2

The Earth's Atmosphere

I. THE ATMOSPHERE

Before we can determine the extent of air pollution, we need a baseline to which present conditions can be compared. While dynamic, the atmosphere can be characterized quantitatively.

On a macroscale (Fig. 2.1) as the earth's atmospheric temperature varies with altitude, as does the density of the substances comprising the atmosphere.[1] In general, the air grows progressively less dense with increasing altitude moving upward from the troposphere through the stratosphere and the chemosphere to the ionosphere. In the upper reaches of the ionosphere, the gaseous molecules are few and far between as compared with the troposphere.

The ionosphere and chemosphere are of interest to space scientists because they must be traversed by space vehicles en route to or from the moon or the planets, and they are also regions in which satellites travel in the earth's orbit. These regions are also of interest to communications scientists because of their influence on radio communications. However, these layers are of interest to air pollution scientists primarily because of their absorption and scattering of solar energy, which influence the amount and spectral distribution of solar energy and cosmic rays reaching the stratosphere and troposphere.

The stratosphere is of interest to aeronautical scientists because it is traversed by airplanes; to communications scientists because of radio and television communications; and to air pollution scientists because global transport of pollution, particularly the debris of aboveground atomic bomb tests and volcanic eruptions, occurs in this region and because absorption

[1] U.S. Environmental Protection Agency, SI:409 Basic Air Pollution Meteorology, 2007: Accessed at: http://yosemite.epa.gov/oaqps/eogtrain.nsf/DisplayView/SI_409_0-5?OpenDocument

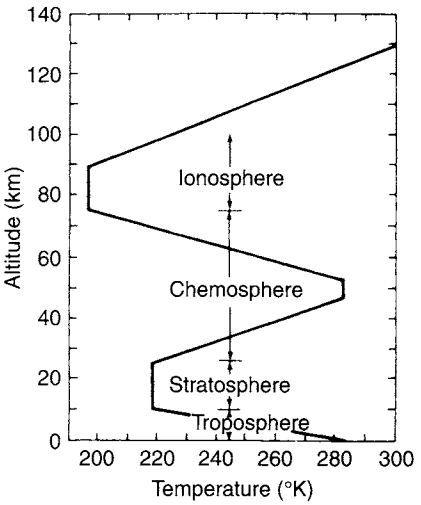


Fig. 2.1. The regions of the atmosphere.

and scattering of solar energy also occur there. The lower portion of this region contains the stratospheric ozone layer, which absorbs harmful ultraviolet (UV) solar radiation. Global change scientists are interested in modifications of this layer by long-term accumulation of chlorofluorocarbons (CFCs) and other gases released at the earth's surface or by high-altitude aircraft.

The troposphere is the region in which we live and is the primary focus of this book; however, we will discuss stratospheric ozone formation and destruction in some detail in Chapter 15.

II. BASELINE CONDITIONS: UNPOLLUTED AIR

The gaseous composition of unpolluted tropospheric air is given in Table 2.1. Unpolluted air is a concept, i.e., what the composition of the air would be if humans and their works were not on earth. We will never know the precise composition of unpolluted air because by the time we had the means and the desire to determine its composition, humans had been polluting the air for thousands of years. Now even at the most remote locations at sea, at the poles, and in the deserts and mountains, the air may be best described as dilute polluted air. It closely approximates unpolluted air, but differs from it to the extent that it contains vestiges of diffused and aged human-made pollution.

The real atmosphere is more than a dry mixture of permanent gases. It has other constituents—vapor of both water and organic liquids, and particulate matter (PM) held in suspension. Above their temperature of condensation, vapor molecules act just like permanent gas molecules in the air. The predominant vapor in the air is water vapor. Below its condensation temperature,

TABLE 2.1

The Gaseous Composition of Unpolluted Air (Dry Basis)

	ppm (vol.)	$\mu g\, m^{-3}$
Nitrogen	780 000	8.95×10^8
Oxygen	209 400	2.74×10^8
Water	—	—
Argon	9300	1.52×10^7
Carbon dioxide	315	5.67×10^5
Neon	18	1.49×10^4
Helium	5.2	8.50×10^2
Methane	1.0–1.2	$6.56\text{–}7.87 \times 10^2$
Krypton	1.0	3.43×10^3
Nitrous oxide	0.5	9.00×10^2
Hydrogen	0.5	4.13×10^1
Xenon	0.08	4.29×10^2
Organic vapors	*ca.* 0.02	—

if the air is saturated, water changes from vapor to liquid. This phenomenon gives rise to fog or mist in the air and condensed liquid water on cool surfaces exposed to air. The quantity of water vapor in the air varies greatly from almost complete dryness to supersaturation, i.e., between 0% and 4% by weight (see Fig. 2.2). If Table 2.2 is compiled on a wet air basis at a time when the water vapor concentration is 31 200 parts by volume per million parts by volume of wet air (Table 2.3), the concentration of condensable organic vapors is seen to be so low compared to that of water vapor that for all practical purposes the difference between wet air and dry air is its water vapor content.

Gaseous composition in Tables 2.1 and 2.2 is expressed as parts per million by volume—ppm (vol). (When a concentration is expressed simply as ppm, it is unclear whether a volume or weight basis is intended.) To avoid confusion caused by different units, air pollutant concentrations in this book are generally expressed as micrograms per cubic meter of air ($\mu g\, m^{-3}$) at 25°C and 760 mmHg, i.e., in metric units. To convert from units of ppm (vol.) to $\mu g\, m^{-3}$, it is assumed that the ideal gas law is accurate under ambient conditions. A generalized formula for the conversion at 25°C and 760 mmHg is

$$\begin{aligned} 1\ \text{ppm(vol) pollutant} &= \frac{1\,\text{L pollutant}}{10^6\,\text{L air}} \\ &= \frac{(1\,\text{L}/22.4) \times \text{MW} \times 10^6 \mu\text{g} \times \text{gm}^{-1}}{10^6\,\text{L} \times 298^\circ\text{K}/273^\circ\text{K} \times 10^{-3}\ \text{m}^3 \times \text{L}^{-1}} \\ &= 40.9 \times \text{MW}\ \mu\text{g/m}^{-3} \end{aligned} \tag{2.1}$$

where MW equals molecular weight. For convenience, conversion units for common pollutants are shown in Table 2.3.

TABLE 2.2

The Gaseous Composition of Unpolluted Air (Wet Basis)

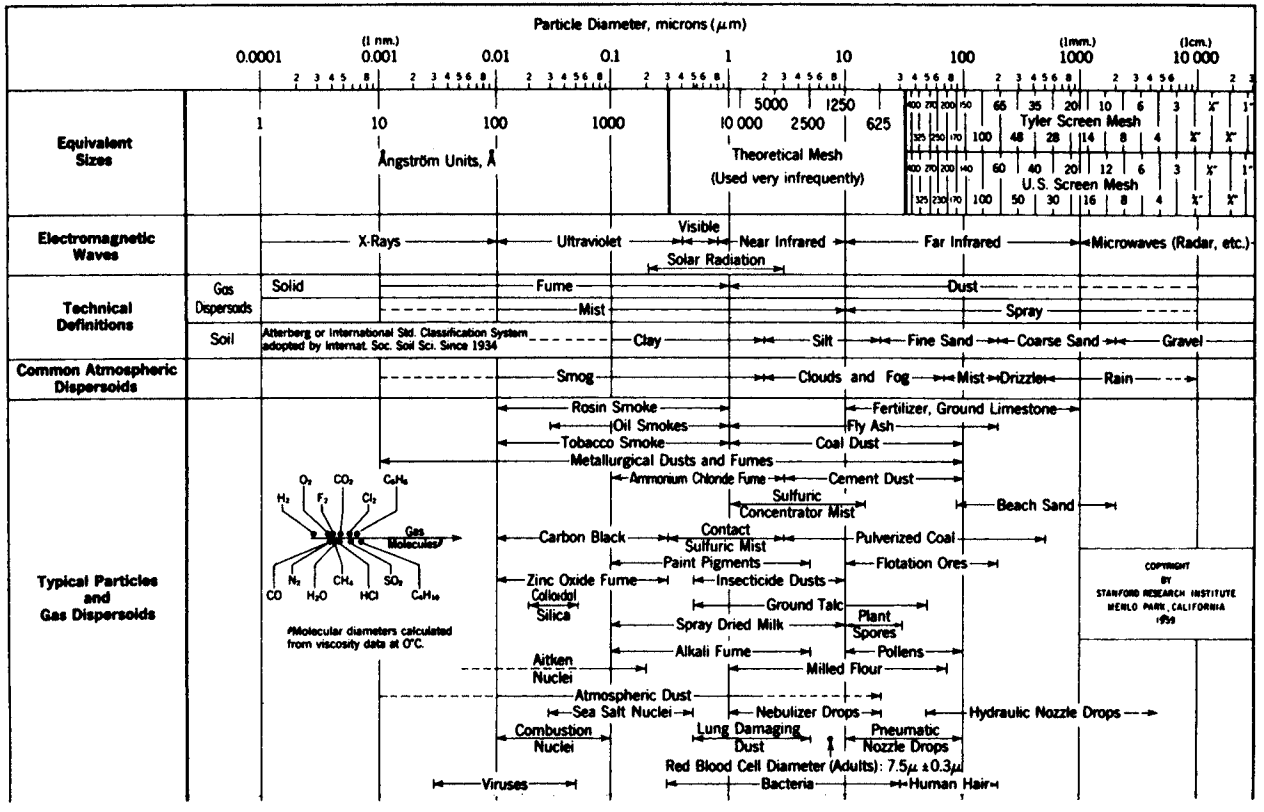
	ppm (vol.)	$\mu g\, m^{-3}$
Nitrogen	756500	8.67×10^8
Oxygen	202900	2.65×10^8
Water	31200	2.30×10^7
Argon	9000	1.47×10^7
Carbon dioxide	305	5.49×10^5
Neon	17.4	1.44×10^4
Helium	5.0	8.25×10^2
Methane	0.97–1.16	$6.35–7.63 \times 10^2$
Krypton	0.97	3.32×10^3
Nitrous oxide	0.49	8.73×10^2
Hydrogen	0.49	4.00×10^1
Xenon	0.08	4.17×10^2
Organic vapors	*ca.* 0.02	—

TABLE 2.3

Conversion Factors Between Volume and Mass Units of Concentration (25°C, 760 mmHg)

	To convert from	
Pollutant	ppm (vol.) to $\mu g\, m^{-3}$, multiply by	$\mu g\, m^{-3}$ to ppm (vol.), multiply by ($\times 10^{-3}$)
Ammonia (NH_3)	695	1.44
Carbon dioxide	1800	0.56
Carbon monoxide	1150	0.87
Chlorine	2900	0.34
Ethylene	1150	0.87
Hydrogen chloride	1490	0.67
Hydrogen fluoride	820	1.22
Hydrogen sulfide	1390	0.72
Methane (carbon)	655	1.53
Nitrogen dioxide	1880	0.53
Nitric oxide	1230	0.81
Ozone	1960	0.51
Peroxyacetylnitrate	4950	0.20
Sulfur dioxide	2620	0.38

A minor problem arises in regard to nitrogen oxides. It is common practice to add concentrations of nitrogen dioxide and nitric oxide in ppm (vol.) and express the sum as "oxides of nitrogen." In metric units, conversion from ppm (vol.) to $\mu g\, m^{-3}$ must be done separately for nitrogen dioxide and nitric oxide prior to addition.


Particle Diameter, microns (μm)
0.0001
(1 nm.)
0.001
0.01
0.1
1
10
100
(1mm.)
1000
(1cm.)
10 000
Equivalent Sizes
Ångström Units, Å
Theoretical Mesh
(Used very infrequently)
Tyler Screen Mesh
U.S. Screen Mesh
Electromagnetic Waves
X-Rays
Ultraviolet
Visible
Near Infrared
Far Infrared
Microwaves (Radar, etc.)
Solar Radiation
Technical Definitions
Gas Dispersoids
Solid
Fume
Dust
Mist
Spray
Soil
Atterberg or International Std. Classification System adopted by Internat. Soc. Soil Sci. Since 1934
Clay
Silt
Fine Sand
Coarse Sand
Gravel
Common Atmospheric Dispersoids
Smog
Clouds and Fog
Mist
Drizzle
Rain
Typical Particles and Gas Dispersoids
Rosin Smoke
Fertilizer, Ground Limestone
Oil Smokes
Fly Ash
Tobacco Smoke
Coal Dust
Metallurgical Dusts and Fumes
Ammonium Chloride Fume
Cement Dust
Sulfuric Concentrator Mist
Beach Sand
Gas Molecules*
Carbon Black
Contact Sulfuric Mist
Pulverized Coal
Paint Pigments
Flotation Ores
Zinc Oxide Fume
Insecticide Dusts
Colloidal Silica
Ground Talc
Plant Spores
Spray Dried Milk
Alkali Fume
Pollens
Aitken Nuclei
Milled Flour
Atmospheric Dust
Sea Salt Nuclei
Nebulizer Drops
Hydraulic Nozzle Drops
Combustion Nuclei
Lung Damaging Dust
Pneumatic Nozzle Drops
Red Blood Cell Diameter (Adults): 7.5μ ±0.3μ
Viruses
Bacteria
Human Hair
*Molecular diameters calculated from viscosity data at 0°C.
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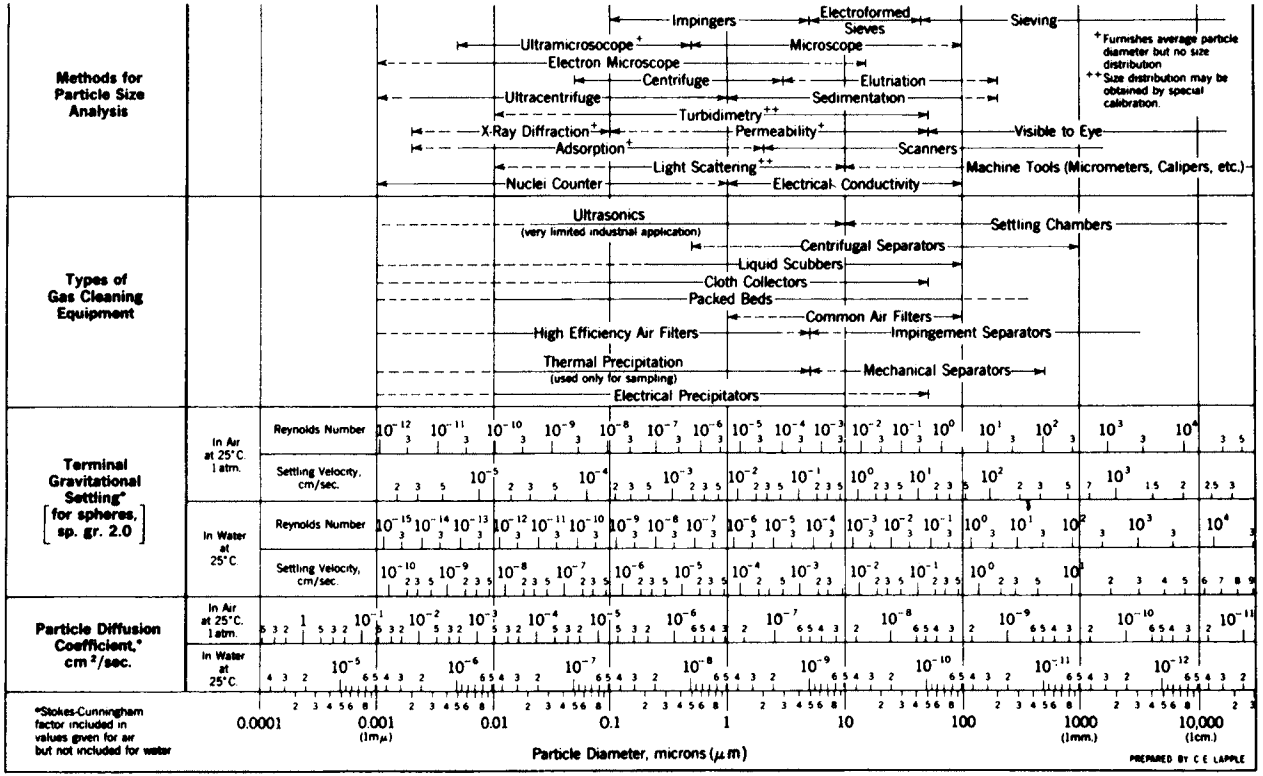

Fig. 2.2. Characteristics of particles and particle dispersoids. Adapted from figure reproduced by permission of SRI International, Menlo Park, CA, 1959.

III. WHAT IS AIR POLLUTION?

In Chapter 1, we attempted to define air pollution. Let us now consider what distinguishes polluted air from acceptable air quality. Over the past few decades the central feature of air pollution has been its association with harm, especially harm to humans in terms of diseases, such as respiratory diseases associated with air pollutants. Harm implies a value; i.e., something that society values is lost or diminished. In the United States, a handful of commonly found air pollutants are known to cause three specific types of harm. They impair health, destroy and adversely affect environmental resources, and damage property. To address these harms, as mentioned in Chapter 1, the Clean Air Act of 1970 established the National Ambient Air Quality Standards to address six so-called "criteria air pollutants":

1. particulate matter (PM),
2. ozone (O_3),
3. carbon monoxide (CO),
4. sulfur dioxide (SO_2),
5. nitrogen dioxide (NO_2),
6. lead (Pb).

They are called criteria air pollutants because the US Environmental Protection Agency (EPA) regulates them by using two sets of criteria for pollutant standards. The first set of standards is designed to protect public health based on sound science. This set of limits (known as *primary standards*) protects health. A second set of limits (known as *secondary standards*) aims to prevent environmental and property damage. When an urban area or other geographic area has concentrations of a criteria pollutant below the standard it is said to be "in attainment" and the area is declared to be an "attainment area." Conversely, any area that has concentrations of a criteria pollutant above the standard is called a "nonattainment area." Such a designation is not only problematic because of the potential health and environmental effects, but also because it means that the local and state governments will have to take actions to bring the area into attainment. The Clean Air Act gives the federal government a range of possible sanctions to encourage these actions, including withholding certain federal funds (e.g. road-building and other transportation projects). At present, many urban areas are classified as nonattainment for at least one criteria air pollutant. In fact about 90 million Americans live in nonattainment areas.[2]

The public's apprehensions, however, extend beyond the criteria pollutants and increase with the growing wariness about "toxic" chemicals added to the more familiar "conventional" pollutants. The clearest association of toxic air pollutants in recent decades has been with cancer, although neurotoxicity (especially in children) from lead and mercury grew in importance in the 1970s and 1980s. By the end of the twentieth century, new toxic pollutants also

[2] US Environmental Protection Agency, *Plain English Guide to the Clean Air Act*, http://www.epa.gov/oar/oaqps/peg_caa/pegcaa03.html#topic3a; accessed on October 6, 2006.

competed for the public's attention, including air pollutants that threaten hormonal systems in humans and wildlife, as well as those associated with immune system disorders.

IV. PARTICULATE MATTER

Neither Table 2.1 nor Table 2.2 lists among the constituents of the air the suspended PM that it always contains. The gases and vapors exist as individual molecules in random motion. Each gas or vapor exerts its proportionate partial pressure. The particles are aggregates of many molecules, sometimes of similar molecules, often of dissimilar ones. They age in the air by several processes. Some particles serve as nuclei upon which vapors condense. Some particles react chemically with atmospheric gases or vapors to form different compounds. When two particles collide in the air, they tend to adhere to each other because of attractive surface forces, thereby forming progressively larger and larger particles by agglomeration. The larger a particle becomes, the greater its weight and the greater its likelihood of falling to the ground rather than remaining airborne. The process by which particles fall out of the air to the ground is called *sedimentation.* Washout of particles by snowflakes, rain, hail, sleet, mist, or fog is a common form of agglomeration and sedimentation. Still other particles leave the air by impaction onto and retention by the solid surfaces of vegetation, soil, and buildings. The particulate mix in the atmosphere is dynamic, with continual injection into the air from sources of small particles; creation of particles in the air by vapor condensation or chemical reaction among gases and vapors; and removal of particles from the air by agglomeration, sedimentation, or impaction.

Before the advent of humans and their works, there must have been particles in the air from natural sources. These certainly included all the particulate forms of condensed water vapor; the condensed and reacted forms of natural organic vapors; salt particles resulting from the evaporation of water from sea spray; wind-borne pollen, fungi, molds, algae, yeasts, rusts, bacteria, and debris from live and decaying plant and animal life; particles eroded by the wind from beaches, desert, soil, and rock; particles from volcanic and other geothermal eruption and from forest fires started by lightning; and particles entering the troposphere from outer space. As mentioned earlier, the true natural background concentration will never be known because when it existed humans were not there to measure it, and by the time humans started measuring PM levels in the air, they had already been polluting the atmosphere with particles resulting from their presence on earth for several million years. The best that can be done now is to assume that the particulate levels at remote places—the middle of the sea, the poles, and the mountaintops—approach the true background concentration. The very act of going to a remote location to make a measurement implies some change in the atmosphere of that remote location attributable to the means people used to travel and to maintain themselves while obtaining the measurements. PM is measured on

a dry basis, thereby eliminating from the measurement not only water droplets and snowflakes but also all vapors, both aqueous and organic, that evaporate or are desiccated from the PM during the drying process. Since different investigators and investigative processes employ different drying procedures and definitions of dryness, it is important to know the procedures and definition employed when comparing data.

Although many of the air pollutants discussed in this book are best classified by their chemical composition, particles are first classified according to their physical properties. PM is a common physical classification of particles found in the air, such as dust, dirt, soot, smoke, and liquid droplets.[3] Unlike other US criteria pollutants [O_3, CO, SO_2, NO_2 and lead (Pb)], PM is not a specific chemical entity but is a mixture of particles from different sources and of different sizes, compositions, and properties. However, the chemical composition of PM is very important and highly variable. In fact, knowing what a particle is made of tells us much about its source, e.g. receptor models use chemical composition and morphology of particles as a means to trace pollutants back to the source.

The chemical composition of tropospheric particles includes inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal (e.g. carbonates and compounds of alkali and rare earth elementals) substances. For example, the mean 24 h $PM_{2.5}$ concentration measured near Baltimore, Maryland in 1999 was composed of 38% sulfate, 13% ammonium, 2% nitrate, 36% organic carbon, 7% elemental carbon, and 4% crustal matter.[4] In addition, some atmospheric particles can be hygroscopic, i.e., they contain particle-bound water. The organic fraction can be particularly difficult to characterize, since it often contains thousands of organic compounds.

The size of a particle is determined by how the particle is formed. For example, combustion can generate very small particles, while coarse particles are often formed by mechanical processes (see Fig. 2.3). If particles are sufficiently small and of low mass, they can be suspended in the air for long periods of time. Larger particles (e.g. $>10\,\mu m$ aerodynamic diameter) are found in smoke or soot (see Fig. 2.4), while very small particles ($<2.5\,\mu m$) may be apparent only indirectly, such as the manner in which they diffuse, diffract, absorb, and reflect light (see Fig. 2.5).

Sources of particles are highly variable. They may be emitted directly to the air from stationary sources, such as factories, power plants, and open burning, and from moving vehicles (known as "mobile sources"), first by direct emissions from internal combustion engines, but also when these and other

[3] UK Department of Environment, Food, and Rural Affairs, Expert Panel on Air Quality Standards, 2004, *Airborne Particles: What Is the Appropriate Measurement on Which to Base a Standard? A Discussion Document.*

[4] Bonne, G., Mueller, P., Chen, L. W., Doddridge, B. G., Butler, W. A., Zawadzki, P. A., Chow, J. C., Tropp, R. J., and Kohl, S. *Proceeding of the PM2000: Particulate Matter and Health Conference, Composition of PM2.5 in the Baltimore-Washington Corridor*, pp. W17–W18. Air & Waste Management Association, Washington, DC, January 2000.

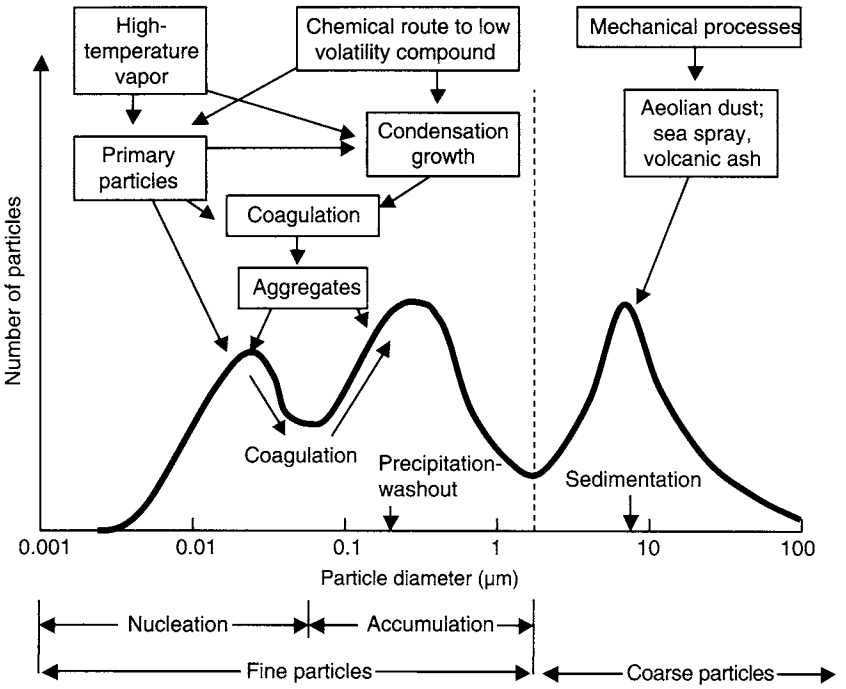

Fig. 2.3 Prototypical size distribution of tropospheric particles with selected sources and pathways of how the particles are formed. Dashed line is approximately 2.5 μm diameter. Adapted from: United Kingdom Department of Environment, Food, and Rural Affairs, Expert Panel on Air Quality Standards, 2004, *Airborne Particles: What Is the Appropriate Measurement on which to Base a Standard? A Discussion Document.*

particles are re-entrained due to the movement of vehicles (e.g. in a "near-road" situation). Area or non-point sources of particles include construction, agricultural activities such as plowing and tilling, mining, and forest fires.

Particles may also form from gases that have been previously emitted, such as when gases released from burning fuels react with sunlight and water vapor. A common production of such "secondary particles" occurs when gases undergo chemical reactions in the atmosphere involving O_2 and water vapor (H_2O). Photochemistry can be an important step in secondary particle formation, resulting when chemical species like ozone (O_3) are involved in step reactions with radicals, e.g. the hydroxyl (OH) and nitrate (NO_3) radicals. Photochemistry also incurs in the presence of air pollutant gases like sulfur dioxide (SO_2), nitrogen oxides (NO_x), and organic gases emitted by anthropogenic and natural sources. In addition, nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere, condensation of low-vapor pressure gases on aerosols already present in the atmosphere, and coagulation of aerosols can contribute to the formation of particles. The chemical composition, transport, and fate of particles are directly associated with the characteristics of the surrounding gas.

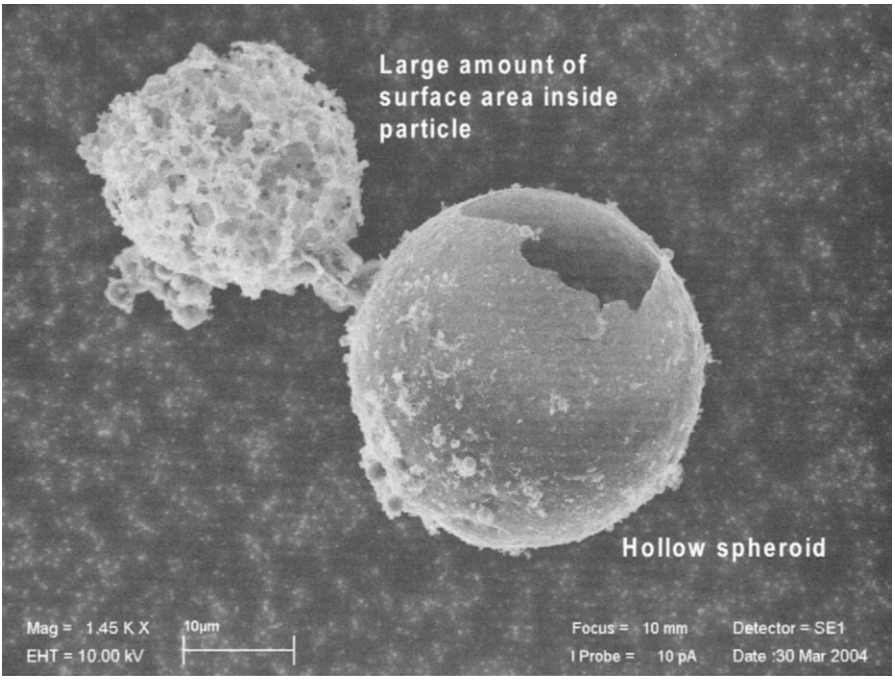

Fig. 2.4. Scanning electron micrograph of coarse particles emitted from an oil-fired power plant. Diameters of the particles are greater than 20 μm optical diameter. Both particles are hollow, so their aerodynamic diameter is significantly smaller than if they were solid. *Source*: Source characterization study by Stevens, R., Lynam, M., and Proffitt, D., 2004. Photo courtesy of Willis, R., ManTech Environmental Technology, Inc., 2004; used with permission.

The term "aerosol" is often used synonymously with PM. An aerosol can be a suspension of solid or liquid particles in air, and an aerosol includes both the particles and all vapor or gas phase components of air.

As mentioned, very small particles may remain suspended for some time, so they are can be particularly problematic from a pollutant transport perspective because their buoyancy allows them to travel longer distances. Smaller particles are also challenging because they are associated with numerous health effects (mainly because they can penetrate more deeply into the respiratory system than larger particles).

Generally, the mass of PM falling in two size categories is measured, i.e. $\leq 2.5\,\mu m$ diameter, and $\geqslant 2.5\,\mu m$ and $\leqslant 10\,\mu m$ diameter. These measurements are taken by instruments (see Fig. 2.6) with inlets using size exclusion mechanisms to segregate the mass of each size fraction (i.e. "dichotomous" samplers). Particles with diameters $\geqslant 10\,\mu m$ are generally of less concern, since these particles rarely travel long distances; however, they are occasionally measured if a large particulate emitting source (e.g. a coal mine) is nearby, since these particles rarely travel long distances.

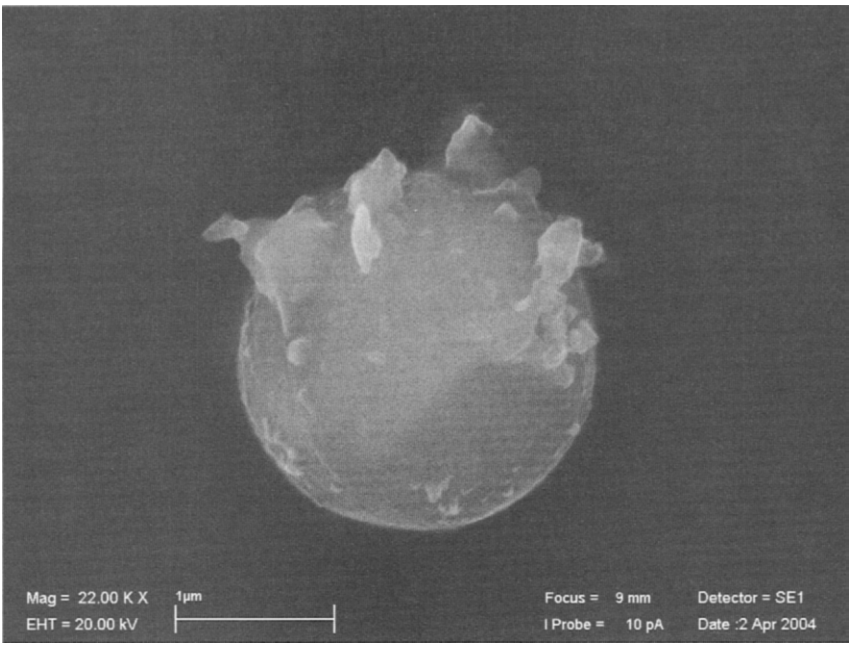

Fig. 2.5. Scanning electron micrograph of spherical aluminosilicate fly ash particle emitted from an oil-fired power plant. Diameter of the particle is approximately 2.5 μm. Photo courtesy of Willis, R., ManTech Environmental Technology, Inc., 2004; used with permission.

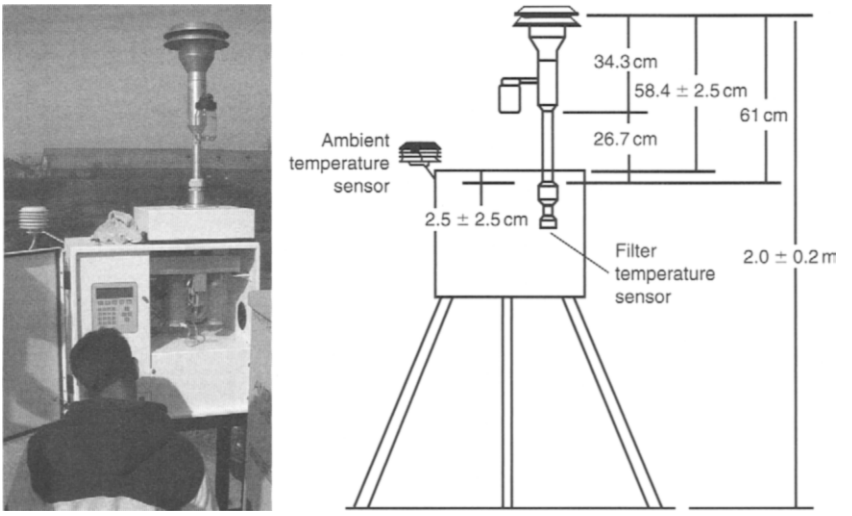

Fig. 2.6. Photo and schematic of sampling device used to measure particles with aerodynamic diameters ≤2.5 μm. Each sampler has an inlet (top) that takes in particles ≤10 μm. An impacter downstream in the instrument cuts the size fraction to ≤2.5 μm, which is collected on Teflon filter. The filter is weighed before and after collection. The Teflon allows construction for other analyses, e.g. X-ray fluorescence to determine inorganic composition of the particles. Quartz filters would be used if any subsequent carbon analyses are needed. Photo and schematic courtesy of US EPA.

Mass can be determined for a predominantly spherical particle by microscopy, either optical or electron, by light scattering and Mie theory, by the particle's electrical mobility, or by its aerodynamic behavior. However, since most particles are not spherical, PM diameters are often described using an equivalent diameter, i.e., the diameter of a sphere that would have the same fluid properties. Another term, optical diameter, is the diameter of a spherical particle that has an identical refractive index as the particle. Optical diameters are used to calibrate the optical particle sizing instruments, which scatter the same amount of light into the solid angle measured. Diffusion and gravitational settling are also fundamental fluid phenomena used to estimate the efficiencies of PM transport, collection, and removal processes, such as in designing PM monitoring equipment and ascertaining the rates and mechanisms of how particles infiltrate and deposit in the respiratory tract.

Only for very small diameter particles is diffusion sufficiently important that the Stokes diameter is often used. The Stokes diameter for a particle is the diameter of a sphere with the same density and settling velocity as the particle. The Stokes diameter is derived from the aerodynamic drag force caused by the difference in velocity of the particle and the surrounding fluid. Thus, for smooth, spherical particles, the Stokes diameter is identical to the physical or actual diameter. The aerodynamic diameter (D_{pa}) for all particles greater than 0.5 μm can be approximated[5] as the product of the Stokes particle diameter (D_{ps}) and the square root of the particle density (ρ_p):

$$D_{pa} = D_{ps}\sqrt{\rho_p} \tag{2.2}$$

The units of the diameters are in μm and the units of density are in g cm^{-3}.

Fine particles (<2.5 μm) generally come from industrial combustion processes (such as the particles in Fig. 2.4) and from vehicle exhaust. As mentioned, this smaller sized fraction has been closely associated with increased respiratory disease, decreased lung functioning, and even premature death, probably due to their ability to bypass the body's trapping mechanisms, such as cilia in the lungs, and nasal hair filtering. Some of the diseases linked to PM exposure include aggravation of asthma, chronic bronchitis, and decreased lung function.

In addition to health impacts, PM is also a major contributor to reduced visibility, including near national parks and monuments. Also, particles can be transported long distances and serve as vehicles on which contaminants are able to reach water bodies and soils. Acid deposition, for example, can be as dry or wet precipitation. Either way, particles play a part in acid rain. In the first, the dry particles enter ecosystems and potentially reduce the pH of receiving waters. In the latter, particles are washed out of the atmosphere and, in the

[5] Aerosol textbooks provide methods to determine the aerodynamic diameter of particles less than 0.5 μm. For larger particles gravitational settling is more important and the aerodynamic diameter is often used.

process; lower the pH of the rain. The same transport and deposition mechanisms can also lead to exposures to persistent organic contaminants like dioxins and organochlorine pesticides, and heavy metals like mercury that have sorbed in or on particles.

In addition to their inherent toxicity, particles can function as vehicles for transporting and transforming chemical contaminants. For example, compounds that are highly sorptive (e.g. those with large K_{oc} partitioning coefficients) can use particles as a means for long-range transport. Also, charge differences between the particle and ions (particularly metal cations) will also make particles a means by which contaminants are transported.

There are ways of measuring PM other than by weight per unit volume of air. They include a count of the total number of particles in a unit volume of air, a count of the number of particles of each size range, the weight of particles of each size range, and similar measures based on the surface area and volume of the particles rather than on their number or weight. Some particles in the air are so small that they cannot be seen by an optical microscope, individually weighing so little that their presence is masked in gravimetric analysis by the presence of a few large particles.

The mass of a spherical particle is

$$w = \frac{4}{3}\pi p r^3 \tag{2.3}$$

where w is the particle mass (g), r is the particle radius (cm), and p is the particle density ($g\,cm^{-3}$).

The size of small particles is measured in microns (μm). One micron is one-millionth of a meter or 10 000 Å (angstrom units)—the units used to measure the wavelength of light (visible light is between 3000 and 8000 Å) (Fig. 2.2) [2]. Compare the weight of a 10-μm particle near the upper limit of those found suspended in the air and a 0.1-μm particle which is near the lower limit. If both particles have the same density (p) the smaller particle will have one-millionth the weight of the larger one. This is because the radius term is cubed. The usual gravimetric procedures can scarcely distinguish a 0.1-μm particle in the presence of a 10-μm particle. To measure the entire size range of particles in the atmosphere, several measurement techniques must therefore be combined, each one most appropriate for its size range (Table 2.4). Thus, the smallest particles—those only slightly larger than a gas molecule—are measured by the electric charge they carry and by electron microscopy. The next larger size range is measured by electron microscopy or by the ability of these particles to act as nuclei upon which water vapor can be condensed in a cloud chamber. (The water droplets are measured rather than the particles themselves.) The still larger size range is measured by electron or optical microscopy; and the largest size range is measured gravimetrically, either as suspended particles separated from the air by a sampling device or as sedimented particles falling out of the air into a receptacle.

TABLE 2.4

Particle Size Ranges and Their Methods of Measurement

Particle size range (μm)	Ions	Nuclei	Visability	Suspended or settleable; nonairborne	Dispersion aerosol	Condensation aerosol	Pollen and spores	Sedimentation, diffusion, and settling
10^{-4}–10^{-3}	Small	—	—	Suspended	—	Gas molecules	—	Diffusion
10^{-3}–10^{-2}	Intermediate and large	Aitken nuclei	Electron microscope	Suspended	—	Vapor molecules	—	Diffusion
10^{-2}–10^{-1}	Large	Aitken and condensation nuclei	Electron microscope	Suspended	—	Fume-mist	—	Diffusion
Air pollution								
10^{-1}–10^{0}	—	Condensation nuclei	Microscope: electron and optical	Suspended	Dust-mist	Fume-mist	—	Diffusion and sedimentation
10^{0}–10^{1}	—	—	Microscope: optical	Suspended and settleable	Dust-mist	Fume-mist	—	Sedimentation
10^{1}–10^{2}	—	—	Eye, sieves	Settleable	Dust-mist	Mist-fog	Pollen and spores	—
10^{2}–10^{3}	—	—	Eye, sieves	Nonairborne	Dust-spray	Drizzle-rain	—	Sedimentation
10^{3}–10^{4}	—	—	Eye, sieves	Nonairborne	Sand-rocks	Rain	—	Sedimentation

1. *Fibers*

Generally, when environmental scientists discuss particles, they mean those that are somewhat spherical or angular like soil particles. Particles that are highly elongated are usually differentiated as "fibers." Such elongation is expressed as a particle's aspect ratio, i.e. the ratio of the length to width. Fibers generally have aspect ratios greater than 3:1. Environmentally important fibers include fiberglass, fabrics, and minerals (see Figs. 2.7 and 2.8). Exposure to fiberglass and textile fibers is most commonly found in industrial settings, such as it has been associated with the health problems of textile workers exposed to fibrous matter in high doses for many years. For example, chronic exposure to cotton fibers has led the ailment, byssinosis, also referred to as "brown lung disease," which is characterized by the narrowing of the lung's airways. However, when discussing fibers, it is highly likely that first contaminant to come to mind is asbestos, a group of highly fibrous minerals with separable, long, and thin fibers. Separated asbestos fibers are strong enough and flexible enough to be spun and woven. Asbestos fibers are heat resistant, making them useful for many industrial purposes. Because of their durability, asbestos fibers that get into lung tissue will remain for long periods of time.

2. *Asbestos: The Fiber of Concern*

There are two general types of asbestos, *amphibole* and *chrysotile*. Some studies show that amphibole fibers stay in the lungs longer than chrysotile, and this tendency may account for their increased toxicity.

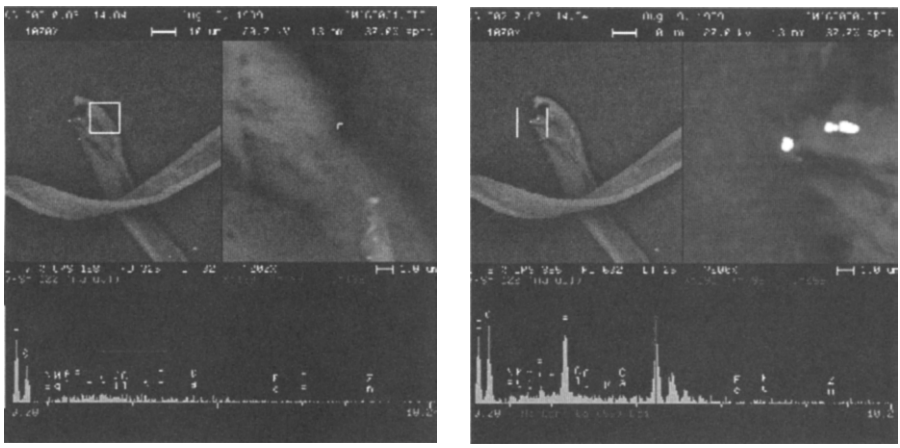

Fig. 2.7. Scanning electron micrograph of cotton fibers. Acquired using an Aspex Instruments, Ltd., Scanning electron microscope. *Source*: US Environmental Protection Agency, 2004. Note the different chemical composition at different locations of the same fiber as indicated by X-ray diffraction (XRD) spectrometry. Each peak at the bottom of the left and right micrographs indicates a different chemical element; the higher the peak, the greater the concentration of that element. Photo courtesy of Conner, T.; used with permission.

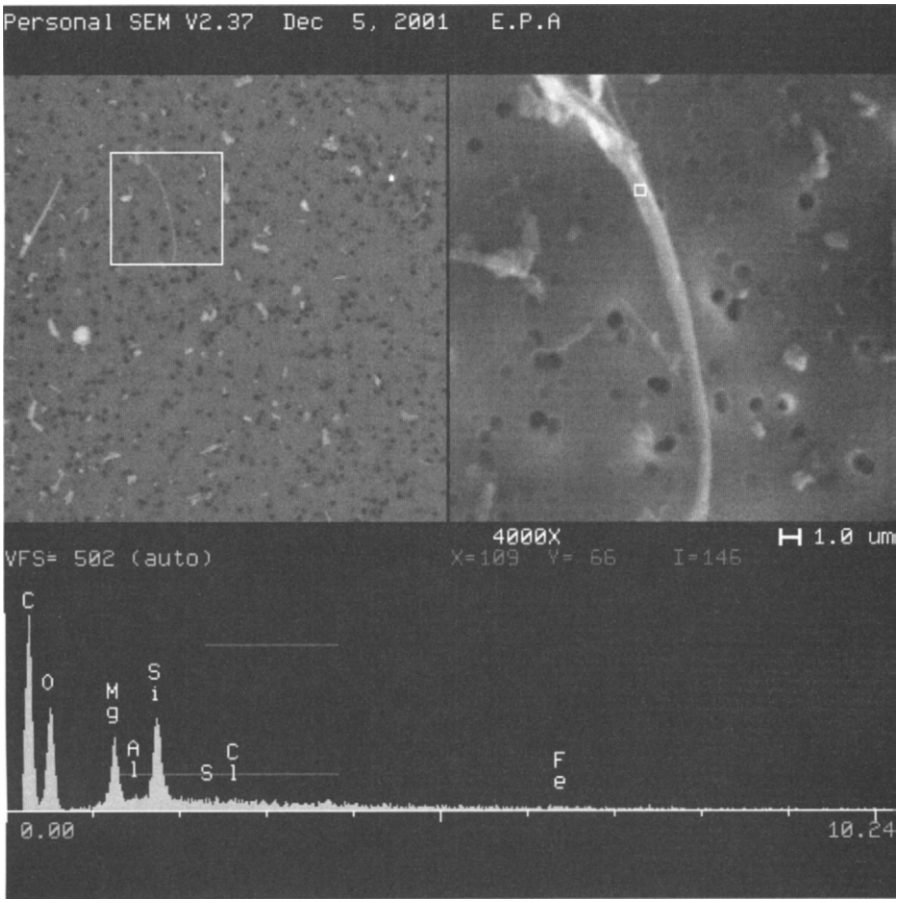

Fig. 2.8. Scanning electron micrograph of fibers in dust collected near the World Trade Center, Manhattan, NY, in September 2001. Acquired using an Aspex Instruments, Ltd., Scanning electron microscope. The bottom of the micrograph represents the elemental composition of the highlighted 15-μm long fiber by energy dispersive spectroscopy (EDS). This composition (i.e. O, Si, Al, and Mg) and the morphology of the fibers indicate they are probably asbestos. The EDS carbon peak results from the dust being scanned on a polycarbonate filter. *Source*: US Environmental Protection Agency, 2004. Photo courtesy of Conner, T.; used with permission.

Generally, health regulations classify asbestos into six mineral types: chrysotile, a serpentine mineral with long and flexible fibers; and five amphiboles, which have brittle crystalline fibers. The amphiboles include actinolite asbestos, tremolite asbestos, anthophyllite asbestos, crocidolite asbestos, and amosite asbestos (see Fig. 2.9).

3. Asbestos Routes of Exposure

Ambient air concentrations of asbestos fibers are about 10^{-5}–10^{-4} fibers per milliliter (fibers mL^{-1}), depending on location. Human exposure to concentrations much higher than 10^{-4} fibers mL^{-1} is suspected of causing health

Fig. 2.9. Scanning electron micrograph of asbestos fibers (amphibole) from a former vermiculite-mining site near Libby, Montana. *Source*: US Geological Survey and US Environmental Protection Agency, Region 8, Denver, CO.

effects.[6] Asbestos fibers are very persistent and resist chemical degradation (i.e. they are inert under most environmental conditions) so their vapor pressure is nearly zero meaning they do not evaporate, nor do they dissolve in water. However, segments of fibers do enter the air and water as asbestos-containing rocks and minerals that are weathered naturally or when extracted during mining operations. One of the most important exposures is when manufactured products (e.g. pipe wrapping and fire-resistant materials) begin to wear down. Small diameter asbestos fibers may remain suspended in the air for a long time and be transported advectively by wind or water

[6] For more information on asbestos exposure, see the Public Health Statement on Asbestos: ATSDR, 2001, Public Health Statement for Asbestos, http://www.atsdr.cdc.gov/toxprofiles/phs61.html.

before sedimentation. Like particles, heavier fibers settle more quickly. Asbestos seldom moves substantially via soil. The fibers are generally not broken down to other compounds in the environment and will remain virtually unchanged over long periods. Although most asbestos is highly persistent, chrysotile, the most commonly encountered form, may break down slowly in acidic environments. Asbestos fibers may break into shorter strands and, therefore, increased number of fibers, by mechanical processes (e.g. grinding and pulverization). Inhaled fibers may become trapped in the lungs and with chronic exposures build up over time. Some fibers, especially chrysotile, can be removed from or degraded in the lung with time.

Type of Control Dependent on Particle Characteristics

Recall from Figure 2.3 that numerous physical processes are at work in the formation of particles in the troposphere. These processes give a clue as to how to control particle emissions.

By measuring each portion of the particle size spectrum by the most appropriate method, a composite diagram of the size distribution of the atmospheric aerosol can be produced. Figure 2.10 shows that there are separate size distributions with respect to the number, surface area, and volume (or mass) of the particles. The volume (mass) distribution is called *bimodal* because of its separate maxima at about 0.2 and 10 μm, which result from

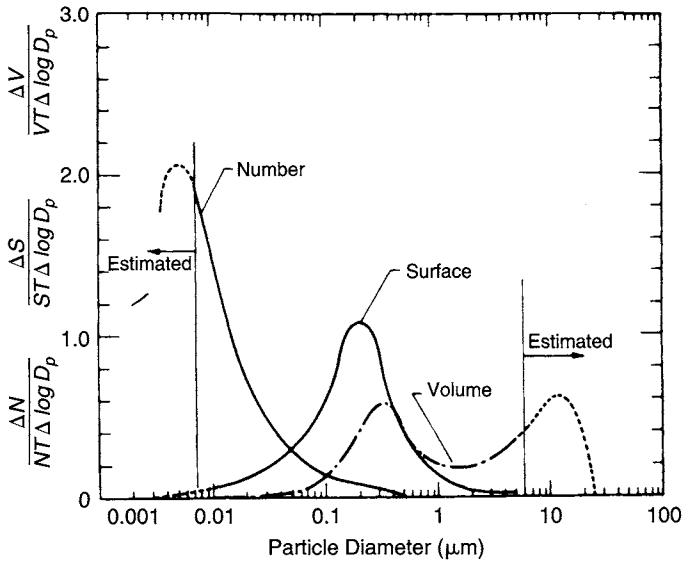

Fig. 2.10. Grand average number (N), surface area (S), and volume (V) distribution of Los Angeles smog. The linear ordinate normalized by total number (NT), area (ST), or volume (VT) is used so that the apparent area under the curves is proportional to the quantity in that size range. *Source*: Corn, M., Properties of non-viable particles in the air, in *Air Pollution*, 3rd ed., Vol. 1 (Stern, A. C., ed.), p. 123. Academic Press, New York, 1976.

different mechanisms of particle formation. The mode with the 0.2-μm maximum results from coagulation and condensation formation mechanisms. As mentioned, these particles are created in the atmosphere by chemical reaction among gases and vapors. They are called *fine* particles to differentiate them from the particles in the 10-μm maximum mode, which are called *coarse.* These fine particles are primarily sulfates, nitrates, organics, ammonium, and lead compounds. The mode with the 10-μm maximum are particles introduced to the atmosphere as solids from the surface of the earth and the seas, plus particles from the coagulation–condensation mode which have grown larger and moved across the saddle between the modes into the larger size mode. These are primarily silicon, iron, aluminum, sea salt, and plant particles. Thus, there is a dynamism that creates small particles, allows them to grow larger, and eventually allows the large particles to be scavenged from the atmosphere by sedimentation (in the absence of precipitation), plus washout and rainout when there is precipitation.

Understanding these mechanisms is the key to controlling air pollution. Designing and operating pollution control equipment effectively must account for the number, surface characteristics, volume, and shape of particles.

The majority of particles in the atmosphere are spherical in shape because they are formed by condensation or cooling processes or they contain core nuclei coated with liquid. Liquid surface tension draws the material in the particle into a spherical shape. Other important particle shapes exist in the atmosphere; e.g. asbestos is present as long fibers and fly ash can be irregular in shape.

The methods just noted tell something about the physical characteristics of atmospheric PM but nothing about its chemical composition. One can seek this kind of information for either individual particles or all particles *en masse.* Analysis of particles *en masse* involves analysis of a mixture of particles of many different compounds. How much of each element or radical, anion, or cation is present in the mixture can be determined. Specific organic compounds may be separated and identified. Individual particles may be analyzed by electron microscopy

Much of the concern about PM in the atmosphere arises because particles of certain size ranges can be inhaled and retained by the human respiratory system. There is also concern because PM in the atmosphere absorbs and scatters incoming solar radiation. For a detailed discussion of the human respiratory system and the defenses it provides against exposure of the lungs to PM, see Chapter 11.

V. CONCEPTS

A. Sources and Sinks

The places from which pollutants emanate are called *sources.* There are natural as well as anthropogenic sources of the permanent gases considered to be

pollutants. These include plant and animal respiration and the decay of what was once living matter. Volcanoes and naturally caused forest fires are other natural sources. The places to which pollutants disappear from the air are called *sinks*. Sinks include the soil, vegetation, structures, and water bodies, particularly the oceans. The mechanisms whereby pollutants are removed from the atmosphere are called *scavenging mechanisms*, and the measure used for the aging of a pollutant is its *half-life*—the time it takes for half of the quantity of pollutant emanating from a source to disappear into its various sinks. Fortunately, most pollutants have a short enough half-life (i.e. days rather than decades) to prevent their accumulation in the air to the extent that they substantially alter the composition of unpolluted air shown in Table 2.1. Several gases do appear to be accumulating in the air to the extent that measurements have documented the increase in concentration from year to year. The best-known example is carbon dioxide (Fig. 2.11; see also Fig. 15.1). Other accumulating gases are nitrous oxide (N_2O), methane (CH_4), CFCs, and other halocarbons. All of these gases have complex roles in climate change processes, particularly global warming concerns. CFCs are chemically very stable compounds in the troposphere and have half-lives from tens of years to over 100 years. One of the sinks for CFCs is transport to the stratosphere, where shortwave UV radiation photodissociates the molecules, releasing chlorine (Cl) atoms. These Cl atoms are projected to reduce the steady-state stratospheric ozone concentration, in turn increasing the penetration of harmful UV radiation to the earth's surface.

Oxidation, either atmospheric or biological, is a prime removal mechanism for inorganic as well as organic gases. Inorganic gases, such as nitric oxide (NO), nitrogen dioxide (NO_2), hydrogen sulfide (H_2S), sulfur dioxide

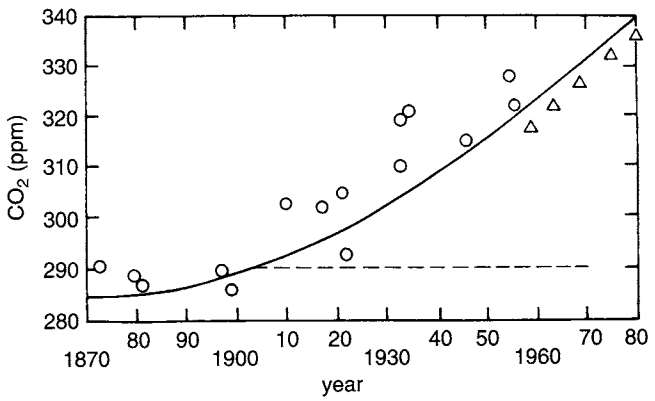

Fig. 2.11. Average CO_2 concentration: North Atlantic Region ○?, Pacific Region △. (The dashed line is the nineteenth-century base value: 290 ppm.) *Source*: Combination of data from Callender, G. C., *Tellus*, 10, 243 (1958), and Council on Environmental Quality, *Global Energy Futures and the Carbon Dioxide Problem*. Superintendent of Documents, US Government Printing Office, Washington, DC, 1981 (see also Fig. 15.1).

(SO_2), and sulfur trioxide (SO_3), may eventually form corresponding acids:

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \tag{2.4}$$

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3 \tag{2.5}$$

$$H_2S + \frac{2}{3}O_2 \rightarrow SO_2 + H_2O \tag{2.6}$$

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \tag{2.7}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{2.8}$$

Oxidation of SO_2 is slow in a mixture of pure gases, but the rate is increased by light, NO_2, oxidants, and metallic oxides which act as catalysts for the reaction. The formed acids can react with PM or ammonia to form salts.

B. Receptors

A *receptor* is something which is adversely affected by polluted air. A receptor may be a person or animal that breathes the air and whose health may be adversely affected thereby, or whose eyes may be irritated or whose skin made dirty. It may be a tree or plant that dies, or the growth yield or appearance of which is adversely affected. It may be some material such as paper, leather, cloth, metal, stone, or paint that is affected. Some properties of the atmosphere itself, such as its ability to transmit radiant energy, may be affected. Aquatic life in lakes and some soils are adversely affected by acidification via acidic deposition.

C. Transport and Dispersion

Transport is the mechanism that moves the pollution from a source to a receptor. The simplest source–receptor combination is that of an isolated point source and an isolated receptor. A point source may best be visualized as a chimney or stack emitting a pollutant into the air; the isolated point source might be the stack of a smelter standing by itself in the middle of a flat desert next to the body of ore it is smelting. The isolated receptor might be a resort hotel 5 miles distant on the edge of the desert. The effluent from the stack will flow directly from it to the receptor when the wind is along the line connecting them (Fig. 2.12). The wind is the means by which the pollution is transported from the source to the receptor. However, during its transit over the 5 miles between the source and the receptor, the plume does not remain a

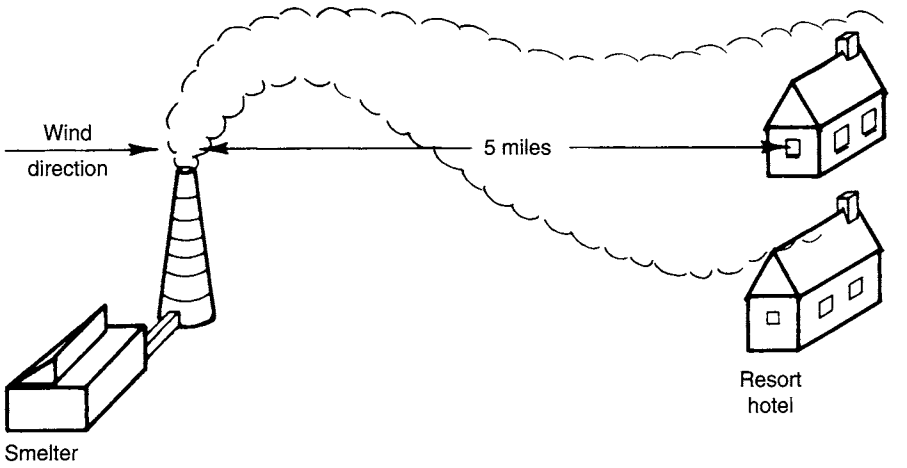

Fig. 2.12. Transport and dispersion from source to receptor.

cylindrical tube of pollution of the same diameter as the interior of the stack from which it was emitted. Instead, as it travels over the 5-mile distance, turbulent eddies in the air and in the plume move parcels from the edges of the plume into the surrounding air and move parcels of surrounding air into the plume. If the wind speed is greater than the speed of ejection from the stack, the wind will stretch out the plume until the plume speed equals wind speed. These two processes—mixing by turbulence and stretch-out of the plume, plus a third one—meandering (which means that the plume may not follow a true straight line between the source and the receptor, but may meander somewhat about that line as wind direction fluctuates from its mean value over the time of transit between the two points)—tend to make the concentration of the plume as it arrives at the receptor less than its concentration on release from the stack. The sum of all these processes is called *diffusion*. However, the term diffusion has a substantially different meaning in chemistry. Substances diffuse according to Fick's law of diffusion, wherein the concentration diminishes with distance from the source. This is known as a concentration gradient. Therefore, dispersion is the preferred term.

If the plume being transported is above the height where ground-based convective and turbulent processes will bring it down to the ground reasonably close to its origin, it may travel for hundreds of miles at that height before being brought to earth, by these processes, in a remote community. This is known as *long-range* or *long-distance transport*.

D. Significant Deterioration of Air Quality

It may be desirable to curtail transport of pollution to areas whose air is presently quite clean, even though, after such transport, the air quality of the

area would be considerably cleaner than would be required by air quality standards. This concept is called prevention of significant deterioration (PSD) of the air quality in such areas. It requires definition of how much deterioration can be considered insignificant. PSD is needed:

1. to protect public health and welfare;
2. preserve, protect, and enhance the air quality in national parks, national wilderness areas, national monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value;
3. to ensure that economic growth will occur in a manner consistent with the preservation of existing clean air resources; and
4. to view regulatory actions that allow certain levels of air pollutant releases from the perspective of the cumulative impact in any area.

Preserving air quality depends on knowing which sources are contributing to the deterioration. When the results of air pollution measurements are interpreted, one of the first questions asked by scientists, engineers, and policy makers is where did it come from? Sorting out the various sources of pollution is known as *source apportionment*. A number of tools are used to try to locate the sources of pollutants. A widely used approach is the "source–receptor model" or as it is more commonly known, the *receptor model.*

Using receptor models can be distinguished from the dispersion models in that dispersion models usually start from the source and estimate where the plume and its contaminants is heading (see Fig. 7.2). Conversely, receptor models are based upon measurements taken in the ambient environment and from these observations, make use of algorithms and functions to determine pollution sources. For a discussion of source–receptor relationships and modeling, see Discussion Box: Source Apportionment, Receptor Models, and Carbon Dating in Chapter 7 (p. 208).

E. Polluted Atmosphere

When is air polluted? This chapter presents principles by which materials are released into the atmosphere, move, transform, and are removed from the atmosphere. The definition of air pollutant or air pollution depends on the context of time, space, and impact for a particular set of circumstances. We have attempted to distinguish unpolluted from polluted air. However, the same chemical compounds or particles from a natural source (e.g. a volcano) elicit the same adverse effects as when they are emitted by anthropogenic sources.

Thus, unpolluted air is merely a benchmark to show the extent and trends of air pollution. Governments around the world have established and are continuously evaluating the impact of elevated levels of myriad gases and particulate material in the atmosphere. Clearly, these agencies are charged with addressing polluted air so that it is healthy to breathe, supports ecosystems,

and supports other welfare uses, such as visibility and integrity of buildings and other structures. This leads to the need to consider the risks brought about by a polluted atmosphere.

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QUESTIONS

1. Prepare a graph showing the conversion factor from ppm (vol.) to $\mu g\,m^{-3}$ for compounds with molecular weights ranging from 10 to 200 at 25°C and 760 mmHg as well as at 0°C and 760 mmHg.
2. (a) Convert 0.2 ppm (vol.) NO and 0.15 ppm (vol.) NO_2 to $\mu g\,m^{-3}$ NO_x at 25°C and 760 mmHg. (b) Convert 0.35 ppm (vol.) NO_x to $\mu g\,m^{-3}$ at 25°C and 760 mmHg.
3. Prepare a table showing the weight in g and the surface area in m^3 of a 0.1-, 1.0-, 10.0-, and 100.0-μm-diameter spherical particle of unit density.
4. What is the settling velocity in $cm\,sec^{-1}$ in air at 25°C and 1 atm for a 100 mesh size spherical particle, i.e., one which just passes through the opening in the sieve (specific gravity = 2.0)?
5. How does the diameter of airborne pollen grains compare with the diameter of a human hair?
6. What are the principal chemical reactions that take place in the chemosphere to give it its name? How do they influence stratospheric and tropospheric chemical reactions?
7. What are the source and nature of the condensable organic vapors in unpolluted air?
8. Has the composition of the unpolluted air of the troposphere most probably always been the same as in Tables 2.1 and 2.2? Will Tables 2.1 and 2.2 most probably define unpolluted air in the year 2085? Discuss your answer.
9. Describe the apparatus and procedures used to measure atmospheric ions and nuclei.
10. What do the terms "dispersion" and "diffusion" have in common? How do they differ?
11. Why is it so difficult to establish a baseline of clean air?