

# Stable carbon ratios of aerosols separated by size-exclusion chromatography:

## Methodology and early results

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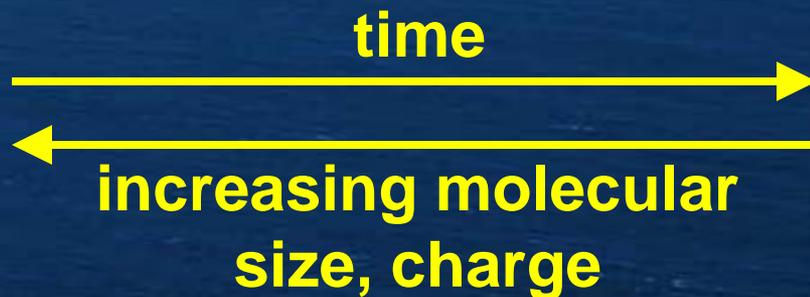
Matthew McCarthy, UC Santa Cruz

Patrick Chuang, UC Santa Cruz

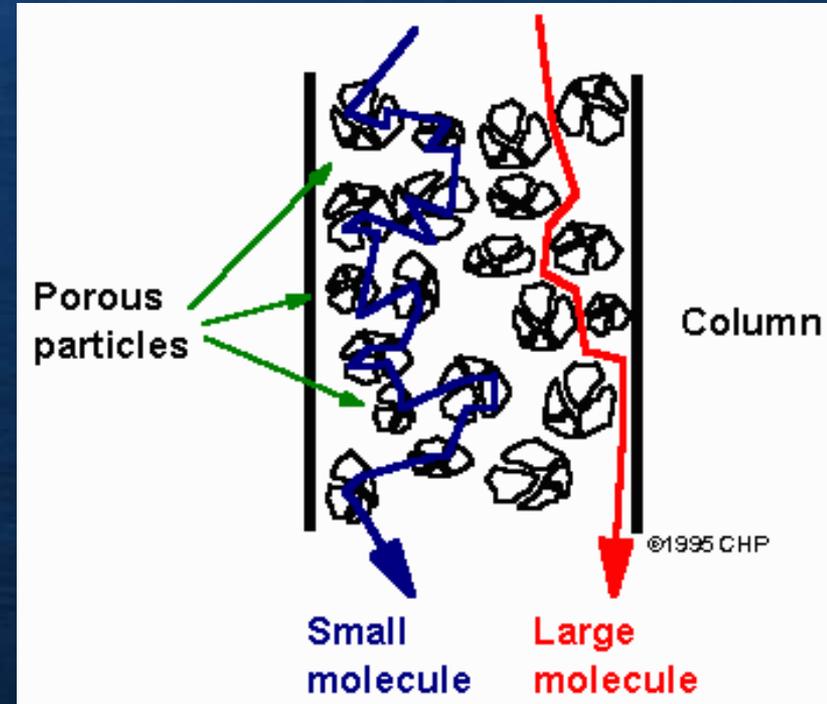


# Size-exclusion chromatography (SEC)

Aqueous SEC: Water-soluble organic carbon (WSOC) separated by hydrodynamic diameter



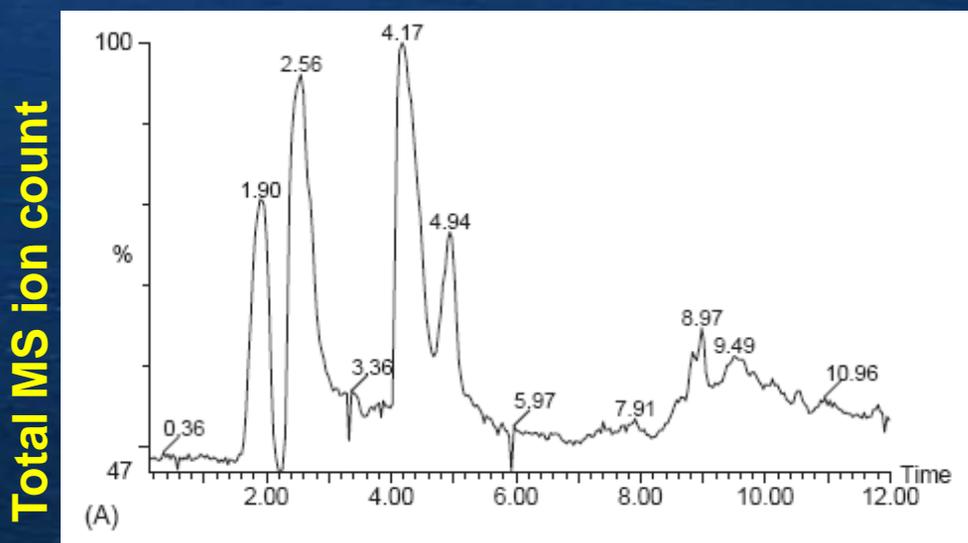
- Nearly the entire WSOC fraction is analyzed
- Vary pH of mobile phase
- Large molecules can be isolated



<http://elchem.kaist.ac.kr/>

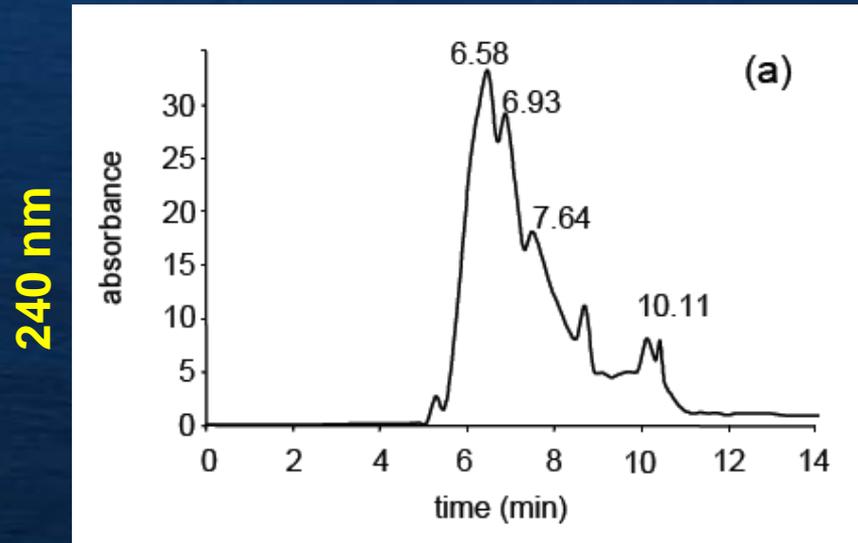
# Examples of previous SEC analysis of aerosol samples

Kiss et al. (Atm. Env. 2003)



$H_2O \rightarrow$  isopropanol  
(organics isolated by  
solid phase extraction)

Samburova et al. (Atm.  
Chem. Phys. 2005)

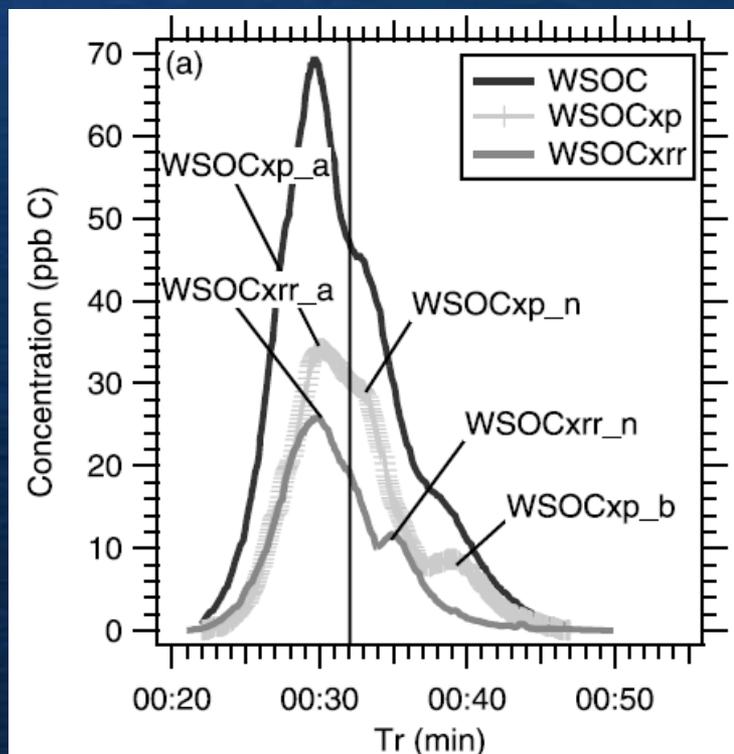


0.3M NaCl, 0.03M  $NH_4Cl$  (pH 10–11)

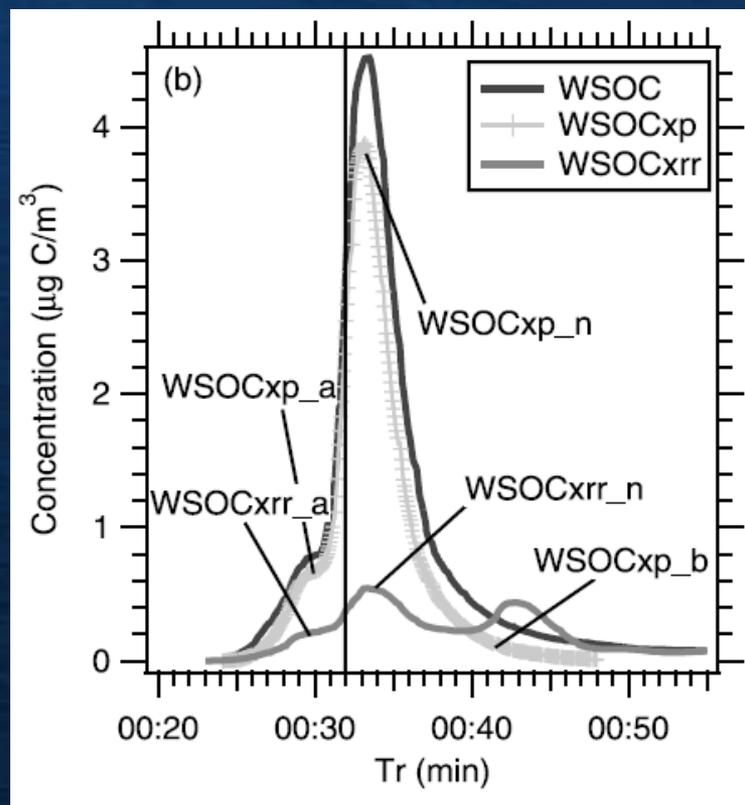
# One more example of a previous SEC analysis of aerosol samples

Sullivan & Weber (J. Geophys. Res. 2006)

summer



biomass burning

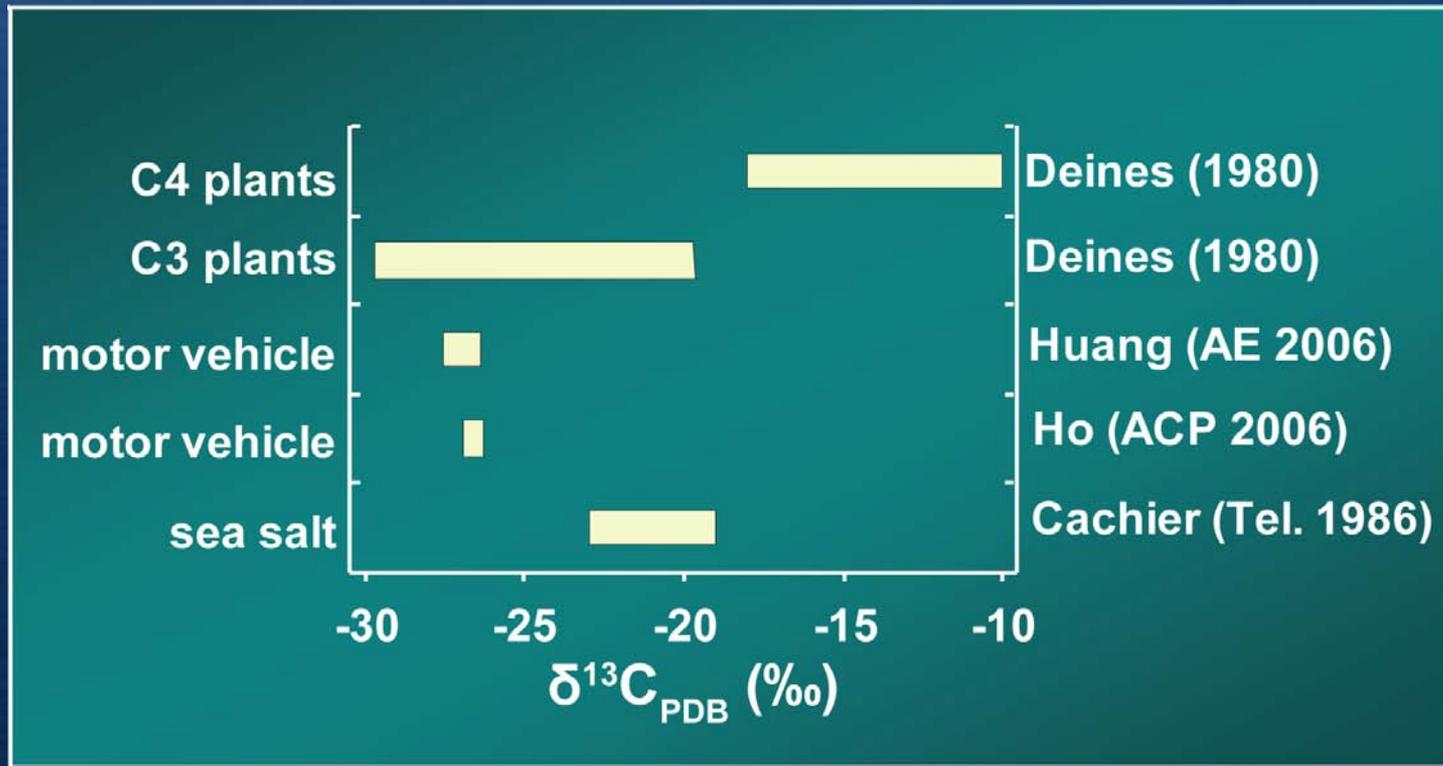


XAD-8  
fractions  
of WSOC

TOC  
analyzer

Low pressure SEC, cationic stationary phase, pH 6.8 buffer

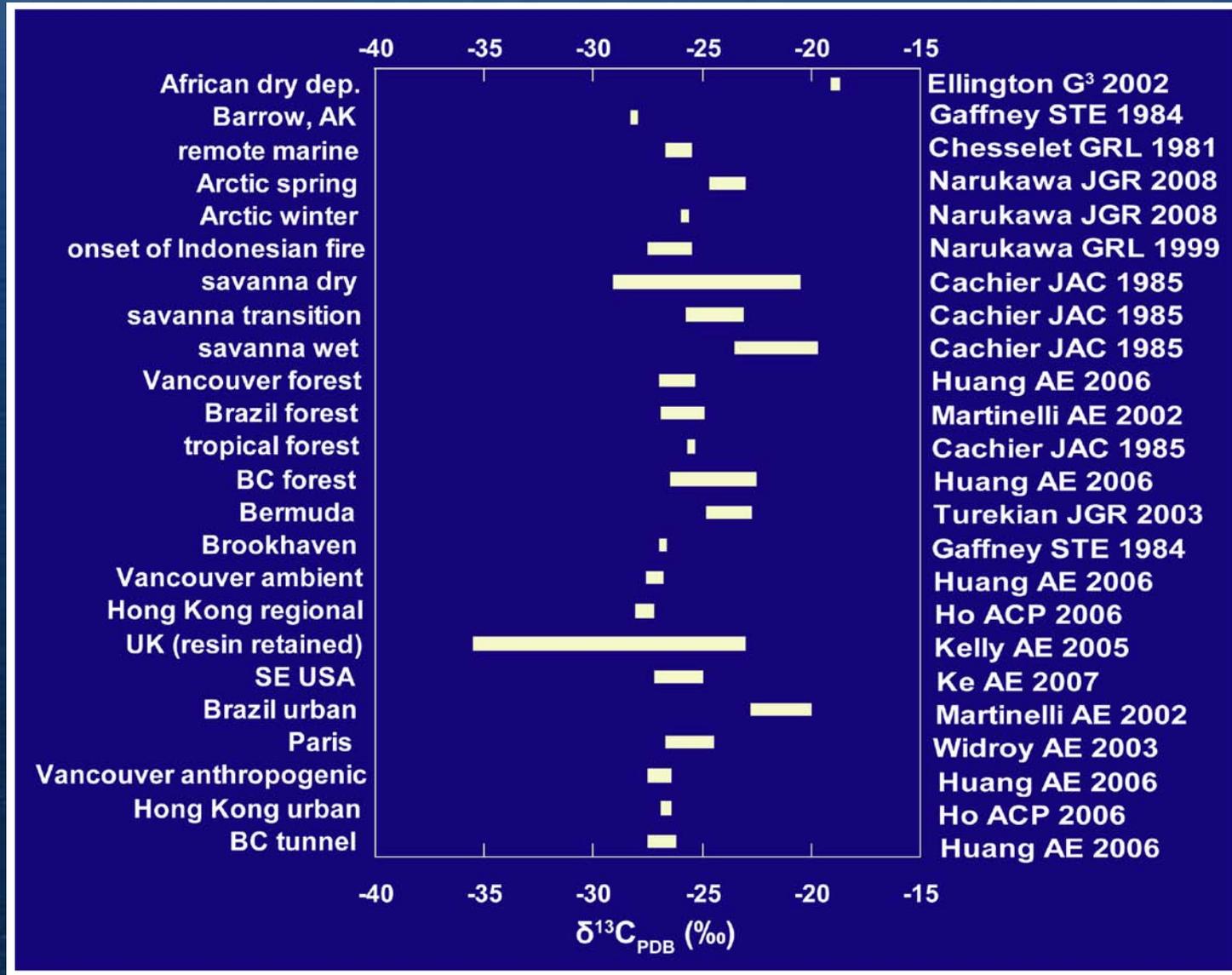
# Stable isotopes of carbon ( $\delta^{13}\text{C}$ )



$$\delta^{13}\text{C} (\text{‰}) = 1000 \frac{(^{13}\text{C}_{\text{aer}}/^{12}\text{C}_{\text{aer}} - ^{13}\text{C}_{\text{PDB}}/^{12}\text{C}_{\text{PDB}})}{(^{13}\text{C}_{\text{PDB}}/^{12}\text{C}_{\text{PDB}})}$$

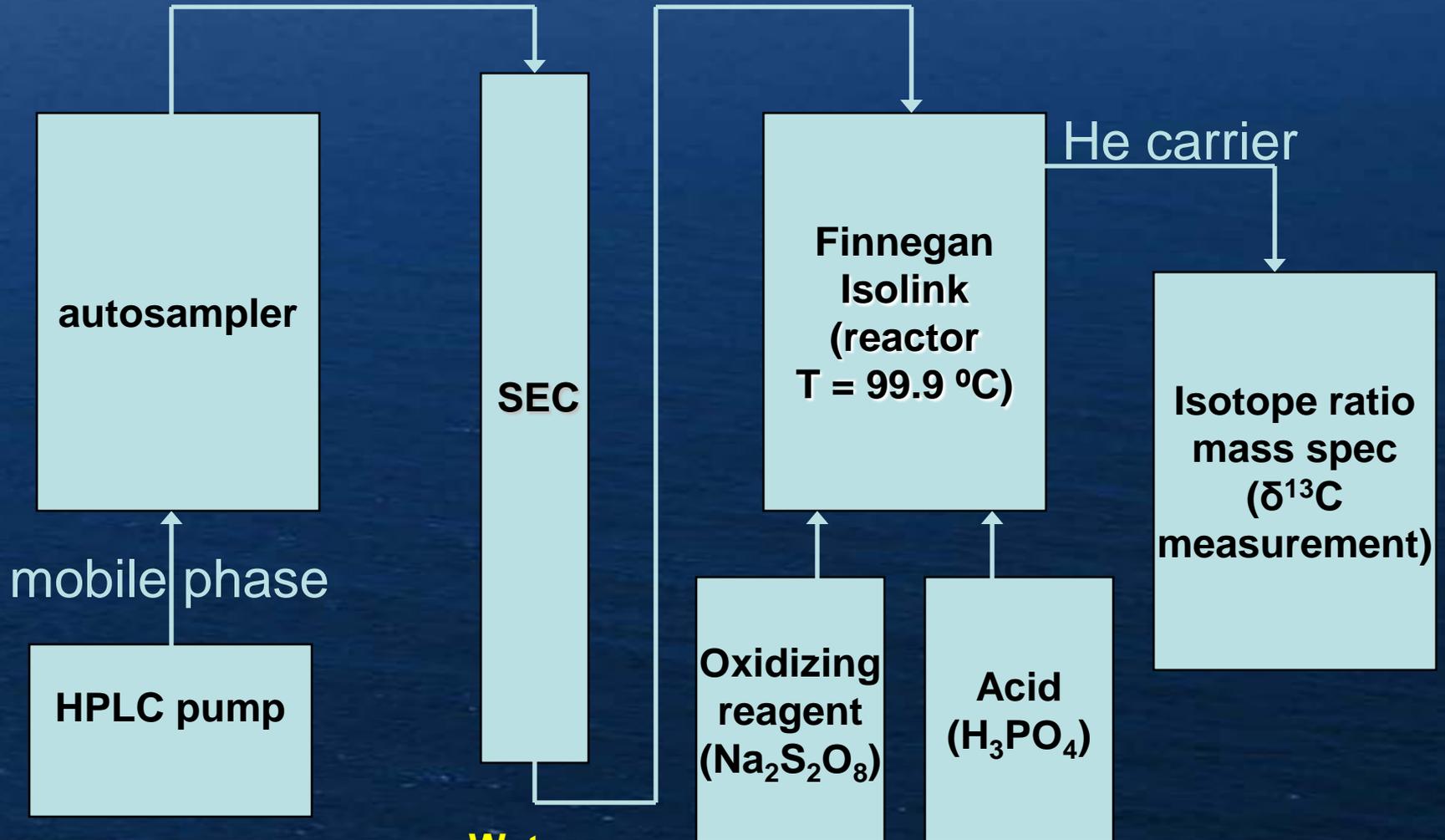
Source attribution:  
C3 vs. C4 plants  
anth. vs. marine

# Some previous measurements of aerosol $\delta^{13}\text{C}$



Much compound-specific work has also been done

# Experimental setup



**Waters  
Ultrahydrogel  
(MW 100-1000)**

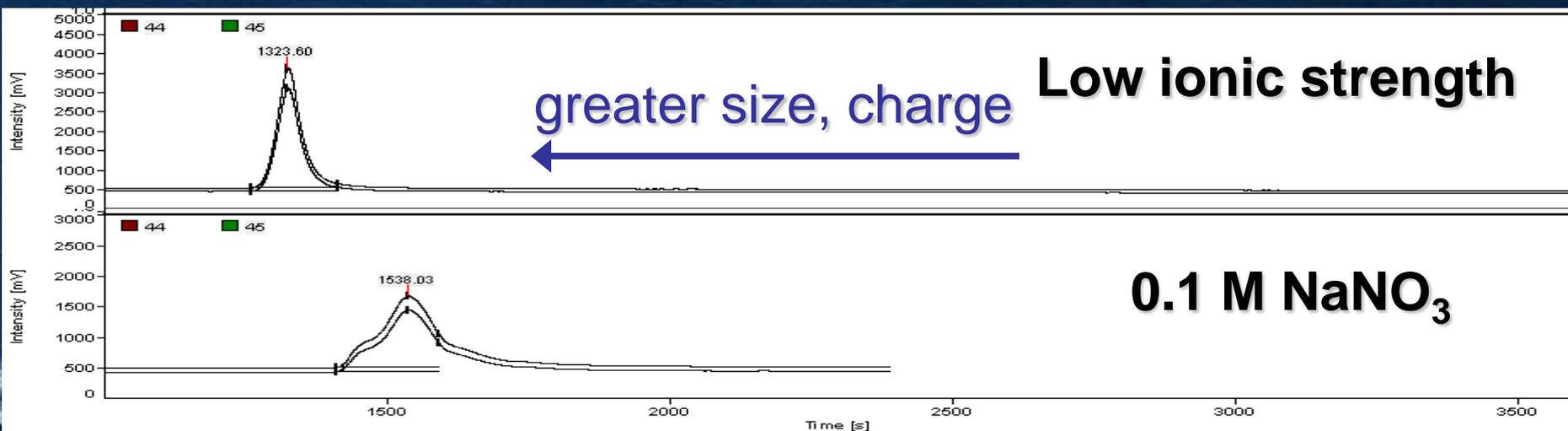
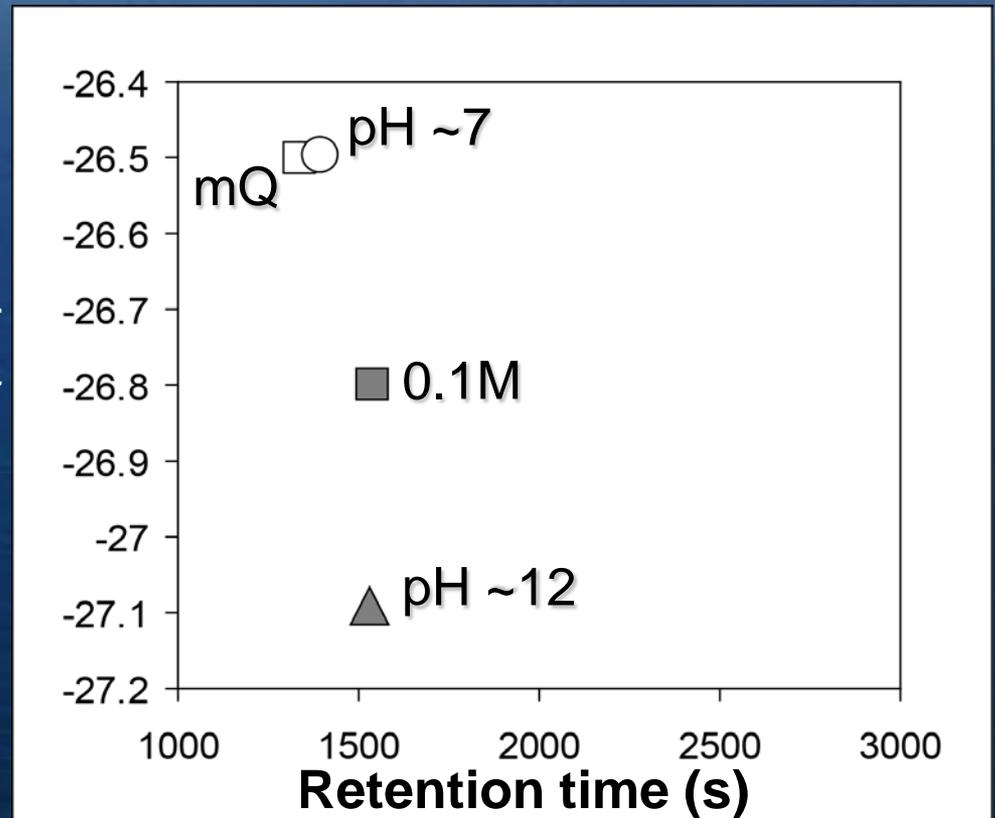
# Suwannee River Fulvic Acid

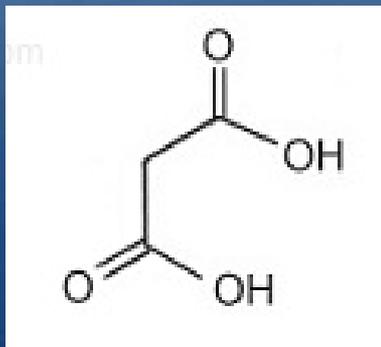
(IHSS standard,  $\delta^{13}\text{C} = -27.6\text{‰}$ )

0.1M refers to  $\text{NaNO}_3$  (ionic strength)

pH values refer to phosphate buffer

$\delta^{13}\text{C}$  (‰)



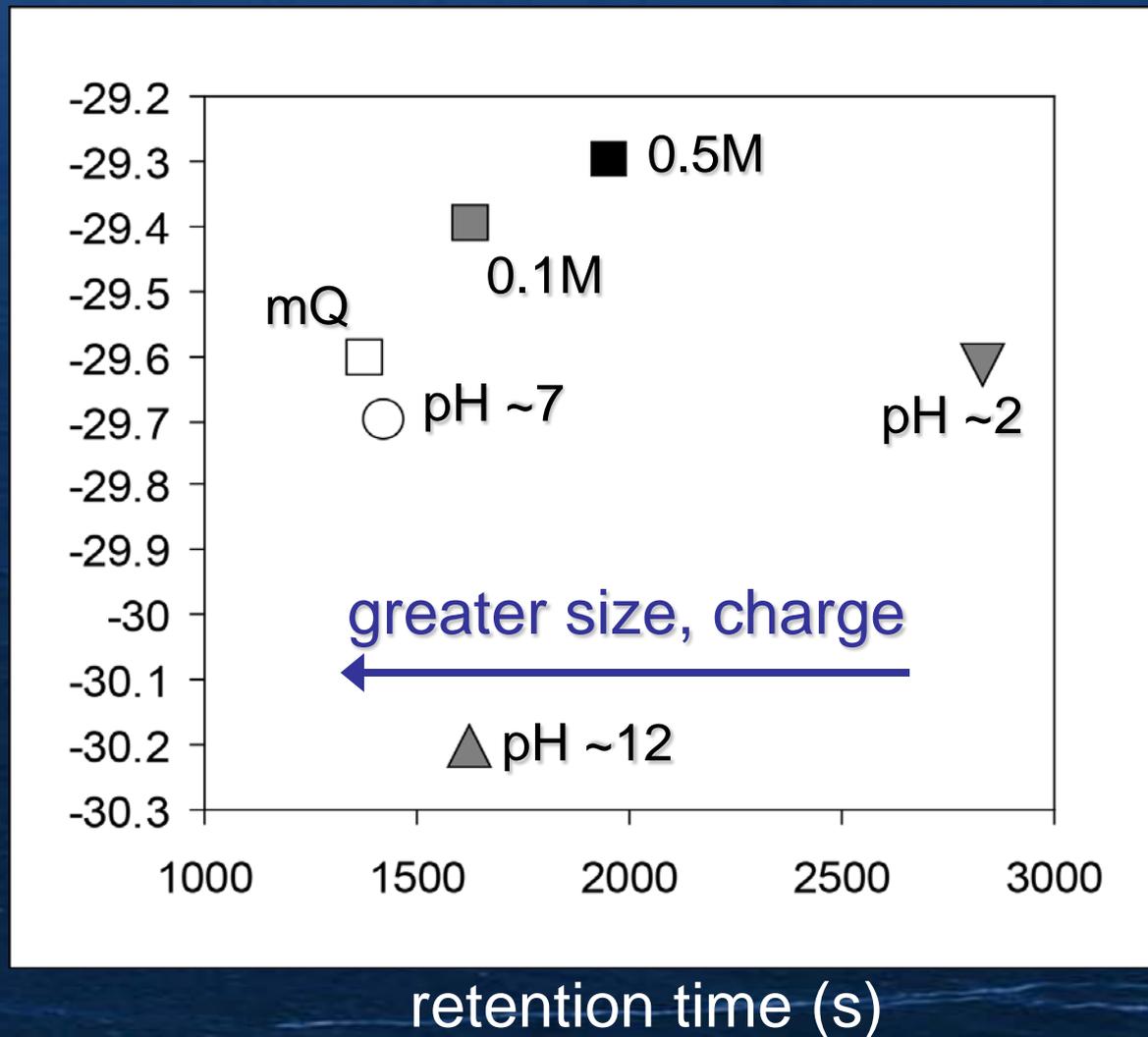


# Malonic acid

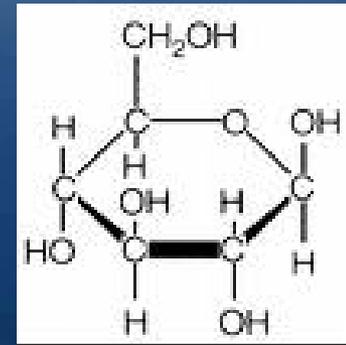
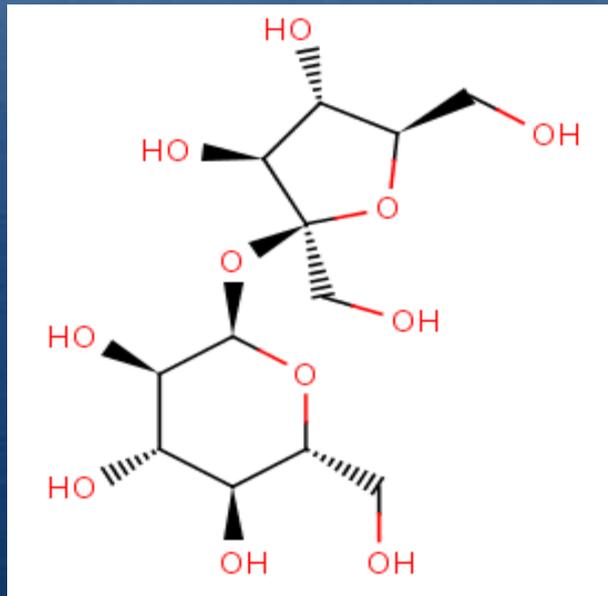
0.1M and 0.5M refer to  $\text{NaNO}_3$  (ionic strength)

pH values refer to phosphate buffer

$\delta^{13}\text{C}$  (‰)

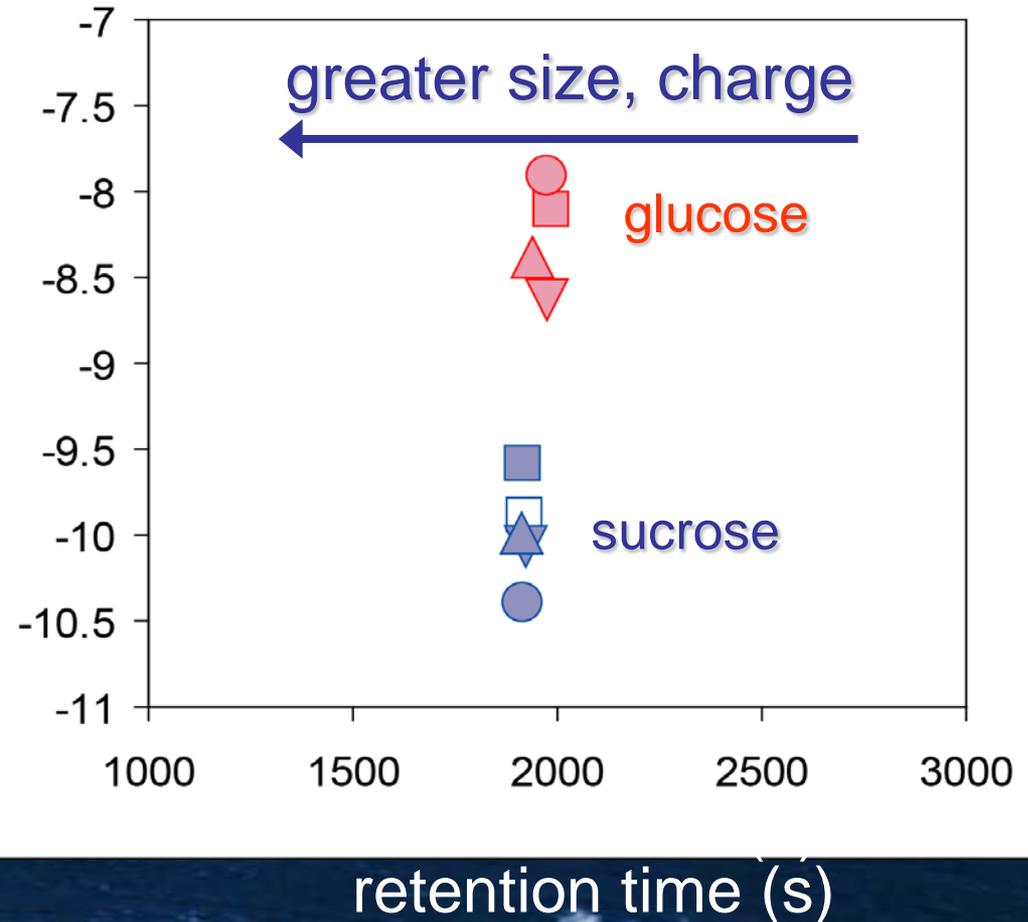


# Sucrose and glucose

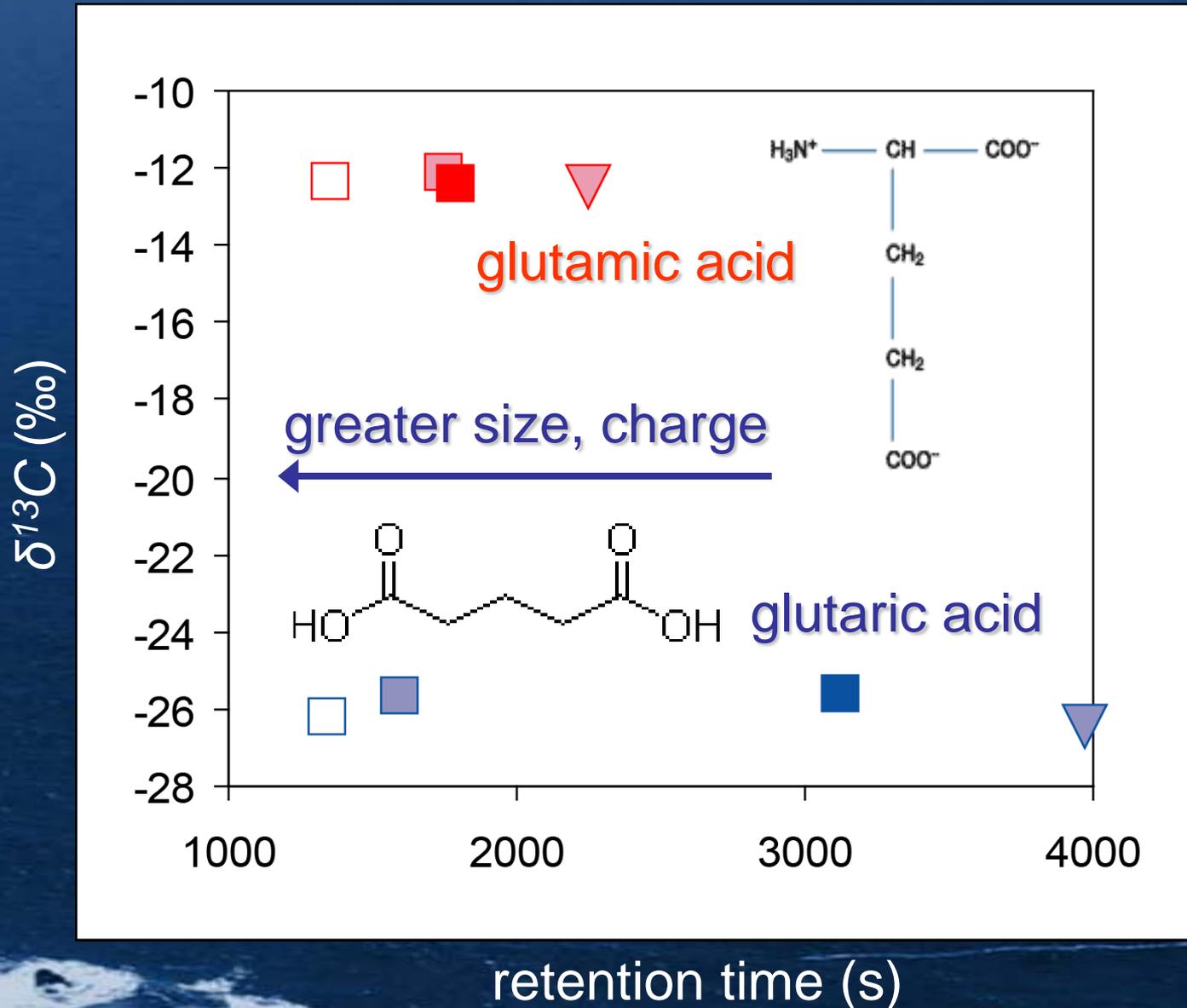


Sugars insensitive  
to SEC pH & ionic  
strength

$\delta^{13}\text{C}$  (‰)

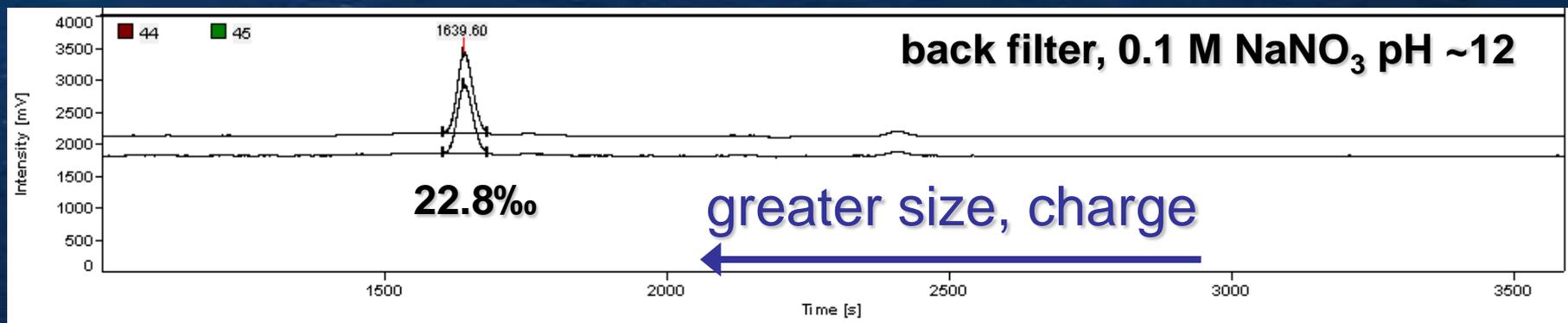
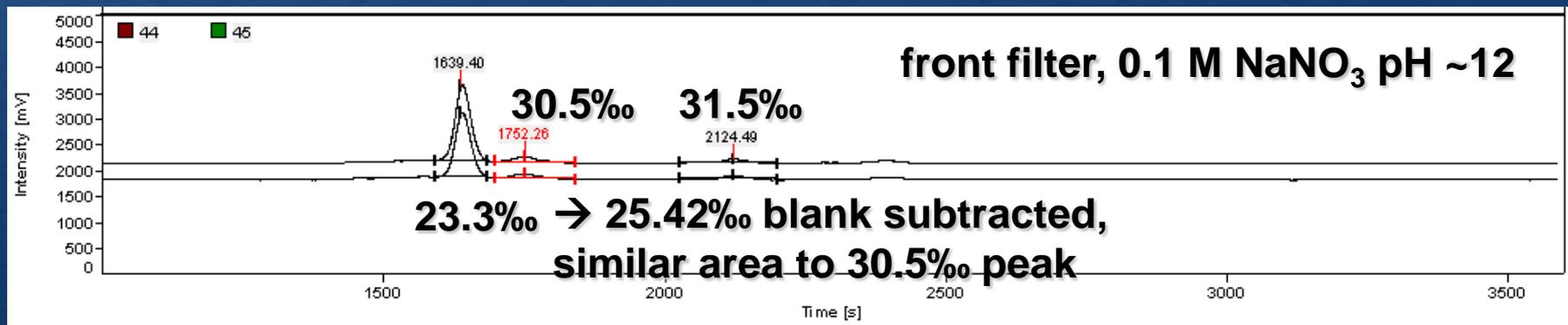


# glutaric and glutamic acid



Acids/bases sensitive to SEC pH & ionic strength

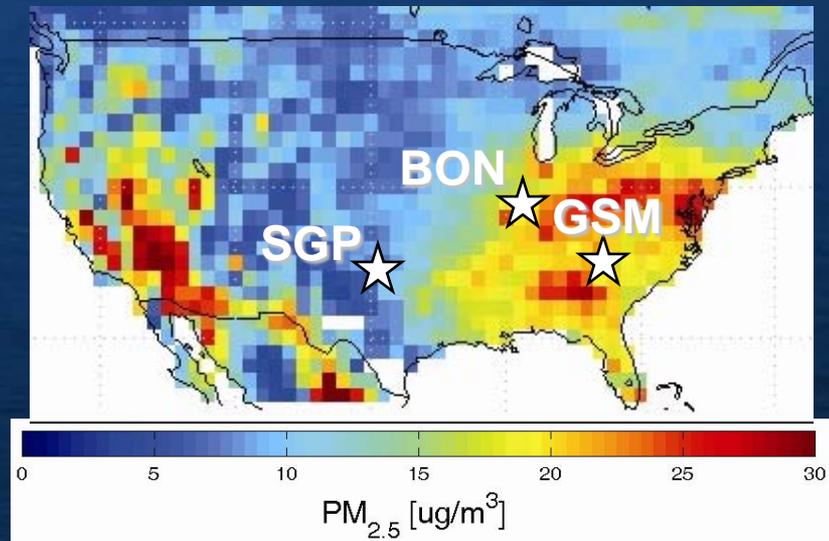
# Smog chamber samples from Jason Surratt (Cal Tech)



Particles depleted in <sup>13</sup>C relative to gaseous precursor?  
Could different peaks represent different n-mers? Would a trend in δ<sup>13</sup>C vs. time suggest oligomerization?

# Ambient aerosol samples

- Submicron ( $D < 1.2 \mu\text{m}$ ) particles sampled at three locations
  - Look Rock, GSM NP, TN
  - Bondville, IL
  - SGP ARM site, OK

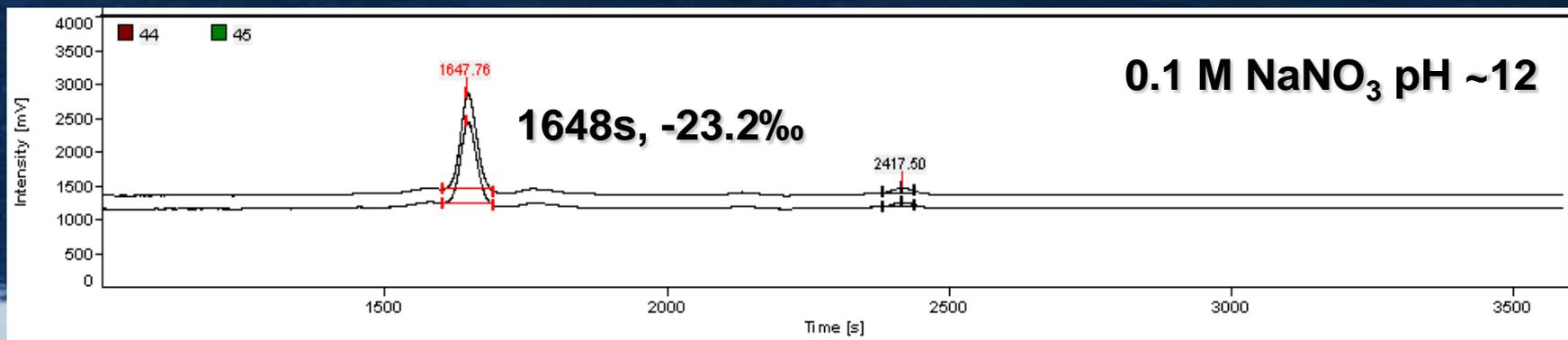
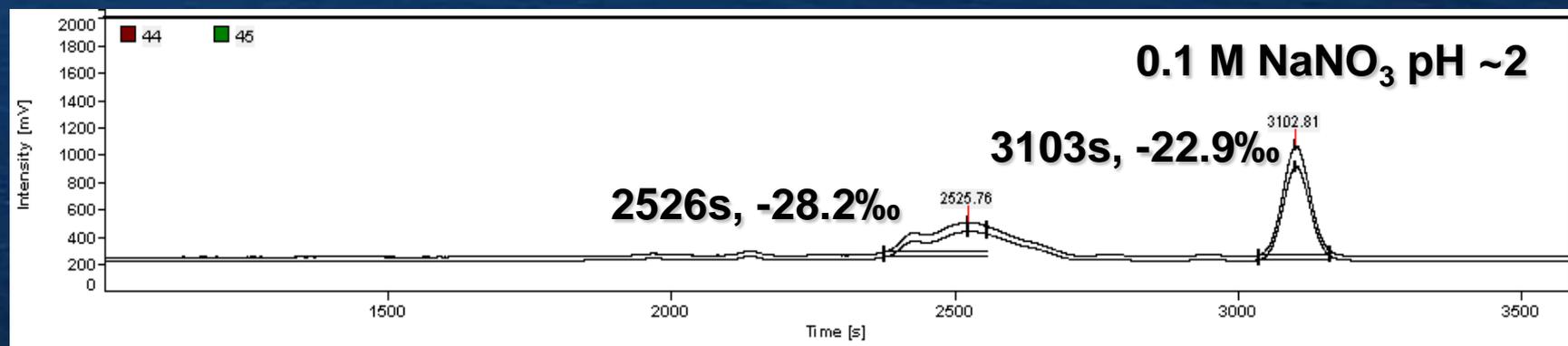
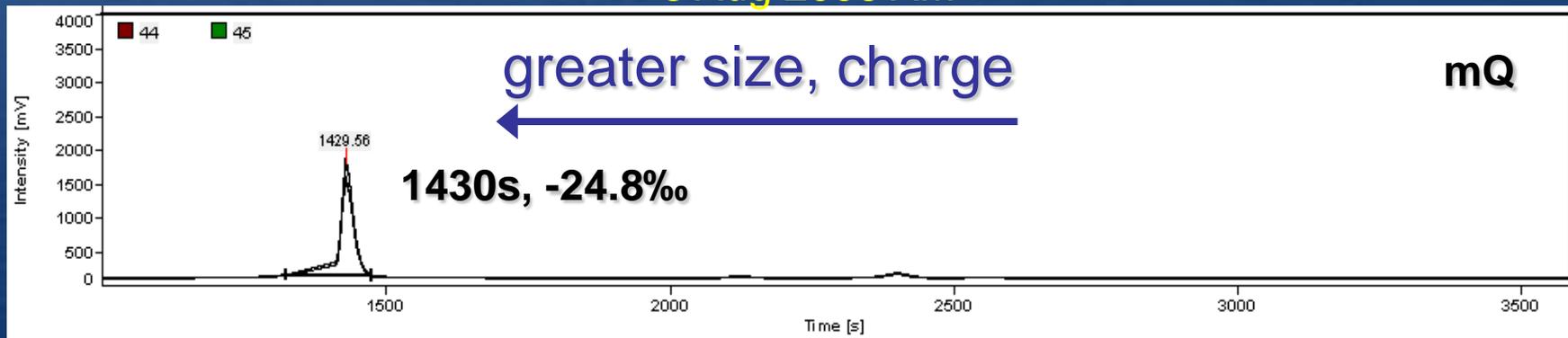


MODIS data from van Donkelaar et al., *JGR* 2006

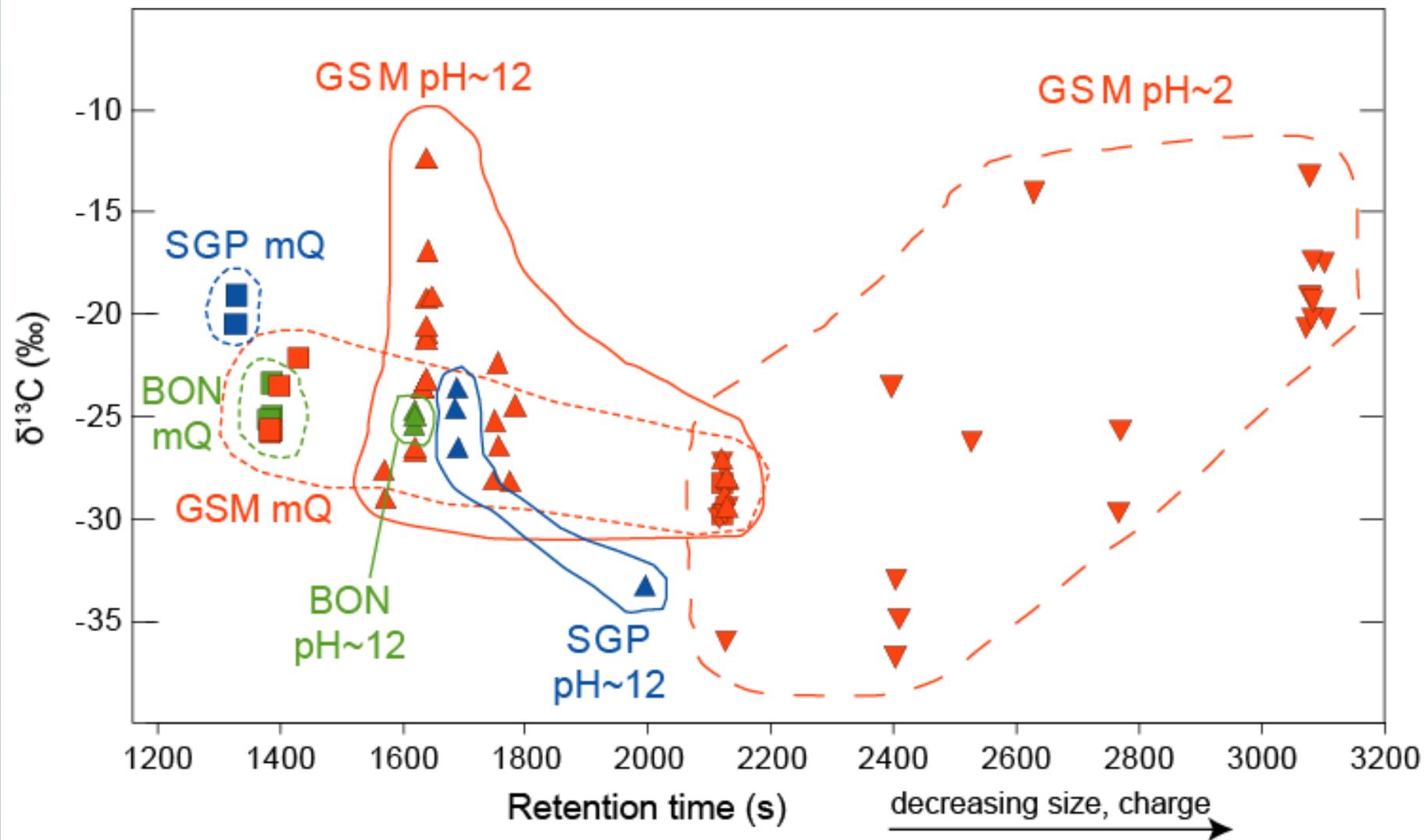
- Filters were extracted in water, filtered ( $0.22 \mu\text{m}$ ), and analyzed without further treatment
  - In some cases, atmospheric carbon dioxide contaminated samples

# Great Smoky Mountain NP

8 Aug 2006 AM



# Summary of ambient samples



# Early conclusions re:SEC- $\delta^{13}\text{C}$

## 1) Analysis of standards

- $\delta^{13}\text{C}$  independent of pH, ionic strength
- SEC retention time of sugars (i.e. neutrals) independent of pH, ionic strength
- SEC retention time of acids, bases a strong function of ionic strength and pH

## 2) Analysis of ambient aerosols

- GSM had small amounts of neutral and larger amounts of acidic OA.
- SEC produced most number of peaks at low pH, pattern of  $\delta^{13}\text{C}$  could be caused by oligomerization
- Less variability in SGP and BON results (but low pH runs have not been done yet).

## 3) “Pure” WSOC, potential probe into SOA mechanisms, could complement compound-specific source apportionment

# Acknowledgements

- 1) UCSC light isotope lab, Dyke Andreasen, manager
- 2) Jason Surratt, Cal Tech, for supplying smog chamber samples
- 3) Field site help – Jim Renfro (GSM NP), David Gay (BON), DOE staff at SGP ARM site
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Chuang research group

