Section 2: Measurement of Particulate Matter Physical Properties

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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 = particle number concentration (typical unit is $1/cm^3$)
Dp = particle diameter (typical unit is μm)

The size distribution function: n(Dp), n(lnDp), n(logDp)

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

Think of as n(Dp) = dN/dDp or ΔN/ΔDp : the number concentration is normalized by the size range of particles (ie "distribution function).

Thus dN or ΔN = n(Dp) x dDp

Not usually plotted in this form since generally the x-axis (Dp) is on a logarithmic scale. To make the shape of the plotted curve meaningful, size distribution function is plotted as dN/dlnDp or n_N(lnDp) (units $1/cm^3$)

dN/dlnDp = number of particles between lnDp and d lnDp

$$dN/d\ln Dp = dN/dDp * Dp$$

or base 10 log;

$$dN/d\log Dp = dN/dDp * Dp * \ln(10)$$

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

ie.
Surface Area: n_A(lnDp) or dA/dlnDp units $\mu m^2/cm^3$

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.

$dA = dN * \pi\ Dp^2$
$dV = dN * \pi/6\ Dp^3$
$dM = \rho(Dp)\ dV$

Moments of the size distribution

Total number concentration –the zeroth moment (Dp^0)

$$N = \int_0^\infty n_N(Dp) \cdot dDp \quad = \quad \int_0^\infty n_N(\ln Dp) \cdot d\ln Dp \quad = \quad \sum_0^\infty dN$$

The first moment (Dp^1)

$$Mean\ \ Dp = 1/N \int_0^\infty Dp \cdot n_N(Dp) \cdot dDp \quad = \quad \frac{\sum_0^\infty Dp\, dN}{N}$$

The second moment (Dp^2)

$$Total\ \ Surface\ \ Area = \int_0^\infty \pi\, Dp^2 \cdot n_N(Dp) \cdot dDp \quad = \quad \sum_0^\infty \pi\, Dp^2\, dN$$

The third moment (Dp^3)

$$Total\ \ Volume = \int_0^\infty \frac{\pi}{6}\, Dp^3 \cdot n_N(Dp) \cdot dDp \quad = \quad \sum_0^\infty \frac{\pi}{6}\, Dp^3\, dN$$

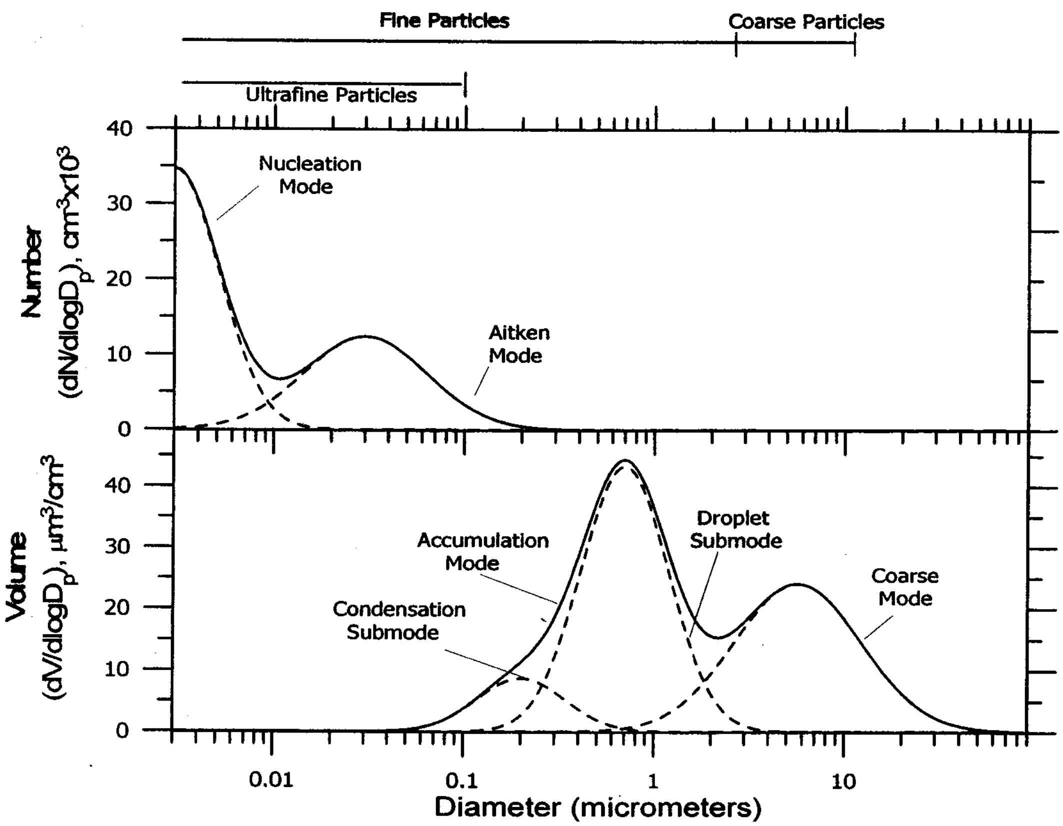
$$Total\ \ Mass = \int_0^\infty \rho\ \frac{\pi}{6}\, Dp^3 \cdot n_N(Dp) \cdot dDp \quad = \quad \sum_0^\infty \rho\ \frac{\pi}{6}\, Dp^3\, dN$$

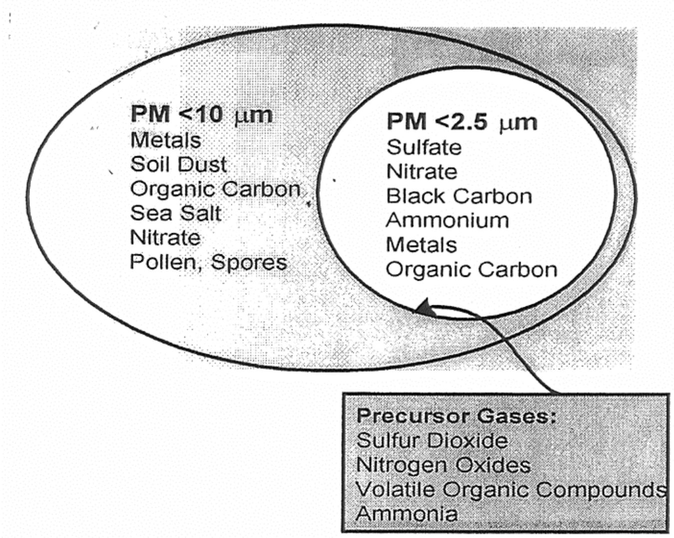
Tabulated Calculations: an instrument typically measures dN over a number of size ranges (dDp). From this, the size distribution for various weightings can be constructed.

i.e.

dDp	dN	Dp	dN/dlnDp	dA	dV	dM	dA/dlnDp	dV/dlnDp
.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
Sum	N			A	V	M		

2.3 Ambient aerosol size distributions and factors affecting size distributions





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

Sources and Processing of fine and coarse atmospheric particles.

Table 1.1. Comparison of ambient particle fractions.

	Fine		Coarse
	Nuclei	Accumulation	
Formed from:	Combustion, high-temperature processes, and atmospheric reactions		Break-up of large solids/droplets
Formed by:	Nucleation Condensation Coagulation	Condensation Coagulation Evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (crushing, grinding, and abrasion of surfaces) Evaporation of sprays Suspension of dusts Reactions of gases in or on particles
Composed of:	Sulfates Elemental carbon Metal compounds Organic compounds with very low, saturation vapor pressure at ambient temperature	Sulfate, $SO_4^{=}$ Nitrate, NO_3^{-} Ammonium, NH_4^{+} Hydrogen ion, H^{+} Elemental carbon Large variety of organic compounds Metals: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc.	Suspended soil or street dust Fly ash from uncontrolled combustion of coal, oil, and wood Nitrates and chlorides from HNO_3 and HCl Oxides of crustal elements (Si, Al, Ti, and Fe) $CaCO_3$, NaCl, and sea salt Pollen, mold, and fungal spores Plant and animal fragments
		Particle-bound water	Tire, brake pad, and road wear debris
Atmospheric half-life:	Minutes to hours	Days to weeks	Minutes to hours
Removal processes:	Grows into accumulation mode	Forms cloud droplets and rains out Dry deposition	Dry deposition by fallout Scavenging by falling rain drops
Travel distance:	<1 to 10s of km	100s to 1000s of km	<1 to 10s of km (100s to 1000s in dust storms)

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)

Instruments that measure particle number distribution:

1) **DMA- Differential Mobility Analyzer**

   (3nm-30nm nano-DMA; 15 nm -0.3 um long DMA)
2) APS- Aerodynamic Particle Sizer (0.2 um to 10 um)
3) OPC – Optical Particle Counter (0.1 um to 10 um, Lab 2)
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.