Emissions Inventory and Process Reconciliation Using Molecular Markers and Hybrid/Inverse Photochemical Modeling with Direct Sensitivity Analysis

U.S. EPA STAR PM Source Apportionment
Progress Review Workshop

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Bo Yan, Mei Zheng, Jaemeen Baek, Yongtao Hu and Ted Russell

Georgia Institute of Technology

Overview

- Introduction
- Objectives
- Field studies and measurements
- Inverse modeling
- Summary

Objectives

- Further develop and apply of a method for assessing emissions estimates of pollutant precursors and their impact on air quality by reconciling bottom-up and top-down emissions estimates using inverse modeling.
- Assess and improve the emissions inventory for primary organic particulate matter in the eastern United States with particular focus on the Southeast.
- Quantify the fraction of primary vs. secondary organic aerosol (SOA) and the fractions of SOA that are biogenic and anthropogenic. These results will be compared with results using other methods.
- Estimate the response of ambient PM2.5 to emissions changes by source category.
- Quantify uncertainties in emissions and source-receptor relationships for the major sources of primary organic matter and precursors to SOA.
- Assess the information added by using molecular markers in the inverse modeling and using longer periods with more routine measurements.
- Provide information on the impact of SOA parameters on simulated OC levels.
- Improve the current methodology by detecting more polar compounds and lower the detection limit for organic tracer analysis by silylation.
- Optimize the number of species applied in the chemical mass balance model so that only a subset of the important and necessary tracers will be included in the model.
- Investigate the sensitivity of the organic tracer-based receptor model technique by comparing the chemical mass modeling results with using different number of tracers, different source profiles, and including or excluding more inorganic tracers.

Approach

- Take advantage of Supersites, SEARCH, ASACA, STN and othetr special study data to better understand the sources of carbonaceous species and methods to identify their sources
  - Focus on SE, particularly Atlanta:
    - Atlanta Supersite: Extensive PM and gaseous data in summer 1999
    - SEARCH: SE, detailed PM and gaseous data since 1998
    - ASACA: Atlanta, daily PM composition since 1999
    - STN
    - Highway-urban-rural measurements
    - Prescribed and wildfire burning episodes
  - Larger scale focus using ESP data (July-August, 2001; January, 2002)
- Use water soluble organic carbon measurements for comparison

Study Area and Periods

Modeling periods:

August 1999

July 2001

January 2002

July 2005

January 2006

Base inventories

EPA NEI

Point sources in Georgia

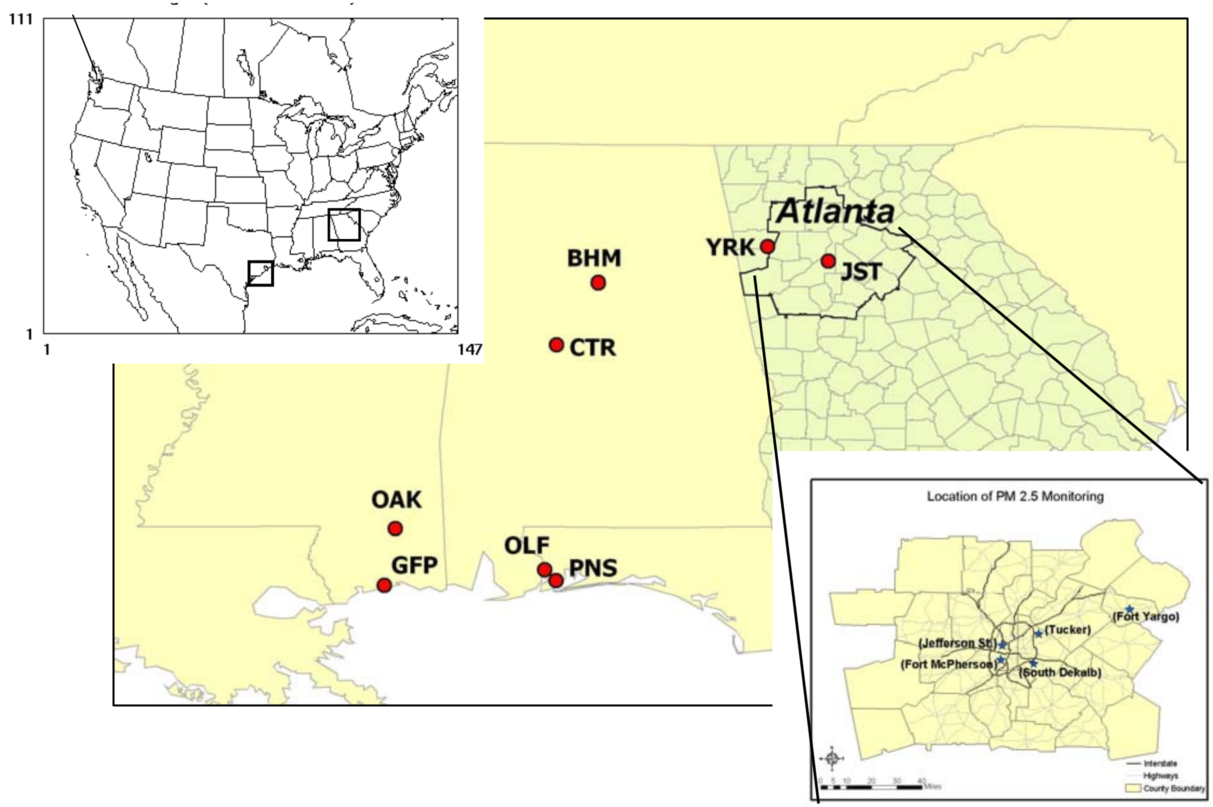
EPA NEI 2002 (draft), CEM data

Forest fire, land clearing debris in 2002

VISTAS, 2005

Residential meat cooking

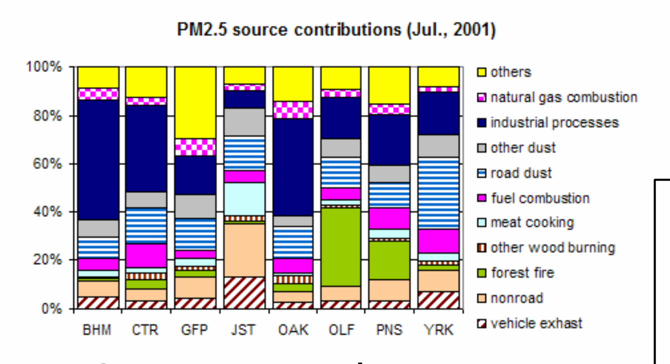
New emissions were added



SEARCH monitoring sites ***ASACA***

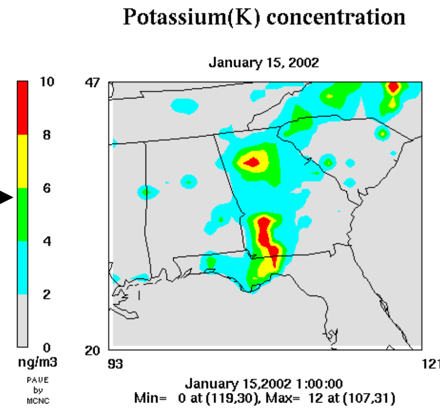
- Urban sites : Atlanta, Jefferson St. (JST) Birmingham (BHM), Gulf port (GFP), Pensacola (PNS)
- Suburban sites: Pensacola (OLF)
- Rural sites: Oak Grove (OAK), Centreville (CTR), Yorkshire (YRK)

Inverse Modeling Using Source Tracers and DDM



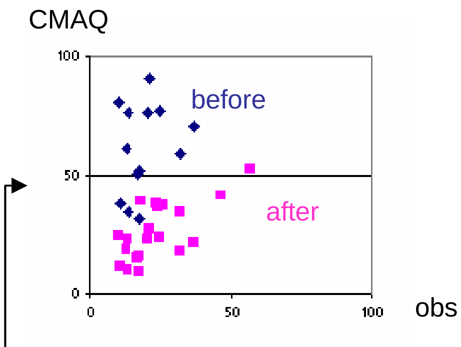
Source apportionment using CMAQ-Markers

Multiplication

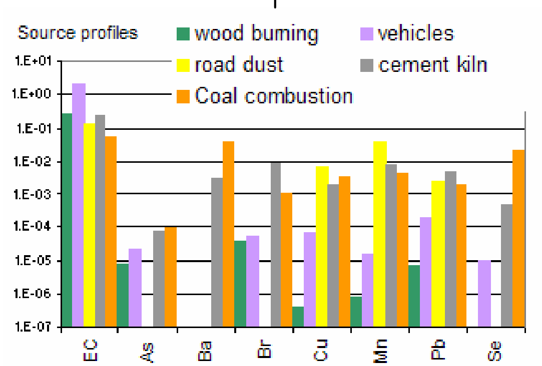


Tracer species concentration

Regression analysis

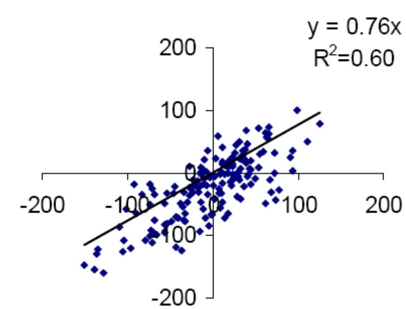


Scaling factors



Source profiles Used in CMB

Observations

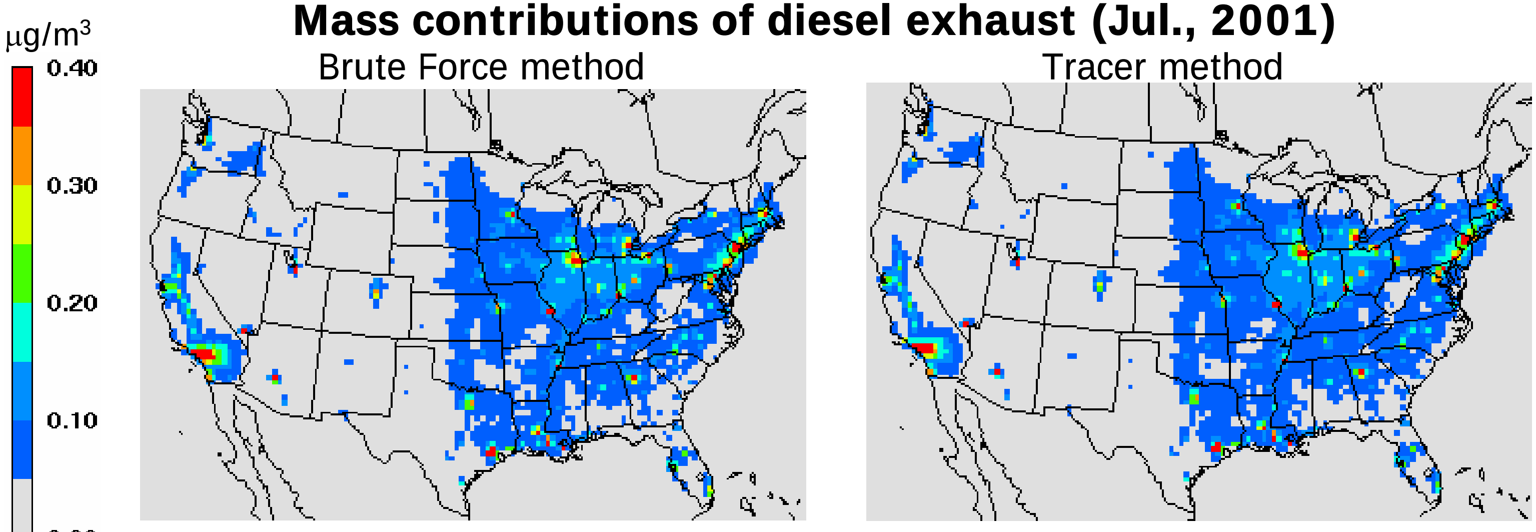


Improved CMAQ simulations

CMAQ-Tracer method

- Method
  - Add tracers for primary organic aerosols categorized into 34 sources, such as wild fires, fireplaces, natural gas combustion, etc.
    - Size resolved (using CMAQ sizes)
    - Flexible species resolution (i.e., not really resolved during calculation)
- Usefulness
  - Detailed source apportionment of primary aerosols
  - Enhanced integrated emission-based/receptor model method

Mass contributions of diesel exhaust (Jul., 2001)



Quantitative Analysis: Regression analysis using tracer species

- Assumptions
  - Tracer species such as organic markers are non-reactive and conservative in the atmosphere
- Advantages
  - Require less resources
    - Combined CMAQ Tracer & DDM (e.g., for secondary species) methods
  - Site specific information
  - Flexible source specific information
    - Can re-optimize profiles

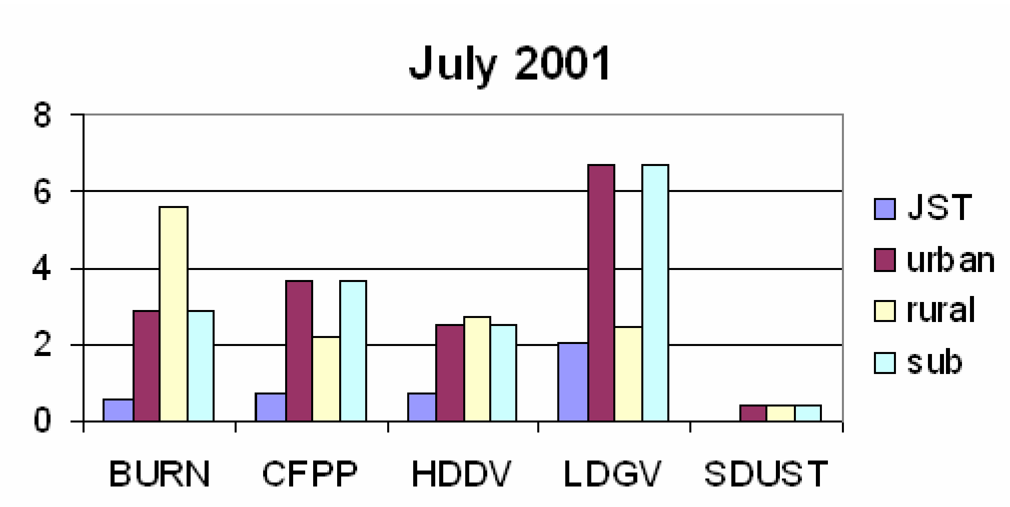
Regression analysis using tracer species – Scaling factors of each source

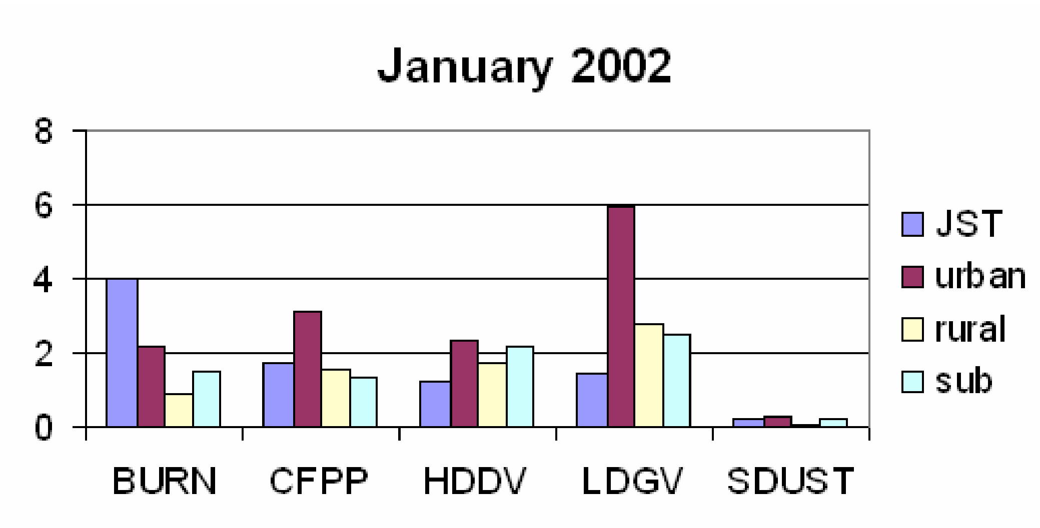
- Regression analysis
- Least square error fitting method

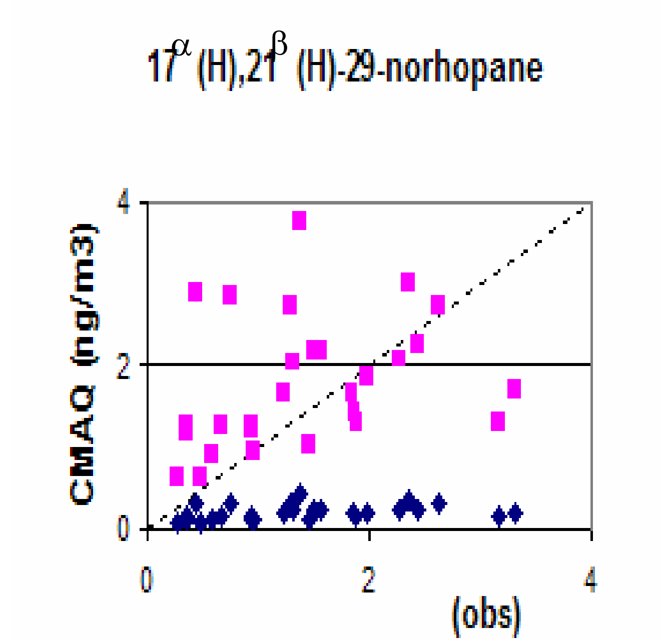
$$\sum_i w_i e_i^2 = \sum w_i (y_i - x_{s,i}\beta_s)^2 + \sum \lambda (f_s - 1)^2$$

- Choose λ that minimizes residual error and physically meaningful

Scaling factors of each source







n.b.: Results are meant to be suggestive of possible biases, and can results from profile and other issues as well

EC Inverse Modeling

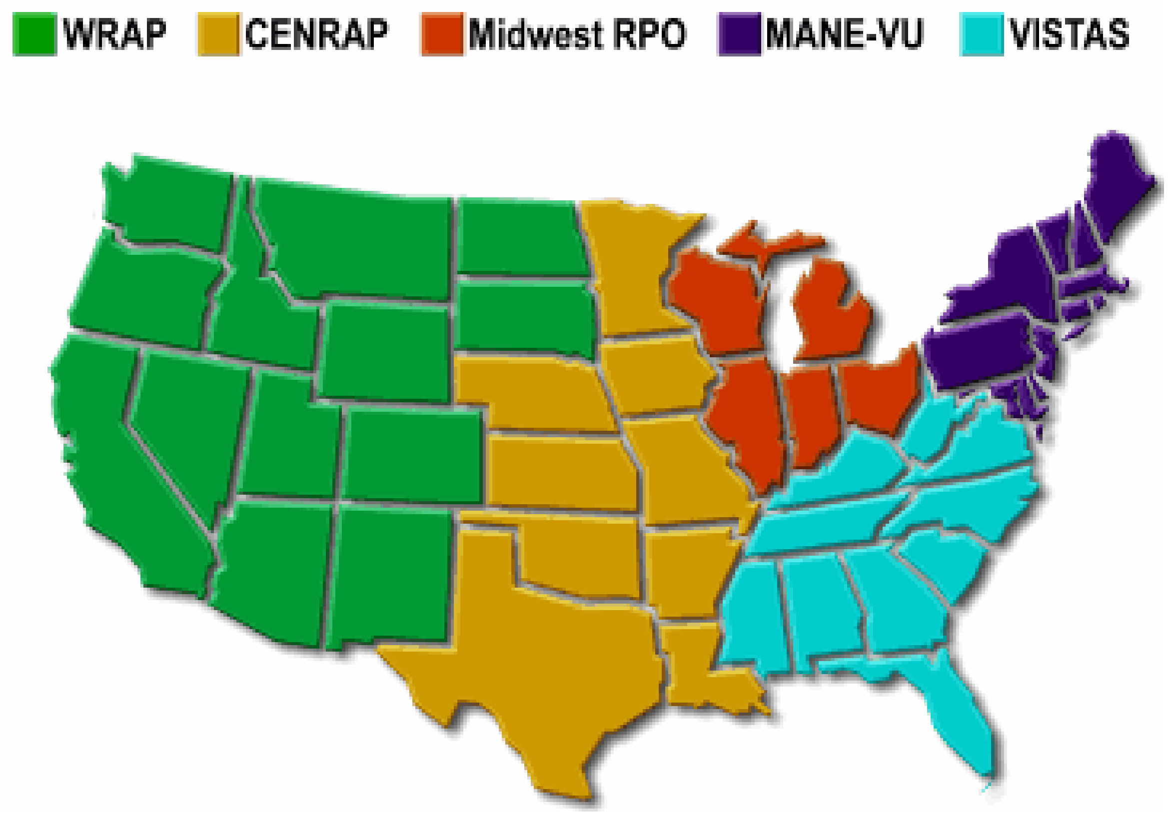
One-year CMAQ simulation in 2004 on a 36-km grid covering continental United States as well portions of Canada and Mexico. The 2002 VISTAS emissions inventory was projected to 2004 and used as the a priori inventory.

Utilizing surface black-carbon observations from networks of STN, IMPROVE, SEARCH and ASACA. TOT measurements from STN and ASACA converted to TOR.

The difference between the CMAQ simulations and the observations, along with the DDM-3D derived sensitivities of BC concentrations to each source group, are used to estimate how much BC emissions from a specific source should be adjusted to optimize the CMAQ BC performance through ridge regression.

Scale BC emissions by five RPO regions and five source category splits as well as Canada and Mexico totals

RPO regions



Emission Splits

On-road

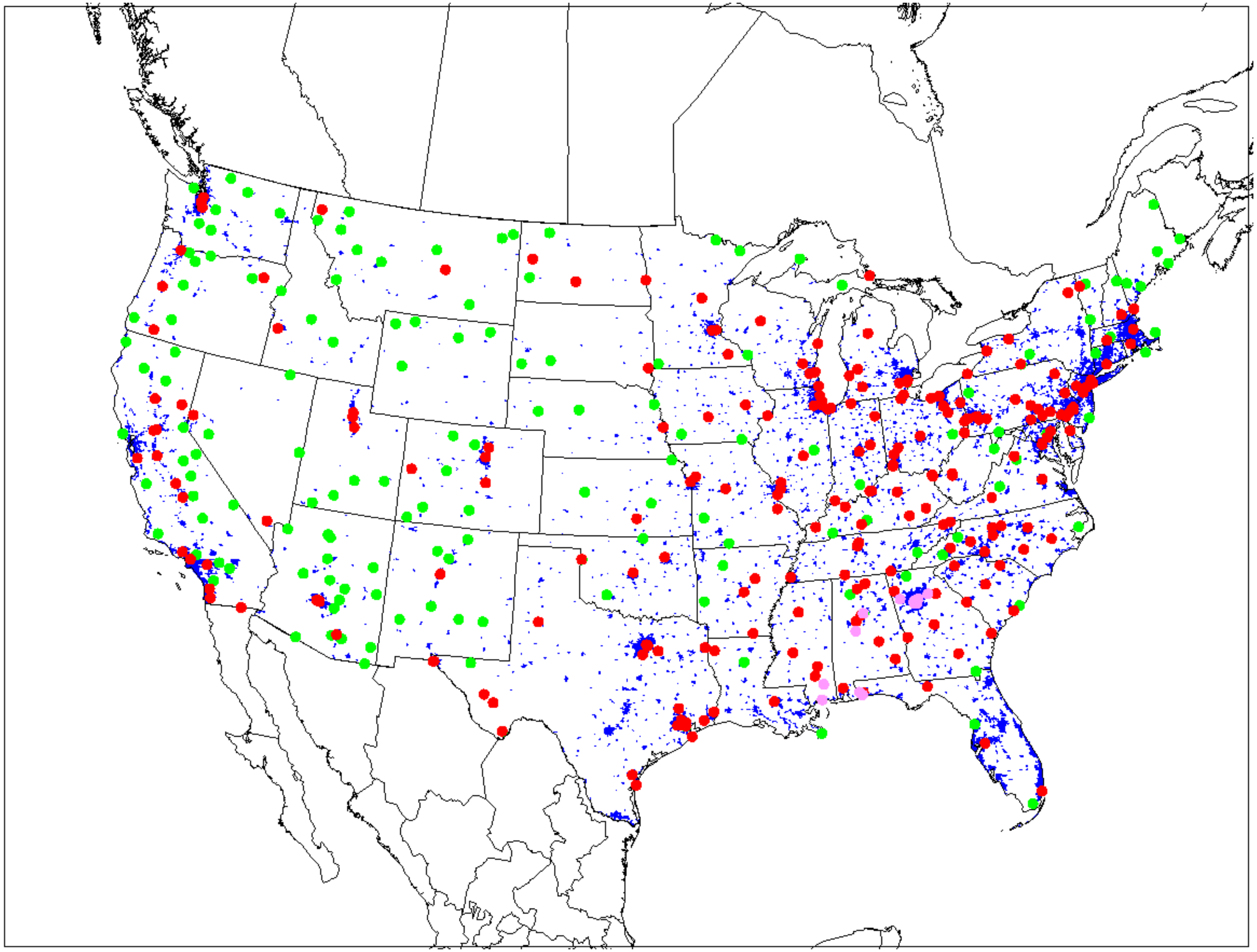
Non-road

Fire

Wood-fuel

“Others”

The modeling domain with 36-km resolution, BC(EC) monitoring networks: IMPROVE (green dots), STN (red dots) and SEARCH and ASACA (pink dots). Urban areas shown in blue.



Preliminary results: the a priori vs. the a posterior (tons/day)

Groups	May 2004		August 2004	
	A priori	A posteriori	A priori	A posteriori
By regions				
CENRAP	254	344	198	236
MANE_VU	132	120	124	122
MIDWEST	149	271	122	174
VISTAS	241	325	232	274
WRAP	266	244	268	244
By Categories				
Fire	188	241	125	141
On-road	72	91	71	100
Non-road	500	607	568	517
“Others”	122	185	130	240
Wood-fuel	161	181	49	52
Totals				
US-total	1043	1304	944	1050
Domain-Total	1219	1665	1081	1315

Roadside, Nearby, Regional OC Study

- Objectives
  - chemical composition of PM2.5 at a few typical sites and seasons (done)
  - apportion source contributions using molecular marker-based CMB (CMB-MM) and model using CMAQ with fine resolution (1km)
  - Assess particle-phase molecular markers of biogenic SOA for comparison with model (CMAQ) results
  - Evaluate and improve CMB-MM and CMAQ performances with the identified biogenic molecular markers

Approach

- Measure PM composition at three distinct sites, two seasons
  - Roadside site
    - I75/85 highway connector located in midtown Atlanta
  - Near-Road site
    - Roof of ES&T building in Georgia Tech located near to midtown Atlanta
  - Rural site
    - Yorkville (YRK), GA, located about 55 km northwest of Atlanta
  - Jefferson Street data available as well
    - About 4 km away

I75/85 Roadside vs Near-Road in GT Campus

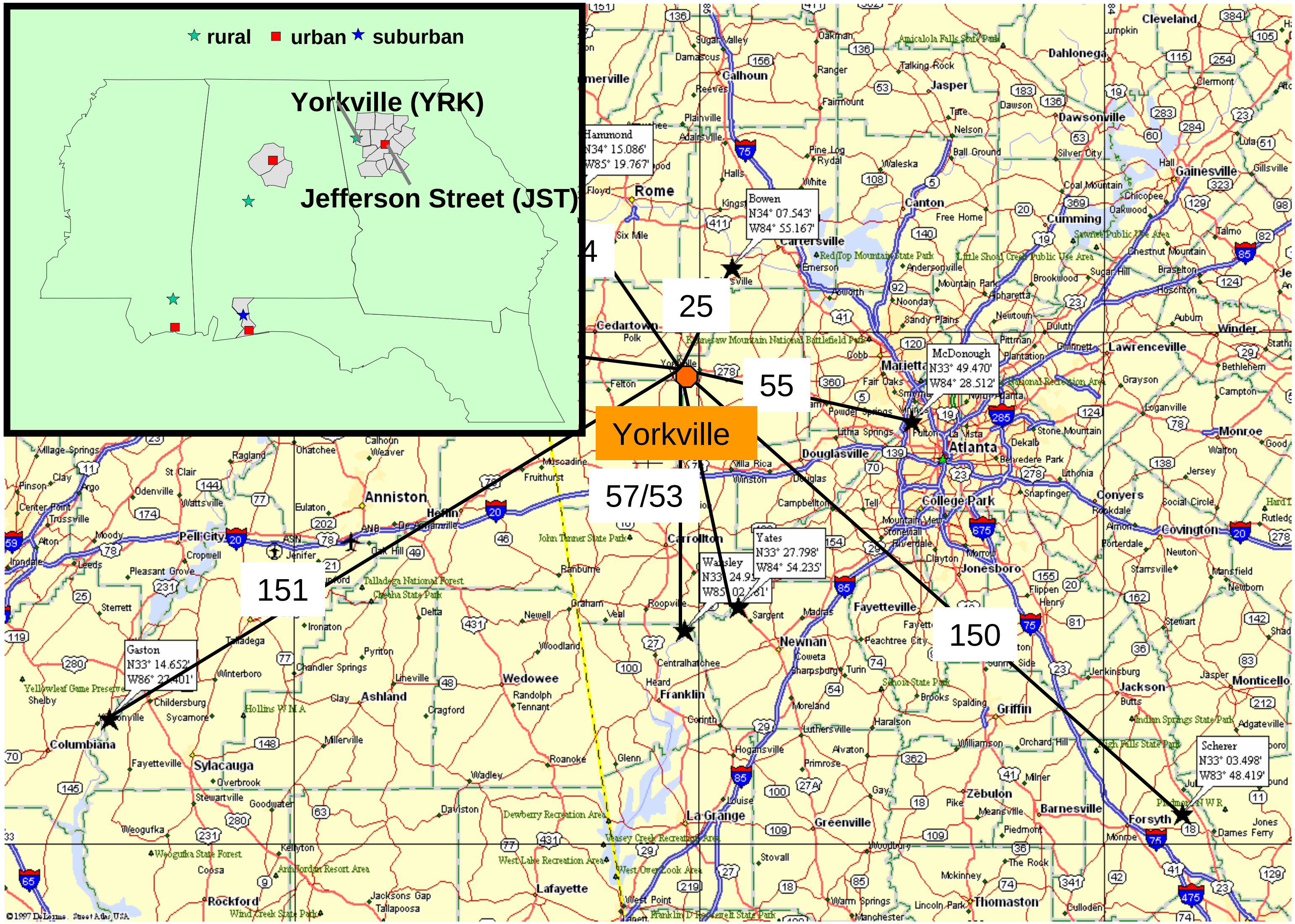
Samplers Next to I75/I85
Highway Connector
- dominated by on-road
emissions

Samplers At Penthouse Lab
(Roof of E.S.&T.Building)
- typical urban site

http://maps.google.com/

Distance between sampling sites is around 450 m

Yorkville - biogenic emission and regional transport impacted



SEARCH

Distances between sampling sites is around 55 km

Sampling Events

- Summer Events in 2005 (n=38 samples)

  06/15 – 06/18 (12-hr)

  06/26 – 07/01 (24-hr)

  0708 – 07/26 (24-hr)

- Winter Events in 2006 (n=47 samples)

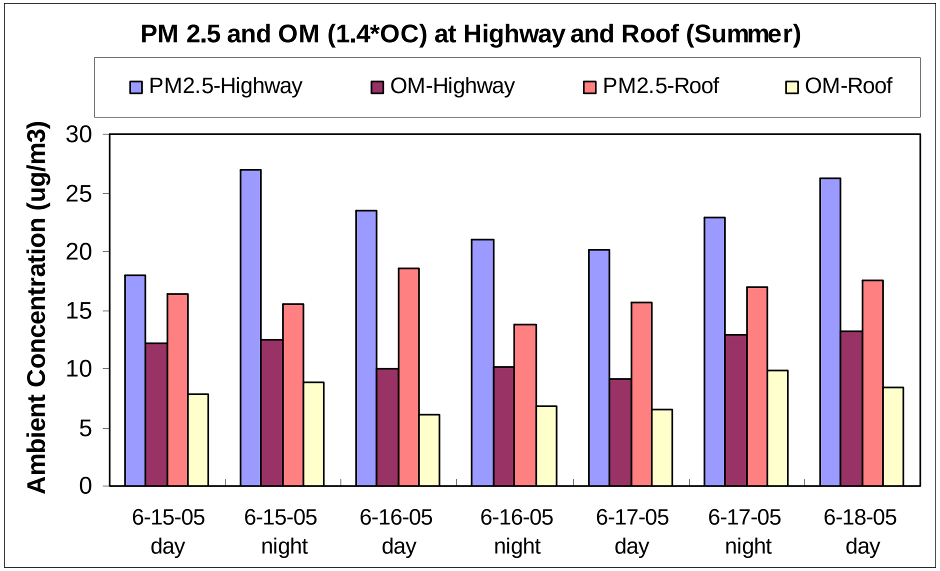
  01/19 – 01/26 (12-hr or 24-hr)

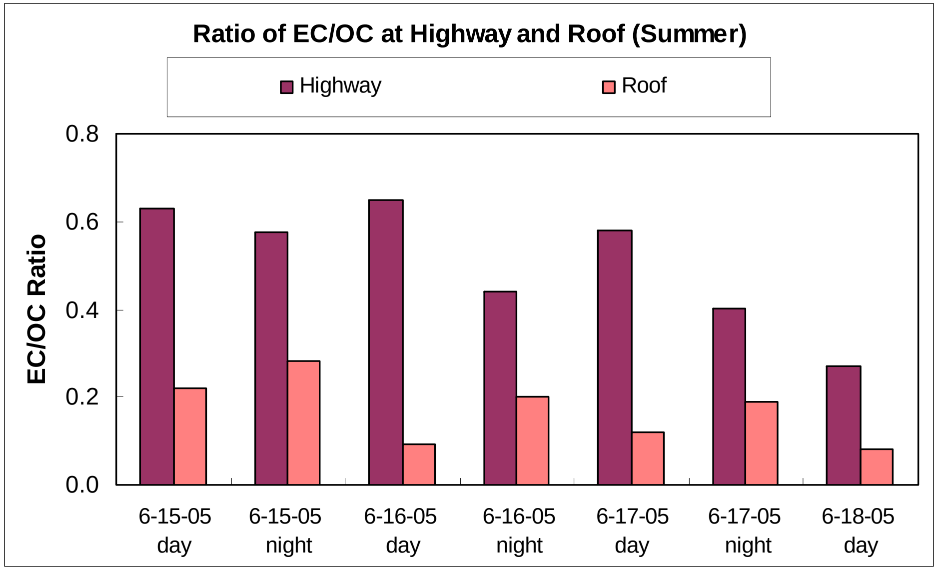
  01/27 – 01/31 (24-hr)

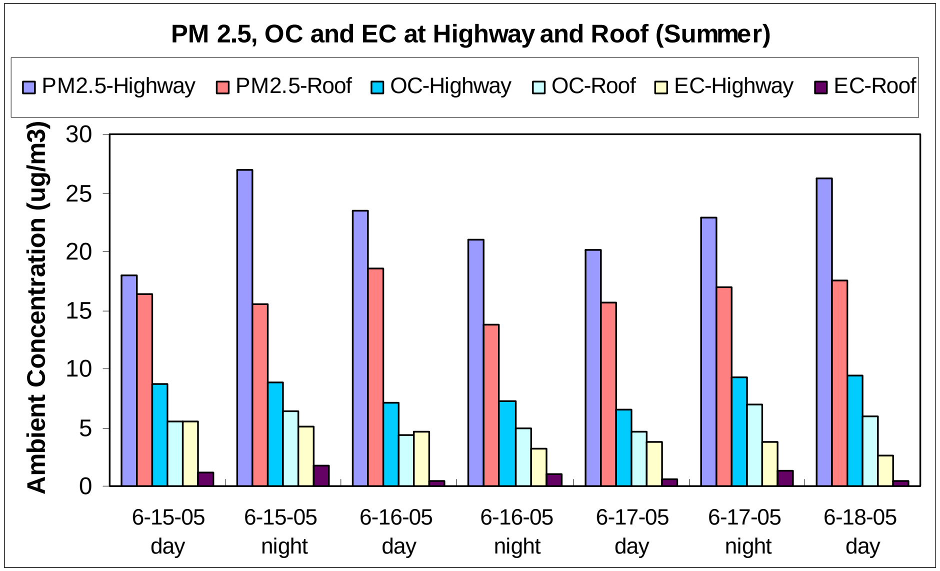
Measurements by Georgia Tech

- PM2.5 mass
- OC and EC
  - thermal optical transmittance (TOT)
- Ions (NH_4^+, NO_3^-, SO_4^{2-}, K^+, etc.)
  - ion chromatography (IC)
- Trace metals (by DRI)
  - X-ray fluorescence (XRF), 40 elements
- Organic Compounds
  - GC-MS, 113 organic compounds quantified
    - Including 2-methyltetrols, pinonic & pinic acids
- WSOC
  - Weber et al.

Highway vs Roof (Summer): PM2.5, OM, OC, EC







OM/PM2.5 (Summer)

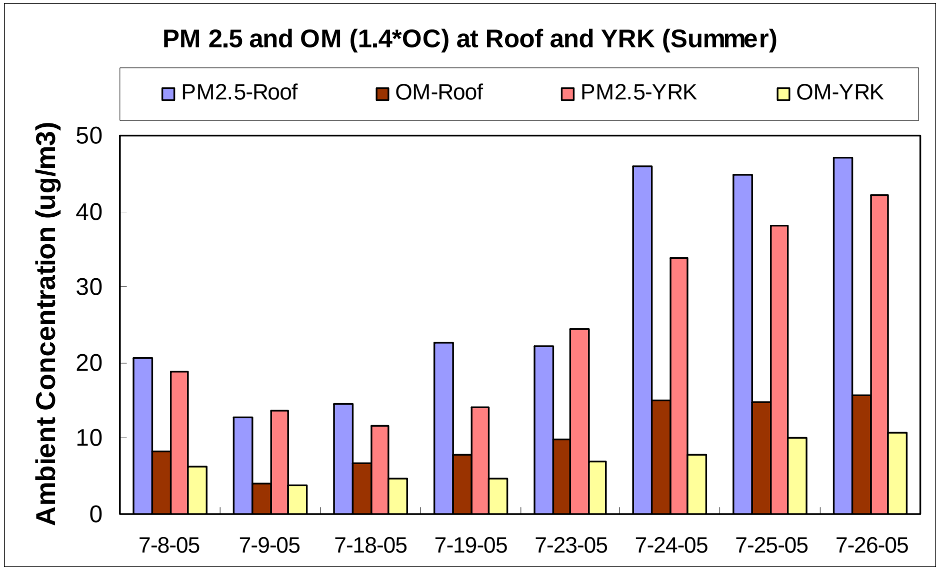
Highway : 46%;   Roof: 39%

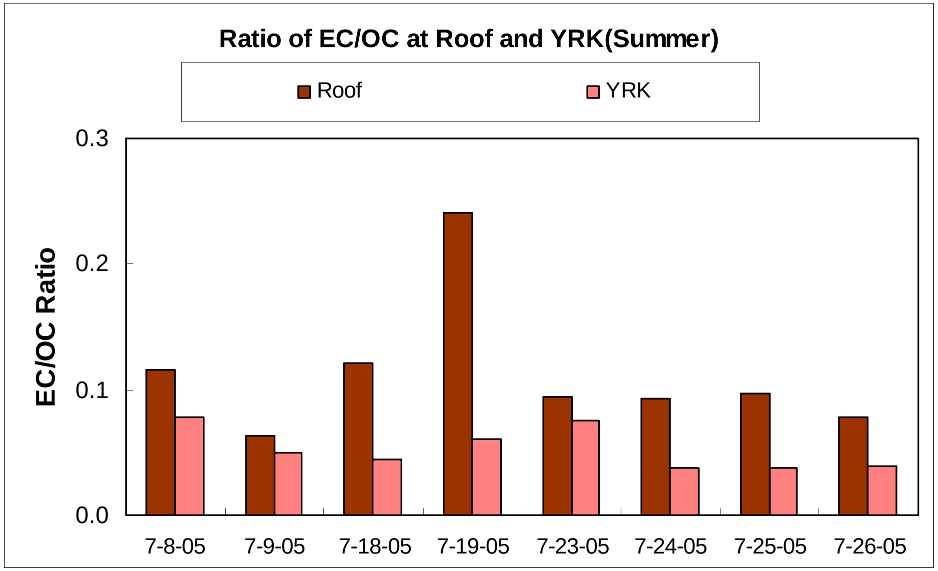
EC/OC ratio (summer)

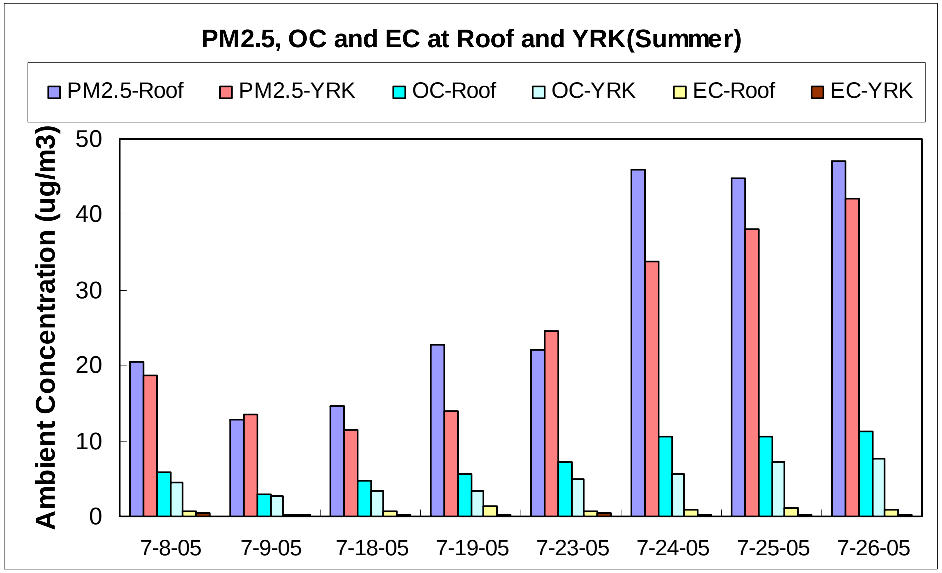
Highway: 0.50;   Roof: 0.18

Diesel vehicle source profile
EC/OC = 1.3 (Schauer et al., 1999)
Gasoline vehicle source profile
EC/OC = 0.02 (Schauer et al., 2002)
Motor vehicle source profiles
EC/OC = 0.94 (DRI, 1998)

Roof vs YRK (Summer): PM2.5, OM, OC, EC







<u>OM/PM2.5 (Summer)</u>

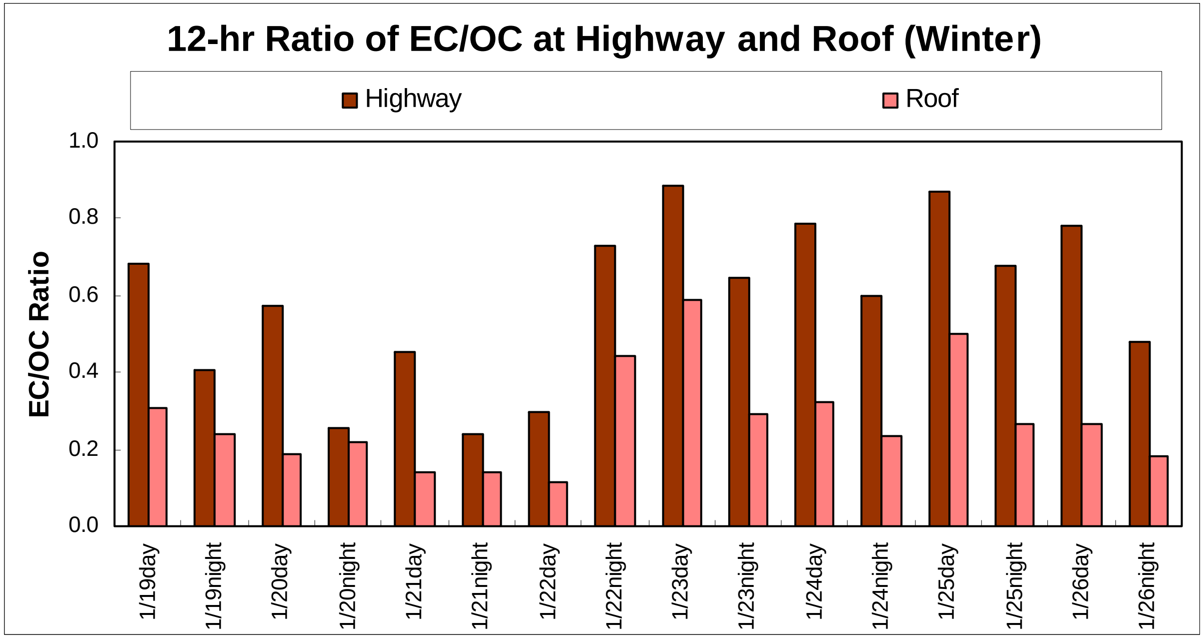
Roof : 36%; YRK: 28%

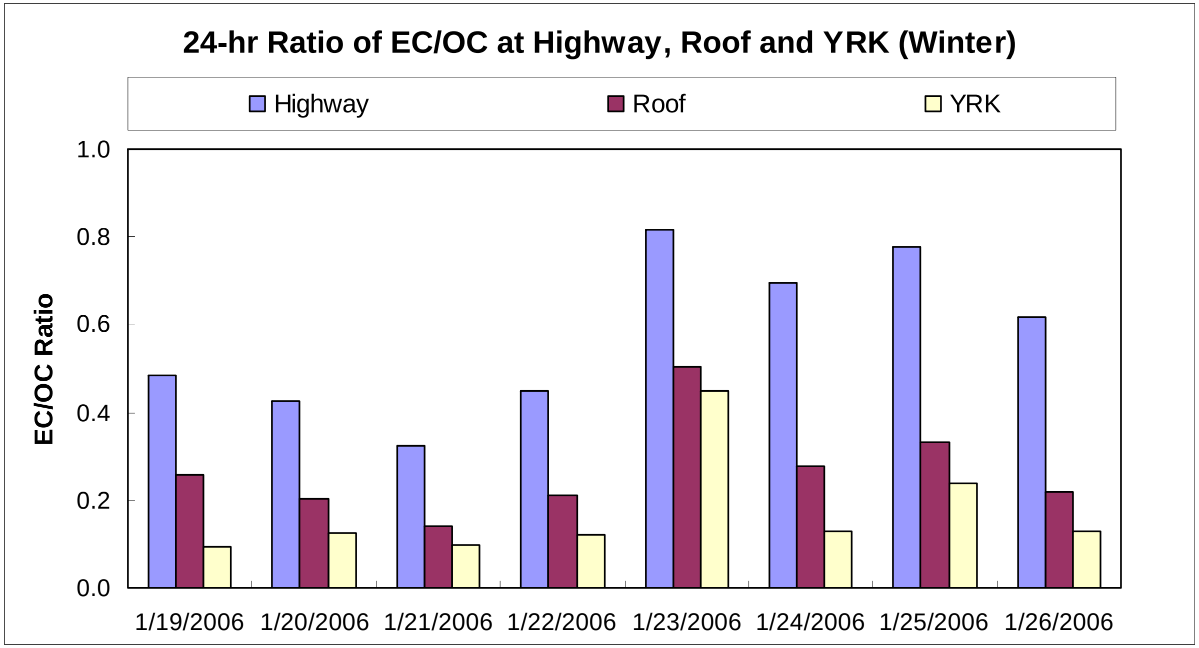
<u>EC/OC ratio (summer)</u>

Roof: 0.11; YRK: 0.05

Haze happened from 07/24 to 07/26

Highway, Roof and YRK (Winter): EC/OC Ratio





<u>EC/OC ratio (Winter)</u>

Highway: 0.59

Daytime: 0.67

Nighttime: 0.50

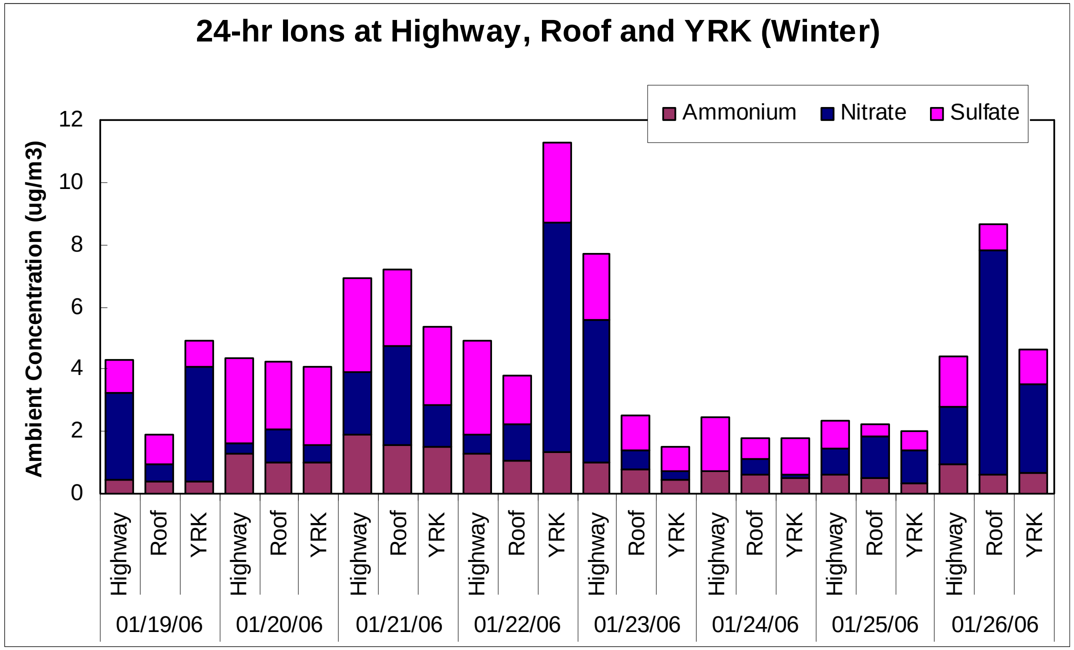
Roof: 0.28

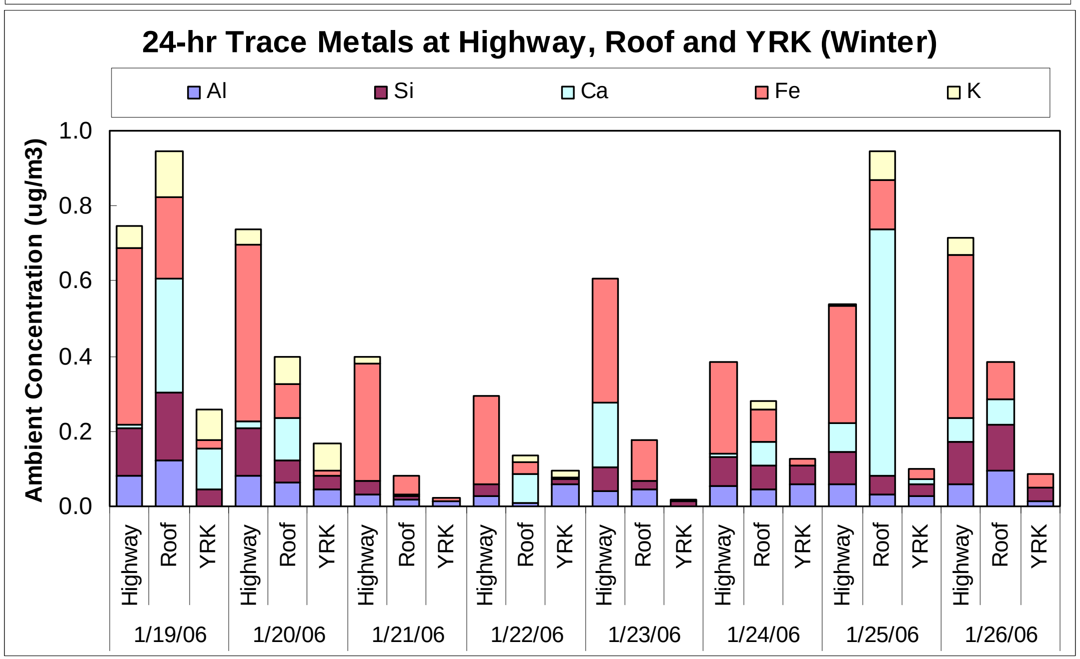
Daytime: 0.30

Nighttime: 0.25

YRK: 0.13

Highway, Roof and YRK (Winter): Ions, Metals





NH_4^+ (winter, $\mu g/m^3$)

Highway: 1.03; Roof: 0.82

YRK: 0.77

NO_3^- (winter)

Highway: 1.62; Roof: 1.95

YRK: 2.16

SO_4^{2-} (winter)

Highway : 2.01; Roof: 1.27

YRK: 1.52

Al (winter)

Highway: 0.05; Roof: 0.05

YRK: 0.03

Si (winter)

Highway: 0.08; Roof: 0.06

YRK: 0.03

Ca (winter)

Highway: 0.04; Roof: 0.16

YRK: 0.02

Fe (winter)

Highway: 0.35; Roof: 0.10

YRK: 0.02

K (winter)

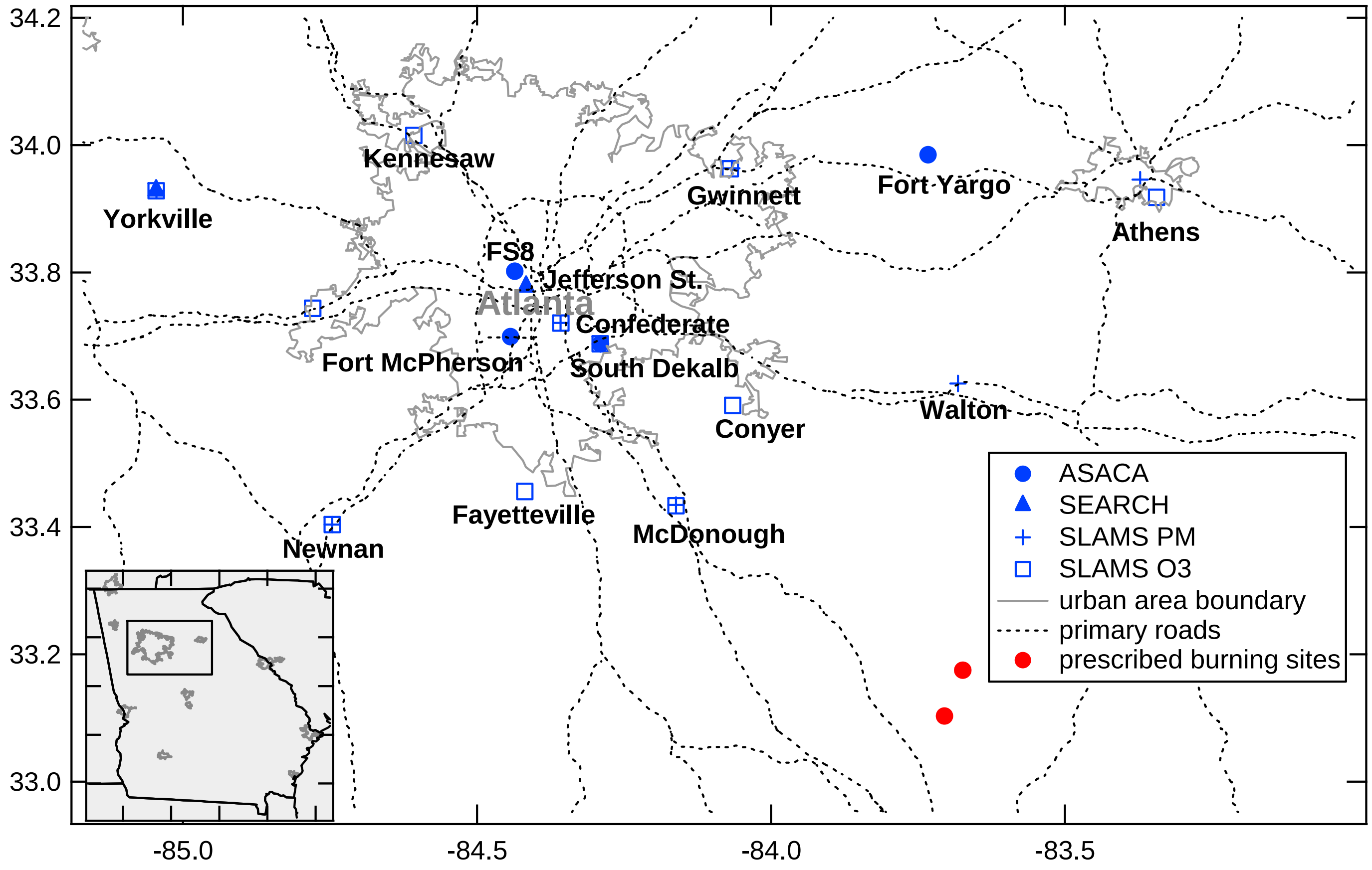
Highway: 0.02; Roof: 0.04

YRK: 0.02

Understanding Fire Impacts

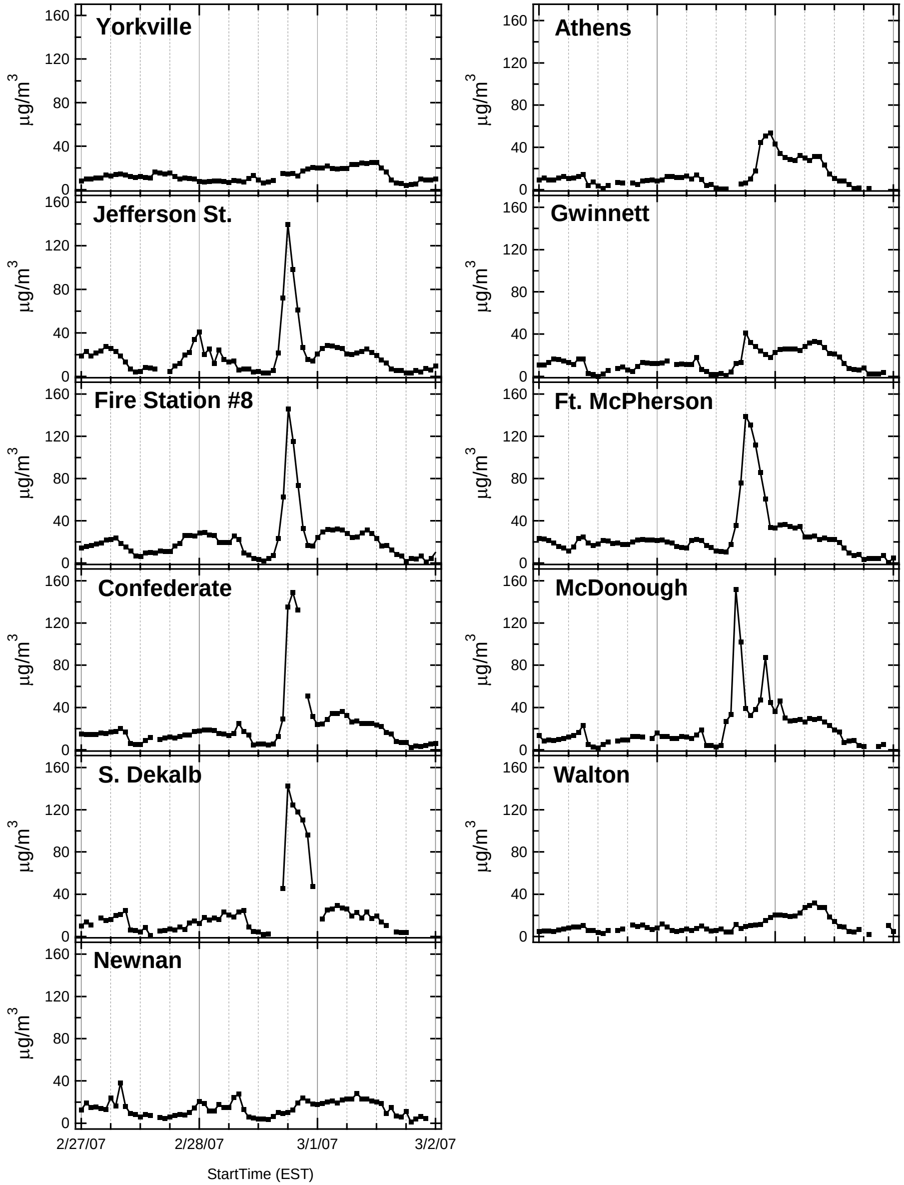
- As sulfate, nitrate and mobile source OC/EC come down, fire-derived carbon will become a more dominant PM component
  - Increased prescribed burning (and possibly wildfires)
- Objective
  - Extend fire emissions studies to measuring plume composition
    - Originally thought about going to prescribed burn sites, but luckily, the plume came to us
- Fire Studies
  - Measurements
    - Prescribed fire, February 28
      - PM2.5 increase over 100 ug m^{-3}
    - Wildfire impacts: May and June
  - Modeling
    - Identification of issues

Monitors



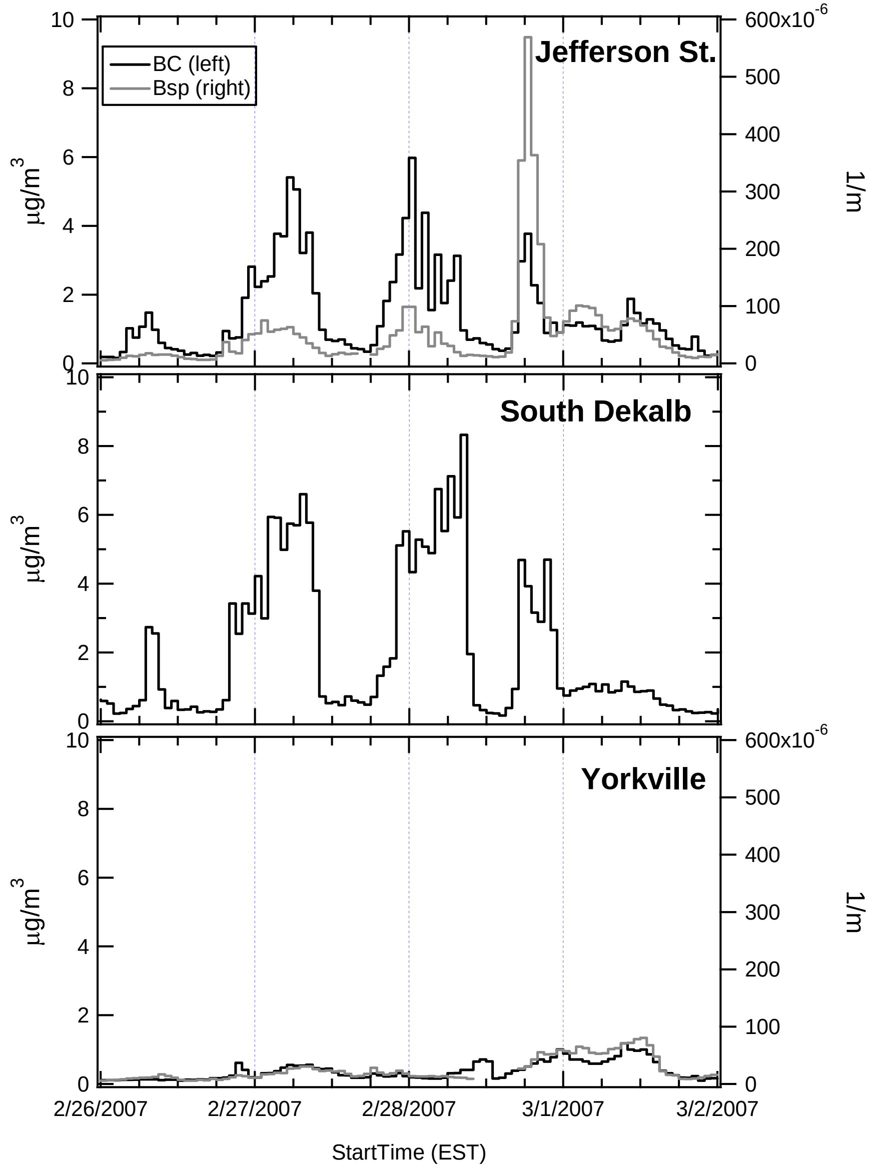
34.2
34.0
33.8
33.6
33.4
33.2
33.0
-85.0
-84.5
-84.0
-83.5
Kennesaw
Yorkville
Gwinnett
Fort Yargo
Athens
FS8
Jefferson St.
Atlanta
Confederate
Fort McPherson
South Dekalb
Walton
Conyer
Fayetteville
McDonough
Newnan
ASACA
SEARCH
SLAMS PM
SLAMS O3
urban area boundary
primary roads
prescribed burning sites

Hourly PM

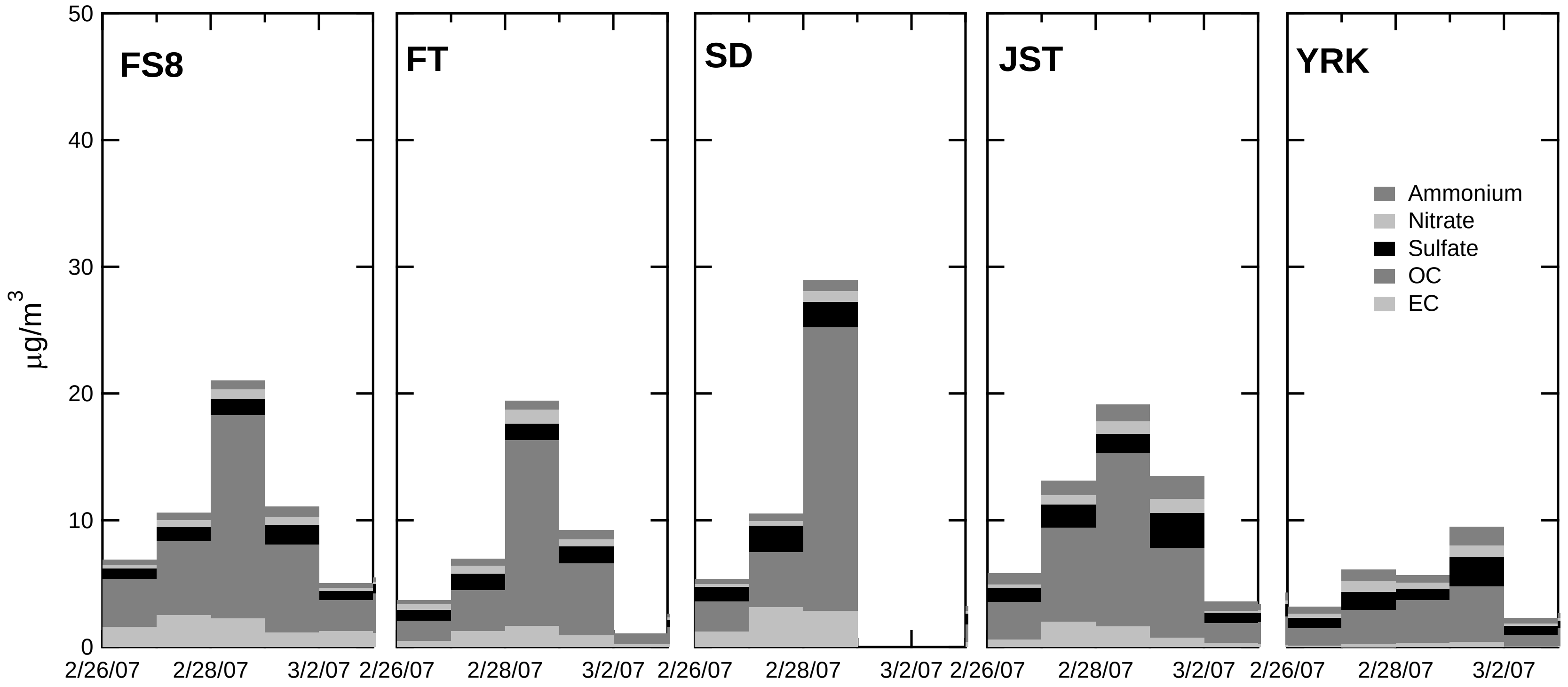


Yorkville
Athens
Jefferson St.
Gwinnett
Fire Station #8
Ft. McPherson
Confederate
McDonough
S. Dekalb
Walton
Newnan
µg/m3
0
40
80
120
160
2/27/07
2/28/07
3/1/07
3/2/07
StartTime (EST)

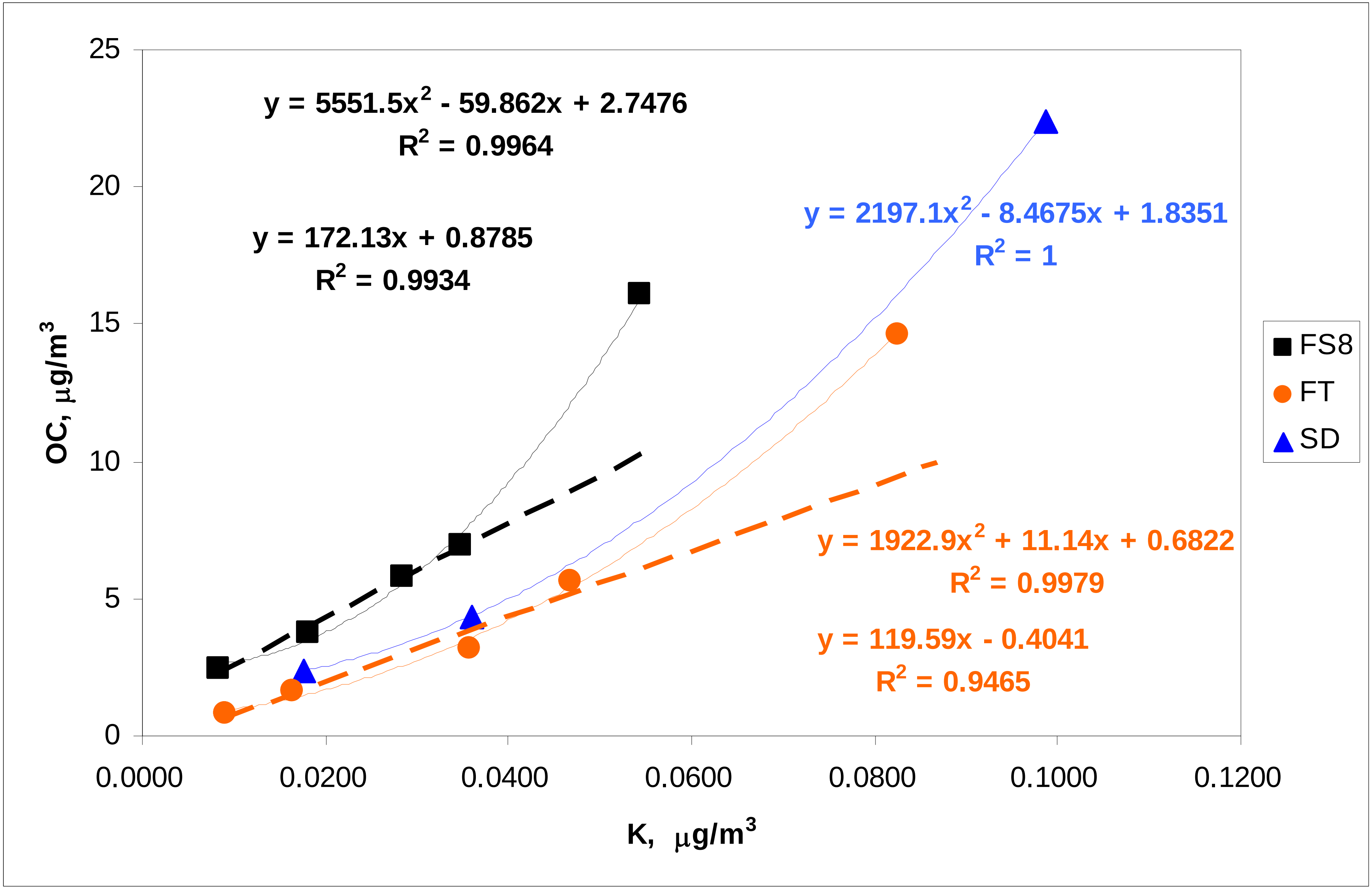
Aethalometer



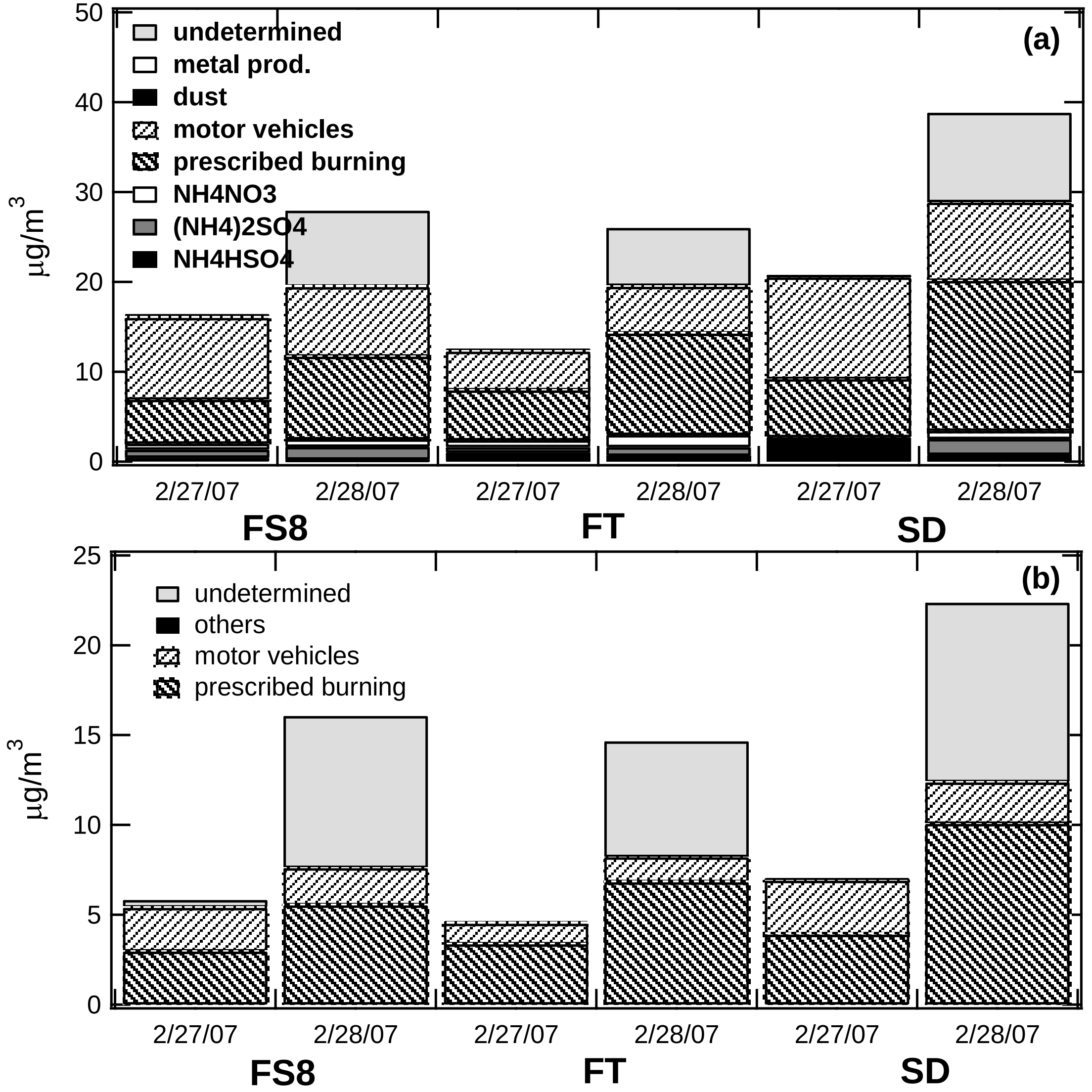
Chemical Composition



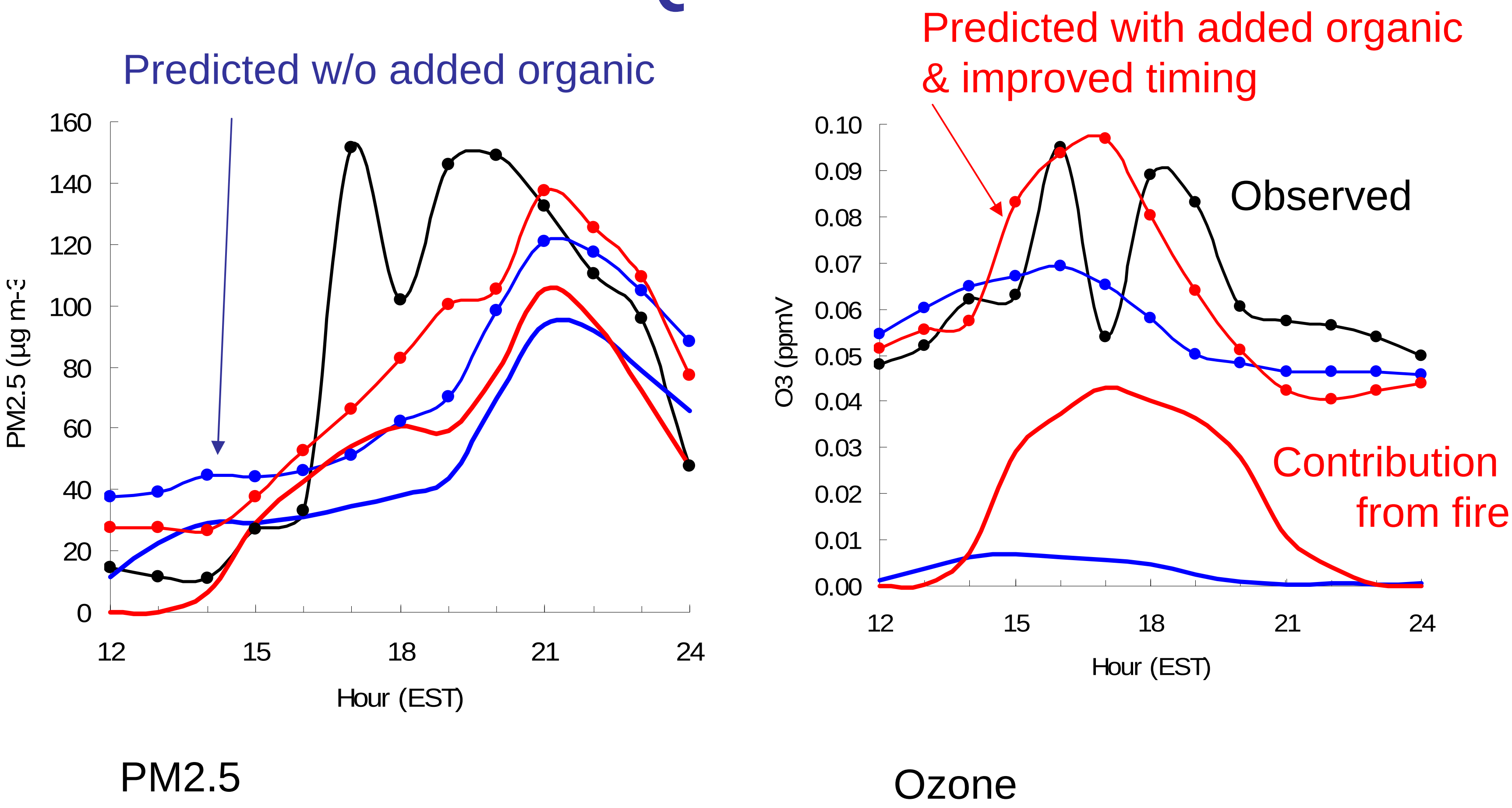
OC-Potassium Relationship



Source Apportionment



CMAQ Results

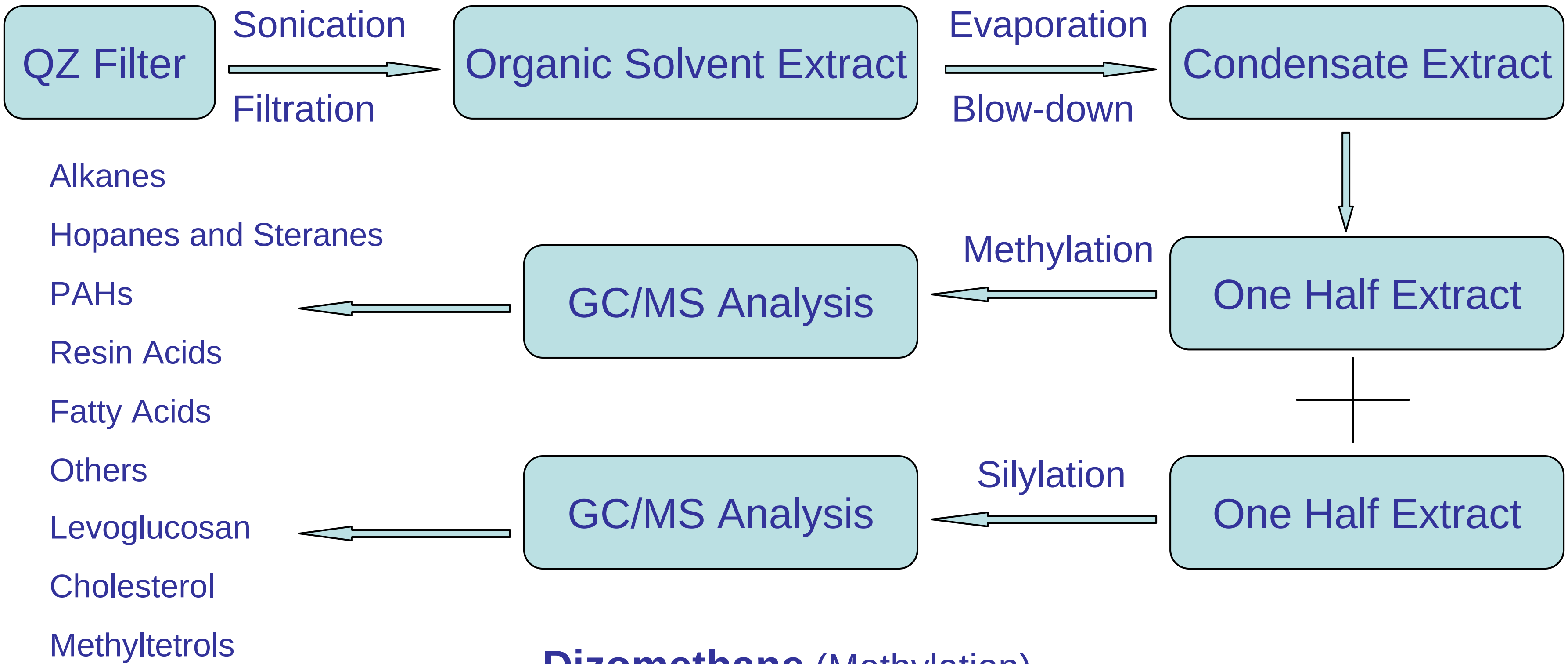


Shown are peak levels at any monitor in the Atlanta area.

Summary

- Comparison of simulated molecular markers and CMAQ results suggests possible increases in emission sources in the Southeast, but...
- Comparison of EC and STN, IMPROVE, SEARCH, ASACA nationally suggest relatively minor changes
- Roadway-Near field-Regional Analysis of molecular markers underway
  - Including products of biogenic VOC oxidation
- Captured a number of fire events
  - Prescribed (mainly pine forest)
    - Suggests need for increased terpenoid emissions in inventory
  - Wild (mixed forest, scrub)

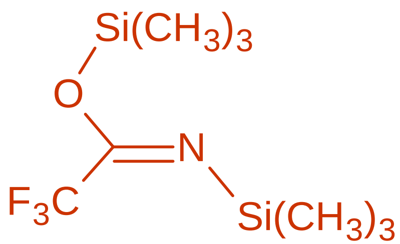
Procedure of GC/MS Analysis



Dizomethane (Methylation)

R-COOH + CH2N2 → R-COO-CH_3 (M+15)

BSTFA (Silylation)



R-OH → R-O-$Si(CH_3)_3$ (M+73)

R-COOH → R-COO-$Si(CH_3)_3$ (M+73)