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Chapter 4: Tropospheric Aerosols

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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. Studies by Charlson, Rodhe, Lovelock and their colleagues have emphasised the substantial role of natural and anthropogenic sulphate aerosol for the radiative properties of the atmosphere and Earth's climate. Studies on the causes of the Antarctic ozone hole have clearly demonstrated the large role of reactions that take place only on ice and aerosol surfaces. When such reactions are possible in the stratosphere, the more they can influence the troposphere with its abundance of various kinds of aerosol. Considering these factors, and especially because of various breakthroughs in experimental techniques, there is little doubt 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, 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 that now in most cases involve only sulphur chemistry have not been sufficiently tested against observations, despite the potentially great cooling effects of aerosol on earth surface temperatures, which so far may well have substantially counteracted the radiative forcing by the greenhouse gases (Crutzen, 1998).

One of the most important advances in the last decade in aerosol research has been the realisation that we will not be able to understand (and even less be able to predict) the chemical state of the atmosphere without taking into account its multi-component and multiphase nature. In contrast to gas phase species where specifying concentrations at a given point in time and space is sufficient to characterise the single-phase system, a range of variables is necessary for aerosol species.

Figure 1 shows in a generic way that aerosol particles have a range of sizes from nanometers to micrometers, a range of shapes, and how the chemical composition usually differs among the size ranges and even among individual particles within a given size range.

1   Aerosol particles are strongly coupled with gas phase chemistry and clouds, and an

2   understanding of their properties and effects, and of the atmosphere in general, requires that

3   gases, particles and clouds be treated as one single system. The scales involved in this

4   system range from molecules and nanometer-sized aerosol particles to frontal cloud systems

5   spanning hundreds of kilometres.

6   An example for the gas/particle/cloud connection is that aerosol particles and cloud

7   droplets can influence gas-phase chemistry as sinks of reactive species by diminishing

8   photo-actinic flux and also as reaction vessels that can contribute reactive species back to

9   the gas phase. As such, aerosol particles and cloud droplets affect the so-called oxidation

0   capacity of the atmosphere, which determines the chemical lifetimes of atmospheric trace

1   substances including condensed species.

2   An example highlighting the range of scales is that clouds cover roughly half of the

3   earth's surface; yet any individual cloud is composed of billions of individual droplets or

4   crystals, each of which started its life as an aerosol particle. Thus, understanding and

5   predicting the characteristics and behaviour of clouds on a global scale will not be possible

6   without an understanding of the microscale processes that create and control them.

7   Aerosol particles have a multitude of sources. They derive from "primary" sources

8   involving direct emissions of particles, and by "secondary" processes, reactions of gaseous

9   precursor emissions in the atmosphere to form particles.

0   Table 1 summarises the natural processes leading to particle production and the

1   anthropogenic processes leading to changes in natural aerosol. The table shows that the

2   effect of man on the atmospheric particle burden can be direct, through changing and

3   adding emissions of particles or their precursors, or indirect, through changing the

4   transformation processes leading to secondary aerosols (e.g., increased oxidising capacity of

5   the atmosphere) or through climate change. The effects of climate change relevant for

6   particle production are exemplified in the last column

1   The systemic view and the detailed discussion of recent developments presented below

2   clearly point to a highly exciting future of aerosol research as an integrative component of

3   atmospheric chemistry.

2.   Integrated view of present state of knowledge of atmospheric aerosols

6   During the past decade, model calculations, *in situ* observations, and measurements from

7   satellites have looked in different ways at the atmospheric aerosol at the global scale. The

8   first space borne radiometers that probed the troposphere revealed, in first instance, the

9   transport of aerosols on regional and global scales. Measuring campaigns, focusing on areas

0   of interest revealed by those satellite images, documented a large variety of aerosol physical

1   and chemical properties, which guided the way to a better understanding of the processes

2   controlling the evolution of the aerosol particles. Model calculations eventually provided

3   links between aerosol sources, atmospheric chemistry, transport, and some of the

4   characteristics of the observed fields.

5   What emerged from these different perspectives is that there is no such thing as "the

6   global aerosol". Instead there exists a superposition of largely independent regional aerosol

7   "plumes" and "layers", each having an active source(s), a unique spatial and seasonal

8   pattern, as well as specific microphysical and chemical characteristics. In parallel to these

9   findings improvements in process understanding have given the atmospheric community a

0   better grasp on this observed variability.

1

2.1   Space borne measurements

2.1.1   Horizontal maps of aerosol optical depth from space borne radiometers

(POLDER)

Figure 2 shows the global horizontal patterns of aerosol optical thickness and Ångström

exponent over the oceans derived from the POLDER sensor for December 1996 and June

1997.

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. These continental aerosol plumes are characterised by high

concentrations near the coastal areas and a monotonic decrease with distance from the

coast. This aerosol pattern arises from continental emissions, followed by atmospheric

dispersion and decay in the downwind direction. In well-defined flow fields such as the

trade winds, the continental plumes are elongated and extend over several thousand

kilometres.

With some a priori knowledge on source distributions, the plumes in Figure 2 can be

attributed to mineral dust, biomass burning and industrial emission. The dominant plumes

are in the tropics/subtropics and are due to mineral dust emissions and biomass burning and

the aerosol levels generally peak in the summer hemispheres.

Sand dunes are shown on Figure 2a and b as yellow patches over the Sahara and north-

western China. However, it should be noted that sand dunes are not necessarily strong or

exclusive sources of wind-blown dust. The emission of windblown dust is seasonal and it is

driven by highly episodic windy conditions. The characteristic dust particle is in the coarse

particle mode (see Figure 4i). Its composition does not always reflects the local sand

composition, but might be enriched by sulphates and nitrates from anthropogenic origin.

Biomass fires are shown as red dots. Note that the fire locations in December (Figure

2a) are distinctly different from those recorded in June (Figure 2b). The regular yearly

biomass burning regions of the world are distributed over central and sub-Saharan Africa,

1   Central and South America, as well as Indonesia and Indochina. More sporadic fires are

2   recorded over the boreal forests of Canada and Siberia. Biomass smoke particles are

3   composed of organic species, elemental carbon, ionic species (sulphate, ammonium, and

4   potassium) and other combustion residues and they are generally of sub-micrometer size

5   (see Figure 4d).

6   Anthropogenic sulphur sources (IGAC GEIA, shown as purple areas) are broadly

7   representative of other types of industrial aerosol emissions and their precursors (e.g.,

8   organic species, nitrates, black carbon, etc.). Most anthropogenic emissions are located in

9   the Northern Hemisphere and are concentrated in mid-latitudes. The three major

0   anthropogenic sulphur emitting regions are eastern North America, Europe, and eastern

1   Asia. The anthropogenic sulphate particles are of sub-micrometer size and often co-exist

2   with condensable organic species (see Figure 4c).

3   Oceanic sources of atmospheric aerosols are also of interest. Unfortunately, there are no

4   satisfactory proxy indicators for oceanic sulphur emission patterns. For example, oceanic

5   emissions of dimethylsulphide (DMS) do not appear to be related to chlorophyll

6   distributions in the ocean (Bates *et al.*, 1993; Covert *et al.*, 1992) which can be measured by

7   satellite. However, DMS emissions are seasonally and regionally dependent with the

8   highest emissions in the middle and high latitudes during the summer months (Bates *et al.*,

9   1987; Kettle *et al.*, 1999).

0   The ocean is also a source of sea-salt particles to the atmosphere through the bursting of

1   air bubbles associated with breaking waves (film and jet droplets) and the mechanical

2   tearing (spume droplets) and spilling over (splash droplets) of wave crests (reviewed by

3   Andreas *et al.* (1995)). While the total number concentration of these mechanically

4   produced sea-salt particles is relatively small even in the remote MBL (Figure 4f), they can

5   dominate the mass size distribution (Quinn *et al.*, 1996b) and thus have a significant effect

6   on chemical reactions occurring in the MBL (Sievering *et al.*, 1992)*,* the formation of new

7   particles (Covert *et al.*, 1996a, 1996b)*,* the production of cloud condensation nuclei

1   (O'Dowd *et al.*, 1997b)*,* and the light scattering by aerosols (Quinn *et al.*, 1996b, 1998). The

2   magnitude of the ocean-atmosphere flux of sea-salt particles is a function of the wind-

3   dependent sea state (Monahan, 1986), while the instantaneous atmospheric sea-salt

4   distribution is a function of the ocean-atmosphere flux, mixing between the MBL and FT,

5   size- dependent removal processes and advection.

6

7   2.1.2 Vertical cross sections from space borne lidar

8   Figure 3a shows the vertical distribution of aerosol plumes (and clouds) over the Atlantic.

9   By a favourable coincidence, the LITE (Lidar Technology in Space Experiment, September

0   1996) lidar recorded the vertical distribution of both the Sahara dust plume and the biomass

1   smoke plume emanating from southern Africa.

2   The picture provides clear illustrations of aerosol-cloud interactions. For instance at

3   12ºN the marine boundary layer (MBL) extends to about 2 km and there is evidence of dust

4   entrainment into the MBL and into the clouds. The cloudiness associated with the Inter-

5   Tropical Convergence Zone is also clearly visible at about 5ºN. The entire convergence

6   zone is relatively aerosol-free, possibly due to the intense cloud processing and removal.

7   The picture, however, also shows that significant amounts of aerosol are transported above

8   clouds and well separated from the boundary layer. The slow removal within the free

9   troposphere allows the long-range transport of these plumes over many thousand kilometres

0   until they are entrained into precipitating cloud systems.

1   Figure 3b depicts the biomass burning haze layer over the Amazon basin. The layer

2   extends from the basin floor to about 3000 m asl. It is remarkable that the aerosol layer is

3   spatially homogeneous over the entire 1000 km cross section along the spacecraft track.

4   During the LITE passage over this part of South America, the free troposphere above 5km

5   was remarkably aerosol free. The Andes constitute a strong barrier to the dispersion of the

6   South American smoke layers

7

1   ## **2.2   *In situ* measurements**

2   There has been a large development in instrumentation for the physical and chemical

3   characterisation of aerosol particles. Their implementation according to well-designed

4   strategies in IGAC and other experiments (see Section 4) has provided more precise data

5   concerning aerosol microphysical and chemical characteristics, at least in those areas visited

6   by these experiments. A compilation of size distributions and chemical compositions is

7   shown in Figure 4, and discussed below. The degree to which they lead to a 3-D picture of

8   the global aerosol is discussed subsequently.

9

0   ### 2.2.1   Particle size distributions

1   In the global atmosphere, the size distribution of aerosol particles is highly variable but

2   generally presents itself as a superposition of more or less distinguishable modes. Each of

3   these modes can be represented by a log-normal distribution. Following the original work of

4   Whitby (1978) and Hoppel (1988), it has been accepted to name these modes "nucleation

5   mode" (particles with $D_p < 0.01$ μm), "Aitken mode" ($0.01 < D_p < 0.1$ μm)), "accumulation

6   mode" ($0.1 < D_p < 1$ μm), and "coarse mode" ($D_p > 1$ μm). The modes become more readily

7   apparent when either the number, surface or volume size distribution is plotted. The modes

8   result from specific emissions and atmospheric processes. The nucleation mode is the result

9   of recent nucleation events involving formation of new particles from gases. The Aitken

0   mode results from condensation on, and self-coagulation of nucleation mode particles as

1   well as from primary emissions during high temperature combustion. The accumulation

2   mode typically results from coagulation and from the formation of particle mass by in-cloud

3   chemistry. Primary emissions from the mechanical break-up of bulk material will contribute

4   to the number of the accumulation mode particles as well; however, they will dominate the

5   mass of the coarse mode.

6   Number concentrations typically drop below a diameter of 10 nm, because the smallest

7   particles and clusters have a high mobility and will rapidly diffuse to surfaces or coagulate

1　with other larger particles. When a high number of nucleation mode particles is observed, as

2　in the urban and sub-urban environment (Figures 4a and b) and in the clean MBL of the

3　Southern Ocean (Figure 4f), it means that nucleation has taken place recently. Over the

4　Southern Ocean, this is thought to happen aloft in the neighbourhood of frontal clouds**.** Note

5　that the actual process of nucleation involves particles of 1 nm in size and less. These are

6　not detectable with the present instrumentation, which has a lower limit of (2-3 nm in D_p).

7　　　Number concentrations also drop above a diameter of about 500 nm, because of

8　impaction or gravitational settling of those large particles. Significant number

9　concentrations of coarse particles are again found in the presence of primary emissions, e.g.,

0　of sea-salt (Figures 4c,d,e,f) or road dust (Figure 4b). The Saharan dust layer in the free

1　troposphere (Figure 4i) still contains relatively high numbers of coarse particles, even

2　several hundreds of kilometres from the emission area. Distribution above the polar pack

3　ice does not show any contribution of sea-spray (Figure 4g).

4　　　In the size range $10 < D_p < 500$ nm, the number size distributions exhibit one or several

5　maxima. When pollution particles, e.g., from industry (Figure 4c) or biomass burning

6　(Figure 4d), "ages" during transport away from its source, a typical mono-modal

7　accumulation mode develops centred around about 100 nm D_p, primarily through the effect

8　of coagulation and cloud processing. These aged aerosols are also present over the

9　continents where they can mix with freshly locally produced aerosol (e.g., Figure 4a,b).

0　　　In the clean marine boundary layer and in the Arctic, far from anthropogenic influences,

1　the sub-micrometer size distribution is typically bimodal (Figure 4e,f,g). The Aitken mode

2　is presently explained by entrainment of free tropospheric aerosol (Figure 4h) into the

3　boundary layer, whereas the accumulation mode results from processing in non-

4　precipitating clouds.

5

1   2.2.2   Chemical composition

2   Urban aerosols are often dominated by organic species (Figure 4a,b) from the inefficient

3   combustion of fossil fuels. Other products from fossil fuel burning, such as nitrate, sulphate,

4   and black carbon, are also present in this aerosol. The acidic fraction of the particles is

5   partially neutralised by ammonia which is a product of animal waste. Outside of the urban

6   environment, the dominant regional continental sub-micrometer aerosol (Figure 4c) is

7   generally $(NH_4)_XH_YSO_4$. The primary source of this sulphur (Figure 2) is industrial fossil

8   fuel combustion. Although the measurement of the organic constituents is fraught with large

9   uncertainties, there are indications that organics form a large fraction of the sub-micron

0   aerosol in the free troposphere (Figure 4) (Novakov *et al.*, 1997; Putaud *et al.*, 2000).

1   The aerosol products of biomass burning are enriched in organic and black carbon, KCl

2   and NH_4Cl. The chloride is generally displaced by sulphate a short distance from the fires

3   (Liu *et al.*, 2000).

4   Sea-salt generally dominates the mass of supermicrometer particles over the ocean

5   (Figure 4c, f) and can dominate the mass of the submicrometer particles in the remote

6   marine environment (Figure 4f) (Huebert *et al.*, 1998; Quinn and Coffman, 1998). In

7   moderate to high wind speed conditions such as over the Southern Ocean (ACE 1), sea-salt

8   controls the magnitude of aerosol light scattering (Carrico *et al.*, 1998; Murphy *et al.*, 1998;

9   Quinn and Coffman, 1998) and the number of cloud condensation nuclei (Covert *et al.*,

0   1998; O'Dowd *et al.*, 1997b). Single particle analysis during ACE-1 revealed that over 90%

1   of the aerosol particles with diameters >130 nm (Murphy *et al.*, 1998) and up to 70% of the

2   particles with diameters >80 nm (Kreidenweis *et al.*, 1998) contained sea-salt. In the sub-

3   tropical N. Atlantic (ACE-2) the contribution of sea-salt to the sub-micron aerosol (and

4   hence to the effects) was less dominant (compare Figure 4e and 4f), even in air masses with

5   marine origin. In continental air masses the sea-salt in all size classes was depleted in

6   chloride (55% on average), indicating the interaction of sea-salt with anthropogenic acids

7   (Quinn *et al.*, 2000).

1

2   2.2.3   The 3–dimensional distribution of the atmospheric aerosol based on *in*

3   *situ* measurements

4   Measurements such as those shown in Figure 4 must be compiled to construct 4-D global

5   aerosol climatologies. Such climatologies are necessary for model testing, for ground-

6   truthing of satellite observations and, eventually, for any quantitative regional or global

7   assessment of aerosol effects on the Earth's system. Obviously the community is far from

8   achieving that goal.

9   For marine areas a climatology has recently been compiled (Heintzenberg *et al.*, 2000).

0   Well-calibrated and parameterised submicrometer size distributions are available for only

1   about a quarter of the oceanic surfaces. For bulk chemical composition the corresponding

2   coverage is somewhat better (60%), but still far from satisfactory. Much of the progress in

3   marine aerosol characterisation came through the large IGAC field experiments of the mid-

4   nineties (ACE 1, Bates *et al.*, 1998) *(*ACE 2, Raes *et al.*, 2000a). For continental aerosols,

5   no comprehensive parameterisation of the size distribution of continental aerosols has been

6   accomplished since the pioneering work of K.T. Whitby (see Whitby, 1978), despite the

7   availability of commercial and specialised methodology that can reveal many more details

8   than was possible 25 years ago (e.g., Heintzenberg *et al.*, 1998). No climatologies of aerosol

9   size distributions over the continents exist. Regional air pollutant networks such as EMEP

0   in Europe and IMPROVE in the US have been collecting data on aerosol chemical

1   composition (typically sulphates, nitrates, black carbon) which are of some use, and the

2   Global Atmospheric Watch programme of WMO started archiving various aerosol

3   parameters at its World Data Centre of Aerosols. The latter have been used for a validation

4   exercise of global chemistry and transport models of the sulphur cycles (Barrie *et al.*, 2000).

5   Knowledge about the vertical aerosol distribution is even more limited than the surface

6   distribution. Over the continents there has been only one long-term effort in vertical aerosol

7   profiling by *in situ* measurements (Hofmann, 1993; Hofmann *et al.*, 1998), yielding

1   valuable data on the effects of volcanoes, of the increase of air traffic and of decreasing

2   surface emissions on the upper troposphere and lower stratosphere. A series of research

3   flights complemented to some extent the continental data with measurements over the

4   Pacific and north Atlantic region (Clarke, 1993; Clarke *et al.*, 1996, 1997, 1999a;

5   Heintzenberg *et al.*, 1991; Weber *et al.*, 1999).

6   After about five years of technical development a first aerosol payload is now flying

7   frequently on a commercial aircraft (Brenningkmeijer *et al.*, 1999). On flights between

8   Europe and the Indian Ocean the first aerosol climatology for the tropopause region has

9   been accumulated by these flights (Hermann, 1999), showing clear influences of surface

0   aerosol sources in the tropics and in the mid-latitudes over Europe.

1   A few aerosol lidars have monitored the vertical aerosol distribution over extended time

2   scales (Ansmann *et al.*, 1997; Jäger and Carnuth, 1994; Reiter and Jäger, 1986).

3

4   **2.3   Process understanding**

5   The understanding of processes underlying the observed variability in Figs. 2, 3 and 4 has

6   evolved over the past decade. This includes understanding of both the microphysical and

7   chemical processes involved in aerosol particle formation, evolution and removal, as well as

8   large-scale meteorological processes.

9

0   2.3.1   Microphysical and chemical processes

1   Figure 5 depicts schematically the microphysical and chemical processes that influence the

2   size distribution and chemical composition of atmospheric aerosol particles. It illustrates the

3   wide range of sizes involved in the formation and evolution of aerosol particles, and the

4   existence of primary particles and secondary particles. Figure 5 also highlights how aerosol

5   particles participate in atmospheric chemical processes through homogeneous,

6   heterogeneous and in-cloud reactions.

1   Primary particles that are derived from division of bulk material and subsequent

2   suspension by the wind, such as sea-salt, soil dust, and biological material, have most of

3   their mass associated in the coarse particle range. However their highest numbers occur in

4   the 0.1-1 μm range. Because of their low concentrations and large sizes, primary particles

5   derived from division of bulk material generally do not coagulate with one another, but can

6   become mixed with other species through uptake of condensable material from the gas

7   phase.

8   An important type of primary particle is so-called "soot", emitted from combustion of

9   carbonaceous fuels. It consists of black carbon-containing material that has not been fully

0   oxidised in the combustion process, often mixed with refractory metal oxides. Soot is

1   formed in the combustion of carbonaceous fuels as particles with a diameter 5 to 20 nm.

2   Such particles rapidly coagulate to form fractal-like aggregates, which in turn collapse to

3   more compact structures having a diameter of several tens of nanometers under the

4   influence of capillary forces of condensing vapours.

5   Gas-to-particle conversion (i.e., condensation and nucleation) in the atmospheric

6   aerosol occurs when a volatile species reaches a concentration that exceeds its equilibrium

7   vapour pressure, resulting in a thermodynamic driving force for condensation. In the

8   atmosphere, this situation can be driven by chemical reactions leading to products with very

9   low vapour pressure (e.g. SO_2 H_2SO_4, -pinene   pinonic acid). Alternatively, this

0   situation can be reached simply by a reduction in temperature, which has the effect of

1   reducing the species' equilibrium vapour pressures. A recently suggested alternative

2   possible mechanism is the co-condensation of several species, so that the equilibrium

3   vapour pressure of the single compounds above the particle is lowered by the presence of

4   the other species in the particle.

5   Nucleation is energetically less favourable than condensation, and it will be facilitated

6   by the absence of pre-existing particulate surface or by very low temperatures. Once it

7   occurs, the new particles grow by condensation and self-coagulation. As particles reach a

1   diameter of the order of the mean free path length of the condensing molecule, condensation

2   becomes diffusion-limited and slows down. Also, self-coagulation, which is a second-order

3   process, eventually slows down as number concentrations fall. Under background

4   tropospheric conditions, particles formed initially by nucleation require days to weeks to

5   grow larger than about 0.1 μm solely by condensation and coagulation (Walter, 1973).

6   Under polluted, urban type conditions, this growth can occur within a day because of the

7   strong supply of condensable material from homogeneous gas phase reactions (Raes *et al.*,

8   1995).

9   Another growth process is by chemical processing in non-precipitating clouds

0   (Friedlander, 1978; Hoppel *et al.*, 1990; Hoppel *et al.*, 1994). This process begins with the

1   uptake of water vapour with increasing relative humidity. According to traditional Köhler

2   theory, a critical supersaturation (RH > 100%) exists above which water vapour condenses

3   in an uncontrolled way and cloud droplets form. This critical supersaturation depends on

4   particle size and chemical composition. Once a drop of sufficient volume is formed,

5   gaseous species like SO_2 can dissolve and be oxidised in the aqueous phase. On average,

6   nine out of ten clouds evaporate rather than precipitate. When the droplets evaporate, larger

7   particles reform as a result of the additional oxidised material, e.g. sulphate (Birmili *et al.*,

8   1999; Yuskiewicz *et al.*, 1999).

9   Reactions that occur in cloud water also occur in wet particles present in sub-saturated

0   (non-cloudy) conditions, however with different efficiencies because of the higher ionic

1   strength. Additionally, adsorbed gases react on the particle (dry) surfaces yielding products

2   that might either remain on the particle or return to the gas phase.

3   Aerosols are removed from the atmosphere by dry and wet processes. For particles

4   below $D_p < 0.1$ μm the dominant dry removal mechanism involves diffusion to the surface,

5   a process which becomes less efficient as particle size increases. Coarse particles ($D_p > 1$

6   μm) settle gravitationally, a process which becomes less efficient as particle size decreases.

7   In the range $0.1 < D_p < 1$ μm, dry removal is very slow, and the formation and growth

1   processes discussed above tend to accumulate condensed material in this size range in the

2   sense of extreme atmospheric residence times. Provided their condensational growth is not

3   hindered by any of the above factors, these particles are removed mainly by growth to cloud

4   drops during cloud formation and subsequent removal from the atmosphere in precipitation.

5

6   2.3.2   Meteorological processes

7   The aerosol plumes and layers depicted in Figures 2 and 3 are a result of meteorological

8   transport, including exchange between the lower and upper troposphere by dry or wet

9   convection. The characteristic time of many of the microphysical aerosol processes depicted

0   in Figure 5 is days up to several weeks. This is typically longer than the time between

1   emission/formation of aerosols in the boundary layer and their cloud transport into the free

2   troposphere. Hence, to understand aerosol properties, one cannot confine the discussion to

3   such compartments as the continental or marine boundary layer or the free troposphere, but

4   one needs to view aerosol microphysical processes as embedded within the context of the

5   general atmospheric circulation that connects those compartments (Raes *et al.*, 2000b).

6   Elements of the general circulation also affect the microphysical processes and influence

7   the size distribution and chemical composition of the particles. For example, during vertical

8   transport in convective precipitating clouds a separation occurs between soluble compounds

9   that are rained out and insoluble compounds that are pumped up aloft (Rodhe, 1983). In the

0   outflow regions of such clouds, optimal conditions exist for nucleation which has been

1   modelled (Raes et al., 2000b) and has been observed (Clarke *et al.*, 1999b; Perry and

2   Hobbs, 1994). Aerosol layers observed in the free troposphere are possibly the result of

3   such cloud outflows and the associated stratification that keeps the aerosols originating

4   from the different clouds separated.. On the other hand, entrainment of free tropospheric

5   aerosol into the mixed boundary layer may be a source of Aitken mode particles and quench

6   nucleation. The depth of the mixed layer may at times be very shallow (about 100m), as for

7   example when nocturnal temperature inversions are present or in the polar regions. Strong

1   concentration gradients of aerosol will form above the top of the inversion layer and small

2   perturbations of mixed depth will cause very large changes in aerosol concentrations and

3   characteristics observed at the surface (Bigg *et al.*, 1996).

4

5   ## 2.4   Global aerosol models

6   The enhanced process understanding is making its way into numerical models describing

7   the emissions, transport, transformation, and deposition of aerosols and their precursors on a

8   variety of scales, from urban air sheds to global. In the last decade major progress has been

9   achieved in simulating the global distribution of tropospheric aerosol *mass* using global

0   CTMs. The first simulation of the global distribution of biogenic and anthropogenic sulphur

1   (Langner, 1991) led to the recognition that anthropogenic sulphate aerosols may have a

2   significant impact on the global radiation balance (Charlson *et al.*, 1991). This spurred a

3   large interest, and simulations of the global mass distributions for the aerosols types listed

4   in Table 1 followed**.** Despite the simplification of considering each aerosol type

5   independently, these studies were important to relate emissions to global distributions, to

6   construct global and regional budgets, to estimate the contribution of anthropogenic sources

7   to the burden of aerosol species that are also produced naturally, and to draw attention to

8   elements of the general circulation that are important in aerosol transport, in particular deep

9   convection (Feichter and Crutzen, 1990). As an example, Figure 6 shows calculated global

0   fields of mineral dust, sulphate and "smoke", calculated with a CTM using actual

1   meteorology. Many of the calculated features can be compared with the observations from

2   space, shown in Figure 2.

3

3.   Detailed discussion of selected recent developments

3.1   Primary emissions

3.1.1   Mineral soil-derived and industrial dust

The majority of soil-derived dust particles are lofted into the atmosphere by aeolian (wind) erosion of arid and semi-arid regions, which cover approximately one third of the global land area. However, any type of land surface can be a potential source of dust particles. Surface soil properties (e.g., texture, roughness, composition, moisture), vegetation, and production mechanisms are key factors determining the emission of dust for specific meteorological events (Gillette *et al.*, 1980).

Current estimates of global annual mean dust burden range from 1000 to 5000 Tg year^{-1} (Duce, 1995). The large uncertainties of dust burden are mainly due to complexity of dust production mechanisms, which exhibit a large spatio-temporal variability. Despite great progress in developing dust emission schemes for Saharan desert dust (Marticorena and Bergametti, 1995), these schemes cannot be directly extended for other main production regions due to a lack of data on surface properties. In addition, emission schemes will need to include explicit information on the particle size distribution and mineralogical composition of dust to allow for better physically based treatments of key processes (Claquin *et al.*, 1999; Sokolik *et al.*, 1998).

Various human activities (such as land use practice, construction, etc.) can extend the geographical area of dust sources and increase dust loading into the atmosphere. This portion of dust is called anthropogenic dust, and it is of special interest in climate change studies. Recent estimates show that the anthropogenic fraction of dust could be as much as 30% to 50% of total dust production, but this remains uncertain (Sokolik and Toon, 1996; Tegen and Fung, 1995). The dependence of dust emissions on climatic parameters, such as wind speed and rainfall, strongly suggests that the atmospheric dust load could be

1   significantly affected by any climatic change either natural or anthropogenic origin. How

2   climate change may affect dust emission remains to be quantified.

3   Another type of anthropogenic dust is industrial dust (or fly ash) produced by some

4   combustion processes, cement manufacturing, metallurgy, etc. (Flagan and Friedlander,

5   1978). Current estimates give a global emission for industrial dust of about 130 Tg year^{-1}

6   (Andreae, 1995). The rapid economic expansion and industrialisation in the developing

7   countries may result in further increase of industrial dust burden.

8   Both natural and anthropogenic fractions of dust must be better quantified to predict the

9   overall effects of dust on atmospheric chemistry and on the climate system.

0

1   **BOX 4.1.** Aviation-produced particles

2

3   Aircraft impact atmospheric aerosols and cirrus (ice) clouds by releasing particles

4   directly into the upper troposphere and lower stratosphere and by causing the appearance of

5   contrails (Penner et al., 1999). At cruise altitudes, concentrations of atmospheric aerosol

6   particles are much lower and their associated residence times are much longer compared to

7   regions closer to the Earth's surface. Two major particle types can be distinguished

8   (Kärcher, 1999): ultrafine liquid particles (diameter range 5-10 nm) formed by nucleation

9   during cooling and dilution of the exhaust, mainly composed of water, sulphuric acid, and

0   particulate organic matter; solid soot particles (20-60 nm), composed of carbonaceous

1   agglomerates formed during fuel combustion containing sulphur and organic compounds.

2   Charged molecular clusters (chemi-ions) produced via high temperature chemical

3   reactions in engine combustion chambers are believed to play a central role in the formation

4   and evolution of the liquid particles. In the dispersing aircraft plumes, the particles grow in

5   size by coagulation and condensation processes, forming an internal soot-sulphate mixture,

6   which adds to the ambient aerosol.

7   Perturbations of CN number densities in aircraft corridors have been observed at

8   regional scales and are supported by model simulations. The aircraft fleet may increase

cirrus cloudiness (Jensen and Toon, 1997). Satellite and *in situ* observations demonstrate that persistent contrails may develop into cirrus clouds. Aircraft-produced particles may also trigger cirrus indirectly, that is, without contrails or after the disappearance of short-lived contrails. Exhaust soot particles coated with sulphates could be more efficient freezing nuclei than ambient aerosol particles. The potential for heterogeneous nuclei to cause ice formation at relative humidities that are lower than those needed to form ice homogeneously in sulphate aerosols raised concerns about the role of aircraft soot in modifying existing or nucleating new cirrus clouds (Jensen and Toon, 1997). Observational evidence exists for aircraft soot influencing cirrus (Ström and Ohlsson, 1998), but the physical mechanisms are not understood. While the direct radiative forcing associated with aircraft-produced particles are estimated to be small compared with those originating from greenhouse gases or contrails, the indirect impact of these particles on cloud formation and modification could become substantial in the future. A better understanding of the physico-chemical and ice forming particle properties is required before the impact of aviation on cloud formation and heterogeneous chemistry can be fully addressed.

3.1.2   Sea spray

Sea-salt particles are produced at the ocean surface by the bursting of air bubbles resulting from entrainment of air induced by wind stress. On bursting, these bubbles produce film and jet drops (Andreas, 1998; Blanchard and Woodcock, 1957). These bubbles are most concentrated in whitecaps associated with the breaking of waves which commences at wind speed approximately 3-4 m s^{-1}. Each bubble can generate jet drops with a typical size of 5 μm diameter, and film drops in the sub-micrometer range (Woolf *et al.*, 1987). At wind speeds in excess of 7-11 m s^{-1}, the tearing of wave crests results in the injection into the marine boundary layer of ultra large spume sea-salt particles (O'Dowd *et al.*, 1997b).

Although number concentration is dominated by the smallest, sub-micrometer salt particles, surface area is dominated by the jet drops and volume is dominated by spume

1   drops when present. Number and mass concentrations are strongly dependent on wind

2   speed, typically adhering to an exponential relationship in the form of log C = aU_{10} + b,

3   where C is the concentration, U_{10} is the wind speed at 10 meter height, and *a* and *b* are

4   parameters that depend on particle size (O'Dowd *et al.*, 1997b). For moderately high wind

5   speeds of 17-18 m s^{-1}, these relationships predict number concentrations of 80-100 cm^{-3} in

6   the film drop mode, 3-5 cm^{-3} in the jet drop mode, and   0.005 cm^{-3} in the spume drop

7   mode. Investigations of the relationship between sea-salt mass, measured using impactor

8   techniques (e.g., review by Fitzgerald, 1991) exhibit good agreement with the optical

9   particle counter techniques for relevant size overlap. Other experimental techniques such as

0   growth factor analysis (Berg *et al.*, 1998) and mass spectroscopy (Murphy *et al.*, 1998) also

1   confirmed the presence of significant concentrations (up to 100 cm^{-3}) of sea-salt particles at

2   sub-micrometer sizes over the southern oceans.

3

4   ## 3.2   Emissions of particle precursors

5   ### 3.2.1   Dimethylsulphide

6   The emission of DMS from the world's oceans is a major sulphur source (yielding gaseous

7   sulphur dioxide, sulphuric acid, methanesulphonic acid and particulate sulphate and

8   methanesulphonate) to the atmosphere (Bates *et al.*, 1992; Kettle *et al.*, 1999; Spiro *et al.*,

9   1992) and contributes to both the marine boundary layer and free tropospheric (over areas

0   of active cloud convection) sulphur burden (Chin *et al.*, 1996). Recent global estimates of

1   DMS flux from the oceans range from 250 to 1600 Gmol S yr^{-1} (Kettle *et al.*, 1999;

2   Spiro *et al.*, 1992). This accounts for at least 50% of natural emissions from ocean, plants

3   and soils taken together (Bates *et al.*, 1992). Altogether the natural sulphur flux is estimated

4   to be of the same order of magnitude as the anthropogenic sulphur emissions, mainly from

5   fossil fuel combustion, which are currently estimated at 2100 Gmol S yr^{-1} (Benkovitz *et al.*,

6   1996, see also Section 3.1.3.4). The relatively large uncertainty in the reported estimates of

7   the oceanic DMS flux is partly due to differences in the transfer velocities used in the sea to

1   air calculations, but mainly to the different assumption made when making seasonal and

2   latitudinal extrapolations of the DMS seawater measurements. In particular, there is a

3   paucity of data for seawater DMS concentrations in the winter months and at high latitudes.

4   This very important natural precursor of sulphate particles and its biogeochemical cycling

5   in the water column is discussed in more detail in Chapter 2. For a discussion on

6   uncertainties involved in DMS transfer velocity estimates and calculated DMS sea to air

7   fluxes, see also Chapter 2.

8   The chemical and physical pathways, which lead from atmospheric DMS to sulphur

9   particles, are very complex and still poorly understood. Over the past ten years, DMS

0   chemistry has been studied extensively by comparing model simulations with laboratory

1   experiments and atmospheric observations. One of the main findings of these investigations

2   has been the important role of heterogeneous reactions on pre-existing secondary and

3   primary (sea-salt) generated aerosols and cloud drops in producing particulate non-sea-salt

4   sulphate (nss-SO_4^{2-}) and methanesulphonate (MSA), the two most important end products

5   from DMS oxidation via the formation of gases sulphur dioxide ($SO_2(g)$), sulphuric acid

6   ($H_2SO_4(g)$) and methanesulphonic acid (MSA(g)) (Campolongo *et al*., 1999; Capaldo and

7   Pandis, 1997; Davis *et al*., 1999; Yin *et al*., 1990a,b). Additional oxidation products are

8   dimethylsulphoxide (DMSO) and dimethylsulphone ($DMSO_2$).

9   The unimolecular decomposition pathways of both $CH_3SO_2(g)$ and $CH_3SO_3(g)$ are

0   acknowledged to be of high importance in affecting the yield of $SO_2(g)$ and of $H_2SO_4(g)$ and

1   MSA(g). Unfortunately these decomposition rates and their temperature dependence are

2   poorly known and subject to an intense debate. For example, reported values of $CH_3SO_3(g)$

3   decomposition rates span between 0.004 and 510 s^{-1} (Campolongo, et al., 1999).

4   Temperatures are thought to affect the decomposition rate to a very large degree. Yin *et al*.

5   (1990a) suggest that the decomposition rate constant of the $CH_3SO_2(g)$ radical will be

6   reduced by about a factor of 40 for a temperature change from 310 to 270K. Turnipseed and

7   Ravishankara (1993) suggests that for CH_3SO_3 the rate constant could change by a factor of

1   two when the temperature changes from 274 to 270 K. Future research on the atmospheric

2   life cycle of DMS should concentrate on reducing these uncertainties and their implications

3   for a potential DMS-climate feedback connection.

4

5   3.2.2   Volcanic SO_2-emissions

6   The most important components of volcanic degassing are H_2O, CO_2 and sulphur as SO_2,

7   H_2S and SO_4^{2-} in varying fractions depending on the magma type. Sulphur dioxide

8   emissions are measured remotely with Correlation Spectrometers (COSPEC) or Fourier

9   Transform Infrared Spectrometers (FTIR). Satellite observations (TOMS and GOME) are

0   feasible only for strong sources (Bluth *et al.*, 1993). The concentration of SO_2 in the plume

1   over a certain time interval is overlaid by the wind to estimate the flux. This strongly

2   increases the uncertainly of the measurements. In addition, only few of the about 560

3   potential volcanic sources, which are geographically well organised, ever have been

4   measured, and only a handful of these were observed more than episodically. For some

5   important regions (e.g., Kamchatka) there exist no data at all.

6   As active volcanoes generally reach considerable elevations, most of their emissions are

7   injected into the free troposphere, well above the planetary boundary layer. There, removal

8   processes are slower and the volcanic sulphur has longer atmospheric residence times

9   leading to more efficient large-scale mixing than for low elevation anthropogenic

0   emissions. Most active volcanoes are found in the Northern Hemisphere (80%). The

1   strongest source region is Indonesia.

2   Changes in sulphur emissions at (and between) single sources over orders of magnitude

3   can take place depending on the state of activity (magma type).

4   The total amount of volcanic tropospheric sulphur emissions was estimated at 14 ± 6 Mt

5   S per year (Graf *et al.*, 1997) in accordance with other recent estimates (e.g., Andres and

6   Kasgnoc, 1998) based solely on published observations which exclude important regions.

1   This is much less than the 25 Mt S per year that was estimated by Lambert *et al.* (1988)

2   from the $SO_2/^{210}Po$ ratio.

3   Mean volcanic sulphur emissions are as important for the atmospheric sulphate burden

4   as anthropogenic ones because they determine the sulphate concentration in the middle and

5   upper troposphere while anthropogenic emissions control sulphate in the boundary layer.

6   Volcanic emissions are highly variable in space and time, so there is need to constrain better

7   these sulphur sources at least by exemplary long-term measurements at the sources and

8   extrapolation to include the potential sources. There is also need to estimate transformation

9   rates of SO_2 into SO_4^{2-} in the warm, moist plumes, and the contribution of H_2S, SO_4^{2-} and

0   SO_2 associated with plume particles, because these species are not measured by the

1   conventional methods. Finally, there is need to determine three-dimensional SO_2 and

2   sulphate fields instead of surface data only.

3

4   3.2.3   Volatile organic compounds

5   Reactive organic gases (ROGs) are emitted into the troposphere from anthropogenic and

6   biogenic sources. Anthropogenic sources comprise organics such as alkanes, alkenes,

7   aromatics, and carbonyls, whereas biogenic sources include organics such as isoprene,

8   mono- and sesquiterpenes as well as a series of oxygen-containing compounds. Because the

9   volatility of the oxidation products is one of the most important parameters that determines

0   the significance of precursor gases in terms of their particle forming potential, only

1   hydrocarbons with more than six carbon atoms are considered to contribute to secondary

2   organic particles under atmospheric conditions (Seinfeld and Pandis, 1998). Thus, natural

3   SOA formation is believed to result mainly from the oxidation of C_{10}- and C_{15}-terpenoids.

4   Based on laboratory data of biogenic ROG particle yields and emission inventories

5   *(*Andreae and Crutzen, 1997) estimated 30 to 270 Tg year^{-1} for the production of secondary

6   organic particles from natural ROGs. Because the estimated global emissions of

7   anthropogenic ROGs are significantly lower, their contribution to organic particles on a

1   global scale would appear to be small when compared with natural terrestrial sources.

2   However in the urban atmosphere during severe smog episodes, anthropogenic SOA

3   formation can make a major contribution to fine particulate mass. Among the anthropogenic

4   precursor gases, aromatics have been identified to dominate the process of SOA formation;

5   this suggests that anthropogenic SOA formation in an urban air shed can be modelled based

6   on the aromatic content of the complex hydrocarbon mixture (Odum *et al.*, 1997).

7

8   3.2.4   Industrial SO_2- emissions

9   A primary advance that has enabled the modelling of spatially and temporally varying

0   aerosol concentrations has been the development of spatially disaggregated inventories. The

1   Global Emissions Inventory Activity (GEIA) has been particularly successful in engaging

2   researchers from different countries to prepare separate country-level inventories

3   (Graedel *et al.*, 1993). For the industrial SO_2 inventory, as a default, in regions where local

4   inventories were not available, the GEIA inventory specified an inventory based on a single

5   emission factor for fossil fuels and distributed emissions according to population. In regions

6   with more specific country level information, the individual country level emissions were

7   used (Benkovitz *et al.*, 1996). This method of inventory preparation suffers from the lack of

8   uniform methods for development among different countries, but is expected to be more

9   accurate than previous inventories which used a single emission factor for fossil fuel

0   emissions from different locations. In addition, emissions from industrial activities (i.e.,

1   smelting) can be more accurately estimated. A continuing concern with the inventories is

2   the estimate of sulphur released as primary sulphate. Estimates range from less than 1%

3   (Dietz and Wieser, 1983; Saeger *et al.*, 1989) to 5% (Eliassen, 1978; Eliassen and

4   Saltbones, 1983).

5   The developed inventory (for calendar year 1985) indicates that about 81% of

6   anthropogenic sulphur emissions are from fossil fuel combustion while 16% are from

7   industrial processes, 3% are from large-scale biomass burning or waste treatment activities,

1   and 1% is from the combustion of biofuels. The current inventory is in need of substantial

2   revision for other years. Between 1985 and 1997 SO_X emissions have decreased by about

3   12% in the U.S. (EPA, 1997; EPA, 1998). The collapse of the economic system in Eastern

4   Europe has caused a decrease of about 25% in sulphur emissions from 1990 to 1993

5   (Tuovinen *et al.*, 1994), and installation of flue gas cleaning equipment alone has accounted

6   for a decrease of about 10% in SO_X emissions in Europe. In contrast, emissions in China

7   have increased by about 10% since 1985 (Kato and Akimoto, 1992).

8   Estimates for total emissions from fossil fuel burning and industrial activities for 1985

9   were given as 76 Tg S year^{-1}, accurate to approximately 20–30% (Benkovitz *et al.*, 1996;

0   Penner *et al.*, 2000)

1

2   **3.3   Formation, evolution and removal of condensed material**

3   3.3.1   Nucleation

4   Homogeneous nucleation has been investigated in the laboratory for several inorganic and

5   organic chemical systems pertinent to the atmosphere. The inorganic system that has

6   received most attention is the binary sulphuric acid (H_2SO_4)- water vapour (H_2O) system. A

7   limited amount of work on ion-induced nucleation has been reported. Nucleation from a

8   variety of gas phase organic precursors has been studied in smog chambers.

9   Despite reasonable agreement between prediction of binary H_2SO_4 nucleation theory

0   and laboratory experiments large discrepancies between this theory and field data have been

1   reported. Based on measurements in a continuous flow reactor it was concluded that

2   discrepancies between measured and theoretical nucleation rates were correlated with the

3   number of acid molecules in the critical cluster (Wyslouzil *et al.*, 1991). Their results were

4   found to be roughly an order of magnitude higher than laboratory results. In experiments at

5   25 ºC in a steady-flow reactor reasonable agreement with previous work and with the binary

6   theory was reported when hydrates were included (Viisanen and Kulmala, 1997). The

7   addition of NH_3 was also shown to dramatically increase nucleation rates and to reduce the

1   functional dependence on H_2SO_4 (Ball *et al.*, 1999). These laboratory studies have all been

2   done at sulphuric acid vapour concentrations that are much higher than values measured in

3   the atmosphere in order to quickly grow particles to a sufficient size to be detected in the

4   laboratory systems. Additional recent advances include the first direct measurements of

5   molecular cluster distributions growing past the critical cluster size in the H_2SO_4-H_2O

6   nucleating system (Eisele and Hanson, 2000) and measurements of the RH dependence of

7   the first two H_2O clusters associated with the H_2SO_4 monomer (Hanson and Eisele, 2000).

8   Several other laboratory studies of multicomponent nucleation significant to the

9   atmosphere have been reported, e.g., on measurements of binary nucleation in the

0   methanesulphonic acid (MSA)/water system. There it was found that nucleation occurred at

1   partial pressures below those required for either pure species (Kreidenweis *et al.*, 1989). It

2   is unlikely, however, that atmospheric concentrations of MSA are high enough for binary

3   MSA/H_2O nucleation to play an important role. Likewise, it is unlikely that ternary

4   nucleation involving H_2SO_4/MSA/H_2O might be important (Van Dingenen and Raes, 1993).

5   Recent experiments have shown that multicomponent nucleation rates are even enhanced

6   for substances that are immiscible in bulk solutions (Strey and Viisanen, 1995).

7   Particle formation from dimethylsulphide (DMS) and DMS precursors has been

8   investigated (Kreidenweis *et al.*, 1991) and Raes *et al.* (1992) reported similar work on

9   particle formation from sulphur dioxide. Uncertainties in rate constants and other

0   parameters precluded definitive comparisons between binary nucleation theory and

1   experiment.

2   Recent studies of particle production by ionising radiation have also been reported (He

3   and Hopke, 1995; Kim *et al.*, 1998; Mäkelä, 1992; Yu and Turco, 1997; Yu and Turco,

4   2000). These studies have shown that small ions enhance nucleation rates in systems that

5   are chemically similar to the atmosphere and that ammonia (NH_3) enhances nucleation rates

6   when SO_2 is irradiated in air containing H_2O. Understanding of clustering on small ions is

1   not yet adequate, however, to permit quantitative estimates of the importance of ion-

2   induced nucleation in the atmosphere.

3   Data from smog chamber studies of the formation of organic aerosols have been

4   analysed to make inferences about homogeneous nucleation (Pandis *et al.*, 1991;

5   Stern *et al.*, 1987; Wang *et al.*, 1992). However, organic precursors typically produce

6   multiple particulate products, and the molecular identity and physical and chemical

7   properties of these products is often unknown. Nevertheless, summary yields and product

8   information can be gained through this approach (Hoffmann *et al.*, 1998; Hoffmann *et al.*,

9   1997; Odum *et al.*, 1996)..

0   Nucleation is often observed during daylight hours in the vicinity of convective clouds

1   in continental (Radke and Hobbs, 1991) and marine environments (Clarke *et al.*, 1998;

2   Hegg *et al.*, 1990; Perry and Hobbs, 1994). A definitive explanation for this phenomenon is

3   not yet established. Atmospheric experiments (Weber *et al.*, 1999) yielded that nucleation in

4   cloud outflows often occurs at H_2SO_4 relative acidities consistent with those predicted by

5   the classical binary theory for H_2SO_4-H_2O nucleation. Hoppel *et al.* (1994) also observed

6   nucleation near clouds but found difficulties in matching the nucleation to expected

7   production of H_2SO_4. De Felice and Cheng (1998) proposed that numerous smaller particles

8   were produced from residues of rapidly evaporated cloud drops during the process of

9   crystallisation. Leck and Bigg (1999) suggested that if the residues contained the amino

0   acid L-methionine, derived from primary particles of marine biological origin, nucleation

1   would also result. In the upper tropical troposphere observations suggest that nucleation is a

2   significant global source of atmospheric particles (Brock *et al.*, 1995; Clarke, 1993).

3   Evidence has also been reported for nucleation in the mid-latitude upper free troposphere

4   (Schröder and Ström, 1997).

5   Nucleation has been observed occasionally in the cloud free marine boundary layer

6   (MBL) (Covert *et al.*, 1992; Clarke *et al.*, 1998a), and more frequently in coastal areas

7   during on-shore flow (McGovern *et al.*, 1996; Grenfell *et al.*, 1999; O'Dowd *et al.*, 1999a).

1   Nucleation events have also been observed at many ground level continental sites

2   (Birmili, 1998; Hörrak *et al.*, 1998; Koutsenogii and Jaenicke, 1994; Kulmala *et al.*, 1998b).

3   These events typically follow regular diurnal patterns, with concentrations of nucleation

4   mode particles increasing several hours after sunrise and reaching peak concentrations in

5   the range 10^4 cm^{-3} or higher after several hours. The chemical mechanisms of nucleation in

6   these regions have not yet been established. One possible explanation comes from Kulmala

7   *et al.* (2000).

8   Nucleation events following regular diurnal patterns have been recorded at mountain

9   sites (Marti, 1990; Raes *et al.*, 1997; Shaw, 1989; Weber *et al.*, 1997). Rates of new particle

0   formation (nucleation rates) were found to be orders of magnitude higher than can be

1   explained by the H_2SO_4-H_2O theory. The observations of Wiedensohler *et al.* (1997) are

2   intriguing as they document the occurrence of freshly nucleated particles downwind of an

3   orographic cloud on two occasions at night. However, nucleation models including several

4   chemical systems were unable to explain their observations.

5   In summary, a great deal of new insight into the nucleation process has been gained in

6   the past decade. Binary H_2SO_4-H_2O theory may explain a limited number of field

7   observations, but probably not most. When there is a discrepancy, nucleation rates are

8   typically higher than predictions rather than lower. These results suggest the presence of a

9   stabilising compound(s) such as ammonia, hydrocarbons or an electrically charged

0   precursor (ions) to reduce the dissociation rate of a pre-nucleation molecular cluster.

1   Laboratory finds have helped to confirm these expectations, at least qualitatively for the

2   H_2SO_4-H_2O-NH_3 system. Clearly far more atmospherically relevant studies are needed in

3   this area.

4

5   3.3.2   Combustion processes

6   There are two main sources of combustion aerosols: fossil fuel burning and biomass

7   burning. The main components are organic and black carbon. The formation of particulate

1   matter (PM) depends strongly on the properties of the combustion process, especially the

2   temperature, the efficiency of combustion, and the nature of the fuel. Higher temperature

3   favours the production of larger amounts of black carbon (BC). Inefficient combustion

4   increases total PM production.

5   Biomass burning sources are derived from agricultural burning, burning associated with

6   fuel use, and savannah and forest burning associated with both land clearing and

7   deforestation. Development of an understanding of the temporally and spatially varying

8   emissions requires an estimation of total fuel burned and emissions factors.

9   A number of IGAC-sponsored field studies have helped to quantify emissions factors

0   from biomass burning, especially in the major savannah and forest burning regions in the

1   tropics (e.g., Andreae *et al.*, 1998; see also Chapter 2). These emissions factors have been

2   used in developing inventories of both total particulate matter and BC from biomass

3   burning (Liousse *et al.*, 1996; Cooke and Wilson, 1996; Cooke *et al.,* 1996). The amount of

4   fuel burned has been based on FAO and U.N. reports of wood and agricultural grain

5   production and amount of deforestation and estimates of frequency of savannah burning.

6   Data from satellites promise to provide more quantitative estimates of area burned

7   (Barbosa *et al.*, 1998) which, together with vegetation maps, can be used to determine more

8   quantitative estimates. Development of emissions estimates from other biomass activities

9   may require data on individual country practices.

0   At the present time, estimates for total biomass burning range from 5390 to 8910 Tg dry

1   mass per year (cf. Chapter 2). The total smoke production associated with these estimates

2   ranges from 60 to 100 Tg year^{-1} with approximately 10% of this total associated with BC

3   from biomass burning.

4   Fossil fuel sources of combustion aerosols are associated with specific burning

5   practices in individual regions and the type of fuels burned. First estimates for BC

6   emissions are available from Penner *et al. (*1993), Cooke and Wilson (1996) and Cooke *et*

7   *al.* (1996). Bond *et al.* (1998) suggested that new emissions factors should be produced

1   based on the absorption properties of the emitted compounds, but insufficient data of this

2   nature are available to develop a complete inventory.

3   A simple estimate of organic carbon (OC) from fossil fuel combustion was based on

4   observed ratios of BC to OC in source regions (Liousse *et al.*, 1996). Cooke *et al.* (1999)

5   attempted a more detailed estimate based on emissions factors and fuel use, however, the

6   total inventory was of order half as large as that estimated in Liousse *et al.* (1996) and

7   underestimated observed OC when used in a model study. Significant effort is needed to

8   improve this situation either by identifying larger sources of secondary organic aerosol than

9   are now estimated (Penner *et al.*, 2000) or through improving the emission factors used in

0   the current study. The current estimated range of mass emissions associated with organic

1   carbon is 10 to 30 Tg year^{-1}. If we assume the measured ratio of BC to OC summarised by

2   Liousse *et al.* (1996), this translates to a source strength for fossil fuel BC ranging from 2.3

3   to 7 Tg C year^{-1}.

4

5   3.3.3   Aerosol growth in concentrated liquid phase chemical reactions

6   Tropospheric aerosol particles are exposed to ubiquitous water vapour in the troposphere.

7   The physical matrix of highly concentrated or even supersaturated aqueous electrolyte

8   particles suspended in air hosts a variety of chemical species which may be involved in

9   solution-phase aqueous reactions (see, e.g., Zellner and Herrmann, 1995). A chemical

0   reaction for a given electrolyte solution composition, acidity, and temperature could be

1   described correctly when either all activity coefficients involved or the rate constant for the

2   reaction under the given set of conditions are known. Difficulties will arise for the

3   determination of the needed activity coefficients in complex matrices.

4   Kinetic salt effects in ion-ion reactions (addressed as 'type 1') can be treated by the

5   Debye-Hückel theory and its extensions (for an overview, see Robinson and Stokes, 1959).

6   In reactions involving neutrals only, or one ion and a neutral, a primary kinetic salt effect is

7   also clearly identified (Debye and McAulay, 1925; Herrmann and Zellner, 1998). This

1   effect, which is suggested to be addressed as primary kinetic salt effects - type 2, can

2   currently not be treated other than by experimental examination of each reaction in each

3   matrix separately.

4   Equilibrium constants are affected by ionic strength (secondary kinetic salt effect) as

5   they represent the ratio of two rate constants which are both subject to the above primary

6   kinetic salt effects. Overviews are given in Harned and Owen (1958) and Robinson and

7   Stokes (1959). These effects have been considered in cloud models in the same manner as

8   the primary kinetic salt effect for ion-ion-reactions (Jacob, 1986).

9   Ionic strength effects may be treated kinetically by the ion pairing approach. Stability

0   constants for ion pairs are available from literature (Högfeldt, 1982; Perrin, 1979) or may be

1   calculated according to the Fuoss-Eigen equation (see Davies, 1962 for an overview). The

2   observed rate constant as a function of ion concentration then results from two parallel

3   elementary reactions coupled by the ion pair formation equilibrium. Such treatment was

4   suggested by Olson and Simonson (1949).

5   The experimental data set for a more complete description of aerosol chemistry is very

6   sparse. In the case of non-radical reactions various data sets relating to S(IV) oxidation now

7   exist (Lagrange *et al.*, 1993, 1995, 1999a,b) and modelling the impact of the described ionic

8   strength effects under tropospheric aerosol conditions should be performed in the near

9   future. In the field of radical chemistry it is striking that especially for OH no single ionic

0   strength dependency has been measured for a system of relevance in tropospheric aerosol

1   chemistry. This is probably due to the wide-spread view that ionic strength effects involving

2   one neutral species can generally be neglected. While this is true for the original Debye-

3   Hückel theory in the concentration range for which the theory has been derived, electrolyte

4   contents of several mol/l may change a rate constant for a reaction involving a neutral by

5   about one order of magnitude, as was shown for NO_3 reactions (Herrmann and Zellner,

6   1998). Recently, ionic strength dependencies have been studied in H-abstraction reactions

7   of Cl_2^- (Jacobi *et al.*, 1999).

1   At present, no tropospheric aerosol model is known which takes into account the

2   available kinetic data described here. Further systematic laboratory studies are clearly

3   required. Apart from experimental data for single reactions such studies may also result in

4   correlations which, in the future, may allow the estimation of rate constants at elevated

5   ionic strength in different cases chosen according to electrolyte compositions, e.g., for a

6   marine or continental tropospheric aerosol.

7   For reactive species, including radicals in aqueous solutions, ionic strength

8   dependencies have been studied only for a few systems. Here the approach of fitting

9   experimental data to an ion-pairing mechanism appears useful, but, at least at present, leads

0   to the need for an explicit investigation for every reaction in each given electrolyte system.

1   The ion-pairing approach for chemical conversion reactions of highly reactive species

2   implies a clear physico-chemical mechanism to describe kinetically at least ion-neutral

3   reactions. It should be combined with the treatment of stable and moderately reactive

4   species by their activities obtained from the Pitzer approach (Pitzer, 1991) or by extended

5   Debye-Hückel treatments as far as applicable. More experimental studies on kinetic primary

6   ionic strength effects, resulting correlations and the development of sound theories are

7   required in order to better understand tropospheric aerosol chemistry.

8

9   **Box 4.2.** Sulphur oxidation in sea-salt

0   Measurements in the marine boundary layer (MBL) indicate that as much as 50 to 90%

1   of nss-sulphate mass is internally mixed with sea-salt (O'Dowd *et al.*, 1997a; Sievering,

2   1984). This implies that non-sea-salt sulphate (NSS) is being formed directly on sea-salt

3   particles. Furthermore, due to the relatively short lifetime of these large particles, the

4   oxidation of SO_2 on sea-salt may act as a kind of short-circuit to the marine sulphur cycle,

5   limiting the formation of longer-lived sub-micrometer NSS.

6   Sea-salt particles in the marine boundary layer are about 80% water, with an initial pH

7   of 8. Their alkalinity determines the viability of these particles as chemical reaction sites for

1   SO_2. Chameides and Stelson (1992) showed that as O_3 oxidation of SO_2 proceeds in the sea-

2   salt water, its pH will drop until—at a pH of 6 or less—oxidation by O_3 is quenched. Thus,

3   the magnitude of NSS-sulphate produced by this mechanism should not exceed the

4   alkalinity present in the sea-salt-bound condensed water (about 1 nmol m^{-3}). However, ion-

5   balance relationships in polluted marine air indicate 5-10 times more NSS than alkalinity in

6   sea-salt aerosols (Keene *et al.*, 1998).

7   One hypothesis is that the effective alkalinity is greater than that usually attributed to

8   sea-salt. Super-micrometer particulate excess calcium (non-soil-derived Ca^{++}) was found to

9   be nearly equal to the observed alkalinity during ACE 1. If this calcium was present as

0   $CaCO_3$ when sea-salt particles were emitted from the sea surface, the buffering capacity of

1   sea-salt could have been roughly doubled. The sum of alkalinity and calcium excess

2   buffering capacity could allow the O_3 oxidation mechanism to explain 70-90% of the super-

3   micrometer NSS observed in the pristine air at Cape Grim during ACE-1 (Sievering *et al.*,

4   1999). Another candidate mechanism is the halogen release proposed by Vogt *et al.* (1996),

5   which has not yet been experimentally verified. The tendency of halogen acid vapours to

6   buffer sea-salt particles to lower pH (Keene *et al.*, 1998) should in fact reduce the efficiency

7   of the O_3 oxidation mechanism, implying that another mechanism must dominate.

8   One more possible explanation for this high fraction of nss-sulphate in sea-salt particles

9   may be the enhanced buffering capacity of cloud droplets formed on sea-salt nuclei. The

0   cloud could behave as a virtual buffer, maintaining pH high and allowing sulphate

1   production beyond the carbonate buffer equivalent. Numerical simulations suggest that

2   during cloud formation, the increasing water volume maintains a pH on the order of seven

3   in droplets derived from super-micrometer sea-salt particles (O'Dowd *et al.*, 2000).

4   While it is not yet clear which of these mechanisms dominates, it is clear that sea-salt

5   exerts an important control on the fate of marine SO_2. To be realistic, future simulations of

6   marine sulphate aerosol formation clearly need to include the impact of sea-salt particles.

1   But this brings us back to the field and the laboratory: the impact of sea-salt particles cannot

2   be properly modelled until the responsible mechanisms can be identified and quantified.

3

4   3.3.4   Cloud processes

5   The life cycle of a cloud - its formation, development (both microphysical and chemical),

6   and dissipation - is intimately linked to the nature of the aerosol on which the cloud forms.

7   In this section we will discuss the life cycle of a cloud with particular emphasis on new

8   developments that have increased our knowledge of the underlying processes. The

9   processing of chemical compounds by liquid water droplets influences the chemical

0   composition of the troposphere (e.g., Lelieveld and Crutzen, 1991). A proper description of

1   liquid phase chemical processes is therefore necessary to assess the role of clouds in a

2   changing atmosphere.

3   Aerosol Scavenging. In most clouds, the fraction of aerosol that is taken up (scavenged)

4   into the cloud droplets is less than unity, both in terms of particle number and mass

5   (Leaitch *et al.*, 1992; Noone *et al.*, 1992). The ability of particles to act as cloud

6   condensation nuclei is dependent on their chemical composition and size. Different

7   chemical species are scavenged with different efficiencies, either because these species are

8   distributed differently across the aerosol size spectrum, or because of the chemical nature of

9   the substance itself (Facchini *et al.*, 1999; Hallberg *et al.*, 1992). This initial scavenging step

0   determines the initial chemical composition of the cloud droplets.

1   Recent new insights into the classical treatment of activation of aerosol particles into

2   cloud droplets have expanded on the notion that chemical effects, and not simply aerosol

3   size, are important determining factors in droplet nucleation. Slightly soluble substances (in

4   particular certain organic compounds) may influence droplet surface tension and

5   equilibrium vapour pressure, thus influencing the aerosol scavenging process

6   (Laaksonen *et al.*, 1998; Shulman *et al.*, 1996). Also, this effect has important implications

7   for indirect aerosol radiative forcing by affecting the drop size distribution. Another

1 potential factor in determining which particles form cloud droplets is the process of co-

2 condensation of soluble gas-phase species other than water onto aerosol particles. Model

3 calculations have indicated that co-condensation of HNO_3 can increase the scavenging

4 efficiency of particles in clouds (Laaksonen *et al.*, 1997; Laaksonen *et al.*, 1998).

5 Aqueous-phase Processes. Clouds constitute an efficient reaction medium for chemical

6 transformations. After cloud formation, the composition of the droplets can be modified by

7 the dissolution of soluble gas-phase species. Two families of chemical species are key

8 participants in the cloud liquid phase chemical reactions: sulphur species and organic

9 compounds. The chemistry of oxidised (NO_X) and reduced (NH_3) nitrogen species is of

0 lesser importance, although gas phase-derived HNO_3 and NH_3 are key compounds in

1 determining pH of cloud droplets and thus affect aqueous chemistry.

2 S(IV) oxidation reactions occur in clouds at a much faster rate than in the clear air:

3 model calculations (Langner and Rodhe, 1991) have shown that, on a global scale,

4 tropospheric in-cloud SO_2 oxidation is from two to five times more important than out-of-

5 cloud oxidation. Laboratory studies have identified the reactions responsible for S(IV)

6 oxidation in the atmospheric liquid phase and in determining the associated rate coefficients

7 (Huie, 1995; Warneck, 1991; Zellner and Herrmann, 1995).

8 Very little is known on aqueous phase chemistry of organic species. In current box

9 models the description of organic chemistry in cloud water is limited to gas phase-derived

0 C_1 and C_2 compounds (Herrmann *et al.*, 1999). Recent work has, however, shown that cloud

1 condensation nuclei (CCN) contain a high percentage of soluble organic species

2 (Facchini *et al.*, 1999; Noone *et al.*, 2000; Saxena and Hildemann, 1996; Zappoli *et al.*,

3 1999). Very little is known of the nature, physical and chemical properties and liquid phase

4 chemical reactions of these species.

5 A further complication of the picture concerning cloud process derives from the size-

6 dependence of cloud water chemical composition, which was stressed by Ogren and

7 Charlson (1992). Because the concentration and composition of cloud droplets is not

1   uniform, the transfer of gas-phase species into the droplets will not be uniform

2   (Twohy *et al.*, 1989). Model results (Hegg and Larson, 1990; Pandis *et al.*, 1990) have also

3   shown the importance of size-dependent cloud droplet chemistry, demonstrating that bulk

4   cloud water parameters are not applicable to processes taking place within individual cloud

5   droplets.

6   Cloud Dissipation. Upon evaporation, gases and particles contained in the droplets are

7   released back to the atmosphere. The particles after evaporation are likely to be quite

8   different (in both physical and chemical properties) from those that entered the cloud

9   because of in-cloud processes. Both modelling and experimental results have shown that

0   sulphate particle concentrations before and after passage through a cloud differ

1   significantly, with much larger concentrations and modified size-distributions in the

2   outflows of the cloud systems (Bower *et al.*, 1997; Hoppel *et al.*, 1986; Laj *et al.*, 1997;

3   Wiedensohler *et al.*, 1997). The effects of multiple cloud passages on CCN have important

4   implications for the direct aerosol radiative forcing by increasing the efficiency of light

5   scattering due to in-cloud particle growth (Yuskiewicz *et al.*, 1999).

6

7   **Box 4.3.** The utility of the CCN concept

8   The concept of CCN has been accepted by the cloud physics community and by most of

9   the aerosol research community for many decades. Its attractiveness stems partly from the

0   pioneering work of Twomey (1959) who introduced measured supersaturation (CCN)

1   spectra into cloud modelling. Visualising a distinct "subset" of the very complex

2   atmospheric aerosol as a well-defined and measurable quantity which is sufficient for a

3   description of the interaction of aerosols and clouds is another factor contributing to the

4   attractiveness and the wide application of the CCN concept.

5   However, there are over-simplifications inherent to this concept that become

6   increasingly difficult to justify with the rapidly increasing experimental and modelling

7   capabilities of atmospheric aerosol research. The concept or definition of CCN is at best

1   operational and any quantification of CCN with existing instrumentation is strongly

2   dependent on the thermodynamic evolution forced upon an aerosol sample in any particular

3   CCN counter. An intrinsic problem is that the thermodynamic evolution occurring in any

4   experimental CCN device bears rather little resemblance to the condensational growth that

5   happens in any real cloud. There are many physical and chemical factors contributing the

6   actual subset of the total particle population, which is incorporated into a particular growing

7   cloud. Even certain gaseous species can strongly affect the growth of cloud elements

8   (Kulmala *et al.*, 1993).

9   Additionally, the concentration of CCN at a particular supersaturation is not necessarily

0   applicable to the prediction of cloud droplet concentration. Even the generally accepted

1   hypothesis that an increased in concentration of CCN leads to an increase in cloud droplet

2   concentration is not necessarily correct, particularly in a mixed population of CCN species.

3   For example, an enhancement in CCN concentration measured at 0.2% supersaturation,

4   which is typical of moderate stratocumulus clouds, would suggest a similar increase in

5   cloud droplet concentration within these cloud types. However, if the additional CCN are

6   activated at supersaturations considerably lower than 0.2%, the resulting depletion of water

7   vapour and a suppression of peak supersaturation in a real cloud can inhibit activation of a

8   significant fraction of the pre-existing CCN population. This results in a reduction in cloud

9   drops (O'Dowd *et al.*, 1999).

0   Avenues of research that may be expected to resolve the CCN-problem include more

1   detailed experimental studies of the condensational growth properties of size-resolved

2   atmospheric particles and ensuing parameterisations for cloud models, and cloud simulation

3   experiments with more realistic flow-through cloud simulators.

4

5   3.3.5   Atmospheric deposition processes

6   Wet deposition and dry deposition are predominant removal pathways for a variety of

7   important trace gases as well as for suspended particulate matter. As such they act as key

1   determinants of the residence times and concentrations of tropospheric aerosols as well as a

2   large variety of pollutant gases.

3   Deposition processes often involve multistage pathways and include interactions

4   between gaseous and particulate pollutants. This is especially true with wet deposition,

5   which often occurs through a complex interaction involving various combinations of

6   sorption, solubilisation, nucleation, aerosol capture, aqueous reaction, precipitation

7   formation, and precipitation delivery. Dry-deposition processes, while not so multifaceted

8   in nature, nevertheless can be complicated by fast chemical reactions (e.g., the O_3 — NO —

9   NO_2 system; (cf. Gao *et al.*, 1993) and by condensational particle growth in humidity

0   gradients (Zufall *et al.*, 1998).

1   The level of scientific effort in deposition research during the past ten years — while

2   appreciable — is significantly less than corresponding efforts during the 1970's and 1980's,

3   when these subjects were receiving much more attention. As a consequence, some of the

4   older reviews of dry deposition (e.g., Hicks *et al.*, 1990) and wet deposition (e.g., Hales,

5   1990) still provide useful and relatively up-to-date synopses. Significant advances during

6   the past decade are summarised below.

7

8   3.3.5.1 Dry deposition

9   Wesely and Hicks (2000) present a recent review of dry-deposition research which,

0   combined with Hicks *et al*. (1990), provides an up-to-date summary of scientific

1   understanding in this field. Brook *et al.* (1999a) review past measurements of deposition

2   velocities and model results. Recent scientific progress in this area has been limited by

3   complexities in four main areas, as follows:

4   Measurement. Air/surface exchange fluxes to and from natural surfaces are, typically,

5   exceedingly difficult to measure — a feature resulting in a profusion of (relatively) direct as

6   well as indirect surrogate and inferential measurement methods (Wesely and Hicks, 2000).

7   Techniques such as eddy-correlation, eddy accumulation, and profile methods directed

1   toward measuring Reynolds fluxes (i.e., those associated with turbulent pollutant transport)

2   are generally favoured for gas-flux measurement when practicable, but require pollution-

3   monitoring equipment that has fast time-response, high precision, or both. Such methods are

4   applicable for measuring fine-particle fluxes as well, but are inappropriate for larger

5   particles, whose gravitational settling rates contribute significantly to the total deposition

6   flux. Much of the advancement in air/surface gas-exchange measurement during the past

7   decade derives from the advent of newer, fast-response instrumentation, allowing Reynolds-

8   flux measurement for a number of additional gases and particles (Gallagher *et al.*, 1997;

9   Shaw *et al.*, 1998).

0   <u>Conceptual Microscale Model Development</u>. Most recent development has occurred in

1   two separate but related areas. The first of these, which is basically an extension of the

2   traditional "resistance" analogy, results from more detailed description of the

3   micrometeorological and deposition-substrate processes within complex canopies, such as

4   forests and croplands. Although founded on simplified concepts that sometimes do not

5   conform with actual two way exchange processes, such conceptual models often involve

6   considerable complexity.

7   The second area of research progress is basically an attempt to replace the irreversible

8   deposition approach with a conceptual model that includes the complex of physical,

9   chemical, and biological interactions occurring on and within the deposition substrate. For

0   practical reasons these complex features are usually characterised in terms of their off-

1   gassing potential, typically embodied in the form of a "compensating" surface concentration

2   at which the deposition and emission fluxes balance. Measurements of compensation points

3   for various depositing species and receptors are becoming more prevalent with modern

4   chamber and cuvette studies, as well as with advanced Reynolds-flux methods. Other

5   simplified approaches include the incorporation of capacitance as well as resistances into

6   modified electrical analogue models. Owing to the obvious complexity of the physical

7   systems being simulated, these attempts are currently at an early development stage.

1   Large-Scale Parameterisations. Significant advances in dry-deposition parameterisation

2   for large-scale chemical-transport models during the past ten years have occurred through

3   extension of traditional procedures (Brook *et al.*, 1999b) as well as incorporation of satellite

4   land-use mapping (Gao, 1995; Gao and Wesely, 1995).

5   Advanced Monitoring and Field Studies. Resulting in part from the advent of the newer

6   instrumentation noted above, a number of advanced field studies have been conducted,

7   which have contributed significantly to the general understanding of dry-deposition rates

8   and processes. The comprehensive investigation of dry deposition in the Speulder forest in

9   the Central Netherlands is a prime example of such efforts (cf. Erisman *et al.*, 1997 and

0   companion articles in that issue).

1

2   3.3.5.2 Wet deposition

3   Many of the more recent scientific advancements in wet-deposition and precipitation-

4   scavenging research have been associated with large, multi-participant efforts such as those

5   in the European Ground-Based Cloud Experiment (Fuzzi *et al.*, 1992; Wobrock *et al.*, 1994)

6   and the High Alpine Aerosol and Snow Chemistry Study (Nickus *et al.*, 1997).

7   Major features of the precipitation-scavenging sequence were understood scientifically

8   by the close of the 1980's. Because of this, advancements since that time can be considered

9   either as mechanistic augmentations to existing theory or as extensions to composite

0   modelling of the scavenging phenomenon. Particularly important advances have been made

1   in the areas of aqueous-phase chemistry, aerosol interactions *(*especially with regard to

2   nucleation phenomena), and composite modelling. Advances in key categories during the

3   past decade are summarised below.

4   Aqueous-Phase Chemistry. Jacob (2000) presents a review of progress in aqueous-

5   phase chemistry processes of importance to scavenging processes. Much of the more recent

6   advancement in this area pertains to the behaviour of in-cloud HO_X chemistry. Aqueous

1   reaction chemistry of a number of pollutant species (e.g., SO_X, NO_Y, soluble organics) is

2   believed to be linked closely with this oxidant chemistry.

3   Aerosols and Cloud Nucleation. During the past decade a number of field, laboratory,

4   and theoretical studies have been aimed at evaluating cloud nucleation rates of mixed

5   aerosol particles in competitive environments as functions of particle size, particle

6   composition, and saturation conditions. These studies are particularly important to

7   scavenging research because they have the potential of shedding considerable light on

8   relative efficiencies for scavenging specific pollutant aerosol-particle classes as functions of

9   storm type and intensity. Several examples of field measurements of related phenomena

0   appear in references associated with the multi-participant studies cited above. Abdul-

1   Razzak and Ghan (2000) provide a recent example of theoretical analysis of aerosol

2   activation by multiple aerosol types.

3   Composite Modelling. Although several global and regional models of the 1990's have

4   incorporated increasingly complex characterisations of wet chemistry and precipitation

5   scavenging (Rasch *et al.*, 2000), the results of these efforts shed comparatively little light on

6   physical and chemical mechanisms for of the scavenging process. On the other hand a

7   number of mesoscale modelling efforts have occurred during the past decade which

8   potentially can provide valuable mechanistic insights, especially when linked appropriately

9   with modern field studies. The paper by Voisin *et al.* (2000) provides a recent example of

0   such an effort.

1

2   **3.4   Aerosol effects**

3   Aerosols influence the earth's radiative balance both directly and indirectly (through their

4   influence on cloud properties). The magnitude and sign of these influences are variable, and

5   the controlling properties and processes behind the radiative effects are presently not well

6   understood. Understanding these controlling properties and processes, and quantifying the

7   influence of aerosols on the radiative balance of the earth will be a major component of

1   aerosol research in the next decade. Aerosols also affect the actinic flux and, as such,

2   photochemistry.

3

4   3.4.1   Direct radiative effects

5   Aerosols both scatter and absorb incoming solar radiation. If incoming radiation is scattered

6   back to space, the energy contained in the scattered photons is lost. In this case, aerosols

7   would have a cooling effect. If the incoming radiation is absorbed in an aerosol layer above

8   the earth's surface, the energy contained in the absorbed photons is transformed to heat, and

9   would result in a warming of the absorbing layer.

0   On a mass basis at a wavelength of 0.55 μm, the scattering efficiency of spherical

1   particles is approximately log-normally distributed with the most efficient size range for

2   scattering occurring between particle diameters of about 0.2 and 1.0 μm. Scattering can be

3   apportioned to the various chemical constituents that make up the atmospheric aerosol, and

4   which particular component dominates scattering will depend on geographical location,

5   time, and a number of other factors.

6   Sulphate aerosol has received the most attention in assessing the direct radiative effects

7   of aerosols (Charlson *et al.*, 1990, 1992), but later work has shown that other chemical

8   components are also important. Over the oceans, sea-salt can contribute substantially to the

9   total aerosol optical depth. Based on measured sea-salt concentrations at the surface and

0   submicrometer and supermicrometer sea-salt mass scattering efficiencies of 8.7 ± 4.4 m^2 g^{-1}

1   and 1.9 ± 0.28 m^2 g^{-1}, respectively, sea-salt is estimated to contribute $90 \pm 10\%$ to aerosol

2   optical depth in the 20°S to 20°N latitude band at 140°W (Quinn and Coffman, 1999).

3   Using sea-salt distributions from a chemical transport model and similar mass scattering

4   efficiencies, Tegen (1999) estimated an 87% relative contribution from sea-salt in this same

5   region, a 57% contribution for the world's oceans, and a 44% contribution to the global

6   aerosol optical depth. Similarly, based on a comparison of clear-sky, top of the atmosphere

7   solar irradiances observed by the Earth Radiation Budget Experiment with those calculated

1   from a general circulation model, Haywood *et al.* (1999) reported that sea-salt is the leading

2   particulate contributor to the global mean clear sky radiation balance over oceans. Organic

3   aerosols can also be a significant contributor to particulate scattering. From aircraft flights

4   off the east coast of the U.S., Hegg *et al.* (1997) show that organic aerosols accounted for a

5   substantial fraction of aerosol light scattering. Mineral dust has also been shown to have

6   large influences on the radiative balance (Li *et al.*, 1996; Sokolik and Toon, 1996).

7   The radiative forcing, defined as the change in the radiative fluxes at the top of the

8   troposphere or top of model domain due to a given aerosol component, has been calculated

9   by off-line and by on-line models for a wide variety of different particle distributions and

0   emission scenarios (Houghton *et al.*, 1996; Shine and de F. Forster, 1999; Tegen and Miller,

1   1998). Estimates of the global mean direct forcing range (for sulphate) between –0.20

2   (Hansen *et al.*, 1997a) and –0.82 W m^{-2} (Haywood and Ramaswamy, 1998). Based on the

3   very few studies estimating effects of other materials than sulphate, the radiative forcing of

4   carbonaceous particles is about –0.4 W m^{-2} (Cooke *et al.*, 1999; Hansen *et al.*, 1997a;

5   Penner *et al.*, 1998), that of anthropogenically disturbed mineral dust +0.09 W m^{-2} (with

6   –0.25 in the solar and +0.35 in the infrared part of the spectrum) (Miller and Tegen, 1998).

7   Haywood *et al.* (1999) calculated short-wave forcing by major natural and anthropogenic

8   constituents. Reported top-of-atmosphere global-annual forcing (in W m^{-2}) were natural

9   sulphate, -0.93; anthropogenic sulphate, –0.72; organic carbon, –1.02; black carbon +0.17;

0   natural dust –0.58; anthropogenic dust –0.54. Two estimates were given for sea-salt based

1   on low and high emission values, –1.51 and –5.03 W m^{-2}, respectively.

2   The wide range of values for the calculated global direct radiative forcing of aerosols

3   clearly shows that we need more information about the chemical components of the aerosol,

4   their state of mixing in the atmosphere, their relative contribution to light scattering and

5   absorption, their response to varying relative humidity conditions, and a better

6   understanding of the cycles of the various species that make up the aerosol. The large

1 uncertainty in direct aerosol forcing also precludes robust quantitative estimates of climate

2 response.

3

4 3.4.2   Indirect effects

5 The indirect aerosol effect is presently the most uncertain of the known forcing mechanisms

6 in the prediction of climate change. The indirect effect refers to potential changes of cloud

7 properties at the global scale due to anthropogenic perturbations of the concentrations and

8 physical and chemical properties of the particles which form cloud drops or ice crystals.

9 Bridging the scales involved is one of the major challenges in understanding and predicting

0 the indirect radiative effect of aerosols. While the radiative effect itself is global, the

1 processes causing the effect happen on spatial scales of micrometers and temporal scales of

2 seconds. Thus, the global-scale phenomenon cannot be quantitatively understood and

3 predicted without an understanding of the microscale processes that cause it.

4   The basis of the indirect effect is a link that was established by Twomey (1974),

5 between aerosol properties, cloud droplet concentrations and cloud albedo. For a given

6 cloud liquid water content and vertical extent, Twomey showed that an increase in aerosol

7 particle number could lead to an increase in cloud droplet number concentration and a

8 decrease in mean drop size, which would cause an increase in cloud albedo. The increase in

9 cloud albedo would lead to cooling, and partially counteract part of the warming due to

0 greenhouse gases (Slingo, 1990). The main contribution to the indirect effect is thought to

1 come from marine stratocumulus clouds (Randall *et al.*, 1984) However, cirrus clouds may

2 also be influenced by anthropogenic aerosol emissions, and in the cirrus case not even the

3 sign of the global radiative effect is yet known. Additional feedback mechanisms potentially

4 responsible for the uncertainty in the prediction of the effect are the extension of cloud

5 cover with increasing global temperature (Arking, 1991), the reduction of cloud

6 precipitation efficiency in clouds causing an increase in their lifetime or extent (Albrecht,

7 1989), the coupling between diabatic processes and cloud dynamics (Martin and Jonas,

1   1997; Pincus and Baker, 1994), and the radiative effect of in-cloud absorption on short

2   wave radiation (Boers and Mitchell, 1994).

3   A number of experiments have been carried out with the aim of better understanding the

4   aerosol/cloud interactions responsible for the indirect radiative effect. In marine

5   stratocumulus clouds, ship tracks have been used as a natural laboratory to better

6   understand how anthropogenic aerosol emissions cause observable increases in cloud

7   albedo (Durkee *et al.*, 2000b; King *et al.*, 1993; Radke *et al.*, 1989). In another approach,

8   Brenguier *et al.* (2000) reported observations in marine stratocumulus clouds during the

9   second Aerosol Characterisation Experiment (ACE-2). In these studies, simultaneous *in situ*

0   measurements of cloud microphysical properties and remote sensing of the cloud radiances

1   in the visible and near-infrared provided direct evidence of changes in cloud radiative

2   properties related to changes in the aerosol background. Drizzle suppression has also been

3   observed in clouds influenced by anthropogenic pollution, both from *in situ* measurements

4   (Ferek *et al.*, 2000) and from satellite observations (Rosenfeld, 2000). Anthropogenic

5   effects on cirrus cloud radiative properties have also been investigated in recent years,

6   particularly in terms of the effects of aircraft emissions on cirrus cloud properties. Wyser

7   and Ström (1998) showed that the balance between shortwave cooling and longwave

8   heating effects of cirrus clouds could be very sensitive to changes in crystal size caused by

9   aerosol emissions from aircraft. Several recent research programs have been specifically

0   aimed at assessing the effects of aircraft emissions on cirrus cloud properties

1   (Brasseur *et al.*, 1998; Schumann *et al.*, 2000; Toon and Miake-Lye, 1998).

2   Detecting large-scale changes in cloud properties from satellites has proven to be

3   challenging. As examples, Han *et al.* (1994) showed that cloud fields immediately

4   downwind of continental pollution sources were brighter than similar mid-ocean clouds - a

5   result consistent with the ship tracks observations, but on a much larger scale. Indications of

6   the indirect effect are also presented in Rosenfeld and Lensky (1998). These authors analyse

7   AVHRR images of cumulus fields and derive the cloud top temperature and droplet

1   effective radius. Variations of the relationship between those two parameters were

2   interpreted as a sign of changes in cloud radiative properties due to continental pollution.

3   Several global-scale model studies have been undertaken to try to explore the

4   consequences of anthropogenic aerosol emissions on cloud radiative properties. While the

5   parameterisations used in the models are limited by an incomplete understanding of the

6   processes involved and a lack of data on nearly all scales, the results indicate that the

7   indirect effect may be very important.

8   The first studies of the indirect effect considered anthropogenic sulphate as calculated

9   by Langner and Rodhe (1991) as a surrogate for all particles produced by anthropogenic

0   emissions and used an empirical relationship to relate the particle mass to the number of

1   cloud drops (Boucher and Lohmann, 1995; Hegg, 1994; Jones *et al.*, 1994). These studies

2   calculated only the possible effect of anthropogenic sulphate particles on the cloud albedo.

3   Glantz and Noone (2000) have recently presented an algorithm for relating accumulation-

4   mode particle mass to cloud droplet number for use in regional or global scale models that

5   follows the physical processes that occur in the atmosphere. In a next step the sulphur

6   chemistry has been coupled with the cloud microphysics to estimate the effect of particles

7   on the cloud life-time and the cloud water content (Jones *et al.*, 1999; Lohmann and

8   Feichter, 1997; Rotstayn, 1999a). Mechanistic approaches which relate the particle number

9   to the cloud droplet number concentration have been proposed by several groups

0   (Chuang *et al.*, 1997b; Ghan *et al.*, 1997; Lohmann *et al.*, 1999a).

1   For indirect forcing by sulphate model estimates range from –0.4 to –2.1 W m^{-2}

2   (Boucher and Lohmann, 1995; Chuang *et al.*, 1997a; Feichter *et al.*, 1997; Jones *et al.*,

3   1999; Jones and Slingo, 1996; Kiehl *et al.*, 2000; Lohmann and Feichter, 1997;

4   Lohmann *et al.*, 1999b; Rotstayn, 1999a,b).

5   The relationship between radiative forcing and climate response was examined for a

6   wide range of different artificial perturbations by Hansen *et al.* (1997b). The direct and

7   indirect climate effects of anthropogenic sulphate were examined for equilibrium (constant)

1   or transient changes in sulphate distributions, and with prescribed or interactively calculated

2   forcing. Tegen and Miller (1998) calculated the climate effect of mineral dust interactively

3   in an equilibrium simulation. Besides the uncertainties associated with the distribution and

4   the optical properties of aerosol particles, climate models exhibit a wide scatter in the

5   climate sensitivity (defined as the ratio of the change in the global mean surface air

6   temperature to the global mean radiative forcing) arising from differences in approaches to

7   treating cloud physical processes and in the assumed optical properties of clouds (e.g.,

8   Cess *et al.*, 1996). Again in view of the many uncertainties associated with understanding

9   and description of aerosol sources and processes and with parameterisation of these

0   processes, such forcing and ensuing climate responses simulated by models must still be

1   considered rather tentative.

2

3   **Box 4.4**. Effects of volcanoes

4   In addition to their considerable contribution to the tropospheric sulphur budget,

5   episodic strong volcanic eruptions reaching the stratosphere cause measurable climatic

6   effects over a few years. Such events with injection of more than   3 Mt SO_2 to the

7   stratosphere occur with a mean recurrence time of about one per decade. The increase of

8   stratospheric sulphate aerosol after these events by one to two orders of magnitude brings

9   about a reduction of solar radiation reaching the troposphere of 2-5 W/m^2 in the global

0   mean, thus overcompensating the anthropogenic greenhouse effects for 1-2 years. The

1   resulting radiative cooling was observed and modelled to be -0.3 to -0.5 K (global annual

2   mean). Discrepancies between observations and model results based on only solar radiation

3   effects were overcome by the inclusion of terrestrial radiative heating of the stratospheric

4   aerosol layer (Graf *et al.*, 1993). The 2-4 K warming of the low-latitude lower stratosphere

5   by this effect intensifies the polar winter vortex with consequences for the structure of

6   tropospheric planetary waves. This dynamical effect results in advective "continental winter

1 warming" (Robock and Mao, 1992) after tropical eruptions in the northern mid- and high

2 latitudes reaching maxima of +6 K over Siberia.

3   The size distribution and optical properties of background and disturbed stratospheric

4 aerosol is known better than for most tropospheric aerosols and was successfully modelled

5 in a CTM (Hamill *et al.*, 1997) and in a climate model (Timmreck *et al.*, 1999).

6   Mainly during volcanically disturbed episodes the gravitational setting of stratosphere

7 sulphate aerosols considerably contributes to upper tropospheric aerosol. Tropopause falls

8 also during other times bring stratosphere aerosol to this region and enhance the occurrence

9 of cirrus clouds. After the eruptions of El Chichòn (1982) and Pinatubo (1991) (sub)visible

0 cirrus increased by   10%. Due to heterogeneous reactions with anthropogenic chlorine the

1 enhanced sulphate aerosol also leads to a decrease of stratospheric ozone (Brasseur and

2 Granier, 1992), which reduces the net heating of the aerosol layer.

3

4 3.4.3   Aerosol effects on actinic flux

5   Solar radiation, especially in the ultraviolet (UV) range, is a driving force of

6 tropospheric photochemistry. The presence of tropospheric aerosols results in additional

7 scattering and absorption of the UV radiation and, hence, affects photolysis rates. Several

8 recent studies pointed out that this aerosol effect might strongly perturb the formation of

9 ozone and other trace gases in the lower atmosphere (Dickerson *et al.*, 1997). For given

0 meteorological conditions and levels of photochemically active gases, photolysis rates and

1 ozone production are most sensitive to the aerosol loading and aerosol optical properties.

2 The strong UV-absorbing aerosols (such as soot and mineral dust) cause a decrease in

3 photolysis rates, which, in turn, inhibits ozone production. The presence of purely scattering

4 aerosol (such as sulphate) or clouds in the boundary layer can increase photolysis rates near

5 the ground and enhance ozone production in the upper atmosphere (He and Carmichael,

6 1999). However, near-ground photolysis rates decrease as aerosol loading increases.

7 Because the distribution of tropospheric aerosols and clouds are highly variable in space

1   (vertically and horizontally) and time, the quantification of the aerosol impact on the

2   photochemical oxidant cycle remains a challenging problem.

3

4.   Research approaches

5

4.1   *In situ* observations with intensive campaigns

7   To a great extent the revolution in atmospheric aerosol research during the past decade can

8   be attributed to a change in the way aerosol measurements and chemical atmospheric

9   measurements in general are being conducted. Investigators and funding agencies are

0   recognising that meaningful progress in understanding atmospheric aerosol properties and

1   processes requires a large number of measurement capabilities to be brought to bear at the

2   same time. This research strategy results in over-determined data sets that can be used in

3   closure studies (Ogren, 1995; Quinn *et al.*, 1996a). From the beginning, closure studies

4   were seen as tools to summarise critically and quantitatively the state of knowledge about

5   characteristics, processes and effects of the atmospheric aerosol. This strategy is adding

6   new rigor to aerosol field measurements and becomes increasingly important as the

7   complexity of the aerosol mixture increases. To date this approach has been used

8   successfully in ACE-1 (Covert *et al.*, 1998; Huebert *et al.*, 1998; Quinn and Coffman,

9   1998), TARFOX (Russell *et al.*, 1999) and ACE-2 (Collins *et al.*, 2000; Durkee *et al.*,

0   2000a; Livingston *et al.*, 2000; Neusüß *et al.*, 2000; Putaud *et al.*, 2000; Russell and

1   Heintzenberg, 2000; Schmid *et al.*, 2000) and it is a key strategy of INDOEX and ACE-

2   Asia.

3   A second and related advance in the past decade is the conduct of aerosol investigations

4   over rather large arenas, thousands of kilometres or more, in order to capture significant

5   aerosol processes that are taking place over such geographical scales. These studies require

6   resources—ships, aircraft, and surface-based stations, as well as large numbers of

7   investigators and specialised instruments—resources that are often beyond those available

1   to single agencies or even single countries. With such resources it has been possible to

2   conduct Lagrangian experiments. This Lagrangian research strategy, where an atmospheric

3   air parcel is identified and followed during its transport, has been employed in several of

4   these large-scale experiments (ASTEX-MAGE (Huebert *et al.*, 1996); ACE-1 (Bates *et al.*,

5   1998); ACE-2 (Raes *et al.*, 2000a)) and has yielded process information with less

6   confounding effects of air mass changes.

7   Large-scale projects also require the active participation of meteorologists and

8   modellers who can provide descriptions of the governing transport fields that are necessary

9   for the interpretation of the observations and recently, in forecast mode, for aiding in

0   targeting aircraft missions. Mathematical models are the integrator of our understanding of

1   atmospheric processes and field data analyses are now being carried out hand-in-hand with

2   model implementation and evaluation. Moreover, some models are being used prior to the

3   field experiment in the design of the best possible measurement strategy. The increasing

4   interaction of experimentalists, modellers and meteorologists is a third major advance in the

5   past decade that is helping to advance rapidly our understanding of aerosol processes.

6   A fourth related advance and a major research strategy in these large international

7   experiments has been the open sharing of data among research participants and with the

8   broader research community, thereby greatly enhancing the utilisation and value of the data.

9   Similarly, much of the ability of meteorologists to contribute to these studies relies on the

0   availability of synoptic-scale meteorological data from the operational weather forecasting

1   community. The open sharing of meteorological data, derived data products and field data

2   has been a major international achievement.

3   Quality control of the host of particle instruments remains a crucial problem that limits

4   the gains of these large experiments as compared to focused small scale process studies.

5

1 **4.2   *In situ* observations using long term monitoring networks**

2 Although large, intensive projects like ACE-1 and ACE-2 contribute a lot to the

3 understanding of aerosol characteristics and the underlying processes, they are not sufficient

4 to produce the needed 4-D aerosol climatologies. A major factor limiting the extent and

5 quality of present aerosol climatologies is the lack of well-defined and calibrated aerosol

6 monitoring programs. Worth mentioning are the networks operated by the University of

7 Miami until the mid 1990s (e.g. Prospero, 1996; Prospero *et al.*, 1983; Saltzman *et al.*,

8 1986) which provided a unique record of aerosol chemistry properties in the marine

9 environment, but were closed due to termination of funding. NOAA CMDL have records of

0 aerosol physical properties dating from the 1970s at their baseline stations, but limited

1 aerosol chemistry data (Bodhaine, 1989; Bodhaine and DeLuisi, 1985; Bodhaine *et al.*,

2 1986). There are other noteworthy individual efforts from, for example, Cape Grim

3 (Ayers *et al.*, 1991, 1995; Gras, 1995), Jungfraujoch (Baltensperger *et al.*, 1997;

4 Weingartner *et al.*, 1999), Hohenpeissenberg (Fricke *et al.*, 1997), Spitsbergen

5 (Heintzenberg and Leck, 1994), and Alert (Sirois and Barrie, 1999). In addition, regional

6 acid deposition networks such as EMEP in Europe, CAPMon, NAPAP and CaSTNET, and

7 air pollution networks such as IMPROVE, make selective measurements of aerosol

8 properties, but as the purpose of the networks is not primarily aerosol characterisation, the

9 resulting data are not always appropriate for climatological use.

0   For lack of suitable methodology and local competence the initial global aerosol

1 monitoring program designed by WMO (1993) has been of somewhat limited value so far.

2 This program had adopted a design philosophy of monitoring stable long-lived trace gases,

3 which adds little of value to interpretation of aerosol measurements. There are renewed

4 efforts to extend the Global Atmosphere Watch (GAW) program to detailed aerosol

5 measurements *(*GAW, 1994), and the World Data Centre for Aerosols

6 (http://www.ei.jrc.it/wdca/) has made progress in constructing an archive of existing data.

1   The latter has been used in the IGAC/WCRP intercomparison and validation study of global

2   CTMs of the sulphur cycle (Barrie *et al.*, 2000).

3

4   ## 4.3   Remote sensing of aerosols

5   Although much aerosol research has traditionally focused on *in situ* measurements, a major

6   exception has been remote sensing by sun photometry. The past decade has seen the

7   fielding of networks of well-calibrated instruments capable of measuring aerosol optical

8   thickness with high accuracy. The availability of such data on the web greatly enhances

9   their utility in developing aerosol climatologies and as observations against which models

0   can be evaluated. Surface-based Lidars are beginning to become routinely employed in

1   networks, and limited experience shows that these can provide vertical resolution that is

2   otherwise not available, and if multiple wavelengths are employed, useful microphysical

3   information. Another extremely valuable source of data to the aerosol research community

4   is satellite-borne instruments. Most data so far have come from passive instruments such as

5   radiometers; often the aerosol signal is obtained as a residual after subtraction of other

6   known or assumed contributions, and products such as aerosol optical thickness are

7   somewhat model dependent. Still the availability of such data has been a great stimulus to

8   aerosol researchers. Active devices such as satellite-borne Lidars hold great promise for the

9   future (see Chapter 5).

0

1   ## 4.4   Aerosol modelling

2   The need for improved aerosol models to address questions ranging from local and regional

3   air pollution to the direct and indirect radiative influence of aerosols on a global scale is

4   placing increasing demands on the aerosol modelling community. Most work to date has

5   focused on particulate mass of one given chemical species, particulate matter being treated

6   as a chemical species analogous to a gaseous compounds, without treatment of the

7   dynamics governing the size distribution. Several groups have represented in global scale

1   models mass loadings of key aerosol constituents--sulphate, nitrate, organics, elemental

2   carbon, sea-salt, dust--but the accuracy of these models is not yet well established. At the

3   subhemispheric scale measured and modelled daily-average concentrations of sulphate

4   agree typically within a factor of two.

5   Considerable effort is now being directed to developing models of aerosol

6   microphysical processes to gain predictive capability for the aerosol size distribution and

7   size-distributed composition. Representation of size-resolved aerosols is necessary for

8   accurate evaluation of radiative forcing, especially the indirect forcing, in which cloud and

9   aerosol microphysics play the central role. Likewise, from the perspective of developing

0   strategies to control local and regional particulate air pollution, it is necessary to develop

1   model-based representations of the processes responsible for aerosol loading that can

2   confidently relate this loading to sources of particulate matter and to other controlling

3   variables. However in view of the still limited understanding of many of the processes that

4   must be represented in the models it is clear that much effort must be directed to gaining

5   enhanced understanding before these processes can confidently be represented in models.

6   A major objective of global-scale aerosol modelling is evaluation of aerosol influences

7   on climate at present, over the industrial period, and for the future, for assumed emissions

8   scenarios. Until recently such assessments have used temporally-averaged aerosol fields or

9   surface albedo calculated in transport-transformation models that are run separately from

0   the climate model that is used to assess the climate influence; that is, the aerosol field is

1   calculated "off line". It is now recognised that such an approach may misrepresent key

2   features of aerosol-climate interactions, for example correlations between relative humidity

3   and particulate mass that might enhance direct forcing, or more intrinsically, the influence

4   of aerosols on precipitation development and resultant changes in the hydrological cycle.

5   For these reasons it is considered necessary ultimately to represent aerosols "on line" in

6   climate models. This may be expected to add considerable computational burden to climate

7   models, and it will be a challenge to the aerosol modelling community to develop accurate

1   and efficient methods of representing size- and composition-dependent aerosol processes

2   suitable for incorporation in climate models.

3

4   **5.   Research needs**

5   **5.1   Characterisation of the atmospheric aerosol**

6   Important uncertainties still remain on crucial parameters and measurements are needed to

7   understand better the emissions and characteristics of carbonaceous particles, to determine

8   optical properties of black carbon and particulate organic matter including information on

9   size distribution, optical properties and state of mixture.

0   Characterisation of primary particulate matter from combustion should include

1   divisions by mass into the fractions that are optically relevant: ash, organic carbon, black

2   carbon, and possibly sulphates. Particular attention is needed for the combustion practices

3   thought to contribute the largest fractions to the global burden of primary particles, such as

4   domestic coal and wood burning and industrial combustion in less-developed countries. The

5   hygroscopicity of these particles should be investigated as a first step in estimating their

6   lifetimes and contribution to cloud droplet nuclei. These studies are most important for

7   long-lived submicrometer particles.

8   A tabulation of combustion practice by region is needed for more accurate development

9   of emission inventories. Information on practice in non-OECD countries is particularly

0   lacking. There are no quantitative estimates of global fly ash source strength, in particular

1   concerning fly ash from biomass burning. There is also missing information on primary

2   mineral matter from sources other than combustion for heat and power.

3   Given that volcanic sulphur emissions are comparable to the much discussed

4   anthropogenic emissions for the atmospheric sulphate burden (and radiative effects), and

5   given that the volcanic emissions are highly variable in space and time, there is a need to

6   constrain better volcanic emission data. For a general background the volcanic sources

1   should be grouped according to their respective magma provinces. A combination with the

2   status of activity can then give better spatial and temporal information about the pattern of

3   emissions. In order to get better data on the absolute emission, more systematic

4   measurements are needed at least for those sources that contribute most. Exemplary long-

5   term (few years) measurements have to be made at some typical volcanoes and the

6   effectiveness of concentration measurements has to be tested against flux measurements.

7

8   ## 5.2   Formation and growth of particulate matter

9   Laboratory studies are needed to test further classical bimolecular nucleation theory and to

0   investigate more quanitatively the influence of ambient levels of ammonia and various other

1   potential biogenic and anthropogenic precursor compounds on nucleation rates. Also, a

2   quantitative study of ion-induced nucleation needs to be undertaken. As new potential

3   nucleation precursors are identified, field measurements including the development of new

4   techniques for quantification of these compounds will be needed to confirm or refute their

5   role in nucleation. Models should be developed to help explain laboratory results and to

6   help short-circuit the arduous path of investigating all possible combinations of nucleation

7   precursors. Models should also be run to determine where climatic and health influences of

8   this highly non-linear nucleation process are most sensitive to changes in precursor

9   concentrations.

0   There is a need to assess the relevance of the individual oxidation pathways to form

1   condensable species under environmental conditions, especially in the case of natural

2   precursors, and to understand the chemical mechanisms leading to very low volatility

3   oxidation products of ROGs. Also the influence of humidity on product yields and particle

4   yields requires further study. The speculation that organic particles might also affect the

5   oxidation capacity of the troposphere by representing a potential sink for atmospheric

6   radicals needs to be evaluated

1   The experimental data set for a more complete description of aerosol chemistry is very

2   sparse. Further systematic laboratory studies are required. Apart from experimental data for

3   single reactions such studies may also result in correlations which, in the future, may allow

4   the estimation of rate constants at elevated ionic strength in different cases chosen

5   according to electrolyte compositions.

6   The current level of understanding chemical reactions in matrices at elevated ionic

7   strengths is unsatisfactory and requires extensive further study. Here the approach of fitting

8   experimental data to an ion-pairing mechanism requires the use of experimentally

9   determined data only, but, at least at present, leads to the need of an explicit investigation

0   for every single reaction in each given electrolyte system. The ion-pairing approach for

1   chemical conversion reactions of highly reactive species implies a clear physico-chemical

2   mechanism to describe kinetically at least ion-neutral reactions. It should be combined with

3   the treatment of stable and moderately reactive species by their activities obtained from the

4   Pitzer approach or by extended Debye-Hückel treatments as far as applicable. More

5   experimental studies on kinetic primary ionic strength effects, resulting correlations and the

6   development of sound theories are required in order to better understand tropospheric

7   aerosol chemistry.

8

5.3   Aerosol/cloud interactions

0   The need to predict cloud element formation from given aerosol size distributions in models

1   provides a strong motivation for identifying the source of the apparent disparities between

2   aerosol physico-chemical measurements and cloud droplet number concentrations. Future

3   investigations will need to examine the influence of soluble gases, partly soluble material

4   and surface active materials on water uptake by aerosol particles and drops. There is need

5   for a co-ordinated effort to investigate CCN properties.

6   In the area of cloud chemistry current research is centred on the interaction of radicals

7   with organics which may also heavily influence the rate of S(IV) oxidation in droplets, alter

1   the pattern of precipitation composition, and may also lead to the production of harmful

2   substances. The radical-driven oxidation of S(IV) to S(VI), after a great deal of research,

3   constitutes an extensive research topic of its own. Attention needs to be given to understand

4   better occurrence and liquid phase chemistry of organic species via laboratory studies,

5   focused field campaigns and modelling efforts. Current efforts to measure and model size-

6   dependent cloud chemical composition should also be improved.

7   The challenge for the prediction of the indirect radiative forcing through aerosol/cloud

8   interaction (IAE) is to develop physically based GCM parameterisations from process

9   parameterisations. The predictable parameters in a GCM are much less numerous than the

0   measured parameters in a closure experiment and they characterise properties averaged over

1   a scale much larger than the typical process scale. The basic information for simulation of

2   the IAE are the characterisation of aerosol nucleation properties and the dynamic and

3   thermodynamic properties of the cloud field. Numerous questions have to be answered

4   collaboratively by experimentalists and modellers.

5   Most global climate model studies so far have only considered the bulk particulate mass

6   of few specific components rather than the size distributions of an externally and internally

7   mixed aerosol and size-dependent chemical composition. This was despite recognition that

8   the size distribution and the chemical composition of the particles controls the activation of

9   particles to cloud elements. Moreover, the cycles of aerosol particles are closely connected

0   with hydrological processes. Therefore, models have to consider the complexity of a multi-

1   phase system. Certainly a weak point of the climate models is the parameterisation of cloud

2   processes and properties and the cloud-radiation feedback. Uncertainties in the calculated

3   cloud properties are hard to quantify because satellite retrievals are not very accurate and *in*

4   *situ* measurements cannot be extrapolated.

5   Potentially, dynamic and precipitation effects through ice nucleation and crystal

6   multiplication processes have great global importance so that they should not be

7   disregarded in future aerosol research. However, there are large uncertainties in the

1   understanding of basic ice formation processes and their connection with the atmospheric

2   aerosol that need to be reduced before new experimental approaches for measuring ice

3   nuclei can be developed. With these new methodologies global inventories need to be

4   established which in turn will need to be connected to cloud microphysics and precipitation

5   data.

6   Physical techniques will continue to play a vital role in atmospheric science. The high

7   sensitivity that can be achieved means that extremely small sample masses are required.

8   Bulk aerosol compositional data provided by these techniques can be used for studies of

9   environmental cycling of various elements, aerosol mass closure studies and source

0   apportionment based on receptor modelling.

1   Single-particle analysis can certainly tell very interesting tales on the origin and

2   evolution of the atmospheric aerosol, for instance regarding the degree of external and

3   internal mixture and new particle formation. Single-particle compositional data still remain

4   to be reconciled with measurements of other properties performed *in situ* on individual

5   particles, such as hygroscopic and cloud-nucleating behaviour.

6   Concerning aerosol process modelling there is still a strong need for improvement

7   concerning the time efficiency and accuracy of these techniques, especially for applications

8   in atmospheric transport models. One of the most important questions today is how to

9   describe properly gas-to-particle mass transfer especially for organic material, i.e., how to

0   account for particle nucleation and growth processes when organic species are involved.

1   Models to calculate heteromolecular nucleation rates for organic species in atmospheric

2   systems are still either completely lacking or have large uncertainties, and probably will

3   continue to do so in the near future.

4

6.   Conclusions

6   The decade of the nineties has been one of major progress in the recognition of the role of

7   aerosols in global atmospheric chemistry, in describing concentrations and properties of

1   tropospheric aerosols and their geographical distribution, and in understanding the

2   controlling processes.

3   Much of this revolution has been fuelled by new measurement capabilities. Extension

4   of the range of differential mobility analysers and condensation particle counters down to

5   particle diameters of a few nanometers has revealed the episodic nature of nucleation

6   events, though the substances responsible for these events still remain a mystery. Single-

7   particle mass spectrometers have revealed that the internal and external state of mixing of

8   particles is much richer than had previously been imagined. This richness is a challenge to

9   explain but it provides a means of identifying the processes responsible for formation of

0   particulate matter in the atmosphere. To a great extent the revolution in atmospheric aerosol

1   research can be attributed also to a change in the way aerosol measurements and

2   atmospheric chemistry measurements generally are being conducted. Investigators and

3   funding agencies are recognising that meaningful progress in understanding atmospheric

4   chemistry processes requires a large number of measurement capabilities to be brought to

5   bear at the same time.

6   The enhanced understanding is making its way into numerical models describing the

7   emissions, transport, transformation, and deposition of aerosols and their precursors on a

8   variety of scales, from urban air sheds to global.

9   During the past decade it has become clear that human activities have dramatically

0   modified the regional distributions of atmospheric aerosols. It is also evident that

1   anthropogenic aerosols play a major role in the determination of local and regional climatic

2   regimes, through both direct and indirect radiative forcing of climate. Increases in

3   anthropogenic aerosols can cause potentially disruptive changes to sociologically and

4   economically important factors such as regional hydrological cycles.

5   While we now know the nature of many of the processes responsible for these impacts,

6   in many cases our understanding is not yet sufficiently quantitative for accurate prediction

7   of the severity of impacts. Fortunately, the rapid progress of the last decade in the

1   development of new observational and simulation tools and of new strategies for employing

2   them in concert suggests that we will be able to develop a useful predictive capability.

3   The aerosol-related activities of IGAC have played a leading role in bringing our

4   understanding of atmospheric aerosols and their effects to its present state.

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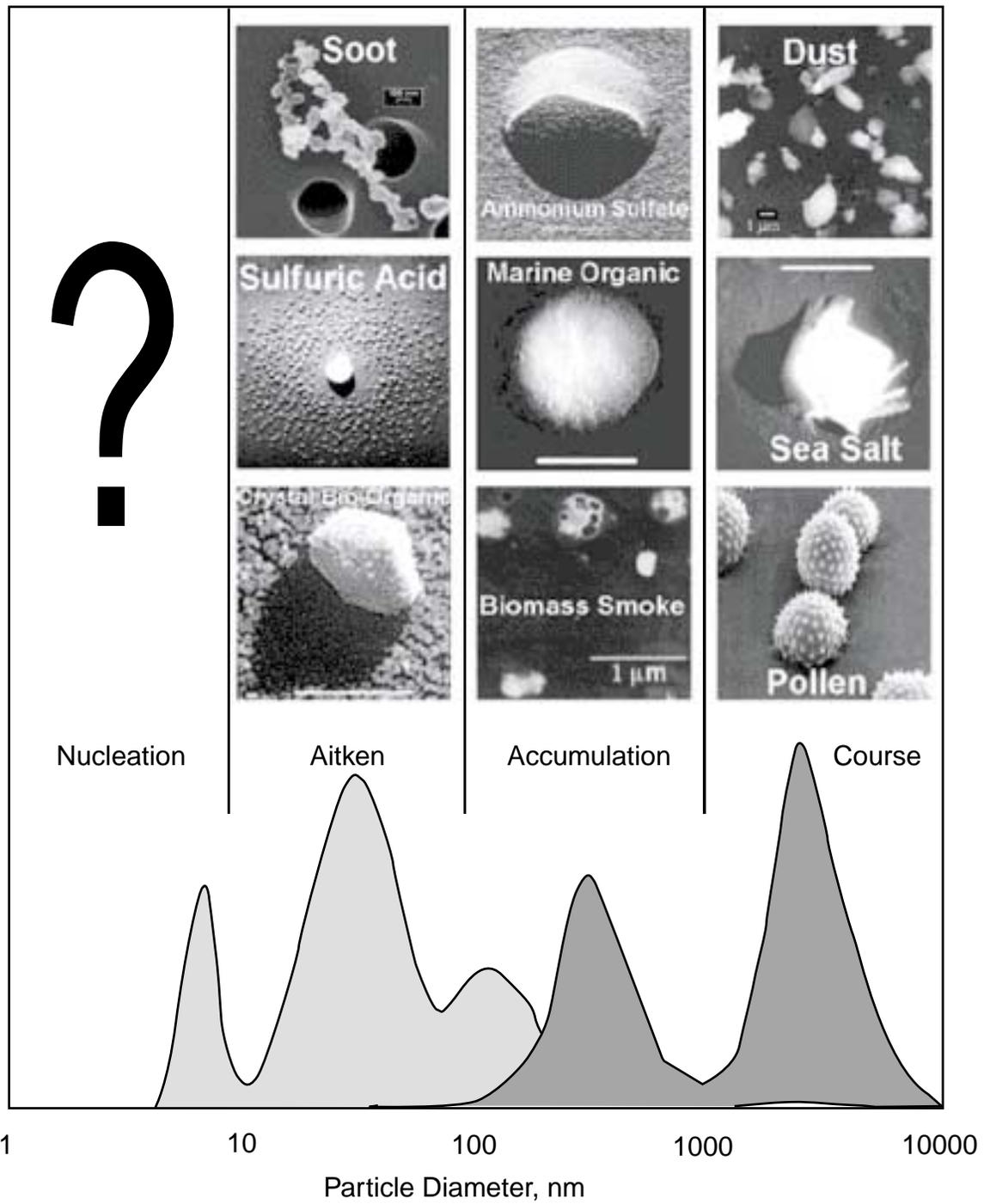
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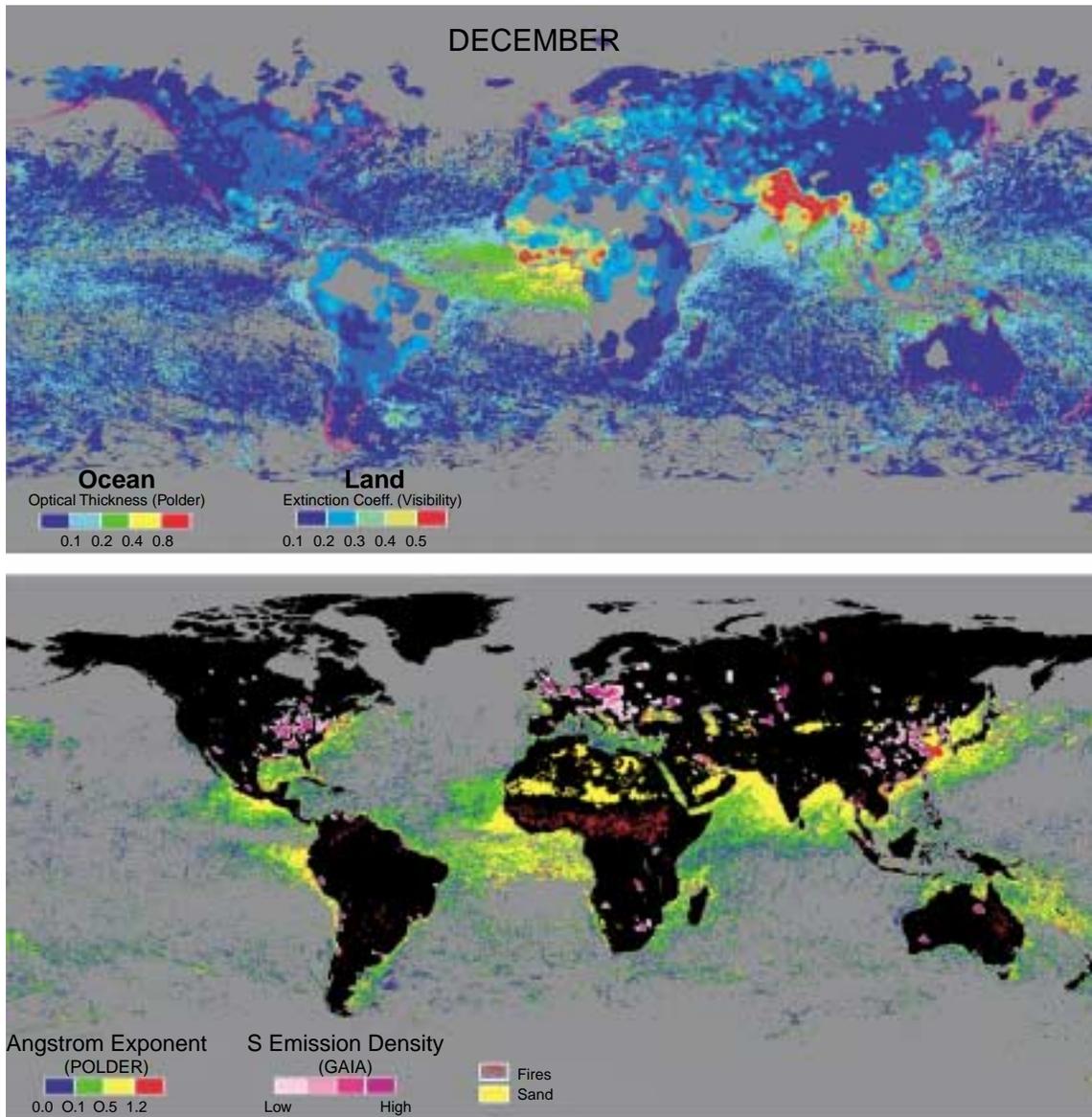
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Table 1. Natural processes leading to particle production and anthropogenic processes leading to changes of the natural aerosol.

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 PARTICLES

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
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

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
Dimethyl-sulfide	Phytoplankton degradation	Increased oxidation capacity	Increased sulfate	Changing winds hence air-sea exchange
SO_2	Volcanic emissions	Fossil fuel combustion	Increased sulfate	
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	

Soot

Ammonium Sulfate

Dust

1 μm

Sulfuric Acid

Marine Organic

Sea Salt

Crystal Bio-Organic

Biomass Smoke

1 μm

Pollen

?

Nucleation Aitken Accumulation Course
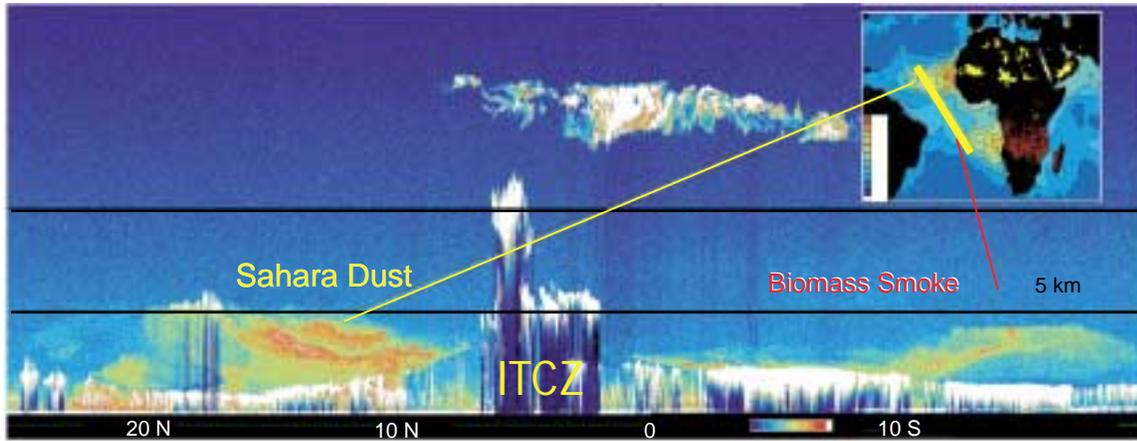
1 10 100 1000 10000

Particle Diameter, nm

Figure 2a. Global map at 18 km resolution showing monthly average aerosol optical thickness at 865 nm over water surfaces for June, 1997, derived from radiance measurements by the POLDER (POLarization and Directionality of the Earth's Reflectance) radiometer aboard the ADEOS (ADvanced Earth Observing Satellite) platform. Reproduced with permission of Laboratoire d'Optique Atmospherique (LOA), Lille, FR; Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif sur Yvette, FR; Centre National d'etudes Spatiales (CNES), Toulouse, FR; and NAtional Space Development Agency (NASDA), Japan.
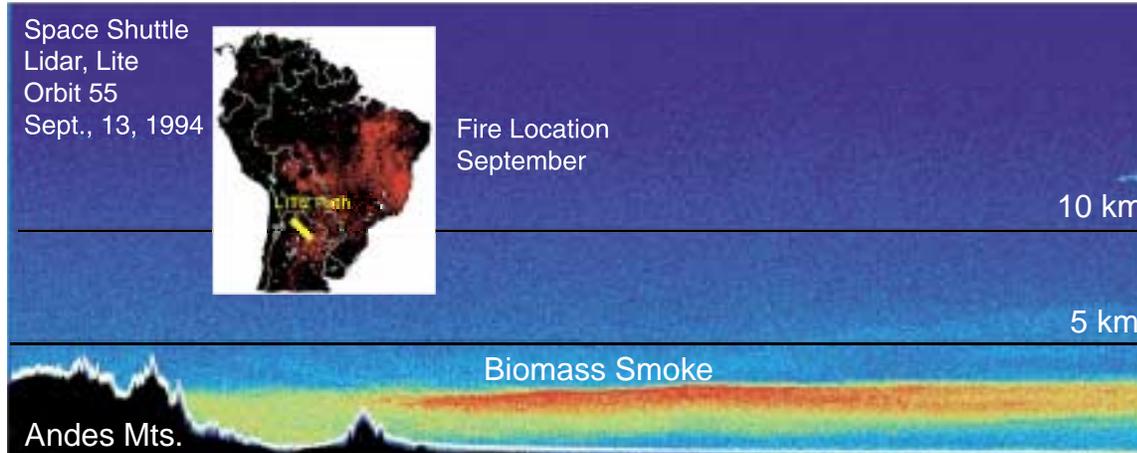
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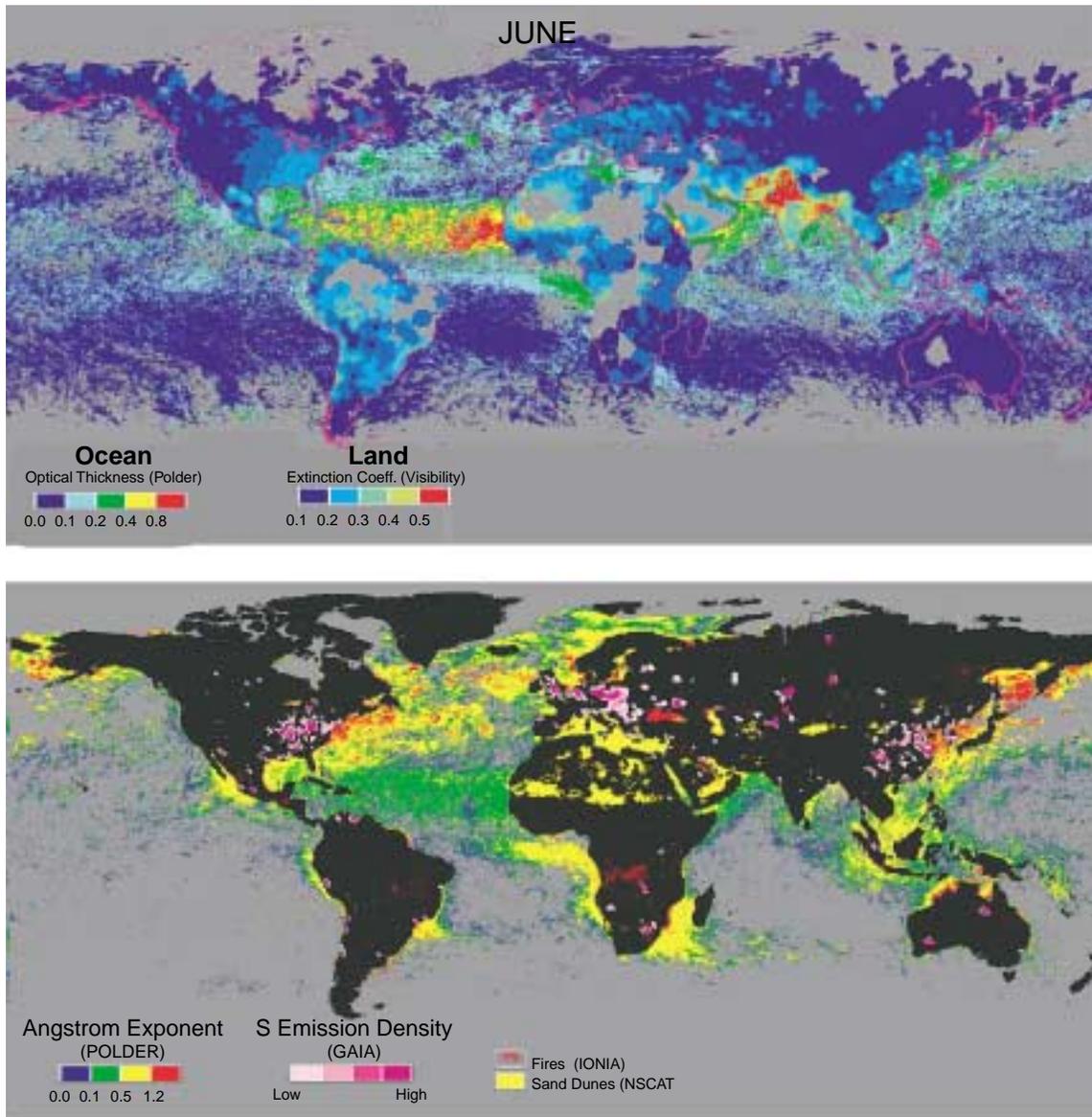
Figure 2b. Ångström exponent of the aerosol optical depth derived from channels 670 and 865 nm of the same data set. This parameter is a rough indicator of particle size and allows the geographic separation of windblown dust (large particles: low values) from biomass smoke or sulfate haze (small particles: high values). For further information see http://earth-sciences.cnes.fr:8060/polder/Mission.html.
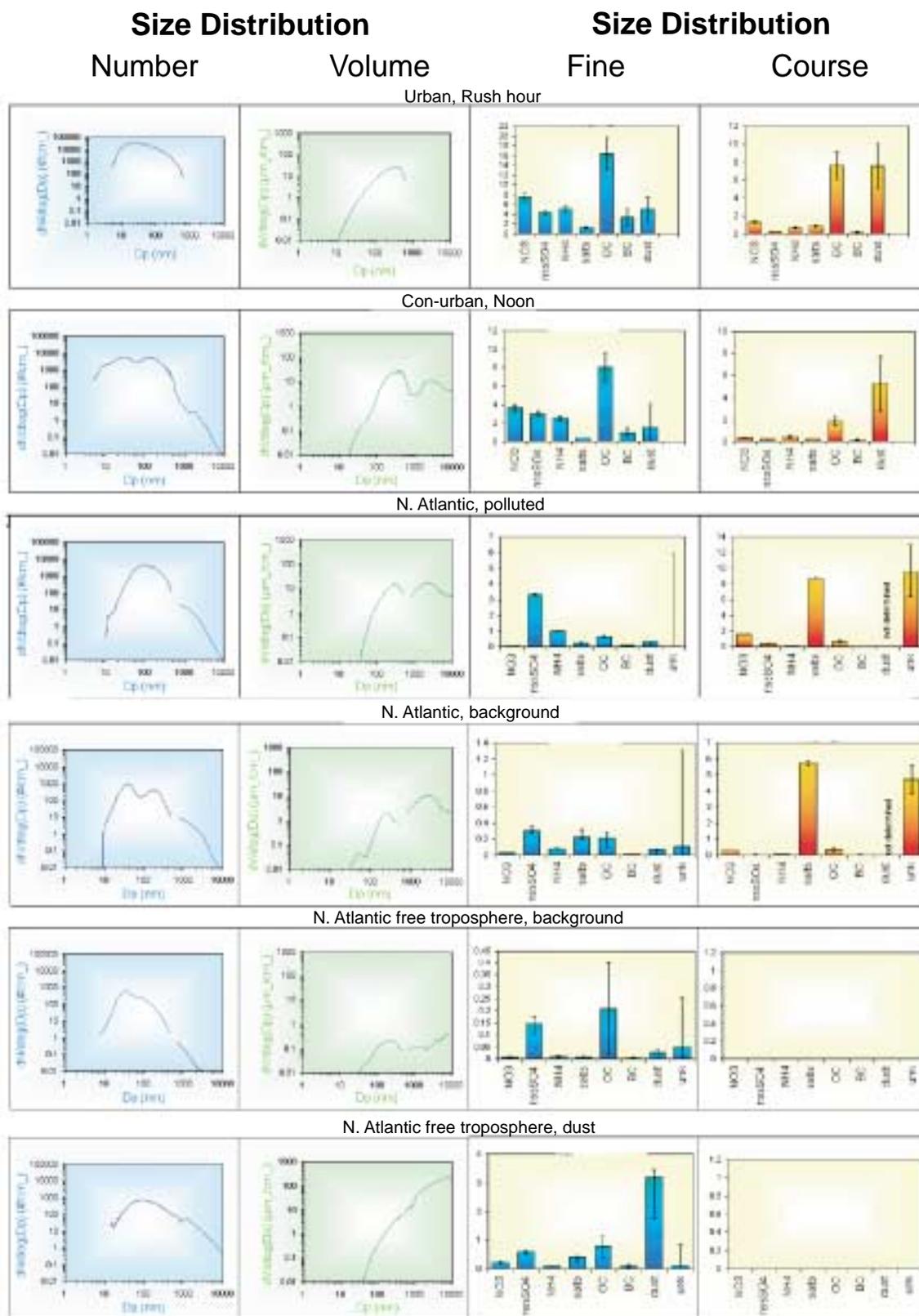
Sahara Dust and Biomass Smoke over the Atlantic

Sahara Dust

Biomass Smoke

5 km

ITCZ

20 N   10 N   0   10 S

Biomass Smoke over South America

Space Shuttle
Lidar, Lite
Orbit 55
Sept., 13, 1994

Fire Location
September

10 km

5 km

Biomass Smoke

Andes Mts.

Figure 3. Aerosol vertical profiles over **a)** the Atlantic and **b)** over South America based on the LITE space-borne lidar instrument.

Size Distribution
Number   Volume

Size Distribution
Fine   Course

Urban, Rush hour

Con-urban, Noon

N. Atlantic, polluted

N. Atlantic, background

N. Atlantic free troposphere, background

N. Atlantic free troposphere, dust

Figure 4. Compilation of size distributions and of sub-micrometer and super-micrometer chemical composition typical for a number of source regions, aerosol plumes or layers.

Chapter 4, 5
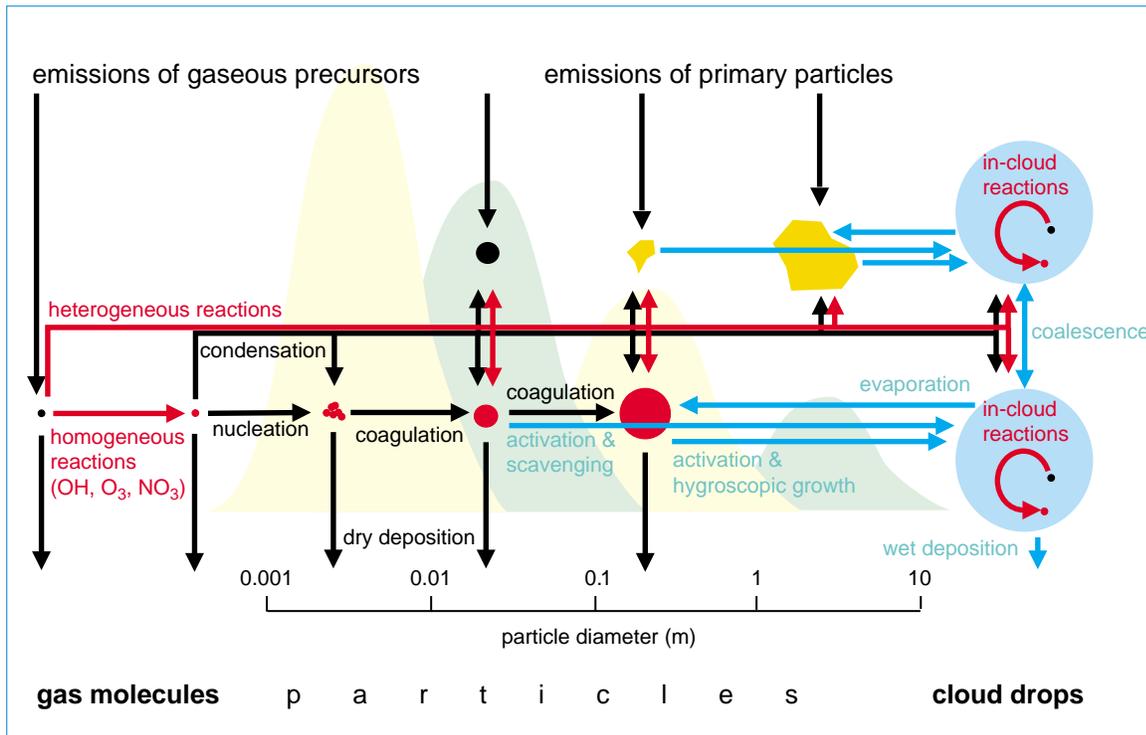
Figure 5. Schematic picture of the microphysical processes that influence the number size distribution and chemical composition of the atmospheric aerosol particles (Raes *et al*., 2000b). A number size distribution, with nucleation, Aitken, accumulation and coarse mode, is schematized in the background, illustrating that the highest number of particles are usually found with the smallest particles.
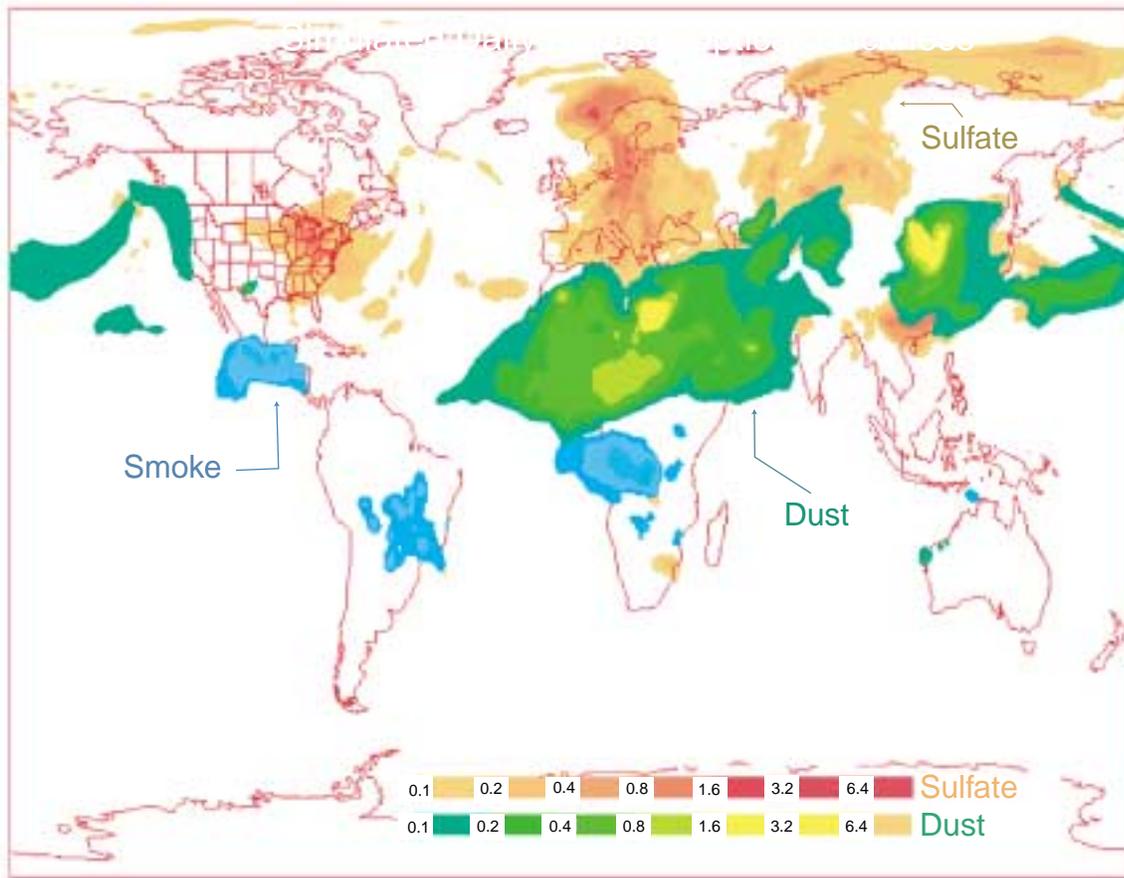
Figure 6. Calculated global fields of mineral dust, sulfate and smoke, calculated with a CTM using actual meteorology. Many of the calculated features can be compared with observations from space (Figure 2).

Chapter 4, 7