EVE 402/502
Air Pollution Generation and Control

1. Introduction to Particulate Matter
2. Real (old) data in Atlanta

Background

- *What is $PM_{2.5}$?*
  - Solid (or liquid) particles with aerodynamic diameters < 2.5 µm
- *Why is the 2.5 µm distinction used?*
  - Fine particles: insufficient inertia to deposit in nasal passages (imbed deep within lungs)
  - Toxicity: particles of this size contain chemicals that may be toxic

Background

- *What are the sources of $PM_{2.5}$?*
  - Anthropogenic
    - Primary: IC engines, fireplaces, meat-cooking operations, industrial processes
    - Secondary: atmospheric conversions of SO_2 and NO_x to SO_4^{2-} and NO_3^-, respectively
  - Biogenic
    - Primary: volcanoes, soil erosion, sea spray
    - Secondary: atmospheric conversion of organic gases to particulate organic carbon

Background

- *What are the effects of $PM_{2.5}$?*
  - Environmental impacts: visibility degradation, natural water acidification
  - Human health impacts
    - Morbidity (decreased lung function, increased respiratory hospitalizations, school absenteeism)
    - Mortality (cancer, cardiovascular disease)

Background

- *What are the current rules for $PM_{2.5}$?*
  - USEPA National Ambient Air Quality Standards (NAAQS)
    - 35 $\mu g/m^3$ 24-hr average, 98th percentile (3 yr avg.)
    - 12 $\mu g/m^3$ annual mean, averaged over 3 years
  - NAAQS require monitoring (attainment status may affect federal funding)
  - Constitutionality of EPA's role in setting NAAQS has been debated (and debated) in US courts

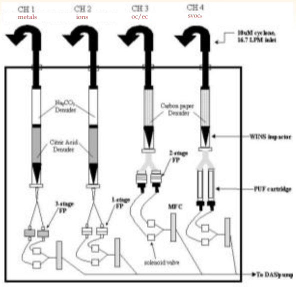
Problem Identification and Research Objectives

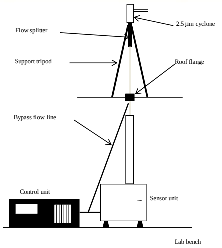
- ASACA goal: *Fully characterize $PM_{2.5}$ spatially and temporally over one year*
- Specific objectives of this work:
  - Develop an urban $PM_{2.5}$ monitoring network
  - Describe temporal and spatial distributions of $PM_{2.5}$ (assess homogeneity)
  - Develop statistical models for estimating $PM_{2.5}$ levels
  - Estimate secondary organic aerosol formation
  - Source ID; Increase power of health studies

Sampling Methods

- Particulate Composition Monitor (PCM)
  - Manual, filter-based multi-channel system
  - 24-hr integrated samples: ions, metals, carbon-containing species
- TEOM®
  - Commercially available, continuous mass
  - Retrofit with Nafion® dryer to minimize volatilization

Schematics of PCM and TEOM





Analytical Methods

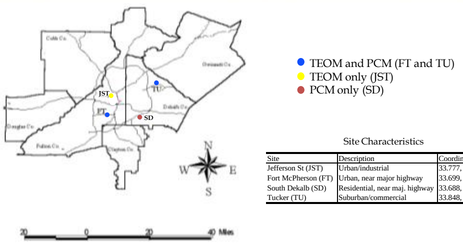
- Ion chromatography (SO_4^{2-}, NO_3^-, NH_4^+)
  - Species extracted from nylon filters using 30 ml ultrapure water and 1 ml CH_3OH
  - 97% extraction efficiency (Russel and Cass, 1984)
- Thermal-optical transmittance (OC/EC)
  - OC and EC volatilized in two stages
  - Oxidation to CO_2, reduction to CH_4, FID quant.
  - “Split point” determined by laser transmittance
- ICP-AES (crustal and trace metals)
  - Species extracted from teflon filters in acid solution
  - Extract “nebulized” into Ar plasma (10,000°C); valence e- excited; characteristic photon emitted

Uncertainties

- Flow meas. and control, < 10%
  - 16.7±1.5 lpm (Temp, Pres. fluctuations)
- Water content (mass meas.), < 5%
  - Nafion dryer for TEOM (RH ≈ 20%)
  - 24-hr equilibration for FRM
- Artifacts
  - Volatilization can be high in summer; refrigeration
  - Adsorption limited by denuders, filter material
- Extraction and analytical instruments, 5-10%
  - Blanks, repeats
- Average uncertainty: 10-15% per measurement

Monitoring Locations and Site Characteristics

ASACA Domain



Site Characteristics

Site	Description	Coordinates
Jefferson St (JST)	Urban/industrial	33.777, -84.414
Fort McPherson (FT)	Urban, near major highway	33.699, -84.443
South Dekalb (SD)	Residential, near maj. highway	33.688, -84.290
Tucker (TU)	Suburban/commercial	33.848, -84.214

Temporal Analysis of $PM_{2.5}$ Mass Data

- Summary statistics

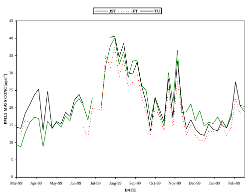
Site	Ann. Mean ± SD [ug/m^3]	Spr. Mean [ug/m^3]	Sum. Mean [ug/m^3]	Aut. Mean [ug/m^3]	Win. Mean [ug/m^3]	Max 1-hr [ug/m^3]	Max 24-hr [ug/m^3]
JST	21.0 ± 13.8	14.1	28.1	24.3	17.7	97.3	48.6
FT	19.3 ± 11.4	Inc. data	26.8	19.8	14.7	90	45.1
TU	21.2 ± 11.9	18.1	30.8	22.6	16.5	87.9	51.5
SD	19.9 ± 9.7	18.1	27.4	20.5	15	--	140*

* Possible outlier (10/15/99)

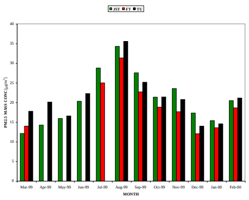
Temporal Analysis of $PM_{2.5}$ Mass Data

- Weekly-averaged and seasonal trends in $PM_{2.5}$ mass

(a) Weekly-averaged trends in $PM_{2.5}$ mass



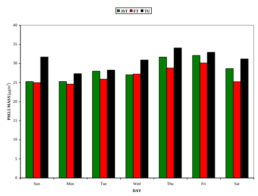
(b) Seasonal variations in $PM_{2.5}$ mass



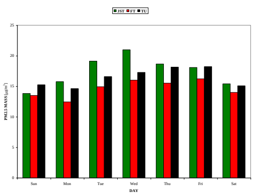
Temporal Analysis of $PM_{2.5}$ Mass Data

- Day-of-week variations in $PM_{2.5}$ mass

(a) Day-of-week $PM_{2.5}$ variations in summer 1999



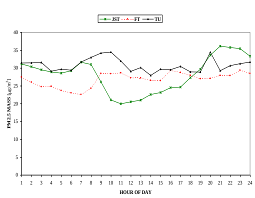
(b) Day-of-week $PM_{2.5}$ variations in winter 1999-2000



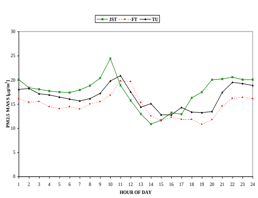
Temporal Analysis of $PM_{2.5}$ Mass Data

- Diurnal variations in $PM_{2.5}$ mass

(a) Diurnal $PM_{2.5}$ variations in summer 1999*



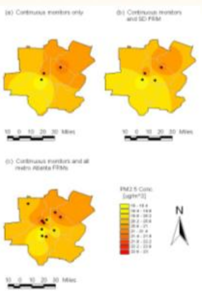
(b) Diurnal $PM_{2.5}$ variations in winter 1999-2000



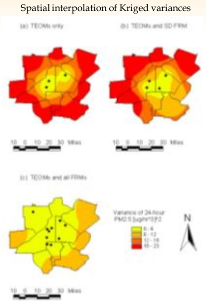
* Potential problems with JST TEOM

Spatial Distributions

Spatial interpolation of annual $PM_{2.5}$ data



Spatial interpolation of Kriged variances

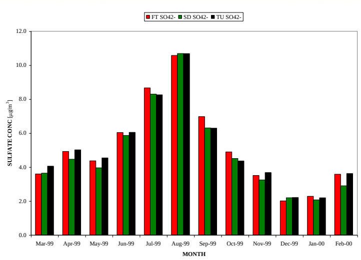


$PM_{2.5}$ Mass Results

- Temporal
  - Highest values in summer
  - Lowest values on Monday
  - Highest values at night and AM rush
- Spatial
  - Overall, little spatial variation
  - Kriged estimates improved with more sites (Georgia DNR data)

Temporal Analysis of SO_4^{2-}

- Seasonal SO_4^{2-} variations and Spearman rank correlation coefficient matrix



Sulfate *R*-values

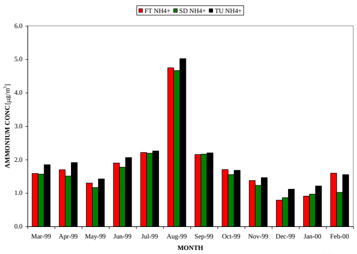
	FT	TU	SD
FT	--		
TU	0.94	--	
SD	0.93	0.93	--

Summary statistics

		SO_4^{2-} Conc. [μg/m^3]		
Site	#Samples	Mean	StDev	Range
FT	331	5.2	3.6	0 - 18.2
SD	313	5.1	3.6	0 - 16.9
TU	326	5.2	3.6	0 - 17.9

Temporal Analysis of NH_4^+

- Seasonal NH_4^+ variations and Spearman rank correlation coefficient matrix



Ammonium *R*-values

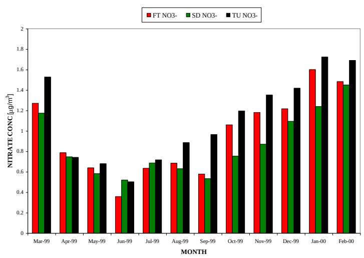
	FT	TU	SD
FT	--		
TU	0.92	--	
SD	0.90	0.92	--

Summary statistics

		NH_4^+ Conc. [µg/m³]		
Site	#Samples	Mean	StDev	Range
FT	331	1.9	1.3	0 - 7.1
SD	313	1.9	1.4	0.1 - 7.0
TU	326	2.0	1.4	0 - 7.1

Temporal Analysis of NO_3^-

- Seasonal NO_3^- variations and Spearman rank correlation coefficient matrix



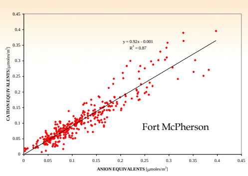
Nitrate *R*-values

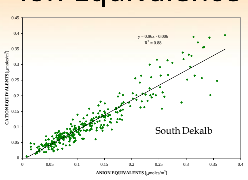
	FT	TU	SD
FT	--		
TU	0.73	--	
SD	0.71	0.74	--

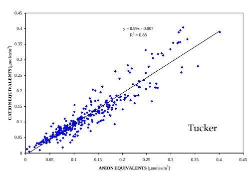
Summary statistics

		NO_3^- Conc. [µg/m³]		
Site	#Samples	Mean	StDev	Range
FT	331	0.9	0.7	0 - 4.2
SD	313	0.8	0.6	0 - 3.8
TU	326	1.1	0.8	0 - 5.1

Data Validation – Ion Equivalence





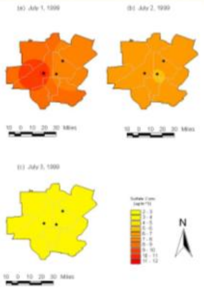


$$anion\ equiv = \frac{Cl^-}{35.453} + \frac{NO_3^-}{62.005} + \frac{SO_4^{2-}}{48.03}$$

$$cation\ equiv = \frac{Na^+}{23.0} + \frac{K^+}{39.098} + \frac{NH_4^+}{18.04}$$

Spatial Analysis of SO_4^{2-} Episode

Spatial interpolation results of a SO_4^{2-} episode, July 1-3, 1999



Wind data during SO_4^{2-} episode

Date	Fort McPh. SO_4^{2-} [μg/m³]	S. Dekalb SO_4^{2-} [μg/m³]	Tucker SO_4^{2-} [μg/m³]	Prev. day wind speed [m/s][a]	Prev. day wind dir. [deg.][a]
July 1	10.3	7.2	7.7	1.1	228.0
July 2	6.3	5.9	6.5	1.2	191.1
July 3	3.8	3.1	4.0	0.9	122.5
July 4	2.2	2.6	2.6	1.0	132.6

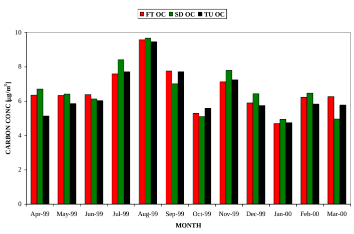
[a]Average wind vector from Tucker and S. Dekalb

Major Ionic Species Results

- SO_4^{2-}
  - Peak values in summer
  - Highest when wind from west (180-360°)
  - Spatially homogeneous
- NO_3^-
  - Peak values in winter
  - Spatially homogeneous
- NH_4^+
  - Peak values in summer
  - Associated with SO_4^{2-} and NO_3^-
  - Spatially homogeneous

Temporal Analysis of OC

- Seasonal OC variations and Spearman rank correlation coefficient matrix



OC *R*-values

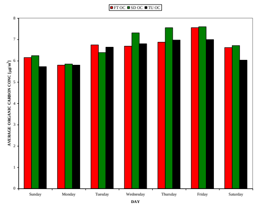
	FT	SD	TU
FT	--		
SD	0.86	--	
TU	0.83	0.86	--

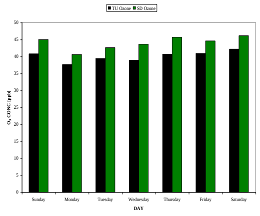
Summary statistics

		Org. Carbon Conc. [μg/m³]		
Site	#Samples	Mean	StDev	Range
FT	328	6.7	3.2	0.7 - 17.8
SD	325	6.8	3.4	0.5 - 20.9
TU	330	6.4	3	0.6 - 16.4

Temporal Analysis of OC

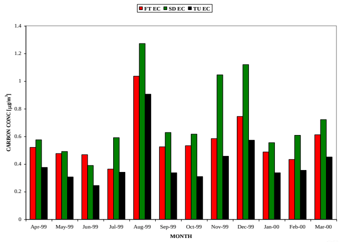
- Day-of-week variations in OC and O_3 concentrations





Temporal Analysis of EC

- Seasonal EC variations and Spearman rank correlation coefficient matrix



EC *R*-values

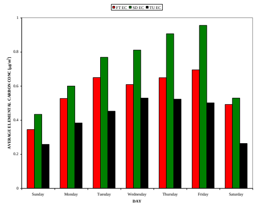
	FT	SD	TU
FT	--		
SD	0.58	--	
TU	0.61	0.8	--

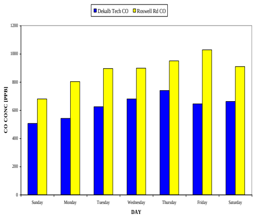
Summary statistics

		Ele. Carbon Conc. [µg/m^3]		
Site	#Samples	Mean	StDev	Range
FT	328	0.6	0.5	0 - 3.09
SD	325	0.7	0.6	0 - 3.31
TU	330	0.4	0.3	0 - 2.44

Temporal Analysis of EC

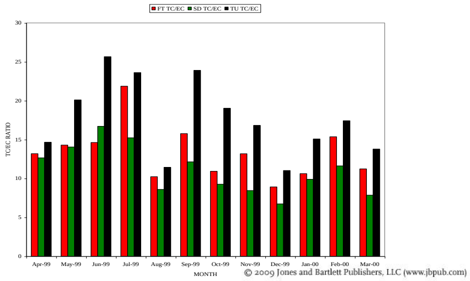
- Day-of-week variations in EC and CO concentrations





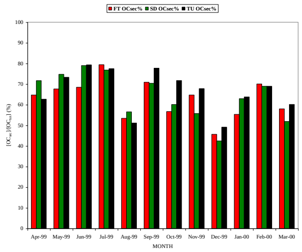
Indicators of Secondary Aerosol Production

- Total carbon (TC=OC+EC) to EC ratio



Estimation of Secondary Aerosol Production

- Method of Turpin and Huntzicker (1991) and Castro et al. (1999)

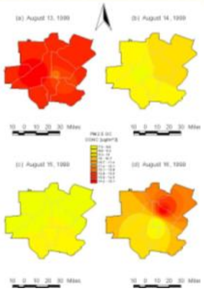


$OC_{sec} = OC_{tot} - OC_{pri}$
$OC_{pri} = EC \times (OC/EC)_{pri}$

OC_{sec} = secondary OC
OC_{tot} = total OC
OC_{pri} = primary OC
$(OC/EC)_{pri}$ = primary ratio estimate

Spatial Analysis of Summer OC Episode

Spatial interpolation results for summer episode



Wind data for summer OC episode, August 13-16, 1999

Date	Fort McPh. OC [μg/m^3]	S. Dekalb OC [μg/m^3]	Tucker OC [μg/m^3]	Prev. day wind speed [m/s][a]	Prev. day wind dir. [deg.][a]
Aug. 13	15.1	12.5	14.0	0.6	214.7
Aug. 14	8.3	9.5	9.9	0.8	236.8
Aug. 15	8.6	9.3	7.9	1.4	291.4
Aug. 16	12.3	11.7	14.1	1.0	173.6

[a]Average wind vector from Tucker and S. Dekalb

OC/EC Results

- Organic carbon
  - Peak values in summer
  - Lowest values on Monday
  - Significant secondary contribution (43-80%)
  - Spatially homogeneous
- Elemental carbon
  - Peak values in summer (August anomaly)
  - Lowest values on weekends

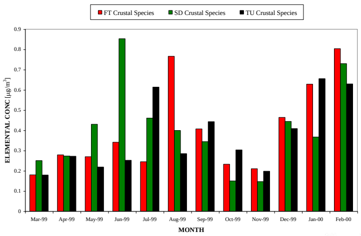
Temporal Analysis of Crustal and Trace Metal Species

- Summary statistics

	Fort McPherson		South Dekalb		Tucker	
Chemical Species	Average ($\mu g/m^3$)	Maximum ($\mu g/m^3$)	Average ($\mu g/m^3$)	Maximum ($\mu g/m^3$)	Average ($\mu g/m^3$)	Maximum ($\mu g/m^3$)
Silicon (SI)	0.044	0.83	0.076	4.05	0.028	0.81
Aluminum (Al)	0.23	1.7	0.19	1.8	0.21	1.7
Calcium (Ca)	0.11	1.1	0.095	0.85	0.099	1.01
Iron (Fe)	0.037	0.93	0.043	0.79	0.033	2.6
Magnesium (Mg)	0.014	0.16	0.012	0.20	0.014	0.16
Nickel (Ni)	0.0027	0.16	0.0046	0.32	0.0036	0.39
Vanadium (V)	0.0005	0.0092	0.0009	0.067	0.0005	0.0098
Cadmium (Cd)	0.0003	0.0056	0.001	0.19	0.0002	0.0052
Chromium (Cr)	0.0015	0.22	0.0031	0.22	0.0035	0.52
Copper (Cu)	0.0019	0.062	0.0028	0.25	0.0021	0.18
Manganese (Mn)	0.0077	0.14	0.0063	0.13	0.0067	0.14
Potassium (K)	0.12	1.8	0.18	3.8	0.13	1.03
Titanium (Ti)	0.0097	0.16	0.0093	0.34	0.0078	0.16
Zinc (Zn)	0.015	0.088	0.015	0.29	0.013	0.24
Lead (Pb)	0.0093	0.063	0.017	2.3	0.0082	0.059
Selenium (Se)	0.073	0.97	0.07	2.7	0.059	1.02

Temporal Analysis of Crustal Species

- Seasonal variation in crustal species and Spearman rank correlation coefficient matrix

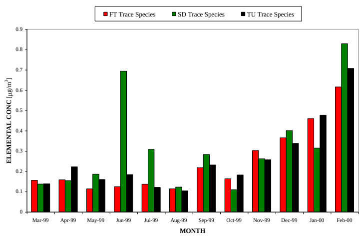


Crustal *R*-values

	FT	SD	TU
FT	--	--	--
SD	0.34	--	--
TU	0.35	0.3	--

Temporal Analysis of Trace Species

- Seasonal variations in trace species and Spearman rank correlation coefficient matrix

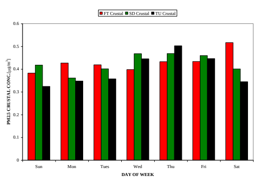


Trace metal *R*-values

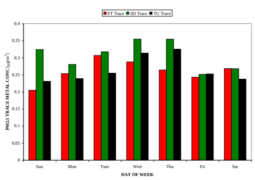
	FT	SD	TU
FT	--	--	--
SD	0.3	--	--
TU	0.43	0.25	--

Temporal Analysis of Crustal and Trace Metal Species

Day-of-week variations in crustal species



Day-of-week variations in trace species



Principal Components Analysis (PCA) for Source Attribution

- Multivariate model – compresses dataset into fewer dimensions (components)
- Minimum number of components contain maximum amount of variance
- Component groupings indicate sources
- Roscoe et al. (1982), Hopke (1983), Biegalski et al. (1998)

Fort McPherson PCA

Element	Component 1	Component 2	Component 3	Component 4	Component 5
Si	--	0.40	--	--	--
Al	0.39	--	--	--	--
Ca	--	--	--	0.37	--
Fe	0.39	--	--	--	--
Mg	--	0.43	--	--	--
Ni	0.30	--	--	--	--
V	0.34	--	--	--	--
Cd	--	--	0.33	--	--
Cr	0.31	--	--	--	--
Cu	--	--	--	--	--
Mn	--	0.51	--	--	--
K	0.39	--	--	--	--
Ti	--	0.49	--	--	--
Zn	--	--	--	--	0.55
Pb	--	--	--	0.73	--
Se	--	--	--	--	0.38
Variance	4.28	2.87	1.87	1.30	1.10

Component		
1	Coal-fired boiler	Cheng et al. (1976)
2	Agr. And natural soil	Chester and Stoner (1974)
3	Motor vehicles	Lee et al. (1999)
4	Mix (veg. burn., mv, cfb)	Edgerton et al. (1984); Huang et al. (1994)
5	Incinerator	Mamame (1988)

South Dekalb PCA

Element	Component 1	Component 2	Component 3	Component 4
Si	0.30	--	--	--
Al	--	--	0.55	--
Ca	--	--	--	0.95
Fe	--	--	--	--
Mg	--	0.45	--	--
Ni	0.32	--	--	--
V	0.31	--	--	--
Cd	0.33	--	--	--
Cr	--	--	--	--
Cu	0.33	--	--	--
Mn	--	0.55	0.37	--
K	--	--	--	--
Ti	--	0.40	--	--
Zn	--	--	0.33	--
Pb	0.33	--	--	--
Se	--	--	--	--
Variance	8.64	2.00	1.44	1.04

Component

1. Coal-fired boiler/incinerator
2. Agricultural and natural soils
3. Motor vehicles
4. Incinerator/coal-fired boiler or soil (Soils dominate for PM_{10})

Tucker PCA

Element	Component 1	Component 2	Component 3	Component 4	Component 5	Component 6
Si	--	0.31	--	--	--	--
Al	0.31	--	--	--	--	--
Ca	--	--	--	0.39	--	0.68
Fe	0.45	--	--	--	--	--
Mg	--	0.36	--	--	--	--
Ni	0.43	--	--	--	--	--
V	--	--	--	--	--	0.30
Cd	--	--	--	--	0.37	--
Cr	0.42	--	--	--	--	--
Cu	--	--	--	--	--	--
Mn	--	0.53	--	--	--	--
K	0.33	--	0.35	--	--	--
Ti	--	0.52	--	--	--	--
Zn	--	--	--	--	--	--
Pb	--	--	--	0.70	--	--
Se	--	--	--	--	0.74	--
Variance	3.63	2.60	2.05	1.36	1.04	1.03

Component

1. Coal-fired boiler
2. Agricultural and natural soils
3. Coal-fired boiler or soil or veg. Burning
4. Motor vehicles
5. Smelting
6. Incinerator (urban mix)

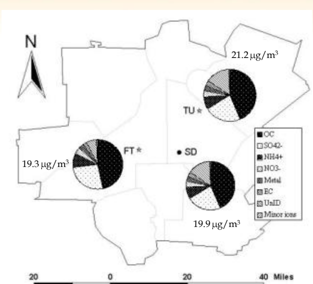
Elemental Species Results

- Crustal and trace metals
  - Both appear bi-modal (summer, winter)
  - June spike at SD due to road construction
  - Significant spatial variation
- Principal components analysis
  - Motor vehicles, coal-fired power plants, soils dominant
  - Sometimes difficult to distinguish sources

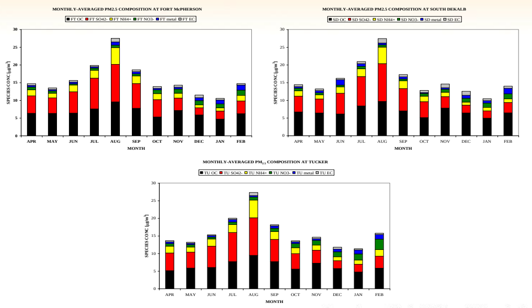
Material Balance

- Sum of chemical constituents vs. TEOM and FRM mass values
  - Carbon
    - "Organic material" = 1.4×OC
      - Accounts for O, H associated with OC (but not quantified via TOT)
  - Crustals
    - To account for oxides (Al_2O_3, SiO_2, CaO, Fe_2O_3)
    - 1.89×Al, 2.14×Si, 1.4×Ca, 1.43×Fe

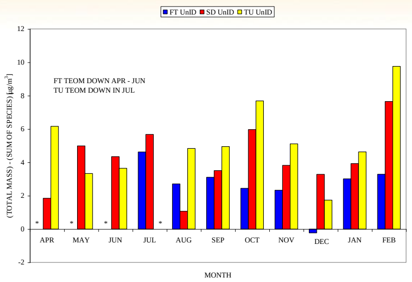
Average Chemical Composition



Seasonal Mass Balance



Seasonal Variation in Unidentifiable Material



Material Balance Results

- Chemical composition
  - 31% Organic material (1.4×OC)
  - 22% SO_4^{2-}
  - 9% NH_4^+
  - 6.4% NO_3^-
  - 3.2% Metals
  - 2% EC
  - 26.4% Unidentifiable material
- UM seasonally invariant

Statistical Modeling of $PM_{2.5}$ Mass

- Used for estimating $PM_{2.5}$ levels when data unavailable
- Models developed for "O_3 season" (April – October 1999)
- Available data
  - Tucker
    - O_3, NO_2, SO_2, T, WSP, WDR, RH, PRECIP, SR, UV
  - South Dekalb (problem with $PM_{2.5}$ data)
    - Same as above, except SR, UV
  - Fort McPherson
    - No supplementary measurements (TU, SD data used)
  - CO measured at two other locations in metro Atl.

Model Development

- Raw data examined for normality
  - Log-transformations indicated
- Multiple linear regression equations derived for 4 cases
  - Case 1: Filling in missing day when prior and subsequent day's values available
  - Case 2: Only prior day's value available
  - Case 3: Only subsequent day's value avail.
  - Case 4: "Back-casting"

Case 1 Results: Previous and Next Days' Values Available

	Fort McPherson		South Dekalb		Tucker	
Term	Coeff.	p-val	Coeff.	p-val	Coeff.	p-val
Intercept	-1.9198	<0.0001	-0.7588	0.1641	-1.3758	<0.0001
Previous day $PM_{2.5}$ (PD)	0.2421	<0.0001	0.4185	<0.0001	0.3986	<0.0001
Next day $PM_{2.5}$ (ND)	0.1169	0.0785	0.2142	0.0044	0.3187	<0.0001
Ozone (O_3)	0.5112	<0.0001	0.2401	0.0062	0.2598	<0.0001
Nitrogen dioxide (NO_2)	0.2837	<0.0001	0.1887	0.0021	0.3183	<0.0001
Carbon monoxide (CO)	0.1972	0.0008	0.0332	0.4853	--	--
Sulfur dioxide (SO_2)	--	--	--	--	0.0705	0.1118
Sin[wind direction], (WDR)	--	--	--	--	0.0458	0.0028
Relative humidity (RH)	0.6077	0.0060	0.3139	0.2348	--	--
Adj. R^2 (%)	75		56		70	
p-val	<0.0001		<0.0001		<0.0001	

Spatially-averaged model for Case 1:

$$[PM_{2.5}] = 0.222[\mathrm{PD}]^{0.38}[ND]^{0.33}[NO_2]^{0.17}[O_3]^{0.34}[CO]^{0.12}[RH]^{0.52} \quad R^2 = 0.74$$

Case 2 Results: Only Previous Day's Values Available

	Fort McPherson		South Dekalb		Tucker	
Term	Coeff.	p-val	Coeff.	p-val	Coeff.	p-val
Intercept	-1.9585	<0.0001	-0.3900	0.0446	-0.5714	<0.0001
Previous day $PM_{2.5}$ (PD)	0.2301	<0.0001	0.3673	<0.0001	0.4427	<0.0001
Ozone (O_3)	0.5680	<0.0001	0.1793	0.0051	0.1843	<0.0001
Nitrogen dioxide (NO_2)	0.3225	<0.0001	0.2147	<0.0001	0.2382	0.0006
Carbon monoxide (CO)	0.2364	<0.0001	0.0619	0.0853	0.2471	0.0001
Sulfur dioxide (SO_2)	--	--			0.1762	0.0002
Temperature (T)	--	--	0.4143	0.0316	--	--
Sin[wind direction], (WDR)	--	--			0.0423	0.0139
Relative humidity (RH)	0.5932	0.0065			--	--
Adj. R^2 (%)	75		53		65	
p -val	<0.0001		<0.0001		<0.0001	

Spatially-averaged model for Case 2:

$$[PM_{2.5}] = 0.0234[PD]^{0.40}[O_3]^{0.41}[CO]^{0.24}[RH]^{0.49}[SO_2]^{0.15}[NO_2]^{0.13} \quad R^2 = 0.69$$

Case 3: Only Next Day's Values Available

	Fort McPherson		South Dekalb		Tucker	
Term	Coeff.	p-val	Coeff.	p-val	Coeff.	p-val
Intercept	-2.0577	<0.0001	-0.4931	0.0047	-0.3909	0.0067
Next day $PM_{2.5}$ (ND)	0.0940	0.1691	0.2900	0.0003	0.3915	<0.0001
Ozone (O_3)	0.6627	<0.0001	0.2738	0.0008	0.2615	<0.0001
Nitrogen dioxide (NO_2)	0.3277	<0.0001	--	--	0.3172	<0.0001
Nitrogen monoxide (NO)	--	--	0.0954	<0.0001	--	--
Carbon monoxide (CO)	0.2289	0.0002	--	--	--	--
Sulfur dioxide (SO_2)	--	--	--	--	0.0957	0.0604
Temperature (T)	--	--	0.8761	<0.0001	0.4653	<0.0001
Sin[wind direction], (WDR)	--	--	--	--	0.0552	0.0018
Relative humidity (RH)	0.6750	0.0035	--	--	--	--
Total UV Radiation (UV)	--	--	-0.2300	0.0065	-0.2197	0.0007
Adj. R^2 (%)	73		53		60	
p -val	<0.0001		<0.0001		<0.0001	

Spatially-averaged model for Case 3:

$$[PM_{2.5}] = 10^{(0.035WDR - 2.16)}[ND]^{0.35}[O_3]^{0.40}[RH]^{0.71}[T]^{0.51}[NO_2]^{0.36}[CO]^{0.11}$$

$R^2 = 0.66$

Case 4: Back-casting

	Fort McPherson		South Dekalb		Tucker	
Term	Coeff.	p-val	Coeff.	p-val	Coeff.	p-val
Intercept	-2.1269	<0.0001	-2.1595	0.0010	-0.5583	0.0012
Ozone (O_3)	0.7078	<0.0001	0.3328	<0.0001	0.2587	<0.0001
Nitrogen dioxide (NO_2)	0.3668	<0.0001	0.1484	0.030	0.3671	<0.0001
Carbon monoxide (CO)	0.2545	<0.0001	--	--	0.1550	0.0376
Sulfur dioxide (SO_2)	--	--	--	--	0.1993	0.0003
Temperature (T)	--	--	1.2989	<0.0001	0.5346	<0.0001
Sin[wind direction], (WDR)	--	--	--	--	0.0633	0.0020
Relative humidity (RH)	0.6812	0.0027	--	--	--	--
Solar Radiation (SR)	--	--	1.2484	0.0118	--	--
Total UV Radiation (UV)	--	--	-1.6117	0.0036	-0.1417	0.0467
Adj. R^2 (%)	73		51		52	
p -val	<0.0001		<0.0001		<0.0001	

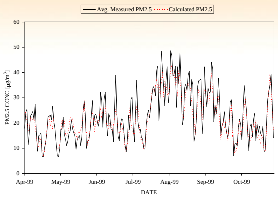
Spatially-averaged model for Case 3:

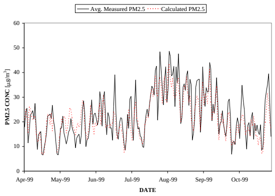
$$[PM_{2.5}] = 10^{(0.059WDR - 2.02)}[O_3]^{0.43}[RH]^{0.58}[T]^{0.61}[NO_2]^{0.32}[CO]^{0.13}[SO_2]^{0.22}$$

$R^2 = 0.63$

Comparison of Models: Case 1 and Case 4

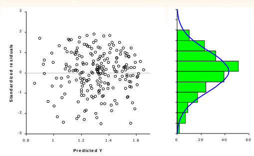
Case 1: $R^2 = 0.74$



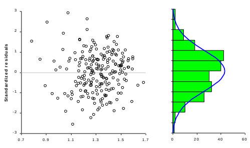


Case 4: $R^2 = 0.63$

Residual analysis



Case 1 Model



Case 4 Model

Statistical Modeling Results

- Significant potential for retrospective estimation
  - Up to 74% of variance explained
- Spatial estimates limited by site-to-site inconsistencies
  - Loss of detail acceptable (lack of spatial variability)

Conclusions

- Temporal variation in $PM_{2.5}$ concentrations greater than spatial
- Mean 24-hour levels: 19.3 - 21.2 μg/m^3
  - Annual NAAQS: 15 μg/m^3 (3 yrs data)
- Peak levels in summer (mass and all species except NO_3^-)
  - August 1999 was anomalous
- Slight increase in $PM_{2.5}$ during work week
- Late-night, early-morning diurnal peaks

Conclusions

- Major ions accounted for ~40% of mass
- OC largest single species (~31% of mass)
  - Secondary formation important (43-79%)
- Metal species bi-modal
  - Significant spatial variability
  - PCA: coal-fired boilers, soils, motor vehicles dominate
- Unidentifiable material invariant with season
- Statistical modeling explained >70% of variance
  - Spatial modeling proved unproductive