

# Investigation of the Physical Properties of Fine Particle Water-Soluble Organic Carbon Aerosols

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# Outline

- Water-Soluble Organic Carbon (WSOC)
- Brief overview of method to group/speciate WSOC involving XAD-8 resin and Size-Exclusion Chromatography (SEC)
- Solid State  $^{13}\text{C}$ -Nuclear Magnetic Resonance ( $^{13}\text{C}$ -NMR) on WSOC, hydrophilic, and recovered hydrophobic fractions from an urban site and biomass burning
- Light Absorption
- Summary

## Why is WSOC of interest?

- A large fraction of total organic carbon (OC)
- Secondary Organic Aerosol (SOA) formation leads to WSOC
- WSOC has unique and important physical properties

## But:

- Only small fraction of WSOC identified because polar oxygenated organic compounds not analyzable by GC-MS

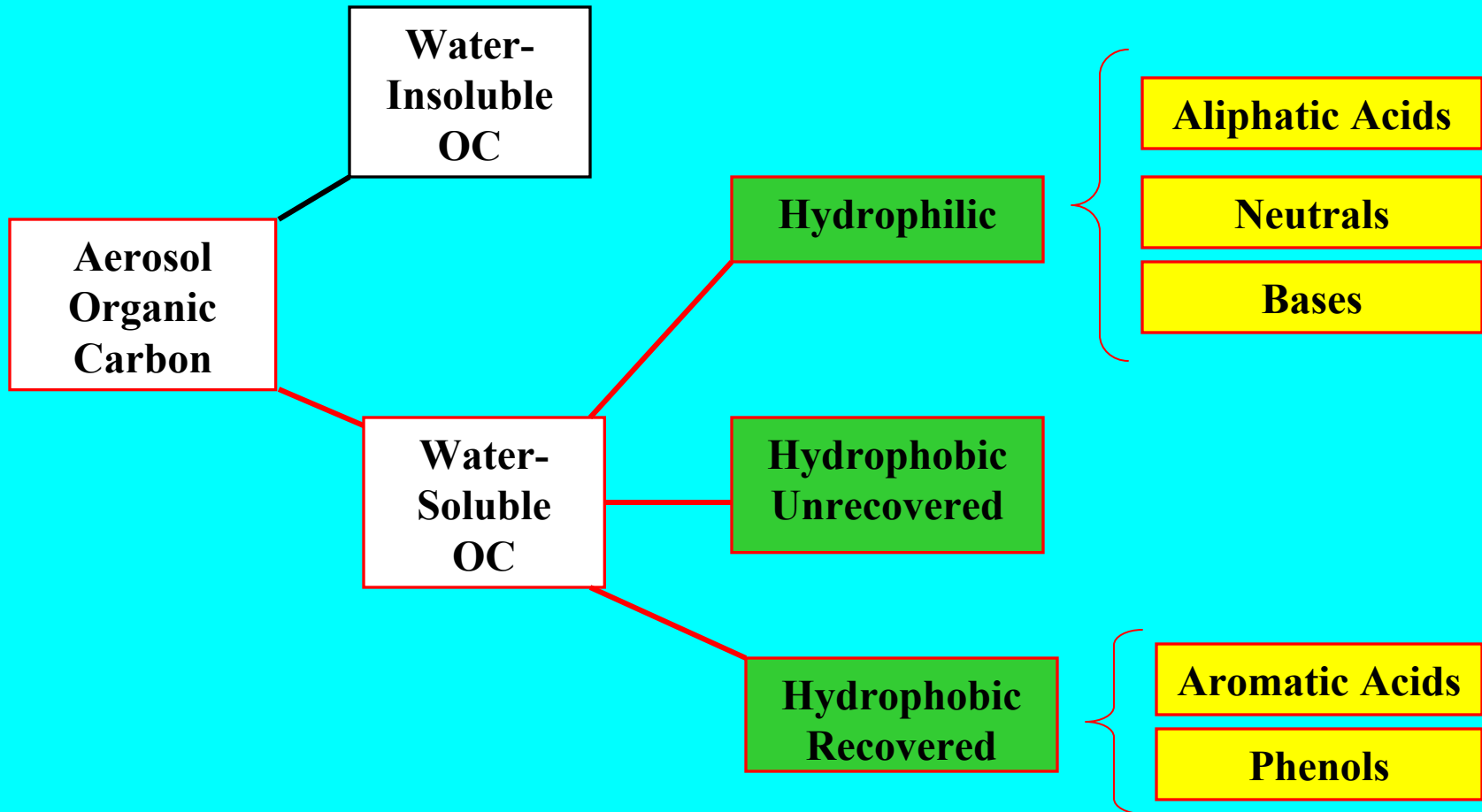
## Solution:

- Use methods to comprehensively group speciate WSOC (e.g. Decesari et al., *JGR*, 2000)
- Isolated fractions of WSOC can be analyzed
  - Droplet surface tension (Asa-Awuku et al., *AAAR*, 2005)
  - <sup>13</sup>C-NMR
  - **Visible Light Absorption**

# Overview of Method to Chemically Fractionate WSOC

**Step 1**  
**XAD-8**

**Step 2**  
**SEC**



# XAD-8 Calibration (based on 36 standards)

	100% Penetration	0% Penetration	
	Hydrophilic	Recovered Hydrophobic	Unrecovered Hydrophobic
<b>Mono-, Di-, Oxocarboxylic Aliphatic Acids</b>	<b>Carbons &lt; 4</b>		<b>Carbons &gt; 4</b>
<b>Carbonyls</b>	<b>Carbons &lt; 4</b>		<b>Carbons &gt; 4</b>
<b>Saccharides</b>	<b>X</b>		
<b>Amines</b>	<b>X</b>		
<b>Aromatics</b>		<b>X</b>	
<b>Cyclic Acids</b>			<b>X</b>
<b>Organic Nitrates</b>			<b>X</b>

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<b>Cyclic Acids</b>			<b>X</b>
<b>Organic Nitrates</b>			<b>X</b>

# Solid State $^{13}\text{C}$ -NMR of Organic Fine Aerosol Particles

Investigate Urban and Biomass Burning Particles:

1. WSOC
2. Hydrophilic WSOC
3. Recovered Hydrophobic WSOC

Sannigrahi, Sullivan, Weber, Ingall, *ES&T*, in press.

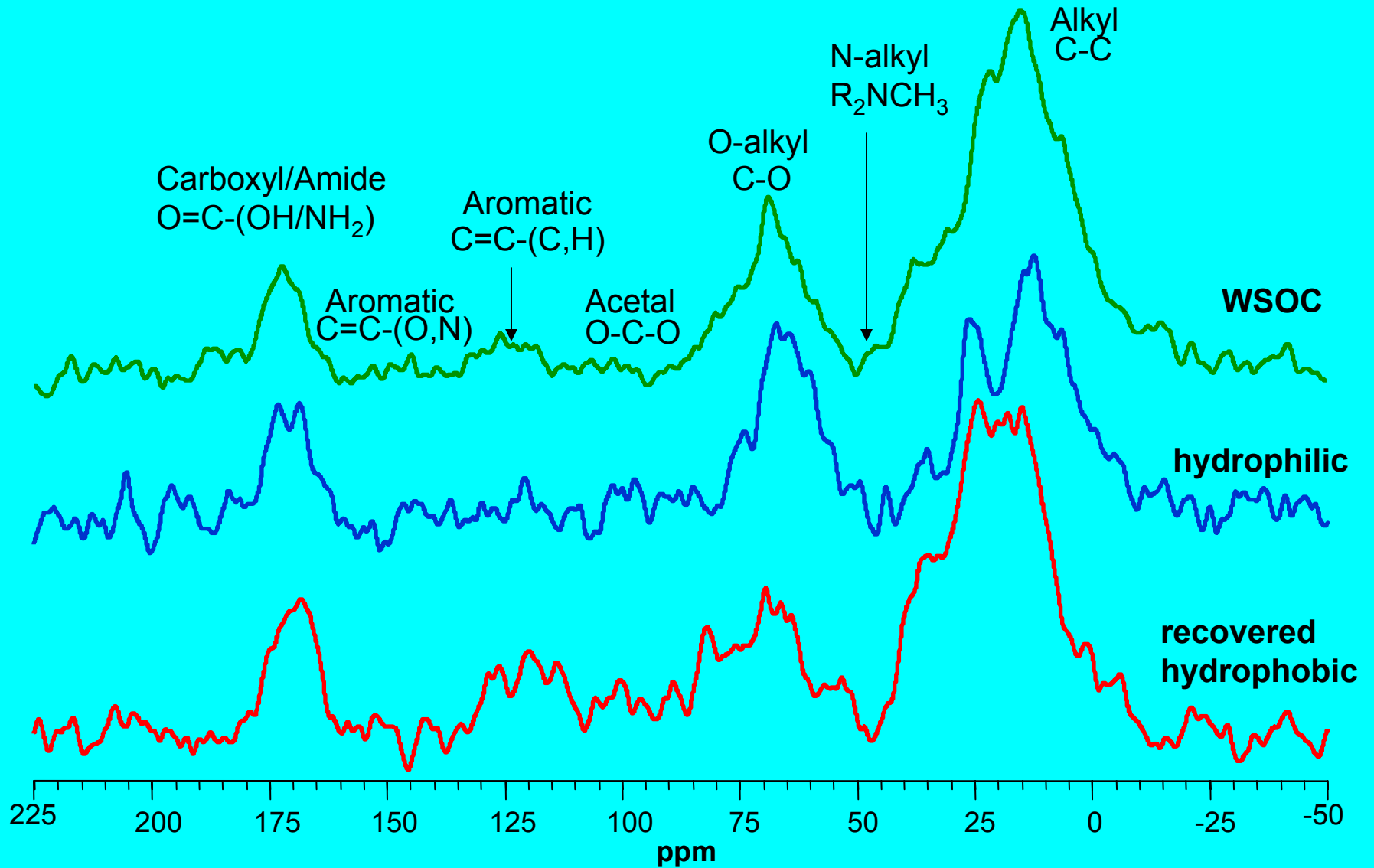
# Solid State $^{13}\text{C}$ -NMR

- Provides independent measure of XAD-8 isolated sample composition
- Provides a comprehensive and semi-quantitative measure of types of carbon bonds in sample
- Disadvantage:
  - Low sensitivity, required 8 24-hour integrated Hi-Volume filter samples from urban Atlanta

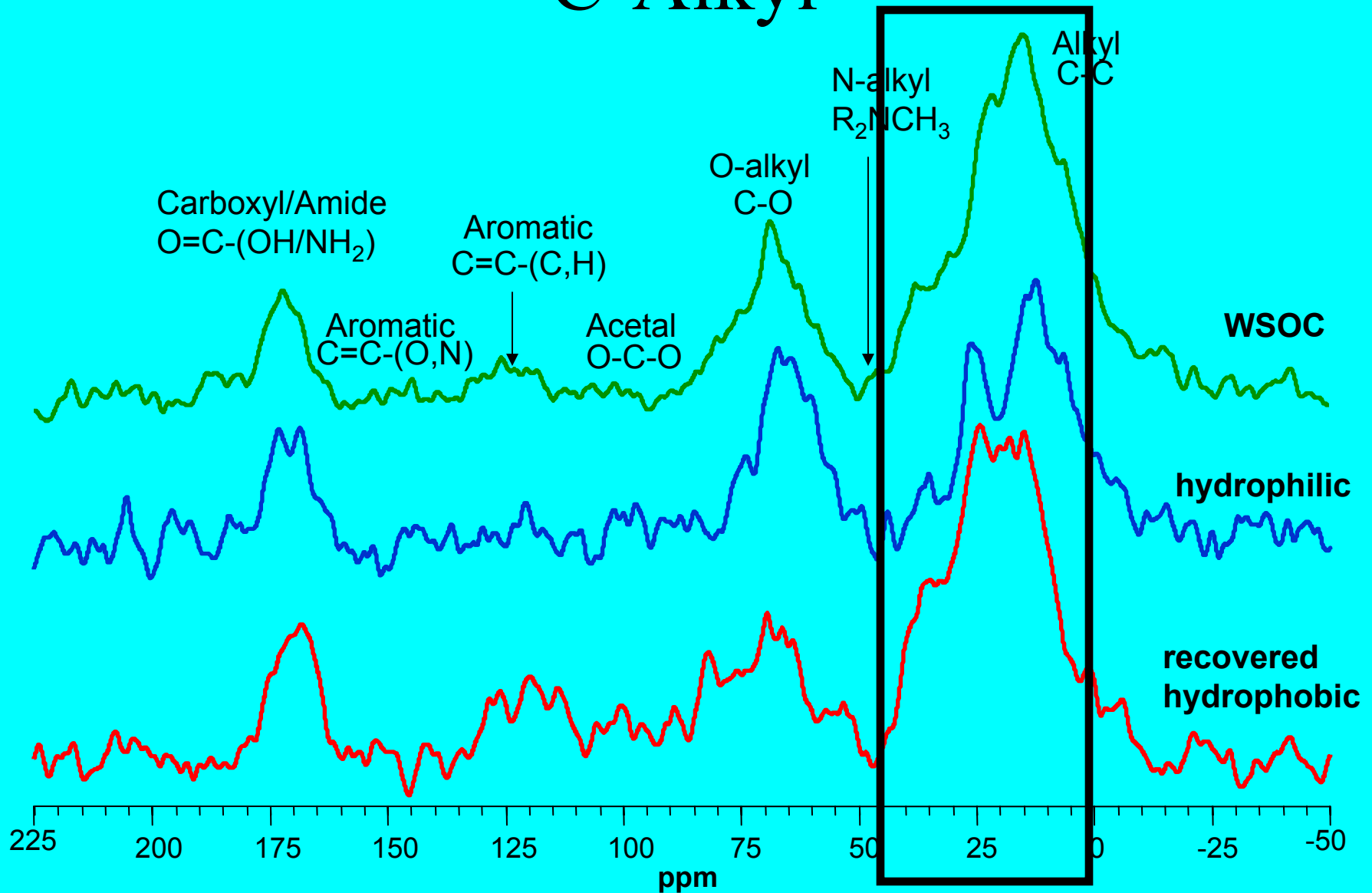
# Solid State $^{13}\text{C}$ -NMR

- 25-30 mg C (40-70 mg total sample) obtained by freeze drying XAD-8 liquid extracts
- Spectra split into 7 spectral regions on ppm scale and integrated using a commercial software package
- From peak areas able to understand major overall trends in organic C composition

# Atlanta Summer

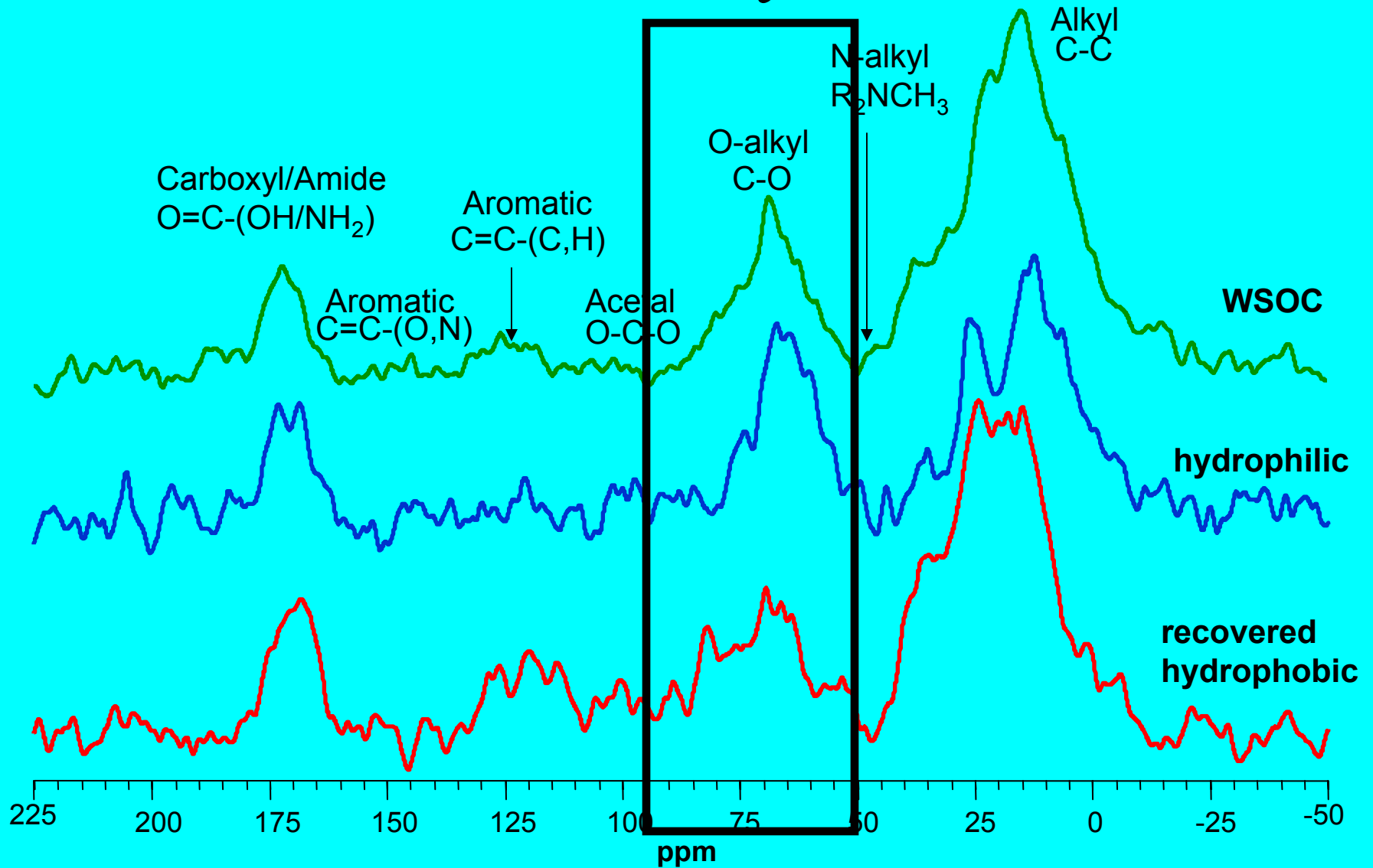


# C-Alkyl



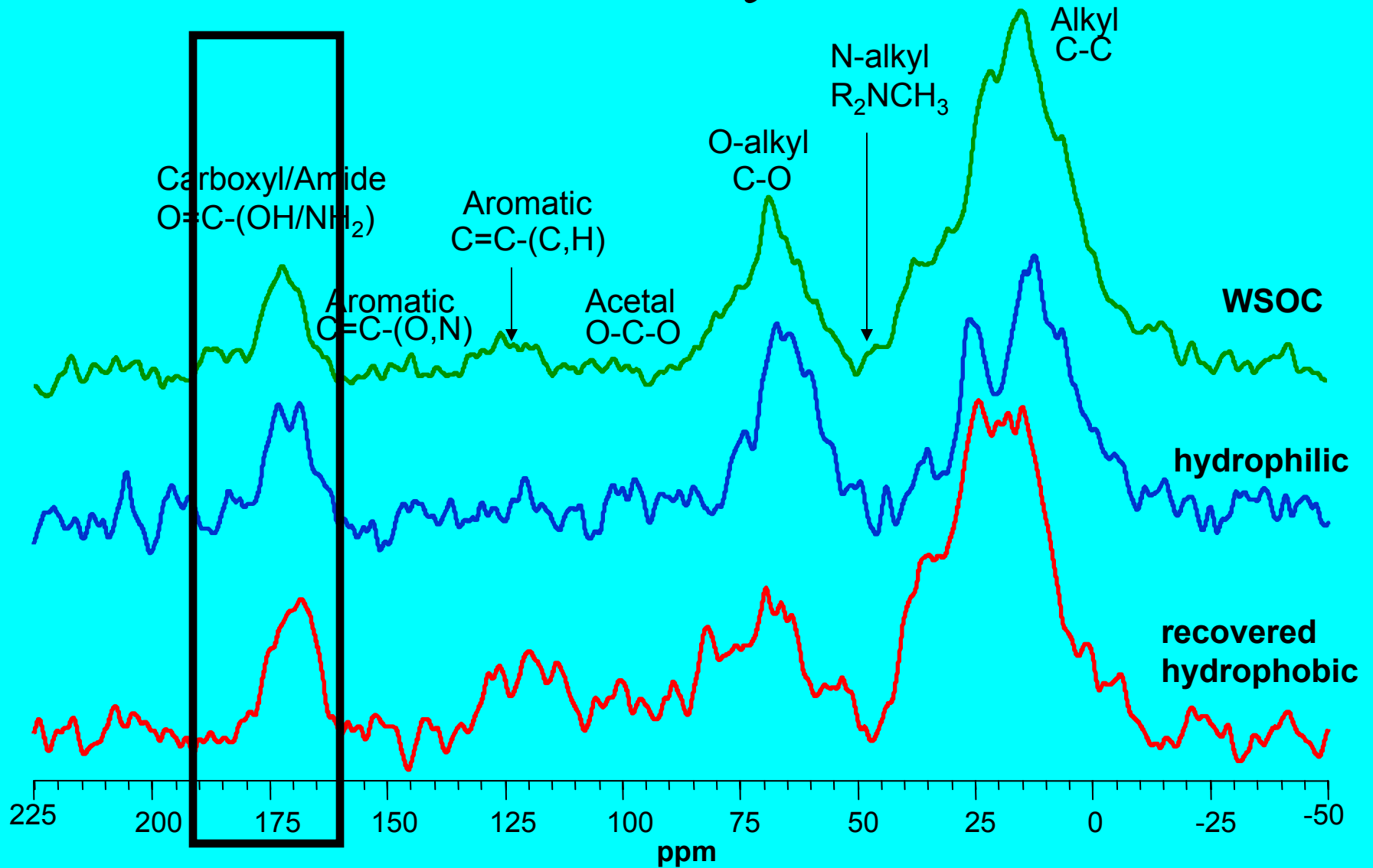
-Aliphatic and aromatic C in carboxylic acids, amides, and alcohols

# O-Alkyl



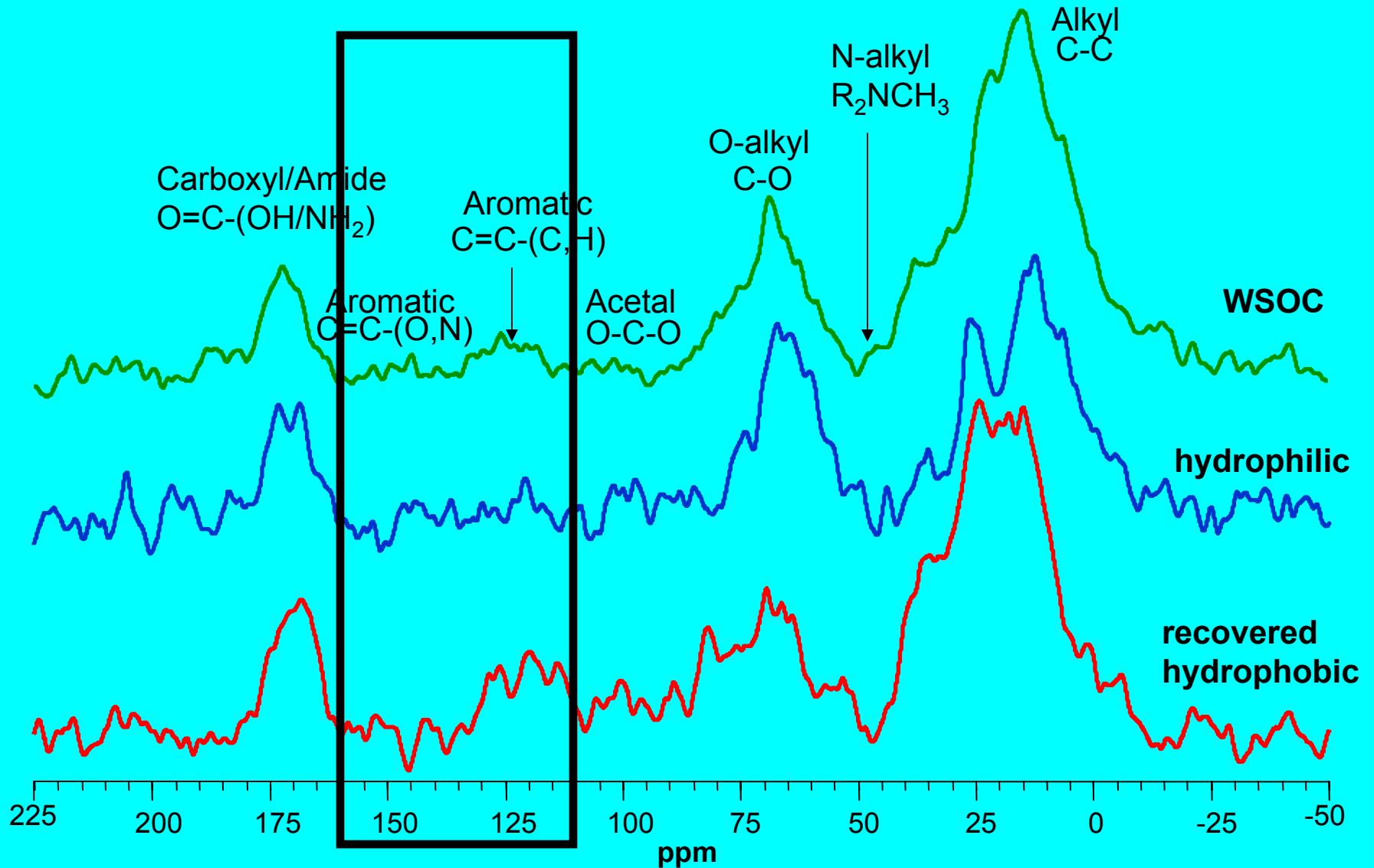
-10:1 ratio of O-alkyl to anomeric peak suggesting not associated with ring polysaccharides

# Carboxylic



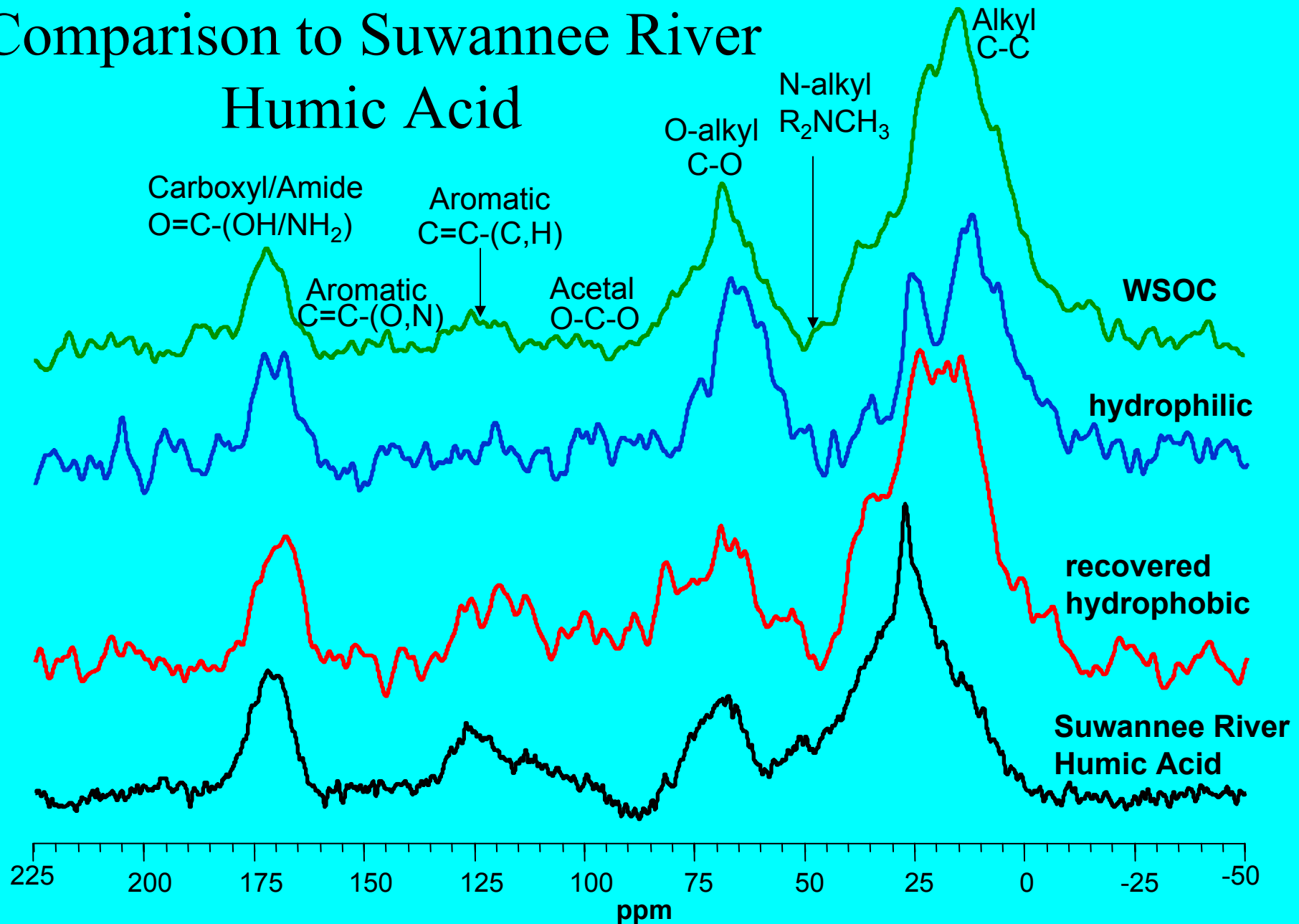
-10% of carbon associated with carboxylic acids, likely aliphatic

# Aromatic



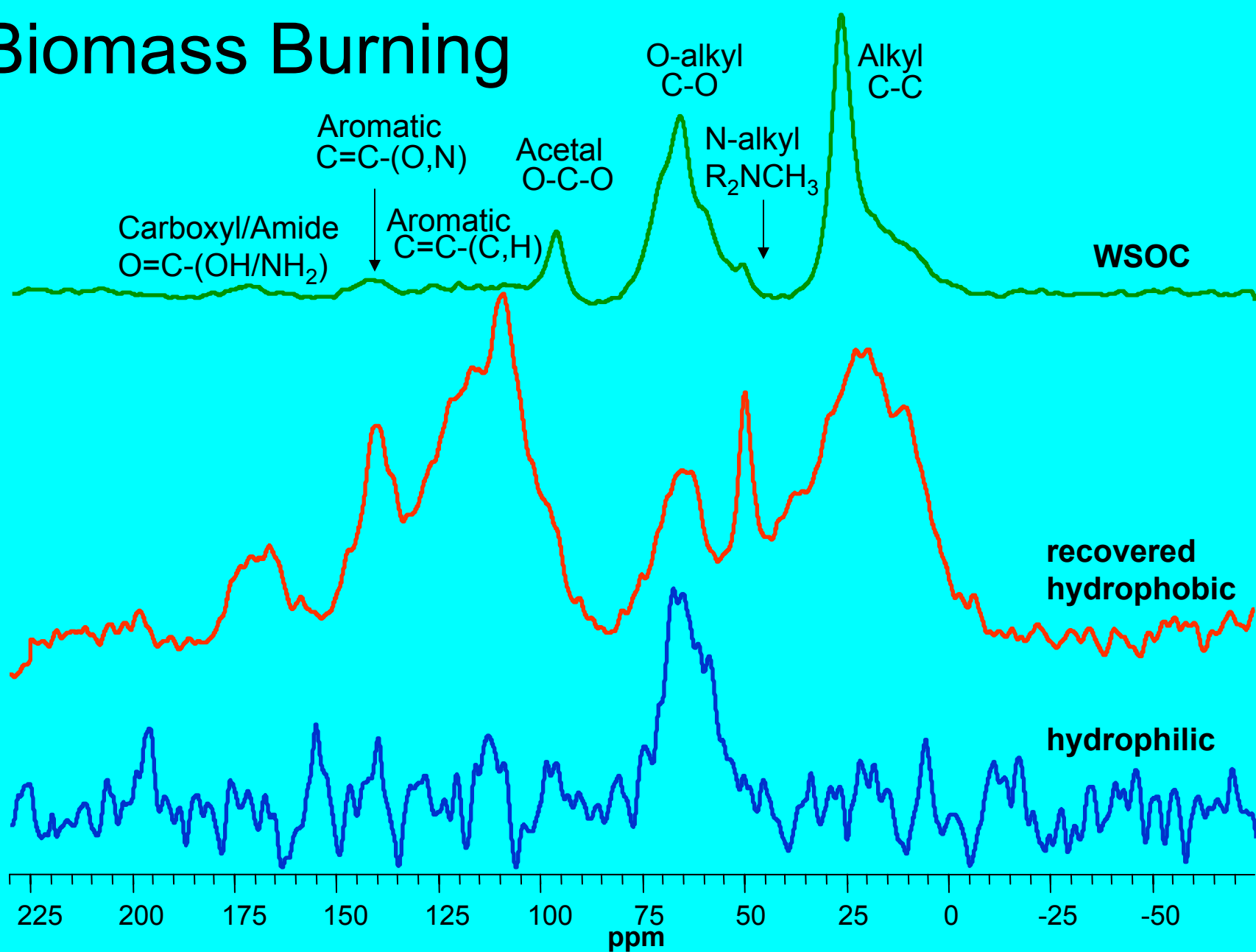
- Only detected in WSOC and recovered hydrophobic fraction
- Unsubstituted or substituted by C-alkyl, carboxylic acid, or O-alkyl

# Comparison to Suwannee River Humic Acid

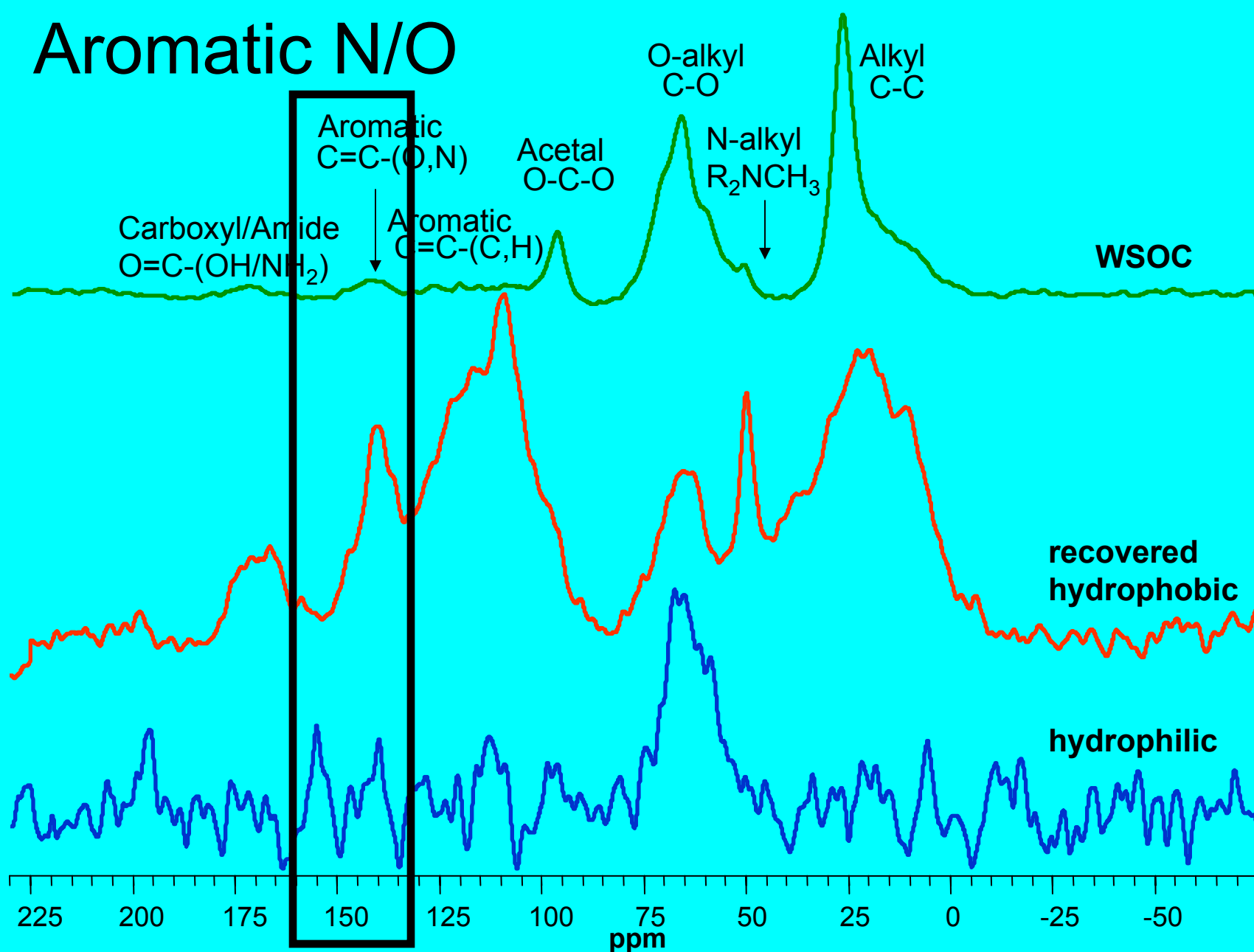


-Only qualitatively similar, Suwannee River humic acid higher carboxylic acid/aromatic and lower C/O-alkyl

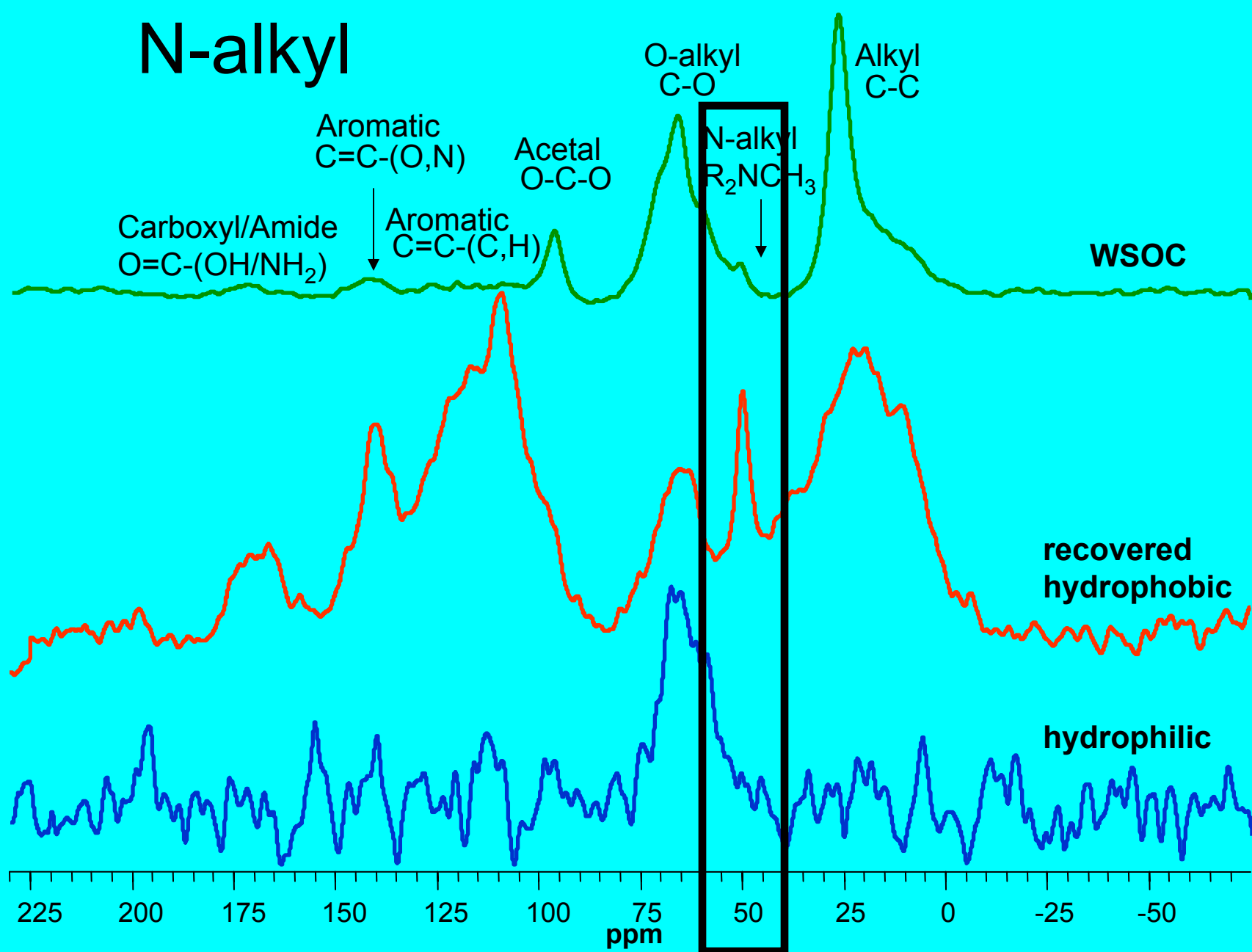
# Biomass Burning



# Aromatic N/O

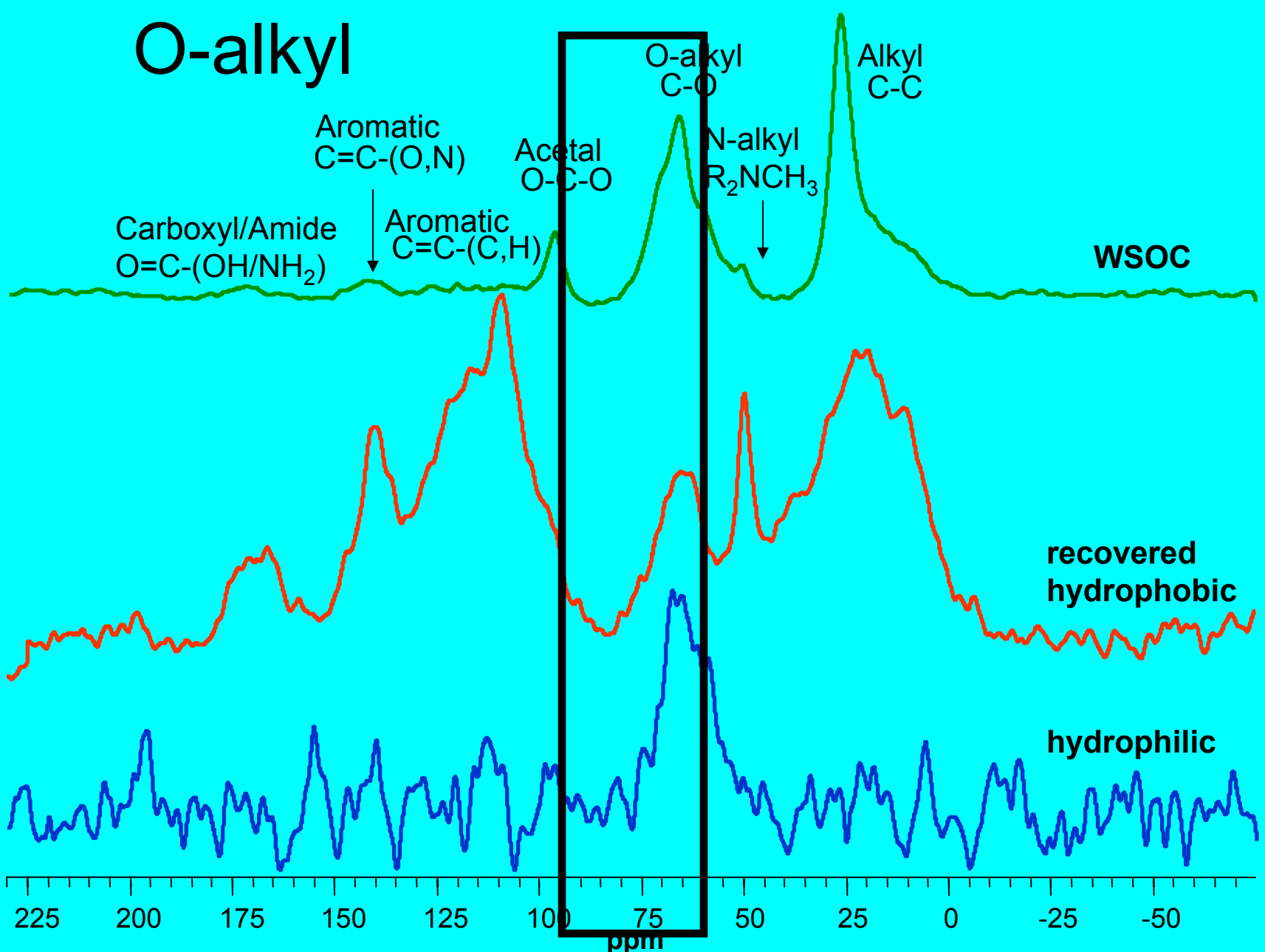


-Peak at ~145 ppm in WSOC and recovered hydrophobic fraction



-Larger N-alkyl peak, can be present in aliphatic amines

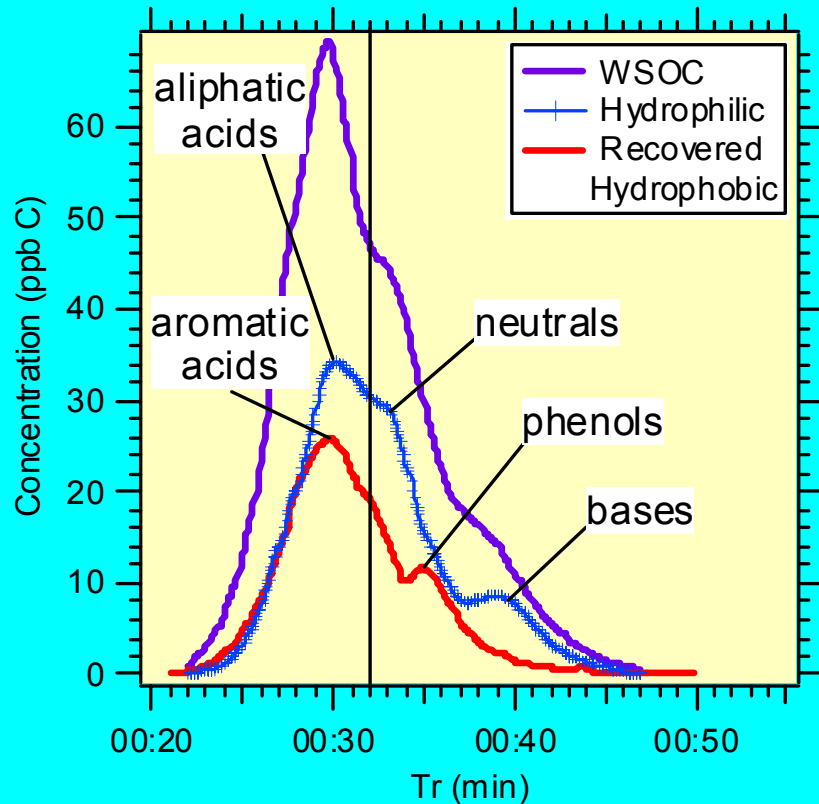
# O-alkyl



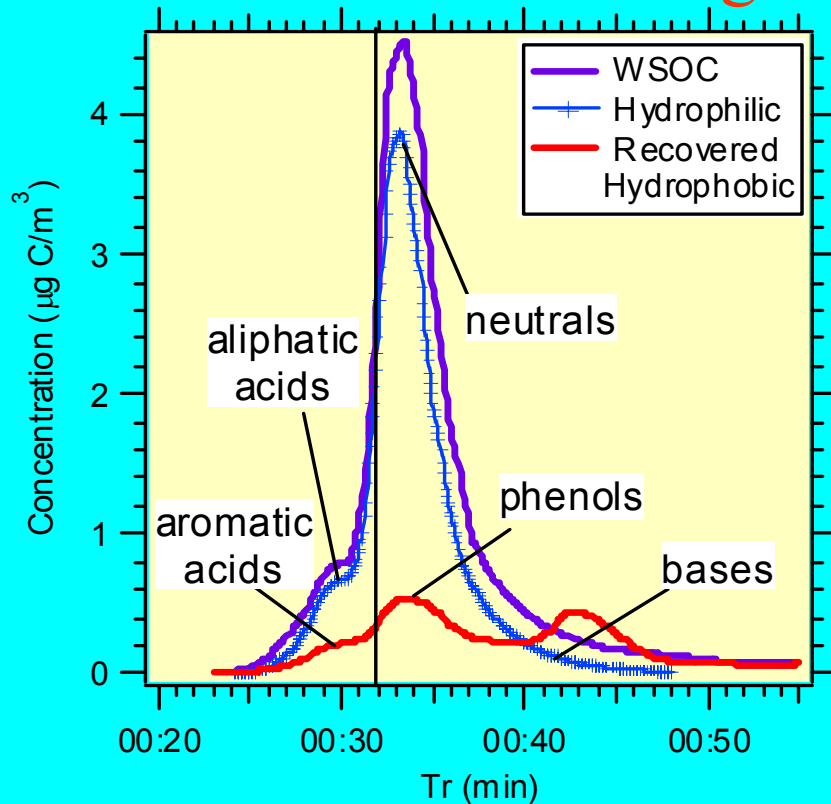
-5:1 ratio of O-alkyl to anomeric peak suggesting associated with ring polysaccharides

# SEC Chromatograms of $^{13}\text{C}$ -NMR Samples

Summer



Biomass Burning



- Use SEC to determine the % of each functional group in hydrophilic and recovered hydrophobic fractions
- Compare SEC to % peak area from  $^{13}\text{C}$ -NMR

# Hydrophilic Comparison

## Summer

SEC

$^{13}\text{C}$ -NMR

58% aliphatic acids

60% C-alkyl

23% neutrals

24% O-alkyl

16% unrecovered

10% carboxylic

2% bases

7% N-alkyl

## Biomass Burning

SEC

$^{13}\text{C}$ -NMR

67% neutrals

76% O-alkyl

28% unrecovered

24% N-alkyl

5% aliphatic acids

All others 0

0% bases

\*XAD-8/SEC is by functional group vs.  $^{13}\text{C}$ -NMR is by C bond

-SEC and  $^{13}\text{C}$ -NMR qualitatively agree

-No aromatic peaks found in  $^{13}\text{C}$ -NMR spectra of hydrophilic fraction, agrees with XAD-8 calibration results

# Recovered Hydrophobic Comparison

Summer		Biomass Burning	
SEC	<sup>13</sup> C-NMR	SEC	<sup>13</sup> C-NMR
34% aromatic acids	60% C-alkyl	47% phenols	36% C-alkyl
11% phenols	18% O-alkyl	0% aromatic acids	22% alkyl aromatics
54% unrecovered	9% carboxylic	53% unrecovered	12% anomeric/ acetal C
	8% alkyl aromatic		9% O-alkyl, N/O aromatics

- Based on calibration results would expect <sup>13</sup>C-NMR to be mostly aromatics, not C-alkyls
- Aromatics may be highly substituted?

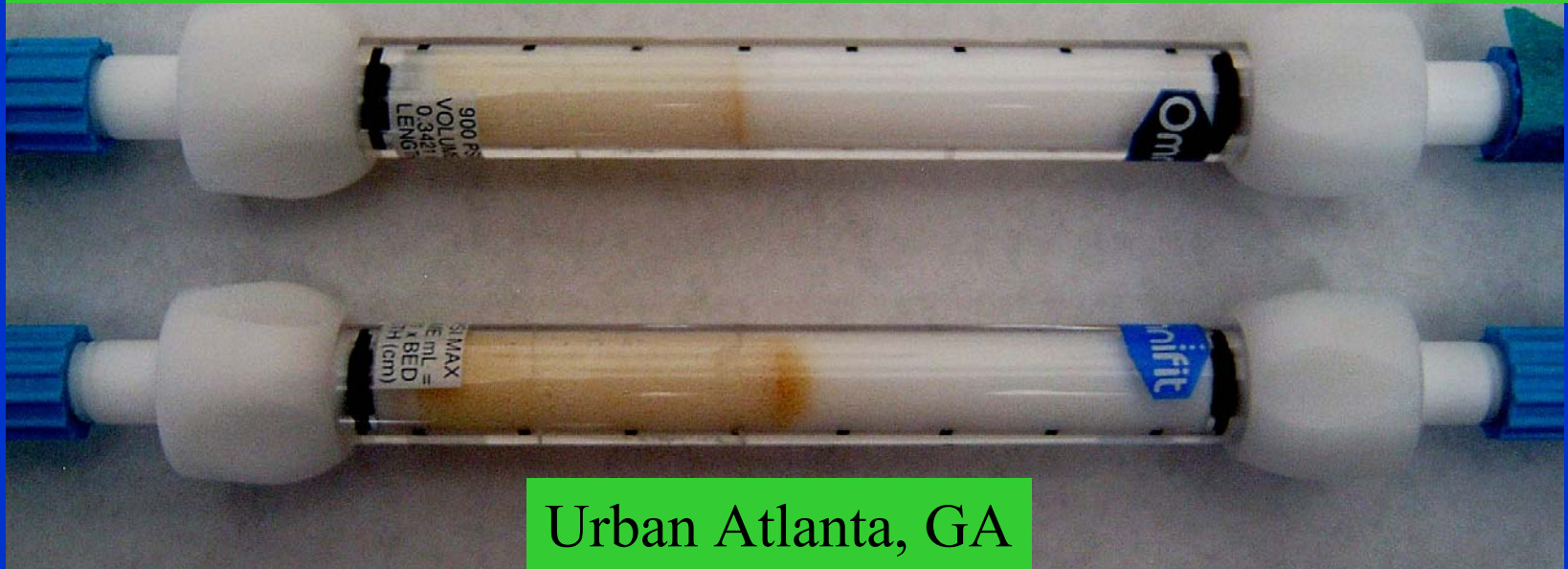
# Light Absorption by Organic Fine Aerosol Particles

## -Preliminary Results-

- Many studies report HULIS (polyacids, high molecular weight compounds) is brown
- Ambient studies suggest OC is light absorbing (e.g. Malm et al., *JGR*, 1996)
- Of our isolated compounds, which absorb light?

# Color of XAD-8 Retained Compounds of the Ambient $PM_{2.5}$ Organic Aerosol

Biomass Burning Smoke from Ft. Benning in Columbus, GA



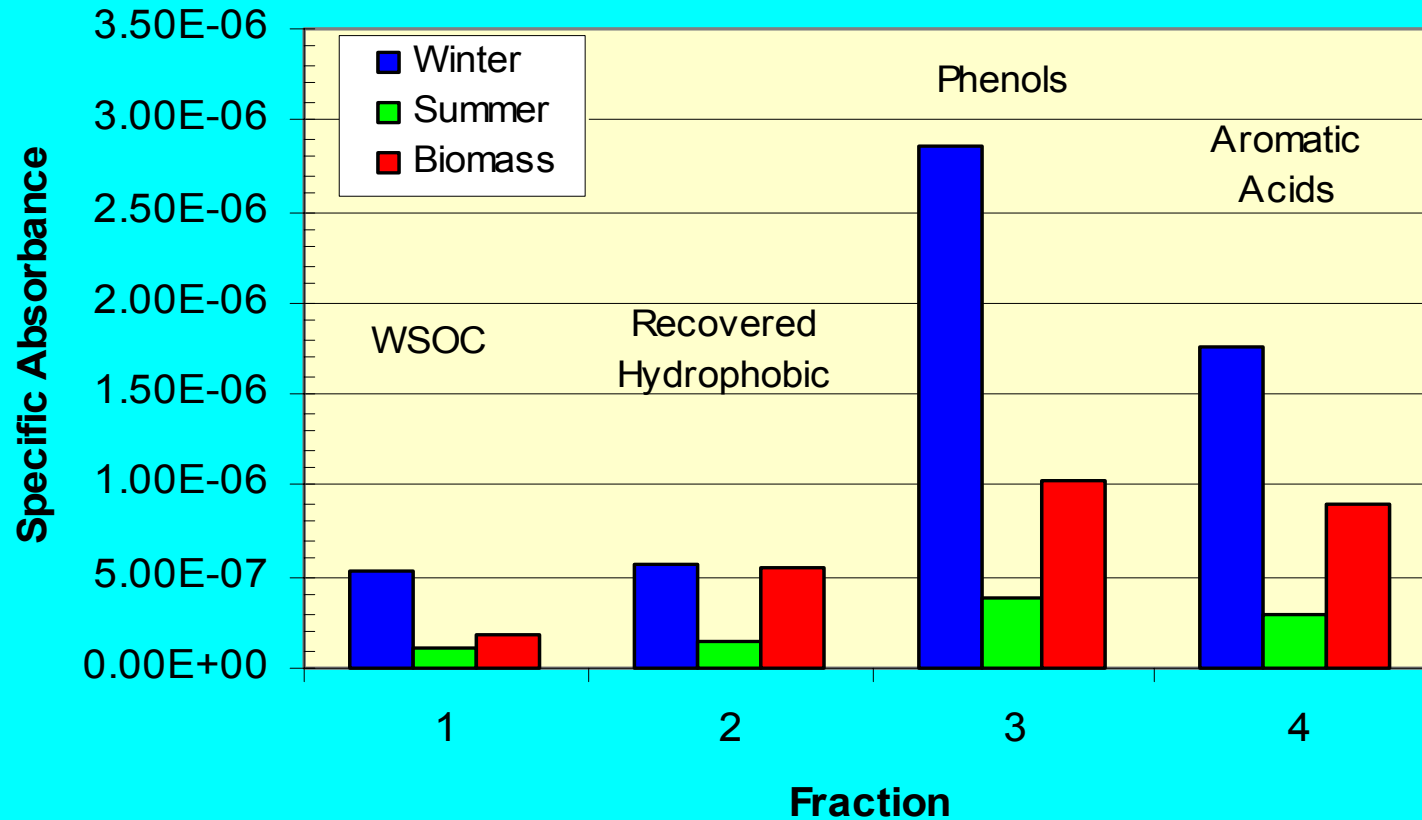
Urban Atlanta, GA

- Significant color is removed when column extracted with sodium hydroxide (NaOH), implying the color is due in part to recovered hydrophobic compounds
- No color observed in hydrophilic species

# Light Absorption Method

- Integrated filter samples included Atlanta Summer, Atlanta Winter, and Biomass Burning
- Collected aromatic acids (<34 minutes) and phenols (>34 minutes) from SEC of recovered hydrophobic XAD-8 fraction
- Blank (or Reference Cell) was deionized water passed through XAD-8/SEC
- Measured carbon concentration for all fractions with TOC Analyzer
- Absorption Detector = Hewlett Packard 8451a diode array spectrophotometer scanning from 400-800 nm

# Visible Light Absorption Results (Absorbance per Carbon Mass)



- Phenols more effective light absorbers than the aromatic acids, especially in Winter followed by Biomass Burning
- Winter aromatics differ from summer aromatic composition?

# Summary

- $^{13}\text{C}$ -NMR useful for investigating WSOC composition
  - Provides information on carbon bonds
  - Spectra simplified by first separating WSOC into fractions
- General agreement of  $^{13}\text{C}$ -NMR and XAD-8 calibration results
  - ❖ Aromatics found only in recovered hydrophobic fraction
- Atlanta summer mainly C/O-alkyl and carboxylic acids, whereas biomass burning additionally had phenolic compounds and N-alkyl

- Ambient samples only qualitatively similar to Suwannee River Humic Acid
- Light Absorption by WSOC compounds
  - Urban Atlanta Winter, Biomass Burning, and then Atlanta Summer are most effective absorbing compounds per carbon mass
    - In each group, phenolic absorbance > aromatic acids absorbance
      - Evidence for conjugated bonds
      - $^{13}\text{C}$ -NMR suggests aromatics highly substituted
  - Hydrophilic compounds (C < 4 or 5 aliphatic acids and neutrals) don't effectively absorb light