# A Method to Isolate Carbonaceous Aerosols Soluble in Water by Organic Functional Group Using Solid Phase Extraction and Size-Exclusion Chromatography

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# Outline

- Group speciation and water-soluble organic carbon (WSOC)
- Method to group speciate WSOC involving XAD-8 resin and Size-Exclusion Chromatography (SEC)
- Ambient results from an urban site and prescribed burning
- Summary

# Group Speciation

- Organics are too complex for complete speciation with current technology
- One approach is to isolate organic aerosols into broad and comprehensive fractions
- Grouping may be driven by question of interest
  - What are the sources?
  - What are their properties/effects?
    (e.g. light absorption, toxicity, CCN activity…)

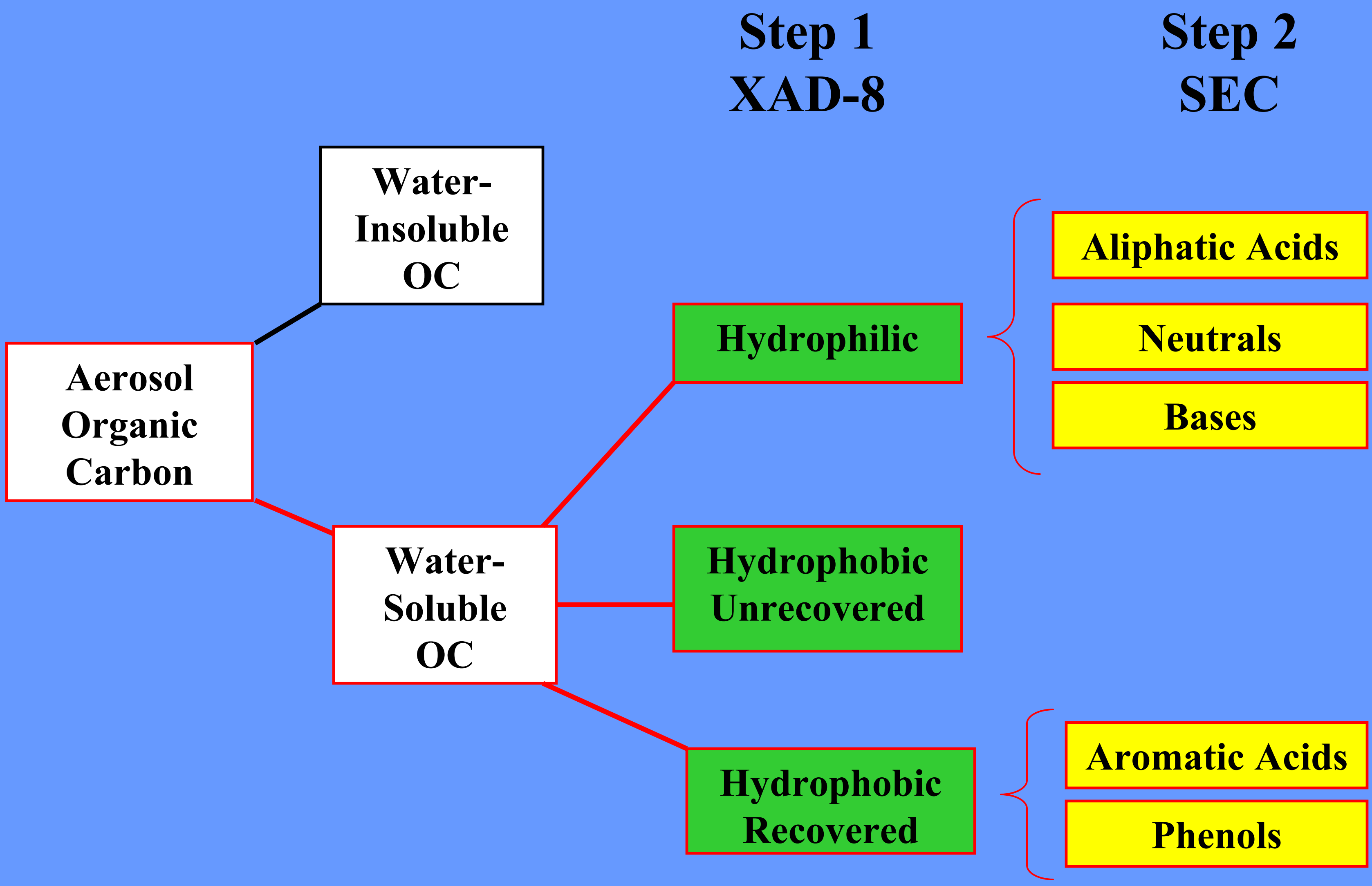
# Water-Soluble Organic Carbon: Why Measure?

- Little known about its chemical nature and abundance
  - Polar compounds not effectively measured via GC-MS
- Water is a natural solvent in the atmosphere
- WSOC can be large fraction of the total organic carbon (OC) (40 to 80%)
- Secondary Organic Aerosol (SOA) formation believed to be one of its major sources
- WSOC fraction may have unique and relevant physical properties

# The Off-line Method

- Collected integrated Hi-Volume quartz filter samples
- Extracted ¼ of filter in 125 ml Deionized Water
- Step 1 – Isolated hydrophilic and hydrophobic fractions with XAD-8 column
- Step 2 - Analyzed XAD-8 fractions with Size-Exclusion Chromatography (SEC) to obtain functional groups
- Obtained quantitative data from both steps using Total Organic Carbon (TOC) Analyzer
  - key to this approach is no organic eluents are needed

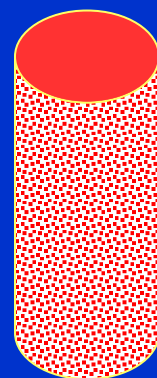
# Overview of Combined Methods



# Step 1: XAD-8 Column Sampling

Filtered (0.22μm) Liquid Sample
from Extracted Filter

0.1 M HCl
Adjust pH~2



-XAD-8 resin adsorbs hydrophobic acids and "neutrals" (**Hydrophobic** fraction)

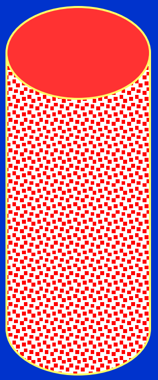
Penetrates

Sievers TOC analyzer

Measures **Hydrophilic** fraction (hydrophobic bases and hydrophilic acids, bases, neutrals)

# Step 1: XAD-8 Column Extraction

0.1 M NaOH



-**Unrecovered Hydrophobic fraction** remains adsorbed to XAD-8 (*aliphatics*)

Penetrates

Sievers TOC analyzer

Measures **Recovered Hydrophobic fraction (***aromatics***)**

# XAD-8 Penetration Tests

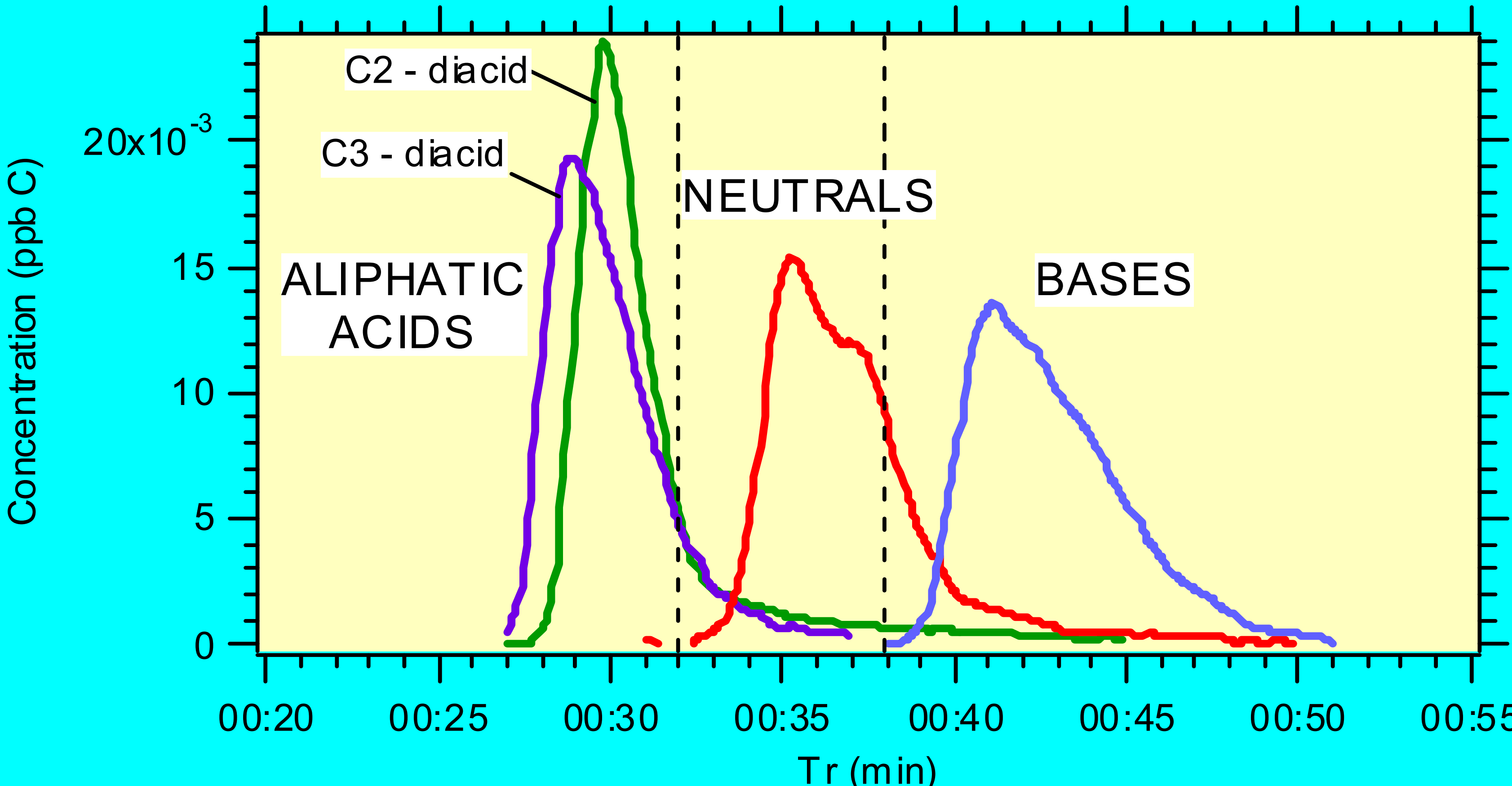
| | Hydrophilic | Recovered Hydrophobic | Unrecovered Hydrophobic |
|---|---|---|---|
| Mono-, Di-, Oxocarboxylic Aliphatic Acids | Carbons < 4 | | Carbons > 4 |
| Carbonyls | Carbons < 4 | | Carbons > 4 |
| Saccharides | X | | |
| Amines | X | | |
| Aromatics | | X | |
| Cyclic Acids | | | X |
| Organic Nitrates | | | X |

*Based on calibrations with 36 different compounds

# Step 2: SEC

- Traditionally used to determine the molecular weight of complex mixtures
- By not adjusting ionic strength and by buffering sample, able to separate organics by functional group with acids eluting first, bases last, and neutrals in between
  - Exploits secondary electrostatic interactions typically suppressed in SEC analysis
- 1 ml sample loop and 1 cm ID x 30 cm length glass column hand-packed with Superdex™-30 resin
- Eluent: pH 6.8 phosphate buffer
- ~85% recovery of compounds regardless of their functional group or XAD-8 fraction

# Hydrophilic SEC Calibration
## (Typical Results)

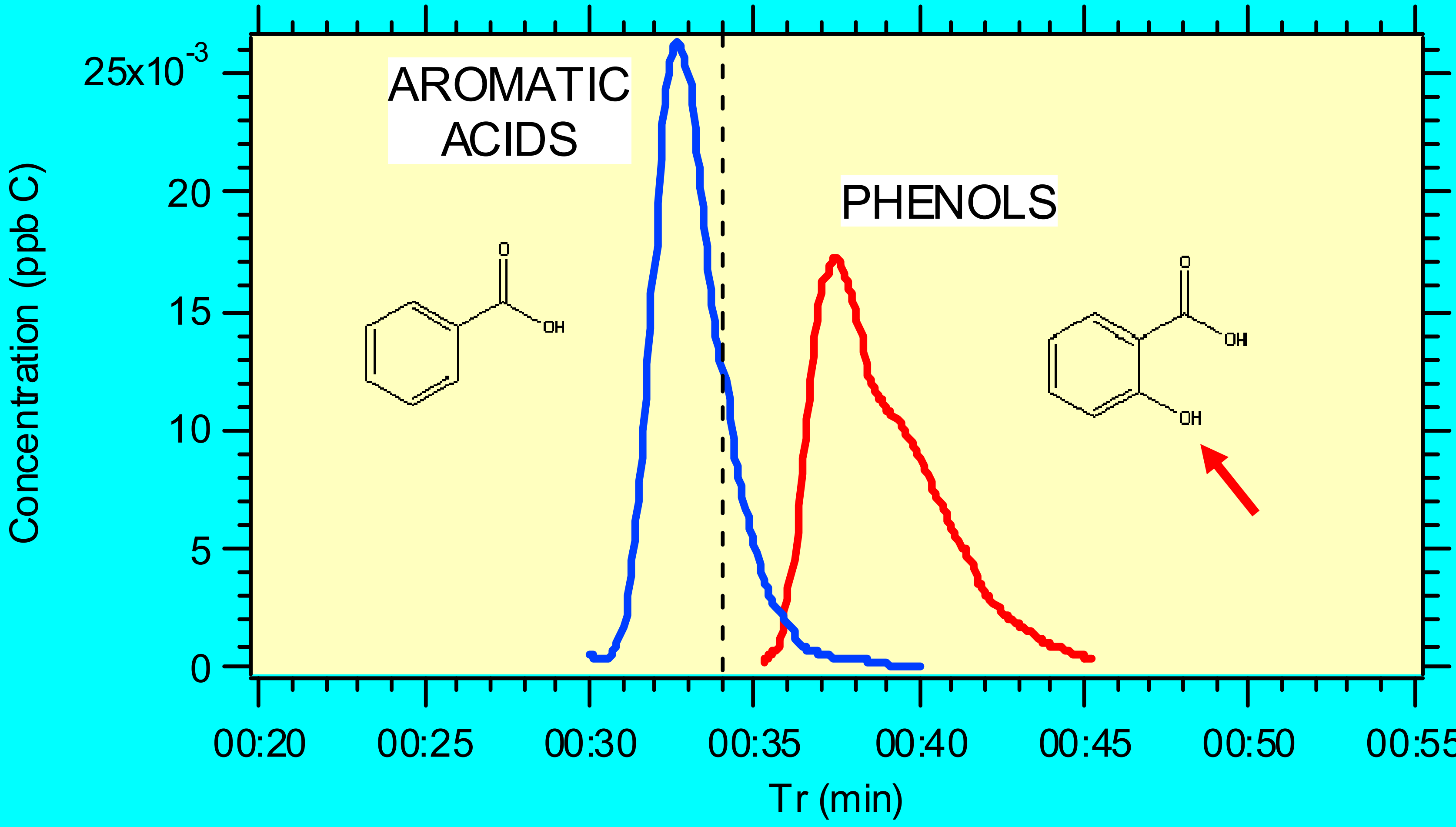



-Retention time < 32 min. = aliphatic acids

-32 min. < Retention time < 38 min. = neutrals

-Retention time >38 min. = bases

# Recovered Hydrophobic SEC Calibration
## (Typical Results)

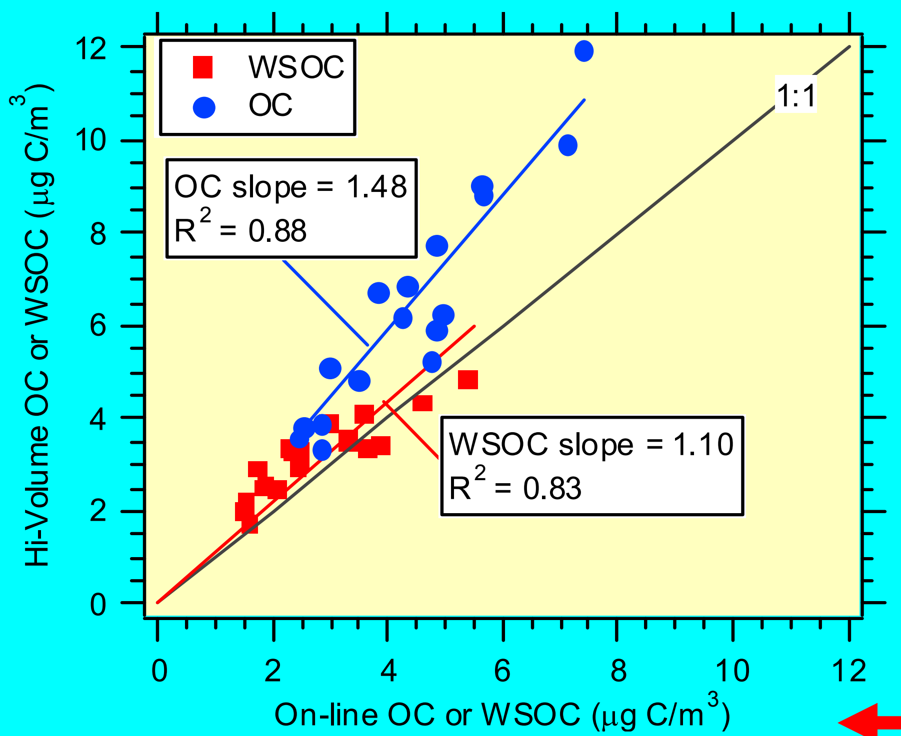



-Retention time < 34 min. = aromatic acids

-Retention time >34 min. = phenols

# Artifacts
# Hi-Volume Filter vs. Denuded On-line

Not Denuded

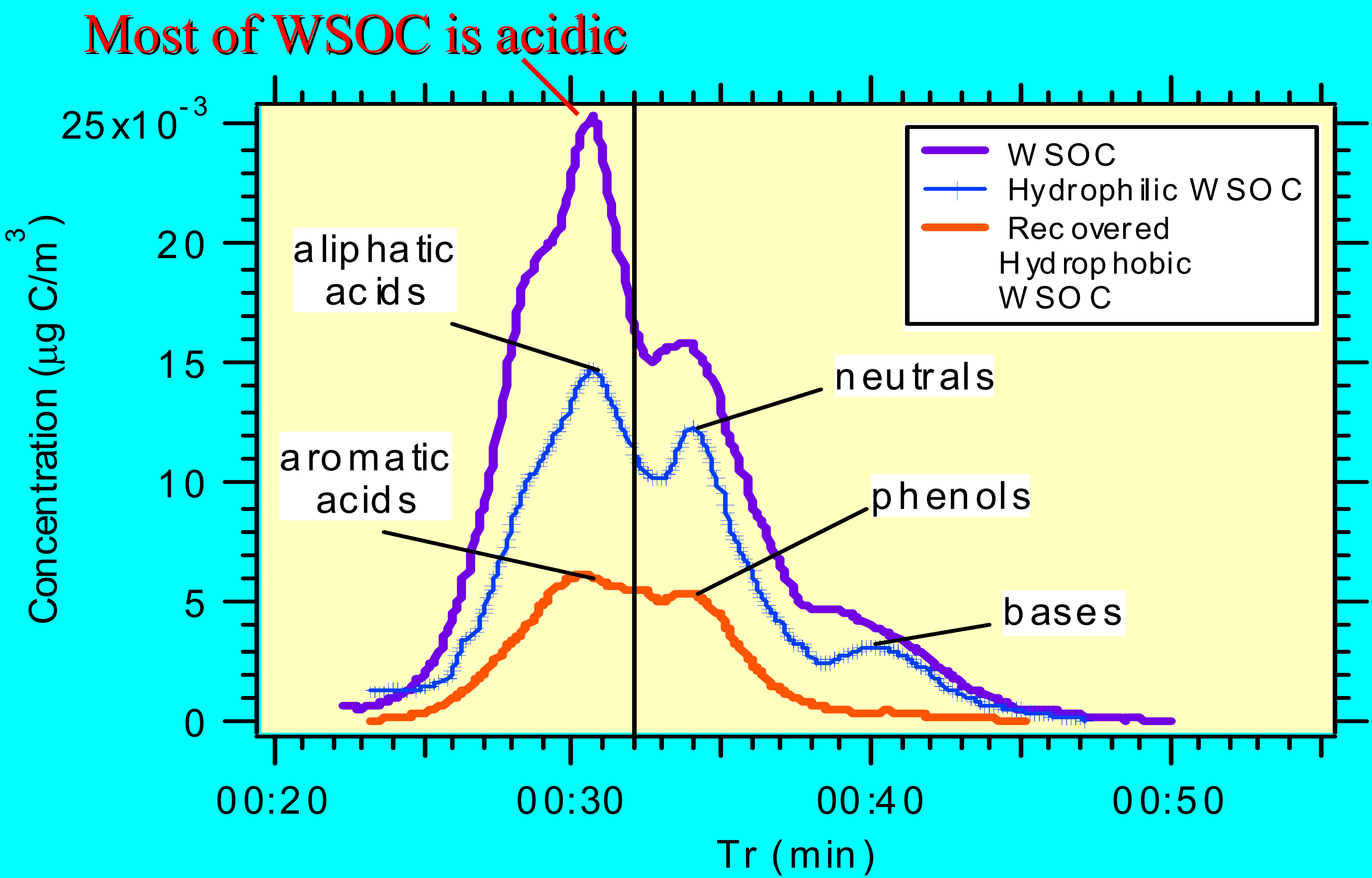



Denuded

<u>Positive Artifacts</u>:
-No evidence for a large positive artifact

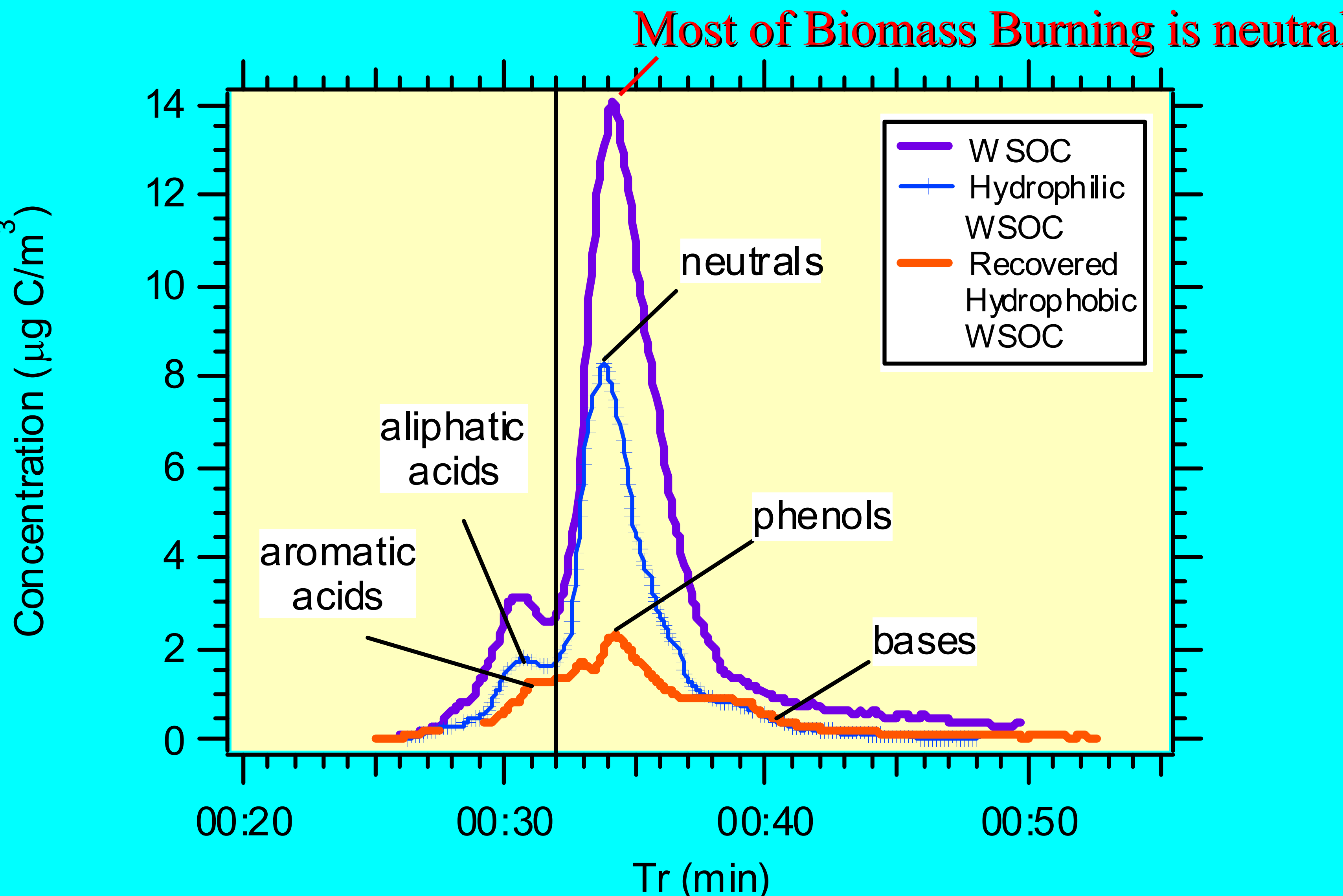
<u>Negative Artifacts</u>:
-Semi-volatile organic compounds likely not measured

# Example of Ambient Sample: **Atlanta Summer**



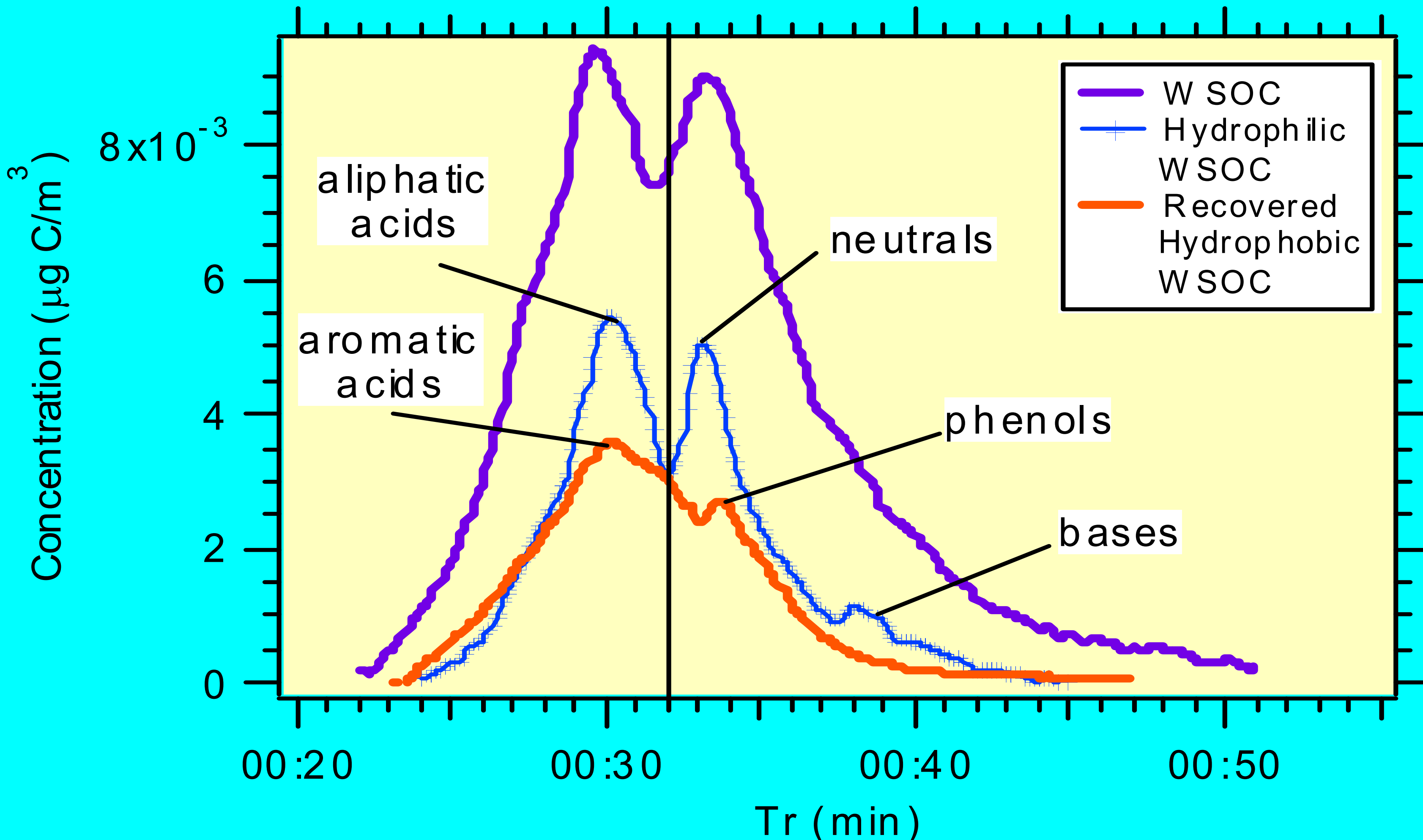

-Acidic peak dominates, consistent with current view that oxidation processes lead to acidic aerosol particles

# Example of Ambient Sample: **Biomass Burning**




-Contains mainly neutrals (i.e. saccharides) and phenolic compounds

# Example of Ambient Sample: **Atlanta Winter**

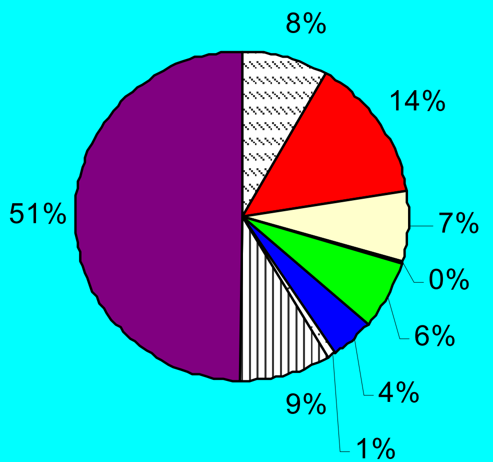



-Combination of summer and biomass; suggesting oxidation processes and larger contribution of biomass-like components?

# Fraction of OC

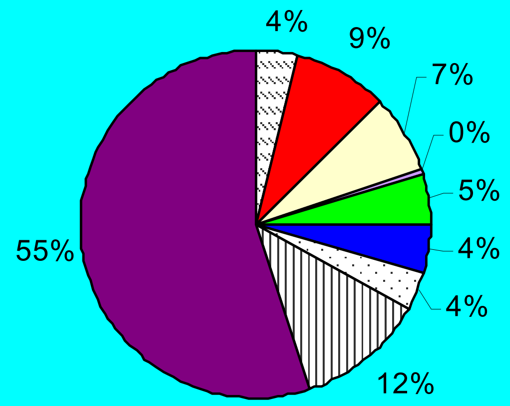
- Aliphatic Acids
- Neutrals
- Bases
- Hydrophilic SEC Unrecovered
- Aromatic acids
- Phenols
- Hydrophobic SEC Unrecovered
- XAD-8 Hydrophobic Unrecovered
- Water-Insoluble OC

**Summer**
**N = 21**



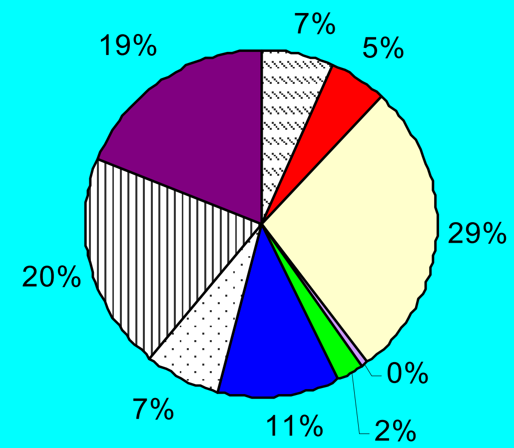

**~20% acids**
**mostly C < 4 acids**

**Winter**
**N = 10**




**highest WIOC**

**Biomass Burning**
**N = 2**

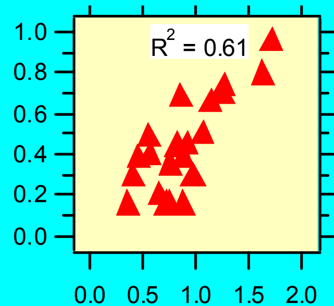



**highest**
**neutrals/phenols**

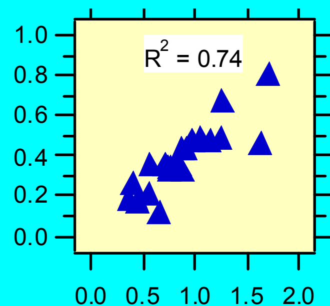
# Atlanta Summer Correlations

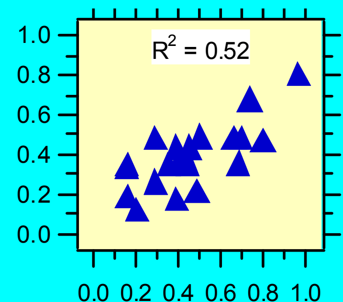
Hydrophilic aliphatic acids | Hydrophilic neutrals | Hydrophobic aromatic acids

## Hydrophilic neutrals

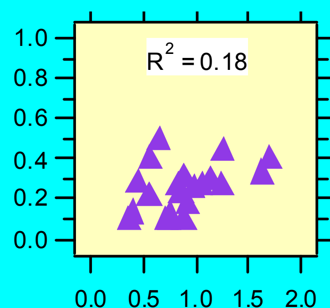


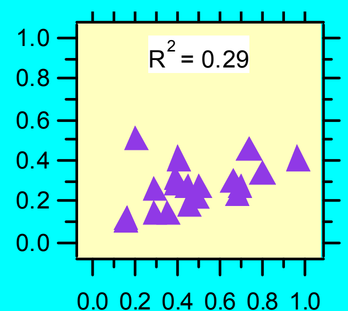

## Hydrophobic aromatic acids

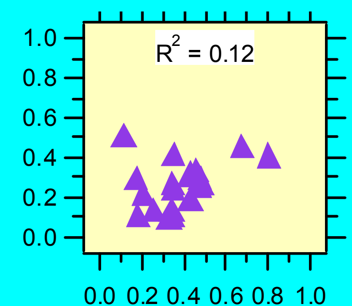



## Hydrophobic phenols



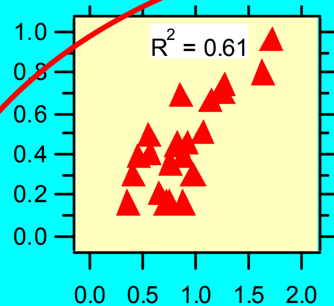



# Atlanta Summer Correlations

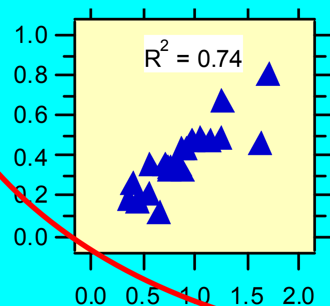
Hydrophilic aliphatic acids | Hydrophilic neutrals | Hydrophobic aromatic acids

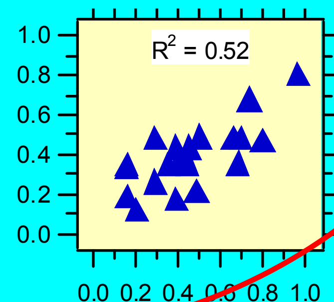
**Hydrophilic neutrals**



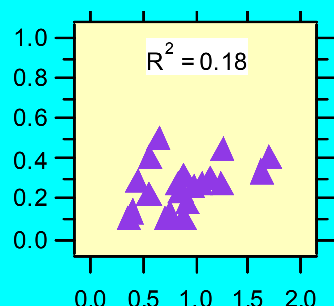

**Aliphatic acids and aromatic acids most correlated**

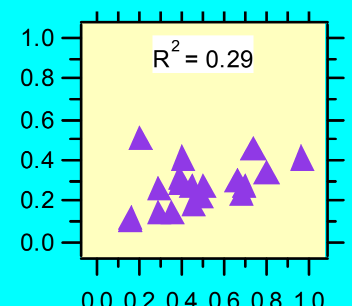
**Hydrophobic aromatic acids**

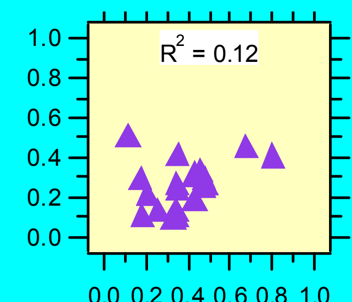



**Hydrophobic phenols**



# Other Summer Facts

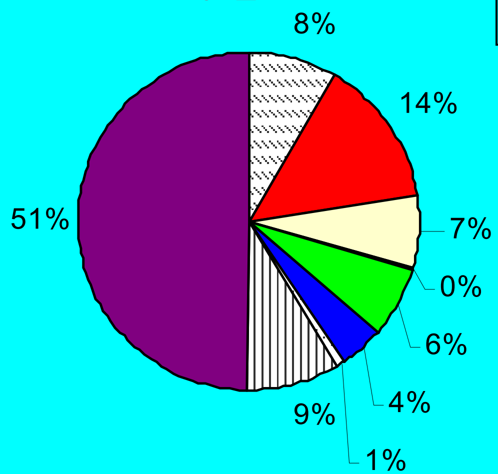
- Based on 24-hour averaged data, aliphatic (C<4) and aromatic acids correlated with:
  - Carbon monoxide ($R^2$ = 0.65 to 0.73)
  - Elemental carbon ($R^2$ = 0.64 to 0.66)
- Correlation with EPA PAMS Volatile Organic Compounds (VOCs)
  - Aliphatic acids with compounds from mobile source emissions
  - Neutrals and phenols not significantly correlated
- Oxalate only ~3% of aliphatic acid fraction suggesting this fraction may instead be oxocarboxylic acids
  - (Semi-volatile organics not measured effectively with Hi-Volume sampler?)
- No functional groups correlated with temperature

# Atlanta Summer: Typical vs. PM Event

- Aliphatic Acids
- Aromatic acids
- XAD-8 Hydrophobic Unrecovered
- Neutrals
- Phenols
- Bases
- Hydrophobic SEC Unrecovered
- Water-Insoluble OC
- Hydrophilic SEC Unrecovered

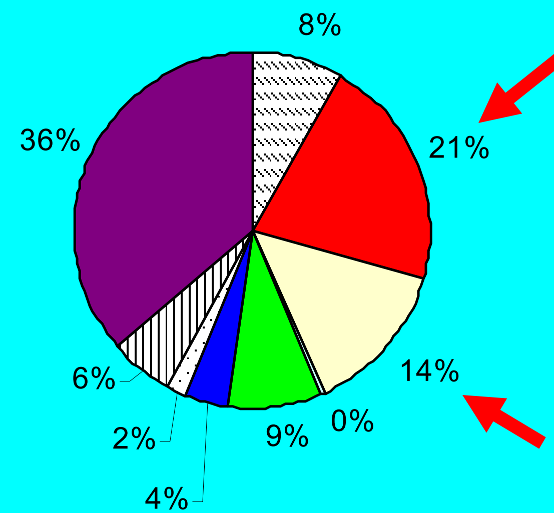
Fractions of OC

## Typical




WSOC/OC = 0.49
~14% of OC aliphatic acids
Ozone = 0.025 ppmv

## PM Event




WSOC/OC = 0.64
~21% of OC aliphatic acids
Ozone = 0.069 ppmv

# Other Supporting Results

(More details in talk 6D5 on Wed. at 12:15 pm)

- Solid State $^{13}$C-NMR (Sannigrahi, Sullivan, Weber, Ingall, *ES&T*, in press)
  - $^{13}$C-NMR on summer and biomass burning sample
  - No aromatic peaks found in hydrophilic spectra, agrees with XAD-8 calibration results
  - C-alkyl peaks highest in recovered hydrophobic fractions suggesting highly substituted aromatics

- Surface Tension Depression
  - Tensiometer measurements show only hydrophobics reduce surface tension, hydrophilics do not
  - More details in talk 11A3

- Light Absorption (absorbance per carbon mass)
  - Phenolic compounds followed by aromatic acids most effective light absorbers, evidence for conjugated bonds

# Summary

- SEC performed on XAD-8 isolated fractions with direct TOC analysis can chemically quantify WSOC hydrophilic and hydrophobic functional groups
  - Enables quantitative chemical group speciation of over 50% of OC, higher during summer PM events

- Speciation results correspond with current views:
  - **Atlanta Summer** – aliphatic acids 29% µg C/µg C of WSOC
  - **Biomass Burning** – neutrals 34% µg C/µg C of WSOC and phenols 14% µg C/µg C of WSOC
  - **Atlanta Winter** – mixture of other two

- Atlanta PM events (SOA) leads to largest increases in C<4 aliphatic acids and neutrals. Investigate with LC-MS (oxocarboxylic acids)?

- During summer (e.g. higher SOA) aliphatic acids correlated with
  - Aromatic acids – $R^2 = 0.74$
  - Elemental Carbon – $R^2 = 0.64$
  - Carbon monoxide – $R^2 = 0.73$
  - VOCs from mobile sources
  - Oxidation of mobile source emissions leads to small-chain aliphatic and aromatic acids? Role of biogenics?