

instrumentation for measuring aerosol physical and chemical properties. It is now possible, for example, to measure physical size distributions down to 3 nm diameter with a time resolution of several minutes, and instruments for measuring the composition of individual particles in real time are being developed and used for atmospheric studies. While most measurements of aerosol composition to date have involved the analysis of samples collected on filters, instruments are currently being developed that provide real-time information on aerosol composition with a much better time resolution than can be obtained with filters. These advances are leading to significant refinements in our understanding of the origins of atmospheric particles and of the role they play in atmospheric chemistry.

See also

Aerosols: Climatology of Tropospheric Aerosols; Physics and Chemistry of Aerosols; Role in Cloud Physics; Role in Radiative Transfer. **Satellite Remote Sensing:** Aerosol

Measurements. **Tropospheric Chemistry and Composition:** Aerosols/Particles.

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Physics and Chemistry of Aerosols

J Heintzenberg, Institute for Tropospheric Research, Leipzig, Germany

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Introduction

The atmosphere is an aerosol, that is, a mixture of carrier gases suspending liquid or solid particles. The literature abounds with confusing usage of the term aerosol (often used synonymously with the condensed phase of this multiphase system). In the present article, the term aerosol is used exclusively for the complete multiphase system. In the atmosphere, there are good reasons to include aerosols and clouds in one definition. Both systems often exhibit comparable lifetimes. The traditional separation into aerosol particles and ‘activated’ cloud elements appears untenable and counterproductive because there is mounting evidence for a humidity-dependent unbroken continuum in particle sizes, related atmospheric processes, and effects from dehydrated submicrometer particles to decamicrometer cloud drops (**Figure 1**).

Monitoring and analytical demands in ultraclean, nanotechnologies and defence technologies have led to the development of a rapidly growing number of high-sensitivity particle sensors and methods. Additionally, some ten years ago atmospheric aerosols were recog-

nized as major controllers of global climate. Taken together, these two independent developments have led to tremendous advances in atmospheric aerosol research over the past 15 years. Consequently, numerous details of the physical and chemical characteristics of the atmospheric aerosol can be summarized after introductory remarks on nomenclature in the first two sections of this article. Through new aerosol instrumentation and theoretical considerations, the state of

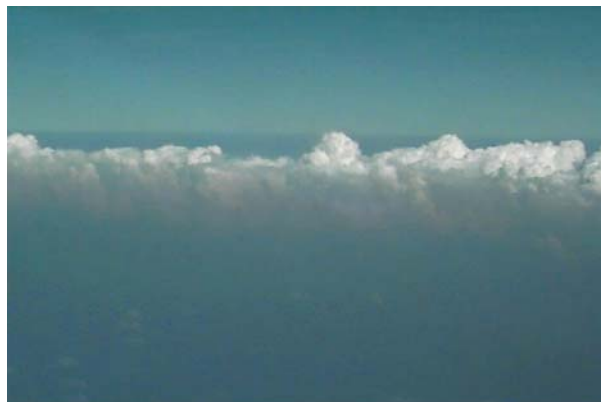


Figure 1 Trade Wind clouds surrounded by thick haze near the surface of the Indian ocean. (Courtesy of A. D. Clarke, University of Hawaii.)

mixture of aerosols emerges as a new dimension affecting all atmospheric aerosol processes and effects. The article will thus conclude with an introduction to this aerosol descriptor.

Nomenclature

Source processes, particle origin, and particle size (in this article the diameter of a reference sphere) are the main descriptors in the current nomenclature of the atmospheric aerosol. Primary particles are emitted into the atmosphere from their source as particles. Examples are pollen, sea salt, and soot from combustion sources. New secondary particles are formed in the atmosphere by the nucleation of one or several precursor gases, while condensation of gas phase material (most frequently water vapor) on existing particles adds secondary particulate matter to the aerosol. Crustal particles have their aeolian origin in the eroded crustal surface of the Earth. Conversely, sea salt particles originate mostly from bubbles bursting at the sea surface. Differentiating natural and anthropogenic particles in the atmospheric aerosol becomes increasingly difficult because environmental changes caused by human activities on a global scale affect all aerosol source processes.

The coarsest size-related particle nomenclature is also connected to particle source processes. Fine particles below roughly $1\ \mu\text{m}$ are mainly secondary in nature or result from combustion processes whereas coarse particles with diameters larger than $1\ \mu\text{m}$ are mainly primary in nature and result from the surface of the Earth (sea, land, vegetation). For technical reasons, coarse particle chemical data are given in this article for an upper size limit of $10\ \mu\text{m}$. The regular structure of the size distribution of atmospheric aerosol particles has stimulated the naming of sub-ranges of particle size. Particles below roughly $20\ \text{nm}$ are called ultrafine. Aitken particles are larger than ultrafine particles, ranging up to about $100\ \text{nm}$. A third subrange, or mode, of fine particles is called the accumulation mode and includes sizes between about $100\ \text{nm}$ and $1\ \mu\text{m}$.

Distribution and Physical Properties

Our knowledge of the three-dimensional distribution of the atmospheric aerosol is rather incomplete. Satellite data and global chemical transport models give the best overviews. These show that crustal aerosols are concentrated in and downwind of the deserts of Africa, Arabia, and Eurasia, whereas the maxima of sea salt particles in both hemispheres are collocated with the stormy mid- and high-latitudinal

west wind zones. Anthropogenic aerosols are concentrated (in order of importance) around and downwind of the major population centres of East Asia, the Indian subcontinent, North America, and Europe.

Dominating aerosol sources are located at or near the ground. Consequently, most integral aerosol properties decrease strongly with altitude. Known exceptions are total number and possibly particle surface, which show secondary peaks near the tropopause where both natural and anthropogenic (air traffic) particle sources have local maxima. In the stratosphere, there is a perennial aerosol layer between 15 and $25\ \text{km}$, the so-called Junge layer. It is maintained by oxidation products of sulfur gases emitted from the Earth's surface, with sporadic strong replenishments from volcanic eruptions. Typical size distribution parameters of major aerosol types are collected in **Table 1**. Global coverage of size distribution data is far from satisfactory. Over the oceans, surface coverage is about 28% , whereas no comparable number exists for the continents or upper atmospheric layers.

Including nonprecipitating clouds, the sizes of atmospheric aerosol particles are distributed over more than four orders of magnitude from $1\ \text{nm}$ to about $100\ \mu\text{m}$. This distribution of particle numbers over particle diameter D is conveniently approximated by a superposition of a number of log-normal distributions, each characterized by the three parameters of geometric mean diameter d_g , geometric standard deviation σ_g , and total number concentration N (eqn [1]).

$$\frac{dn}{d \ln D} = \frac{N}{\sqrt{2\pi} \ln \sigma_g} \exp \left[-\frac{(\ln D - \ln D_g)^2}{2(\ln \sigma_g)^2} \right] \quad [1]$$

Here $dn/d \ln D$ is the number of particles per logarithmic size interval and volume of air. Apart from mathematical convenience, there is no physical basis for this particular choice of distribution function, except for crustal particles. For this particle type, models of the primary processes of particle formation on the Earth's surface have been formulated with log-normal distributions.

With additional assumptions about particle shape and composition, the integral properties of surface, volume, and mass concentrations can be derived analytically from the three basic distribution parameters. They vary over more than six orders of magnitude in the Earth's atmosphere. Models of aerosol dynamics have been formulated that are based on moments of log-normal size distributions.

Table 1 compares log-normal distribution parameters for major natural aerosol types and reservoirs with those for anthropogenic particles and low stratiform clouds. For sea salt particles the distribution

Table 1 Geometric mean diameter d_g , geometric standard deviation σ_g and total number concentration N_t in cm^{-3} for major atmospheric aerosol types and reservoirs in the ultrafine, Aitken, and coarse particle size ranges and for low stratiform clouds.

Region \log-normal parameters	No. ^a	Ultrafine			Aitken			Accumulation			Coarse			Stratus		
		N_t	d_g (nm)	σ_g (nm)	N_t	d_g (nm)	σ_g (nm)	N_t	d_g (nm)	σ_g (nm)	N_t	d_g (μm)	σ_g (μm)	N_t	d_g (μm)	σ_g (μm)
Arctic	1	120	14	1.4												
Ocean, fine	2				280	40	1.4									
Ocean, fine	3							170	160	1.5						
Sea salt (film)	4							3.4	200	1.9						
Sea salt (jet)	5										1.1	2.0	2.0			
Crustal, mode 1	6										4.5	0.64	1.7			
Crustal, mode 2	7										0.15	3.5	1.6			
Crustal, mode 3	8										0.013	8.7	1.5			
Anthropogenic, fine	9	630	5.9	1.3												
Anthropogenic, fine	10	2010	16	1.6												
Anthropogenic, fine	11				2300	58	1.7									
Anthropogenic, fine	12							500	199	1.52						
Anthropogenic, coarse	13										1.5	0.73	1.9			
Upper troposphere	14				4400	24	1.7									
Stratosphere	15				50	80	1.5									
Marine Stratus	16													74	13	1.5
Continental Stratus	17													288	7.7	1.5

^aThe number identifies the curves in **Figure 2**.

parameters for the two major source processes of film and jet drop production are listed in **Table 1** for a wind speed at 10 m height (U_{10}) of 10 m s^{-1} . Number concentrations of film (N_{film}) and jet particles (N_{jet}) at other wind speeds follow eqns [2] and [3], respectively.

$$\ln N_{\text{film}} = 0.095U_{10} + 0.283 \quad [2]$$

$$\ln N_{\text{jet}} = 0.0422U_{10} - 0.288 \quad [3]$$

Crustal particle sources are also strongly wind-driven. Total mass concentration of crustal particles c in $\mu\text{g m}^{-3}$ is related empirically to the wind speed at 2 m height (U_2) by eqn [4].

$$\log c = 0.3U_2 + 52.77 \quad [4]$$

Note that the substantial mass concentrations implied by eqn [4] at zero local wind speed are due to the fact that regional dust sources will maintain the crustal aerosol even without local wind. For the size distribution of crustal particles, a superposition of three modes has been suggested. The corresponding modal parameters for experimentally determined mass proportions of these three modes averaged over different wind conditions in two source regions are listed in **Table 1**. The mass-related crustal data have been converted, using a particle density of 2.65 g cm^{-3} , to respective total number concentrations for $c = 52.77 \mu\text{g m}^{-3}$. With eqn [4] these number concentrations can be scaled to different wind speeds (neglecting the fact that the proportions of the three modes also show some

wind speed dependence). Only for the summer Arctic have statistical data for a marine ultrafine mode been secured. Global annual average Aitken and accumulation mode distribution parameters, on the other hand, have been published and are listed as ‘Ocean, fine’ in **Table 1**. Anthropogenic fine and coarse particle distribution parameters have been derived from about two years’ of continuous data near Leipzig, Germany. Upper troposphere parameters are derived from 21 flights with a commercial aircraft of the CARIBIC project between Germany and the Indian Ocean. The stratus data are derived from 14 marine and 14 continental cloud studies.

Figure 2 illustrates the shapes of the different particle size distributions of **Table 1**. Size, position, and total number of the submicrometer modes are controlled by the strengths of the related gas-to-particle sources combined with the effects of aerosol dynamics and liquid phase chemical reactions. The different modes depicted in **Figure 2** will never be present at the same time and place in the atmosphere. Numerical models of atmospheric aerosol dynamics predict transformations between the modes depicted in relation to the source and sink processes controlling a particular setting. It is interesting to note that despite the very wide range of median particle sizes the geometric standard deviations of the distributions vary only between 1.4 and 2.

As indicated by the thick haze surrounding the clouds in **Figure 1**, there is no size gap around 1000 nm in the real cloudy planetary boundary layer between

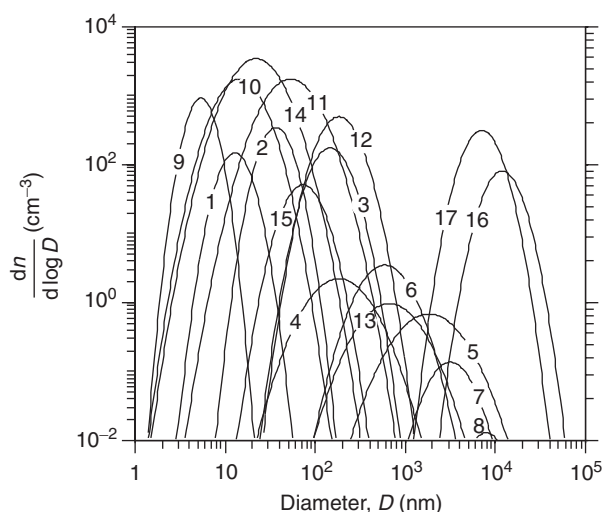


Figure 2 Number size distributions of major aerosol types and reservoirs. For comparison, number size distributions of low stratiform clouds are shown (16,17). Numbers on the curves refer to the curve parameters in Table 1.

aerosol and cloud drop size distribution, such as may be inferred from Figure 2. Recent studies of the transition from haze to fog with new drop spectrometers have shown that there is a continuous range of particle sizes from the accumulation mode to micrometer-sized and supermicrometer-sized haze and cloud drops with increasing relative humidity (RH). By means of measured horizontal visibilities, this transition can be divided into three meteorological regimes: haze with a visibility larger than 1000 m; mist with a visibility between 500 and 1000 m; and fog with visibilities below 500 m. Average particle size distributions in the highly polluted Po Valley, Italy, for the three regimes are displayed in Figure 3. Counting statistics limit the size range for the cases of haze and mist. The corresponding average visibilities are 1770 m, 790 m, and 190 m, respectively.

The *in situ* particle or drop size distributions clearly demonstrate the evolution of a continuous size distribution from submicrometer particle sizes to decameter sized drops in the transition from haze to fog (or other stratiform clouds).

Chemical Composition

The chemical composition is a major factor that controls the atmospheric effects of aerosol particles. The many possible source processes and source types coupled with physical and chemical atmospheric transformation processes lead to a large variability in aerosol composition. This variability, combined with

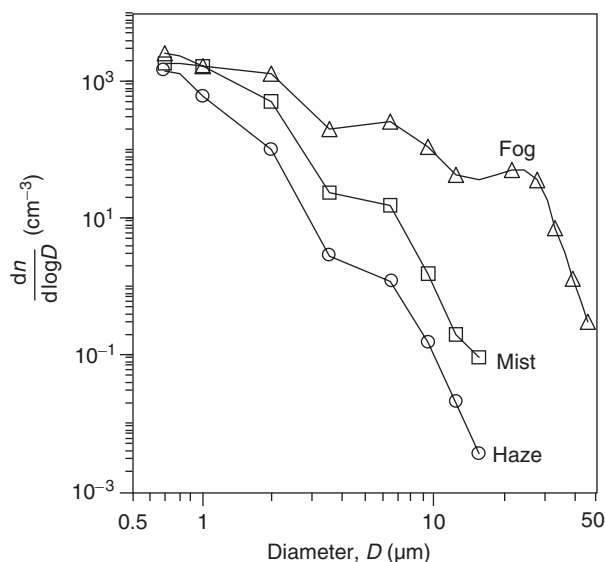


Figure 3 Average number size distributions of haze, mist and fog particles from experiments in the Po Valley, Italy.

very low mass mixing ratios of particulate matter in the atmosphere (mostly much less than parts per million), puts very high demands on chemical analyses. Consequently, global coverage and chemical completeness of aerosol analyses are far from satisfactory for most aerosol-related issues. As an example, only about 65% of the oceans are covered by the simplest non-size-resolved chemical analyses of the surface aerosol. For want of adequate global chemical aerosol data, the following section presents typical examples from larger aerosol experiments in polluted central Europe and from low-pollution marine regions.

With a size segregation into fine and coarse particles, chemical balances of gravimetric particulate mass have been constructed. For mass closure, estimates of particulate organic carbon (POM) and elemental carbon (EC) from thermal analyses and water as calculated with the measured ionic composition and sample relative humidity have been included. The sum of crustal dust is estimated from analyzed crustal components such as iron, aluminum, and silicon. Figure 4 summarizes the chemical mass balances over central Europe for summer and winter. Ammonium sulfate and carbonaceous components, both largely due to combustion sources, dominate fine particle composition. The higher mass fraction of elemental carbon in winter results from increased combustion of fossil fuels during the cold season. For ammonium nitrate, the partitioning between the gas phase and the particulate phase is strongly temperature-dependent. Additionally, the Kelvin effect (curvature-dependent vapor pressure) disfavors particulate nitrate in small

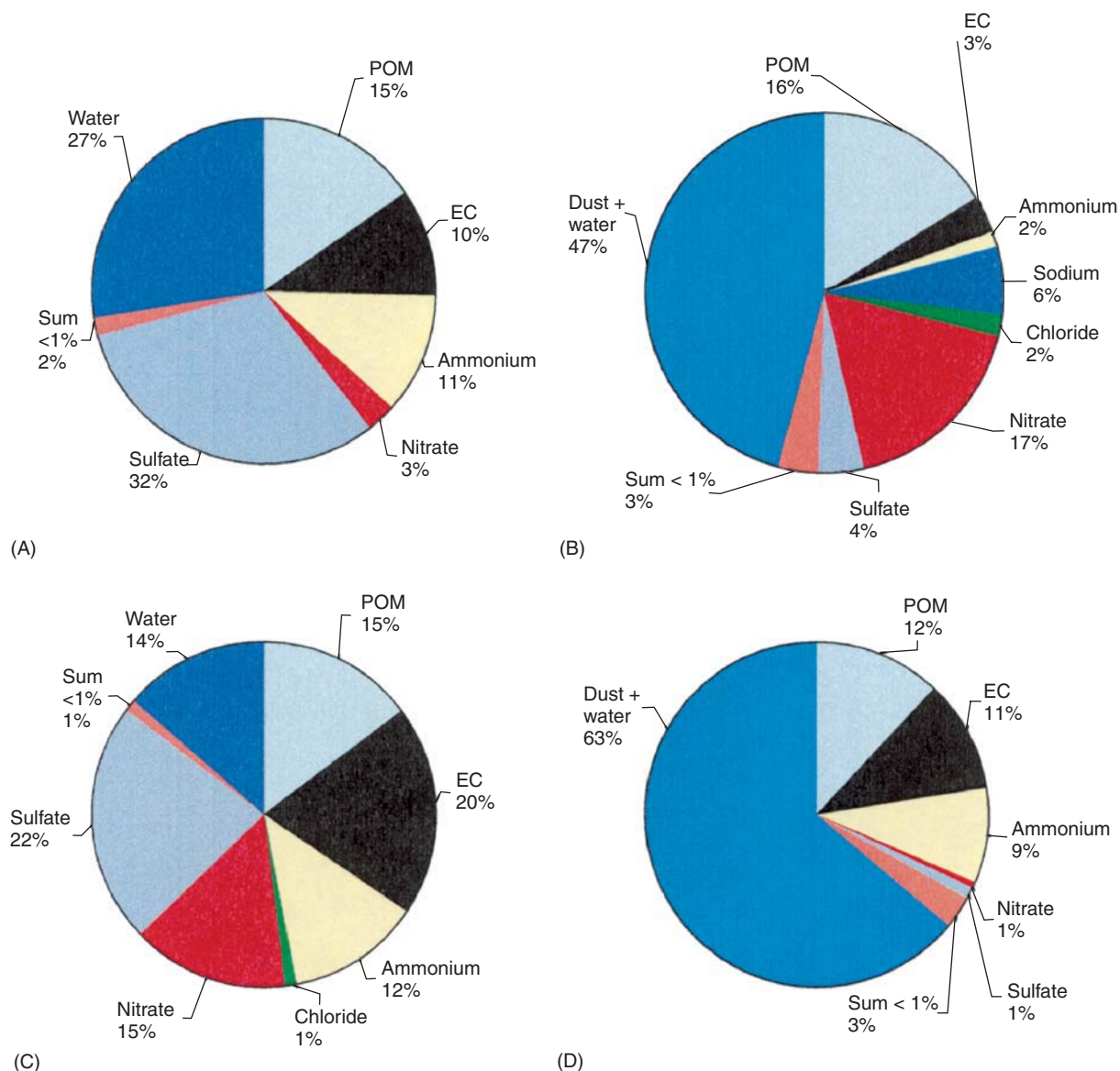


Figure 4 Mass fractions of major chemical components of fine and coarse particles over central Europe: (A) fine particles, summer; (B) coarse particles, summer; (C) fine particles, winter; (D) coarse particles, winter. Total mass concentrations in $\mu\text{g m}^{-3}$ are (A) 8.6, (B) 3.9, (C) 25, (D) 4.5. EC = elemental carbon; POM = particulate organic matter. Sum < 1% = sum of all analyzed components with individual mass concentrations less than 1%.

submicrometer particles. Consequently, most particulate nitrate is found in coarse particles in summer, whereas submicrometer particles show highest nitrate contents in winter.

The marine aerosol data shown in Figure 5 are aggregated from recent cruises in the North and South Atlantic and in the Indian Ocean (without direct influence from the Indian subcontinent), from which the first chemical mass closures of size-segregated aerosol were reported.

The significant contribution of continental dust to submicrometer particle composition and the even

stronger contribution to coarse particle composition is due to the ship passing through the Saharan plume over the Atlantic. Supermicrometer composition in Figure 5B is just meant to indicate that the two major possible contributors are sea salt and dust, with their actual proportion being controlled by local wind speed and the distance to the nearest continental crustal source. The relatively high mass fraction of elemental carbon is due to the African biomass burning plume reaching out over the tropical Atlantic. Note that nearly 90% of the particulate mass is in the coarse particle range.

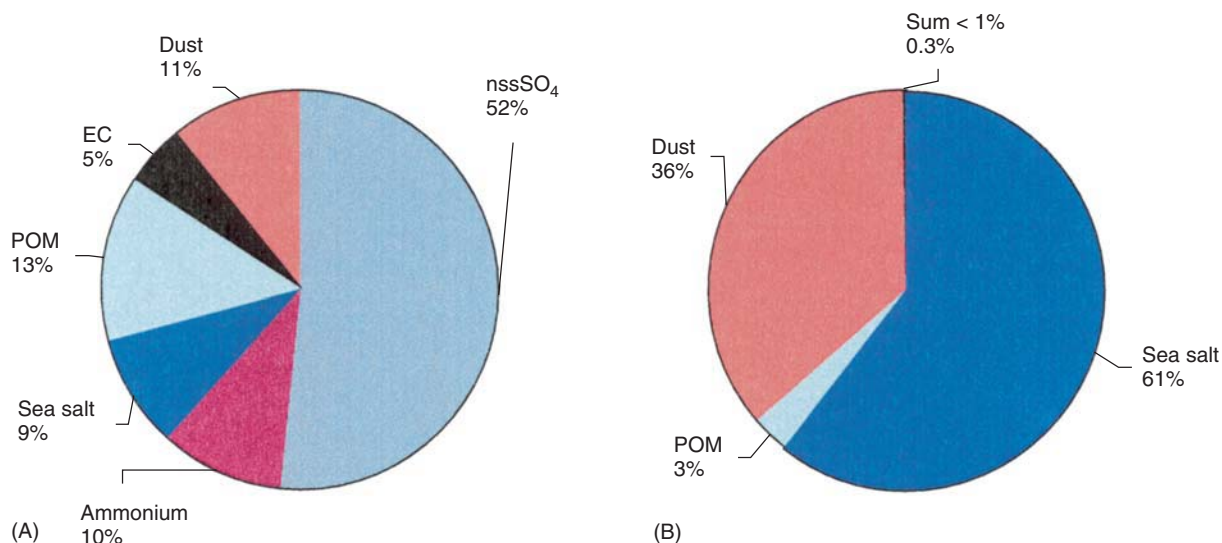


Figure 5 Mass fractions of major chemical components of fine and coarse particles over the oceans: (A) fine particles; (B) coarse particles. Total mass concentrations in $\mu\text{g m}^{-3}$ are (A) 1.7, (B) 14. EC = elemental carbon; POM = particulate organic matter. Sum < 1% = sum of all analyzed components with individual mass concentrations less than 1%.

State of Mixture

All aerosol characteristics and aerosol effects are controlled by the properties of the individual particles. A volume of air contains many particles in any given particle size interval, which can be expected to have individual properties because of the multitude of possible source and transformation processes. The available physical and chemical aerosol information, on the other hand, mostly concerns bulk properties of a rather large number of particles as required for the quantification in specific aerosol analytical instruments after sampling from the atmosphere.

The distribution of particle properties among a population of particles with a common sorting property such as their electrical mobility or mass is called the state of mixture. This state varies between the extreme possibility of an external mixture, in which essential particle properties such as their light absorption differ between particles of a given sorting property, and an internal mixture, in which all particles of a given size range have very similar properties. The traditional methods of quantifying the state of mixture are based on topochemical or electron-microscopic studies of individual deposited particles. With recent advancements of electrical and mass spectroscopy of airborne particles, new information on the state of mixture has been derived that is consistent with and extends microscopic data.

Owing to atmospheric transformation processes, we expect a general trend from a more externally mixed aerosol in source regions to a more internal mixture near the end of the atmospheric residence time

of the particles. The main reasons for this trend are Brownian coagulation, condensation from the gas phase, and in-cloud processes evening out interparticle differences with time.

This trend is most clearly seen in measurements of the hygroscopic particle properties, which can be made with high size resolution for individual particles in their airborne state. At any given submicrometer particle size these measurements frequently indicate the existence of at least two particle populations, one that is more and one that is less hygroscopic; that is, an external mixture of hygroscopic behavior. **Figure 6** shows the number fraction of submicrometer less hygroscopic particles as a function of distance from major anthropogenic source regions. This graph

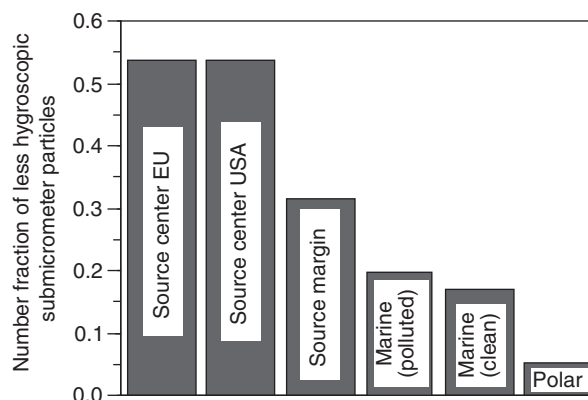


Figure 6 Number fraction of less hygroscopic submicrometer particles from aerosol source to sink regions.

illustrates the change in the state of mixture from aerosol source to sink regions. To date, no large-scale aerosol dynamics model takes this aerosol parameter into account.

See also

Aerosols: Climatology of Tropospheric Aerosols; Observations and Measurements; Role in Cloud Physics; Role in Radiative Transfer. **Arctic Haze. Biogeochemical Cycles:** Sulfur Cycle. **Cloud Microphysics. Satellite Remote Sensing:** Aerosol Measurements. **Stratospheric Chemistry and Composition:** HO_x; Halogen Sources, Anthropogenic; Halogen Sources, Natural; Halogens; Hydrogen Budget; Reactive Nitrogen (NO_x and NO_y). **Tropospheric Chemistry and Composition:** Aerosols/Particles.

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Role in Cloud Physics

S M Kreidenweis, Colorado State University, Fort Collins, CO, USA

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Introduction

Without aerosol particles, cloud formation in the atmosphere would not occur at the temperatures and relative humidities at which clouds are observed to exist. Pure water droplets can form from the vapor phase only at very high supersaturations – that is, at partial pressures well above the equilibrium vapor pressure for water at a given temperature. The presence of aerosols in the atmosphere provides nuclei onto which liquid water or ice can condense at much lower partial pressures, initiating droplet formation and eventually growing the nuclei to sizes recognized as cloud particles. At the same time, incorporation into cloud water and precipitation is the main mechanism by which small particles are removed from the atmosphere. Thus to some extent aerosol particles can affect their own atmospheric removal rates, by influencing the conditions for cloud formation and the properties of the clouds into which they become incorporated.

Atmospheric Particulate Matter

A broad range of chemical species is found in atmospheric particulate matter, reflecting the variety of sources that contribute particles of different sizes and properties. A basic distinction is drawn between ‘primary’ particles, those emitted directly from a source, and ‘secondary’ particles, particulate matter formed in the atmosphere via gas-to-particle conversion processes. Examples of the former are soot particles generated in combustion processes, wind-blown dust particles, and sea salt particles. An important example of gas-to-particle conversion (GTPC) is the oxidation of reduced sulfur gases, such as SO₂, to oxidized sulfur compounds (e.g., sulfuric acid), that have very low vapor pressure and remain in the particulate phase. In this case the primary emission is the sulfurous gas, and the formation of particulate matter can take place at large distances from the gas emission source. Further, the oxidation can occur either slowly in the gas phase, generally initiated by attack of the OH• radical, or rapidly in the aqueous phase (cloud or fog water) by the reaction of dissolved SO₂ with a dissolved oxidant such as ozone (O₃) or hydrogen peroxide (H₂O₂). Thus it can be quite difficult to unambiguously and quantitatively link