

Investigation into Secondary Organic Aerosol Formation in Metro Atlanta

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Outline

- Motivation
- Overview of methods
 - Components of PILS-TOC (On-line)
 - Group speciation of WSOC involving XAD-8 resin and Size-Exclusion Chromatography (SEC) (Off-line)
- Ambient results from urban Atlanta and its surrounding regions during summer
 - Airborne on-line WSOC measurements
 - Off-line WSOC group speciation at various locations
- Summary

Motivation

- Sources of organic carbon (OC) not fully known, esp. secondary products.
- EC tracer method suggests 50% of Atlanta OC secondary, can be near 90% on short time scales [Lim and Turpin, *ES&T*, 2002].
- Chamber studies show biogenic emissions (e.g., terpenes) are readily oxidized to form Secondary Organic Aerosol (SOA).
- Southeastern urban centers densely forested with coniferous trees implying that biogenic precursors are major contributor to SOA.

How can WSOC Measurements Help?

- SOA formation is thought to be one of the major sources of WSOC

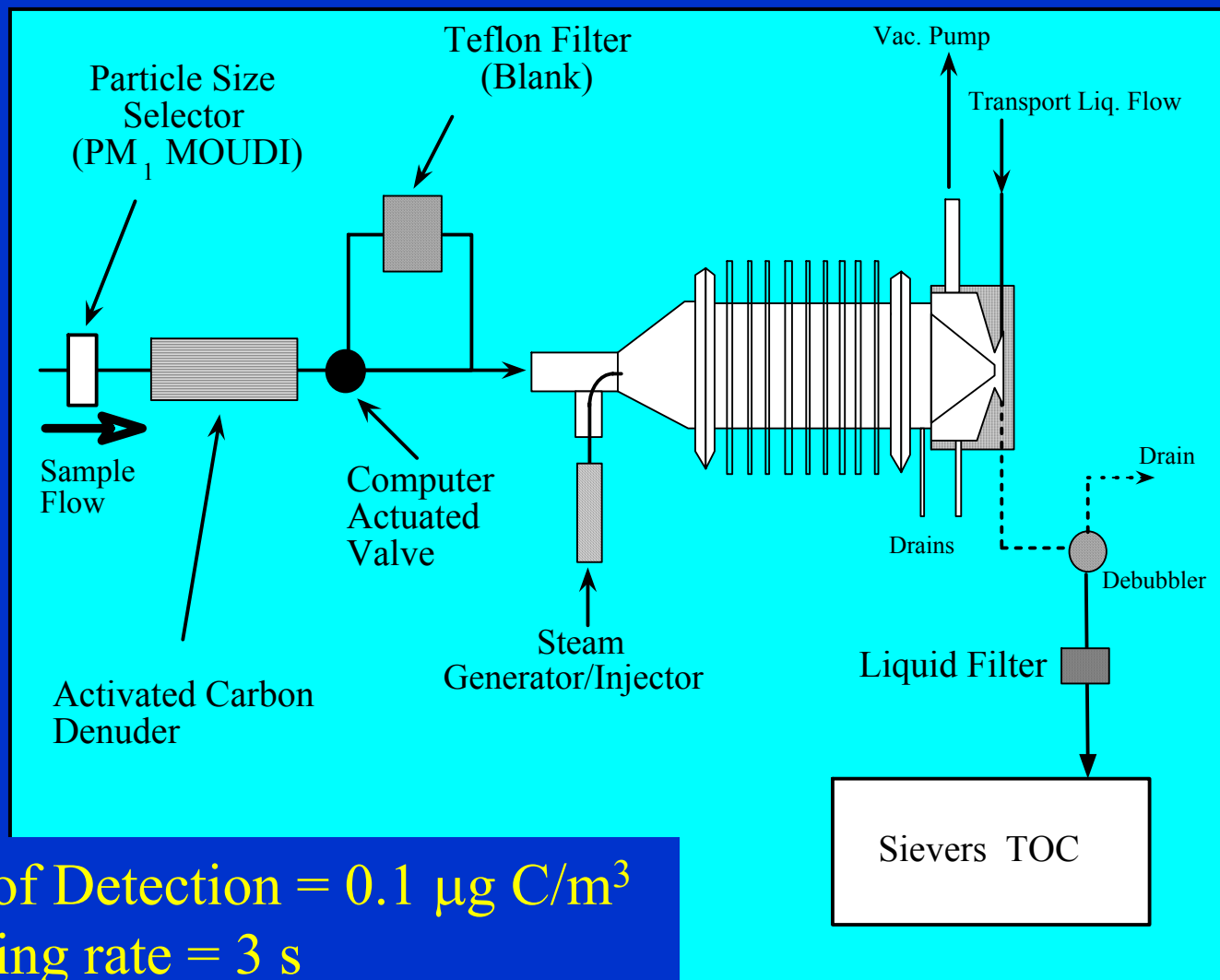
Maybe:

$WSOC = SOA$ (to 1st approx. when no biomass burning)

- Chemical analysis of WSOC could be used to investigate SOA products.

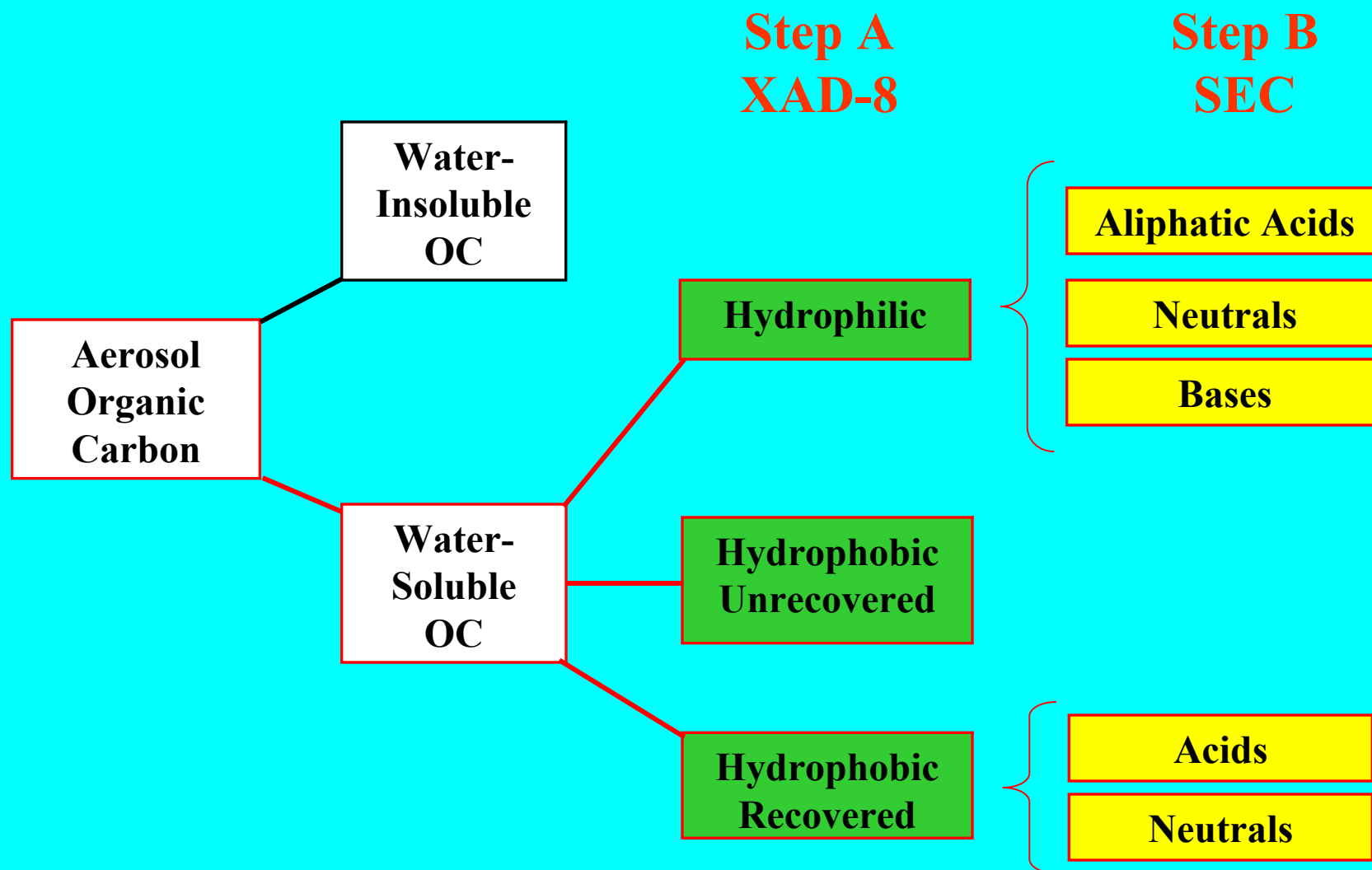
Method 1: On-line Measurement of WSOC

Schematic of PILS-TOC



- Limit of Detection = $0.1 \mu\text{g C/m}^3$
- Sampling rate = 3 s

Method 2: Off-line Group Speciation of WSOC



-Analysis performed on Hi-Volume integrated filters

Step A: XAD-8 Separation

(Calibration based on 36 "standards")

WSOC Extracted From Filter



Un-Recovered
Hydrophobic
> C₄ acids
> C₄ carbonyls
Cyclic Acids
Organic Nitrates

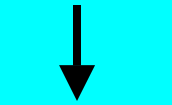
Recovered
Hydrophobic
Aromatics
(aromatic-like)

Hydrophilic
C₁-C₄ acids
C₁-C₄ carbonyls
Saccharides

Measured directly with TOC

Step 2B: Modified SEC Method

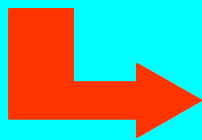
WSOC, Hydrophilic, or
Recovered Hydrophobic
Sample



S
E
C

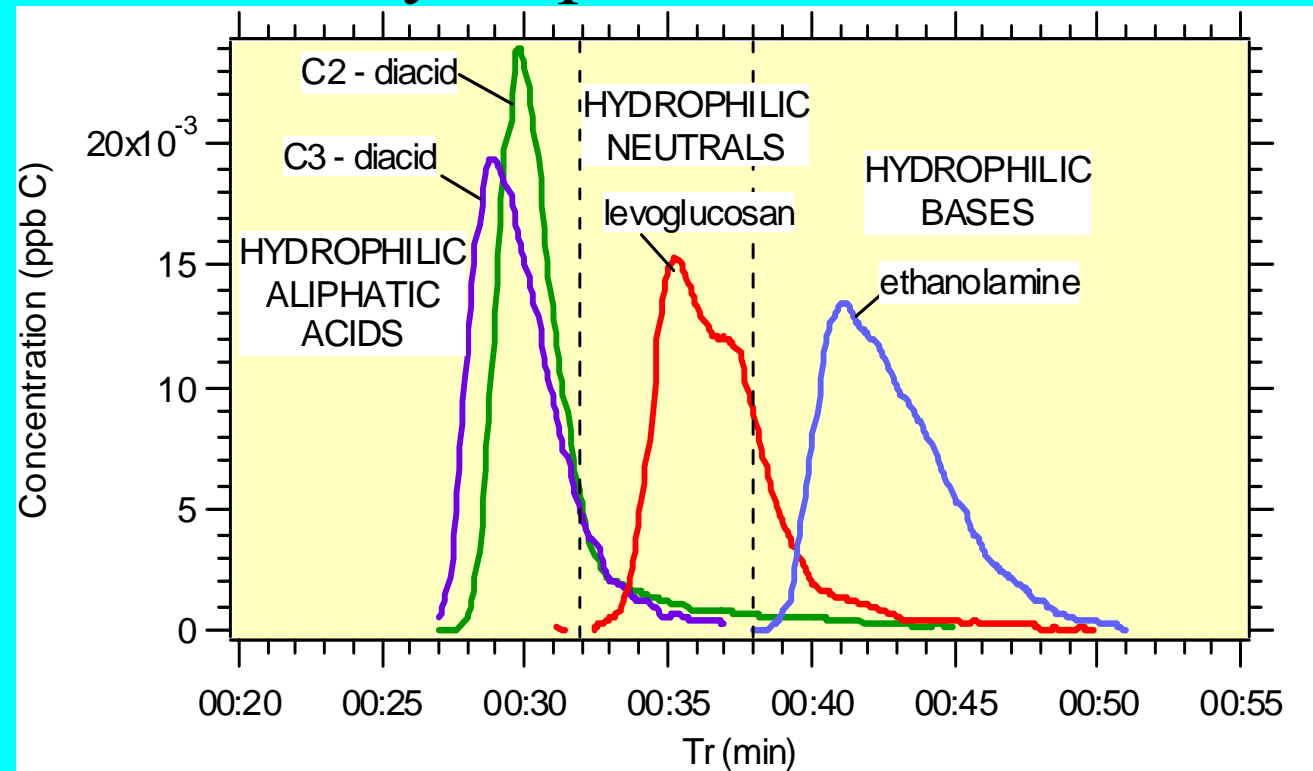


Total Organic
Carbon Analyzer



By not adjusting ionic strength and buffering sample (pH 6.8) obtain separation by functional groups

Hydrophilic Calibration



Ambient Results

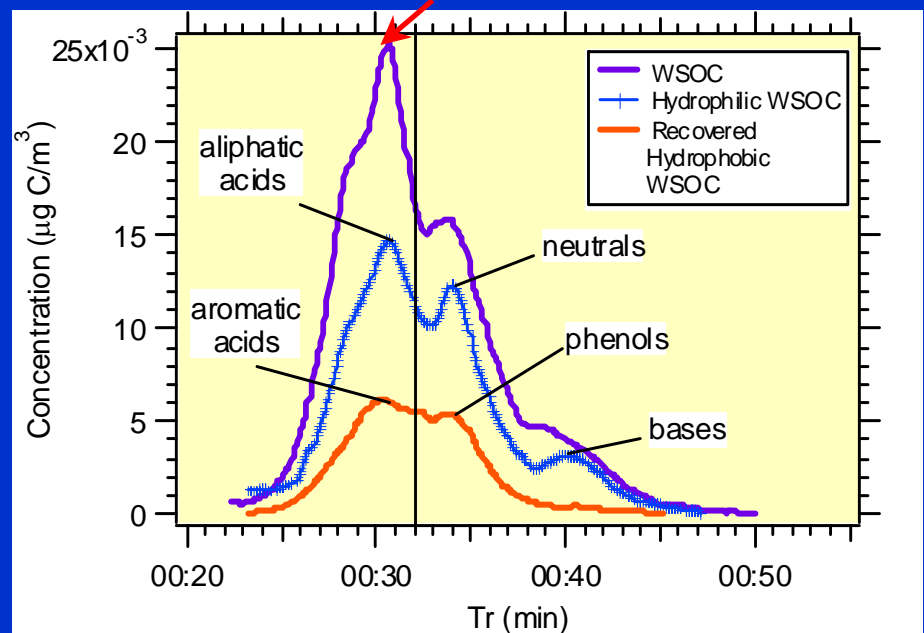
XAD-8 & SEC on 24-hr
integrated Hi Vol Filters

Urban Atlanta Summer
2004

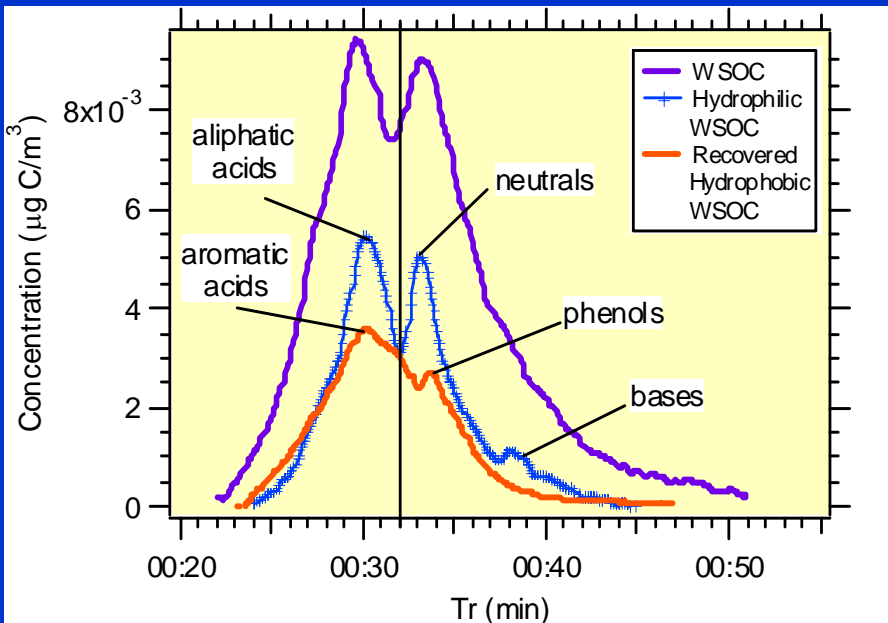
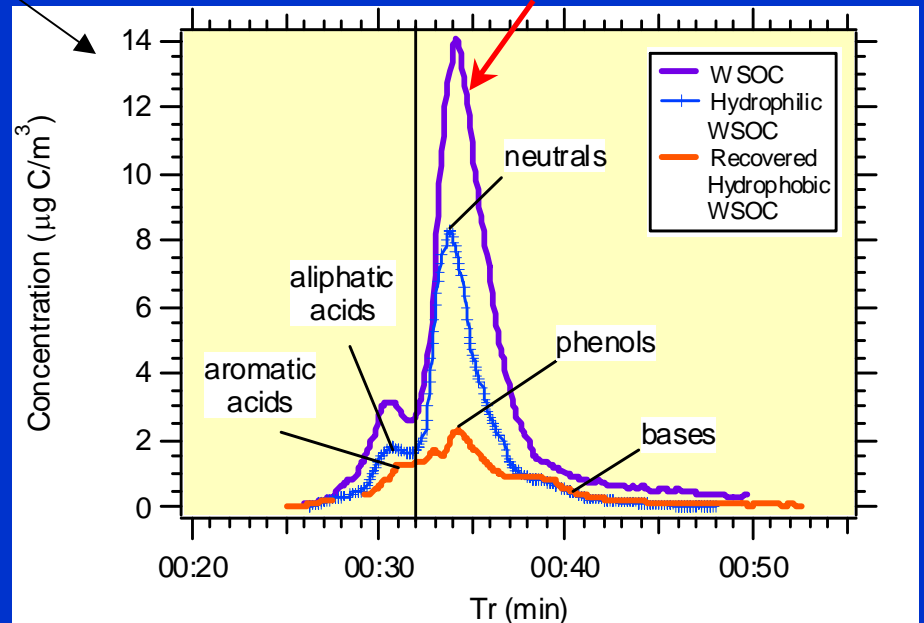
Atlanta Winter 2004

Biomass Burning
Fort Benning

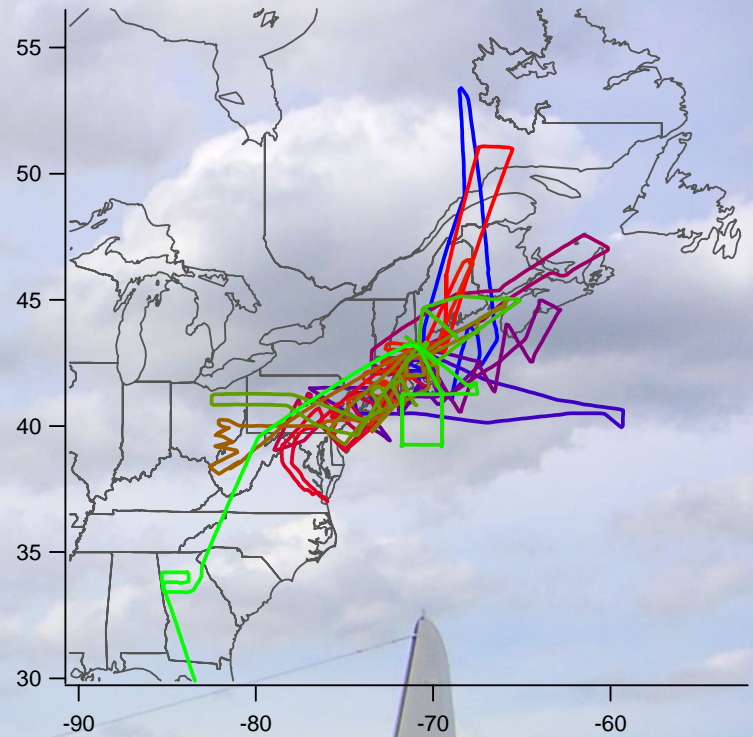
Most of Summer WSOC is acidic



Most of Biomass Burning is neutral

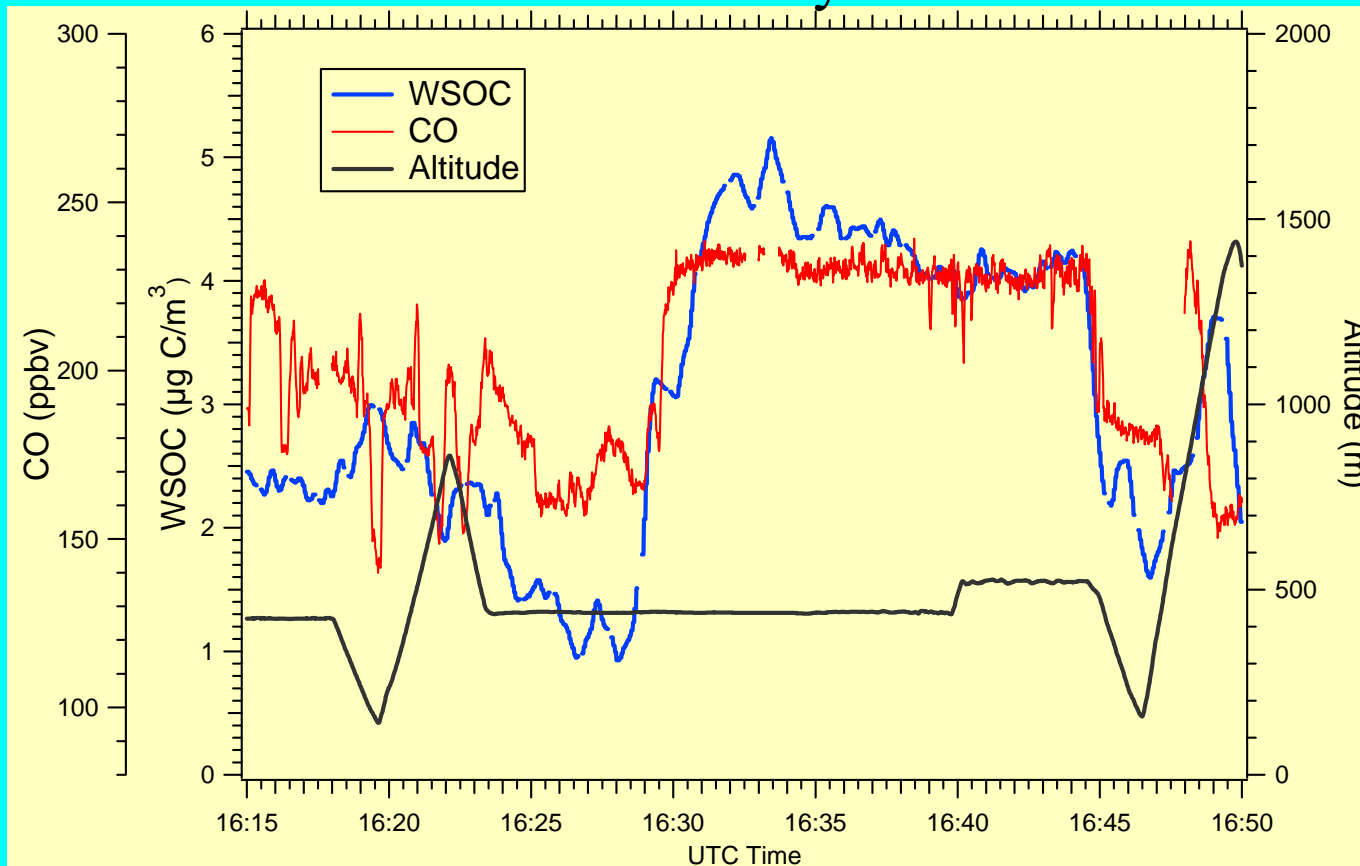


ICARTT: ITCT 2004 Online WSOC



Non-Biomass Near-Surface Data: WSOC versus CO (acetonitrile < 200 pptv and altitude < 2 km)

New York City Plume



WSOC-CO $R^2 = 0.82$, highly correlated in specific urban plumes

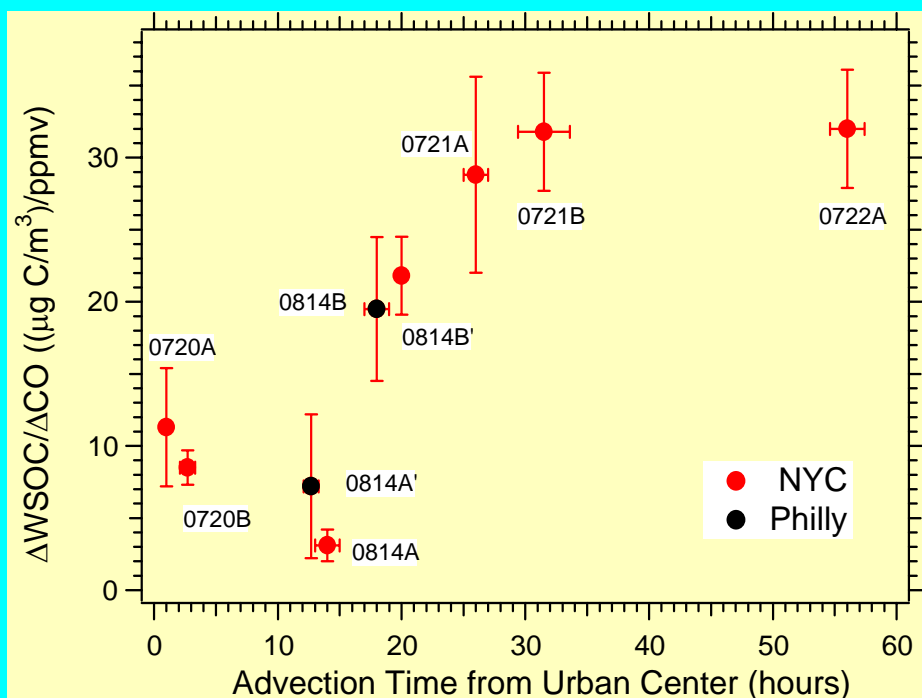
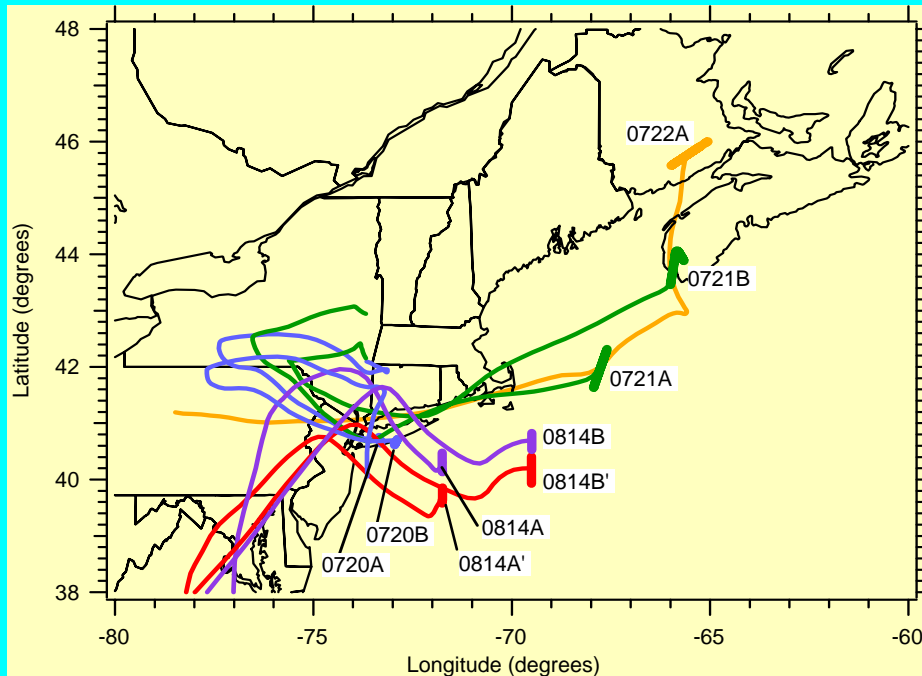
All Data: WSOC-CO $R^2 = 0.53$, fairly well correlated

WSOC Evolution in Urban Plumes

Back trajectories of WSOC plumes that intercepted NYC.

Δ WSOC/ Δ CO

- Lowest near city.
- Begins to level off after ~ 1 day to 32 ± 4 ($\mu\text{g C}/\text{m}^3$)/ppmv.
- WSOC produced from compounds co-emitted with CO.
- Urban emissions rapidly converted to secondary products?



Other Studies: WSOC and AMS Oxygenated OC

AMS Oxygenated and Hydrocarbon OC versus WSOC

AMS

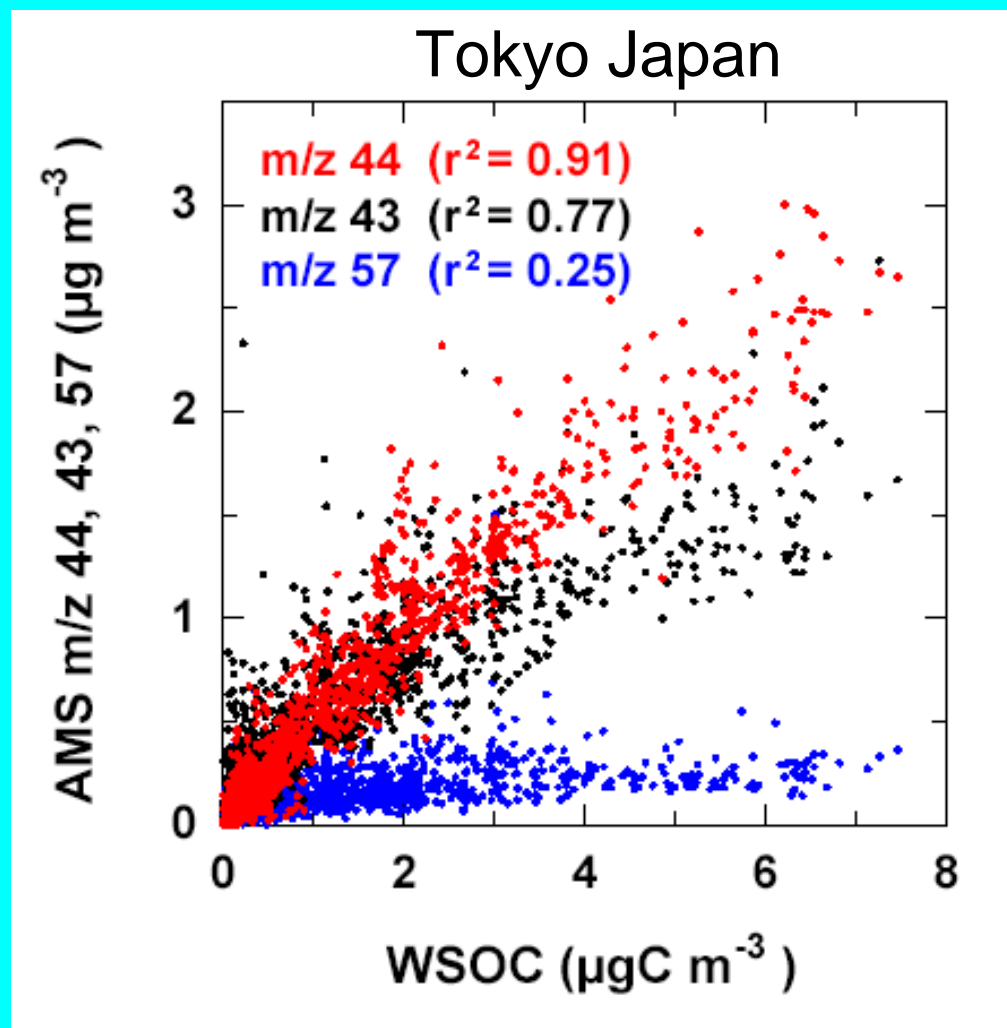
m/z 44 - oxygenated OA, accumulation mode

m/z 57 - hydrocarbon OA, ultrafine mode

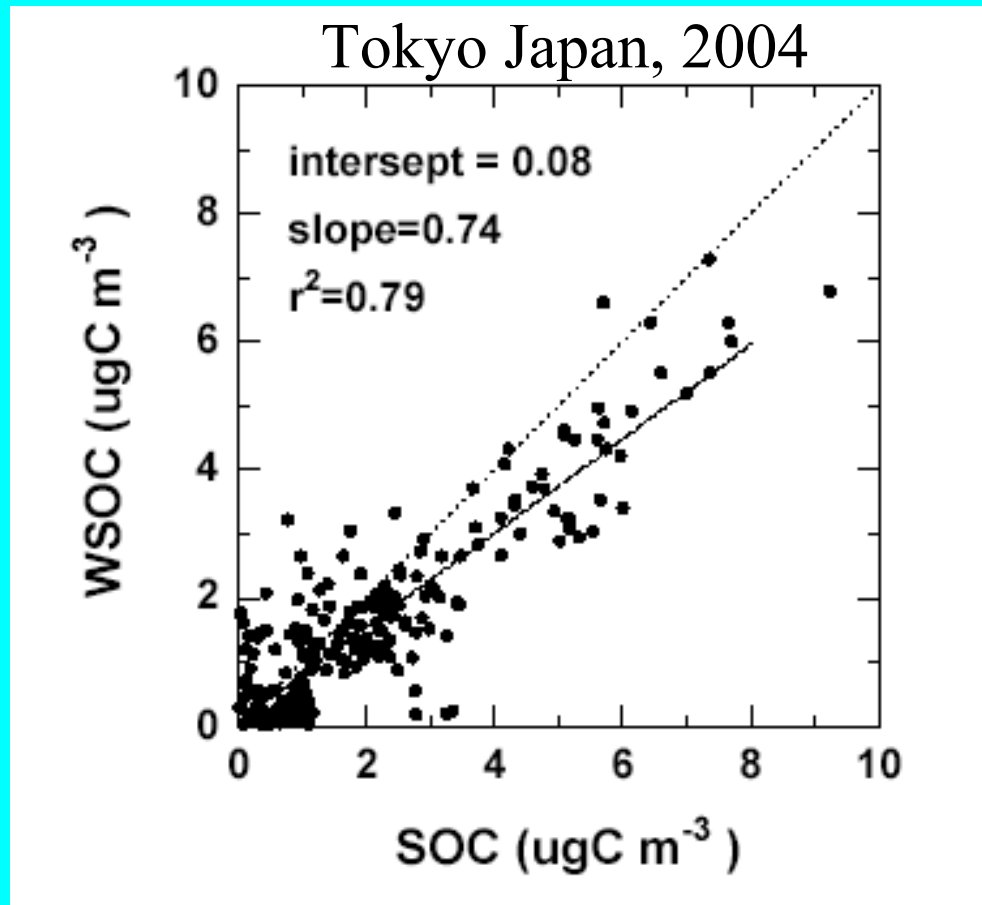
WSOC = 0.8 (OOA)
Secondary?

(OOA = oxygenated organic aerosol $\mu\text{gC}/\text{m}^3$)

Y. Kondo et al, GRL, submitted, 2005



Other Studies: WSOC and SOA from EC Tracer Method



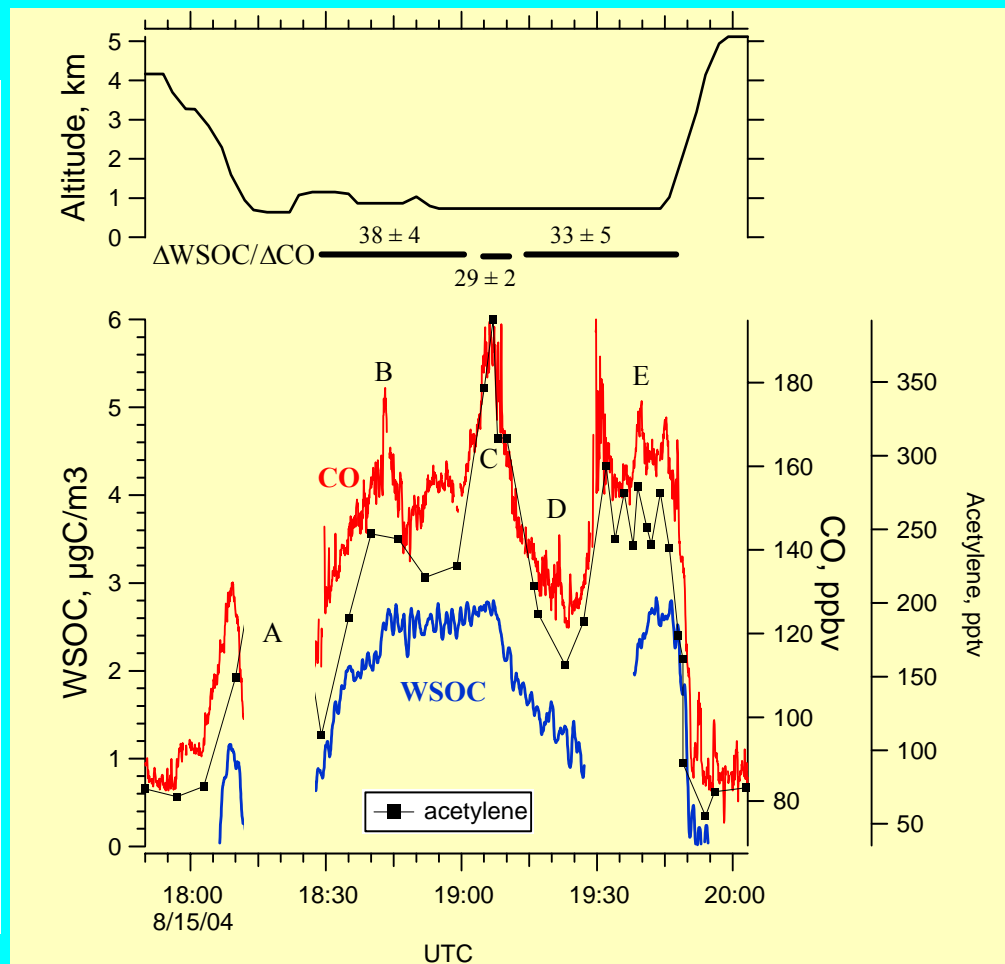
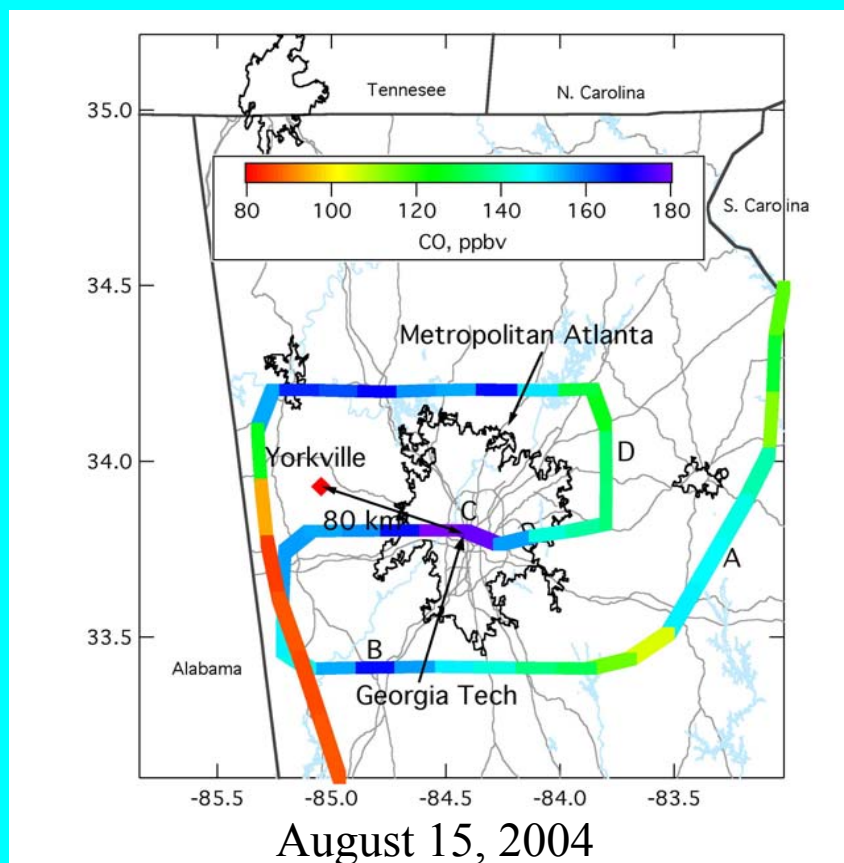
Y. Miyazaki et al,
submitted, 2005

$$\text{SOC} = \text{OC} - [\text{OC}/\text{EC}]_{(\text{pri})} \text{EC}$$

$$\text{WSOC} = 0.75 \text{ SOC}: r^2 = 0.79$$

WSOC appears to be mainly from SOA formation

Atlanta Fly-Over: WSOC-CO



- Wide-spread elevated CO and WSOC in boundary layer

- WSOC-CO $R^2 = 0.83$
- WSOC doesn't track in fresher CO plumes (point C)

$\Delta\text{WSOC}/\Delta\text{CO} \sim 33 \pm 5$ ($\mu\text{g C}/\text{m}^3$)/ppmv, similar to NYC (32 ± 4)

Sampling Sites For WSOC Group Speciation

Georgia Institute of Technology (GIT)
Roof top of ES&T Building



Hi-Volume Samplers: B. Yan and M. Zheng,
Georgia Institute of Technology

Next to I-75/85
~400 m from GIT and
~1 m from highway



Yorkville, GA
~80 km west of GIT
(during period of poor air quality)



Paired Experiments

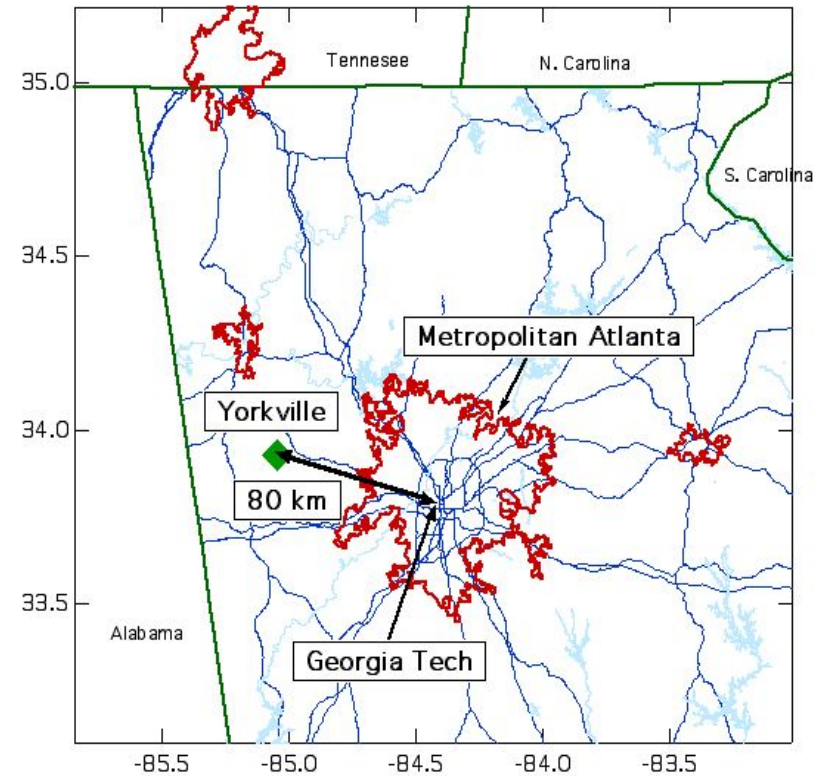
GIT vs. Highway

From: <http://maps.google.com/>



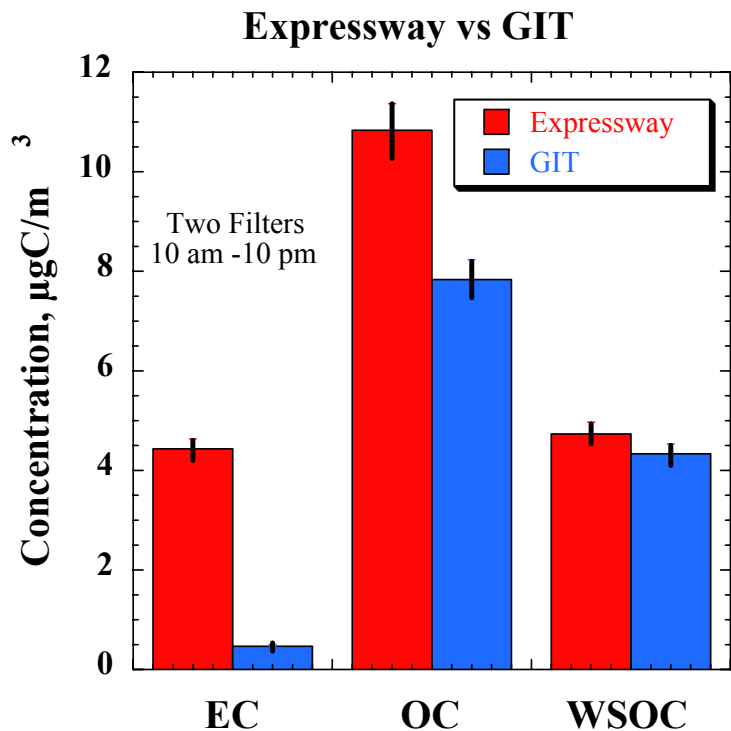
400 m

GIT vs. Yorkville

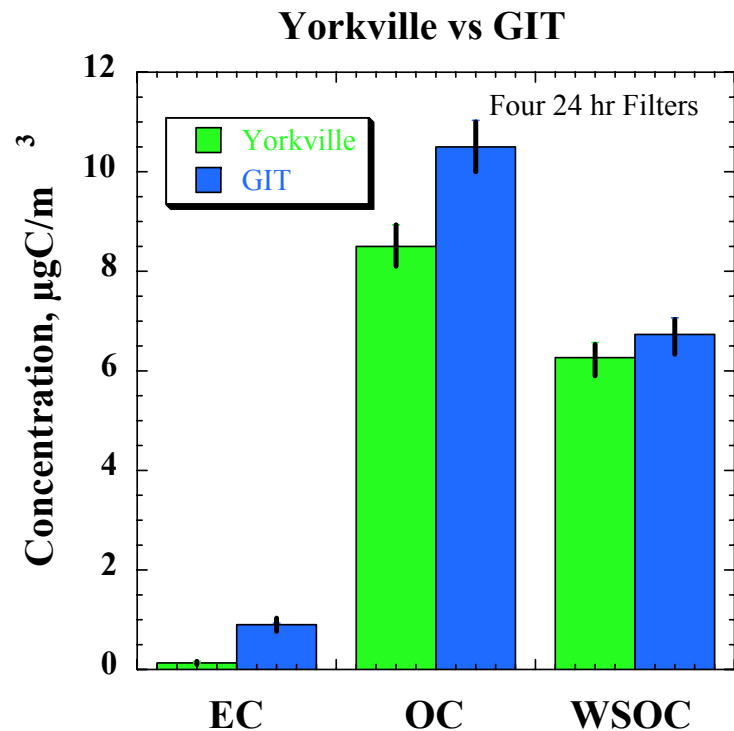


80 km

Ground-Based Measurements with Integrated Filters



Uncertainty is 5%, based on side by side comparisons



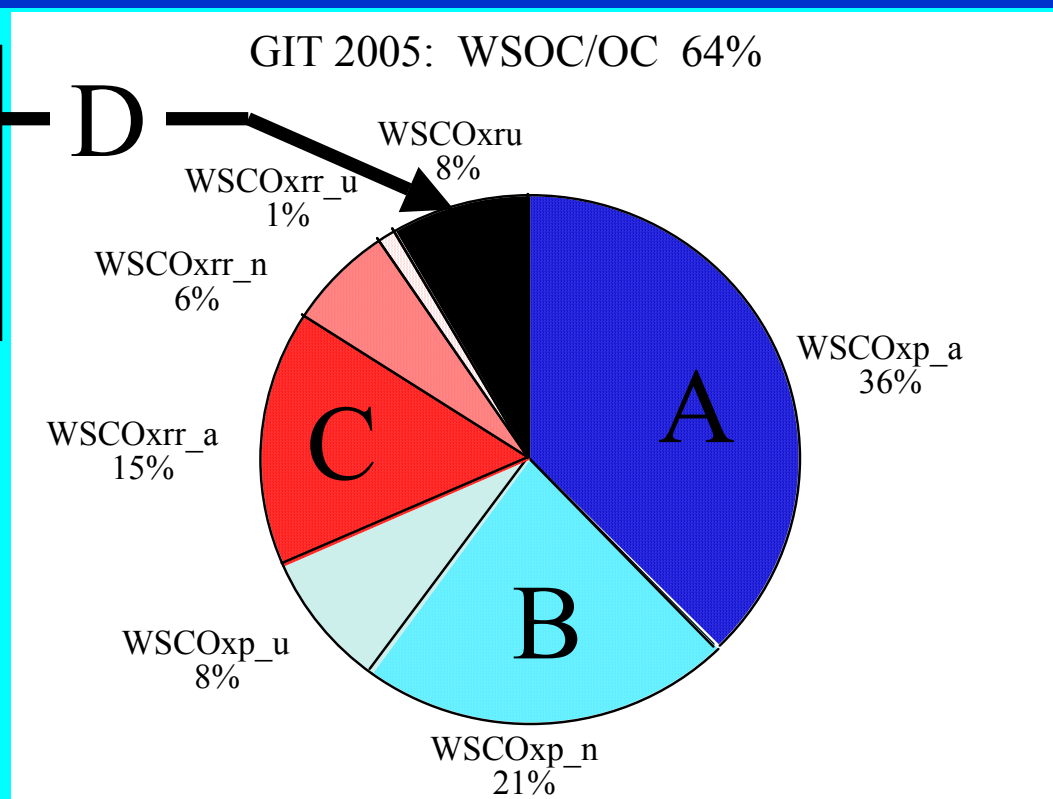
EC = Primary: Greater near expressway

OC = Primary + Secondary: Somewhat higher near expressway

WSOC = Not Primary, Secondary ?: Little difference between sites

Three Main Chemical Components of WSOC

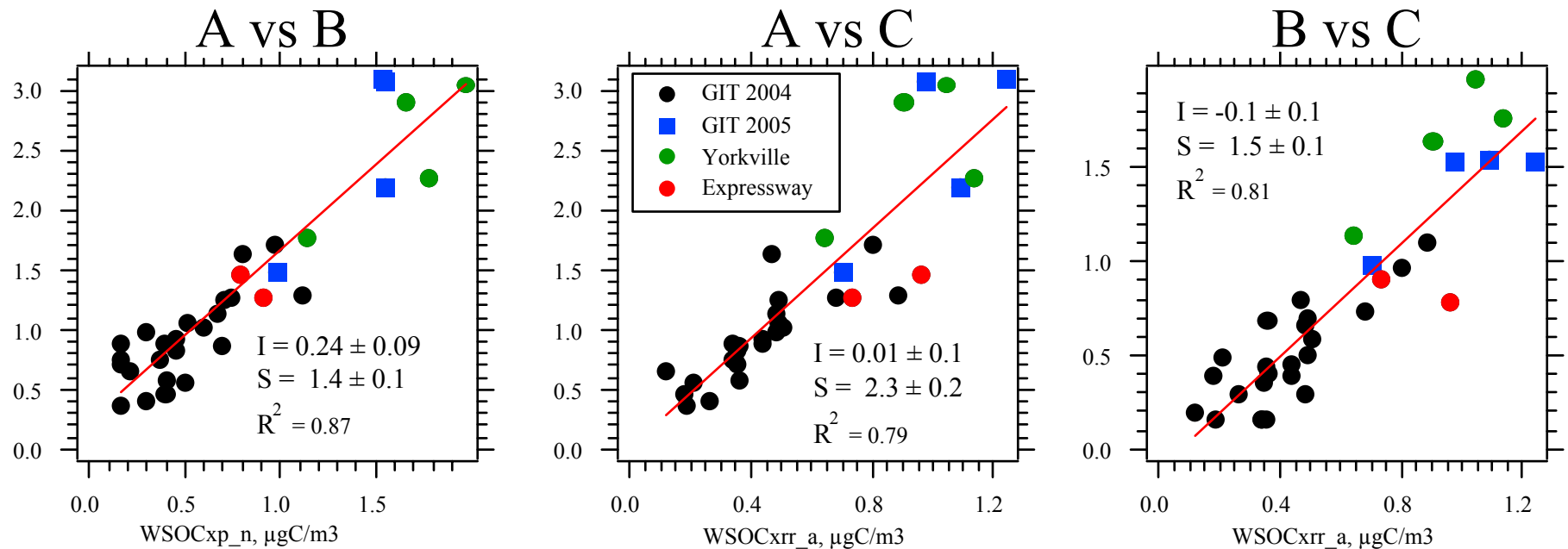
Includes expected biogenic SOA products



- A. Hydrophilic aliphatic acids, e.g., $C < 5$ acids
- B. Hydrophilic neutrals, e.g. saccharides and $C < 5$ carbonyls
- C. Recovered hydrophobic acids, e.g. aromatic acids or compounds with similar properties.

Three Main Components of WSOC Measured at Various Sites In Summer 2004 & 2005

Fractions are correlated: $R^2 > 0.79$

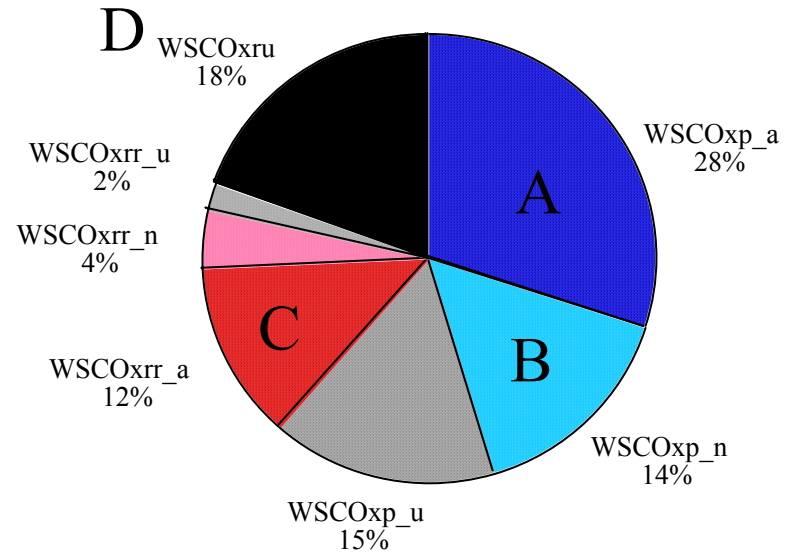


Major fractions of WSOC are linked to same source?

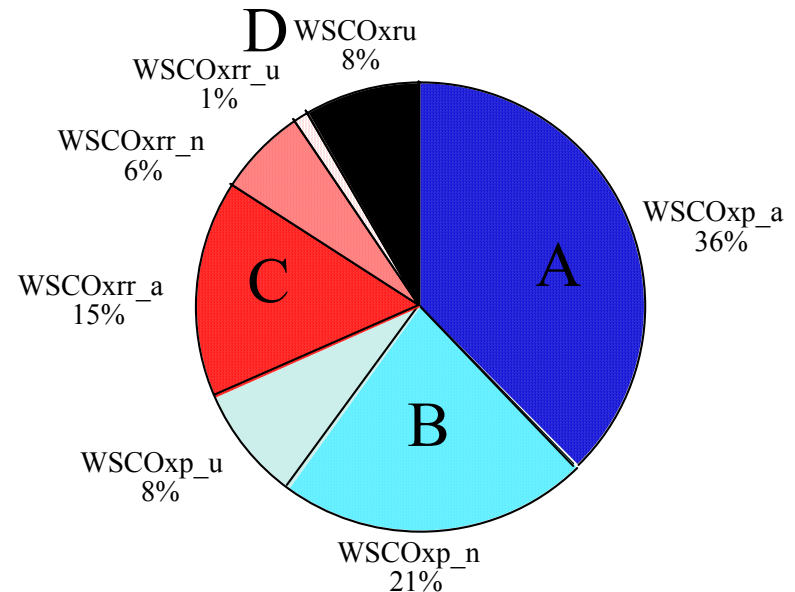
WSOC Chemistry vs A.Q.

Means	Atl. 2004	Atl. 2005
Daily Peak O ₃ , ppbv	61	100
PM2.5, μg/m ³	17	36
EC, μgC/m ³	0.4	0.9
OC, μgC/m ³	6.4	11
A+B+C, μgC/m ³	1.7	4.9
D, μgC/m ³	0.6	0.5

GIT 2004: WSOC/OC 50%



GIT 2005: WSOC/OC 64%



Summary: Based on a limited number of samples

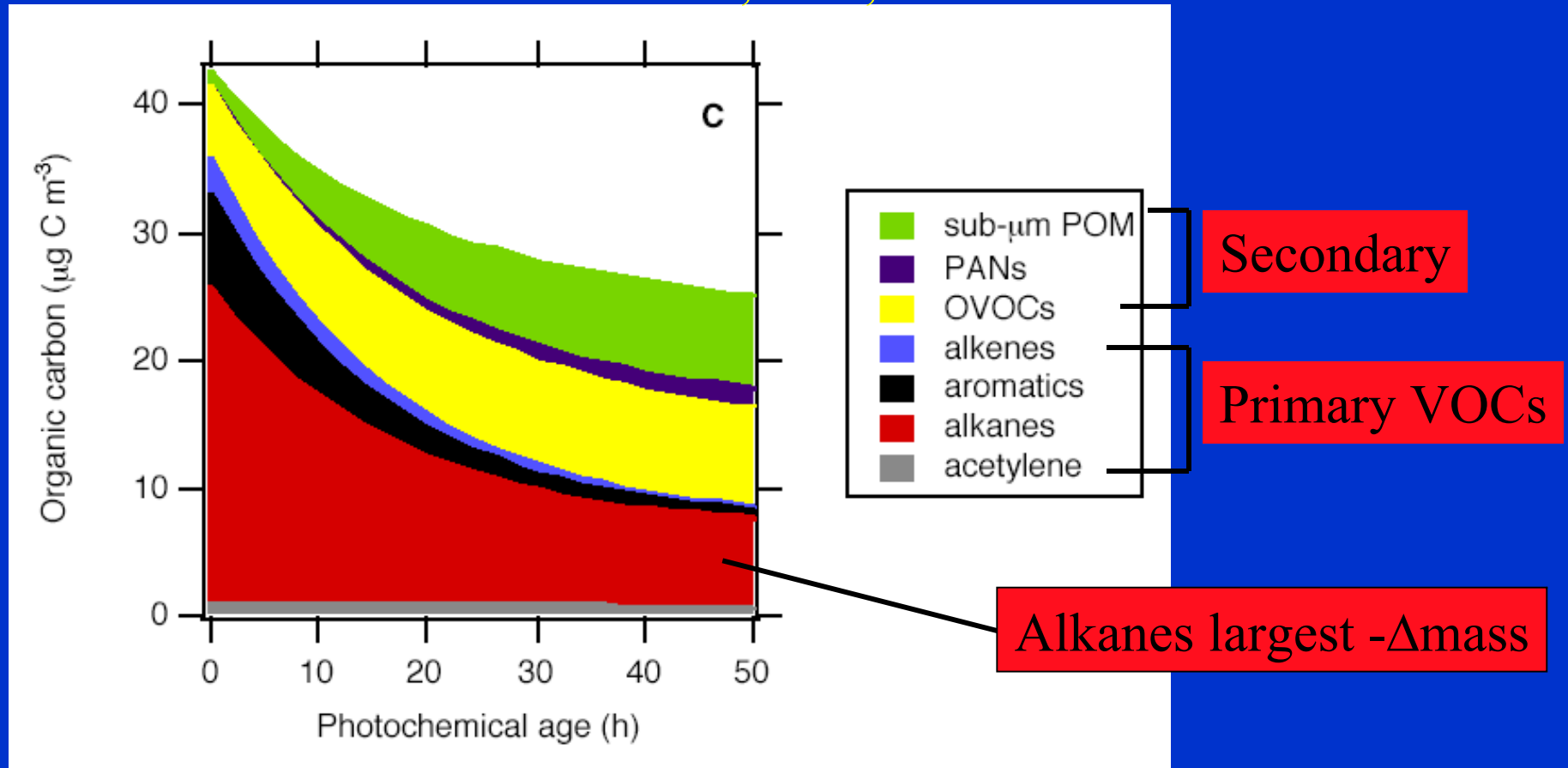
- In summer urban Atlanta and its surrounding areas WSOC has a regional characteristic and the source appears to be largely SOA formation.
 - Spatially uniform compared to primary particles (EC)
 - $\Delta\text{WSOC}/\Delta\text{CO}$ NYC plume evolution suggest secondary.
 - Comparisons with AMS & SOA by EC-tracer in Tokyo.
- No clear evidence for strong biogenic SOA signal, instead points to precursors from mobile sources
 - Supported by:
 - High WSOC-CO correlations on large spatial scale
 - Similar $\Delta\text{WSOC}/\Delta\text{CO}$ in Atlanta and NYC
 - Known biogenic SOA products small fraction of WSOC, remains constant during poorest AQ
 - Three major components of SOA linked to common source and highest under poorest AQ.

Implication that mobile source emissions play a large role in the formation of WSOC and hence SOA in summer-time metropolitan Atlanta

No known (to me) chemical mechanism to explain observations.

Mass Balance on Measured VOCs and OC (POM) from NEAQS 2002

From: J.A. de Gouw et al., *JGR*, 2005



-SOA: little evidence for biogenic, not explained by aromatic VOCs
SOA from anthropogenic VOCs not well understood

What about C¹⁴

Houston: Lemire et al, JGR, 2002

- Higher OC/EC \Rightarrow higher % modern C
 - Suggests that most SOA modern C

Future Work ?

Radio-C analysis on Atlanta WSOC
and isolated fractions.

Acid Catalyzed reactions?

