Chapter 4

Tropospheric Aerosols

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4.1 Introduction

Between 1970 and 1990 the major advances in atmospheric chemistry were made in gas-phase photochemistry, except perhaps for a brief intermezzo of "nuclear winter" studies. This focus is now shifting, as it is recognised that natural and anthropogenic aerosols play a substantial role in the radiative properties of the atmosphere and Earth's climate. In addition, studies on the causes of the Antarctic ozone hole have demonstrated the large role of reactions that take place on ice and particulate surfaces. If such reactions occur in the stratosphere, they must take place also in the troposphere, with its abundance of various types of aerosol. Considering these factors, and especially because of various breakthroughs in experimental techniques, it is likely that aerosol research will be prominent in atmospheric chemistry in the coming decades. This research will involve process studies both in the atmosphere and in laboratories, studies on the sources and sinks of aerosols, chemical analyses of the particulate matter (PM), modelling, and especially regional (campaigns) and global (satellites) observations on the distribution of the atmospheric aerosol. This is all the more important because climate models, which in most cases currently consider only sulphur chemistry, cannot be tested sufficiently for want of data, despite the potentially great climate effects of aerosols. Aerosol particles may already be significantly counteracting the radiative forcing by the greenhouse gases (Ramaswamy et al. 2001).

One of the most important advances in aerosol research in the past decade has been the realisation that it will not be possible to understand (and even less so to be able to predict) the chemical state of the atmosphere without taking into account its multi-component and multi-phase nature. Figure 4.1 shows in a generic way that atmospheric aerosol particles exhibit a wide range of sizes, from nanometers to micrometers, and a range of shapes, and that chemical composition usually differs among the size ranges and even among individual particles within a given size range. These properties distinguish aerosols from trace gases, for which knowledge of the mass concentration or mixing ratio is sufficient to characterise their abundance and to permit specification of their properties, reactions, and effects. Particle size is central to the description of the radiative effects of aerosols and to their influences on clouds. Likewise, composition affects the hygroscopic growth of aerosol particles, again affecting their radiative influences and ability to form cloud droplets. For these reasons the ability to characterise particle size and size-dependent composition and to represent these properties in large-scale chemical transport models is essential.

As aerosol particles are strongly coupled with gas-phase chemistry and clouds, an understanding of their properties and effects, and of the atmosphere in general, requires that gases, aerosol particles, and clouds be treated as a single system. The scales to be considered in this system range from molecules and nanometer-sized aerosol particles to frontal cloud systems spanning hundreds of kilometres.

An example for the gas-particle-cloud coupling is that aerosol particles and cloud droplets can influence gas-phase chemistry by acting as sinks of reactive species and by decreasing or increasing actinic flux. Clouds also serve as reaction media that can release reactive species to the gas-phase. As such, aerosol particles and cloud droplets affect the so-called oxidising capacity of the atmosphere, which determines the chemical lifetimes of atmospheric trace substances including condensed phases (see Chap. 3).

An example highlighting the range of scales that must be considered is that clouds cover roughly half of the Earth's surface; yet any individual cloud is composed of billions of individual droplets or crystals, each of which started its life as an aerosol particle. Thus, understanding and predicting the characteristics and behaviour of clouds on a global scale will not be possible without an understanding of the microscale processes that create and control clouds.

Aerosol particles have a multitude of sources. They derive from primary sources, involving direct emissions of particles, and from secondary processes, i.e. reactions of gaseous precursors in the atmosphere to form particles. Some of the natural processes leading to particle production and the anthropogenic processes leading to

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In *Atmospheric Chemistry in a Changing World - An Integration and Synthesis of a Decade of Tropospheric Chemistry Research*, G. Brasseur, R. G. Prinn, and A. A. P. Pszenny, Eds., pp. 125-156, Springer, Berlin, 2003.

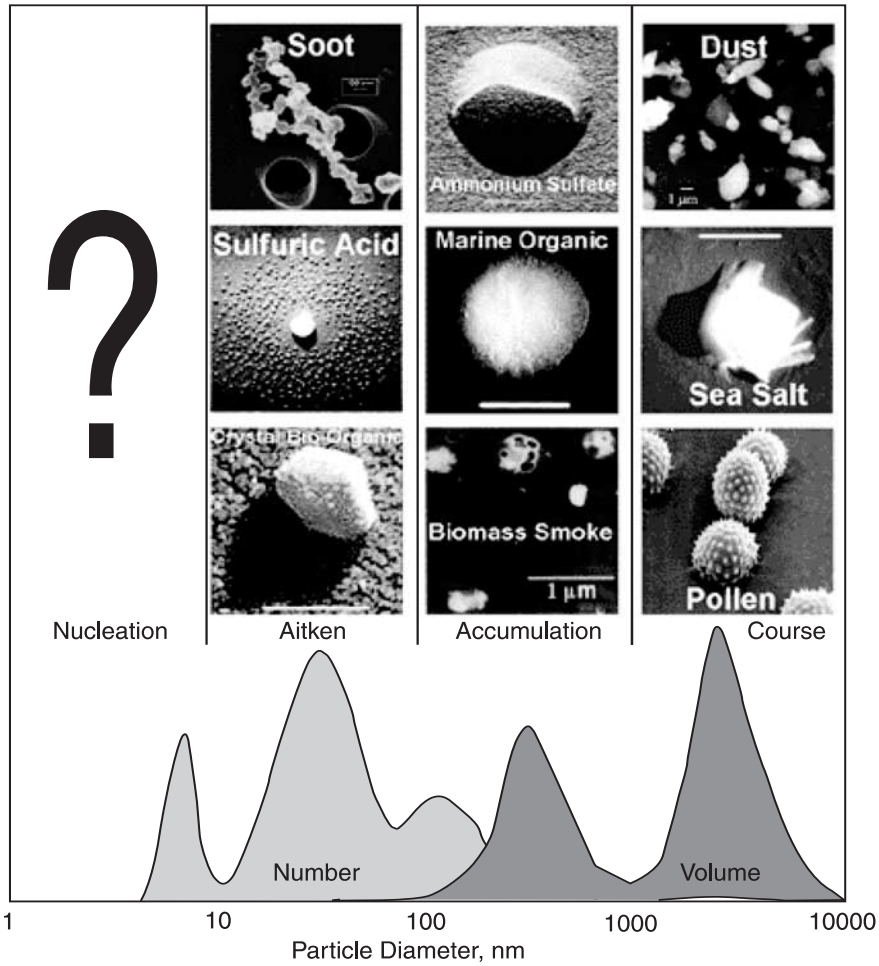


Fig. 4.1. Generic presentation of the range of particle shapes and chemical composition of the atmospheric aerosol

Table 4.1. Natural processes leading to particle production and anthropogenic processes leading to changes of the natural aerosol

Species	Natural processes	Anthropogenic processes	Present day particle burden compared to pre-industrial time	Elements of climate change potentially affecting emissions of species in column 1
Primary particle				
Mineral dust	Wind erosion	Land use change; Industrial dust emissions	Increased dust	Changing winds and precipitation
Sea salt	Wind			Changing winds
Biological particles	Wind, biochemical processes	Agriculture	?	Changing winds
Carbonaceous particles	Vegetation fires	Fossil fuel; Biomass burning	Increased carbonaceous particles	Changing precipitation (droughts…)
Precursors of secondary particles				
Dimethylsulphide	Phytoplankton degradation	Increased oxidising capacity	Increased sulphate	Changing winds hence air-sea exchange
SO_2	Volcanic emissions	Fossil fuel combustion	Increased sulphate	
NH_3	Microbial activity	Agriculture	Increased ammonium nitrate	
NO_x	Lightning	Fossil fuel combustion	Increased nitrate	Change in convective activity hence lightning
Volatile organic compounds	Emission from vegetation	Increased oxidation capacity; Industrial processes	Increased organic aerosol	

changes in natural aerosol are summarised in Table 4.1. Anthropogenic effects on the atmospheric particle burden can be direct, through changing and adding emissions of particles or their precursors. The effects can also be indirect, as consequences of changing the transformation processes leading to secondary aerosol particles (e.g. altered oxidising capacity of the atmosphere), or of climate change. The effects of climate change relevant for particle production are exemplified in the last column of Table 4.1.

The discussion of recent developments presented in this chapter points to a highly exciting future of this subject as an integrative component of atmospheric chemistry.

Box 4.1. Definitions

Optical thickness: A measure of extinction of direct solar beam by transmittance through the atmosphere. The fractional transmittance of the direct beam for solar zenith angle, θ, is expressed in terms of the optical thickness, τ, at a given wavelength as $\exp(-\tau / \cos\theta)$; that is, τ is the optical thickness for overhead sun. Optical thickness consists of additive contributions from Rayleigh scattering, gaseous absorption, and aerosol scattering and absorption.

Ångström exponent: A measure of the dependence of aerosol optical thickness τ_a on wavelength λ, $\alpha = -d \ln \tau_a / d \ln \lambda$. A greater value of Ångström exponent corresponds to smaller size aerosol particles.

S(IV): The Roman numeral IV in parentheses indicates the oxidation number of +4 of the sulphur atom S in SO_2 and its family of aqueous dissolution products, i.e., bisulphite (HSO_3^-) and sulphite (SO_3^{2-}). The S atom in sulphate (SO_4^{2-}) has a higher oxidation number of +6 and is a member of the S(VI) family. Oxidation numbers are discussed in most general chemistry texts.

4.2 Integrated View of Present State of Knowledge of Atmospheric Aerosols

During the past decade, model calculations, *in situ* observations, and measurements from satellites have looked in different ways at the atmospheric aerosol. The first space-borne radiometers that probed the troposphere revealed the transport of aerosols on regional and global scales. Measuring campaigns focussing on areas of interest revealed by those satellite images documented a large variety of aerosol physical and chemical properties, which guided the way to a better understanding of the processes controlling the evolution of the aerosol particles. Model calculations helped to identify links between aerosol sources, atmospheric chemistry, transport, and some of the characteristics of the observed fields.

What emerged from these different perspectives is that there is no such thing as a global aerosol. Instead there exists a superposition of largely independent regional aerosol plumes and layers, each having unique sources and correspondingly differing spatial and seasonal patterns as well as specific microphysical and chemical characteristics.

4.2.1 Space-Borne Measurements

4.2.1.1 *Maps of Aerosol Optical Depth from Space-Borne Radiometers*

Global horizontal patterns of aerosol optical thickness and Ångström exponent (see Box 4.1 for definitions) over the oceans derived from the POLDER instrument for December 1996 and June 1997 are shown in Fig. 4.2a,b. The oceanic aerosol optical depth maps reveal two distinctly different spatial patterns: aerosol plumes originating from continents and oceanic aerosol patches that are detached from the continents. Near coastal areas the continental aerosol plumes are characterised by high concentrations, which decrease with distance from the coast. This pattern arises from aerosol emissions from the continents, followed by atmospheric dispersion, transformation, and decay in the downwind direction. In large-scale flow fields, such as the trade winds, these continental plumes persist over several thousand kilometres.

With some *a priori* knowledge of source distributions, the plumes illustrated in Fig. 4.2 can be attributed to mineral dust, biomass burning, and industrial emissions. The dominant plumes are in the Tropics and subtropics and are due to mineral dust emissions and biomass burning; the aerosol levels generally peak in the dry seasons in the respective hemispheres.

The Ångström exponent shown in Fig. 4.2a exhibits a very different pattern from that of the aerosol optical thickness; specifically, it exhibits high values in or near industrialised regions and regions of biomass burning, indicative of small particles arising from direct emissions from combustion sources and/or gas-to-particle conversion, and low values associated with large particles in plumes of soil dust from deserts and in sea salt aerosols.

Sand dunes are shown on Fig. 4.2b as yellow patches over the Sahara and northwestern China. However, it should be noted that sand dunes are not necessarily strong or exclusive sources of wind-blown dust. The emission of wind-blown dust is seasonal and it is driven by highly episodic windy conditions. Frequently the sources of such aerosols are pans of dry silty soil that have resulted from prior rain events. The characteristic dust particle is in the coarse particle mode (see Fig. 4.4i). Its composition does not always reflect the local sand composition, but might be enriched by anthropogenic sulphates and nitrates.

Biomass fires are shown as red dots. Note that the fire locations in December (Fig. 4.2a) are distinctly dif-

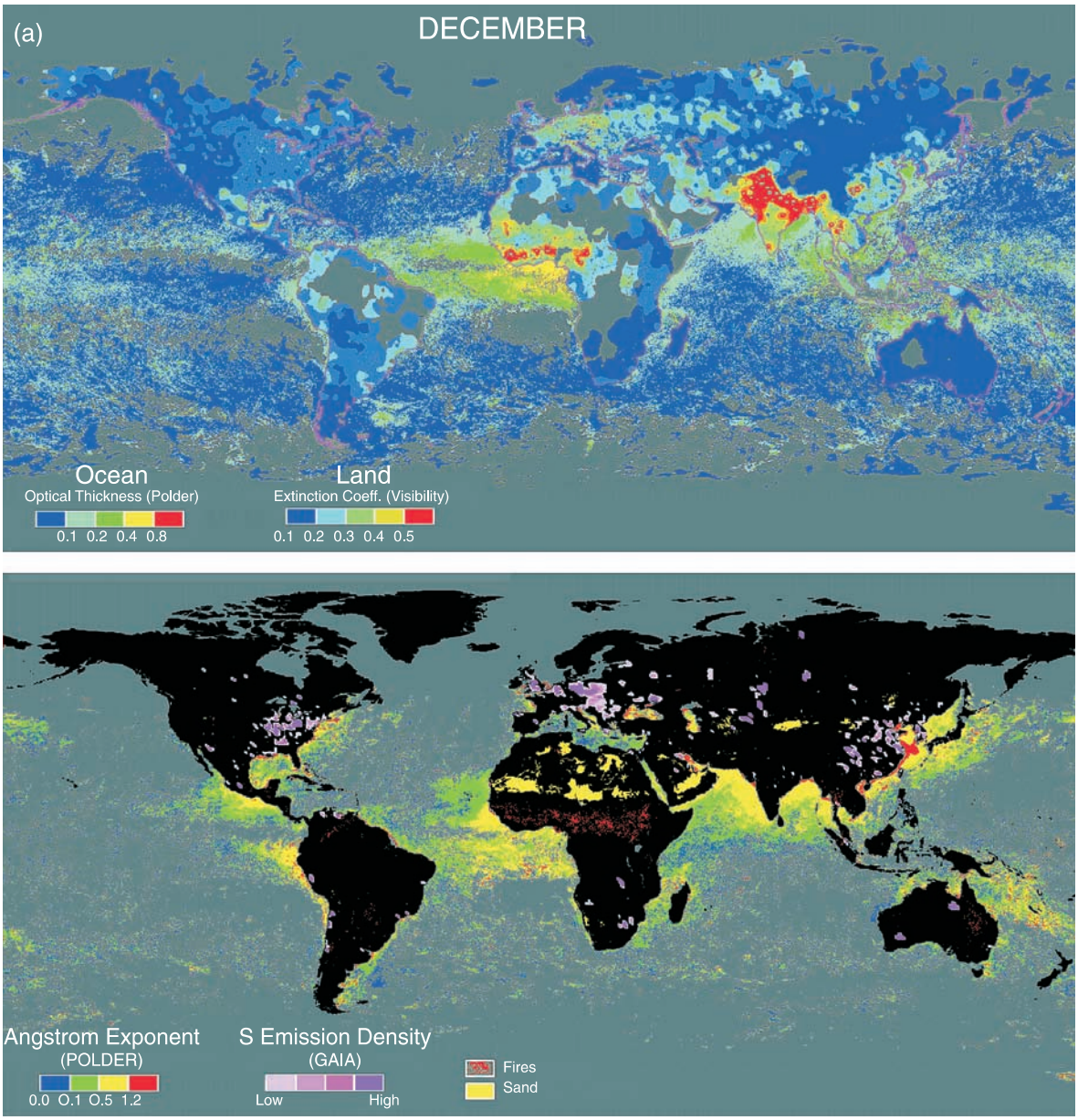


Fig. 4.2a. Global horizontal patterns for December 1996 of aerosol optical thickness and Ångström exponents over the oceans from the POLDER instrument aboard the ADEOS satellite and extinction coefficients over land areas from visibility data (reproduced with permission of Laboratoire d'Optique Atmospherique (LOA), Lille; Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-sur Yvette; Centre National d'Etudes Spatiales (CNES), Toulouse, France; and the National Space Development Agency (NASDA), Japan)

ferent from those recorded in June (Fig. 4.2b). The regular yearly biomass burning regions of the world are distributed over central and sub-Saharan Africa, Central and South America, as well as Indonesia and Indochina. More sporadic fires are recorded over the boreal forests of Canada and Siberia. Biomass smoke particles are composed of organic species, elemental carbon, ionic species (sulphate, ammonium, and potassium), and other combustion residues, and they are generally submicrometer in size (see Fig. 4.4d).

Anthropogenic sulphur sources obtained from the IGAC GEIA inventory (see Sect. 4.3.2.3), shown as purple areas, are broadly representative of other types of industrial aerosol emissions and their precursors (e.g. organic species, nitrates, black carbon, etc.). Anthropogenic emissions are located mainly in the Northern Hemisphere and mainly in midlatitudes. The three major anthropogenic sulphur-emitting regions are eastern North America, Europe, and eastern Asia. Anthropogenic sulphate particles are sub-micrometer in

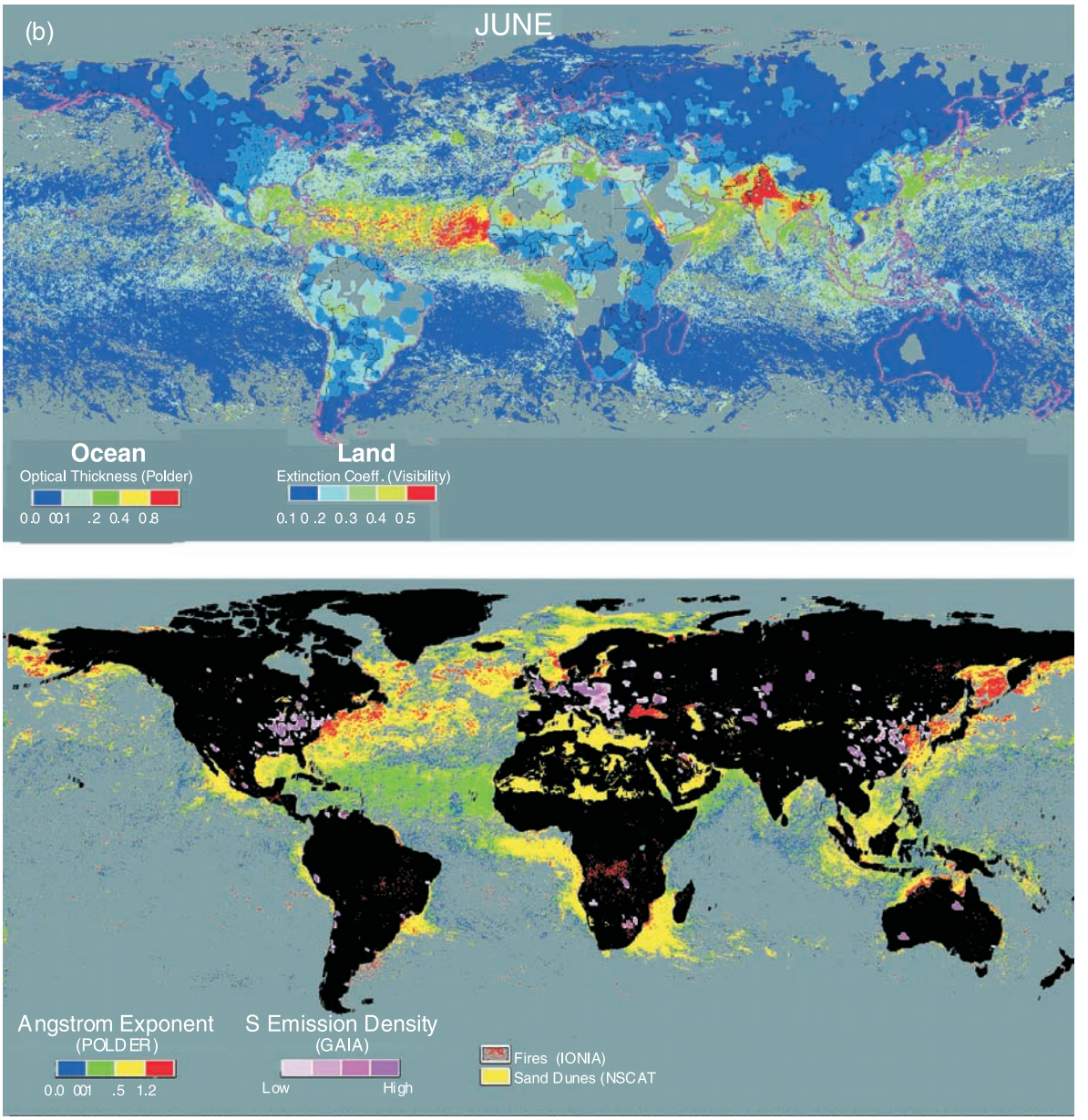


Fig. 4.2b. Global horizontal patterns for June 1997 of aerosol optical thickness and Ångström exponents over the oceans from the POLDER instrument aboard the ADEOS satellite and extinction coefficients over land areas from visibility data (reproduced with permission of Laboratoire d'Optique Atmospherique (LOA), Lille; Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-sur Yvette; Centre National d'Etudes Spatiales (CNES), Toulouse, France; and the National Space Development Agency (NASDA), Japan)

size and often co-exist with condensable organic species (see Fig. 4.4c).

The oceans are also sources of aerosols and precursor gases, especially dimethylsulphide (DMS). DMS emissions are seasonally and regionally dependent with the highest emissions in the middle and high latitudes during the summer months (Kettle et al. 1999). Unfortunately, there are no satisfactory proxy indicators for oceanic sulphur emission patterns. For example, oceanic emissions of DMS do not appear to be related to chlorophyll distributions in the ocean (e.g. Leck 1990), which can be measured by satellite. The sea is also a source of primary particles to the atmosphere through bubble bursting and shearing of wave crests. Although the total number concentration of mechanically produced super-micrometer sea salt particles is relatively small even in the remote marine boundary layer (MBL, cf. Fig. 4.4f), they can dominate light scattering by aerosol particles (Quinn et al. 1996c).

4.2.1.2 *Vertical Aerosol Distributions from Space-Borne Lidar*

The vertical distribution of aerosol plumes (and clouds) over the Atlantic Ocean is shown in Fig. 4.3a. By a favourable coincidence, the LITE (Lidar Technology in Space Experiment, September 1996) lidar recorded the vertical distribution of both the Sahara dust plume and the biomass smoke plume emanating from southern Africa.

The picture provides clear illustrations of aerosol-cloud interactions. For instance at 12° N the marine boundary layer (MBL) extends to about two km and there is evidence of dust entrainment into the MBL and the clouds. The cloudiness associated with the Inter-Tropical Convergence Zone is also clearly visible at about 5° N. The entire convergence zone is relatively aerosol-free, possibly because of the intense cloud processing and removal of particles by precipitation. The picture, however, also shows that significant amounts of aerosol are transported above clouds and become well separated from the boundary layer. The slow removal within the free troposphere allows the long-range transport of these plumes over many thousand kilometres until they are entrained into precipitating cloud systems.

The biomass burning haze layer over the Amazon basin is depicted in Fig. 4.3b. The layer extends from the basin floor to about 3 000 m altitude. It is remarkable that the aerosol layer is spatially homogeneous over the entire 1 000 km cross section along the track of the spacecraft. During the LITE passage over this part of South America, the free troposphere above 5 km was remarkably aerosol-free. The Andes constitute a strong barrier to the dispersion westward of the smoke layers.

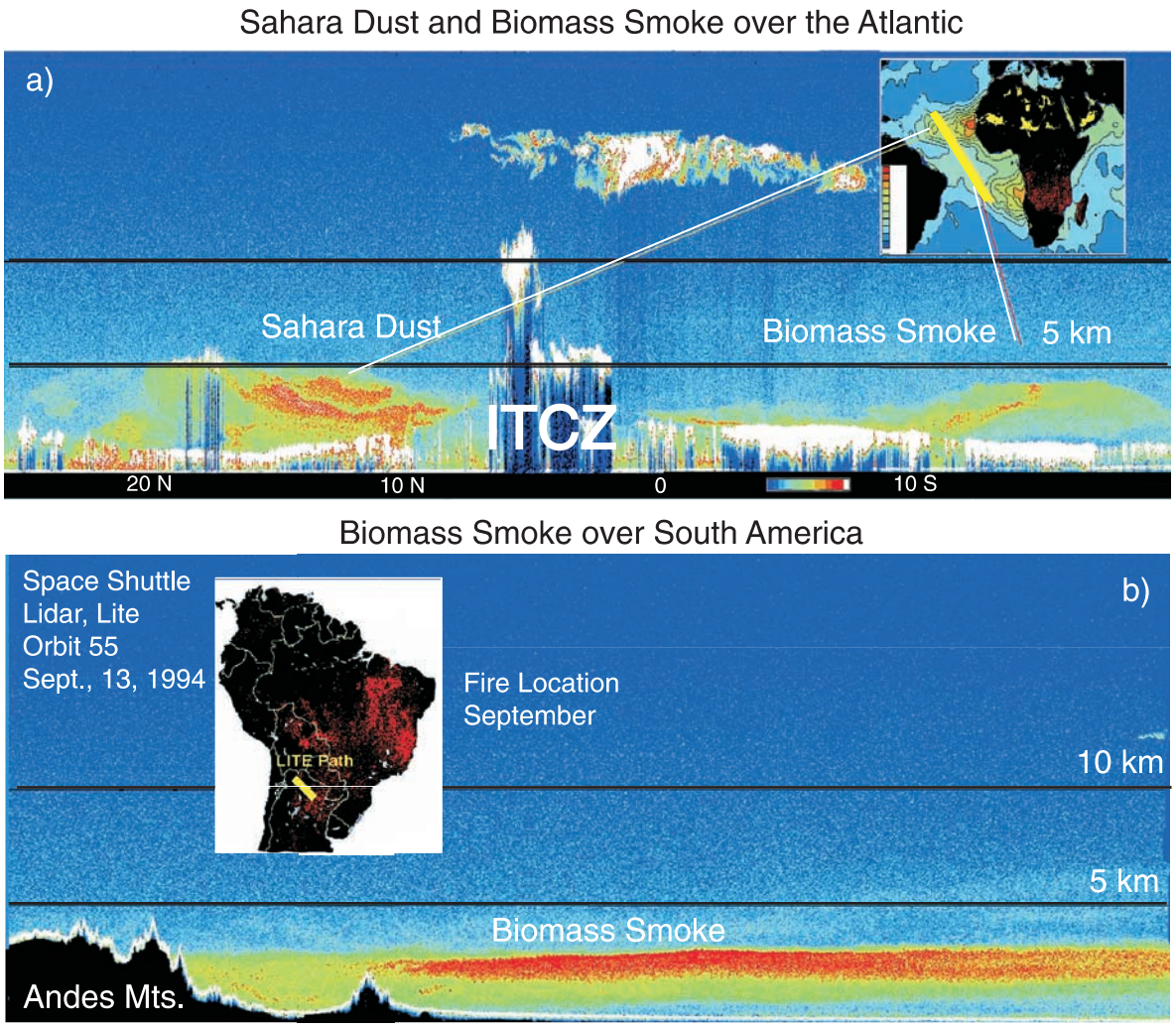


Fig. 4.3. Vertical distribution of aerosol plumes (and clouds) from the Lidar Technology in Space Experiment (LITE) instrument, over **a** the Atlantic Ocean, and **b** South America

4.2.2 *In situ* Measurements

There has been extensive development in instrumentation for the physical and chemical characterisation of aerosol particles. Implementation of these instruments in well-designed field studies in IGAC and elsewhere (see Sect. 4.4) has provided considerable new information on aerosol microphysical and chemical characteristics, at least in those areas visited by these experiments. A compilation of particle size distributions and their chemical composition is shown in Fig. 4.4, and discussed below. The degree to which they lead to a three dimensional picture of the global aerosol is discussed subsequently.

4.2.2.1 *Particle Size Distributions*

In the global atmosphere, the size distribution of aerosol particles, while highly variable, generally can be represented as a superposition of more or less distinguishable modes. These modes are often approximated as log-normal distributions. Following the original suggestions of Whitby (1978), these modes are generally referred to as the nucleation mode (particles with diameter $D_p < 0.01$ µm), the Aitken mode ($0.01 < D_p < 0.1$ µm), the accumulation mode ($0.1 < D_p < 1$ µm), and the coarse mode ($D_p > 1$ µm). Each mode results from specific emissions and atmospheric processes. The nucleation mode is the result of recent nucleation of new particles from gases. The Aitken mode results from condensation on and coagulation of nucleation-mode particles, as well as from primary emissions during combustion. The accumulation mode typically results from coagulation and from the formation of particle mass by chemical reactions in cloud droplets. Primary emissions from the mechanical break-up of bulk material also contribute to accumulation mode particles, but they dominate the mass of the coarse mode.

Particle number concentrations typically decrease for particles with diameters below 10 nm, because the smallest particles and clusters have a high mobility and therefore rapidly diffuse to surfaces or coagulate with other particles. The presence of high numbers of nucleation-mode particles, for example, in urban and suburban environments (Fig. 4.4) and (on occasion) in the clean MBL of the Southern Ocean (Fig. 4.4f) indicates that nucleation has taken place recently. Over oceans, this is thought to happen aloft in the neighbourhood of clouds (e.g. Hegg et al. 1990). The nucleating particles are 1 nm and less in diameter and they are not detectable with the present instrumentation, which has a lower limit of 2–3 nm.

Number concentrations also decrease for particles with diameters above about 500 nm, because of impaction or gravitational settling. Significant number concentrations of coarse particles are found in the presence of primary emissions, e.g. of sea salt (Fig. 4.4c–f) or crustal dust (Fig. 4.4b). The Saharan dust layer in the free troposphere (Fig. 4.4i) contains relatively high numbers of coarse particles even several hundreds of kilometres from the emission area. In the diameter range 10 to 500 nm, the number size distributions exhibit one or more maxima. When particles resulting from industrial activity (Fig. 4.4c) or biomass burning (Fig. 4.4e) age during transport from their sources, primarily because of coagulation and cloud processing, a single accumulation mode develops with diameter typically centred near 100 nm. These aged aerosols are also present over the continents where they can mix with freshly produced aerosols (e.g. Fig. 4.4a,b).

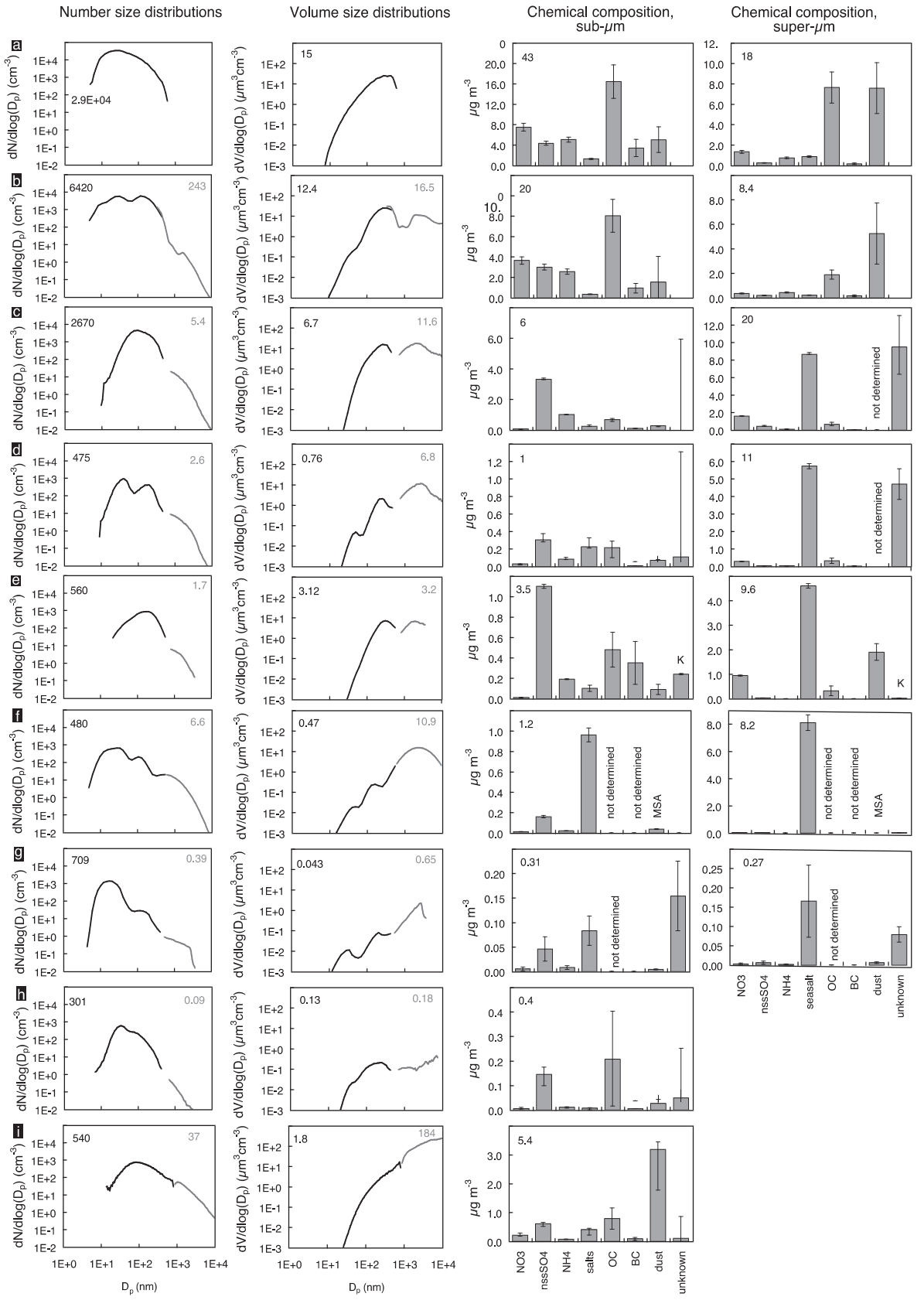
In the clean MBL, far from anthropogenic influences, the sub-micrometer size distribution is typically bimodal (Fig. 4.4d,f,g). The Aitken mode is thought to arise from entrainment of free tropospheric aerosol (Fig. 4.4h) into the boundary layer, whereas the accumulation mode results from the growth of smaller particles, mainly by chemical reactions in non-precipitating clouds. In the summer Arctic three sub-micrometer modes have consistently been found (Covert et al. 1996b).

4.2.2.2 *Chemical Composition*

Within a given environment the chemical composition of sub-micrometer particles ($D_p < 1$ µm) is generally different from that of coarse mode particles ($D_p > 1$ µm), reflecting the different formation mechanisms (Fig. 4.3). In the following discussion we will focus on the sub-micrometer fraction, which is most relevant for many of the aerosol effects.

Urban aerosols are often dominated by sulphate and by organic species that derive from the incomplete combustion of fossil fuels. Other products from fossil fuel burning, such as nitrate and black carbon, are also present in this aerosol. The acid fraction of the particles is partially neutralised by ammonia. Figure 4.4a and b show data for the city of Milan (Italy) during summertime. Aerosols in cities in northern Europe contain a smaller contribution of organic particulate matter and exhibit significant seasonal variations. Outside of the urban environment, the regional continental sub-micrometer aerosol (Fig. 4.4c) is generally dominated by sulphuric acid and its partial neutralisation products with ammonia $(NH_4)_xH_ySO_4$, where x and y range from zero to two and two to zero, respectively. The dominant source of the sulphur in this aerosol is industrial fossil fuel combustion.

Although the measurement of the organic constituents is fraught with large uncertainties, there are indications that organics also form a large fraction of the


Number size distributions
Volume size distributions
Chemical composition, sub-μm
Chemical composition, super-μm
a
b
c
d
e
f
g
h
i
dN/dlog(Dp) (cm-3)
dV/dlog(Dp) (μm3cm-3)
μg m-3
Dp (nm)
2.9E+04
15
43
18
6420
243
12.4
16.5
20
8.4
2670
5.4
6.7
11.6
6
20
475
2.6
0.76
6.8
1
11
560
1.7
3.12
3.2
3.5
K
9.6
K
480
6.6
0.47
10.9
1.2
8.2
709
0.39
0.043
0.65
0.31
0.27
301
0.09
0.13
0.18
0.4
540
37
1.8
184
5.4
not determined
MSA
NO3
nssSO4
NH4
seasalt
OC
BC
dust
unknown
salts

sub-micrometer aerosol in the free troposphere (see Fig. 4.4h) (Novakov et al. 1997; Putaud et al. 2000).

The particulate products of biomass burning (see Fig. 4.4e) are enriched in black carbon, potassium, ammonium, and chlorine. Some chlorine can be displaced by sulphate over short distances from the fires (Liu et al. 2000).

Sea salt generally dominates the mass of super-micrometer particles over the ocean (Fig. 4.4c,f) and can dominate the mass of the sub-micrometer particles in the remote marine environment (Fig. 4.4f). Single particle analysis during ACE-1 revealed that over 90% of the aerosol particles with diameters >130 nm (Murphy 1998, #1 097) and up to 70% of the particles with diameters >80 nm (Kreidenweis et al. 1998) contained sea salt. In the subtropical North Atlantic (ACE-2) the contribution of sea salt to the sub-micrometer aerosol was less dominant (compare Fig. 4.4e and f), even in air masses of marine origin.

Over the oceans, in plumes originating over the polluted continent, the sea salt becomes depleted in chloride (55% on average during ACE-2, see Fig. 4.4c), indicating the interaction of sea salt with anthropogenic acids (Quinn et al. 2000) or perhaps other mechanisms (Keene et al. 1990). In such plumes, the contribution of nitrate to the sub-micrometer aerosols is also very small. This can be explained by the displacement of the equilibrium $NH_4NO_3 \longleftrightarrow NH_3 + HNO_3$ through the reaction of HNO_3 with : $NaCl + HNO_3 \longrightarrow NaNO_3 + HCl$.

During transport events out of North Africa, mineral dust is the main component of sub-micrometer aerosol particles in the free troposphere (see Fig. 4.4i). However, the presence of nitrate and sulphate and the high SO_4^{2-}/Ca^{2+} ratio suggest that dust plumes over the Atlantic tend to be mixed with aerosol resulting from industrial activity.

◀ **Fig. 4.4.** A compilation of particle size distributions and their chemical composition representative of different atmospheric settings. Size distributions below 1 000 nm are obtained with differential mobility analyser (*black line*), above 1 000 nm with optical particle counter or aerodynamic particle sizer (APS) (*gray line*). Aerodynamic diameters have been converted to geometric diameters for consistent representation. *Numbers* inside the size distribution panels indicate integrated number (resp. volume) concentration for the sub-µm (*black*) and the super-µm (*gray*) size range in the same unit as indicated in the Y-axis. *Numbers* inside the chemical composition panels indicate gravimetric mass ($\mu g\, m^{-3}$) for the respective size ranges. Labels for the composition bars are as in the lower panels, unless indicated otherwise (*black bars*). The unknown fraction is the difference between gravimetric mass and the sum of quantified compounds. **a** Urban background during rush hour; **b** Suburban at local noon; **c** N. Atlantic MBL, continentally influenced; **d** N. Atlantic MBL, background; **e** N. Atlantic MBL, biomass burning influenced; **f** Southern Ocean MBL, background; **g** Arctic MBL, background during clear sky; **h** N. Atlantic free troposphere, background; **i** N. Atlantic free troposphere, Saharan dust plume; (courtesy of R. Van Dingenen, J. P. Putaud, EC Joint Research Centre, Ispra, Italy; T. S. Bates, P. K. Quinn, NOAA PMEL, Seattle, WA; C. Leck, MISU, Stockholm, Sweden, H. Maring, RSMAS, University of Miami, FL)

4.2.2.3 *The 3-Dimensional Distribution of the Atmospheric Aerosol Based on in situ Measurements*

Measurements such as those shown in Fig. 4.4 must be compiled to construct global aerosol climatologies. Such climatologies are necessary for testing models, for verifying satellite observations and, eventually, for quantitatively assessing any regional or global aerosol effects in the Earth system. This goal is far from being achieved.

A compilation of surface-based aerosol measurements has recently been published for marine areas (Heintzenberg et al. 2000). Well-calibrated and parameterised sub-micrometer particle size distributions are available for only about a quarter of the oceanic surfaces. For bulk chemical composition the corresponding coverage is somewhat better (≈60%), but still far from satisfactory. Significant progress in marine aerosol characterisation came through the large IGAC field experiments of the 1990s: ASTEX (Huebert et al. 1996); ACE-1 (Bates et al. 1998; Bates 1999); TARFOX (Russell et al. 1999); and ACE-2 (Raes et al. 2000a).

For continental aerosols, no comprehensive parameterisation of the size distribution of continental aerosols has been accomplished since the pioneering work of K. T. Whitby (see Whitby 1978), despite the availability of commercial and specialised methodology that can reveal many more details than was possible 25 years ago (e.g. Heintzenberg et al. 1998). Regional air pollutant networks such as EMEP in Europe (*http://www.nilu.no/projects/ccc/emepdata.html*) and IMPROVE in the US (*http://vista.cira.colostate.edu/IMPROVE*) have been collecting data on aerosol chemical composition (typically sulphates, nitrates, and black carbon), which are of some use, and the Global Atmospheric Watch programme of WMO has started archiving various aerosol parameters at its World Data Centre for Aerosols (*http://www.ei.jrc.it/wdca/*). The latter have been used for a validation exercise of global chemistry and transport models of the sulphur cycle (Barrie et al. 2000).

Knowledge of the vertical aerosol distribution is even more limited than that of the surface distribution. Over the continents there has been only one long-term effort in vertical aerosol profiling by *in situ* measurements (Hofmann 1993); valuable data were obtained on the effects on the upper troposphere and lower stratosphere of volcanoes, of the increase of air traffic, and of decreasing surface emissions. A series of research flights complemented the continental data to some extent with measurements over the Pacific and North Atlantic region (e.g. Clarke 1993; Heintzenberg et al. 1991; Hobbs and Yates 1985). As an example, all Pacific measurements from major aircraft experiments made over a ten-year period are summarised in Fig. 4.5. The measurements

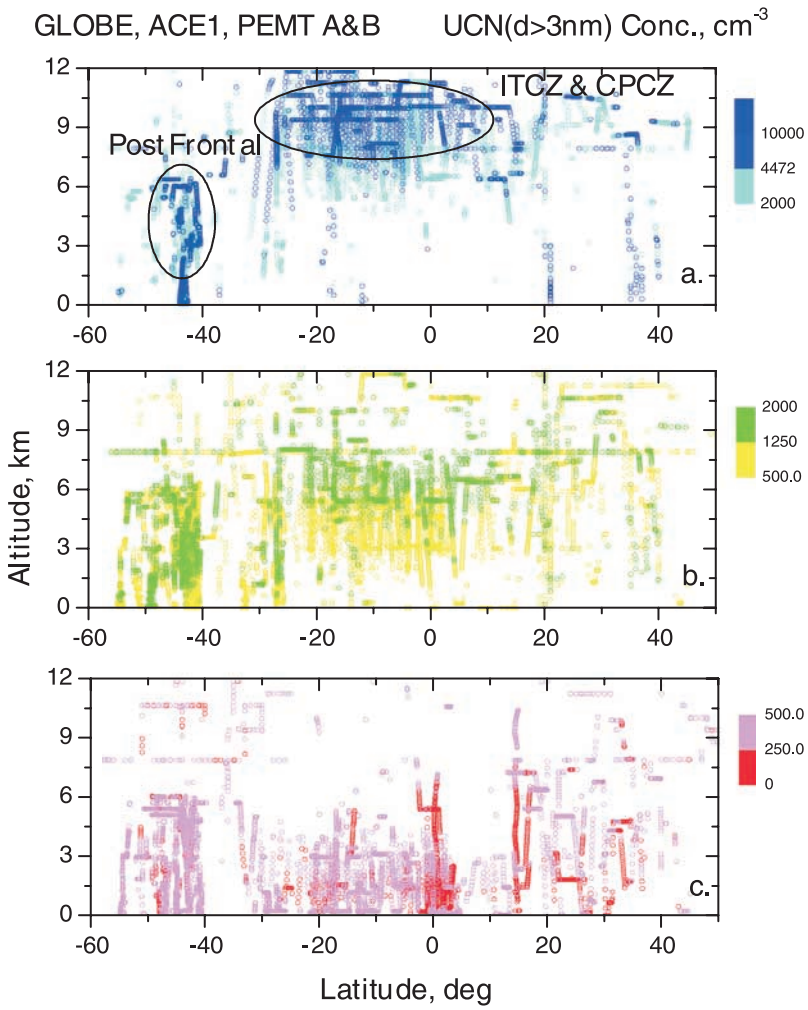


Fig. 4.5. Ultrafine particles (diameter $D_p > 3$ nm) in particles cm^{-3}, STP as a function of latitude and altitude from five major aircraft experiments: GLOBE (1989, 1990); ACE-1 (1995); and PEM-Tropics A and B (1996, 1999, respectively) above the Pacific Ocean. Because of data point overlap, the data have been separated into three panels with indicated concentration ranges of 0–500 cm^{-3} (*red-pink*); 500–2 000 cm^{-3} (*yellow-green*) and 2 000–10 000 cm^{-3} (*light-dark blue*) (data courtesy of A. Clarke, University of Hawaii, and B. Anderson, NASA, Langley Research Center)

reveal the occurrence of large-scale natural aerosol production over the Pacific. For these extensive regions the highest concentrations are generally most common aloft in the Tropics and near deep convective regions near the south polar front and elsewhere. These are regions of well scavenged air with very low particle surface area and new particle production that appears to be linked to cloud pumping of precursors aloft where low surface area, low temperatures, and high humidity favour nucleation (Clarke et al. 1998, 1999a,b; Weber et al. 1999). Lower concentrations are more common at higher latitudes in both hemispheres. In spite of fewer flights in the higher altitude and latitude regions, it appears likely that these differences reflect air masses de-coupled from the tropical latitudes, as would be expected for typical characteristics of the Hadley circulation.

Lower number concentrations but larger particles were frequently observed in the North Pacific midlatitude free troposphere (FT). Here aged "rivers" of continental aerosol are present frequently, often internally mixed with a non-volatile residual indicative of soot and/or externally mixed with dust. The higher concentrations of small volatile nuclei often observed near combustion source regions tend to be depleted in the aged plumes, perhaps because of coagulation with the high available surface areas. The FT in the subtropics tends to show frequent and marked transitions and mixing between these clean and continental aerosol types.

Vertical aerosol distributions have also been monitored over several years by a few lidars over the European continent (Ansmann et al. 1997; Jäger and Carnuth 1994) and more recently by Raman lidar at a site in central North America (Peppler et al. 2000).

After about five years of technical development, an aerosol payload is now flying frequently on a commercial aircraft (Brenninkmeijer et al. 1999). An aerosol climatology for the tropopause region has been accumulated for several years during scheduled flights between Europe and the Indian Ocean (Hermann 1999). As over the Pacific (cf., Fig. 4.5) there is a clear influence of surface aerosol sources in the Tropics and in the midlatitudes over Europe (Fig. 4.6). In the latter region aircraft emissions contribute to aerosol sources in the tropopause region.

Box 4.2. Aviation-produced particles

Aircraft affect atmospheric aerosols and cirrus (ice) clouds by releasing particles directly into the upper troposphere and lower stratosphere and by producing contrails (condensation trails) (Penner et al. 1999). At cruise altitudes (9–12 km), concentrations of atmospheric aerosol particles are much lower, and their associated residence times are much longer, than for regions closer to Earth's surface. Two major particle types can be distinguished in aircraft exhaust (Kärcher 1999): (*1*) ultrafine liquid particles (diameter range 5 to 10 nm) formed by nucleation during cooling and dilution of the exhaust, which are composed of water, sulphuric acid, and organic matter; and (*2*) solid soot particles (20 to 60 nm) composed of carbonaceous agglomerates containing sulphur and organic compounds formed during combustion.

Charged molecular clusters (chemi-ions) produced via high temperature chemical reactions in engine combustion chambers are believed to play a central role in the formation and evolution of the liquid particles (Yu and Turco 2000). In the dispersing aircraft plumes, the particles grow by coagulation and condensation to form internally mixed soot-sulphate particles.

Perturbations in particle number concentrations in aircraft corridors have been observed at regional scales. The aircraft fleet may increase cirrus cloudiness (Jensen and Toon 1997). Satellite and *in situ* observations show that persistent contrails may develop into cirrus clouds. Aircraft-produced particles may also trigger cirrus indirectly, after the disappearance of short-lived contrails. Exhaust soot particles coated with hygroscopic sulphates could be more efficient freezing nuclei than ambient aerosol particles. Concerns have been raised about the role of aircraft soot in modifying existing or stimulating formation of new cirrus (Jensen and Toon 1997) because there is the potential for heterogeneous nuclei to cause ice formation at relative humidities that are lower than those needed to form ice homogeneously on sulphate particles.

Observational evidence exists for aircraft soot influencing cirrus (Ström and Ohlsson 1998), but the physical mechanisms are not understood. Whereas direct radiative forcing associated with aircraft-produced particles is estimated to be small compared with that originating from greenhouse gases now, the effect of these particles on cloud formation and modification could become substantial in the future. A better understanding of physico-chemical and ice-forming particle properties is required before the impact of aviation on cloud formation and heterogeneous chemistry can be addressed fully.

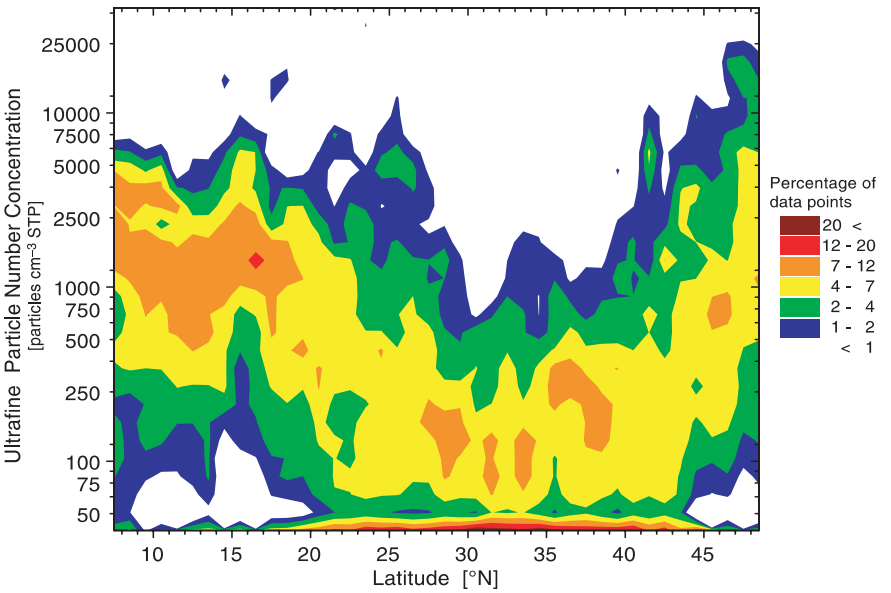


Fig. 4.6. Climatology of particles ($4\ \text{nm} \le D_p \le 12\ \text{nm}$) in (# cm^{-3}, STP) in the middle and upper troposphere as a function of latitude from scheduled flights during the period 1997–2000 with a commercial aircraft between Europe and the Indian Ocean

4.2.3 Process Understanding

An increased understanding of the processes underlying the observed variability in Fig. 4.2, 4.3, and 4.4 has evolved over the past 10 to 20 years. This includes both the microphysical and chemical processes involved in aerosol particle formation, evolution, and removal, as well as the role of large-scale meteorological processes.

4.2.3.1 *Microphysical and Chemical Processes*

The main microphysical and chemical processes that influence the size distribution and chemical composition of atmospheric aerosol particles are depicted schematically in Fig. 4.7. The figure illustrates the existence of primary and secondary particles and also the wide range of sizes involved in their formation and evolution. How aerosol particles participate in atmospheric chemical processes through homogeneous, heterogeneous, and in-cloud reactions is also highlighted in Fig. 4.7.

Primary particles that derive from the comminution of bulk material and subsequent suspension by the wind, such as sea salt, soil dust, and biological material, have most of their mass in the coarse particle mode. However, their highest numbers occur in the sub-micrometer range. Because of their small numbers and large sizes, these primary particles generally do not coagulate. They can, however, become more heterogeneous

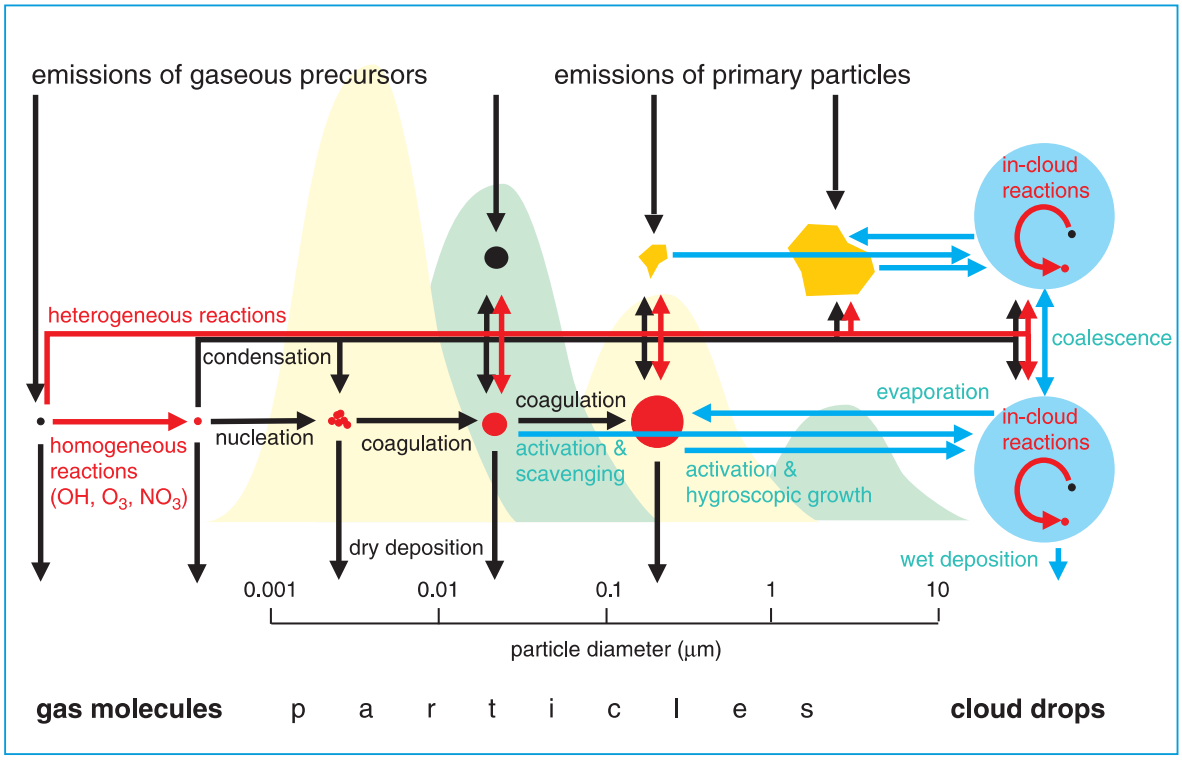


Fig. 4.7. Major microphysical and chemical processes that influence the size distribution and chemical composition of atmospheric aerosol particles

through uptake and chemical processing of condensable gases.

An important type of primary particle is so-called soot emitted from combustion of carbonaceous fuels. Soot consists of black carbon-containing material, which has not been fully oxidised in the combustion process; it is often mixed with refractory metal oxides. Primary soot particles have diameters from about 5 to 20 nm. Such particles coagulate rapidly to form fractal-like aggregates, which in turn collapse under the influence of capillary forces of condensing vapours to form more compact structures having diameters of up to micrometer size.

Gas-to-particle conversion (i.e. nucleation of new particles or condensation on existing particles) occurs when a volatile species reaches a concentration that exceeds its equilibrium vapour pressure, resulting in a thermodynamic driving force for condensation. In the atmosphere, this situation can be driven by chemical reactions leading to products with very low equilibrium vapour pressures (e.g. $SO_2 \longrightarrow H_2SO_4$, α-pinene $\longrightarrow$ pinonic acid). Alternatively, this situation also can be reached by a reduction in temperature, which reduces equilibrium vapour pressures. Another suggested mechanism is the co-condensation of several substances for which the equilibrium vapour pressure is lowered by the presence of other compounds in the particle. For example, the co-condensation of small amounts of ammonia has been predicted to enhance greatly the binary nucleation of H_2SO_4 and water vapour (Kulmala et al. 2000). Nucleation is energetically less favourable than condensation onto existing surfaces because of the free energy penalty associated with formation of new surface area. Therefore, nucleation is facilitated by the absence of pre-existing particulate surface. After nucleation occurs, the new particles grow further by condensation and coagulation. As particles reach a diameter of the order of the mean free path of the condensing molecule, typically ca. 0.1 µm, condensation becomes diffusion limited and slows down. Also, coagulation eventually slows down as the number concentrations of particles decrease. Under background tropospheric conditions particles formed initially by nucleation require from days to weeks to grow larger than about 0.1 µm solely by condensation and coagulation (Walter 1973). Under polluted conditions this growth can occur within a day because of the strong supply of condensable material (Raes et al. 1995).

Another growth process is by chemical processing in non-precipitating clouds (e.g. Bower et al. 1997; Laj et al. 1997). This process begins with the uptake of water vapour by the particle with increasing relative humidity (RH). According to traditional Köhler theory, a critical supersaturation exists, slightly above 100% RH. For RH exceeding this critical value, water vapour condensation is energetically favoured, leading to rapid growth of sub-

micrometer aerosol particles to supermicrometer cloud drops. This critical supersaturation depends on size and chemical composition of the particle as well as the concentrations of soluble gases in the surrounding air. Some soluble gases, most prominently SO_2, are oxidised in the aqueous phase. As most clouds evaporate before the onset of precipitation, larger particles result from the additional oxidised material, e.g. sulphate (Birmili et al. 1999b; Yuskiewicz et al. 1999).

Reactions that occur in cloud water also occur in wet particles under sub-saturated (non-cloudy) conditions. However, reaction rates are generally much lower because of lower liquid water content; reaction rate expressions also differ because of the higher ionic strengths in the wet particles. Additionally, adsorbed gases react on the particle surfaces yielding products that might either remain on the particle or return to the gas phase.

Particles are removed from the atmosphere by dry and wet processes. For particles whose diameter is less than 0.1 μm, the dominant dry removal mechanism involves turbulent diffusion followed by Brownian diffusion to the surface through a viscous sub-layer, typically about 1 mm thick; this process becomes less efficient as particle size increases. Coarse particles ($D_p > 1$ μm) settle gravitationally, a process that becomes less efficient as particle size decreases. Coarse particle dry deposition is enhanced by impaction, which is wind speed dependent (Slinn and Slinn 1980). In the range $0.1 < D_p < 1$ μm, dry removal is very slow, resulting in long atmospheric residence times (up to weeks). Provided their atmospheric residence time is not limited by any of the above sink mechanisms, these particles are removed mainly by growth to cloud drops during cloud formation and subsequent removal from the atmosphere in precipitation.

4.2.3.2 *Horizontal and Vertical Transport*

The aerosol plumes and layers depicted in Fig. 4.2 and 4.3 result from meteorological transport, including exchange between the lower and upper troposphere by dry or wet convection. The characteristic times of many of the microphysical aerosol processes depicted in Fig. 4.7 are days up to several weeks. This is typically longer than the time between emission/formation of aerosols in the boundary layer and their transport into the free troposphere. Hence, to understand aerosol properties one cannot confine the discussion to such compartments as the continental or marine boundary layers or the free troposphere. Instead, one needs to view aerosol microphysical processes in the context of the atmospheric transport processes that connect those compartments (Raes et al. 2000b). Meteorological processes also affect microphysical processes and influence the size distribution and chemical composition of the particles. For example, during vertical transport in precipitating clouds, a separation occurs between soluble compounds that are rained out and insoluble compounds that are pumped aloft (Rodhe 1983, #1 827). In the outflow regions of such clouds, optimal conditions exist for nucleation, the consequences of which have been both observed (e.g. Perry and Hobbs 1994; Clarke et al. 1999b) and modelled (e.g. Hegg et al. 1990; Wiedensohler et al. 1997). Aerosol layers observed in the free troposphere are possibly the result of such cloud outflows, the structures of which are maintained by meteorological stratification. On the other hand, entrainment of free tropospheric aerosol into the boundary layer may be a source of Aitken-mode particles, which may quench nucleation of new particles. Because strong gradients of particle concentration will form above the inversion layer, turbulent mixing will cause very large changes in particle concentrations and size distributions observed at the surface (Bigg et al. 1996).

4.2.4 Large-Scale Aerosol Models

The advances in understanding of aerosol processes are making their way into numerical models describing the emissions, transport, transformation, and deposition of aerosol particles and their precursors on a variety of scales from local to global (see Chap. 6). Major progress has been achieved over the last decade in simulating the global distribution of tropospheric particulate mass using chemical transport models (CTMs). Simulation of the global distribution of biogenic and anthropogenic sulphur (Langner 1991) led to the recognition that anthropogenic sulphate aerosols may have a significant impact on the global radiation balance (Charlson et al. 1991). This spurred a large interest in simulating global mass distributions of the aerosol types listed in Table 4.1. Despite the simplification of considering each aerosol type independently, these studies were important in several respects. They related emissions to global aerosol distributions, constructed global and regional budgets, estimated the contributions of anthropogenic sources to the aerosol burden, and drew attention to elements of the general circulation that are important for aerosol transport, particularly deep convection (Feichter and Crutzen 1990). As an example, global fields of mineral dust, sulphate, and "smoke", calculated with a CTM driven by observation-derived meteorological data, are shown in Fig. 4.8. Many of the calculated features can be compared with the observations from space, shown in Fig. 4.2a and b. A sub-hemispheric sulphate model driven by observation-derived meteorological data has been evaluated by thousands of daily comparisons with surface measurements (Benkovitz et al. 1994; Benkovitz and Schwartz 1997).

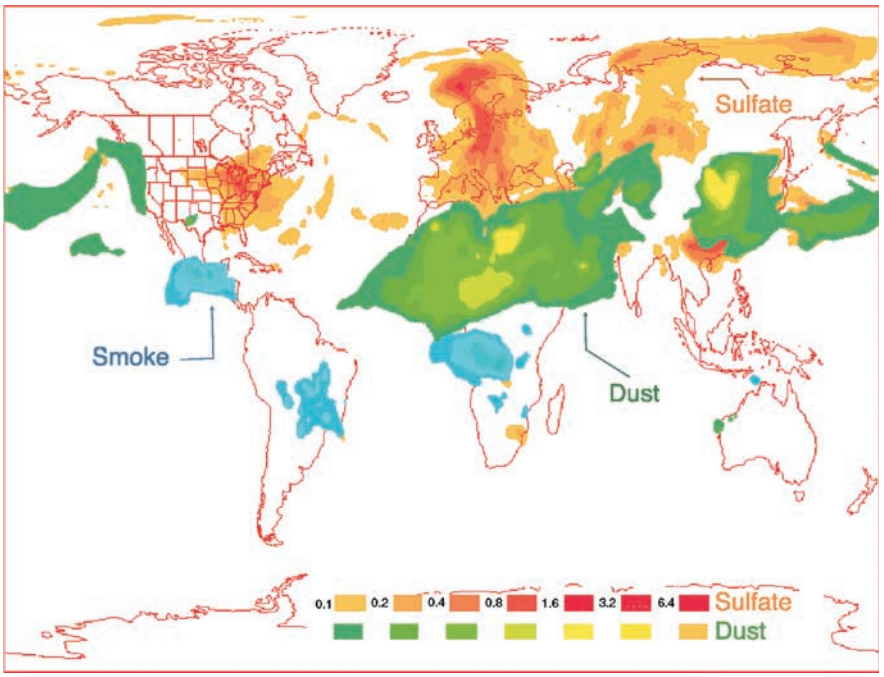


Fig. 4.8. Global fields of mineral dust, sulphate, and "smoke", calculated with a CTM using actual meteorology (*http://www.nrlmty.navy.mil/aerosol/*)

4.3 Selected Recent Developments

4.3.1 Primary Emissions

4.3.1.1 *Soil-Derived and Industrial Dust*

The majority of soil-derived dust particles is lofted into the atmosphere by wind in arid and semi-arid regions, which comprise approximately one third of Earth's land area. However, any type of land surface is a potential source of dust particles. Besides production mechanisms, surface properties (e.g. texture, roughness, composition, moisture, and vegetation) are key factors that determine the emission of dust for specific meteorological events (Gillette et al. 1980).

Estimates of global annual mean dust production range from 1 000 to 5 000 Tg yr^{-1} (Duce 1995). The large uncertainties are due mainly to the complexity of dust production mechanisms, which exhibit a large spatio-temporal variability. Despite progress in developing dust emission schemes for Saharan desert dust (Marticorena and Bergametti 1995), these schemes cannot be extended directly to other source regions due to a lack of data on surface properties. Emission data and models need to include explicit information on the particle size distribution and mineralogical composition to allow for better physically-based treatments of key processes (Sokolik et al. 1998; Claquin et al. 1999).

Anthropogenic dust is of special interest in climate change studies because human activities such as land use practice and construction, etc., can modify the geographical area of dust sources and increase the dust loading of the atmosphere. Recent estimates show that the anthropogenic fraction of dust could be as much as 30 to 50% of total dust production, but these percentages are very uncertain (Sokolik and Toon 1996; Tegen and Fung 1995). The dependence of dust emissions on meteorological parameters, such as wind speed and rainfall, suggests that atmospheric dust concentrations could be affected significantly by climate change.

Another type of anthropogenic aerosol is industrial (fly ash) produced by most combustion processes, cement manufacturing, metallurgy, and so on (Flagan and Friedlander 1978). Current estimates give a global emission for industrial dust of about 130 Tg yr^{-1} (Andreae 1995). The rapid economic expansion and industrialisation in developing countries may result in additional industrial aerosol emissions.

Both natural and anthropogenic fractions of dust must be better quantified to predict the overall effects of dust on atmospheric chemistry and on the climate system.

4.3.1.2 *Primary Particles from the Oceans*

The ocean is a source of primary sea salt particles to the atmosphere through the bursting of bubbles (yielding film and jet droplets), mechanical tearing (spume droplets), and spillover (splash droplets) of wave crests (reviewed by Andreas et al. 1995). Number concentration is dominated by the smallest, sub-micrometer salt particles, whereas surface area is dominated by jet drops, and volume by spume drops when present. Although the total number concentration of mechanically produced super-micrometer sea salt particles is relatively small even in the remote marine boundary layer (MBL, *cf.*

Fig. 4.4f), these particles can dominate the mass size distribution and thus have significant effects on chemical reactions occurring in the MBL (Sievering et al. 1992), the nucleation of new particles (Covert et al. 1996a), and the formation of clouds (O'Dowd et al. 1997b). The magnitude of the ocean-atmosphere flux of sea salt particles depends on the wind-dependent sea state (Woodcock 1953). The instantaneous atmospheric sea salt size distribution depends on the present and prior ocean-atmosphere flux, mixing between the MBL and free troposphere (FT), size-dependent removal processes, and advection. Typically, number and mass concentrations increase with increasing wind speed. Estimates of the source strength of aerosol are quite uncertain. Andreae (1995) gives a best estimate of the annual global mass emission rate of 1 300 Tg yr^{-1} with an uncertainty range of 1 000 to 10 000 Tg yr^{-1}; the estimate of Tegen et al. (1997) is 5 900 Tg yr^{-1}. Estimates of local production flux and its dependence on controlling variables, such as wind speed, are also quite uncertain as are estimates of the size-dependent production flux.

Sea salt aerosol particles also contain biological material. Blanchard (1963) reported surface-active components of the marine aerosol, which he demonstrated were transported into the atmosphere by bubble bursting. Subsequently, Gershey (1983) found that the production of particles by bubbling in seawater discriminated against the more soluble low molecular weight compounds in favour of the more surface-active high molecular weight compounds. These latter compounds are most likely concentrated in the walls of the bubble and are liberated as film drops when the bubble bursts, leading to a considerable enrichment of these organic components in the aerosol relative to the parent water. As a result, primary biological particles in the marine environment will usually contain a wide range of biogenic compounds such as long chain fatty acids, alcohols, esters, and soluble proteins. Some of these compounds are oxidised in the atmosphere to form other products (e.g. fatty acids to oxalic acid and proteins to amino acids).

4.3.2 Emissions of Particle Precursors

4.3.2.1 *Dimethylsulphide*

The emission of dimethylsulphide (DMS) from the oceans is a major sulphur source to the atmosphere (Barnard et al. 1982; Kettle et al. 1999) and contributes to the sulphur burden in both the marine boundary layer and free troposphere (over areas of active cloud convection) (Chin et al. 1996). Recent global estimates of DMS flux from the oceans range from 8 to 51 Tg S yr^{-1} (Kettle et al. 1999; Spiro et al. 1992). This accounts for at least 50% of natural sulphur emissions from ocean, plants, and soils taken together (Bates et al. 1992). Altogether the natural sulphur flux is estimated to be of the same order of magnitude as the anthropogenic sulphur emissions, mainly from fossil fuel combustion, which are currently estimated at 76 Tg S yr^{-1} (Benkovitz et al. 1996) (see also Sect. 4.3.2.3). The relatively large uncertainty in the reported estimates of the oceanic DMS flux is due partly to differences in the transfer velocities used in the sea-to-air calculations, but mainly to the different assumptions involved in seasonal and latitudinal extrapolations of the DMS seawater measurements. In particular, there is a paucity of data for seawater DMS concentrations in the winter months and at high latitudes. This very important natural precursor of sulphate particles and its biogeochemical cycling in the water column is discussed in more detail in Chap. 2.

The chemical and physical pathways that lead from atmospheric DMS to sulphur particles are complex and still poorly understood. Over the past ten years, DMS chemistry has been studied extensively by comparing model simulations with laboratory experiments and atmospheric observations. One of the main findings of these investigations has been the important role of heterogeneous reactions on pre-existing secondary and primary (sea salt) particles and cloud drops in producing particulate non-sea salt sulphate (nss-SO_4^{2-}) and methanesulphonate (MSA). The latter two compounds are the most important end products of DMS oxidation via the formation of gaseous sulphur dioxide, sulphuric acid, and methanesulphonic acid (Campolongo et al. 1999; Capaldo and Pandis 1997; Davis et al. 1999; Yin et al. 1990a,b). Additional oxidation products are dimethylsulphoxide (DMSO) and dimethylsulphone ($DMSO_2$).

Initial reaction products of gas-phase reaction of DMS include CH_3SO_2 and CH_3SO_3. The unimolecular decomposition pathways of both compounds are considered important in affecting the yields of SO_2, H_2SO_4, and MSA. The branching between these pathways determines whether DMS oxidation leads to particle nucleation from H_2SO_4, or to condensation of H_2SO_4 and MSA on existing particles. Unfortunately, the decomposition rates and their temperature dependencies are poorly known and subject to an intense debate. For example, reported CH_3SO_3 decomposition rates range over five orders of magnitude (Campolongo, et al. 1999). Temperature is thought to strongly affect the decomposition rates. Future research on the atmospheric life cycle of DMS should concentrate on reducing these uncertainties and on their implications for a potential DMS-climate feedback.

4.3.2.2 *SO_2 Emissions from Volcanoes*

Volcanoes are a major natural source of atmospheric sulphur species. Most active volcanoes are in the Northern Hemisphere (≈80%). The strongest source region is Indonesia. The most important products of volcanic

degassing are H_2O, CO_2, and sulphur (as SO_2, H_2S, and SO_4^{2-}) in varying fractions depending on the magma type. The measured concentration of SO_2 in volcanic plumes can be combined with wind speeds to estimate the SO_2 fluxes. However, emissions have been measured from only a few of the approximately 560 potential volcanic sources, and only a handful of these have been observed more than episodically. For some important regions (e.g. Kamchatka, Russia) there exist no data at all. Based on published observations, which exclude important regions, the total amount of volcanic tropospheric sulphur emissions has been estimated at 14 ±6 Tg yr^{-1} (Graf et al. 1997) in accordance with other recent estimates (e.g. Andres and Kasgnoc 1998). This is much less than the 25 Tg yr^{-1} estimated by Lambert et al. (1988) from the $SO_2/^{210}Pb$ ratio.

As active volcanoes generally reach considerable elevations, most of their emissions are injected into the free troposphere. There, removal processes are slower and, consequently, the volcanic sulphur species have longer residence times than anthropogenic and biogenic species in the boundary layer, leading to more efficient large-scale transport than for low-elevation emissions.

Mean volcanic sulphur emissions are of comparable importance for the atmospheric sulphate burden as anthropogenic sources because they affect the sulphate concentrations in the middle and upper troposphere whereas anthropogenic emissions control sulphate in the boundary layer. Volcanic emissions are highly variable in space and time, so there is need to quantify these sulphur sources better. There is also need to estimate transformation rates of SO_2 to SO_4^{2-}, in warm, moist volcanic plumes, and the contribution of H_2S, SO_4^{2-}, and SO_2 associated with plume particles, because these compounds are not measured by conventional methods. Finally, there is need to determine three-dimensional SO_2 and sulphate fields.

4.3.2.3 *Industrial SO_2 Emissions*

A key advance that has enabled the modelling of spatially and temporally varying aerosol concentrations has been the development of spatially disaggregated inventories. The Global Emissions Inventory Activity (GEIA) has been particularly successful in engaging researchers from different countries in preparing separate country-level inventories (Graedel et al. 1993). For the industrial SO_2 inventory, in regions where local inventories were not available, GEIA specified an inventory based on a single emission factor for fossil fuels and distributed emissions according to population. Where available, the individual country-level emissions were used (Benkovitz et al. 1996). This method of inventory preparation suffers from the lack of uniform methods for different countries but is expected to be more accurate than previous inventories which used a single emission factor for fossil fuel emissions from different locations. In addition, emissions from industrial activities (e.g. smelting) can be more accurately estimated. A remaining uncertainty with the inventories is the estimate of sulphur released as primary sulphate. Estimates range from less than one percent (Dietz and Wieser 1983; Saeger et al. 1989) to five percent (Eliassen and Saltbones 1983).

The global inventory developed for calendar year 1985 (see Fig. 4.9) indicates that about 81% of anthropogenic sulphur emissions are from fossil fuel combustion, 16% from industrial processes, 3% from large-scale biomass burning or waste treatment activities, and 1% from the combustion of biofuels. The current inventory is in need of substantial revision for other years. Total emissions of SO_2 from fossil fuel burning and industrial activities for 1985 have been estimated as 76 Tg S yr^{-1}, accurate to 20–30% (Benkovitz et al. 1996; Penner et al. 2000).

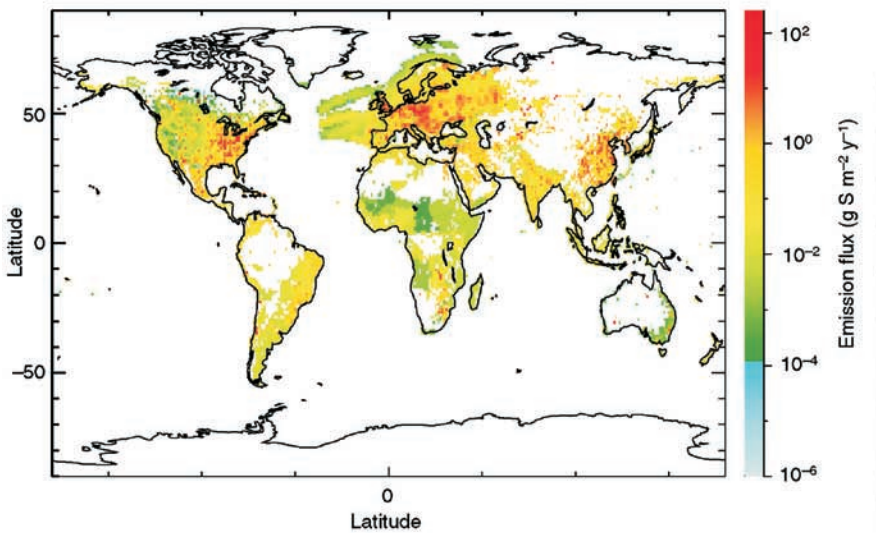


Fig. 4.9.
Global distribution of anthropogenic SO_2 emissions for 1985 as estimated by the IGAC/GEIA Activity (Benkovitz et al. 1996)

4.3.2.4 *Nitrogen Oxides and Ammonia*

In addition to their importance in atmospheric oxidant chemistry (Chap. 2 and 3) nitrogen oxides are important as precursors for nitric acid, which, despite its high vapour pressure, can be bound into the particle phase by the equilibrium reaction with NH_3:

$$HNO_3(g) + NH_3(g) \longleftrightarrow NH_4NO_3(s)$$

Ammonia is important as well because of its role in neutralization of aerosol sulphuric acid and possible role in new particle formation. Rather complex dynamic equilibria will usually exist in the atmosphere between aqueous aerosols and the gas phase (H_2O, HNO_3, H_2SO_4, $NH_3)_{gas} \longleftrightarrow$ (water, sulphate, nitrate…) particle. The emissions of ammonia (NH_3) and nitrogen oxides (NO_X) are discussed in Chap. 2 and 3, respectively.

4.3.2.5 *Organic Carbon and Black Carbon*

There are two main sources of combustion aerosols: fossil fuel burning and biomass burning. The main components are organic and black carbon and, for fossil fuel combustion, sulphate. The formation of particulate matter depends strongly on the conditions of combustion, especially temperature, combustion efficiency, and nature of the fuel. Higher temperature favours the production of larger amounts of black carbon (BC) and a lesser organic fraction. Inefficient combustion increases total particulate matter production.

Biomass burning sources include savannah and forest burning associated with both land clearing and deforestation, burning of agricultural wastes, and domestic burning of biofuels. Development of an understanding of the temporally and spatially varying emissions requires an estimation of total fuel burned and emission factors.

A number of IGAC-sponsored field studies have helped to quantify emissions factors from biomass burning, especially in the major savannah and forest burning regions in the Tropics (e.g. Andreae et al. 1998; see also Chap. 2). These emission factors have been used to develop inventories of both total particulate matter and BC from biomass burning (Liousse et al. 1996). The amount of fuel burned has been based on statistics from the Food and Agricultural Organisation and United Nations for wood and agricultural grain production, amount of deforestation, and estimates of savannah burning frequency. Data from satellites, together with vegetation maps, promise to provide more quantitative estimates of area burned (Barbosa et al. 1998). Development of emissions estimates from other biomass activities may require data on individual country practices.

Current estimates for total biomass burning, expressed as dry mass, range from 4 000 to 10 400 Tg yr^{-1} (see Table 2.4). The total soot production associated with these estimates ranges from 60 to 100 Tg yr^{-1}, with approximately 10% of this total associated with BC.

Fossil fuel emissions of combustion particles depend on burning practices in individual regions and the type of fuels burned. Rough estimates for BC emissions are available from, e.g. Cooke and Wilson (1996). Bond et al. (1998) suggested that new emission factors should be produced, based on the absorption properties of the emitted compounds, but insufficient data of this nature are available to develop such an inventory.

A simple estimate of organic carbon (OC) emissions from fossil fuel combustion was based on observed ratios of BC to OC in source regions (Liousse et al. 1996). Cooke et al. (1999) attempted a more detailed estimate based on emission factors and fuel use. However, their total inventory was about half that estimated in Liousse et al. (1996) and underestimated observed OC when used in a model study. The currently estimated range of emissions of OC is 10 to 30 Tg yr^{-1}. Using the measured ratios of BC to OC summarised by Liousse et al. (1996) yields a source strength for fossil fuel BC ranging from 2.3 to 7 Tg C yr^{-1}.

4.3.2.6 *Volatile Organic Compounds*

Volatile organic carbon compounds (VOCs) are emitted into the troposphere from anthropogenic and biogenic sources. Anthropogenic compounds include organics such as alkanes, alkenes, aromatics, and carbonyls, whereas biogenic gases include isoprene, mono- and sesquiterpenes, and a variety of oxygen-containing compounds. Because the volatility of the oxidation products is one of the most important parameters that determines the significance of precursor gases in terms of their particle-forming potential, only hydrocarbons with more than six carbon atoms are considered to contribute to secondary organic particles under atmospheric conditions (Seinfeld and Pandis 1998). Thus, natural secondary organic aerosol (SOA) formation is believed to result mainly from the oxidation of C_{10}- and C_{15}-terpenoids. Based on emission inventories and laboratory data of biogenic VOC particle yields, Andreae and Crutzen (1997) estimated 30 to 270 Tg yr^{-1} for the production of secondary organic particulate matter from natural VOCs. Because the estimated global emissions of anthropogenic VOCs are significantly lower, their contribution to organic particulate matter on a global scale would appear to be small in comparison. However, in the urban atmosphere during severe smog episodes, anthropogenic SOA formation can make a major contribution to fine particulate mass (see Fig. 4.2b). Among the anthropogenic precursor gases, aromatics have been identified to dominate the process of SOA formation; this suggests that anthropogenic SOA formation in an urban air shed can be modelled based on the aromatic content of the complex organic mixture (Odum et al. 1997).

Box 4.3. The CLAW hypothesis

In 1989, Charlson, Lovelock, Andreae and Warren (Charlson et al. 1987) wrote an influential paper that hypothesised about the role that sulphate particles derived from DMS emissions play in climate control. (The hypothesis is called "Claw," after the first initial of each last name.) In order to explain the relatively stable temperature on Earth over geological times, they proposed a negative feedback cycle with the following elements: DMS emission from oceanic phytoplankton are supposed to increase with increasing temperature. The increase in DMS then leads to an increase in the number of non-sea-salt (nss)-sulphate aerosol particles, which were thought to be the main nuclei on which cloud droplets form in the marine boundary layer. At a given liquid water content, more cloud droplets result in an increased reflectivity of the clouds (Twomey 1974). The latter leads to a cooling, counteracting the initial warming.

The CLAW hypothesis linked oceanic biology, atmospheric chemistry, cloud physics, and climate in an elegant way. As such it spurred extensive new atmospheric and biological research and improved understanding of aspects of the biogeochemical cycling of sulphur and its relationship to climate. In particular it promoted the atmospheric aerosol as a possible key player in the climate system through its indirect radiative effect on clouds. In fact, it was the basis of most of the aerosol work initiated and performed within IGAC.

The CLAW hypothesis was criticised early on the grounds that its proposed sensitivity of cloud albedo to sulphur emissions together with anthropogenic sulphur emissions largely in the Northern Hemisphere would result in a much greater interhemispheric contrast in cloud albedo and temperature change than has been observed (Schwartz 1988). The hypothesis was criticised as well on the grounds that the energy requirements for DMS production by marine phytoplankton were inconsistent with the benefits that would be derived by the individual organisms (Caldeira 1989). Nonetheless after 15 years of research the CLAW hypothesis still stands. However, a number of related mechanisms have been proposed that might dampen the effectiveness of the controlling feedback loop, or that at least might help to explain why a relationship between DMS emissions and cloud-forming particles remains elusive. Figure 4.10 summarises the present thinking, indicating some of these mechanisms:

1. Whereas the CLAW hypothesis assumed that the nss-sulphate particles derived from DMS oxidation are the main contributors to cloud condensation nuclei, it is now accepted that some of the nss-sulphate mass in the MBL is internally mixed with sea salt (e.g. Chameides and Stelson 1992; Sievering et al. 1992). In combination with the analysis of individual sea salt particles during ACE-1, this suggests that a significant fraction of the conversion of DMS-derived SO_2 to sulphate occurs on or in sea-salt particles over the oceans and therefore does not lead to new particle production. Several pH-dependent sulphur oxidation pathways in sea-salt particles have been hypothesised that involve either ozone, hydrogen peroxide, halogens, and/or trace metals (see review by Keene et al. 1998). Sulphur oxidation also occurs in the marine stratiform clouds (e.g. Ayers and Larson 1990; Hegg and Larson 1990; O'Dowd et al. 2000), where it is also pH-dependent. Coarse-mode sea-salt particles dry-deposit to the ocean surface relatively quickly (e.g. Slinn and Slinn 1980) and, thus, remove nss-sulphate from the MBL efficiently. This multiphase processing and removal of biogenic sulphur could be an effective shunt that prevents the formation of new sulphate particles by nucleation, for which gas-phase oxidation of SO_2 is prerequisite.
2. In the original CLAW hypothesis all processes that transform DMS into new or better cloud-forming particles were supposed to take place within the marine boundary layer. A key link in this chain of processes was the nucleation of sulphuric acid into new particles and eventually new cloud-forming particles. Box models of the MBL that described these processes depicted in Fig. 4.7 dealing with sea-salt and sulphate particle formation were in better agreement with the observed size distributions only when entrainment of aerosols from the free troposphere was considered as a source of particle number in the MBL (Raes 1995; Katoshevski et al. 1999). Some measurements have been reported of the frequent occurrence in the summer Arctic (Covert et al. 1996b) of large numbers of ultra-fine particles following rain events or subsidence of free tropospheric air (Covert et al. 1992). Other observations indicate that *in situ* nucleation is absent and that entrainment from the free troposphere is the source of MBL particle number concentration (Clarke et al. 1996).
3. An alternative feedback mechanism has been proposed that involves convection in the MBL rather than the active participation of marine phytoplankton (Shaw et al. 1998a). Based on the accepted view that the frequency of occurrence and intensity of convection increases with sea surface temperature, they suggest that such an increase in convection would increase the formation of free tropospheric sulphate particles, which after subsidence and entrainment would interact with the MBL clouds and increase their reflectivity, leading to cooling of the sea surface. It has been estimated that in the upper troposphere, in particular in the Tropics and the midlatitudes of the Southern Hemisphere, up to 100% of the SO_2 might be derived from DMS (Raes et al. 2000b). Hence a mechanism by which changes in the mass and number of free tropospheric sulphate particles result from changes in convective transport of boundary layer DMS into the free troposphere is a possibility.

4.3.3 Formation, Evolution, and Removal of Condensed Material

4.3.3.1 *Nucleation*

4.3.3.1.1 *Laboratory Studies*

Homogeneous nucleation has been investigated in the laboratory for several inorganic and organic chemical systems pertinent to the atmosphere.

The inorganic system that has received the most attention is the binary sulphuric acid-water vapour system. Recent advances include the direct measurements of molecular clustering in the H_2SO_4-H_2O nucleating system (Eisele and Hanson 2000; Hanson and Eisele 2000). Despite reasonable agreement between prediction of binary H_2SO_4 nucleation theory and laboratory experiments (Viisanen and Kulmala 1997), large discrepancies have been reported between this theory and field data. The addition of ammonia (NH_3) was shown to increase nucleation rates dramatically and to reduce the dependence on H_2SO_4 (Ball et al. 1999). These laboratory studies, however, have all been done at sulphuric acid vapour concentrations that are much higher than those measured in the atmosphere.

Several other laboratory studies of multi-component nucleation significant to the atmosphere have been reported. Binary nucleation in the MSA-water system oc-

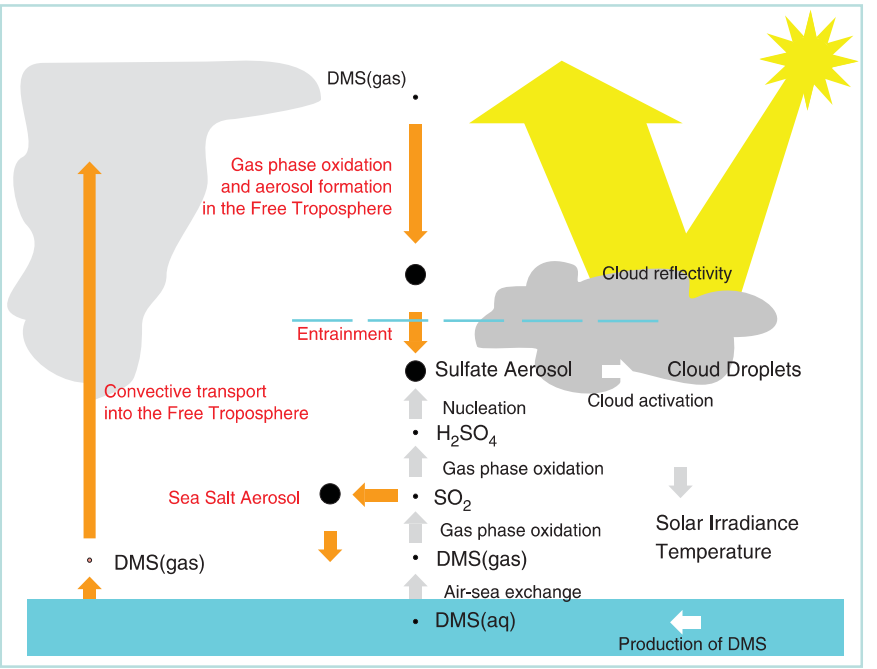


Fig. 4.10.
The original CLAW hypothesis (*in black*) and major additional mechanisms proposed such as: **a** the role of sea-salt; **b** the quenching of nucleation by aerosols entrained from the free troposphere; and **c** the role of convective transport into the free troposphere

curs at partial pressures below those required for either pure species (Kreidenweis et al. 1989). It is unlikely, however, that atmospheric concentrations of MSA are high enough for binary MSA-H_2O nucleation to play an important role. Likewise, it is unlikely that ternary nucleation involving H_2SO_4-MSA-H_2O is important (Van Dingenen and Raes 1993). Recent experiments have shown that multi-component nucleation rates are enhanced even for immiscible substances (Strey and Viisanen 1995).

Recent studies of particle production by ionising radiation (He and Hopke 1995; Kim et al. 1998; Mäkelä 1992) have shown that small ions enhance nucleation rates in systems that are chemically similar to the atmosphere and that NH_3 enhances nucleation rates when SO_2 is irradiated in air containing it and H_2O. Understanding of clustering on small ions is needed to permit quantitative estimates of the importance of ion-induced nucleation in the atmosphere; such studies are proceeding (Yu and Turco 2000).

Data from smog chamber studies of the formation of organic aerosol particles have been analysed to make inferences about homogeneous nucleation (Pandis et al. 1991; Stern et al. 1987; Wang et al. 1992). However, organic precursors typically produce multiple particulate products, and the molecular identity and physical and chemical properties of these products are often unknown. Nevertheless, summary yields and product information can be gained through this approach (Odum et al. 1996).

4.3.3.1.2 *Field Experiments*

Nucleation is often observed during daylight hours in the vicinity of convective clouds in continental (Radke and Hobbs 1991) and marine environments (e.g. Clarke et al. 1998; Hegg et al. 1990). A definitive explanation for this phenomenon is not yet established, but H_2SO_4-H_2O nucleation has most often been invoked (Perry and Hobbs 1994). Atmospheric observations (Weber et al. 1999) suggest that nucleation in cloud outflows often occurs at H_2SO_4 relative acidity (ratio of H_2SO_4 partial pressure to equilibrium vapour pressure) consistent with that predicted by the classical binary theory for H_2SO_4-H_2O nucleation. Hoppel et al. (1994) also observed nucleation near clouds but found difficulties in matching the nucleation to expected production of H_2SO_4. De Felice and Cheng (1998) proposed that numerous smaller particles were produced from residues of rapidly evaporated cloud drops during the process of crystallisation. Leck and Bigg (1999) suggested that nucleation would also result if the cloud residues contained the amino acid L-methionine, derived from primary particles of marine biological origin. In the upper tropical troposphere observations suggest that nucleation is a significant global source of atmospheric particles (Brock et al. 1995; Clarke 1993). Evidence has also been reported for nucleation in the midlatitude upper free troposphere (Schröder and Ström 1997).

Nucleation has been observed occasionally in the cloud-free marine boundary layer (Covert et al. 1992; Clarke et al. 1998), and more frequently during on-shore flow in coastal areas that are exposed at low tide (e.g. O'Dowd et al. 1999).

Nucleation events also have been observed at many different ground-level continental sites (Birmili 1998b; Hörrak et al. 1998; Koutsenogii and Jaenicke 1994; Kulmala et al. 1998). These events typically follow regular diur-

nal patterns, with concentrations of nucleation-mode particles beginning to increase several hours after sunrise, reaching peak concentrations several hours later. The chemical mechanisms of nucleation in these regions have not yet been established, though one possible explanation involves sulphonate clusters (Kulmala et al. 2000).

In summary, a great deal of new insight into the nucleation process has been gained in the past decade. Binary H_2SO_4-H_2O theory may explain a limited number of field observations. When there is a discrepancy, nucleation rates inferred from atmospheric observations are typically higher than those predicted from theory. These findings suggest the presence of stabilising compounds such as ammonia, hydrocarbons, or electrically charged precursors that reduce the dissociation rate of the pre-nucleation molecular clusters. Laboratory studies have provided some support for these speculations. Clearly far more atmospherically relevant studies are needed in this area.

4.3.3.2 *Aerosol Growth through Concentrated Liquid-Phase Chemical Reactions*

Tropospheric aerosol particles are exposed to ubiquitous water vapour. The physical matrix of highly concentrated, or even supersaturated, aqueous electrolyte droplets in air contains a variety of compounds that may be involved in solution-phase aqueous reactions (see, e.g. Zellner and Herrmann 1995). A chemical reaction in a given electrolyte solution could be described correctly if either all activity coefficients involved or the rate constant for the reaction under the given set of conditions (pH, temperature, etc.) were known.

Kinetic salt effects in ion-ion reactions (type 1) can be treated by the Debye-Hückel theory and its extensions (for an overview, see Robinson and Stokes 1959). In reactions involving neutrals only, or one ion and a neutral, a primary kinetic salt effect is also clearly identified (Debye and McAulay 1925; Herrmann and Zellner 1998). This effect (type 2), cannot currently be treated other than by experimental examination of each reaction in each matrix separately.

Equilibrium constants are affected by ionic strength (secondary kinetic salt effect) as they may be viewed as the ratio of two rate constants, both of which are subject to the above primary kinetic salt effects (Harned and Owen 1958; Robinson and Stokes 1959). These effects have been considered in cloud models in the same manner as the type 1 effect for ion-ion reactions (Jacob 1986).

Ionic strength effects may be treated kinetically by the ion pairing approach. Stability constants for ion pairs are available (Högfeldt 1982; Perrin 1979) or may be calculated according to the Fuoss-Eigen equation (Davies 1962). The observed rate constant as a function of ion concentration then results from two parallel elementary reactions coupled by the ion pair formation equilibrium. Such treatment was suggested by Olson and Simonson (1949).

The experimental data set for a more complete description of aerosol chemistry is very sparse. In the case of non-radical reactions, various data sets relating to aqueous sulphur oxidation now exist (Lagrange et al. 1993, 1995, 1999a,b), and modelling the impact of ionic strength effects under tropospheric aerosol conditions should be possible in the near future. Concerning radical reactions, it is striking that even for OH no ionic strength dependency has been measured for a system of relevance in tropospheric aerosol chemistry. This is probably due to the widespread view that ionic strength effects involving one neutral species generally can be neglected. While this is true for the original Debye-Hückel theory in the concentration range for which that theory was derived, electrolyte contents of several mol l^{-1} may change a rate constant for a reaction involving a neutral by about one order of magnitude, as was shown for nitrogen trioxide (NO_3) reactions (Herrmann and Zellner 1998). Recently, ionic strength dependencies have been studied in H-abstraction reactions of chlorine radical anion (Cl_2^-) (Jacobi et al. 1999).

At present, there is no comprehensive tropospheric aerosol model that takes into account the available kinetic data described here. Further systematic laboratory studies are required. Apart from experimental data for single reactions, such studies may also yield correlations which, in the future, may allow the estimation of rate constants at elevated ionic strength in different cases for different electrolyte compositions (e.g. for a marine or continental tropospheric aerosol).

4.3.3.3 *Cloud Processes*

The life cycle of a cloud – its formation, development (both microphysical and chemical), and dissipation – is linked in part to the nature of the aerosol on which the cloud forms. Recent developments have increased knowledge of the underlying processes. The processing of compounds by liquid water droplets influences the chemical composition of the troposphere (e.g. Lelieveld and Crutzen 1991). A proper description of liquid phase chemistry is therefore necessary to assess the role of clouds in a changing atmosphere.

Aerosol scavenging. In most clouds, the fraction of aerosol that is taken up (scavenged) by cloud droplets is less than unity, both in terms of particle number and mass (Leaitch et al. 1992; Noone et al. 1992b). The ability of particles to act as cloud condensation nuclei is dependent on their chemical composition and size. Differ-

ent compounds are scavenged with different efficiencies, either because the particle composition is size dependent, or because of the chemical nature of the substance itself (Facchini et al. 1999; Hallberg et al. 1992). This initial step determines the starting chemical composition of the cloud droplets.

Recent insights into the classical treatment of growth of aerosol particles into cloud droplets have expanded on the classical theory that chemical effects, and not simply particle size, are important factors in droplet formation. Slightly soluble substances (in particular certain organic compounds) may influence droplet surface tension and equilibrium vapour pressure, thus influencing the aerosol scavenging process (Laaksonen et al. 1998; Shulman et al. 1996). Also, this effect has important implications for indirect aerosol radiative forcing (see Sect. 4.3.4.2) by affecting the drop size distribution. Another potential factor that controls the growth of cloud droplets is co-condensation of soluble gases other than water onto aerosol particles. For example, model calculations have indicated that co-condensation of nitric acid (HNO_3) can increase the scavenging efficiency of particles in clouds (Laaksonen et al. 1997). The importance of these effects in the atmosphere has not been demonstrated experimentally.

Aqueous-phase processes. Clouds constitute an efficient reaction medium for chemical transformations. After cloud formation, the composition of the droplets can be modified by the dissolution of soluble gases. Two families of chemical compounds are key participants in cloud liquid-phase chemical reactions: sulphur and organic compounds. The chemistry of oxidised (e.g. NO_x) and reduced (e.g. NH_3) nitrogen compounds is of lesser importance, although their dissolution alters the pH of cloud droplets and thus affects aqueous chemistry.

Sulphur oxidation reactions occur in clouds at a much faster rate than in the clear air. Model calculations (Langner and Rodhe 1991) have shown that, on a global scale, tropospheric in-cloud SO_2 oxidation is from two to five times more important than out-of-cloud oxidation. Laboratory studies have identified the most likely reactions responsible for sulphur oxidation in the atmospheric liquid phase and in determining the associated rate coefficients (Warneck 1991).

Very little is known about atmospheric aqueous phase chemistry of organic compounds. In current box models, the description of organic chemistry in cloud water is limited to dissolved C_1 and C_2 compounds (Herrmann et al. 1999). Recent work has shown that cloud-forming particles contain a high percentage of soluble organic compounds (Facchini et al. 1999; Noone et al. 2000; Saxena and Hildemann 1996; Zappoli et al. 1999).

A further complication concerning cloud chemical processes derives from the size-dependence of cloud droplet chemical composition (Ogren and Charlson 1992). Because the concentration and composition of cloud droplets are not uniform, the transfer of gases into the droplets will depend on droplet size (Twohy et al. 1989). Model results (Hegg and Larson 1990; Pandis et al. 1990) have also shown the importance of size-dependent cloud droplet chemistry, demonstrating that use of bulk cloud water parameters can lead to substantial errors in description of processes taking place within individual cloud droplets.

Box 4.4. The utility of the cloud condensation nucleus (CCN) concept

The concept of CCN has been accepted by the cloud physics community, and by most of the aerosol research community, for many decades. Its attractiveness stems partly from the pioneering work of Twomey (1959), who introduced measured supersaturation spectra of droplets into cloud modelling. Visualising a distinct subset of the very complex atmospheric aerosol as a well-defined and measurable quantity, sufficient for a description of the interaction of particles and clouds, is another factor contributing to the attractiveness and the wide application of the CCN concept.

However, there are over-simplifications inherent in this concept that become increasingly difficult to justify with the rapidly advancing experimental and modelling capabilities of atmospheric aerosol research. The concept or definition of CCN is at best operational because any quantification of CCN with existing instrumentation is strongly dependent on the thermodynamic evolution forced upon an aerosol sample in any particular CCN counter (Nenes et al. 2001). An intrinsic problem is that the thermodynamic evolution occurring in any experimental CCN device bears rather little resemblance to the condensational growth that happens in any real cloud. Most CCN counters have not been characterised sufficiently to justify meaningful connection of their results to droplet growth in real clouds (Nenes et al. 2001). Many physical and chemical factors contribute to the subset of the total particle population that evolves into a cloud droplet population. Even certain soluble gases can strongly affect the growth of cloud elements (Kulmala et al. 1993).

Additionally, the concentration of CCN at a particular supersaturation is not necessarily applicable to the prediction of cloud droplet concentration. Even the generally accepted hypothesis that an increase in concentration of CCN leads to an increase in cloud droplet concentration is not necessarily correct, particularly in a mixed population of CCN (Feingold and Kreidenweis 2000). For example, an enhancement in CCN concentration measured at 0.2% supersaturation, typical of stratocumulus clouds, suggests a similar increase in cloud droplet concentration within this cloud type. However, if the additional CCN are activated at supersaturations considerably lower than 0.2%, the resulting depletion of water vapour and suppression of the peak supersaturation in a real cloud can inhibit activation of a significant fraction of the CCN population. This results in a reduction in the number of cloud drops (O'Dowd et al. 1999).

Avenues of research that may resolve the CCN issue include more detailed experimental studies of the condensational growth properties of size-resolved atmospheric particles, providing parameterisations for cloud models and cloud simulation experiments with more realistic flow-through cloud simulators.

Cloud dissipation. Upon evaporation, gases and particles contained in the droplets are released back to the cloud-free atmosphere. The residual particles are likely to be quite different (physically and chemically) from those that entered the cloud because of in-cloud processes. Field observations and modelling results have shown that sulphate size distributions before and after passage through a cloud differ significantly, with much larger concentrations in the outflows of the cloud systems (Bower et al. 1997; Hoppel et al. 1986; Laj et al. 1997; Wiedensohler et al. 1997). The effects of multiple cloud passages on cloud-processed particles have important implications for direct aerosol radiative forcing (see Sect. 4.3.4.1) by increasing the efficiency of light scattering due to in-cloud particle growth (Yuskiewicz et al. 1999).

4.3.3.4 *Aerosol Deposition Processes*

Wet deposition and dry deposition are important removal pathways for suspended particulate matter. As such they act as key determinants of the residence times and concentrations of tropospheric aerosol particles.

Aerosol deposition processes often involve multistage pathways and can include interactions with gases. This is especially true for wet deposition, which often occurs through a complex interaction involving various combinations of sorption, dissolution, particle capture, aqueous reaction, precipitation formation, and precipitation delivery. Dry deposition processes, while not so multi-faceted in nature, nevertheless can be complicated by condensational particle growth in humidity gradients.

The level of scientific effort in deposition research during the past ten years, while appreciable, was significantly less than corresponding efforts during the 1970s and 1980s. As a consequence, some of the older reviews of dry deposition (e.g. Hicks et al. 1990) and wet deposition (e.g. Hales 1990) still provide useful and relatively up-to-date synopses. Some of the more significant advances during the past decade are summarised below.

4.3.3.4.1 *Dry Deposition*

Wesely and Hicks (2000) present a review of recent dry deposition research which, combined with Hicks et al. (1990), provides an up-to-date summary of scientific understanding in this field. Brook et al. (1999a) review past measurements of deposition velocities and model results. Recent scientific progress in this area has been limited by complexities in four main areas, described below:

Measurement. Air-surface exchange fluxes to and from natural surfaces are exceedingly difficult to measure. This has resulted in a profusion of (relatively) direct as well as indirect surrogate and inferential measurement methods (Wesely and Hicks 2000). Techniques such as eddy correlation, eddy accumulation, and profile methods directed toward measuring Reynolds fluxes (i.e. those associated with turbulent transport) are generally favoured for gas flux measurement when practicable, but require monitoring equipment that has fast time response, high precision, or both. Such methods are applicable for measuring fine particle fluxes as well, but they are inappropriate for larger particles, whose gravitational settling rates contribute significantly to the total deposition flux. Much of the advance in air-surface gas exchange measurement during the past decade derives from the advent of newer, fast-response instrumentation, which allows Reynolds-flux measurement for a number of additional gases and particles (Gallagher et al. 1997; Shaw et al. 1998).

Conceptual microscale model development. Most recent development involved an extension of the traditional resistance analogy (see Chap. 2) through more detailed description of the micrometeorological and deposition processes within complex canopies, such as forests and croplands. Although founded on simple concepts that sometimes do not conform with actual two-way exchange processes, such conceptual models often involve considerable complexity.

Large-scale parameterisations. Significant advances have occurred in dry deposition parameterisation for large-scale CTMs during the past ten years through extension of traditional procedures (Brook et al. 1999b) as well as the employment of satellite land-use mapping (Gao and Wesely 1995a,b).

Advanced monitoring and field studies. Resulting in part from the advent of the newer instrumentation noted above, a number of advanced field studies have been conducted, which have contributed significantly to the general understanding of dry deposition rates and processes. The comprehensive investigation of dry deposition in the Speulder forest in the central Netherlands is a prime example of such efforts (Erisman et al. 1997 and companion articles in that issue).

4.3.3.4.2 *Wet Deposition*

Some of the more recent scientific advances in understanding wet deposition and precipitation scavenging have been associated with large, multi-participant efforts. Examples include the European Ground-Based Cloud Experiments (Fuzzi et al. 1992; Wobrock et al. 1994) and the High Alpine Aerosol and Snow Chemistry Study (Nickus et al. 1997).

Major features of the precipitation scavenging sequence were understood scientifically by the close of the 1980s. Because of this, advances since that time can be considered either as mechanistic extensions to ex-

isting theory or to composite modelling of the scavenging phenomenon. Particularly important advances have been made in the areas of aqueous-phase chemistry, aerosol cloud interactions, and composite modelling. Some of the advances in key categories during the past decade are summarised below.

Aqueous-phase chemistry. Jacob (2000) presents a review of progress in aqueous-phase chemical processes of importance to scavenging. Much of the more recent advance in this area pertains to the behaviour of in-cloud odd hydrogen (HO_x) chemistry. Aqueous reactions of a number of trace substances (e.g. sulphur and nitrogen oxides, soluble organics) are believed to be linked closely with this oxidant chemistry.

Aerosols and cloud formation. During the past decade a number of field, laboratory, and theoretical studies has evaluated cloud formation from mixed aerosol particles in competitive environments as functions of particle size, composition, and saturation conditions. These studies are particularly important because they can elucidate relative efficiencies for the scavenging of specific aerosol particle classes as functions of storm type and intensity. Several examples of field measurements of related phenomena appear in references associated with the multi-participant studies cited above.

Composite modelling. Although several global and regional models of the 1990s have incorporated increasingly complex representations of wet chemistry and precipitation scavenging (e.g. Rasch et al. 2000), the results of these efforts shed comparatively little light on physical and chemical mechanisms of the scavenging process. On the other hand, a number of mesoscale modelling efforts have been undertaken during the past decade that may provide valuable mechanistic insights, especially when linked with modern field studies. The study of Voisin et al. (2000) provides a recent example of such an effort.

4.3.4 Effects of the Aerosol on Radiation in the Atmosphere

Aerosols influence Earth's radiative balance both directly and indirectly, through their influence on cloud properties. The magnitude and sign of their influences are variable, and the controlling properties and processes behind the radiative effects are presently not well understood. Understanding these controlling properties and processes, and quantifying the influence of aerosols on the radiative balance of Earth, is expected to be a major component of aerosol research in the next decade. Aerosols also affect the actinic flux and, as such, photochemistry.

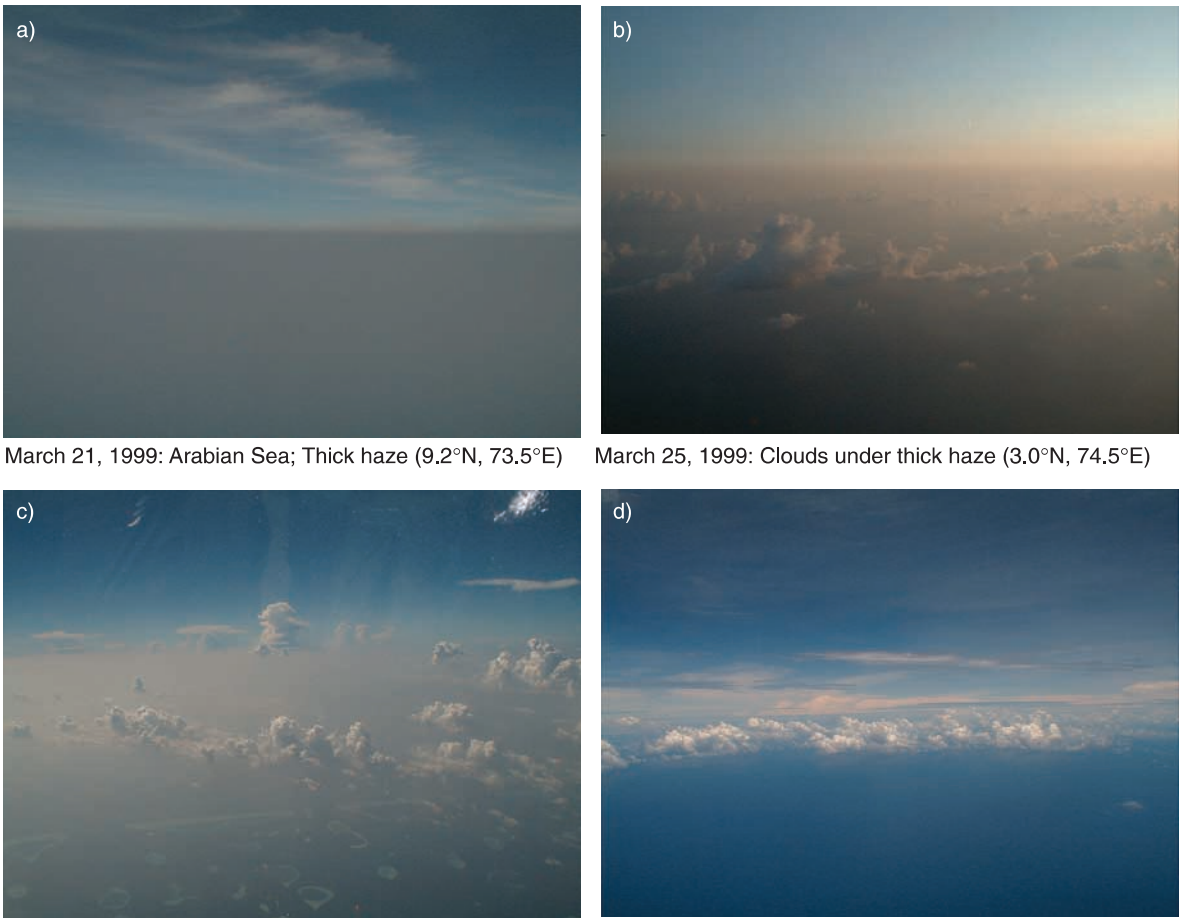
4.3.4.1 *Direct Radiative Effects*

Aerosol particles both scatter and absorb incoming solar radiation, effects that are visible to the naked eye. Figure 4.11a–c shows examples of visibility reductions over the Arabian Sea and Indian Ocean caused by transport of pollution from the Indian sub-continent. Figure 4.11d shows an almost pristine atmosphere south of the Inter-tropical Convergence Zone.

If incoming radiation is scattered back to space, the energy contained in the scattered photons is lost from the system. In this case, aerosols would exert a net cooling effect on the Earth system. If the incoming radiation is absorbed in an aerosol layer above Earth's surface, the energy contained in the absorbed photons is transformed to heat, and can result in a warming of the absorbing layer. This backscattering and absorption in the atmosphere can reduce the amount of solar energy available at the surface for biological processes.

The mass scattering efficiency (scattering coefficient per mass concentration of aerosol) is strongly dependent on wavelength and particle size, reaching a maximum for particle diameter near the wavelength of the light. For radiation near the centre of the visible spectrum (0.53 μm) this maximum occurs at $D_p \approx 0.5$ μm for ammonium sulphate aerosol with value ca. 9 m^2 (g SO_4^{2-})$^{-1}$, and with the most efficient size range for scattering between particle diameters of about 0.1 and 1.0 μm (Ouimette and Flagan 1982; Nemesure et al. 1995; Schwartz 1996). Scattering can be reasonably accurately apportioned among the various chemical constituents that make up the atmospheric aerosol (White 1986; Sloane 1983; Zhang et al. 1994b; McInnes et al. 1998). The particular component that dominates scattering depends on location, time, and other factors.

Sulphate particles have received the most attention in assessing the direct radiative effects of aerosols (Charlson et al. 1990, 1992), but other chemical components are also important. Over the oceans, sea salt can contribute substantially to the total aerosol optical depth. Using sea salt distributions from a chemical transport model and similar mass scattering efficiencies, Tegen (1999) estimated an 87% relative contribution from sea salt in the 20° S to 20° N latitude band at 140° W, a 57% contribution for the world's oceans, and a 44% contribution to the global aerosol optical depth. Similarly, based on a comparison of clear-sky, top-of-the-atmosphere solar irradiances observed by the Earth Radiation Budget Experiment with those calculated from a general circulation model, Haywood et al. (1999) reported that sea salt is the leading particulate contributor to the global mean clear sky radiation balance over oceans. Organic aerosols can also be a significant contributor to particulate scattering. For example, from aircraft flights off the east coast of the U.S., Hegg et al. (1997)



March 21, 1999: Arabian Sea; Thick haze (9.2°N, 73.5°E)

March 25, 1999: Clouds under thick haze (3.0°N, 74.5°E)

February 24, 1999: Just north of ITCZ
Haze extends up to top of CU (0.5°N, 73.3°E)

March 24, 1999: Just south of ITCZ
Almost pristine clouds (7.5°N, 73.5°E)

Fig. 4.11. Aerosols and clouds as observed during the INDOEX experiment. **a** Arabian Sea, thick haze; **b** Indian Ocean, clouds under thick haze; **c** Indian Ocean just north of the ITCZ, haze extends up to the top of cumulus clouds; and **d** Indian Ocean south of ITCZ, almost pristine clouds (photographs from Center for Clouds, Chemistry and Climate, Scripps Institution of Oceanography, USA)

showed that organic particulate matter accounted for a substantial fraction of aerosol light scattering. Mineral dust also exerts a large influence on the radiative balance (e.g. Sokolik and Toon 1996).

Radiative forcing, defined as the change in the radiative fluxes at the top of the troposphere or top of the model domain due to a given aerosol component, has been calculated for a variety of particle distributions and emission scenarios. The most recent summary of forcing results is given by the Intergovernmental Panel on Climate Change (IPCC 2001); see Fig. 1.7. The wide range of values for the calculated global direct radiative forcing of aerosols clearly shows that more information is needed to constrain this forcing. Key information needs are: (*1*) the mass loading and geographical distribution of the aerosol; (*2*) the chemical components of the aerosol, their state of mixing in the atmosphere, their relative contributions to light scattering and absorption, and their response to varying relative humidities; and (*3*) a better understanding of the cycles of the various substances that make up the aerosol. The large uncertainty in direct aerosol forcing limits quantitative estimates of climate response to forcing over the industrial period.

4.3.4.2 *Indirect Effects*

The indirect aerosol effect refers to potential changes of cloud properties at the global scale due to anthropogenic perturbations of the concentrations and physical and chemical properties of the particles that form cloud drops or ice crystals. This indirect aerosol effect is presently the most uncertain of the known forcing mechanisms in the prediction of climate change over the industrial period (see Fig. 1.7). Bridging the scales involved is one of the major challenges in understanding and predicting the indirect radiative effect of aerosols. While the effect itself is global, the processes causing it occur on spatial scales as small as micrometers and temporal scales as short as seconds. Thus, the global-scale phenomenon

cannot be understood and predicted quantitatively without adequate understanding of the microscale processes.

The basis of the indirect effect is a link that was established by Twomey (1974) between aerosol properties, cloud droplet concentrations, and cloud albedo. For a given cloud liquid water content and cloud depth, Twomey showed that an increase in aerosol particle number concentration could lead to an increase in cloud droplet number concentration, which would cause an increase in cloud albedo. The increase in cloud albedo would lead to cooling and partially counteract the warming due to greenhouse gases (Slingo 1990). The main contribution to the indirect effect is thought to come from marine stratocumulus clouds (Randall et al. 1984). However, cirrus clouds may also be influenced by anthropogenic aerosols, but for the cirrus case not even the sign of the global radiative effect is known. Additional feedback mechanisms potentially responsible for the uncertainty in the prediction of the indirect effect include increases in cloud cover with increasing global temperature (Arking 1991), reduction of the precipitation efficiency of clouds causing an increase in their lifetime or extent (Albrecht 1989), coupling between diabatic processes and cloud dynamics (e.g. Pincus and Baker 1994), and the radiative effect of in-cloud absorption on short wave radiation (Boers and Mitchell 1994).

A number of experiments have been carried to understand better the aerosol-cloud interactions responsible for the indirect radiative effect. Ship tracks in marine stratocumulus clouds have been used as a natural laboratory to understand better how anthropogenic aerosol emissions cause observable increases in cloud albedo (Durkee et al. 2000b; Ferek et al. 1998; King et al. 1993; Radke et al. 1989). In another approach, Brenguier et al. (2000) observed marine stratocumulus clouds during the second Aerosol Characterisation Experiment (ACE-2). In these studies, simultaneous *in situ* measurements of cloud microphysical properties and remote sensing of the cloud radiances in the visible and near-infrared provided direct evidence of changes in cloud radiative properties related to changes in the input aerosol. Drizzle suppression has also been observed in clouds influenced by anthropogenic aerosols, through both *in situ* measurements (Ferek et al. 2000) and satellite observations (Rosenfeld 2000).

Anthropogenic effects on cirrus cloud radiative properties have also been investigated in recent years, particularly in terms of the effects of aircraft emissions on cirrus cloud properties. Wyser and Ström (1998) showed that the balance between short-wave cooling and long-wave heating effects of cirrus clouds could be very sensitive to changes in crystal size caused by aerosol emissions from aircraft. Several recent research programmes have been aimed specifically at assessing the effects of aircraft emissions on cirrus cloud properties (Brasseur et al. 1998a; Schumann et al. 2000; Toon and Miake-Lye 1998).

Detecting large-scale changes in cloud properties from satellites has proven to be challenging. For example, Han et al. (1994) showed that effective radius in warm ($T > 273$ K) continental clouds was on average two to three μm smaller than that in marine clouds. They also showed that droplet radii are about one μm smaller in marine clouds of the Northern Hemisphere than in those of the Southern Hemisphere. Likewise, fairly strong spatial correlations have been reported of monthly mean aerosol optical depth and number concentration with effective radius (negative correlation) and optical depth (positive correlation) of low clouds, all of which would be consistent with the Twomey effect (Wetzel and Stowe 1999; Nakajima et al. 2001). However, the expected enhancement of cloud albedo due to the Twomey effect has not been identified in interhemispheric comparisons (Schwartz 1988; Han et al. 1998). Likewise, examination for aerosol enhancement of monthly mean cloud albedo as a function of distance from continents has been negative (Falkowski et al. 1992) or has shown only marginal indication of enhancement (Kim and Cess 1993). Evidence has been presented of enhanced reflectivity of marine stratocumulus clouds in the vicinity of copper smelters in Peru under conditions of offshore flow (Kuang and Yung 2000). Indications of the indirect effect were also presented by Rosenfeld and Lensky (1998), who analysed AVHRR satellite images of cumulus and derived the cloud top temperature and effective radius. Variations of the relationship between those two parameters were interpreted as a sign of changes in cloud radiative properties due to continental pollution.

Several global-scale model studies have been undertaken to explore the consequences of anthropogenic aerosol emissions on cloud radiative properties. While the parameterisations used in the models are limited by an incomplete understanding of the processes involved and by a lack of data on nearly all scales, the results as summarised by Penner et al. (2002) and Ramaswamy et al. (2001) indicate that the indirect effect may be very important (see Fig. 1.7).

The relationship between radiative forcing and climate response was examined for a wide range of artificial perturbations by Hansen et al. (1997b). The direct and indirect climate effects of anthropogenic sulphate were examined for equilibrium and transient responses to anthropogenic sulphate, and with prescribed or interactively calculated forcing. Tegen and Miller (1998) calculated the climate effect of mineral dust interactively in an equilibrium simulation. Climate models exhibit wide scatter in the climate sensitivity (defined as the ratio of the change in the global mean surface air temperature to the global mean radiative forcing). Factors causing this scatter include uncertainties in the distribution and the optical properties of aerosol particles and differences in approaches to treating cloud physical proc-

esses and in the assumed optical properties of clouds (e.g. Cess et al. 1996). In view of the many uncertainties associated with understanding and describing aerosol sources and processes and with their parameterisation, such forcing and the ensuing climate responses simulated by models must be considered tentative.

4.3.4.3 *Aerosol Effects on Actinic Flux*

Solar radiation, especially in the ultraviolet (UV) range, drives tropospheric photochemistry. The presence of tropospheric aerosols results in additional scattering and absorption of UV radiation and, hence, affects photolysis rates. Several recent studies have pointed out that aerosol particles might strongly perturb the formation of ozone and other trace gases in the lower atmosphere (Dickerson et al. 1997). For example, for given meteorological conditions and levels of photochemically active gases, ozone production is sensitive to the aerosol burden and optical properties. Strong UV-absorbing particles (such as soot and mineral dust) cause a decrease in photolysis rates, which, in turn, inhibits ozone production. The presence of purely scattering particles (such as sulphate) or clouds in the boundary layer can increase photolysis rates there and above cloud tops, which enhances ozone production aloft (He and Carmichael 1999). However, near-ground photolysis rates can decrease as particle concentrations increase. Because the distributions of tropospheric aerosols and clouds are highly variable in space and time, the quantification of the effects of the aerosol on photochemical processes remains a challenging problem.

4.3.5 Effects of Aerosols on Atmospheric Photochemistry

Aerosol particles can affect atmospheric photochemistry by changing the actinic UV flux (see Sect. 4.3.4.3), or more directly by acting as sinks or sources of reactive trace gases (Ravishankara and Longfellow 1999). Aerosol growth due to reactions in deliquescent particles at very high relative humidities has already been discussed (Sect. 4.3.3.2). Here we focus on heterogeneous reactions at lower relative humidities and/or on insoluble particulate matter. A textbook example is the hydrolysis of N_2O_5 on particles, which affects the oxidising capacity of the troposphere via the atmospheric residence time of NO_x. The process was shown to be important on a global scale by Dentener and Crutzen (1993) who assumed in their model calculations that the hydrolysis rate is first order in $[N_2O_5]$ and proportional to the surface area of the particulate matter, times a constant reactive uptake coefficient, γ. A value of $\gamma = 0.1$ was used in the base case calculations. More recent aerosol chamber studies yielded significantly lower uptake coefficients, which also depended on the nitrate activity of deliquescent aerosol particles (Mentel et al. 1999).

Considerable attention has been paid to reactions of oxidising species with soot particles from fossil fuel combustion. Several studies yielded relatively large values of γ for the decomposition of ozone on soot (Rogaski et al. 1997) which indicated that ozone destruction on aircraft soot may be significant (Bekki 1997). However, chamber studies yielded much lower time- and concentration-dependent values of γ, implying a complex reaction mechanism which eventually leads to surface passivation (Kamm et al. 1999).

The reduction of HNO_3 and/or NO_2 on soot was also studied in several laboratories, and surprisingly large values of γ were obtained (Rogaski et al. 1997). The latter reaction was found to produce HONO as a by-product (Kalberer et al. 1999), which is a photochemical source of OH in polluted atmospheres. However, simple thermodynamic considerations imply that neither NO_2 nor HNO_3 can be reduced on soot at a constant rate, because some reducing functionalities must be consumed in the process. This was confirmed by a recent aerosol chamber study which yielded much lower upper limits for the time-averaged reactive uptake coefficients of NO_2, HNO_3, and several other oxidising species on soot particles (Saathoff et al. 2001). Multi-day model calculations assuming a large mass concentration of soot particles resulted in up to 10% lower ozone maxima on the second day when the whole set of heterogeneous reactions was included. The reduction was mainly due to the loss of HO_2 on soot, for which $\gamma \leq 10^{-2}$ had been determined. More accurate measurements of $\gamma(HO_2)$ are needed to prove or disprove this result.

Trace gas-soot interactions are comparable to reactions with large polycyclic aromatic hydrocarbons. The oxidation by ozone of benzo-(a)-pyrene adsorbed on soot aerosol has recently been studied in an aerosol flow tube (Pöschl et al. 2001). The surface reaction with the adsorbate is preceded by the reversible adsorption of ozone on soot. The reaction rate decreases in humid air because of competition between water vapour and ozone for adsorption sites. Kirchner et al. (2000) reported that reactions of NO_2 and HNO_3 with soot induce permanent changes in the IR spectra of the particles, confirming the analogy with PAH reactions. They measured concentration- and time-dependent values of γ, which were limited by surface saturation, in good agreement with Kalberer et al. (1999), who observed saturation-limited NO_2-to-HONO conversion on soot particles. Clearly, the assumption that "initial" uptake coefficients, determined under idealised laboratory conditions, can be used to calculate reaction rates on aerosol particles un-

der realistic atmospheric conditions is not justified in general.

The role of mineral particles as a reactive surface in the global troposphere was pointed out by Dentener et al. (1996). Recent laboratory investigations (Hanisch and Crowley 2001) yielded very large slightly humidity-dependent uptake coefficients for HNO_3 on $CaCO_3$ and on authentic samples of desert dust. The release of CO_2 confirms that carbonates are converted to nitrates, thereby changing the hygroscopic properties of the dust.

Sea salt particles are a potential source of photochemically active halogen compounds. It is now quite clear that bromine atoms are involved in polar tropospheric ozone destruction during springtime. Large tropospheric BrO-clouds have been observed by satellite in polar regions of both hemispheres while ozone destruction occurred (Richter et al. 2001). Details of the complex chemistry of sea salt activation have recently been reviewed (De Haan et al. 1999), but further work is needed to understand better the halogen source related to the sea salt aerosol.

In summary, there is now overwhelming evidence that aerosol particles can act as sources and sinks of reactive species in the gas phase. It is, however, important to note that reactions on particles not only impact on gas-phase photochemistry, but also change the bulk and/or surface chemical composition of particulate matter, with important consequences for their hygroscopic and optical properties.

4.3.6 Aerosols and Health

Although aerosol studies within IGAC primarily looked at aerosol effects on radiation and chemistry, it should not be forgotten that a major driver of aerosol research has been their effect on human health. It has been shown that cardio-pulmonary diseases and mortality are related to the presence of particulate matter (e.g. Dockery et al. 1993). Significant correlations have been established between mortality and the levels of PM10 (i.e. the mass concentration of particles with aerodynamic diameters less than 10 μm) and PM2.5 (mass concentration below 2.5 μm); see Table 1.3. As yet, no mechanism is known that relates specific chemical or physical characteristics of the particles to their effects on health. The fact that PM2.5 has a larger effect than PM10 may be explained by the fact that the PM2.5 fraction contains most of the combustion-derived and most soluble particles, or alternatively may be due to the greater depth of penetration of small particles into the lungs. Clearly, the advanced methodologies developed for IGAC experiments and the aerosol characteristics derived in these experiments will be useful for the understanding of aerosol effects on health.

4.4 Research Approaches

4.4.1 *In situ* Observations with Intensive Campaigns

To a great extent the progress in atmospheric aerosol research during the past decade can be attributed to a change in the way aerosol measurements and chemical atmospheric measurements in general are being conducted. Investigators and funding agencies recognised that meaningful progress in understanding atmospheric aerosol properties and processes requires a large number of measurement capabilities to be brought to bear simultaneously. This research strategy results in over-determined data sets that can be used in closure studies (e.g. Ogren 1995; Quinn et al. 1996a), which can summarise critically and quantitatively the state of knowledge about characteristics, processes, and effects of the atmospheric aerosol. This approach has been used successfully during several large, international campaigns (e.g. ACE-1, Bates et al. 1998; Bates 1999; TARFOX, Russell et al. 1999; and ACE-2, Raes et al. 2000a).

A second and related advance in the past decade has been the conduct of aerosol investigations over large areas (thousands of square kilometres or more) in order to capture significant aerosol processes that take place over such geographical scales. These studies require major resources – ships, aircraft, and surface stations, as well as large numbers of investigators and specialised instruments – that often exceed the capabilities of any single agency or even a whole country. With such resources it has been possible to conduct Lagrangian experiments, wherein an air parcel is identified and followed as it is transported. This strategy has been employed in several large-scale experiments (e.g. ASTEX-MAGE, Huebert et al. 1996; ACE-1, Bates et al. 1998; Bates 1999; ACE-2, Raes et al. 2000a; and INDOEX, Satheesh and Ramanathan 2000) and has yielded process information less confounded by effects of advection.

Large-scale projects also require the active participation of meteorologists and modellers who can provide descriptions of the transport fields that are necessary for the interpretation of the observations. Mathematical models are the integrator of understanding of atmospheric processes, and field data analyses are now being carried out hand-in-hand with model implementation and evaluation. Moreover, some models are being used prior to the field experiment in the design of the best possible measurement strategy. Recently, modelling in forecast mode has begun to aid the day-to-day planning of aircraft missions during large campaigns. The increasing interaction of experimentalists, modellers, and meteorologists is a third major advance in the past decade that is helping to advance understanding of aerosol processes.

A fourth related advance, and a major research strategy in large international experiments, has been the open sharing of data among research participants and with the broader research community, which greatly enhances the utilisation and value of the data. Similarly, much of the ability of meteorologists to contribute to these studies relies on the availability of synoptic-scale meteorological data from the operational weather forecasting community.

Quality control of the host of particle instruments remains a crucial problem that limits the gains of these large experiments as compared to focussed small scale process studies. In particular, there are no generally accepted sampling specifications for atmospheric aerosols, neither concerning the range of sampled sizes nor concerning the thermodynamic state of the aerosol. Also, for crucial particle properties such as carbonaceous matter or light absorption there are no internationally established reference methods and standards for calibration.

4.4.2 *In situ* Observations Using Long-Term Monitoring Networks

Although large, intensive projects such as ACE-1 and ACE-2 can contribute much to the understanding of aerosol characteristics and the underlying processes, they are not sufficient to produce needed aerosol climatologies. A major factor limiting the extent and quality of present aerosol climatologies is the rarity of well-defined and calibrated aerosol monitoring programmes. The successful networks operated by the University of Miami (Florida, USA) until the mid 1990s (e.g. Prospero 1996; Prospero et al. 1983; Saltzman et al. 1986) provided a unique record of aerosol chemistry properties in the marine environment. NOAA-CMDL has records of aerosol physical properties dating from the 1970s at its baseline stations, but only limited aerosol chemistry data (Bodhaine 1989; Bodhaine and DeLuisi 1985; Bodhaine et al. 1986). Other noteworthy data sets exist for a few individual stations. Examples include Cape Grim, Tasmania (Ayers et al. 1991, 1995; Gras 1995); Jungfraujoch, Switzerland (Baltensperger et al. 1997; Weingartner et al. 1999); Hohenpeissenberg, Germany (Fricke et al. 1997); Spitsbergen, Norway (Heintzenberg and Leck 1994); and Alert (Ellesemere Island, Canada) (Sirois and Barrie 1999). In addition, regional acid deposition networks such as EMEP in Europe (*http://www.nilu.no/projects/ccc/emepdata.html*), CAPMon (Canadian Air and Precipitation Monitoring Network), NAPAP (U.S. National Acid Precipitation Assessment Program) and CaSTNET (Clean Air Status & Trends Network) (*http://www.epa.gov/castnet/data.html*), and air pollution networks such as IMPROVE (*http://vista.cira.colostate.edu/IMPROVE*), make selective measurements of aerosol properties. Because the primary purpose of these networks, however, is not aerosol characterisation, the resulting data are not always appropriate for aerosol climatological use.

For lack of suitable methodology and local scientific capacity, the initial global aerosol monitoring programmes designed by WMO (1993) has been of somewhat limited value so far. This programmes had initially adopted a design philosophy restricted to monitoring stable long-lived trace gases. However, there are renewed efforts to extend the Global Atmosphere Watch (GAW) programmes to detailed aerosol measurements (GAW 1994) and the World Data Centre for Aerosols (*http://www.ei.jrc.it/wdca/*) has made progress in constructing an archive of existing data. The latter has been used in the IGAC-WCRP intercomparison and validation study of global CTMs of the sulphur cycle (Barrie et al. 2000).

4.4.3 Remote Sensing of Aerosols

Although much aerosol research has traditionally focussed on *in situ* measurements, a major exception has been remote sensing by sun photometry. Networks of well-calibrated instruments capable of measuring aerosol optical thickness with high accuracy have been initiated over the past decade (e.g. AERONET; Holben et al. 1998). The availability of such data on the web greatly enhances their utility both in developing aerosol climatologies and in evaluating models.

Surface-based lidars are starting to be employed in networks, and limited experience thus far shows that they can probe aerosols and provide useful microphysical information with vertical resolutions of a few hundred meters.

An increasingly valuable source of data to the aerosol research community is satellite-borne instruments. Most data so far have come from passive instruments such as radiometers; often the aerosol signal is obtained as a residual after subtraction of other known or assumed contributions; and products, such as aerosol optical thickness, are somewhat dependent on assumptions (Kaufman et al. 1997a and papers in that issue; Wagener et al. 1997; King et al. 1999). Active devices such as satellite-borne lidars and the combination of radiometers and radars on the same satellite hold great promise for the future (see Chap. 5).

4.4.4 Aerosol Modelling

The need to address with models questions ranging from local and regional air pollution to the direct and indirect radiative influence of aerosols on a global scale is placing increasing demands on the aerosol modelling community (see also Chap. 6). Most work to date has focussed on particulate mass of a single substance, ig-

noring the dynamics governing its size distribution. This is a major shortcoming given the strong influence of particle size on aerosol radiative properties (Nemesure et al. 1995; Schwartz 1996; Boucher et al. 1998) and on cloud microphysical influences (Pruppadcher and Klett 1980; Schwartz and Slingo 1996).

Likewise, from the perspective of developing strategies to control local and regional particulate air pollution, it is necessary to develop model-based representations of the processes responsible for aerosol burdens that can confidently relate these burdens to sources of particulate matter and to other controlling variables. Several global-scale models have represented mass concentrations of some key aerosol constituents, e.g. sulphate (Langner and Rodhe 1991; Pham et al. 1995; Chin and Jacob 1996; Chuang et al. 1997; Feichter et al. 1997; van Dorland et al. 1997; Graf et al. 1997; Lelieveld et al. 1997; Restad et al. 1998; Lohmann et al. 1999a; Barth et al. 2000; Rasch et al. 2000); nitrate (van Dorland et al. 1997); and organic and elemental carbon (Liousse et al. 1996; Cooke and Wilson 1996; Cooke et al. 1999; Penner et al. 1998b). Sectional models for a range of particle sizes have been used for (Gong et al. 1997a,b; Tegen et al. 1997) and soil dust (Tegen and Fung 1994); these models are essentially models for the mass of each of the several sections, as there is no dynamical evolution of these materials. Accuracies of these models are generally evaluated by comparison with monthly mean or annual measurements at surface stations. Often agreement is within a factor of 1.5 to 2 in such comparisons, but occasionally much worse. Comparison is occasionally made with aircraft flights, for which agreement is generally less. At the sub-hemispheric scale, for a model driven by observationally derived meteorological data, it has been possible to make comparisons for specific dates; measured and modelled daily-average mass concentrations of sulphate typically agree within a factor of two but with numerous outliers (Benkovitz and Schwartz 1997).

Considerable effort is now being directed toward developing models that explicitly represent aerosol microphysical processes to gain predictive capability of aerosol particle size and size-distributed composition. Approaches to this size-resolved modelling include explicit representation of the size distribution (Meng et al. 1998); modelling the evolution of the amount, peak radius, and standard deviation of each of several aerosol modes (Schulz, et al. 1998); and, modelling the evolution of the moments of the size distribution, from which aerosol physical properties can be calculated (McGraw 1997; Wright et al. 2000; Wright 2000). In view of the still limited understanding of many of the processes that must be represented in the models, it is clear that much effort must be directed to enhance understanding before these processes can be represented realistically.

A major objective of global-scale aerosol modelling is evaluation of aerosol influences on climate at present, over the industrial period, and for the future, for various assumed emission scenarios. Three types of evaluations may be distinguished. Until recently, assessments of aerosol influences on climate have used temporally-averaged aerosol fields calculated in transport-transformation models that are run separately from the radiation transfer model used to assess the climate influence; that is, the aerosol field is calculated off line. This approach may misrepresent key features of aerosol-climate interactions, for example, by not capturing correlations between particulate concentrations and relative humidity or cloudiness that might affect direct forcing. A second approach (e.g. Koch et al. 1999; Adams et al. 1999; Tegen et al. 1997) calculates the aerosol loading and distribution in a model for which the meteorological driver is the output of a GCM, thereby permitting such correlations to be captured. However, even these calculations fail to represent the influence of aerosols on the climate system, such as their influence on precipitation development and resultant changes in the hydrological cycle. In an early study Taylor and Penner (1994) found that inclusion of sulphate aerosol chemistry and transport in their GCM resulted in changes in precipitation patterns that in turn enhanced the sulphate loading. While it is premature to attribute such specific climatic effects and interactions to aerosols with confidence, the fact that such changes are exhibited in on-line aerosol-climate models underscores the need for aerosols ultimately to be represented on line in climate models and for the aerosol influences on the climate system being modelled to be taken into account. This will add considerable computational burdens, which poses a challenge to the aerosol modelling community to develop accurate and efficient methods of representing size- and composition-dependent aerosol processes suitable for incorporation in climate models.

4.5 Highlights and Remaining Challenges

The decade of the 1990s was one of major progress in the recognition of the role of aerosols in global atmospheric chemistry, in describing concentrations and properties of tropospheric aerosols and their geographical distribution, and in understanding the controlling processes. Much of this revolution has been fuelled by new measurement capabilities. Extension of the range of differential electrical mobility analysers and condensation particle counters down to particle diameters of a few nanometers has revealed the episodic nature of nucleation events, though the substances responsible for these events still remain elusive. Single-particle mass spectrometers have revealed that the internal and external state of mixing of particles is much richer than had previously been imagined. This richness is a challenge to explain but it provides a means of identifying

the processes responsible for formation of particulate matter in the atmosphere. To a great extent the revolution in atmospheric aerosol research can be attributed also to a change in the way aerosol measurements and atmospheric chemistry measurements generally are being conducted. Investigators and funding agencies are recognising that meaningful progress in understanding atmospheric chemistry processes requires a large number of measurement capabilities to be brought to bear at the same time, as noted above.

The enhanced understanding is making its way into numerical models describing the emissions, transport, transformation, and deposition of aerosols and their precursors on a variety of scales, from urban air sheds to global.

During the past decade it has become clear that human activities have dramatically modified the regional distributions of atmospheric aerosols. It is also evident that anthropogenic aerosols play a major role in the determination of local and regional climatic regimes, through both direct and indirect radiative forcing of climate. Increases in anthropogenic aerosols can cause potentially disruptive changes to sociologically and economically important factors such as regional hydrological cycles.

While we have learned a lot about aerosol characteristics and the nature of many of the processes responsible for their impacts, in many cases our understanding is not yet sufficiently quantitative for accurate prediction of the severity of impacts. A few future challenges are outlined next.

4.5.1 Characterisation of the Atmospheric Aerosol

Characterisation of primary particulate matter from combustion should include divisions by mass into fractions that are relevant optically: ash, organic carbon, black carbon, and, possibly, sulphates. Particular attention is needed for the combustion practices thought to contribute the largest fractions to the global burden of primary particles, such as domestic coal and wood burning, and industrial combustion in less-developed countries. The hygroscopicity of these particles should be investigated as a first step in estimating their lifetimes and roles in cloud droplet formation.

A tabulation of combustion practices by region is needed for development of more accurate emission inventories. Information on practices in non-OECD countries is particularly sparse. There are no quantitative estimates of global fly ash emissions, in particular fly ash from biomass burning. Information is also lacking on primary mineral matter emissions from sources other than combustion for heat and power.

As volcanic sulphur emissions are comparable to anthropogenic emissions of sulphate, there is a need to estimate volcanic emissions better. Volcanic sources should first be grouped according to their respective magma provinces. Combination with their respective levels of activity will then yield better spatial and temporal emissions patterns. To obtain better data on the absolute emissions from volcanoes, more systematic measurements are needed, at least for those sources that contribute most. Exemplary long-term (few years) measurements must be made at type-representative volcanoes.

Physical techniques based on single particle counting will continue to play a vital role in atmospheric aerosol science. The high counting sensitivity that can be achieved means that extremely small samples are sufficient. Bulk aerosol composition data provided by these techniques can be used for studies of environmental cycling of various elements, aerosol mass closure studies, and source apportionment based on receptor modelling.

Single-particle analysis can provide invaluable information on the origin and evolution of atmospheric particles, such as their degree of external and internal mixture and new particle formation. Single-particle compositional data still remain to be reconciled with measurements of other properties performed *in situ* on individual particles, such as hygroscopic and cloud-nucleating behaviour.

4.5.2 Formation and Growth of Particulate Matter

Laboratory studies are needed to test further binary and ternary nucleation theory and to investigate more quantitatively the influence of ambient levels of ammonia and various other potential biogenic and anthropogenic precursor compounds on particle nucleation rates. Also, a quantitative study of ion-induced nucleation needs to be undertaken. Models should be developed to help explain laboratory results and to help short-circuit the arduous path of investigating all possible combinations of nucleation precursors. Models should also be run to determine where climatic and health influences of this highly non-linear nucleation process are most sensitive to changes in precursor concentrations.

There is a need to assess the relevance of various oxidation pathways to form condensable species under atmospheric conditions, especially in the case of natural precursors, and to understand the chemical mechanisms leading to very low volatility oxidation products of reactive organic gases. The influence of humidity on product and particle yields requires further study. The speculation that aerosol particles (both organic and inorganic) might also affect the oxidising capacity of the troposphere, by serving as sources or sinks for gas-phase radicals, needs to be evaluated.

Further systematic laboratory studies are required to provide fundamental data (e.g. accommodation co-

Box 4.5. Effects of volcanoes

In addition to their considerable contribution to the tropospheric sulphur budget, episodic strong volcanic eruptions reaching the stratosphere cause measurable climatic effects over periods lasting a few years. Injections of volcanic material of more than about 3 Tg SO_2 to the stratosphere occur about once per decade. Such events cause an increase in stratospheric sulphate aerosol particles of one to two orders of magnitude and a reduction of solar radiation reaching the troposphere of ca. 2 $W m^{-2}$ in the global mean, thus compensating much of the anthropogenic greenhouse effect for one to two years. The radiative cooling resulting from the 1991 Mt. Pinatubo eruption was modelled to be –0.3 to –0.5 K (global annual mean) (Hansen et al. 1996); a concomitant global cooling of similar magnitude was observed. Discrepancies between observations and model results based on solar radiation effects alone have been overcome by the inclusion of terrestrial radiative heating of the stratospheric aerosol layer (Graf et al. 1993). The 2–4 K warming of the low-latitude lower stratosphere by this effect intensifies the winter polar vortex, with consequences for the structure of tropospheric planetary waves. This dynamic effect results in advective continental winter warming in the northern mid- and high-latitudes reaching maxima of +6 K over Siberia following the eruption of tropical volcanoes (Robock and Mao 1992).

The particle size distribution and optical properties of background and disturbed stratospheric aerosol are known better than for most tropospheric aerosols, and have been simulated in a CTM (Hamill et al. 1997) and in a climate model (Timmreck et al. 1999).

During volcanically disturbed episodes the gravitational settling of stratospheric sulphate particles contributes significantly to the upper tropospheric (UT) aerosol. Tropopause folds during other times bring stratospheric aerosol to the UT region and increase the frequency of occurrence of cirrus. After the eruptions of El Chichòn (1982) and Pinatubo (1991) subvisible cirrus increased by about 10%. By increasing heterogeneous reactions with anthropogenic chlorine the enhanced stratospheric sulphate aerosol also leads to a decrease of stratospheric ozone (Brasseur and Granier 1992), which reduces the net heating of the aerosol layer.

efficients, rate coefficients) needed for a more complete description of aerosol chemistry. In addition to experimental data for individual reactions, such studies should aim toward developing correlations that could allow the estimation of rate constants at high ionic strength in various electrolytes.

4.5.3 Aerosol-Cloud Interactions

The need to predict cloud droplet formation from given aerosol particle size distributions in models provides a strong motivation for identifying the source of the apparent disparities (e.g. Schwarzenböck et al. 2000) between aerosol physico-chemical measurements and cloud droplet number concentrations. Future investigations must examine more comprehensively the influence of soluble gases, partly soluble material, and surface active materials on water uptake by aerosol particles and drops. There is need for a coordinated effort to investigate the properties of particles on which cloud droplets form.

In the area of cloud chemistry, current theoretical research is centred on the interaction of radicals with organics that may influence the rate of S(IV) oxidation in droplets, alter the pattern of precipitation composition, and possibly lead to the production of harmful substances. The radical-driven oxidation of S(IV) to S(VI) is an extensive research topic of its own. Attention needs to be given to understand better the production and aqueous-phase chemistry of organic species via laboratory studies, focussed field campaigns, and modelling efforts. Current efforts to measure and model size-dependent cloud chemical composition should also be improved.

Potentially, dynamic and precipitation effects through ice nucleation and crystal multiplication processes have great global importance and must receive more attention in future aerosol research. There are large uncertainties in the understanding of basic ice formation processes and their connection with the atmospheric aerosol that need to be reduced before new experimental approaches for measuring ice nuclei can be developed. When improved methodologies are in place, global inventories need to be established that, in turn, must be connected to cloud microphysics and precipitation data.

A challenge for the prediction of indirect radiative forcing through aerosol-cloud interactions is to develop physically based GCM parameterisations from process parameterisations. The predictable parameters in a GCM are far fewer than the measured parameters in a closure experiment, and they characterise properties averaged over a scale much larger than the typical process scale. The basic information needed for simulation of aerosol-cloud interactions is the physical and chemical characteristics of aerosol particles and cloud droplets, interstitial gas composition, and the dynamic and thermodynamic properties of the cloud field. Numerous questions have to be answered collaboratively by experimentalists and modellers.

4.5.4 Modelling Challenges

Concerning aerosol process modelling, there is a strong need for improvements in the time efficiency and accuracy of the computational techniques used, especially for applications to atmospheric transport models. One of the most important questions is how to describe properly gas-to-particle mass transfer, especially for organic material (i.e. how to account for particle nucleation and growth processes when organic species are involved). Models to calculate heteromolecular nucleation rates for organic species in atmospheric systems are few and have large uncertainties associated with them.

Most global climate model studies so far have only considered the bulk particulate mass of few specific components, rather than the size distributions of an externally and internally mixed aerosol and size-dependent chemical composition. This is despite the recognition that the size distribution and the chemical composition of the particles control the activation of particles to cloud elements. Moreover, the cycles of aerosol particles are closely connected with hydrological processes. Models have to consider the complexity of a multiphase system. Certainly a weak point of the climate models is the parameterisation of cloud processes and properties as well as cloud-radiation feedbacks. Uncertainties in the calculated cloud properties are hard to quantify because satellite retrievals are not very accurate and *in situ* measurements cannot be extrapolated.

As always with large-scale models there is a continuing need for evaluation. Future work should take its cue from the recent successful large-scale, multi-investigator field projects that have brought together in an arena covering thousands of kilometres and a variety of platforms, instruments, and techniques, to provide detailed characterisation of aerosol sources, geographical distributions, and chemical and microphysical properties, and of the governing meteorological fields. Data sets resulting from these studies, together with satellite observations, provide the basis for a stringent test of the accuracy with which chemical transport models can represent aerosol loadings and properties that is necessary if these models are to be used with known and reasonable accuracy to calculate aerosol influences on climate at the present, over the industrial period, and for future emissions scenarios.