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"Atmospheric Particles and Nuclei: Aerosols"

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Aerosols

Atmospheric Particles and Nuclei

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2. The atmospheric aerosol

2.1 Introduction

2.1.1 Definition of the aerosol

An aerosol is defined as a dispersed system containing solid or liquid particles suspended in a gas. In the present case the gaseous medium is the air in which aerosol particles of different composition and size are suspended.

In more rigorous terms the principal characteristics of an aerosol or aerocolloidal system, are (HIDY and BROCK, 1970):

a) the sedimentation velocity of the particles is small;

b) inertial effects during particle motions can be neglected (the ratio of inertial forces to viscous forces is small);

c) the Brownian motion of the particles, due to the thermal agitation of gas molecules, is significant and

d) the surface of the particles is large compared to their volume.

The physical meaning of the above criteria will be defined in the following paragraphs. The principal force acting on an aerosol is generally gravitation. This means that the lifetime of a particle in the system is determined by its sedimentation velocity. If the particle radius is greater than the mean free path of gas molecules, the falling velocity v_s is given by the well-known Stokes equation:

$$v_s = \frac{2}{9}\frac{r^2 \varrho_p g}{\mu} \tag{2.1}$$

where r and ϱ_p are the radius and density of the particle, assumed spherical, μ is the dynamic gas viscosity (equal to 1.815×10^{-5} N s m^{-2} at a temperature of 20 °C) while g is the gravitational constant. In the atmosphere, v_s in Eq. (2.1) depends on altitude above the sea level. Furthermore, the updraft motions in the troposphere make the meaning of the sedimentation velocity rather complicated. If, for example, in the surface air a value of 10 cm s^{-1} is accepted as an upper limit, the radius of a spherical particle will be 30 μm if the density is taken to be unity. It must be emphasized, however, that due to the presence of updrafts, larger particles can also be found in the atmosphere at significant distances from their sources.

The ratio of inertial forces to viscous forces is *per definitionem* the Reynolds number (Re) of particles. In this way the second criterion after reduction can be written in the form:

$$\frac{\varrho v r}{\mu} = \mathrm{Re} < 1 \tag{2.2}$$

where ϱ is the air density, while v is the speed of the particle motion caused by some external force. Physically Eq. (2.2) means that in a stable system the product of the particle speed and particle size cannot exceed a given value. Thus, under normal atmospheric conditions the speed of motion of a particle of 10 µm radius could not exceed 30 cm s^{-1}. In the case of $r = 30$ µm the critical velocity is 10 cm s^{-1}. If the external force arises from the gravitational field, this condition is obviously equivalent to the first criterion.

A very characteristic property of aerosol particles is their Brownian motion. This random motion is a result of the fluctuations in the impact of gas molecules on the particles. It goes without saying that the speed of this motion increases with decreasing size. Generally, Brownian motion is considered significant if the particle radius is smaller than 0.5 µm.

Finally, the fourth criterion is satisfied if the particle surface (in cm^2) exceeds the particle volume (in cm^3) at least a thousand times. For this reason, surface phenomena play an important role in the behavior of aerocolloidal systems.

The foregoing conditions determine the upper limit of the particle size. The lower limit can be specified in a very simple way. A system is considered an aerosol when the radius of the particles is greater than that of gas molecules. At the same time $m_a \gg m_g$, where m_a and m_g are the mass of aerosol particles and gas molecules, respectively. Bearing in mind the size of molecules in the air we might define the lower limit to be around 10^{-7} cm ($= 10^{-3}$ µm).

An important consequence of the Brownian motion of aerosol particles is their collision and subsequent coalescence. This so-called coagulation process for a monodisperse aerosol can be characterized by the particle loss per unit time (Hidy and Brock, 1970):

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = 8\pi D r N^2 \tag{2.3}$$

where N is the number of particles per unit volume, t is the time and D is the diffusion coefficient of particles:

$$D = \frac{kT}{6\pi\mu r}\left(1 + \frac{A\lambda}{r}\right) \tag{2.4}$$

In Eq. (2.4) k is the Boltzmann constant (1.31×10^{-23} J/K × molecule), T is the absolute temperature, A is the Stokes-Cunningham correction[1], while λ is the mean free path of gas molecules[2]. Thus, the coagulation equation may be

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[1] $A \cong 1.257 + 0.400 \times \exp(-1.10\, r/\lambda)$

[2] $\lambda = 6.53 \times 10^{-6}$ cm, at a temperature of 20 °C and a pressure of 1013 hPa.

written in the following form:

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{4}{3}\frac{kT}{\mu}\left(1 + \frac{A\lambda}{r}\right)N^2 \tag{2.5}$$

It is concluded on the basis of Eq. (2.5) that the intensity of the particle loss due to thermal coagulation is directly proportional to the square of the particle concentration, while the coagulation efficiency increases with decreasing particle radius. This means that the coagulation of small particles at a high concentration is a very rapid process. Equation (2.5) is valid only for monodisperse aerosols, i.e. aerosols composed of particles of uniform size. However, the same qualitative conclusion can also be drawn in the case of polydisperse systems.

It should be emphasized that the dynamics of aerocolloidal systems is not to be discussed here. For further details the reader is referred to textbooks specialized in the field (e.g. Hidy and Brock, 1970; Twomey, 1977).

2.1.2 Characterization and measurement of atmospheric aerosol particles

As we have emphasized in the introduction of this book the atmospheric aerosol plays an important part in the control of many atmospheric processes: cloud formation, radiation transfer, etc. For the study of the role of atmospheric particles the measurement of their physical and chemical characteristics is of crucial importance.

An essential physical characteristic of the particles is their concentration. We can characterize the particle concentration in two different ways. Firstly, the number concentration can be employed which is the number of the particles in unit gas volume. Secondly, the particle mass in unit gas volume (mass concentration) or in unit mass of air (mixing ratio) can be given. Since, as we have seen previously, the size of the particles varies by several orders of magnitude, for particle characterization the determination of the size distribution is also necessary (see Subsection 2.3.2).

The effects of the particles in the air also depend on their composition. Thus the study of the chemical nature of individual particles or a particle ensemble is also of interest.

In this subsection the physical detection and collection of aerosol particles for further studies will be presented, while the main methods of chemical identification are discussed in a separate subsection (2.4.1).

From the point of view of particle characterization and measurements the aerosol classification of Junge (1963) is very convenient. Junge divided aerosol particles in three groups:

Aitken[1] particles: $r < 0.1$ µm;
large particles: $0.1 \leq r < 1.0$ µm;
giant particles: $r = 1.0$ µm.

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[1] The concentration of these particles is generally measured by means of expansion chambers, the first versions of which were constructed by Aitken.

2.2 Origin of atmospheric aerosol particles

2.2.1 Dispersal of particles of surface origin

Apart from a very minor contribution from meteorites and pollens, atmospheric particles arise from two basic processes[1]:

a) dispersal of materials from the Earth's surface;
b) chemical reaction and condensation of atmospheric gases and vapors.

The dispersal of surface materials produces particles in two major categories: sea salt, and soil or mineral particles.

Sea salt particles can be formed by direct dispersal of ocean water from the foam of the waves. However, these particles are generally too large to remain airborne, even after evaporation of water. A much greater number of particles is produced by the bursting of gas bubbles reaching the water surface. According to the laboratory work of Moore and Mason (1954) this process takes place in two stages. In the first stage, when the bubble arrives to the surface, small particles are ejected from the bursting water film. In the second stage, a thin jet is formed by the water flowing into the cavity remaining in the surface after the rupture. The particles formed in the second stage are less numerous and their sizes are in the giant range (Woodcock, 1953)

The sea salt particles produced in this way are composed mostly of sodium chloride, which reflects the composition of sea water. Among other substances, marine particulate matter also contains a large amount of sulfates. Furthermore, during their rise through the water, bubbles scavenge surface-active organic materials which are partly injected into the air when the bubbles burst.

Woodcock (1953) as well as Moore and Mason (1954) originally demonstrated that the rate of bubble formation increases with increasing wind speed. In a more recent work A. Mészáros and Vissy (1974) reported that over the oceans the correlation between the number of sea salt particles and the wind speed becomes gradually weaker as the particle size decreases. Thus, the smallest sea salt particles ($r < 0.3$ µm) may originate from a type of bubbles the formation of which is independent of the wind speed.

The relation between the bubble size and the number of airborne particles produced upon bursting was studied by Day (1963) during his laboratory investigation. He pointed out that the number of particles increases with increasing bubble size. A bubble with a size of several millimeters forms some hundreds of particles when it bursts. The results of simultaneous observations of size spectra of bubbles in foam patches and giant sea salt particles in the air over a surf zone in Texas show that both spectra follow the gamma distribution function (Podzimek, 1984). On the basis of his atmospheric observations made

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[1] Such processes as particle coagulation may also produce new large particles, but not new particulate matter.

in Hawaii, **Blanchard** (1969) assumed that the intensity of sea salt particle formation is between 25–100 cm^{-2} s^{-1} at the surface of the ocean. This range is in a good agreement with the laboratory results of Moore and Mason (1954).

Airborne sea salt particles are transported to higher levels and over the continents by atmospheric motions. Thus, such particles were observed over Australia (Twomey, 1955), North America (Byers *et al.*, 1957) and Europe (Mészáros, 1964). Due to removal processes near the surface level as well as to convective motions, the concentration of sea salt particles increases with increasing height in the lower troposphere over the continents in contrast to the situation over the ocean where their number decreases with increasing altitude (Woodcock, 1953; Lodge, 1955; Blanchard *et al.*, 1984). Because of the relationship between relative humidity and particle size (see Section 2.5), low relative humidity promotes the transport of sea salt particles.

The other category of particles originates from the solid surface of the Earth. This dispersal is obviously due to the effect of wind on rocks and soils. A well-known and highly visible example of this process is the formation of dust clouds and storms. However, the quantitative explanation of this particle production mechanism is not easy, except when some external mechanical force agitates the surface (vehicles, animals, people, etc.). The main reason for the difficulties in the explanation is the decrease of the wind speed with decreasing height above surface, usually extrapolating to zero wind speed at the surface. It is believed that turbulent flow is necessary (see Twomey, 1977) for the detachment of grains. According to the most acceptable estimates the global strength of this source is 100–500 Tg yr^{-1} (SMIC, 1971[1]; Prospero, 1984).

An important proportion of mineral particles produced by wind erosion is insoluble in water. Their composition can be characterized by determining the so-called aerosol–crust enrichment factor on the basis of the analyses of atmospheric aerosol samples and rocks or soils. The enrichment factor (EF) defined by Rahn (1976) is given by the following expression[2]

$$EF = \frac{(X/\mathrm{Ref})_{\mathrm{aerosol}}}{(X/\mathrm{Ref})_{\mathrm{crust}}} \tag{2.6}$$

where X is the concentration of the element considered in the aerosol or in the crust, while "Ref" is the concentration of a crustal reference element (generally Al, Ti or Fe). It follows from this definition that a certain element is considered of mineral origin if its enrichment factor is near unity. By using this approach and Ti as reference element A. Mészáros *et al.* (1984) demonstrated that, in agreement with the results of many other workers, under continental conditions Al and Si are the most important elements of soil origin, these elements almost certainly occur in silicate compounds.

Some particles of crustal origin are removed from the air in the vicinity of sources, while another fraction is transported to great distances. Thus, particulate matter collected over the Atlantic Ocean contains a significant quantity of Saharan dust under some conditions (Junge and Jaenicke, 1971); in fact, such dust particles were collected and identified even over the West Indies (Prospero, 1968; Blifford, 1970). Furthermore, dust particles from Asian desert were identified by several workers (see Braaten and Cahill, 1986) at the Mauna Loa Observatory in Hawaii. Elements of soil origin like Al and Fe were even found in relatively high concentrations at the South Pole, Antarctica (Zoller *et al.*, 1979). It was also shown (Andreae *et al.*, 1986) that, during their transport over the oceans, silicate species can be mixed with sea salt components.

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[1] SMIC: Study of Man's Impact on Climate.

[2] EF can also be defined to characterize particles of oceanic origin. In this case in the denominator the oceanic ratio should be used (the reference element is generally Na).

2.2.2 Formation of atmospheric aerosol particles by chemical reaction and condensation

Particles formed by the dispersal of surface materials generally have radii larger than about 0.1 μm. This means that Aitken particles must be produced by another mechanism, namely by condensation of vapors, preceded in many cases by gaseous chemical reactions. These reactions are generally initiated by photochemical processes.

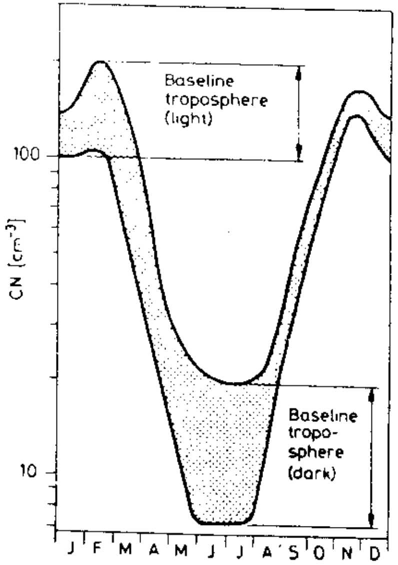

Fig. 2.2

Annual variation of the number concentration of aerosol particles (CN) over Antarctica according to Heitzenberg (1985). The dotted area represents the concentration fluctuation. (By courtesy of Kluwer Academic Press)

Thus, a large set of data obtained by McWilliams (1969) in clear air (W. Ireland) by means of expansion chambers showed that the concentration of Aitken particles is lower in the winter than in the summertime. Furthermore, McWilliams' observations also demonstrated that more aerosol particles can be detected during daylight than at night. This finding was confirmed by the investigations of Vohra *et al.* (1970) and A. Mészáros and Vissy (1974) according to which, in a clean maritime environment, the number of Aitken particles is at a maximum during the afternoon. It was also shown by atmospheric measurements (e.g. Lopez *et al.*, 1973) that after sunrise the aerosol concentration increases, which also points in the direction that particles with radii smaller than 0.1 μm are produced by photochemical reactions. Further, Hogan and Bernard (1978) have reported that over Antarctica there is a steady increase in concentration after astronomical sunrise. Moreover, in Antarctic winter very small concentrations can be measured. This finding was recently confirmed by numerous data published by Bigg *et al.* (1984), Heitzenberg (1985) and Bodhaine *et al.* (1986). The annual variation presented in Fig. 2.2 is taken from the work of Heitzenberg (1985).

The formation of aerosol particles from gaseous components can be investigated under laboratory conditions. In so-called aerosol chambers an artificial atmosphere is created to which small quantities of appropriate trace gases (e.g. SO_2, NO_2, H_2O, NH_3 and organics) are added. It is also possible to use ambient air purified of particulate matter. The chamber may be illuminated to initiate photochemical processes, and the behavior of particles formed is studied by the methods outlined in Subsection 2.1.2, e.g. by electrical mobility analyzers (Whitby *et al.*, 1972).

An important result from aerosol chamber studies was the discovery of Bricard *et al.* (1968) who found that intense aerosol particle production can be observed in the chamber in the dark if ambient filtered air is sampled from a sunlit atmosphere. It is assumed that in the atmosphere some gaseous substance is excited by sunlight and is not collected by the filter used to obtain air that is free of aerosol particles. In the chamber these photochemically excited molecules initiate secondary thermal reactions leading to the formation of some supersaturated vapor (e.g. H_2SO_4) which subsequently condenses.

It was also demonstrated by aerosol chamber investigations that the behavior of particles formed by condensation varies as a function of time. Figure 2.3 reproduces schematically the change in particle number *(N)*, particle surface *(A)* and particle volume *(V)* according to Friedlander (1978). The curves are based on irradiation chamber experiments by Husar and Whitby (1973) and three separate domains are identified. In domain I the formation of new particles is the dominant process. In this stage the number, surface and volume of particles steadily increase. With increase in particle number (domain II), coagulation becomes more and more important (see Subsection 2.1.2). When the *N* curve has a maximum the coagulation loss just balances the particle formation rate. In domain III coagulation and condensation of the vapor on existing particles are the dominant processes. The number concentration decreases in this time interval, while particle volume further increases. The value of the surface area remains approximately constant.

In the atmosphere, a good example of the above particle formation is the production of sulfate and nitrate particles from gaseous precursors. In continental air sulfate and nitrate particles come into being from sulfur dioxide and nitrogen oxides emitted into the atmosphere mostly by different pollution sources (e.g. combustion of fossil fuels). The oxidation of SO_2 and NO_x is due to the presence of hydroxyl radicals (OH) formed by photochemical processes followed by thermal chemical reactions (Logan *et al.*, 1981). The oxidation of the gases mentioned is controlled by the following reaction steps (Calvert *et al.*, 1985):

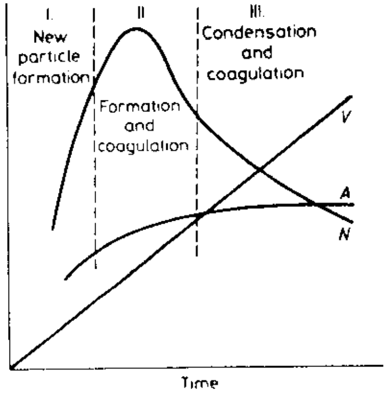

Fig. 2.3

Aerosol formation in an irradiated chamber (Friedlander, 1978). *N*: particle number; *V*: volume of particles; *A*: total particle surface. (By courtesy of Pergamon Press)

$$OH + SO_2\ (+M) \rightarrow HSO_3\ (+M)$$

$$OH + NO_2\ (+M) \rightarrow HNO_3\ (+M)$$

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The end products of these gas-phase reactions are sulfuric and nitric acid vapor. Sulfuric acid vapor condenses in the air by bimolecular condensation (H_2O molecules also take part in the phase transition), while an important part of HNO_3 remains in vapor phase owing to its high saturation pressure (Mirabel and Jaecker-Voirol, 1988). In the case of HNO_3, condensation is promoted by existing aerosol particles which serve as nuclei for the phase transition (for further details see e.g. KIANG *et al.*, 1973 and COX, 1974). The acidic solution droplets formed in this way are neutralized by biogenic NH_3 if this gas is available in the atmosphere.

Concerning the sources and nature of precursor gases under clean tropospheric conditions it was first believed that hydrogen sulfide is the only biogenic sulfur gas of any significance. However, results of more recent research indicate that H_2S is oxidized very rapidly in the ocean water (ANDREAE, 1986), and consequently cannot be released into the air. Many papers suggest (NGUYEN *et al.*, 1983; BIGG *et al.*, 1984; ANDREAE, 1986; ANDREAE and ANDREAE, 1988) that dimethyl sulfide (DMS) of oceanic origin plays an important role in sulfate particle formation. The studies mentioned show that DMS emission is due to microbiological processes in the ocean. A recent work of FALL *et al.*, (1988) demonstrate that the major gas emitted from different terrestrial plants is also DMS. According to the estimate of ANDREAE and ANDREAE (1988) the oceanic emission of DMS is 1 Tmol yr^{-1}, while the magnitude of the biogenic continental emission is 0.1 Tmol yr^{-1}.

In the atmosphere a certain part of DMS molecules is converted to SO_2 and consequently to sulfate particles. Another part of DMS produces first methanesulfonic acid and numerous other compounds. The reactions are initiated by OH and NO_3 radicals (GROSJEAN and LEWIS, 1982; TOON *et al.*, 1987). Methanesulfonic acid was detected in aerosol samples collected in clean maritime atmosphere (SALTZMAN *et al.*, 1983, AYERS *et al.*, 1986) and also in samples from Antarctic ice (SAIGNE and LEGRAND, 1987).

On the other hand, LEGRAND and DELMAS (1986) assumed on the basis of the results of their Antarctic snow analyses that lightning at tropical and/or mid latitudes is the most probable source of Antarctic nitrate. In other words this means that the combination of atmospheric O_2 and N_2 at high temperatures produced by lightning strokes constitutes the main global source of nitrogen-containing precursor gases.

It is further assumed that the sulfate aerosol layer in the stratosphere (see later) is due to sulfur-bearing gases like carbon disulfide and carbonyl sulfide (TURCO, 1982) mostly of biogenic origin. However, during volcanic eruptions a large amount of SO_2 is injected into the stratosphere (BERRESHEIM and JAESCHKE, 1983) which is converted into aerosol (KEESER and CASTLEMAN, 1982).

There is a considerable body of evidence suggesting that small organic particles are also formed by gas-to-particle conversion (DUCE, 1978). Under unpolluted conditions this particle formation is due to the release of natural hydrocarbons from vegetation. In agreement with the original idea of WENT (1966), LOPEZ *et al.*, (1984) assumed that different pinenes, emitted by pine forests, play an important part in the process. Further, natural forest, brush and grass fires also provide an important atmospheric aerosol particle source (see CADLE, 1973). In urban and industrial environments the cooling of vapors with low saturation pressure, released during combustion, produces a large quantity of aerosol particles composed mainly of carbonaceous materials. These processes are essential in particular since on the surface of elemental carbon (soot) particles formed by condensation, adsorbed SO_2 molecules can be converted to sulfuric acid as discussed by NOVAKOV (1984).

A special case of the production of particulate matter by gas-to-particle conversion is provided by the irreversible transformation of trace gases in cloud and fog droplets. A good example of this process is the formation of sulfate from gaseous sulfur dioxide absorbed by cloud/fog elements. It is well documented (PENKETT *et al.*, 1979b) that the oxidation of SO_2 to form sulfate ions proceeds through the action of oxidizing agents like ozone and hydrogen peroxide formed by chemical reactions in the atmosphere (see LOGAN *et al.*, 1981). Laboratory experiments (summarized by BEILKE, 1985) show that at low pH values of cloud water (pH < 5.5), occurring under atmospheric conditions, the oxidation of SO_2 by H_2O_2 is much more effective than the transformation due to ozone molecules. O_2 may also be important in oxidation processes if catalyzed by active sites on soot or by transition metals (JACOB and HOFFMANN, 1983), at least under more polluted conditions. If NH_3 is also absorbed, the sulfuric acid present is transformed into ammonium sulfate. When the cloud/fog partially or totally evaporates[1], ammonium sulfate becomes airborne as demonstrated by the atmospheric observations of HEGG *et al.* (1980).

The formation rate of small Aitken particles in the troposphere was estimated by LOPEZ *et al.* (1974) on the basis of their aircraft measurements carried out over Southwest France. They argued that in an air column with a base area of 1 cm^2, 3×10^4 particles are formed each second. A quarter of this quantity is due to human activity. In a more recent paper, BIGG and TURVEY (1978) assume that the natural particle production rate is only 170 cm^{-2} s^{-1}, by two orders of magnitude smaller than the above estimate. BIGG and TURVEY establish this rate by using the results of their observations, carried out over Australia, together with an acceptable residence time of 3×10^5 s. It follows from this figure that the total Australian source strength is about 10^{19} s^{-1}. This may be compared with the total particle flux of 4×10^{19} s^{-1} produced by only one industrial area (Perth) which exceeds the global natural emission of the continent! The present author feels that the natural production rate proposed by LOPEZ *et al.* (1974) is too high, while BIGG and TURVEY's value is too low, at least for the European continent. Thus, according to SELEZNEVA (1966), who made a large number of aircraft measurements over the European part of Soviet Union, the particle number is 6×10^8 cm^{-2} in a tropospheric air column. Using a residence time of 3×10^5 s, an acceptable production rate of 2×10^3 cm^{-2} s^{-1} is calculated.

2.2.3 Other sources

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2.3 Concentration and size distribution of atmospheric aerosol particles

2.3.1 Concentration and vertical distribution of Aitken particles

In this subsection we will discuss the number concentration of all particles, which is partically equivalent to the number of Aitken particles (see Subsection 2.1.2). All values discussed in the following were obtained using expansion chambers.

The early results of particle concentration measurements carried out under different conditions were compiled by Landsberg (see Junge, 1963). Some of his data are reproduced in Table 2.2. The figures tabulated make it evident that the majority of particles are of continental origin. It is also obvious that man's activity plays an important role in particle production. Furthermore, one can see from Table 2.2 that the number concentration of atmospheric aerosol particles decreases with increasing height.

Table 2.2

Average concentration of Aitken particles under various conditions according to Landsberg (see Junge, 1963). (By courtesy of Academic Press)

Location	Number of observations	Average concentration cm^{-3}
Cities	2500	147 000
Towns	4700	34 300
Country	3500	9 500
Sea shore	7700	9 500
Mountains		
500–1000 m	870	6 000
1000–2000 m	1000	2 130
above 2000 m	190	950
Islands	480	9 200
Oceans	600	940

Observations carried out during the last decades demonstrated that in remote oceanic and continental areas smaller concentrations can be measured than those listed in the table. Thus, according to Junge and Jaenicke (1971), over the northern Atlantic Ocean the concentration is 600 cm^{-3} on an average. Hogan *et al.* (1973) suggest that lowest concentrations in the surface air over the North Atlantic can be measured between 20°–25° N and 30°–50° W. Over this area the mean value is only about 300 cm^{-3}. In clean oceanic air of the Southern Hemisphere a lower average concentration (~ 400 cm^{-3}) can be detected (A. Mészáros and Vissy, 1974) than the value reported by Junge and Jaenicke (1971). Moreover, according to information published by Japanese workers (Ohta and Ito, 1974), concentrations are generally between 150–200 cm^{-3} over the Pacific Ocean. The long-term mean of Aitken particle concentration at American Samoa (also in the Pacific ocean) is 274 cm^{-3} (Bodhaine and DeLuisi, 1985) which is in a good agreement with the average value (300 cm^{-3}) measured in extremely clean air at Cape Grim (Tasmania, Australia) (Heitzenberg, 1984). The results obtained by Hogan and Bernard (1978) over Antarctica demonstrate that the concentration is less than 50 cm^{-3} in wintertime. This finding was recently confirmed by Bodhaine *et al.* (1986) who report monthly average values of about 10 cm^{-3} in Antarctic winter. Further, Gras and Adriaansen (1985) found in Antarctic air during wintertime weekly median concentrations of a few tens of particles per cm^3. According to several authors (Hogan and Bernard, 1978; Ito, 1985; Bodhaine *et al.*, 1986) during Antarctic summer the number of aerosol particles is around 200 cm^{-3}, while others (Gras and Adriaansen, 1985) publish somewhat higher concentrations (300–400 cm^{-3}).

It follows from the data presented that in remote air of the Southern Hemisphere the concentration of Aitken particles is rather homogeneous. Except in austral winter over Antarctica, the particle number is around 200–300 cm^{-3}. However, in the Northern Hemisphere the situation is much more complicated owing to anthropogenic pollution sources. Even under Arctic conditions during late winter and early spring a haze layer (called Arctic haze, discovered by chemical measurements, see 2.4.2) of anthropogenic origin can be observed. Within this layer the Aitken particle concentration is typically 800–1000 cm^{-3}, while in clean air without pollution effects it varies between 50 and 100 cm^{-3} (Schnell, 1984). In summer the concentrations measured in Arctic regions (Jaenicke and Schütz, 1982) are rather similar to those observed in Antarctic areas.

It is questionable whether the higher values reported for the Northern Atlantic Ocean are also caused by anthropogenic pollutant emissions. Unfortunately, it is very difficult to answer this important question, since we have no suitable homogeneous data sets to estimate possible secular concentration trends. However, some information is available concerning variations in the electrical mobility of the air over different oceans. These data show (Cobb and Wells, 1970) that electrical mobility of the surface air over the northern part of the Atlantic Ocean decreased by a factor of 2 during the first 70 years of this century. In contrast this electrical parameter remained constant over the southern regions of the Pacific Ocean. Taking into account the relation between electrical mobility and aerosol particle concentration this finding suggests that the particle number concentration doubled during this century in remote areas of the Northern Hemisphere.

The vertical profile of aerosol particle concentration in the troposphere was widely studied by Soviet research workers. A great number of data obtained by aircraft flights is reviewed by Selezneva (1966). Her compilation indicates that on the average the concentration drops to one-fourth of its ground level value at an altitude of 900 m on an average, and that above 3000–4000 m the particle number becomes constant. SELEZNEVA assumes that this vertical distribution is mostly controlled by atmospheric exchange and particle coagulation (flights were made generally under weather situations without precipitation). In Fig. 2.4 the average results at 3000 m altitude are plotted. One can see that concentrations increase with increasing continental source density. It can also be seen that the concentrations measured at this altitude agree well with those reported for remote oceanic surface air (see above). This means that, except the first few kilometers above the continents, the troposphere is filled with aerosol particles at the same concentration. Disregarding sea salt particles of small number concentration, the composition of this aerosol, termed the tropospheric background aerosol (JUNGE, 1963), is also independent of place and time (see Section 2.4).

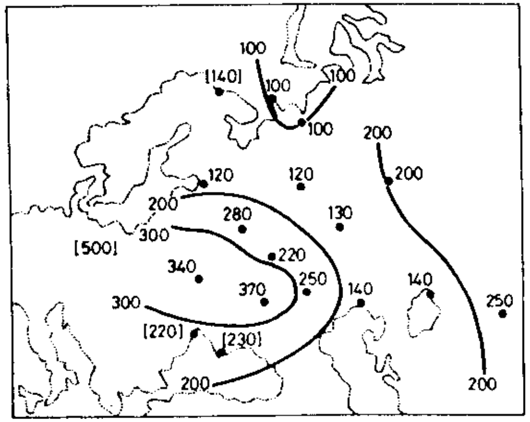

Fig. 2.4

Spatial distribution of the concentration of the Aitken particles at 3000 m over the European part of the USSR (SELEZNEVA, 1966). (By courtesy of *Tellus*)

The concentration of aerosol particles in the stratosphere was firstly measured by JUNGE (1963) by balloon flights over the central part of the USA. He found (see Fig. 2.5) that the number of aerosol particles, in agreement with the Soviet data discussed above, does not change with altitude in the upper troposphere. This constant concentration is around 300 cm^{-3}. Above the tropopause the concentration rapidly decreases with increasing height. Since the character of the vertical profile plotted in Fig. 2.5 was confirmed by several workers (e.g. KÄSELAU *et al.*, 1974; PODZIMEK *et al.*, 1977), it can be considered acceptable for use in further studies. On the basis of the stratospheric concentration distribution, it is believed that particles in this atmospheric domain may be of tropospheric origin. However, it is also possible that stratospheric Aitken

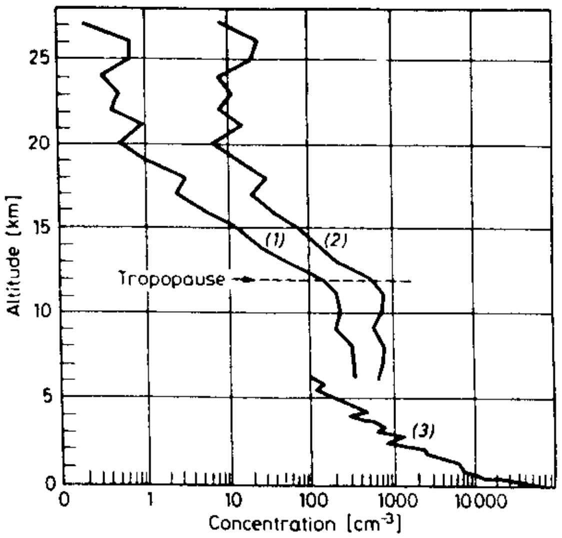

Fig. 2.5

Vertical profile of Aitken particles in the upper troposphere and stratosphere (1) under ambient conditions; (2) at standard temperature and pressure; both according to JUNGE, (1963); and (3) in the lower troposphere according to WEICKMANN (1957). (By courtesy of Academic Press)

particles, formed *in situ* by gaseous reactions, coagulate to create the stratospheric aerosol layer consisting of large particles.

The vertical profile of the concentration of Aitken particles in the lower troposphere over Antarctica was recently studied by HOGAN (1986) and ITO *et al.* (1986). HOGAN's observations indicate an aerosol decrease of 25 particles $\text{cm}^{-3}\ \text{km}^{-1}$. In contrast to this finding the vertical profile in Arctic haze was found to be more complicated as a function of the haze structure (SCHNELL, 1984).

2.3.2 The size distribution

Since the size of atmospheric particles covers several orders of magnitude (see Subsection 2.1.1) the concentration alone is not sufficient to characterize atmospheric particles. For more complete aerosol characterization the size distribution function must be used, which is defined as follows (FUCHS, 1964):

$$\frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}r} = \mathrm{f}(r) \qquad (2.7)$$

where N is the total number concentration while $\mathrm{d}N$ is the same parameter for particles with radii between r and $r + \mathrm{d}r$. It follows from Eq. (2.7) that

$$\int_0^\infty \mathrm{f}(r)\,\mathrm{d}r = 1 \tag{2.8}$$

It is obvious that a similar size distribution function can be given for the surface, volume and mass of aerosol particles. Thus, e.g. the volume concentration (aerosol volume per unit volume of air) is distributed according to particle radius in the following way:

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}r} = \mathrm{F}(r) \tag{2.9}$$

with the condition

$$\int_0^\infty \mathrm{F}(r)\,\mathrm{d}r = 1 \tag{2.10}$$

Of course, the number size distribution may be converted to volume size distribution, given an assumed particle shape. Furthermore, by using a constant particle density the size distribution of particle mass can be calculated from Eq. (2.9) by a simple calculation.

It is customary, in the interconversion of these distribution functions, to assume that the particles are spherical; this simplifies the mathematics, but is somewhat questionable physically. The method of measurement determines the nature of the reported radii of these hypothetical spheres; e.g. in the case of microscopic sizing, the so-called "surface radius" is obtained, which is the radius of a circle having the same surface area as the orthogonal projection of the particle.

On the basis of his atmospheric impactor measurements JUNGE (1963) proposed a power law to describe the size distribution of large and giant particles:

$$\frac{\mathrm{d}N}{\mathrm{d}r} = C_1 r^{-(\beta+1)} \tag{2.11}$$

where C_1 and β are constants. Considering the broad range of particle size, Eq. (2.11) is best rewritten in the following form:

$$\frac{\mathrm{d}N}{\mathrm{d}\log r} = C_2 r^{-\beta} \tag{2.12}$$

In this formula C_2 is a function of concentration, while β gives the slope of the distribution curve. According to JUNGE (1963), β is about 3 under continental conditions.

More recently, WHITBY (1978) has analyzed the results of much more numerous size distribution observations carried out mainly by his group, using a combination of expansion chamber, electrical mobility and optical counter techniques. This analysis clearly shows that the complete size distribution is composed of three separate log–normal distributions as demonstrated in Fig. 2.6. WHITBY assumes that the first distribution, the nuclei mode, is controlled by the condensation of vapor (predominantly H_2SO_4) formed by chemical reactions. Thus, the concentration of these small particles was found to be very significant in the irradiated, polluted atmosphere. On the other hand, the so-called accumulation mode is due to the coagulation of primary particles or to the vapor condensation on secondary particles formed by coagulation or on existing aerosol particles. It follows from this idea that the accumulation mode is a consequence of aging of the primary aerosol. In the air far from gaseous sources the nucleation mode may well be partly or totally missing. The third log–normal distribution consists of particles formed mostly by mechanical disintegration of the material of the Earth's surface. This is the coarse particle

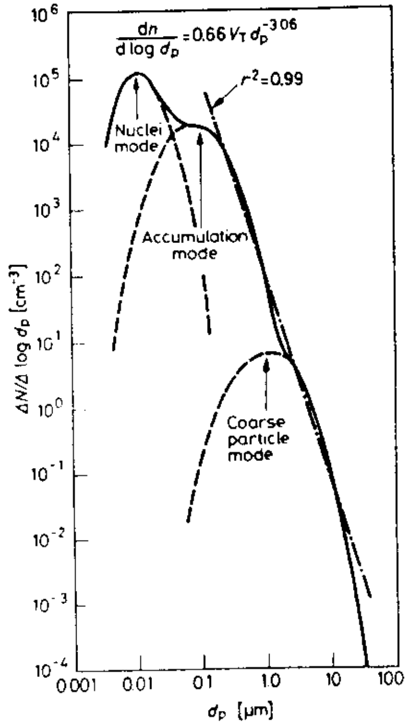

Fig. 2.6

Number size distribution of aerosol particles under urban conditions according to WHITBY (1978). N number of particles; d_p: diameter of particles; V_t: total volume concentration; r: correlation coefficient between power law given in the figure and experimental data. (By courtesy of Pergamon Press)

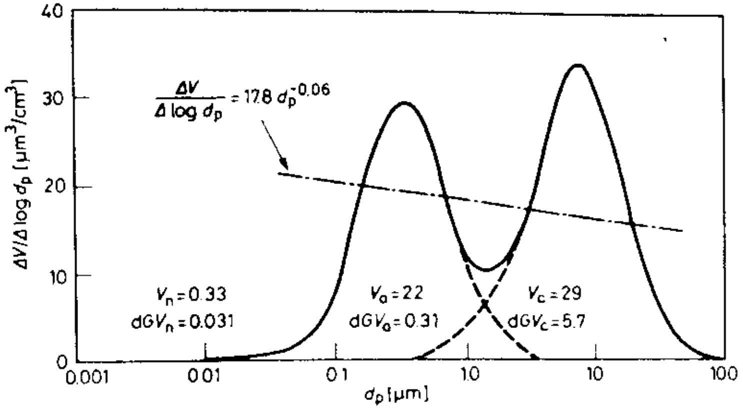

Fig. 2.7

Size distribution of the volume of aerosol particles (solid line) according to WHITBY (1978). Dotted line corresponds to the power law of Fig. 2.6. V: particle volune, n: nuclei mode; a: accumulation mode; c: coarse particle mode; d_pGV: geometric volume mean size. (By courtesy of Pergamon Press)

mode, which is independent of the first two distributions. For this reason the chemical composition of the coarse particles is different from the composition of the smaller particles (see later), called "fine" particles.

To gain further insight into the character of particle size distribution, the volume distribution calculated from the curve of Fig. 2.6 is also presented in Fig. 2.7. It can be seen that on a volume basis the nuclei mode, which determines the particle number, cannot be identified owing to the small size of the primary particles. One can also see that a large fraction of the aerosol mass is found in the range of coarse particles. However, the mass of particles in the accumulation mode is also significant. In our case the particle volume in the two modes is nearly the same. Generally speaking, 2/3 of the total mass is in the coarse and 1/3 in the accumulation mode. Finally, Figs 2.6 and 2.7 show that, while the number size distribution of large and giant particles can be well approximated by the power law, JUNGE's formula is very poor for characterizing the volume distribution. In other words this means that minor deviations from the power law in the number distribution cause significant deviations in the volume distribution.

It should be mentioned that the size distributions presented in Figs 2.6 and 2.7 are typical of a polluted atmosphere. To gain further insight into the tropospheric aerosol structure let us consider Fig. 2.8. These average size distributions were measured by A. MÉSZÁROS under various conditions by using the membrane filter technique. Particles were counted and sized in the radius range of 0.03–64 μm by optical and electron microscopy. In the figure the total concentration of these particles is also shown. Curve 1 was observed near Budapest, Hungary in a locally polluted atmosphere (A. MÉSZÁROS, 1977), while spectrum 2 refers to rural air also in Hungary. Curve 3 represents the size distribution of atmospheric aerosol particles obtained over the oceans of the Southern Hemisphere (the curve does not contain the distribution of sea salt particles dicussed later). Finally, curve 4 is the size distribution of large and giant particles observed at an altitude of 3 km above inversion layers over Central Europe (A. MÉSZÁROS, 1969). It can be seen by comparing these size distributions that the aerosol structure varies considerably as a function of the pollution of the place considered. The difference between curve 1 and 3 is particularly great in the range of smaller particles. The coarse mode is also evident in distributions 1 and 2. The concentration of coarse (or giant) particles is 0.40 and 0.12 cm^{-3}, respectively. Unfortunately, when distribution 4 was measured, only optical microscopic evaluation was made. However, comparison of curves 3 and 4 shows that the distribution of large and giant particles at an altitude of 3 km over continents practically coincides with the spectrum

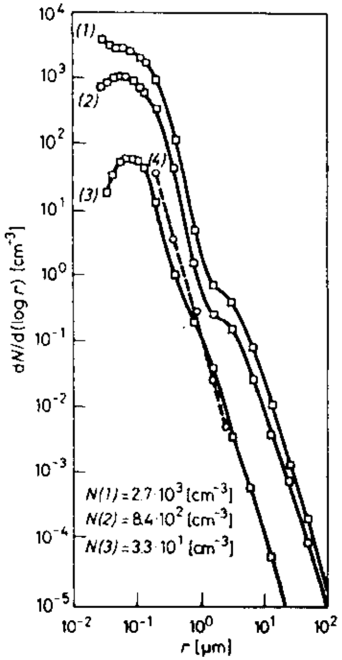

Fig. 2.8

Size distribution of atmospheric aerosol particles under various conditions. (1): urban; (2): continental; (3): tropospheric background; (4): continental at 3000 m above inversions; N: total number of particles with radius larger than 0.03 μm. (Data of A. MÉSZÁROS) of aerosol particles measured in remote oceanic areas without the sea salt component. This fact also supports the concept of a tropospheric background aerosol.

It can also be seen that the maximum of distribution 3, referring to background conditions, occurs around 0.1 μm radius, a value in the range of the accumulation mode. It should be mentioned that the form of this spectrum agrees fairly well with the distributions found by other workers over the North Atlantic (JUNGE and JAENICKE, 1971; TYMEN *et al.*, 1975) and over other remote areas (BIGG, 1980) like Alaska, Hawaii, Tasmania and Antarctica. However, the maximum of the distribution over the Northern Hemisphere is shifted to smaller sizes probably as a result of indirect anthropogenic effects.

On this point, JUNGE and JAENICKE (1971) identified, by the diffusion channel technique, another maximum in the aerosol particle spectrum below 0.01 μm, which proves the presence of primary particles formed by reaction and subsequent condensation (nuclei mode). This finding is supported by data of HAAF and JAENICKE (1980) gained on sunny days during a North Atlantic expedition. Such measurements were not performed by A. MÉSZÁROS and VISSY (1974). However, comparison between the concentration of particles with radii larger than 0.03 μm and the total particle concentration ($\cong 400\ \mathrm{cm}^{-3}$) makes evident the presence of the nuclei mode even over the Southern Hemisphere. This assumption is confirmed by recent observations carried out by ITO (1985) in clean air over Antarctica. He found that while in the polar night months the size distribution of submicrometer particles is monomodal (with a maximum at a radius of 0.03 μm), in the sunlit months the aerosol spectrum is bimodal, having another mode at around 0.005 μm. Again, in Arctic areas the situation is more complicated. In winter the size distribution depends upon the type of air masses, as shown by the aerosol observations of SHAW (1985), made in central Alaska. According to this work, the size distribution during winter months is similar to curve 3 in Fig. 2.8 when the sampling is made in Pacific marine air masses. However, in Arctic air (Arctic haze) the mean size is about 5 times larger and the mass concentration is by an order of magnitude greater than during intrusions of warm Pacific air. Arctic haze is composed of an aged polluted continental aerosol coming from Eurasia, as the analysis of meteorological conditions indicates (RAATZ, 1985).

2.4.2 Chemical composition of tropospheric aerosols

The chemical composition of aerosol particles in the troposphere results from the interaction of many formation and dynamic (e.g. coagulation) processes. For this reason particles are often composed of several materials and the composition varies as a function of time and location. The nature of particulate matter is complicated in particular under locally polluted urban conditions. However, it is not intended here to discuss the chemical composition of aerosol particles in polluted atmosphere[1]. Our aim is to present the chemical composition of the so-called background aerosol influencing the cloud formation as well as solar and terrestrial radiation transfer in the atmosphere on a larger scale. Thus, we will deal with aerosol compositions referring to regional (rural), continental and global scales. As we will see the major part of tropospheric background aerosol consists of water-soluble substances. For this reason we begin the present section with the discussion of the water-soluble part of atmospheric particulate matter important for cloud droplet formation as we will see in the next chapter.

The investigation of the composition of water-soluble particles started with the classical measurements of JUNGE (1963), who collected particles with a

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[1] The interested reader is referred to the review of CORN (1976) and to the book of FINLAYSON-PITTS and PITTS (1986)

two-stage cascade impactor, the two stages corresponded to the large and giant size range, respectively. Samples were washed off the collecting surface with a small quantity of distilled water, and the ions dissolved were analyzed by microchemical methods (bulk analysis). Measurements were carried out in continental air (Frankfurt, FRG) as well as under maritime conditions in eastern USA, Florida and Hawaii. The results indicate that in the large size range water-soluble species consist of ammonium and sulfate and their mass ratio practically coincides with the stoichiometric ratio of SO_4^{2-} to NH_4^+ in ammonium sulfate. In the size range of giant particles over maritime areas chloride and sodium predominate. The major part of nitrate ions is found in the giant size range because of the interaction of gaseous NO_x and sea salt particles[1]. The concentration of chloride ions increases, while the sulfate level decreases in the direction of more maritime environments. However, in the giant range relatively high sulfate concentrations can be detected even under oceanic conditions owing to the sulfate fraction of sea salt.

Table 2.3

Size distribution of the mass of various ions in percentage of the total mass of the ion considered (E. Mészáros, 1968). (By courtesy of *Tellus*)

Size range	NH_4^+	SO_4^{2-}	Cl
Giant	8	12	33
Large	45	45	49
Aitken	47	43	18

The measurement technique of Junge was extended to Aitken particles in the sixties by several workers. In these studies cascade impactors were backed up by suitable filters to capture unimpacted small particles. Table 2.3 shows the results obtained in this way by E. Mészáros (1968) under moderately polluted continental conditions. In the table the values are expressed in percentage of the total mass. It can be seen from these data that approximately half of the *mass* of sulfate and ammonium ions may be found in the Aitken size range, which means that on a *number basis* the great majority of sulfate particles have radii less than about 0.1 μm. This is hardly surprising, considering the formation mechanism of secondary aerosol particles. It is to be noted that the mass median diameter of sulfate particles identified agrees well with the geometric mean of the accumulation mode, as discussed by Whitby (1978; see also Fig. 2.7). In contrast to sulfate- and ammonium-containing aerosol particles, only 20% of chloride ions are detected in the Aitken size range and in this case the fraction found on giant particles is also significant, in agreement with Junge's results discussed above. Mészáros' measurements also showed that the relative quantity of water-soluble substances increases with decreasing particle size, which also suggests that the amount of particulate matter formed by mechanical disintegration is less significant in the range of smaller particles.

An important step in the understanding of the formation and composition of tropospheric background aerosol was provided by the work of Fenn *et al.* (1963) who demonstrated that in aerosol samples collected in Greenland, 40%

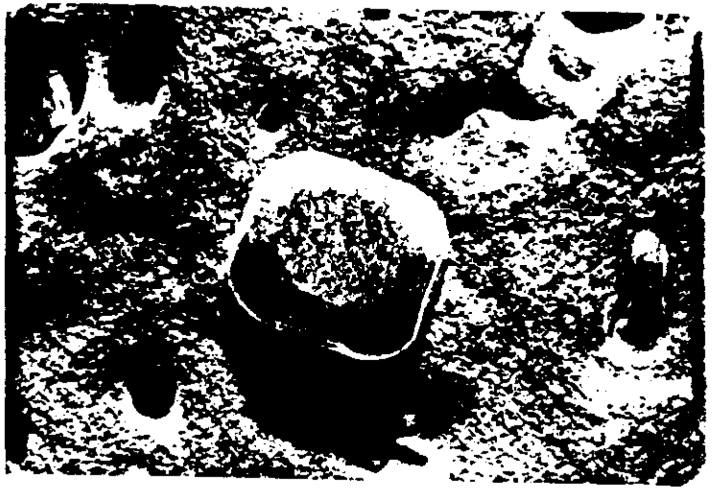

Fig. 2.12a

Fig 2.12b

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[1] During this process sodium nitrate is formed with the liberation of gaseous hydrochloric acid.

Fig. 2.12c

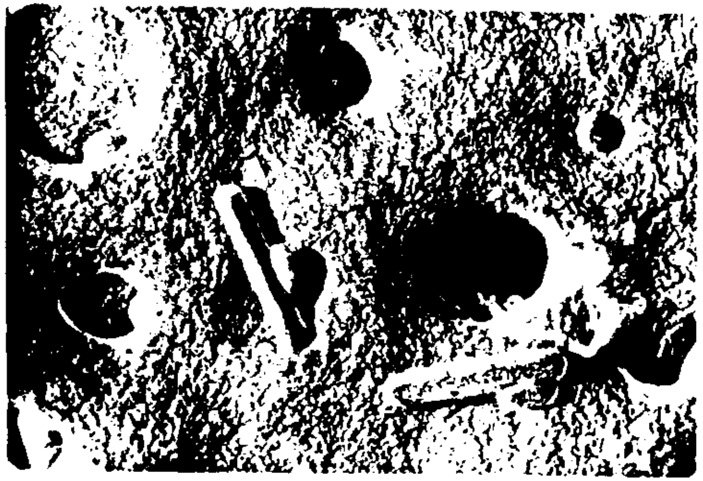

Fig. 2.12d

Electron micrographs of aerosol particles collected on membrane filters under remote maritime conditions (photo: A. MÉSZÁROS). *(a)* sea salt; *(b)* ammonium sulfate; *(c)* sulfuric acid. *(d)* mixed. The size of the field in the pictures is 2.4 × 3.6 μm. (By courtesy of Pergamon Press)

of the large particles consisted of sulfate. This finding was confirmed by American authors (CADLE *et al.*, 1968) who showed by means of special microscopic techniques (e.g. morphological identification) that in Antarctic air the large particles are formed from sulfates.

The composition of background aerosol particles, including a part of the Aitken range, was investigated by morphological identification by A. MÉSZÁROS and VISSY (1974) on the basis of membrane filter samples collected in remote oceanic air in the Southern Hemisphere. They found that 75–95% of the particles was composed of the following four substances (Fig. 2.12):

a) sea salt,
b) ammonium sulfate,
c) sulfuric acid,
d) mixture of sea salt and $(NH_4)_2SO_4$.

Table 2.4

Chemical composition of atmospheric aerosol particles expressed in percentage of the number of particles with radius larger than 0.03 μm (A. MÉSZÁROS and VISSY, 1974). (By courtesy of Pergamon Press)

	Atlantic $0 \leqq \varphi \leqq 20$	Atlantic $40 \leqq \varphi \leqq 60$	Atlantic $\varphi > 60$	Indian Ocean
$(NH_4)_2SO_4$	69	38	33	18
NaCl	1.6	15	7.3	28
H_2SO_4	–	–	7.6	3.2
Mixed	4.9	42	36	31

Note: Collections were made in remote oceanic areas. φ is the geographical latitude in the Southern Hemisphere.

In Table 2.4 the relative quantities of these substances, expressed in percentage of the number concentration of particles with $r \geq 0.03$ μm, are tabulated as a function of geographical position. It can be seen that the fraction that consists of these water-soluble substances is the smallest in the vicinity of the Equator (75%), owing to the fact that in these areas the number of insoluble particles with radii greater than 0.5 μm was relatively significant.

Figure 2.13 represents the average size distribution of sulfate and sea-salt particles observed by A. MÉSZÁROS and VISSY (1974) over different parts of the South Atlantic. One can see that on a number basis (solid lines), sulfate particles with much smaller mean radii predominate, while the major proportion of the particle volume (dotted lines) is occupied by the sea salt fraction in the coarse size range. On the basis of the data plotted, only 4% of the total volume of the particulate matter is composed of sulfates (the total volume is 6.2 μm^3 cm^{-3}). This means that the mass concentration of aerosol particles in remote oceanic areas is also controlled by sea salt.

The quantity of sea salt particles, identified as NaCl, was found to be particularly important over the Indian Ocean. This is explained by stormy weather

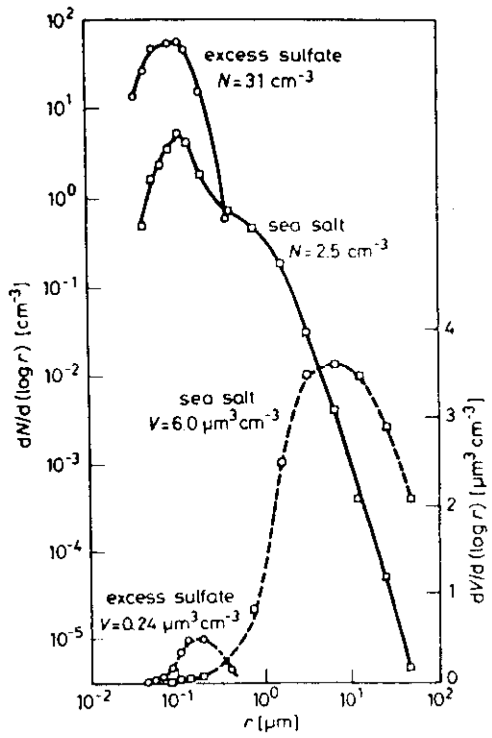

Fig. 2.13

Size distribution of the number *(N)* and volume *(V)* of excess (non sea salt) sulfate and sea salt particles with $r \geq 0.03$ µm. (Data of A. Mészáros)

conditions during the sampling period. Curve 1 in Fig. 2.14 gives the size distribution of sea salt particles measured over the Indian Ocean (the total number concentration, *N*, is also plotted). To represent the advection of sea salt particles over the continents, two other spectra are also shown. Curve 2 was measured by Metnieks (1958) in Ireland, while distribution 3 was observed in the surface air in Hungary (E. Mészáros, 1964). These latter investigators used gelatin layers sensitized with silver nitrate to identify chloride particles. Figure 2.14 makes it clear that the sea salt concentration is very small in a continental environment. Furthermore, the maximum of the distribution is shifted in the direction of larger particles. However, even over the ocean very few sea salt particles have a radius smaller than 0.1 µm (3.2 cm^{-3} in this case) as compared to the total concentration of Aitken particles (Subsection 2.3.1). Finally, over the Indian Ocean practically all giant particles consisted of sea salt.

It follows from Table 2.4 that the great majority of aerosol particles consist either of ammonium sulfate or of a mixture of ammonium sulfate and sea salt. Thus, if we disregard sea salt particles we can conclude that the particulate matter in tropospheric background air consists mainly of sulfur-containing species. This finding was confirmed by Butor (1976) and more recently by Parungo *et al.* (1986) who made samplings over the North Atlantic and Pacific Ocean, respectively, and identified particles by electron microscopy. Moreover, the investigation of A. Mészáros and Vissy also shows that 70% of the number of ammonium sulfate particles are in the range of $0.03 \leq r \leq 0.1$ µm, in agreement with the results of continental observations (see Table 2.4) and with the direct chemical bulk analyses of Winkler (1975) indicating that the main component of the aerosol in the Aitken size range is sulfur under oceanic background conditions.

The composition of aerosol particles in the remote atmosphere was studied

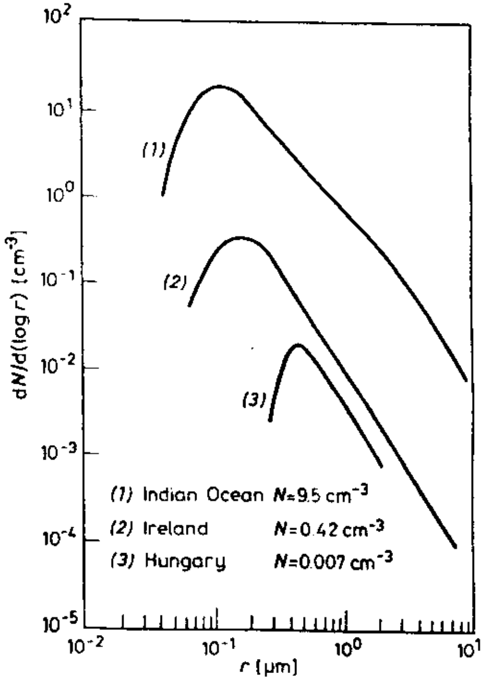

Fig. 2.14

Size distribution and concentration *(N)* of sea salt particles from different geographical regions. *(1)*: according to A. Mészáros and Vissy (1974) (by courtesy of Pergamon Press); *(2)*: according to Metnieks (1958) (by courtesy of School of Cosmic Physics); *(3)*: according to E. Mészáros (1964) (by courtesy of *J. Recherches Atmosphériques*) in detail by **Bigg** (1980) who applied electron microscopy combined with a special single-particle analysis. He collected aerosol particles by electrostatic precipitators and impactors in Alaska, Hawaii, Tasmania and Antarctica. **Bigg** found that, in agreement with previous discussions, smaller particles were composed mainly of sulfuric acid (Alaska and Hawaii) or ammonium sulfate (Tasmania and Antarctica). In the size range of larger particles in Alaska, a lot of mixed particles were identified which consisted of insoluble cores coated by sulfuric acid. On the other hand, in Tasmania particles larger than 0.1 μm were of oceanic origin. At the sampling site in Tasmania (Cape Grim) a mass size distribution similar to the volume spectrum presented in Fig. 2.13 was measured. In remote Everest highlands at altitudes between 5400 and 6500 m **Ono** *et al.* (1983) also found that in the submicrometer size range atmospheric particles consisted of sulfate particles. By using a selective single-particle method, **Ono** and his associates also showed that sulfate particles were in the form of hydrated sulfuric acid solution and/or in the form of supersaturated acidic droplets. In agreement with **Bigg** (1980) and in disagreement with Japanese workers, **Gras** (1983) reports that at the South Pole particulate sulfate is nearly fully neutralized by ammonium. He attributed this neutralization to the mid- and upper-tropospheric transport of gases and aerosol particles. Finally, we note that in the surface air over Antarctica the sulfate level is around 0.1 μg m^{-3} (**Bigg**, 1980). In contrast, in the Arctic region during late winter or spring relatively high sulfate concentrations can be observed (~ 2.0 μg m^{-3}). It is expected that this phenomenon is due to transport from pollution sources in Eurasia (**Rahn**, 1981).

Beside ammonium sulfate and sea salt, nitrate ions constitute another important class of water-soluble materials as originally shown by **Junge** (1963). Unfortunately, the identification of these ions is rather difficult due to the fact that alkaline sites on many filters[1] collect gaseous nitric acid and cause it to be reported as particulate nitrate (**Spicer** and **Schumacher**, 1977). Moreover, it is reasonable to expect that nitric acid vapor reacts with atmospheric NH_3 to form an aerosol of ammonium nitrate. The equilibrium of NH_4NO_3 with NH_3 and HNO_3 (**Stelson** *et al.*, 1979) varies as a function of temperature, which further complicates the interpretation of nitrate measurements. Bearing in mind these problems we note that, within the marine boundary layer[2] over the Pacific, the particulate nitrate level was found to be rather low: 0.1 μg m^{-3} or less (**Huebert** and **Lazrus**, 1978; **Parungo** *et al.*, 1986). Also at Ny-Ålesund, Spitzbergen, very low nitrate concentrations were measured (**Heitzenberg**, 1981).

The above discussion on water-soluble components can be summarized by the results of **Yoshizumi** and **Asakuno** (1986) gained recently in Chichi of the Ogasawara Islands situated in the Pacific Ocean about 1000 km from the main

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[1] Teflon filters minimize sampling artefacts.

[2] Above the boundary layer even lower concentrations were observed (**Huebert** and **Lazrus**, 1978).

island of Japan. During sampling in Chichi particles were separated into several size intervals by a cascade impactor. Species were analyzed by neutron activation and wet chemistry. Sodium nitrate and ammonium nitrate were separated by a method based on the difference in their thermal stability. Table 2.5 gives the concentrations measured in the coarse and fine particle size ranges. It can be seen that sea salt, constituting the majority of the total mass, is in the coarse particle size range. Nitrate ions and soil components[1] are also in the coarse mode. The Cl loss related to Na concentration (3.1%) is comparable to the quantity of $NaNO_3$ on the mole basis. Fine particles consist mostly of sulfate ions. The concentration of ammonium makes it possible that about 75% of sulfate is neutralized by NH_4^+. **Yoshizumi** and **Asakuno** note that the unknown fraction in the fine particle range is probably composed of some organics and elemental carbon not evaluated in their program. In the following we will discuss these two types of carbonaceous particles.

Table 2.5

Characterization of atmospheric aerosols in Chichi of the Ogasawara Islands (**Yoshizumi** and **Asakuno**, 1986). (By courtesy of Pergamon Press)

Component	Concentration (μg m^{-3}) Coarse particle (2 μm <)	 Fine particle (2 μm ≥)
Sea salt*	10.52	0.83
Soil	2.60	0.62
$NaNO_3$	0.69	0.07
NH_4NO_3	0.05	0.08
Secondary SO_4^{2-}	0.04	1.90
NH_4^+ †	0.01	0.54
Total	13.9	4.0
Mass con measured	16.5	7.4
Unknown	2.6	3.4

* Sea salt does not include Na of $NaNO_3$.

† NH_4^+ does not include NH_4^+ of NH_4NO_3.

The organic fraction of atmospheric particulate matter was investigated by **Ketseridis** *et al.* (1976) at several locations, including remote oceanic areas. These authors collected particles on glass fiber filters and determined the total mass of suspended particles by weighing the filters before and after the sampling. They extracted ether-soluble materials from the samples and were able to identify chemically organic acids and phenols, organic bases, aliphatic hydrocarbons, aromatic hydrocarbons and neutral compounds. The results obtained are summarized in Fig. 2.15. The data labelled "Meteor" refer to samplings

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[1] Determined on the basis of Al concentration (see later).

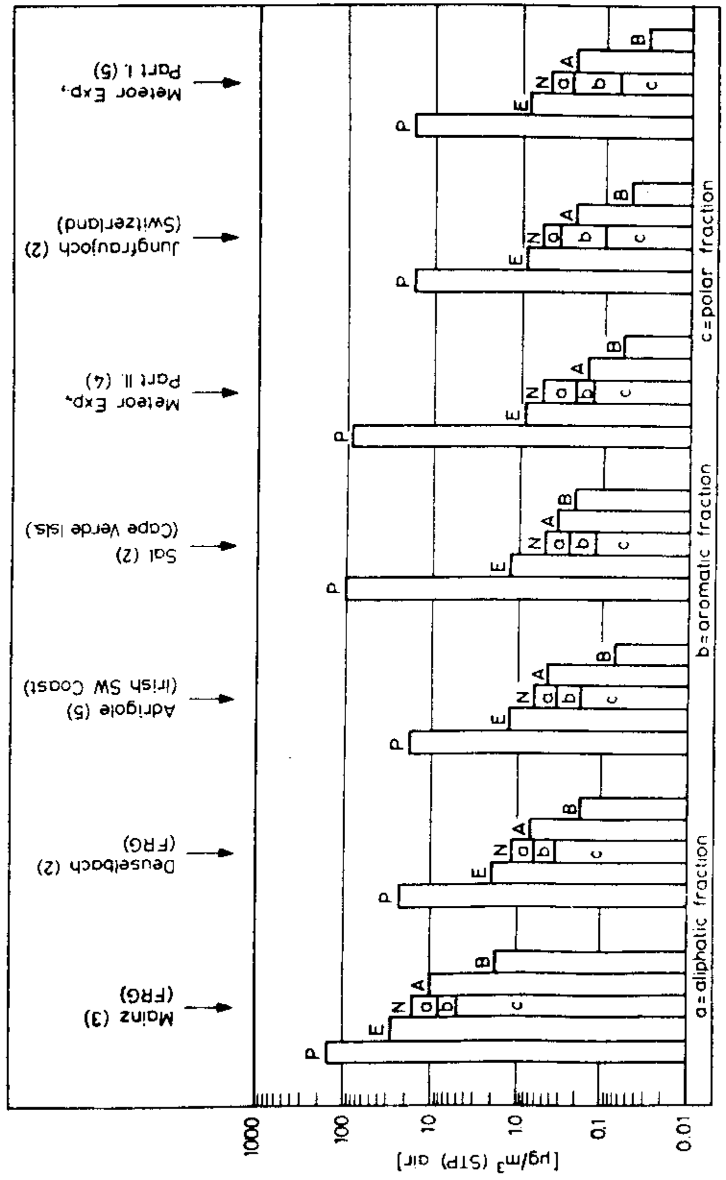

Fig. 2.15

Mass concentration of all aerosol particles (*P*) and of organic particles at different sampling sites according to KETSERIDIS *et al.* (1976). *E*: ether extractable organic material; *N*: neutral organic compounds; *A*: organic acids; *B*: organic bases. (By courtesy of Pergamon Press)

Note: The majority of the mass of all particles under marine conditions is sea salt (see Fig. 2.13). The numbers behind the names of the sampling locations give the number of samples analyzed.

carried out on board of the German research vessel Meteor in 1973 over the North Atlantic. It is to be noted that during Part II of this expedition and during sampling in Cape Verde an advection of Sahara dust was observed. One can see that, except more polluted atmospheres, the concentration of organic material extractable in ether is practically constant at about 1 μg m^{-3} at standard temperature and pressure. The fraction of different components is also independent of the sampling location. At Jungfraujoch and over the Atlantic Ocean (without dust advection) about 5–10% of the aerosol particle mass is composed of organics. KETSERIDIS *et al.* (1976) assumed that this constant concentration of organic particulate matter in tropospheric background is either due to particle advection from highly populated areas or to a constant production mechanism in clean tropospheric air. In another study, KETSERIDIS and EICHMANN (1978) used an impactor to separate particles with radii smaller and larger than 1 μm. They report on the basis of their measurements carried out in Ireland, that the majority of organics are in the smaller size range where these materials comprise 25% of the aerosol mass. It is very probable that organic particles of these sizes are formed by gas-to-particle conversion.

In recent years several analyses have been made to identify organic compounds in the atmospheric aerosol (FINLAYSON–PITTS and PITTS, 1986; SIMONEIT, 1984). These studies show that higher molecular weight solvent-soluble compounds (>C_{12}, lipids) are common species in urban, rural and oceanic aerosols. It is demonstrated that petroleum residues predominate in urban and suburban areas, while waxes from vegetation are the main components under rural and oceanic conditions. Polycyclic aromatic hydrocarbons were also identified in urban and remote atmosphere.

The presence of elemental carbon in the particulate matter has also been demonstrated. It is expected that under polluted conditions elemental carbon particles are mostly emitted by diesel vehicles. In winter these particles are transported to long distances and they constitute an important component of the Arctic haze (ROSEN *et al.*, 1981). Moreover, significant amounts (0.01–0.1 μg m^{-3}) of soot carbon were observed in remote air over the tropical Atlantic and Pacific Oceans (ANDREAE *et al.*, 1984). On the basis of the concentrations of other species in the particulate matter, ANDREAE and his associates estimate that elemental carbon detected over tropical oceans is released into the air by biomass burning in the tropics and subsequently transported over oceanic areas. A. MÉSZÁROS (1984) showed by electron microscopy that elemental carbon can be internally mixed with sulfate, while COVERT and HEITZENBERG (1984) observed a high degree of external mixing between the two species.

According to recent studies of CACHIER *et al.* (1986) the average concentration of giant carbonaceous aerosol particles in remote oceanic air over the Northern and Southern Hemisphere is the same and equal to 0.07 μg m^{-3} expressed in carbon equivalents. On the other hand, the mean concentration for particles with radii smaller than 0.5 μm is rather different over the two hemispheres: it is 0.45 and 0.06 μg m^{-3} for the Northern and Southern Hemisphere, respectively. Carbon isotope measurements of CACHIER *et al.* indicate that carbonaceous

Table 2.6

Elemental composition of atmospheric aerosol particles under different environmental conditions expressed in $\mathrm{ng\ m^{-3}}$

Element	Europe			Asia		Africa		N. America		S. America	Arctic		Antarctica		Pacific O.
–	K-puszta[1] Hungary	Valen[2] Sweden	Jungfraujoch[3] Switzerland	Delhi[4] India	Great Wall[5] near Beijing, China	Gezira[6] Sudan N	S	St. Louis[7] USA	Twin Gorges[8] N. W. Canada	Chacaltaya[9] Bolivia	N. Greenland[10] Summer	Ny-Ålesund[11] Spitzbergen Winter	Summer[12]	Winter[12]	Enewetak Atoll[13] tropical N. Pac.
Si	1350	–	–	–	21	–	–	2260	–	200	43	110	–	–	–
Al	663	–	51	3413	–	3030	293	–	66	62	–	–	0.82	0.4	21
Ca	470	65	–	2600	–	–	–	170	–	~28	9.1	73	0.6	1.6	220
Na	–	–	22	848	–	480	197	–	18	~10	–	130	4.2	26	5200
Fe	285	72	36	2753	7.9	2996	940	960	71	58	6.4	64	0.7	0.3	15
Ti	21	4.5	2.4	–	–	–	–	–	5.0	5.2	0.9	< 5	0.1	0.2	–
S	2270	650	–	–	315	767	1052	4400	–	34	27	690	78	48	–
Cl	18	130	7.2	1978	6.5	970	260	197	9.0	1.4	10	96	4.3	38	8300
Br	3.5	2.1	1.3	–	0.6	14	7.8	177	0.5	0.1	0.2	130	0.9	0.3	0.02
Pb	35	14	4.4	52	5.6	–	–	742	–	1.1	–	–	–	–	–
Cu	8.7	1.8	0.9	39	0.4	49	< 9	–	0.9	0.5	–	< 2	0.004	0.006	0.04
V	3.1	2.1	0.3	–	0.5	9.1	2.6	–	0.2	0.3	0.1	0.2	0.002	0.001	0.08

[1] A. Mészáros *et al.* (1984); [2] Lannefors *et al.* (1977); [3] elevation: 3752 m; Dams and de Jonge (1976); [4] Khemani *et al.* (1985); [5] only fine particles; Winchester *et al.* (1981); [6] Penkett *et al.* (1979a); N: north wind, S: south wind; [7] only inhalable particles ($d < 15\ \mu m$); Spengler and Thurston (1983), [8] Rahn (1976); [9] elevation: 5245 m; Adams *et al.* (1983); [10] Flyger and Heidam (1978); [1] Heitzenberg (1981); [12] Zoller *et al.* (1979); [13] Duce *et al.* (1983)

materials in the giant size range are associated with sea salt, while fine carbonaceous particles are of continental origin.

As mentioned in Subsection 2.4.1, recent research on the composition of aerosol particles has been promoted by the application of non-destructive nuclear analytical methods (PIXE, neutron activation). These procedures have made possible to study simultaneously several elements in particulate matter. As an example, Table 2.6 contains mean concentrations of twelve elements according to the measurements carried out under different atmospheric conditions. Except some data (e.g. concentrations measured in Delhi) the values tabulated were obtained by the nuclear methods mentioned. For the sake of completeness some results for a locally pulluted place (St. Louis, USA) are also given. In this respect we note that according to Khemani *et al.* (1985) the samples collected in Delhi are free from the effects of local pollution sources. Thus, it is proposed that results gained at K-puszta (Hungary) and Valen (Sweden) are representatives of regional background air in Europe, while Chinese and Indian data in the table refer probably to similar conditions in Asia. Further, we believe that Jungfraujoch (Switzerland), Gezira (Sudan), Twin Gorges (Canada) and Chacaltaya (Bolivia) are suitable sites to study the continental background aerosol over Europe, Africa, North America and South America, respectively. Finally, concentrations measured at other stations, except those for Ny-Ålesund and Enewetak Atoll, give information about global tropospheric background air. As we discussed above, data observed in Arctic regions during late winter are related to Arctic haze, while values gained at the station in the Pacific Ocean represent remote oceanic conditions.

If we do not consider the concentrations measured over the Pacific Ocean (which are controlled by sea salt components) one can say that data can be divided into two groups. The first six elements (from Si to Ti) are of soil origin, which is proved by their crustal enrichment factors defined in Subsection 2.2.1. On the other hand, sulfur, chlorine, bromine, copper, lead and vanadium are typically so-called enriched elements, the concentration of which are controlled by different natural and anthropogenic emissions. (Lead and vanadium are notorius man-made elements due to exhaust materials from vehicles and to combustions processes, respectively.) In agreement with the discussion in Section 2.2, elements in the first category are in the coarse particle range, while enriched species can be detected generally in the fine size range (see the references given in the table).

As it can be seen from values tabulated, enriched elements have high concentrations under polluted conditions, while the concentration of elements of soil origin is significant particularly in the air influenced by dust particles coming from deserts (Delhi, Gezira in the case of north winds)[1]. It is interesting to note that the atmospheric level of crustal elements is rather high even at elevated altitudes (Jungfraujoch, Chacaltaya). For Gezira, Arctic and Antarctica the

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[1] It is noted that in Delhi the total mass concentration of aerosol particles is about 100 and 200 $\mu g\ m^{-3}$ for monsoon and dry season, respectively (Khemani *et al.*, 1985), while it is only 3.1 $\mu g\ m^{-3}$ at the Jungfraujoch (Dams and De Jonge, 1976).

concentrations are separated into two classes. In the case of Gezira, data are separated according to the wind direction. This is explained by the fact that at this site an aerosol originating from deserts can be observed if the wind blows from north, while south winds transport to the site aerosol particles of tropical origin. Further, Antarctic concentrations are grouped according to the seasons of the year. This classification clearly shows that sulfate-sulfur, the majority of particulate matter, has a high concentration in summer, in agreement with our discussion about Aitken particles in Subsection 2.3.1. On the other hand, winter Antarctic data indicate that in winter sea salt is an important component of the atmospheric aerosol in this remote area. Finally, the comparison of summer and winter data obtained over Arctic regions makes evident the presence of the Arctic haze during late winter. Data indicate that the ratio of winter to summer concentrations is especially high in the case of sulfur.