Atmospheric Aerosols

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MAGEEP Atmospheric Aerosols Module
Version 1.0

- Ambient aerosol physical and chemical properties and certain effects
  - particle morphology, size and chemical composition
  - particle formation, transport and fate
  - aerosol levels and attribution to emissions sources
- Current module content focuses on urban aerosols at ground level
  - module will be expanded to include aerosols at:
    - remote/rural locations
    - marine locations
    - free troposphere
    - stratosphere
Aerosol Physical Properties

- Complex morphology
  - Typically treat particle as a sphere with equivalent aerodynamic, optical or electric mobility diameter

- Sizes range from a few nanometers to 100s of micrometers
  - Focus on particles up to ~ 10 micrometers (PM-10)
  - Aerosol size distributions by number, surface area, and volume (or mass)
    - size distributions can be stable or can change rapidly in time and by location

Magnified ambient particles from the industrial city of Port Talbot, England.
(www.nasa.gov/vision/earth/environment)
Aerosol Chemical Properties

- Complex chemical properties
  - **internally mixed**: all particles have the bulk mixture composition – vs – **externally mixed**: particles have different composition

Airborne particles sampled above Los Angeles, soot cores with sulfate coatings [Husar et al., *Environ. Sci. Technol.* (1976)]

- atmospheric processing of particles (surface chemical reactions, adsorbed coatings) can alter their properties
Aerosol Physical and Chemical Properties

- Aerosol physical/chemical properties vary with size
  - ideally represented by a size-composition(-morphology) distribution function
  - size-composition distribution function determines:
    - transport and fate characteristics
    - impacts on health, visibility, and radiative forcing
Particles fall into two size categories:

1. Coarse Particles
diameters 2.5 - 10 μm
(These particles usually deposit out of the air close to their source)

2. Fine Particles
diameters < 2.5 μm
(These particles can stay suspended for weeks and are can be transported far from their source)

Fine and coarse particles typically come from different sources and have different compositions
粒物
燃煤飞灰（PM$_{2.5}$）
c煤-burning flyash

燃重油颗粒物
diesel engine combustion

冶金粉尘（PM$_1$）
metal smelter

内燃机排放颗粒物
gasoline engine combustion
Particle Morphology and Composition

- Complex, heterogeneous
- Some particles have euhedral morphologies; more are amorphous/irregularly shaped
- Particles derived from anthropogenic emissions are often spheres
Particle Morphology and Composition

Al-Si-K

Si-O

Fe-Si-O

Biogenic Organic (PRD)

K-S

Fly ash: Fe-Si-O
Iron oxide particle measured downwind of a steel mill near St. Louis (USA)

Willis et al., United States EPA, personal communication (2006)
Soot Measured in Beijing

Soot shows discontinuous onion-like structure of graphitic layers.
Atmospheric Aerosol Sources and Dynamics

Modes / Submodes: Fine Nucleation Aitken Accumulation Coarse

Gases

Low volatility vapors
Hot vapor
Nucleation in the exhaust plume
Nucleation in the engine
Direct emissions
Chemical conversion
Gases

1° vs 2° aerosols

Mechanically Generated Particles
Wind blown dust
Sea spray
Volcanos
Plant Particles

Particle Diameter [μm]

Growth by Condensation and Coagulation
Coagulation
Chain aggregates

Submicron Particles (submicron particles)
Clusters Nucleation and Aitken modes (ultrafine particles) Accumulation mode Coarse particles (supermicron particles) Sedimentation

Rainout Washout
Aerosols and Air Pollution

Local air pollution
- aerosols affect human health
- aerosols reduce visibility

Regional air pollution
- aerosols contribute to acid deposition, affecting forests & lakes
- aerosols contribute to eutrophication, affecting water quality
- aerosol influence photochemistry and ozone production

Global air pollution
- aerosols absorb and scatter solar and surface-radiated light and hence influence climatic change
- aerosols catalyze stratospheric ozone loss/Antarctic ozone hole
Aerosol Pollution in Urban Areas

- Particulate matter (PM) is dominant type of air pollution in most large cities.
- Fine PM mass (and certainly surface area and number) typically dominates PM$_{10}$ mass, leading to deteriorated air quality and poor visibility.
- Significant, and often dominant fraction of fine PM mass is from secondary formation (sulfate, nitrate, ammonium, secondary organic compounds).
  - Difficult to control (precursors, transport, transformation, mechanism, regional problem).
  - Often hygroscopic (grow in size, CCN, climate change).
  - Often hazardous to human health (e.g. PAHs, EC in particles from primary combustion process).
Presentation Highlights

- Ambient aerosol source mixes can be complex
- Ambient aerosol concentration levels can be quite high
- Regional transport can be a significant contributor to particulate matter air quality in urban areas
- Particulate organic matter (POC) is often a significant fraction of ambient aerosol mass
- Aerosol size distributions reflect changing aerosol dynamics which can occur on relatively short time scales
Highlight 1: Aerosol Sources Mix can be Complex

- Mineral Dusts
  - Dust storms
  - Resuspended road dust
  - Other fugitive dusts (unpaved road, construction, soil)
- Combustion process primary emissions
  - Stationary sources such as electric utility and industrial power plants
  - Vehicle emissions
  - Biomass burning
  - Cooking
- Industrial sources such as steel mills and metal smelters
- Natural sources such as sea salt, biogenic
- Secondary processes: sulfate, nitrate, ammonium, secondary organic aerosol (SOA)

Relative contributions from these source types varies between cities
Example: PM$_{2.5}$ Mass Apportionment for East St. Louis (USA)

- Positive Matrix Factorization (PMF)
- 11 “factors” represent the time variation of 31 chemical components
- Four factors contain PM that is mostly transported into St. Louis from other areas
- Mobile = motor vehicles
- Soil = resuspended soil, mostly local sources
- Soil II is a mix of soil and diesel vehicles
- Four factors representing industrial sources

Highlight 2: Concentration Levels can be quite high

<table>
<thead>
<tr>
<th>Type</th>
<th>Concentration (cm(^{-3}))</th>
<th>Surface Area ((\mu m^2cm^{-3}))</th>
<th>Volume ((\mu m^3cm^{-3}))</th>
<th>PM(_{10}) Mass Conc. ((\mu g/m^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number Conc.</td>
<td>(3 \times 10^4 \pm 1.6 \times 10^4)</td>
<td>(1.4 \times 10^3 \pm 1.0 \times 10^3)</td>
<td>(90 \pm 70)</td>
<td>(153)</td>
</tr>
<tr>
<td>Surface Conc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume Conc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM(_{10}) Mass Conc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(PV_1/PV_{10}: 75\%\)
Fine PM Composition in two China Cities

Beijing PM2.5, 105 ug/m3
- Organics: 36%
- Unknown: 23%
- Trace: 4%
- Crustal: 12%
- Ammonium: 9%
- Sulfate: 5%
- Nitrate: 5%
- Chloride: 1%

Guangzhou PM2.5, 67.7 ug/m3
- Organics: 36%
-Unknown: 17%
-Trace: 11%
-Crustal: 12%
-Ammonium: 5%
-Sulfate: 14%
-Nitrate: 2%
-Chloride: 1%

Data for Beijing and Guangzhou, 2000
Highlight 3: Regional Pollution Impacts on Air Quality

Beijing API=39 (I)
Low pollution day

Beijing API=124 (III1)
Lightly polluted day

API = air pollution index

These images are consecutive days!
Daily API in Beijing, October 2004

Date (Beijing Oct.01-19)

API Value

- V Heavily polluted
- IV Polluted
- III Lightly polluted
Air mass back trajectories arriving on Beijing on the noted day

http://www.arl.noaa.gov/ready
Oct. 7, 2004 from Jietai Mao, Chengcai Li
Oct. 9, 2004 from Jietai Mao, Chengcai Li
Fine Particulate Matter Sulfate & Air Mass Back Trajectories

Air mass back trajectories
(NOAA/HYSPLIT)

Weather Systems

06/22/01  06/23/01  06/24/01  06/25/01  06/26/01  06/27/01  06/28/01  06/29/01
Regionally Transported Secondary Sulfate: St. Louis

- formed from atmospheric chemistry of SO$_2$ emissions
- sulfate transported from areas with many coal-burning power plants

Sulfate Potential Source Contribution Function, (PSCF) analysis, incremental probability compared to seasonal climatology...

Hot colors denote air masses coming to St. Louis on days with high sulfate

Cold colors denote air masses coming to St. Louis on days with low sulfate

Source: Sonoma Technology, Inc.
East St. Louis (IL) is approximately 3 km east of the City of St. Louis (MO) central business district.
Park Hills (MO) is a predominantly rural site ~100 km south/southwest of the St. Louis urban core.
Daily-Integrated PM$_{2.5}$ Sulfate

Fine particulate matter sulfate is highly coupled between the two sites separated by 100 km.
Hourly sulfate at two sites separated by ~400 km

Urban: East St. Louis, IL
Rural: Reserve, KS
Highlight 4: Organics often major fraction of PM\textsubscript{2.5} mass

POC from combustion process and biogenic VOC, SOC needs more attention

[POC = primary organic carbon PM; SOC = secondary organic carbon PM, VOC = volatile organic compounds (gases)]

Beijing PM\textsubscript{2.5}, 105 ug/m\textsuperscript{3}

- Trace: 4%
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Data of Beijing and Guangzhou, 2000
Estimated Secondary Organic Carbon (SOC) by Season for Beijing

<table>
<thead>
<tr>
<th>season</th>
<th>(OC/EC)_{pri}</th>
<th>SOC (ugC/m$^3$)</th>
<th>SOC/OC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>daytime</td>
<td>nighttime</td>
<td>mean±σ</td>
</tr>
<tr>
<td>winter</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6±3.1</td>
</tr>
<tr>
<td>spring</td>
<td>1.8</td>
<td>1.5</td>
<td>2.8±2.4</td>
</tr>
<tr>
<td>summer</td>
<td>1.5</td>
<td>1.0</td>
<td>4.5±2.9</td>
</tr>
<tr>
<td>autumn</td>
<td>1.8</td>
<td>1.4</td>
<td>4.1±4.0</td>
</tr>
</tbody>
</table>

SOC concentration: Summer > Fall > Spring ≈ Winter
SOC/OC: Summer > Spring > Fall > Winter

Winter Spring Fall: POC is major fraction of OC;
Summer: SOC can be comparable with POC;
OC in Beijing PM2.5 mainly from primary emission.
Organic Carbon Source Apportionment

East St. Louis, IL / USA
PMF on 2001-2003 data

Interior black line is median
Interior red line is arithmetic mean
Circles are 5th/95th percentiles
Highlight 5: Characteristics & Dynamics of Atmospheric Aerosol Size Distributions (especially nucleation)
Nucleation Events by Season & Location

Rural area, Finland

40% in spring

Urban area, USA

Atmospheric Nucleation Size Distributions

High time resolution (e.g. 5-minute) of aerosol size distributions, size from a few nanometer and up

Often plotted as follows…

Colors indicate number concentration (dN/dlog dp) so a vertical slice of the plot is a size distribution
Classification of New Particle Formation Events

"Clean" event

"Polluted" event

Wu et al., JGR, 2007
New Particle Formation Events

Beijing Urban: 2004

Guangzhou Urban: 2004

Yellow Sea: 2005
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Summary

- Increasing population, vehicles, expansion and economic development can be driving forces for air pollution. These are characteristics of many large cities.
- Urban atmospheric aerosols are chemically complex.
- While characteristic concentrations can be relatively low or quite high, fine PM many urban areas often have similar characteristics.
  - Particulate organic matter is a significant fraction of the fine PM mass.
  - Secondary formation and regional transport often contribute to particulate matter air quality problems.
- An understanding of the transport and transformation of primary emissions and gaseous precursors is necessary to understand regional air pollution.
- Atmospheric nucleation of new particles can occur on clean days and polluted days; a more-detailed understanding the composition and mechanisms of new particle formation is needed.
We welcome your comments and contributions!