Section 2: Measurement of Particulate Matter Physical Properties

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    Number distribution.
      SMPS, APS, OPC, SEM, TEM
    Chemical composition (M. Bergin covers this)
      Size resolved chemistry (Mass Spec, MOUDI, etc)

2.1. Terminology
The aerosol literature has experienced a proliferation of diffusely defined terminology (e.g., fine particles, total suspended particulate matter, aerosols, superfine particles, ultrafine particles, hyperfine particles, nanoparticles, . . . ), a situation which has served to obscure scientific communication in the field. In an attempt to limit this tendency, this Assessment restricts itself to a limited number of terms, which are defined immediately below. This terminology is consistent with that used by the Intergovernmental Panel on Climate Change.

Suspended particulate matter (PM): Any non-gaseous material (liquid or solid) which, owing to its small gravitational settling rate, remains suspended in the atmosphere for appreciable time periods.

Aerosol: A mixture of suspended PM and its gaseous suspending medium.
The terminology denoting suspended PM subclasses is selected primarily, but not totally, on the basis of physicochemical processes involved in formation and growth of the particles (see Chapter 3, Figure 3.2) which describe four “modes”: coarse, accumulation, Aitken, and nucleation.

Ultrafine particles: Particles operationally defined (mainly within the health-sciences community) as those having diameters less than 0.1 µm

Fine particles: Particles operationally defined as those smaller than 2.5 µm aerodynamic diameter.
Fine particle measurements include the accumulation mode (nominally 0.1 to 2.5 µm), where most of the submicron mass is found and, depending on measurement technique, may include ultrafine particles, where most of the particle number concentration is found. Because filter-based PM2.5 sampling techniques collect all particles smaller than 2.5 µm, such “fine particle” samples implicitly include ultrafine particles. However, because the properties and effects of ultrafine particles are different from those of larger particles, it is often useful to separately identify “fine” and “ultrafine” particles as distinct fractions of PM2.5.

Coarse particles: Particles extending through the high end of the aerosol size distribution. This Assessment adopts the proposed regulatory definition, which includes those particles between 2.5 µm and 10 µm aerodynamic diameter (PM10-2.5). Many “coarse-particle” sampling techniques also collect particles in the finer ranges. Thus reported data designated as “coarse-particle” data may or may not include contributions from finer modes, and these contributions can be significant.

PM10: The mass concentration of particles smaller than 10 µm. In practice, PM10 samplers do not provide perfectly sharp cuts at 10 µm. Instead, size-dependent collection efficiencies typically decrease from 100 percent at ~ 1.5 µm to 0 percent at ~15 µm, and are equal to 50 percent at 10 µm.

Primary PM: PM that is emitted directly to the atmosphere in solid or liquid form.

Secondary PM: PM formed in the atmosphere through condensation/deposition of gaseous precursors.
How to specify particle Size

**Geometric Diameter:** unambiguous if particles are liquid, not clear if particles are solid and non-spherical.

**Aerodynamic Diameter:** Measured by inertial methods such as impactors and cyclones, depends on particle shape, density, and size.

**Electrical mobility Diameter:** Measured by electrostatic mobility analyzers. It depends on particle shape and size and is determined by the rate of migration of charged particles in an electrostatic field.

**Optical Diameter:** measured by light scattering detectors. It depends on particle refractive index (chemical composition), shape, and size.

### 2.2. The Size Distribution Function

\[ N = \text{particle number concentration (typical unit is 1/cm}^3\) \]

\[ D_p = \text{particle diameter (typical unit is } \mu\text{m}) \]

The size distribution function: \( n(D_p), n(\ln D_p), n(\log D_p) \)

\( n_n(D_p), \) or \( N(D_p)\): the number density (concentration) distribution function: the number of particles per volume of air with sized between \( D_p \) and \( dD_p \). \{Units particles/(cm}^3\mu\text{m})\} 

Think of as \( n(D_p) = dN/dDp \) or \( \frac{\Delta N}{\Delta D_p} \): the number concentration is normalized by the size range of particles (ie “distribution function).

Thus \( dN \) or \( \Delta N = n(D_p) \times dD_p \)

Not usually plotted in this form since generally the x-axis \( (D_p) \) is on a logarithmic scale. To make the shape of the plotted curve meaningful, size distribution function is plotted as \( dN/d\ln D_p \) or \( n_n(\ln D_p) \) (units 1/cm3)

\[ dN/d\ln D_p = \text{number of particles between } \ln D_p \text{ and } d \ln D_p \]

\[ dN/d\ln D_p = dN/dDp \times Dp \]

or base 10 log;

\[ dN/d\log D_p = dN/dDp \times Dp \times \ln(10) \]

The size distribution can be of any aerosol property. (Demonstrates how the property varies with particle size)

ie.

Surface Area: \( n_A(\ln D_p) \) or \( dA/d\ln D_p \) units \( \mu\text{m}^2/\text{cm}^3 \)
Volume: \( n_v(\ln Dp) \) or \( dV/d\ln Dp \) \( \mu m^3/cm^3 \)
Mass \( n_m(\ln Dp) \) or \( dM/d\ln Dp \) \( \mu g/m^3 \)
(Note, you could have a mass distribution of a specific particle chemical component
(e.g., \( \mu g SO_4^{2-}/m^3 \))

If you know the number distribution and assume the particles are spherical, the other
distributions can be calculated.

i.e.
\[
\begin{align*}
&dA = dN \cdot \frac{\pi Dp^2}{2} \\
&dV = dN \cdot \frac{\pi}{6} Dp^3 \\
&dM = \rho(Dp) \cdot dV
\end{align*}
\]

Moments of the size distribution

Total number concentration –the zeroth moment (\( Dp^0 \))
\[
N = \int_0^\infty n_v(Dp) \cdot dDp = \int_0^\infty n_v(\ln Dp) \cdot d\ln Dp = 0 \cdot dN
\]

The first moment (\( Dp^1 \))
\[
Mean \ Dp = \frac{1}{N} \int_0^\infty Dp \cdot n_v(Dp) \cdot dDp = \frac{0 \cdot Dp \cdot dN}{N}
\]

The second moment (\( Dp^2 \))
\[
Total \ Surface \ Area = \int_0^\infty Dp^2 \cdot n_v(Dp) \cdot dDp = \int_0^\infty \frac{\pi}{6} Dp^2 \cdot dN
\]

The third moment (\( Dp^3 \))
\[
Total \ Volume = \int_0^\infty Dp^3 \cdot n_v(Dp) \cdot dDp = \int_0^\infty \frac{\pi}{6} Dp^3 \cdot dN
\]
\[
Total \ Mass = \int_0^\infty \rho(Dp) \cdot Dp^3 \cdot n_v(Dp) \cdot dDp = \int_0^\infty \frac{\pi}{6} Dp^3 \cdot dN
\]
Tabulated Calculations: an instrument typically measures $dN$ over a number of size ranges ($dDp$). From this, the size distribution for various weightings can be constructed.

i.e.

\[
\begin{array}{cccccccc}
  dDp & dN & Dp & dN/dlnDp & dA & dV & dM & dA/dlnDp & dV/dlnDp \\
  \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
  \text{Sum} & N & A & V & M & & & & \\
\end{array}
\]

2.3 Ambient aerosol size distributions and factors affecting size distributions
<table>
<thead>
<tr>
<th>Emissions</th>
<th>General Source Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crustal / Soil Dust</td>
<td>Paved / unpaved roads, construction, agricultural and forestry operations, high wind events and fires.</td>
</tr>
<tr>
<td>Salt (NaCl)</td>
<td>Oceans, road salt and salt pans / dry lake beds.</td>
</tr>
<tr>
<td>Biogenic material</td>
<td>Pollen, spores and plant waxes.</td>
</tr>
<tr>
<td>Metals</td>
<td>Industrial processes and transportation</td>
</tr>
<tr>
<td>Black carbon</td>
<td>Fossil fuel combustion (especially diesel engines).</td>
</tr>
<tr>
<td>Semi-volatile organic compounds (direct condensation of organic vapors at ambient conditions) and non-volatile organic compounds</td>
<td>Contemporary and fossil fuel combustion, surface coatings and solvents, cooking, and industrial processes.</td>
</tr>
<tr>
<td>Semi- and volatile organic compounds (forming secondary organic aerosols)</td>
<td>Electrical utilities, transportation, mining and smelting, and industrial processes.</td>
</tr>
<tr>
<td>Sulfur dioxide (forming sulfate particles)</td>
<td></td>
</tr>
<tr>
<td>Ammonia (contributing to formation of ammonium sulfate and ammonium nitrate)</td>
<td>Agriculture and animal husbandry, with minimal contributions from transportation and industrial processes.</td>
</tr>
<tr>
<td>Nitrogen oxides (forming ammonium nitrate with ammonia)</td>
<td>All types of fossil fuel combustion, and to minor degree microbial processes in soils.</td>
</tr>
</tbody>
</table>
Sources and Processing of fine and coarse atmospheric particles.

<table>
<thead>
<tr>
<th>Fine</th>
<th>Coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nuclei</strong></td>
<td><strong>Accumulation</strong></td>
</tr>
<tr>
<td>Formed from:</td>
<td>Combustion, high-temperature processes, and atmospheric reactions</td>
</tr>
<tr>
<td>Formed by:</td>
<td>Condensation, Coagulation, Evaporation of fog and cloud droplets in which gases have dissolved and reacted</td>
</tr>
<tr>
<td>Composed of:</td>
<td>Mechanical disruption (crushing, grinding, and abrasion of surfaces), Evaporation of sprays, Suspension of dusts, Reactions of gases in or on particles</td>
</tr>
<tr>
<td>Sulfates, Elemental carbon, Metal compounds, Organic compounds with very low saturation vapor pressure at ambient temperature</td>
<td>Sulfate, $\text{SO}_4^{2-}$, Nitrate, $\text{NO}_3^-$, Ammonium, $\text{NH}_4^+$, Hydrogen ion, H⁺, Elemental carbon, Large variety of organic compounds, Metal: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc.</td>
</tr>
<tr>
<td>Atmospheric half-life:</td>
<td>Minutes to hours, Days to weeks, Minutes to hours</td>
</tr>
<tr>
<td>Removal processes:</td>
<td>Grows into accumulation mode, Forms cloud droplets and rains out, Dry deposition</td>
</tr>
<tr>
<td>Travel distance:</td>
<td>&lt;1 to 10s of km, 100s to 1000s of km, Dry deposition</td>
</tr>
</tbody>
</table>

Source: Adapted from Wilson and Suh (1997).
2.4 Size Distribution Measurement Techniques

Number distribution. {SMPS, APS, OPC, SEM, TEM}

Chemical composition (Mass Spec, MOUDI, etc) (M. Bergin covers this)

Instrument that measure particle number distribution:

1) DMA- Differential Mobility Analyzer
2) APS- Aerodynamic Particle Sizer
3) OPC – Optical Particle Counter (Mike Bergin covers in detail)
4) SEM – Scanning Electron Microscopy
   - Collect particles on a sampling a substrate (e.g., smooth poly carbonate capillary pore filter by impaction)
   - Sample coated with conductive layer (gold or carbon) reduce charge accumulation from electron beam
   - Photograph particles and count numbers in various size bins
5) TEM – Transmission Electron Microscopy
   - Similar to SEM, but higher resolution
   - Can perform chemical analysis on individual particles (elemental composition by EDXA (energy dispersive x-ray analysis) and crystal structure by electron diffraction.