

urban–suburban atmosphere, where maxima well above 200 ppb have been observed (Table 2.16). Ozone concentrations in rural areas tend to be more moderate and rarely exceed 150 ppb. In remote locations, ozone concentrations typically range from 20 to 40 ppb.

2.7 PARTICULATE MATTER (AEROSOLS)

Particles in the atmosphere arise from natural sources, such as windborne dust, sea spray, and volcanoes, and from anthropogenic activities, such as combustion of fuels. Whereas an aerosol is technically defined as a suspension of fine solid or liquid particles in a gas, common usage refers to the aerosol as the particulate component only (Table 2.17). Emitted directly as particles (primary aerosol) or formed in the atmosphere by gas-to-particle conversion processes (secondary aerosol), atmospheric aerosols are generally considered to be the particles that range in size from a few nanometers (nm) to tens of micrometers

TABLE 2.17 Terminology Relating to Atmospheric Particles

Aerosols, aerocolloids, aerodisperse systems	Tiny particles dispersed in gases
Dusts	Suspensions of solid particles produced by mechanical disintegration of material such as crushing, grinding, and blasting. $D_p > 1 \mu\text{m}$.
Fog	A loose term applied to visible aerosols in which the dispersed phase is liquid. Usually, a dispersion of water or ice, close to the ground.
Fume	The solid particles generated by condensation from the vapor state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as oxidation. Often the material involved is noxious. $D_p < 1 \mu\text{m}$.
Hazes	An aerosol that impedes vision and may consist of a combination of water droplets, pollutants, and dust. $D_p < 1 \mu\text{m}$.
Mists	Liquid, usually water in the form of particles suspended in the atmosphere at or near the surface of the Earth; small water droplets floating or falling, approaching the form of rain, and sometimes distinguished from fog as being more transparent or as having particles perceptibly moving downward. $D_p > 1 \mu\text{m}$.
Particle	An aerosol particle may consist of a single continuous unit of solid or liquid containing many molecules held together by intermolecular forces and primarily larger than molecular dimensions ($> 0.001 \mu\text{m}$). A particle may also be considered to consist of two or more such unit structures held together by interparticle adhesive forces such that it behaves as a single unit in suspension or upon deposit.
Smog	A term derived from smoke and fog, applied to extensive contamination by aerosols. Now sometimes used loosely for any contamination of the air.
Smoke	Small gas-borne particles resulting from incomplete combustion, consisting predominantly of carbon and other combustible material, and present in sufficient quantity to be observable independently of the presence of other solids. $D_p \geq 0.01 \mu\text{m}$.
Soot	Agglomerations of particles of carbon impregnated with “tar,” formed in the incomplete combustion of carbonaceous material.

(μm) in diameter. Once airborne, particles can change their size and composition by condensation of vapor species or by evaporation, by coagulating with other particles, by chemical reaction, or by activation in the presence of water supersaturation to become fog and cloud droplets. Particles smaller than $1 \mu\text{m}$ diameter generally have atmospheric concentrations in the range from around ten to several thousand per cm^3 ; those exceeding $1 \mu\text{m}$ diameter are usually found at concentrations less than 1cm^{-3} .

Particles are eventually removed from the atmosphere by two mechanisms: deposition at the Earth's surface (dry deposition) and incorporation into cloud droplets during the formation of precipitation (wet deposition). Because wet and dry deposition lead to relatively short residence times in the troposphere, and because the geographical distribution of particle sources is highly nonuniform, tropospheric aerosols vary widely in concentration and composition over the Earth. Whereas atmospheric trace gases have lifetimes ranging from less than a second to a century or more, residence times of particles in the troposphere vary only from a few days to a few weeks.

2.7.1 Stratospheric Aerosol

The stratospheric aerosol is composed of an aqueous sulfuric acid solution of 60 to 80% sulfuric acid for temperatures from -80 to -45°C , respectively (Shen et al., 1995). The source of the globally distributed, unperturbed background stratospheric aerosol is oxidation of carbonyl sulfide (OCS), which has its sources at the Earth's surface. OCS is chemically inert and water insoluble and has a long tropospheric lifetime. It diffuses into the stratosphere where it dissociates by solar ultraviolet radiation to eventually form sulfuric acid, the primary component of the natural stratospheric aerosol. Other surface-emitted sulfur-containing species, for example, SO_2 , DMS, and CS_2 , do not persist long enough in the troposphere to be transported to the stratosphere.

A state of unperturbed background stratospheric aerosol may be relatively rare, however, as frequent volcanic eruptions inject significant quantities of SO_2 directly into the lower and midstratosphere. Recent major eruptions include Agung in 1963, El Chichón in 1982, and Pinatubo in 1991. The subsequent sulfuric acid aerosol clouds can, over a period of months, be distributed globally at optical densities that overwhelm the natural background aerosol. The stratosphere's relaxation to background conditions has a characteristic time on the order of years, so that, given the frequency of volcanic eruptions, the stratospheric aerosol is seldom in a state that is totally unperturbed by volcanic emissions. With an estimated aerosol mass addition of 30 Tg to the stratosphere, the June 1991 eruption of Mt. Pinatubo was the largest in the 20th century and led to enhanced stratospheric aerosol levels for over 2 years.

2.7.2 Chemical Components of Tropospheric Aerosol

A significant fraction of the tropospheric aerosol is anthropogenic in origin. Tropospheric aerosols contain sulfate, ammonium, nitrate, sodium, chloride, trace metals, carbonaceous material, crustal elements, and water. The carbonaceous fraction of the aerosols consists of both elemental and organic carbon. Elemental carbon, also called black carbon, graphitic carbon, or soot, is emitted directly into the atmosphere, predominantly from combustion processes. Particulate organic carbon is emitted directly by sources or can result from atmospheric condensation of low-volatility organic gases. Anthropogenic emissions leading

TABLE 2.18 Mass Concentrations and Composition of Tropospheric Aerosols

Region	Mass ($\mu\text{g m}^{-3}$)	Percentage Composition				
		C (elem)	C (org)	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
Remote (11 areas) ^a	4.8	0.3	11	7	3	22
Nonurban continental (14 areas) ^a	15	5	24	11	4	37
Urban (19 areas) ^a	32	9	31	8	6	28
Rubidoux, California ^b (1986 annual average)	87.4	3	18	6	20	6

^aHeintzenberg (1989).^bSolomon et al. (1989).

to atmospheric aerosol have increased dramatically over the past century and have been implicated in human health effects (Dockery et al., 1993), in visibility reduction in urban and regional areas (see Chapter 22), in acid deposition (see Chapter 20), and in perturbing the Earth's radiation balance (see Chapter 22).

Table 2.18 presents data summarized by Heintzenberg (1989) and Solomon et al. (1989) on aerosol mass concentrations and composition in different regions of the troposphere. It is interesting to note that average total fine particle mass (that associated with particles of diameter less than about $2 \mu\text{m}$) in nonurban continental, (i.e., regional) aerosols is only a factor of 2 lower than urban values. This reflects the relatively long residence time of particles. Correspondingly, the average compositions of nonurban continental and urban aerosols are roughly the same. The average mass concentration of remote aerosols is a factor of 3 lower than that of nonurban continental aerosols. The elemental carbon component, a direct indicator of anthropogenic combustion sources, drops to 0.3% in the remote aerosols, but sulfate is still a major component. This is attributable to a global average concentration of non-sea-salt sulfate of about $0.5 \mu\text{g m}^{-3}$. Rubidoux, California, located about 100 km east of downtown Los Angeles, routinely experiences some of the highest particulate matter concentrations in the United States.

2.7.3 Cloud Condensation Nuclei (CCN)

Aerosols are essential to the atmosphere as we know it; if the Earth's atmosphere were totally devoid of particles, clouds could not form. Particles that can become activated to grow to fog or cloud droplets in the presence of a supersaturation of water vapor are termed cloud condensation nuclei (CCN). At a given mass of soluble material in the particle there is a critical value of the ambient water vapor supersaturation below which the particle exists in a stable state and above which it spontaneously grows to become a cloud droplet of $10 \mu\text{m}$ or more diameter. The number of particles from a given aerosol population that can act as CCN is thus a function of the water supersaturation. For marine stratiform clouds, for which supersaturations are in the range of 0.1 to 0.5%, the minimum CCN particle diameter is 0.05 to $0.14 \mu\text{m}$. CCN number concentrations vary from fewer than 100cm^{-3} in re-

mote marine regions to many thousand cm^{-3} in polluted urban areas. An air parcel will spend, on average, a few hours in a cloud followed by a few days outside clouds. The average lifetime of a CCN is about 1 week, so that an average CCN will experience 5 to 10 cloud activation/cloud evaporation cycles before actually being removed from the atmosphere in precipitation.

2.7.4 Sizes of Atmospheric Particles

Atmospheric aerosols consist of particles ranging in size from a few tens of angstroms (\AA) to several hundred micrometers. Particles less than $2.5 \mu\text{m}$ in diameter are generally referred to as “fine” and those greater than $2.5 \mu\text{m}$ diameter as “coarse.” The fine and coarse particle modes, in general, originate separately, are transformed separately, are removed from the atmosphere by different mechanisms, require different techniques for their removal from sources, have different chemical composition, have different optical properties, and differ significantly in their deposition patterns in the respiratory tract. Therefore the distinction between fine and coarse particles is a fundamental one in any discussion of the physics, chemistry, measurement, or health effects of aerosols.

The phenomena that influence particle sizes are shown in an idealized schematic in Figure 2.15, which depicts the typical distribution of surface area of an atmospheric aerosol. Fine particles can often be divided roughly into two modes: the *nuclei mode* and the *accumulation mode*. The *nuclei mode*, extending from about 0.005 to $0.1 \mu\text{m}$ diameter, accounts for the preponderance of particles by number; because of their small size, these particles rarely account for more than a few percent of the total mass of airborne particles. Particles in the nuclei mode are formed from condensation of hot vapors during combustion processes and from the nucleation of atmospheric species to form fresh particles. They are lost principally by coagulation with larger particles. The *accumulation mode*, extending from 0.1 to about $2.5 \mu\text{m}$ diameter, usually accounts for most of the aerosol surface area and a substantial part of the aerosol mass. The source of particles in the accumulation mode is the coagulation of particles in the nuclei mode and from condensation of vapors onto existing particles, causing them to grow into this size range. The accumulation mode is so named because particle removal mechanisms are least efficient in this regime, causing particles to accumulate there. The *coarse mode*, from $>2.5 \mu\text{m}$ diameter, is formed by mechanical processes and usually consists of man-made and natural dust particles. Coarse particles have sufficiently large sedimentation velocities that they settle out of the atmosphere in a reasonably short time. Because removal mechanisms that are efficient at the small and large particle extremes of the size spectrum are inefficient in the accumulation range, particles in the accumulation mode tend to have considerably longer atmospheric residence times than those in either the nuclei or coarse mode.

2.7.5 Sources of Atmospheric Particulate Matter

Significant natural sources of particles include soil and rock debris (terrestrial dust), volcanic action, sea spray, biomass burning, and reactions between natural gaseous emissions. Table 2.19 presents a range of emission estimates of particles generated from natural and anthropogenic sources, on a global basis. Emissions of particulate matter attributable to the activities of humans arise primarily from four source categories: fuel combustion, industrial processes, nonindustrial fugitive sources (roadway dust from paved and unpaved

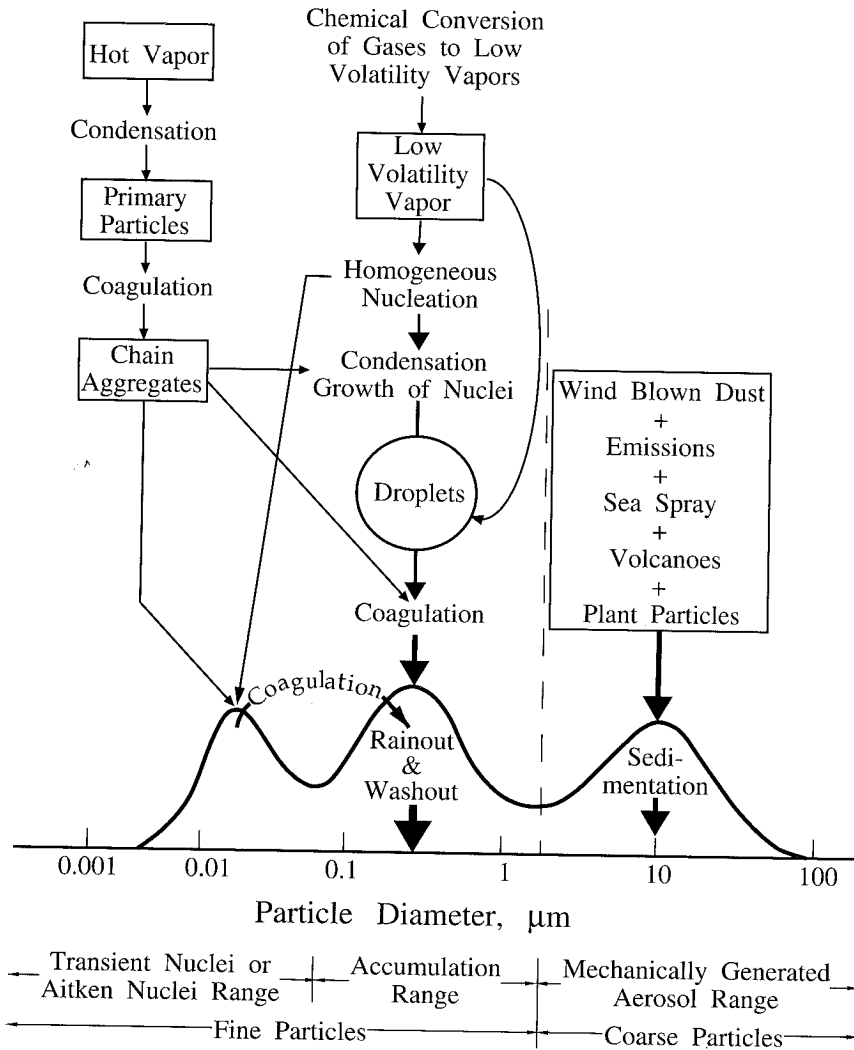


FIGURE 2.15 Idealized schematic of the distribution of particle surface area of an atmospheric aerosol (Whitby and Cantrell, 1976). Principal modes, sources, and particle formation and removal mechanisms are indicated.

roads, wind erosion of cropland, construction, etc.), and transportation sources (automobiles, etc.).

Fugitive particles are those not emitted from a definable point such as a stack. Industrial fugitive dust emissions result from wind erosion of storage piles and unpaved plant roads and from vehicular traffic over plant roads. Fugitive process emissions result from industry-related operations such as materials handling, loading, and transfer operations. Three broad categories account for nearly all of the potential process fugitive emissions—mineral products, food and agriculture, and primary metals. Nonindustrial fugitive particulate emissions, commonly termed *fugitive dust*, are caused by traffic entrainment of dust from

TABLE 2.19 Global Emission Estimates for Major Aerosol Types in the 1980s

Source	Estimated Flux (Tg yr ⁻¹)			Particle Size Category ^a
	Low	High	Best	
NATURAL				
Primary				
Soil dust (mineral aerosol)	1000	3000	1500	Mainly coarse
Sea salt	1000	10000	1300	Coarse
Volcanic dust	4	10000	30	Coarse
Biological debris	26	80	50	Coarse
Secondary				
Sulfates from biogenic gases	80	150	130	Fine
Sulfates from volcanic SO ₂	5	60	20	Fine
Organic matter from biogenic VOC	40	200	60	Fine
Nitrates from NO _x	15	50	30	Fine and coarse
Total natural	2200	23500	3100	
ANTHROPOGENIC				
Primary				
Industrial dust, etc. (except soot)	40	130	100	Fine and coarse
Soot	5	20	10	Mainly fine
Secondary				
Sulfates from SO ₂	170	250	190	Fine
Biomass burning	60	150	90	Fine
Nitrates from NO _x	25	65	50	Mainly coarse
Organics from anthropogenic VOC	5	25	10	Fine
Total anthropogenic	300	650	450	
Total	2500	24000	3600	

^aCoarse and fine size categories refer to mean particle diameter above and below 1 μm , respectively.

Note: Sulfates and nitrates are assumed to occur as ammonium salts. Flux unit: Tg yr⁻¹ (dry mass).

Source: Kiehl and Rodhe (1995).

paved and unpaved roads, agricultural operations, construction, and fires. Except for the last, all these sources entail dust entrainment by the interaction of machinery with materials and by the forces of wind on materials. While it is estimated that fugitive dust emissions exceed particulate emissions from stationary point sources in most areas, their impact is limited because the emissions are mostly large particles that settle a short distance from the source, and fugitive dust sources exist mainly in rural areas.

Transportation source emissions occur in two categories: (1) vehicle exhaust and (2) vehicle-related particles from tire, clutch, and brake wear. Engine-related particulate emissions are composed primarily of lead halides, sulfates, and carbonaceous matter and are mostly smaller than 1 μm in diameter. About 40% of particles from tire wear are less than 10 μm (about 20% are less than 1 μm) and are primarily carbon. Particles from brake linings are less than 1 μm and are composed mainly of asbestos and carbon.

Atmospheric particulate matter samples can be analyzed routinely for more than 50 trace elements. Trace element emissions arise from a large number of different source types in urban areas. For example, motor vehicles burning leaded fuel, electric arc steel furnaces, Kraft recovery boilers, and secondary lead smelters contribute to atmospheric lead concentrations. The wide spectrum of sources, together with the fact that trace metals often are only a minor fraction of the mass emissions from each source, obscure the relative importance of the contributors to atmospheric trace element levels.

As with all atmospheric species, trace metal emissions undergo atmospheric transport and dilution before they reach a particular receptor site. Mathematical models can be constructed based on the fundamentals of atmospheric chemistry and physics that will track the contributions from many emission sources as they undergo atmospheric transport. Indeed, the development of such models will receive considerable attention in this book. In the case of particulate emissions, an alternative is available. It is possible to attack the source contribution identification problem in reverse order, proceeding from measured particulate concentrations at a receptor site backward to the responsible emission sources (see Chapter 24). The unique metals content of the emissions from each source type is viewed as a fingerprint for the presence of material from that source in an ambient aerosol sample.

2.7.6 Carbonaceous Particles

Carbonaceous particles in the atmosphere consist of two major components—graphitic or black carbon (sometimes referred to as elemental or free carbon) and organic material. The latter can be directly emitted from sources or produced from atmospheric reactions involving gaseous organic precursors. Elemental carbon can be produced only in a combustion process and is therefore solely primary. Graphitic carbon particles are the most abundant light-absorbing aerosol species in the atmosphere. Particulate organic matter is a complex mixture of many classes of compounds (Daisey, 1980). A major reason for the study of particulate organic matter has been the possibility that such compounds pose a health hazard. Specifically, certain fractions of particulate organic matter, especially those containing polycyclic aromatic hydrocarbons (PAHs), have been shown to be carcinogenic in animals and mutagenic in *in vitro* bioassays.

2.8 EMISSIONS INVENTORIES

An estimate of emissions of a species from a source is based on a technique that uses “emission factors,” which are based on source-specific emission measurements as a function of activity level (e.g., amount of annual production at an industrial facility) with regard to each source. For example, suppose one wants to sample a power plant’s emissions of SO₂ or NO_x at the stack. The plant’s boiler design and its BTU (British thermal unit) consumption rate are known. The sulfur and nitrogen content of fuel burned can be used to calculate an emissions factor of kilograms (kg) of SO₂ or NO_x emitted per metric ton (Mg) of fuel consumed.

The U.S. Environmental Protection Agency (EPA) has compiled emission factors for a variety of sources and activity levels (such as production or consumption), reporting the results since 1972 in “AP-42 Compilation of Air Pollutant Emission Factors,” for which supplements are issued regularly. Emission factors currently in use are developed from only a