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

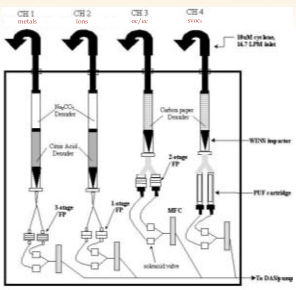
Problem Identification and Research Objectives

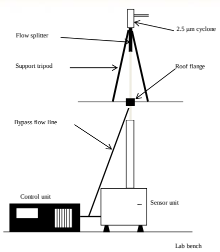
- ASACA goal: *Fully characterize $PM_{2.5}$ spatially and temporally over one year*
- Specific objectives of this work:
  - Develop an urban $PM_{2.5}$ monitoring network
  - Describe temporal and spatial distributions of $PM_{2.5}$ (assess homogeneity)
  - Develop statistical models for estimating $PM_{2.5}$ 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



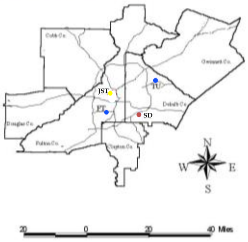


Analytical Methods

- 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

Monitoring Locations and Site Characteristics

ASACA Domain



- TEOM and PCM (FT and TU)
- TEOM only (JST)
- PCM only (SD)

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*

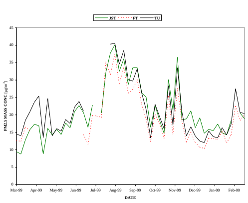
* Possible outlier (10/15/99)

Remember: Annual NAAQS = 12.0 μg/m^3

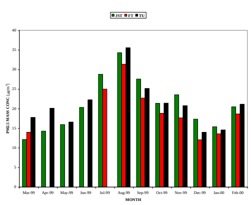
Temporal Analysis of $PM_{2.5}$ Mass Data

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

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



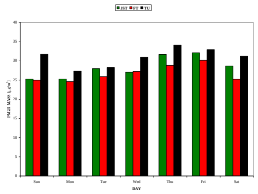
(b) Seasonal variations in $PM_{2.5}$ mass



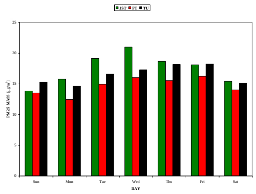
Temporal Analysis of $PM_{2.5}$ Mass Data

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

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



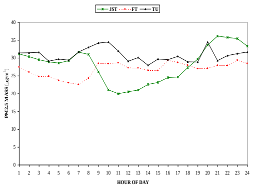
(b) Day-of-week $PM_{2.5}$ variations in winter 1999-2000



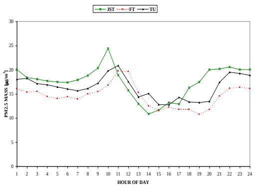
Temporal Analysis of $PM_{2.5}$ Mass Data

- Diurnal variations in $PM_{2.5}$ mass

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



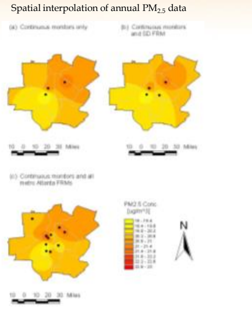
(b) Diurnal $PM_{2.5}$ variations in winter 1999-2000



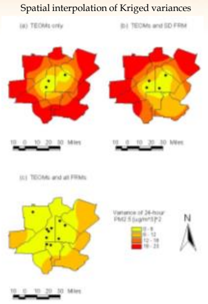
* Potential problems with JST TEOM

Spatial Distributions

Spatial interpolation of annual $PM_{2.5}$ data



Spatial interpolation of Kriged variances



$PM_{2.5}$ Mass Results

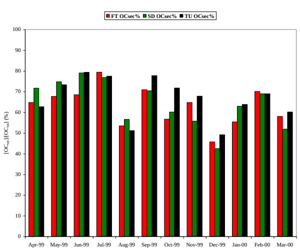
- Temporal
  - Highest values in summer
  - Lowest values on Monday
  - Highest values at night and AM rush
- Spatial
  - Overall, little spatial variation
  - Kriged estimates improved with more sites (Georgia DNR data)

Major Ionic Species Results

- SO_4^{2-}
  - Peak values in summer
  - Highest when wind from west (225-315°)
  - 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

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

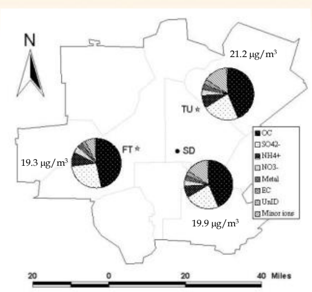
OC/EC Results

- 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

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

Average Chemical Composition



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
    - 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"

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 (back then): 15 μg/m^3 (3 yrs data)
  - Annual NAAQS (current): 12 μg/m^3 (3 yrs data)
- Peak levels in summer (mass and all species except NO_3^-)
  - Highest values in August 1999
- 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 (43-80%)
- 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

Recent Trends