$PM_{2.5}$ Organic Carbon in Atlanta: Measurements and Statistical Relationships to EPA PAMS Data

Paper # 69721

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Motivation

Ambient air quality in Atlanta, GA, Wednesday, Sept 11, 2002 at 11:00am

Abstract

- A four-site monitoring network was established in metropolitan Atlanta, GA to measure fine particulate mass ($PM_{2.5}$) and composition for approximately one year, beginning in March 1999. Approximately 75% of the mass was identified using various chemical speciation analyses. Of the identifiable portion, carbonaceous material was the largest constituent. In addition, two of the $PM_{2.5}$ instruments were co-located with EPA Type 2 PAMS sites, located at South Dekalb and Tucker. This paper presents a short overview of the $PM_{2.5}$ organic carbon (OC) measurements, as well as statistical relationships among OC and many of the volatile organic precursor gases sampled at the PAMS sites.

Background - PAMS

Photochemical Air Monitoring Stations

- 1990 Clean Air Act called for more monitoring of O_3 .
- Ozone is not emitted directly, but forms in the atmosphere:

$$NO_x + VOC + sunlight \rightarrow O_3$$

- 5-site network in Atlanta, including:
  - Tucker
  - South Dekalb
- PAMS collected data for species with both anthropogenic and biogenic origins, as well as corresponding meteorological data
  - 56 gas-phase species sampled using automatic gas chromatography
- Atlanta is currently considered in “serious” nonattainment status for the ozone NAAQS.

Background - ASACA

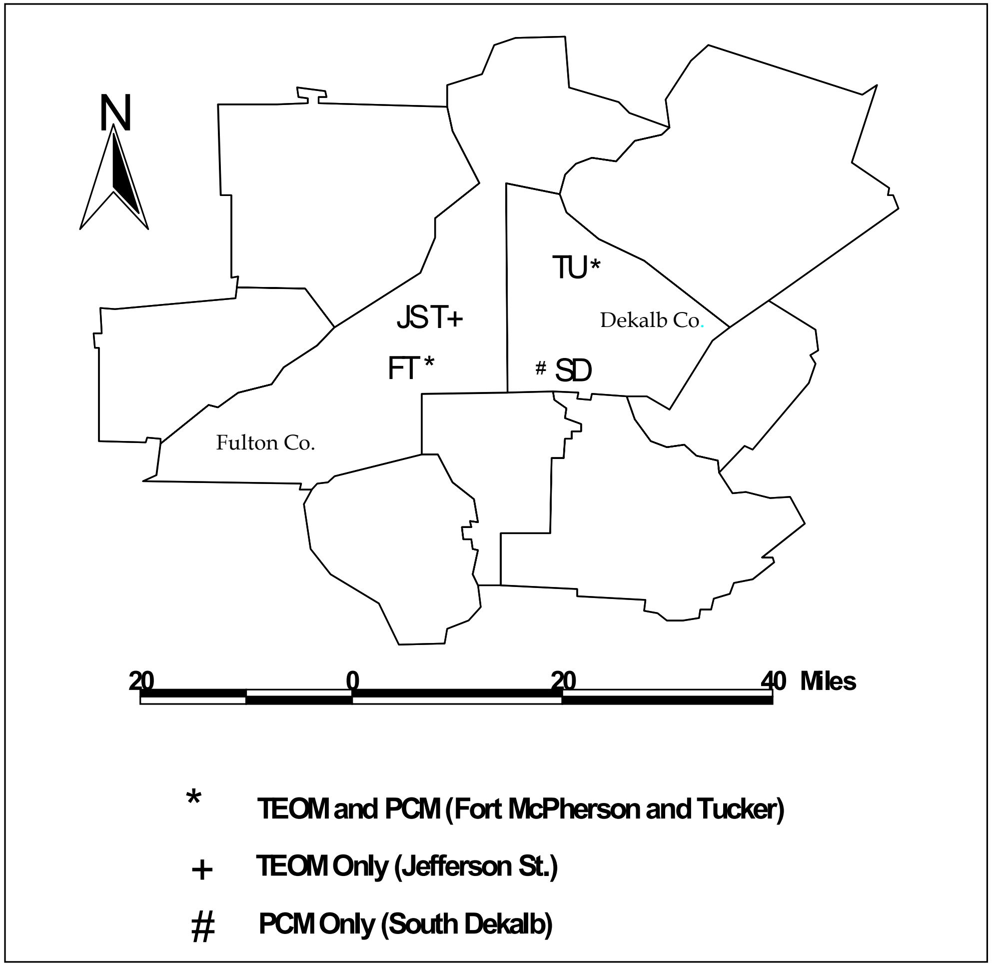
Assessment of Spatial Aerosol Composition in Atlanta

- 4-site monitoring network installed in Atlanta to monitor $PM_{2.5}$ distributions.
  - $PM_{2.5}$: particulates defined by having aerodynamic diameters of ≤ 2.5 microns.
- Auto emissions important in $PM_{2.5}$ formation.
- Ambient levels of $PM_{2.5}$ believed to be closely linked to the formation of ozone in the Atlanta area.
- Integrated, 24-hour measurements of particulate OC in the 2.5 µm size range were obtained; carbonaceous material was the largest constituent.

Objectives

- Two of the three ASACA sites, Tucker and South Dekalb, correspond with the two type 2 PAMS sites; thus the potential exists to examine the relationship between OC concentration and the ozone precursor species.
- The objectives of this work were to:
  - Examine spatial and temporal organic carbon trends at two sites in urban Atlanta during the first year of the ASACA sampling period.
  - Explore PAMS data trends for the summer months of 1999 (June – August).
  - Identify statistical relationships between organic carbon and the many PAMS ozone precursor species.

ASACA Sampling Sites - Locations



Jefferson Street (1999 EPA Supersite)
Urban/commercial
33.777, -84.414

Fort McPherson
Residential (near major highway)
33.699, -84.443

South Dekalb (OC and PAMS data)
Residential (near major highway)
33.688, -84.290

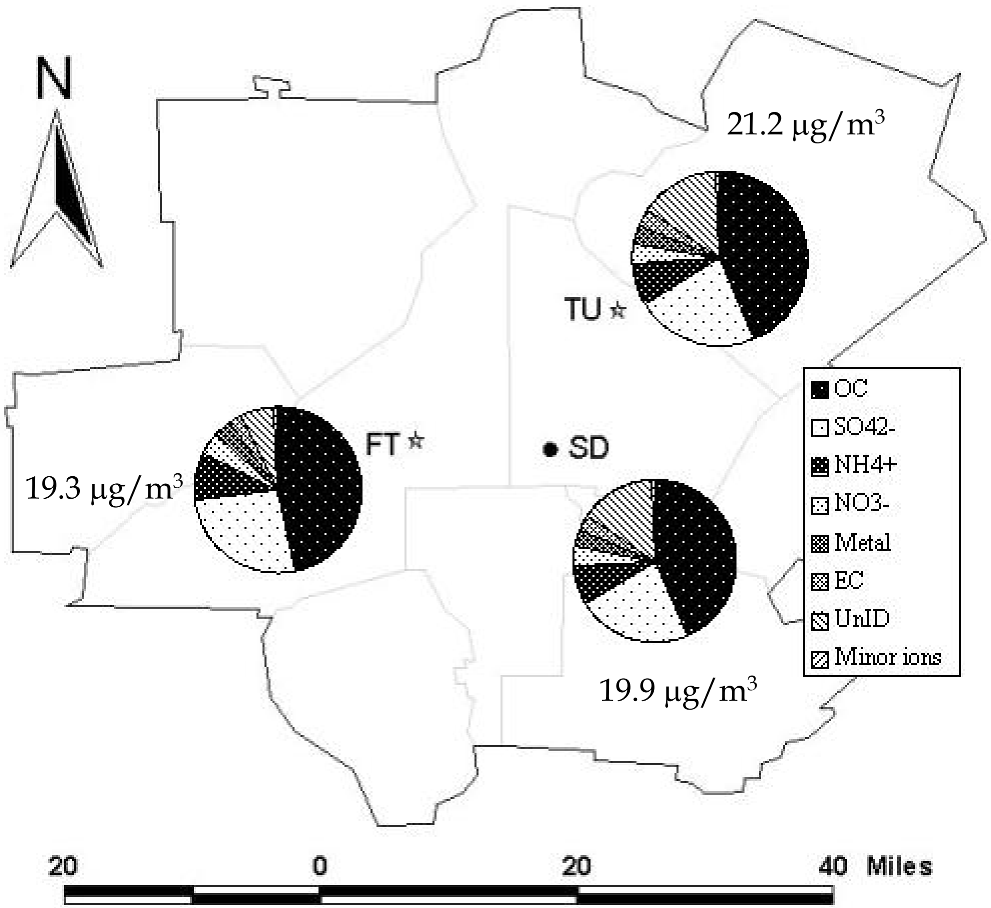
Tucker (OC and PAMS data)
Suburban/commercial
33.848, -84.214

ASACA Sampling Sites - Image

This site is located just west of downtown Atlanta

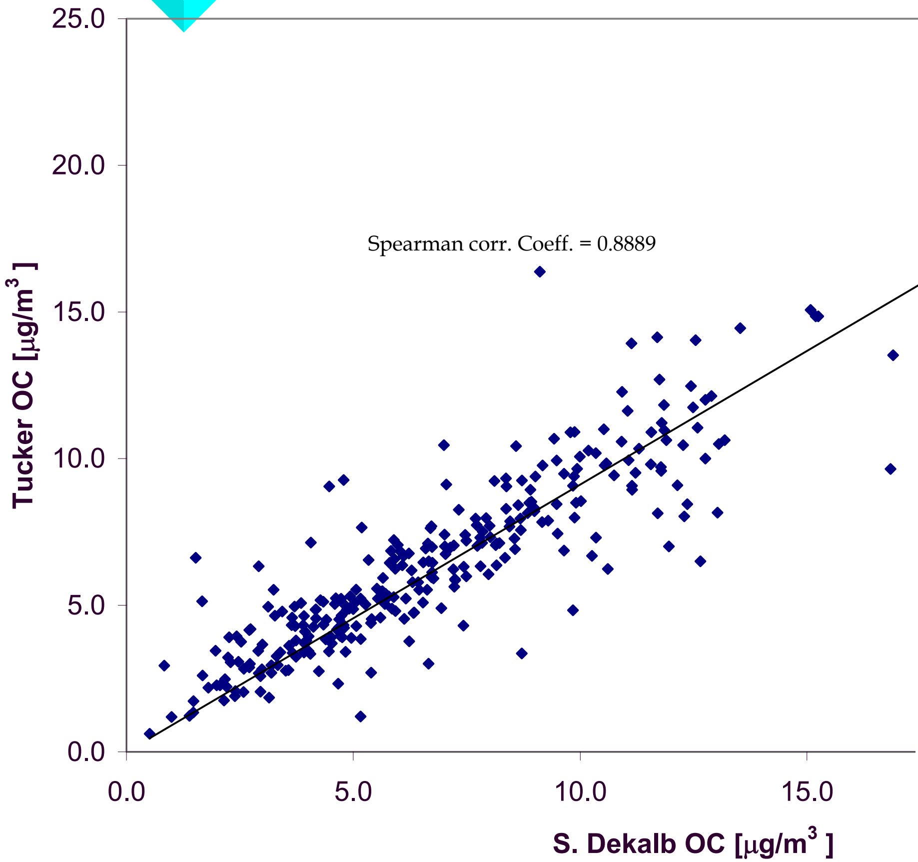
Extensive air quality measurements were made ($PM_{2.5}$, O_3, NO_2, etc.)

Average Chemical Composition



Roughly 40% of the $PM_{2.5}$ mass sampled at the three sites shown was identified as carbonaceous material (the solid black slices of the pie graphs)

Overview of $PM_{2.5}$ OC

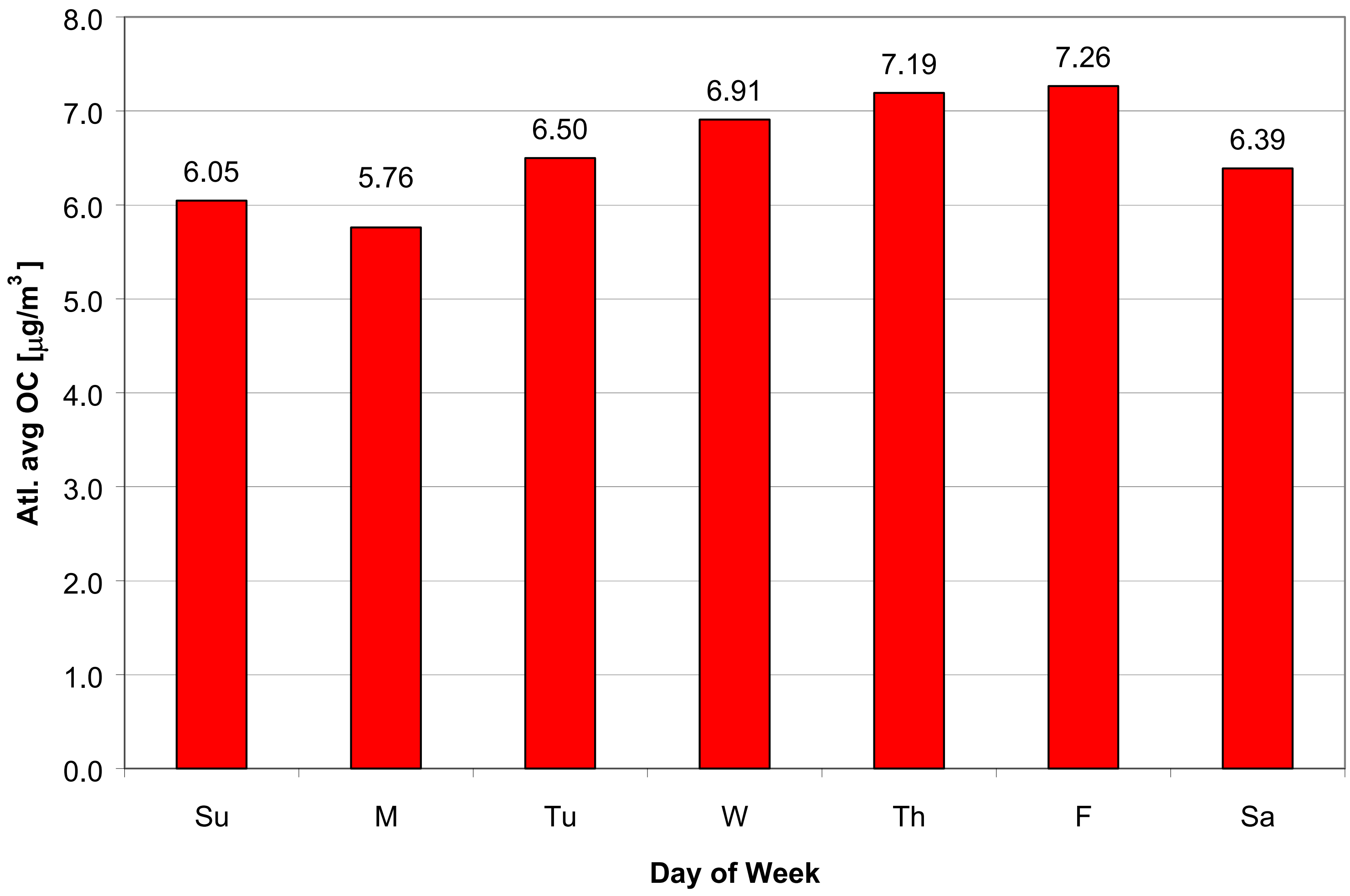


Site-to-site OC correlations
(April 1999 – March 2000)

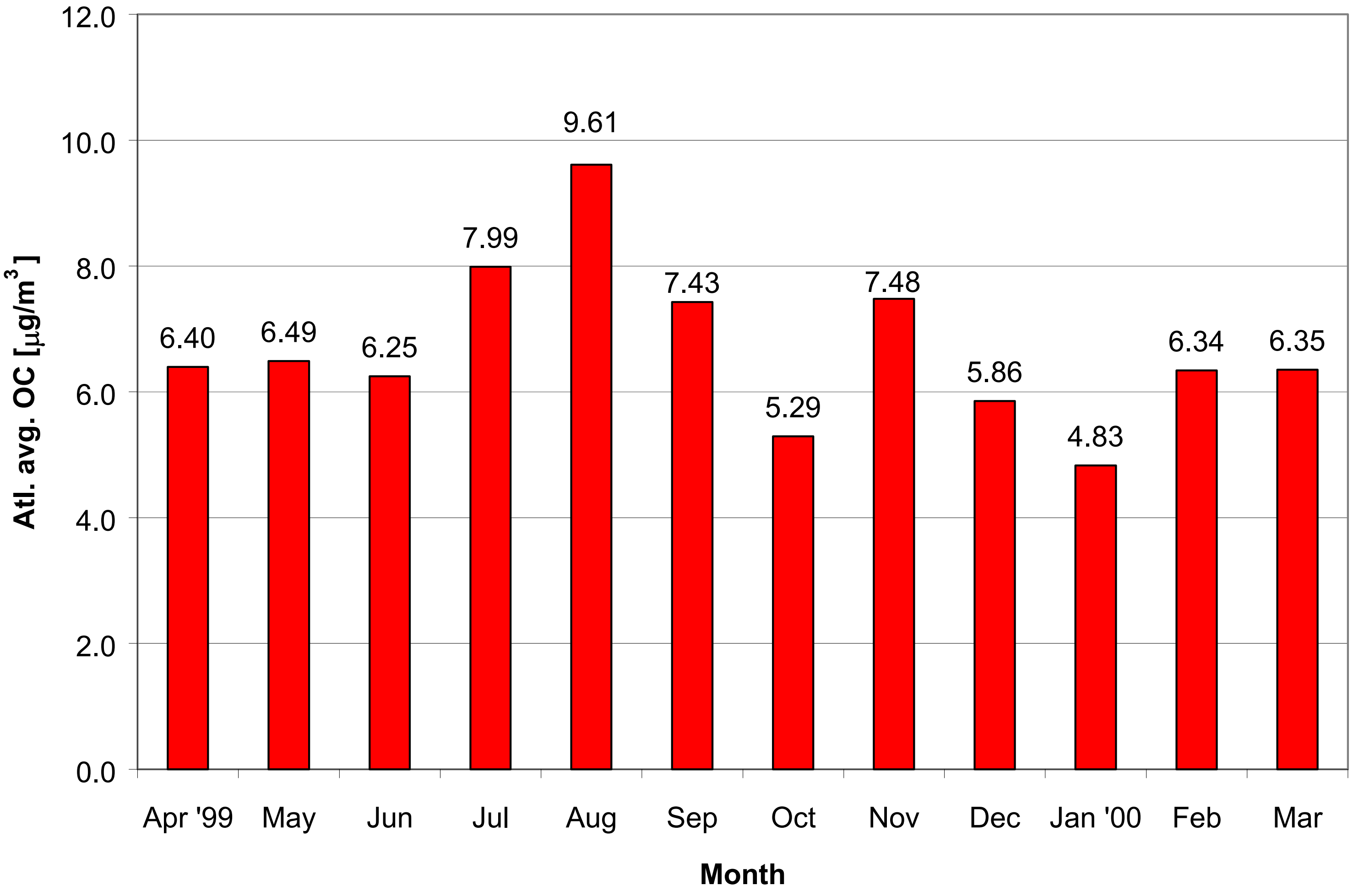
Summary statistics for OC concentrations

	S. Dekalb OC	Tucker OC	Atl. Avg OC
N	305	315	329
Missing	44	34	20
Mean [µg/m^3]	6.8	6.4	6.6
St. Dev. [µg/m^3]	3.4	3.0	3.1
Min. [µg/m^3]	0.5	0.6	0.6
Max. [µg/m^3]	20.9	16.4	16.9

Day of Week OC Trend



Monthly OC Trend



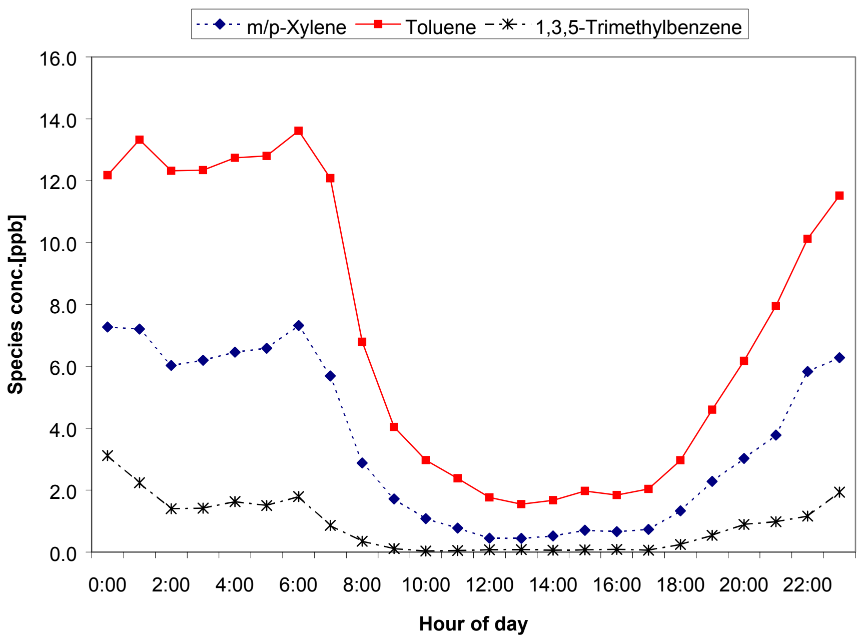
PAMS Target Compounds

Ethylene	2,3-Dimethylbutane	3-Methylheptane
Acetylene	2-Methylpentane	n-Octane
Ethane	3-Methylpentane	Ethylbenzene
Propylene	2-Methyl-1-Pentene	m/p-Xylene
Propane	n-Hexane	Styrene
Isobutane	Methylcyclopentane	o-Xylene
1-Butene	2,4-Dimethylpentane	n-Nonane
n-Butane	Benzene	Isopropylbenzene
trans-2-Butene	Cyclohexane	n-Propylbenzene
cis-2-Butene	2-Methylhexane	m-Ethyltoluene
Isopentane	2,3-Dimethylpentane	p-Ethyltoluene
1-Pentene	3-Methylhexane	1,3,5-Trimethylbenzene
N-Pentane	2,2,4-Trimethylpentane	o-Ethyltoluene
Isoprene	n-Heptane	1,2,4-Trimethylbenzene
trans-2-Pentene	Methylcyclohexane	n-Decane
cis-2-Pentene	2,3,4-Trimethylpentane	1,2,3-Trimethylbenzene
2,2-Dimethylbutane	Toluene	m-Diethylbenzene
Cyclopentane	2-Methylheptane	p-Diethylbenzene
Total NMOC		n-Undecane

Note: α-pinene and β-pinene also collected in Atlanta

PAMS Data Trends (Diurnal)

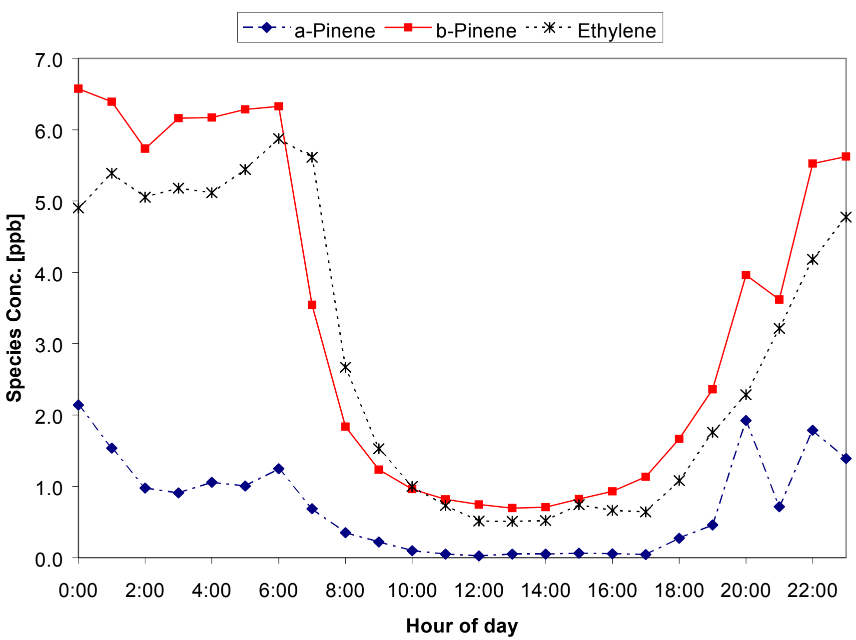
Representative Anthropogenic Species



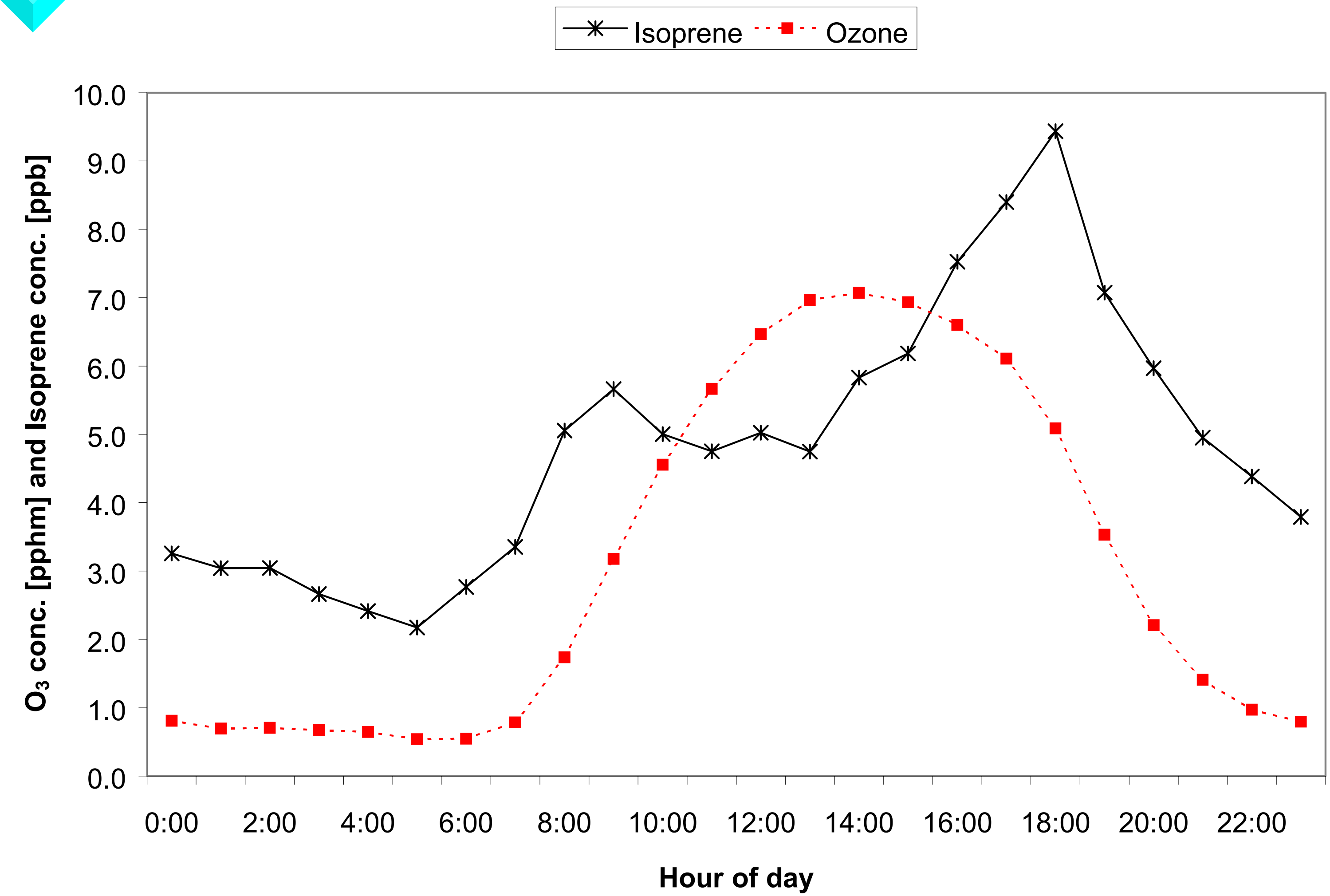
Site-to-site Correlation Coefficients

Compound	Spearman correlation coefficient
α-Pinene	0.6136
β-Pinene	0.4833
Isoprene	0.6469
m/p-Xylene	0.6655
Toluene	0.6831

Representative Biogenic Species

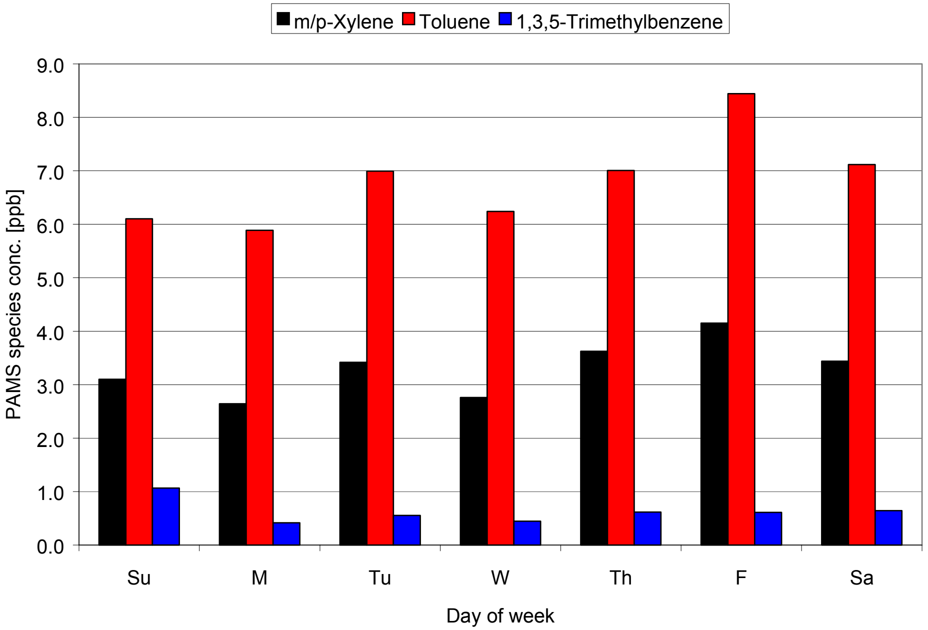


Ozone and Isoprene (Diurnal)

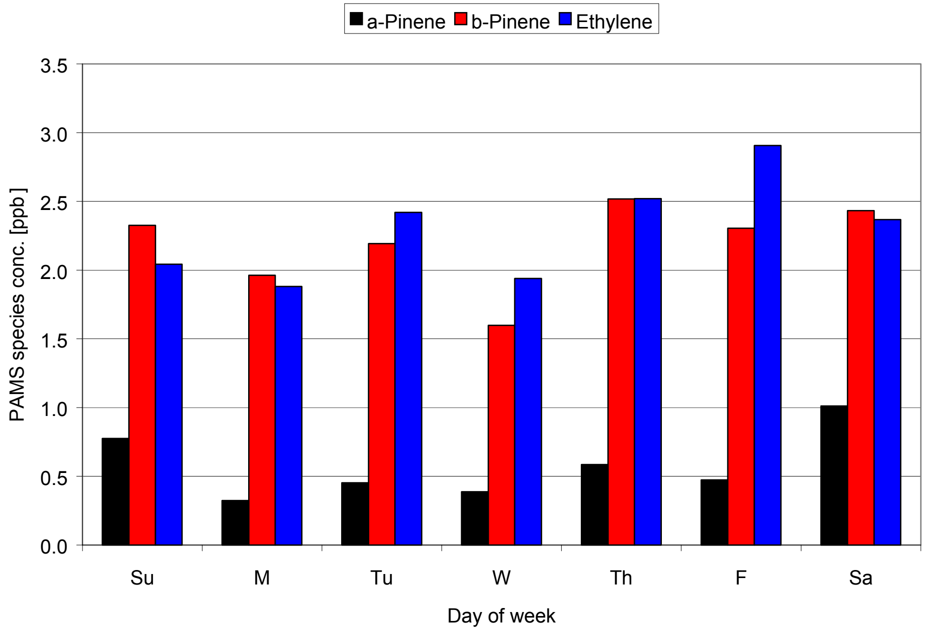


Day-of-week Trends for Selected PAMS Species

Representative Anthropogenic Species



Representative Biogenic Species



OC and PAMS Relationships

- Relationship between isoprene and OC investigated (isoprene's unusual trend)

	OC	Isoprene	O_3
OC	--	0.7525	0.7213
Isoprene	--	--	0.4657

Spearman correlation coefficient matrix

- OC sources may be anthropogenic and secondary (like O_3) and biogenic and primary (like isoprene)

PAMS Species as Precursors of $PM_{2.5}$ OC

- Up to 80% of OC in Atlanta may result from secondary sources
- Results of Grosjean and Seinfeld (1989) used as a starting point
  - "Low" MW gases (< 7 C atoms) irrelevant
  - Estimation of FAC for each PAMS species
- Statistical relationships based on species having appreciable FAC

FAC for PAMS Species (including α-pinene and β-pinene)

FAC expressed as a percentage

Ethylene (0)	3-Methylpentane (0)	**p-Xylene (2.5)**
Acetylene (0)	2-Methyl-1-Pentene (0)	Styrene (0)
Ethane (0)	n-Hexane (0)	**o-Xylene (6.3)**
Propylene (0)	Methylcyclopentane (0.17)	n-Nonane (1.5)
Propane (0)	2,4-Dimethylpentane (0)	Isopropylbenzene (0.7)
Isobutane (0)	Benzene (0)	n-Propylbenzene (0.7)
1-Butene (0)	Cyclohexane (0.17)	**m-Ethyltoluene (2.6)**
n-Butane (0)	2-Methylhexane (0)	**p-Ethyltoluene (2.6)**
trans-2-Butene (0)	2,3-Dimethylpentane (0)	**1,3,5-Trimethylbenzene (2.6)**
cis-2-Butene (0)	3-Methylhexane (0)	**o-Ethyltoluene (2.6)**
Isopentane (0)	2,2,4-Trimethylpentane (0)	1,2,4-Trimethylbenzene (1.7)
1-Pentene (0)	n-Heptane (0)	n-Decane (2.0)
n-Pentane (0)	Methylcyclohexane (1.0)	1,2,3-Trimethylbenzene (1.4)
Isoprene (0)	2,3,4-Trimethylpentane (0)	**m-Diethylbenzene (2.6)**
trans-2-Pentene (0)	Toluene (1.5)	**p-Diethylbenzene (2.6)**
cis-2-Pentene (0)	2-Methylheptane (0.5)	**n-Undecane (2.5)**
2,2-Dimethylbutane (0)	3-Methylheptane (0.5)	**α-Pinene (30)**
Cyclopentane (0)	n-Octane (0.7)	**β-Pinene (30)**
2,3-Dimethylbutane (0)	Ethylbenzene (0.6)	
2-Methylpentane (0)	**m-Xylene (2.5)**	

Spearman corr. coefficients for OC and important PAMS species

Compound	Corr. Coeff.
m/p-Xylene	0.7086
o-Xylene	0.7098
m-Ethyltoluene	0.6219
1,3,5-Trimethylbenzene	0.6891
o-Ethyltoluene	0.6719
m-Diethylbenzene	0.6199
p-Diethylbenzene	0.6383
n-Undecane	0.6007
α-Pinene	0.7003
β-Pinene	0.5513

Multiple Linear Regression Analysis and Results

- Best subsets, stepwise (forward), and stepwise (backward)

Results:

R^2	Adj. R^2	C_p	Variable	Coefficient	p-value
0.8949	0.8885	1.9	α-Pinene (ALPHAP)	2.7146	0.0503
			m-Ethyltoluene (METOL)	2.0158	0.0065
			m/p-Xylene (MPXYL)	3.0502	0.0000
			o-Xylene (OXY)	-4.4527	0.0027
			1,3,5-Trimethylbenzene (TRI)	-4.0556	0.0000

Average conc. (June-Aug. 1999)

Compound	Avg. Conc. [ppb]
α-Pinene	0.57
m-Ethyltoluene	1.88
m/p-Xylene	3.29
o-Xylene	1.32
1,3,5-Trimethylbenzene	0.62

- Both anthropogenic and biogenic sources important; majority of relevant species result from human activity

Concluding Remarks

- Organic carbon trends analyzed over a 12-month sampling period (Apr. 1999 – Mar. 2000) showed late summer peaks, most notably in August, and exhibited slight late- to midweek peaks when analyzed on a day of week basis.
- Two organic carbon sampling sites in Atlanta, Tucker and South Dekalb, showed reasonably high correlations to one another.
- PAMS data showed similar trends, with peak average concentrations in August and a general weekday peak on Friday. However, these trends were not statistically significant.
- Diurnal trends for PAMS species showed early morning peaks and afternoon troughs in all cases except isoprene.
- While both isoprene and ozone are well correlated to OC formation, they are not correlated to one another, suggesting that OC is a product of both anthropogenic and biogenic sources.

Concluding Remarks

- Based on sets of PAMS and OC data collected over the summer of 1999, a simple statistical model was developed with OC as the dependent variable.
- The PAMS compounds relevant to OC formation appear to be α-pinene, o-xylene, m/p-xylene, m-ethyltoluene, and 1,3,5-trimethylbenzene.
- Four of the relevant species have anthropogenic sources, while the other is biogenic in nature.
- The results suggest that formation of OC in Atlanta during the summer months is likely a result of both natural and fuel/combustion emissions, and that a limited number of PAMS species may be secondary sources.

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- Note: This poster was awarded the 3rd Place Prize in the student competition at the 2003 Air & Waste Management Association National Convention, which was held June 21-26 in San Diego, CA.