- groups, not carboxylic acids
- Isomers positively correlate ($r_s > 0.75$; $p < 0.05$)

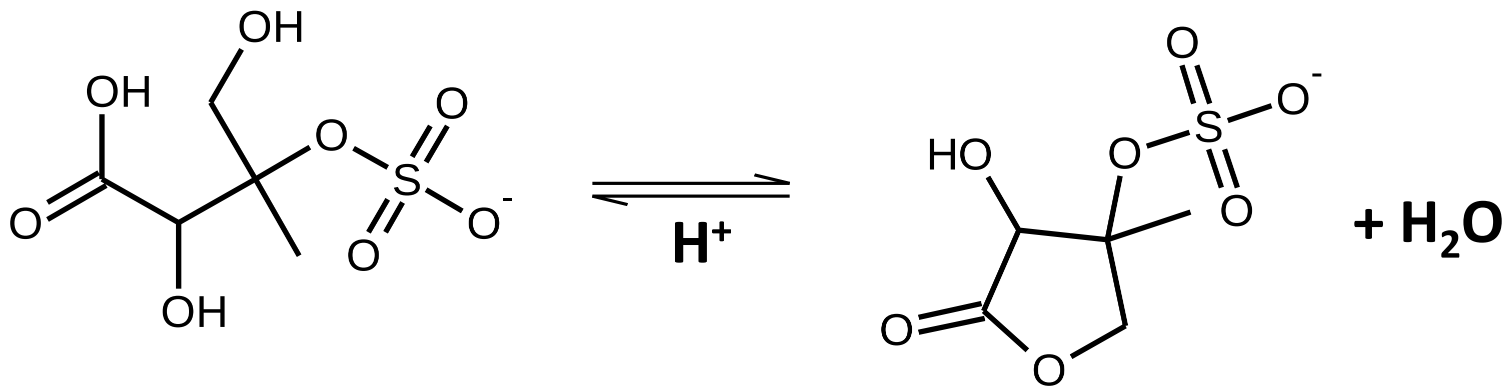


Other biogenic organosulfates (*m/z* 211)

High resolution extracted ion chromatogram



- Forms in chamber experiments of isoprene (Surratt et al. *JPCA,* 2008)
- Similarly, short retention times suggest keto- and hydroxy- groups, not carboxylic acids
- Isomers positively correlate ($r_s > 0.9$; $p < 0.05$)

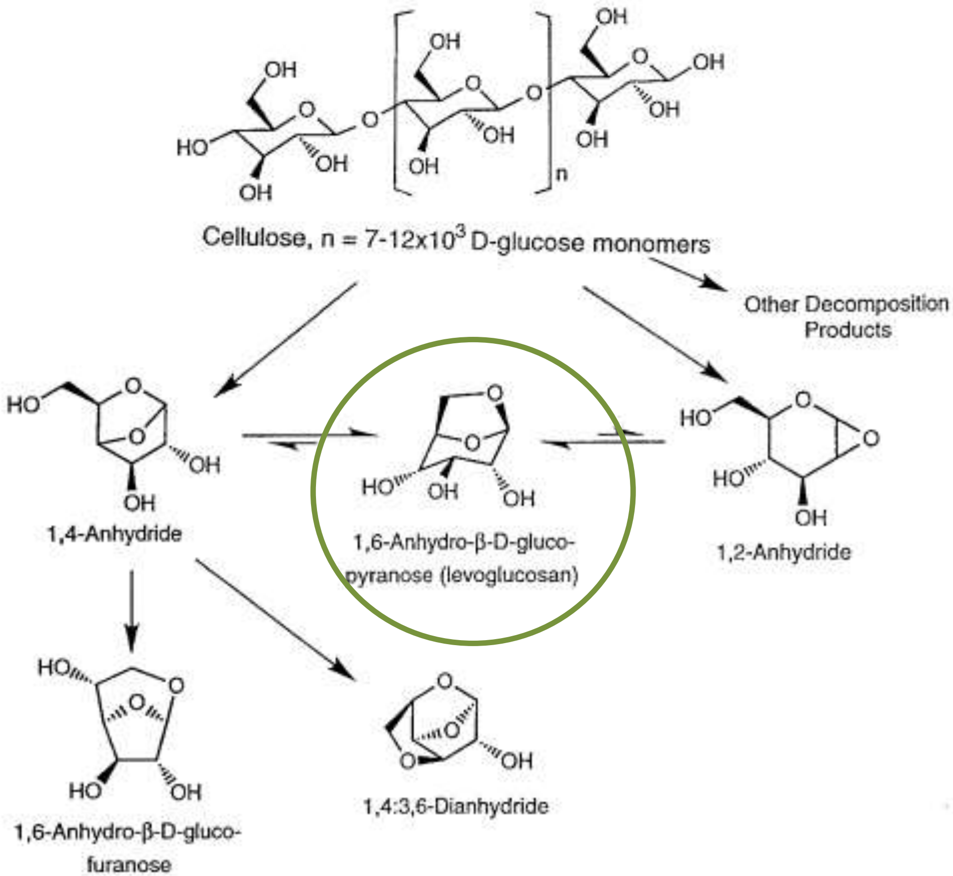


Molecular marker source apportionment

Aerosol Source	**Markers**
Secondary- *biogenic*	Derivatives of isoprene, monoterpenes, *including organosulfates*
Secondary- *anthropogenic*	Aromatic acids
Secondary – *inorganic*	Ammonium sulfate
Primary biogenic (*detritus)*	Linear *n*-alkanes (odd C preference) Linear *n*-alkanoic acids (even C preference)
Diesel engines	Hopanes, steranes, elemental carbon
Gasoline vehicles	Hopanes, steranes, polycyclic aromatic hydrocarbons (PAH)
Biomass burning	Levoglucosan, plant sterols

Biomass burning

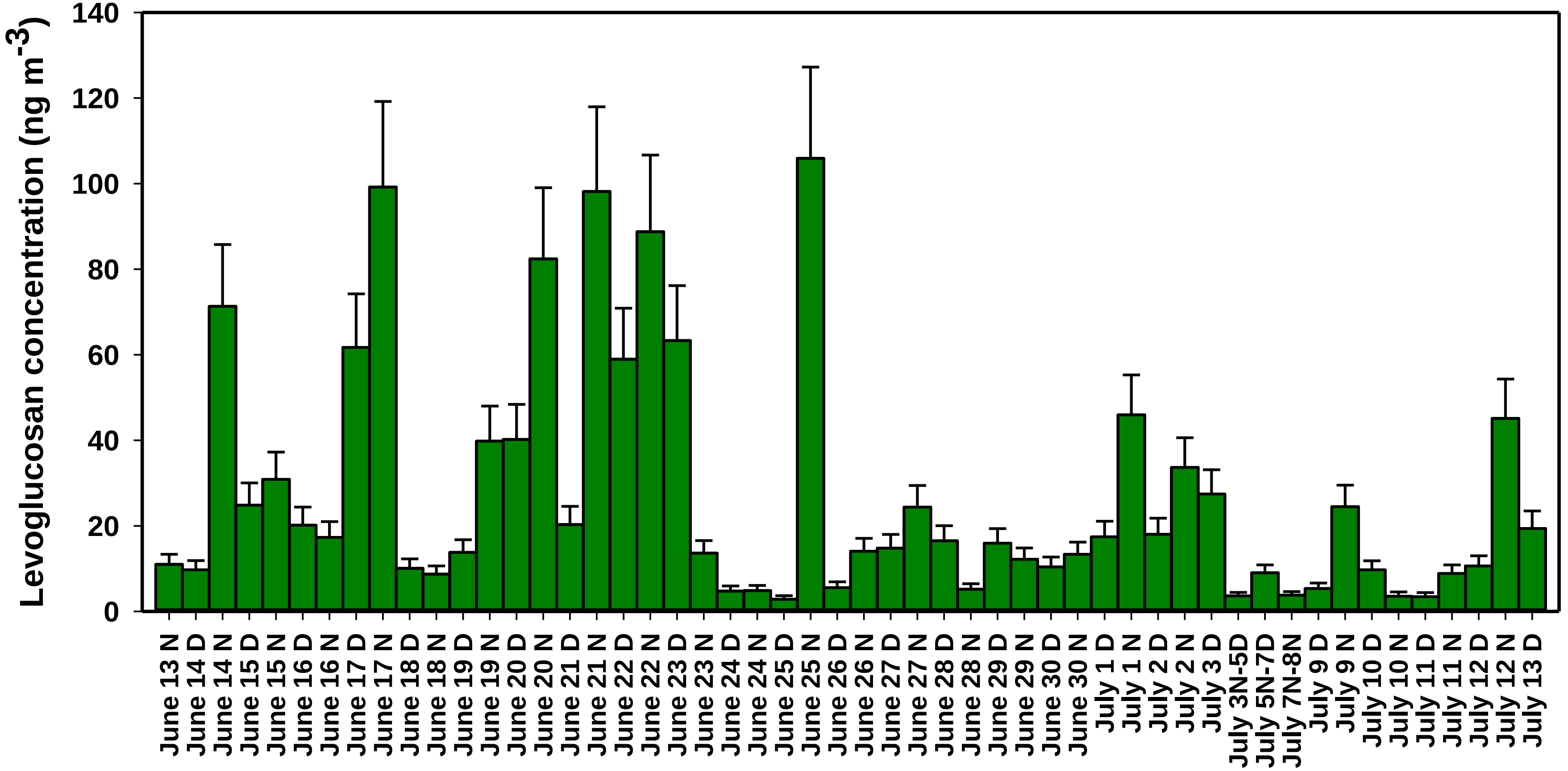
Chemical Signatures: Anhydrosugars



(Simoneit, et al., 1999)

(photo by Joost de Gouw)

Biomass Burning at Centreville



Chemical mass balance source apportionment

EPA CMB v. 8.2

$$c_i = \sum_{i=1}^{p} a_{ij} s_j$$

c_i = ambient concentration of species *i*
a_{ij} = fractional concentration of species *i* at source *j*
s_j = mass contribution of source *j*

Key assumptions:

1) Conservation of mass, i.e. tracers do not react or interact
2) Source compositions are independent of one another
3) Sources have been identified and are characterized

Conclusions

- HILIC chromatography provides improved retention and resolution of carboxy- and hydroxy-substituted organosulfates
  - Diagnostic tool for carboxy-organosulfates
  - Complementary to reversed-phase separations
  - May aid in understanding isoprene SOA product distributions
- Organosulfates in Centerville are largely biogenic, showing consistent signatures from isoprene
  - Correlation analysis implies an important role for sulfate
  - pH is consistently low enough to support their formation
- Preliminary source apportionment indicates a very small role for primary sources relative to secondary in Centreville.

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