Introduction and Fundamentals

Atmospheric Particulate Matter (PM)/Aerosols

**Definition**: An aerosol is a relatively stable suspension of fine solid or liquid particles in a gas. (Commonly refers to the condensed phase component only)

\[
\text{Aerosol} = \text{Particles} = \text{Particulate Matter (PM)}
\]

\[
PM_x: \text{particles with diameters smaller than x \( \mu \text{m} \)} \text{ (e.g., PM}_1, \text{ PM}_{2.5}, \text{ PM}_{10})
\]

PM range in diameters from \(~0.002\) to \(100 \ \mu \text{m} \) (2 – 100,000 nm) and may be in the solid or liquid state. (Gas --- Aerosol --- Fog or Cloud Droplet)

An aerosol can be envisioned as a population of particles consisting of “k” molecules or monomers.
Some Effects of Atmospheric Aerosols

• Health effects:
  – Epidemiological evidence: significant cardiopulmonary response, cancer inducing, impair lung development of children
  – More deadly than car accidents (est. mortality ~ 60,000 people / year in US)
  – Leading cause of excess mortality globally
• Ecological hazards:
  – Acid and nutrient deposition: damage to ecosystems and ecological components, disturb nutrient balance
• Influence atmospheric chemistry:
  – Reaction media
  – Heterogeneous & surface reactions (e.g., polar stratospheric clouds and the ozone hole)
  – Transport media

Figure 2.5. Stylized summary of acute exposure studies, percent change in health endpoint per 10 µg/m³ increase in PM₁₀ (adapted from Pope and Dockery, 1999)
## Aerosol Particle Sizes (aerodynamic diameter)

<table>
<thead>
<tr>
<th>Category</th>
<th>Diameter/Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSP</td>
<td>Total Suspended Particles (all sizes)</td>
</tr>
<tr>
<td>$PM_{10}$</td>
<td>10 µm or smaller</td>
</tr>
<tr>
<td>$PM_{2.5}$</td>
<td>2.5 µm or smaller</td>
</tr>
<tr>
<td>$PM_{1}$</td>
<td>1 µm or smaller</td>
</tr>
<tr>
<td>Ultrafine particles</td>
<td>0.1 µm (100 nm) or smaller</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>0.05 µm (50 nm) or smaller</td>
</tr>
<tr>
<td>Coarse mode</td>
<td>2.5 µm and larger</td>
</tr>
<tr>
<td></td>
<td>(sometimes 2.5 – 10 µm)</td>
</tr>
<tr>
<td>Accumulation mode</td>
<td>0.05 µm (50 nm) – 1 µm</td>
</tr>
<tr>
<td>Nuclei mode</td>
<td>5nm – 50 nm</td>
</tr>
</tbody>
</table>
Size Classifications of Ambient Aerosols: Modes

- **Nucleation mode:** $< 0.01 \mu m$
- **Ultrafine mode:** $< 0.1 \mu m$
- **Accumulation mode:** $0.1 - 2.5 \mu m$
- **Fine mode:** $< 2.5 \mu m$
- **Coarse mode:** $> 2.5 \mu m$
  (sometimes 2.5 to 10 $\mu m$)
Typical PM Size Distributions in Various Atmospheres

Number
Surface
Volume

Urban

Rural

Remote

Desert

Free Troposphere

Polar

Note very large differences in y-axis ranges
Particle Size Distribution Properties (previous slide)

• Number, surface area, and volume (mass = volume x aerosol density) distributions look very different from each other at a given location, and

• Even more different between locations

• Numbers are highest in urban locations, and lowest in polar, FT, and desert locations

• Mass (volume) is greatest in either the accumulation mode (0.5-1 \( \mu m \)) or the coarse mode (2.5 \( \mu m \) and up)
Aerosol Sources

- **Primary** – emitted directly as particles (Globally most atmospheric aerosol is naturally emitted primary particles like windborne dust and sea spray)

- **Secondary** – formed in the atmosphere by gas-to-particle conversion – a large fraction of these are anthropogenic in origin and considered air pollution

  (Particles are removed from the atmosphere by wet and dry deposition processes – not covered here. Lifetime of aerosols ~1 week or less. Shorter for larger particles due to gravitational settling.)
### Aerosol Sources

Many of these values are uncertain by a factor of 2 or more.

<table>
<thead>
<tr>
<th>Source</th>
<th>Annual Emissions (Tg/yr)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural Particles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil &amp; rock debris (^a,b)</td>
<td>1500</td>
<td>Principally coarse particles; contains an anthropogenic component.</td>
</tr>
<tr>
<td>Forest fires &amp; slash burning</td>
<td>50</td>
<td>Principally PM(_{2.5}); contains an anthropogenic component.</td>
</tr>
<tr>
<td>Sea salt (^a,b)</td>
<td>1300</td>
<td>Principally coarse particles</td>
</tr>
<tr>
<td>Volcanic debris</td>
<td>33</td>
<td>Highly intermittent source.</td>
</tr>
<tr>
<td><strong>Gas to particle conversion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate from sulfur gases</td>
<td>102</td>
<td>Principally PM(_1).</td>
</tr>
<tr>
<td>Nitrate from NO(_x)</td>
<td>22</td>
<td>Principally PM(_{2.5}).</td>
</tr>
<tr>
<td>VOC from plant exhalation (^a) &amp; fires</td>
<td>55</td>
<td>Principally PM(_{2.5}).</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>3060</td>
<td></td>
</tr>
<tr>
<td><strong>Anthropogenic Particles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary particles - industrial transportation, etc.</td>
<td>120</td>
<td>Principally PM(_{2.5}).</td>
</tr>
<tr>
<td><strong>Gas to particle conversion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate from SO(_2) ( &amp; H(_2)S)</td>
<td>120</td>
<td>Primarily PM(_{2.5}).</td>
</tr>
<tr>
<td>Nitrate from NO(_x)</td>
<td>36</td>
<td>Primarily PM(_{2.5}).</td>
</tr>
<tr>
<td>VOC conversion</td>
<td>90</td>
<td>Primarily PM(_{2.5}).</td>
</tr>
<tr>
<td><strong>Subtotal conversion</strong></td>
<td>366</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>3430</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) These categories are ambiguous in that they may include anthropogenic disturbances from land use, and prescriptive or accidental burning from man’s activities.

\(^b\) The low initial release height of soil and sea salt makes their raw emission estimates difficult to interpret; their magnitude biases their actual airborne contribution too high, because much suspended material is potentially deposited close to the source, or in the case of soil, removed from the air by collection on vegetation or structures.

\(^c\) There is evidence that trees produce wind blown primary organic emissions as well in the form of waxy alkanes (e.g., Diamond et al., 2000). The magnitude of these emissions is essentially not known.

Anthropogenic particles are only 10% of mass — But they are the fraction we can control! And they tend to be concentrated where people live.
Main Chemical Components

- Carbonaceous materials
  - Organic carbon (many types) - “OC”
  - Elemental or black carbon - “EC”
- Sulfate
- Nitrate
- Ammonium
- Water
- Dust (crustal materials)
- Seasalt (sodium, chloride, other ions)
- Other trace elements (metals)
- Biological material
- ????
Chemical composition reflects the sources and processes of particles:

- Metals/crustal materials (e.g., Al, Fe, Ca, Si): soil erosion, dust
- Na, Cl\(^{-}\): Sea-salt
- Black carbon: Fusil fuel / biomass combustion
- Sulfate, nitrate, ammonium: secondary formation
- Organics: a complex mixture of many individual organic compounds
- H\(_2\)O

Figure 1.2. Representative Composition of PM.
Submicron Aerosol (PM$_1$) Composition

PM$_{2.5}$ Concentration & Composition in US

Atmospheric PM vary greatly in concentration & composition

Figure 6.16. Comparisons of average PM$_{2.5}$ mass and species concentrations at urban and rural locations. The rural data are from the IMPROVE network, while the urban data are from the EPA Speciation Trends Network. Note that urban nitrate concentrations are distinctly higher than rural levels. Direct comparison of the information in these two maps should take into consideration: the fact that they represent different years; that one is an urban network and the other is a rural network; and that there are also differences in instruments and measurement methods (Source: U.S. EPA, 2002).
Particle Nucleation and Growth

- Condensation and nucleation are competing processes.
- Nucleation dominates when PM condensational sink is low.

Possible nucleation mechanisms
a) Binary nucleation (H₂SO₄ + H₂O)
b) Ternary nucleation (H₂SO₄ + NH₃ + H₂O)
c) Organic compounds nucleation
d) Ion-induced nucleation
Key Concept for Aerosol Chemistry

• **Volutility** – the tendency of a substance to vaporize
• This is directly related to the vapor pressure of the substance.
• **Volatile species** (VOCs, gases) reside almost entirely in the gaseous phase
• **Non-volatile species**, or those that become increasingly less volatile as a result of physical or chemical changes tend to exist more in the condensed phase (solid or aqueous).
Secondary Aerosol Growth - Inorganics

• Secondary aerosols are of great interest because their formation is mainly due to air pollution emissions that are chemically transformed and eventually partition to aerosol particles.

• Air pollution control (or air quality management) is concerned with reducing (by regulation and incentives) the emissions that contribute to secondary aerosol formation.

• The transformation of the major inorganic aerosol species (sulfur, oxidized and reduced nitrogen) to aerosol sulfate, nitrate and ammonium is relatively straightforward.
• The gaseous precursors of interest here are SO$_2$ (from coal combustion), NO$_x$ (from large combustion facilities and motor vehicles), and ammonia (from agriculture).

• The SO$_2$ and NO$_x$ are oxidized in the atmosphere to H$_2$SO$_4$ and HNO$_3$ respectively.

• This oxidation lowers their volatility (vapor pressure) considerably – especially for H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Vapor Pressures at 25°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapor</td>
<td>0.032 atm</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>~0.08 atm</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>&lt; 10$^{-6}$ atm</td>
</tr>
</tbody>
</table>
Inorganic Secondary Aerosol Growth (cont.)

• These lower volatility acids can then react with and be neutralized (in an acid-base sense) by gaseous ammonia to form even less volatile species:
  - \(2\text{NH}_3(g) + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{NH}_4)_2\text{SO}_4(s)\) (ammonium sulfate)
  - \(\text{NH}_3(g) + \text{HNO}_3 \rightleftharpoons \text{NH}_4\text{NO}_3(s)\) (ammonium nitrate)

• Both (condensed) species are much more stable than the precursor gases, and important components of ambient aerosol.

• Ammonium sulfate is very stable in the condensed phase at ambient temperatures, while ammonium nitrate is “semi-volatile” – it is stable in the aerosol phase in cold temperatures, and decomposes under warmer (summer) conditions.
Recap (Inorganic SA – highly simplified!)

• Precursor gases are oxidized to acids (fully oxidized forms), with lower volatility.

• These acids react and combine with ammonia in the atmosphere to form stable condensed species.

• These reactions often take place on pre-existing aerosol surfaces, or if in the gas phase, they will quickly condense onto particles.
Elemental & Organic Carbon (EC/OC)

EC: elemental carbon, i.e., black carbon (BC)
OC: organic carbon
Soot: by-product of the combustion, contain both EC and OC. Present as chain agglomerate of small roughly spherical elementary carbonaceous particles.
\[ \rho \approx 2 \text{ g/cm}^3 \]

Atmospheric organic compound classes:
Aliphatics (e.g., alkanes, alkenes)
Aromatics
Aliphatic and aromatic acids
Aliphatic and aromatic carbonyls (i.e., aldehydes & ketones)
Aromatic polycarboxylic acids
Polycyclic aromatic hydrocarbons (PAH)
Peroxides
Nitrogen containing organic compounds (e.g., amines, amides, nitro compounds, nitrates, heterocyclics) …

Thousands of compounds, extremely complex

BaP – benzo[a]pyrene
Primary and Secondary Organic Aerosols

Primary Organic Aerosol (POA)

*Anthropogenic*
- Gasoline
- Diesel
- Wood smoke
- Meat Cooking

*Biogenic*
- Plant debris
- Pollen
- Bacteria

Secondary Organic Aerosol (SOA)

*Particle phase products of anthropogenic & biogenic VOCs (volatile organic compounds)*

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**Figure 3.9.** Schematic of the formation of secondary organic aerosol in the atmosphere.

2003 NARSTO Assessment
Yet another complication of organic aerosols is that they can be semi-stable in the condensed phase (more volatile), and therefore move between vapor and condensed phase quite a bit.

Recall – Volatility is key concept number 1!
Once a multicomponent system contains enough condensable material to form aerosol, equilibrium G/P partitioning is governed by the equation for absorptive gas/liquid partitioning in a potentially nonideal system:

1) \[ p_i = X_i \zeta_i p_{L,i} \]

2) \[ K_{p,i} = \frac{(ng/\mu g)_{\text{ParticlePhase}}}{(ng/m^3)_{\text{GasPhase}}} = \frac{F_i / TSP}{A_i} = \frac{760RTf_{om}}{10^6MW_{om}\zeta_i p_{L,i}^o} \]

- \( p_i \) (torr): the gas-phase partial pressure of species \( i \)
- \( X_i \): the mass fraction of \( i \) in the particle phase
- \( \zeta_i \): the activity coefficient of species \( i \) in the particle phase typically lie in the range 0.3–3.
- \( p^o_{L,i} \) (torr): the compound’s vapor pressure as a pure liquid (subcooled if necessary) at the temperature of interest.
- \( A_i \) (ng m\(^{-3}\)): gas phase conc.
- \( F_i \) (ng m\(^{-3}\)): OM phase conc.
- \( TSP \) (ng m\(^{-3}\)): total suspended PM conc.
- \( R \): the ideal gas constant (8.2E-5 m\(^3\) atm mol\(^{-1}\) K\(^{-1}\))
- \( T \) (K): temperature
- \( f_{om} \): the weight fraction of the TSP that comprises the absorbing OM phase
- \( MW_{om} \) (g mol\(^{-1}\)): the number-average molecular weight of the absorbing OM phase.

**Equilibrium Relation – similar to Henry’s Law Equilibrium**
Volatility Changes

Note that these are multiplicative factors, so addition of these functional groups (via reaction) always leads to lower vapor pressure (lower volatility).

Seinfeld and Pandis, 2016
Oxidation State Changes - 2nd Key Concept

- \( \text{OS}_C \) is the carbon oxidation state
- \( \text{OS}_C \approx 2(\text{O:C}) - \text{H:C} \)
- Oxidation –
  - Increases O:C
  - Decreases H:C
- Van Krevelen plot

Van Krevelen diagram illustrating how functionalization reactions of organic species affect H:C and O:C from an arbitrary starting point. Each arrow corresponds to the addition of a particular functional group to an aliphatic (unfunctionalized) carbon. Lines of constant carbon oxidation state are shown in grey.
Van Krevelen diagram of elemental ratios estimated from HR-AMS measurements of organic aerosol. These include mean observations from field studies (solid circles), lab studies (diamonds), and thermal denuder experiments (open circles). Also shown are the positive matrix factorization components of the MILAGRO observations (1 = HOA, 2 = BBOA, 3 = OOA2, 4 = OOA1) [Aiken et al., 2008]. Line with −1 slope is illustrative and originates at O:C = 0 and H:C = 2, corresponding to an arbitrarily long acyclic alkane.

Interpretation – since the real world oxidation of organic aerosols more or less follows the line with slope = -1, the most important reaction process involves the replacement of a −CH₂− group with a carboxylic acid group - see previous slide.
Example: Combustion Emissions

• The exhaust stream is concentrated with pollutant species, both gas and condensed phase
• (Exhaust plumes are visible mainly due to aerosol or condensed phase species)
• This fresh exhaust is rapidly diluted in the ambient air. Pollutant species become much less concentrated.
• In the diluted air mass there is much less condensed phase for the semi-volatile species to interact with and “stay” condensed
• After dilution, some (maybe most) of the condensed material coming out the exhaust re-evaporates into the gas phase.
• These gas phase species undergo photochemical oxidation (AC lecture 2) and many of these partially oxidized reaction products have lower volatility, as we have just seen.
• The low volatility reaction products condense onto the existing particles.
• In this example PM mass first decreases (dilution and evaporation), then increases due to oxidation reactions producing low volatility products.
When mixture is diluted by a factor of 1000, the $C_{OA}$ drops by a factor of 4000. (Note change of y-axis)

Colored bars represent condensed phase carbon species, white bars represent gas phase carbon species.

X-axis is a representation of the “volatility basis set” for organic carbon species.
Chemical transformation including oxidation to less volatile intermediate products (and eventually to more volatile final products)

FIGURE 4. (a–c) Evolving mass distribution as semi-volatile organics are chemically processed to produce less volatile products (0 days, 2 days, and 4 days, see text). Chemistry eventually drives material into the high volatility bin (c) and then out of the model. (d) Time evolution of the total organic carbon (circles) and condensed-phase organic carbon (squares) in the simple model. With the particular assumed balance between formation of less volatile products and eventual formation of highly volatile products the aerosol mass roughly doubles after 4 days (4 generations), and then declines as the organics are oxidized more completely.