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Marine Aerosols

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The aerosol over the world oceans plays an important role in determining the physical and chemical characteristics of the Earth's atmosphere and its interactions with the climate system. The oceans contribute to the aerosols in the overlying atmosphere by the production and emission of aerosol particles and precursor gases. The marine aerosol, in turn, influences the biogeochemistry of the surface ocean through long distance transport and deposition of terrestrial and marine-derived nutrients and other chemicals. This chapter is an introduction to the physical and chemical properties of marine aerosols, to processes determining their composition and behavior, and to some of the issues driving current research in this field.

1. INTRODUCTION

The aerosol over the world oceans plays an important role in determining the physical and chemical characteristics of the Earth's atmosphere and its interactions with the climate system. For the purposes of this chapter, the "marine aerosol" is defined broadly as including all various types of particles found over the oceans. This includes particles generated mechanically at the sea surface as well as those formed chemically, from the atmospheric reactions of gases emitted from the sea surface. Terrestrial aerosols derived from fossil fuel combustion, biomass burning, dust, and biogenic compounds also contribute to the marine aerosol because atmospheric transport times across the major ocean basins are comparable to the atmospheric lifetime of many aerosols. There is extensive interaction between marine and continentally derived gases and particles. As a result, it can be difficult to strictly segregate aerosols into "marine" and "continental" types.

The marine aerosol is of considerable importance to the biogeochemical state of the underlying ocean. A notable example is the deposition of iron and other micronutrients from dust. Dust deposition is a major factor influencing surface ocean biological productivity in high nutrient, low chlorophyll regions of the oceans [*Duce and Tindale*, 1991; *Falkowski et al.*, 1998]. The aerosol also reflects the biogeochemical state of the underlying oceans. A notable example is the distribution of biogenic sulfate aerosols over the oceans, reflecting production and emissions of dimethylsulfide arising from phytoplankton [*Andreae*, 1990; *Savoie and Prospero*, 1989]. This coupling of the marine aerosol to biogeochemistry raises the potential for numerous feedback mechanisms between climate and ocean biota.

The first major survey of marine aerosols was carried out by the Sea-Air Exchange (SEAREX) program, a 10-year multi-investigator study of the transport of natural and anthropogenic substances to the Pacific ocean [*Duce*, 1989]. To a large extent, the SEAREX program defined the modern view of marine aerosol chemical properties and raised many of the questions driving marine aerosol research today. SEAREX and other research programs clearly demonstrated two important points: (1) that there is a distinct marine aerosol with characteristics related to the underlying ocean and (2) that the marine aerosol is episodically and dramatically influenced by long distance transport from continental regions.

Since that time, considerable progress has been made in terms of documenting the physical and chemical properties

of the marine aerosol and in understanding the processes that influence it. The last decade has seen a great expansion in the field of environmental aerosol science, in general, driven by the recognition of the impact of airborne particulates on global climate change and human health. This has spawned a new generation of field and laboratory instrumentation. However, many fundamental questions remain, and aerosols remain a focus of active research and discovery. Aerosol science has historically been observationally limited. New methods are needed for physical/chemical characterization of marine aerosols from all sources and at all size ranges. New tools for mapping the spatial/temporal distribution of aerosols over the oceans are needed.

This chapter is intended as a basic introduction to the physical and chemical properties of marine aerosols, to some of the processes important in determining their evolution and characteristics, and to current areas of study relevant to the Surface Ocean Lower Atmospheric Studies (SOLAS).

2. AEROSOL BASICS

2.1. Terminology

Aerosol—a dispersion of solid and liquid particles suspended in gas. Note that the strict definition of the word "aerosol" refers to a mixture of particles and gas, but in common practice, it is used to refer to the particles only. Often the term "aerosol particles" is used to refer to the solid/liquid phases only. In this chapter, the term "aerosol" is also used to refer to the suspended particles.

Primary aerosol—atmospheric particles that are emitted or injected directly into the atmosphere. Examples are particles formed in the combustion process or smoke stack, including sulfuric acid, soot, and fly ash particles. Natural examples include, Saharan dust, pollen, and sea spray (salt and organic) from the ocean.

Secondary aerosol—atmospheric particles that are created by in situ aggregation or nucleation from gas phase molecules (gas to particle conversion). These can be formed from both anthropogenic and natural gaseous emissions.

Internal versus external mixture—this term refers to the mixing state of the aerosols. An externally mixed aerosol is composed of particles with varying chemical or mineral composition. For example, in an externally mixed aerosol, sulfate and sea salt might occur in different particles. In an internally mixed aerosol, the different aerosol components are mixed within individual particles.

Homogeneous versus heterogeneous chemistry—in atmospheric chemistry, the term homogeneous chemistry refers to reactions occurring in the gas phase. Heterogeneous chemistry refers to processes involving transfer of chemicals between the gas and particulate phases and usually reaction in or on the particulates.

Hygroscopicity—the tendency of a substance to absorb water vapor from surrounding environment.

2.2. Physical Size Distributions: Number, Surface Area, Volume

Much of what is known about atmospheric aerosols has been learned by examining how the number of particles in air varies as a function of size (diameter). Such physical size distributions are obtained using a variety of instrumentation, including particle counters, electrostatic classifiers, and optical particle analyzers. These devices take advantage of a number of aerosol properties: (1) aerosols are effective light scatterers, being similar in size to the wavelength of visible light, (2) in a supersaturated environment, aerosols will absorb material from the gas phase and grow to larger sizes, and (3) aerosols can be electrically charged and electrostatically steered.

Atmospheric aerosol particle concentrations typically exhibit a log-normal size distribution, i.e., a Gaussian distribution when plotted against the log of the diameter. Figure 1 illustrates the size distribution of the marine aerosol in terms of the number, surface area, and volume, with Dp referring to particle diameter. The left side of Figure 1 is plotted on a
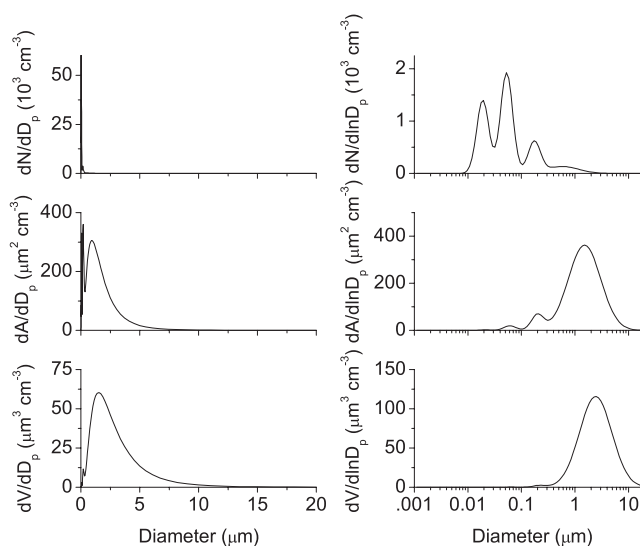

Figure 1. Model marine aerosol size distribution of aerosol number, surface, and volume distributions versus particle size. Left, linear size scales; right, logarithmic size scales. Adapted from *Seinfeld and Pandis* [1998] using aerosol parameters from *Heintzenberg et al.* [2004].

linear size scale, and the units of the number size distribution are given as *number of particles per micron per cm³*. This is commonly called *dN/d*Dp, and is actually the *number of particles per cm³ of air in a 1-μm-wide size bin*. The integrated area under the size distribution therefore represents the total number of particles. The surface area and volume distributions are expressed as *dA/d*Dp and *dV/d*Dp, respectively. The gross features of the distributions are obvious. Most of the particles are in the small size range, while most of the mass is in the larger particles. However, the details of the size distribution are not clear in this view. Aerosol sizes vary over such a large dynamic range that plotting properties on a linear scale is not very illuminating.

Aerosol size distributions are usually plotted against the natural logarithm of the particle diameter. Here, the number size distribution is expressed as *dN/d*lnDp, or the *number of particles per cm³ of air in a size bin 1 lnDp wide*. Because lnDp is unitless, the number distribution has units of *numbers of particles per cm³* or simply *cm⁻³*. The surface area and volume distributions have analogous units. Figure 1b clearly shows that the aerosols are concentrated in distinct modes, or peaks in the distributions, with minima between them. Three major aerosol modes are commonly observed in marine air: the Aitken mode, in the size range Dp < 0.1 μm, the accumulation mode in the size range from 0.1 to 1 μm, and the coarse mode consisting of particles with Dp > 1 μm. A fourth, nucleation mode is sometimes observed, containing very small particles, D p < 0.01 μm. The major aerosol modes have different mechanisms of formation, and removal, and often very different chemical characteristics.

Figure 2 is a process-oriented view of the aerosol size distribution. This view links the size distribution of the aerosols to the source/removal processes that affect it. The diagram is rather simple and hides the extraordinary complexity of the myriad of chemical reactions and physical processes involved in determining the nature of the atmospheric aerosol. The diagram emphasizes three basic aspects of atmospheric aerosols. First, primary aerosols are generated in the nucleation mode by condensation of vapors. In industrial settings, this may involve the cooling of heated gases. In the marine environment, it involves the gas phase production of low volatility compounds such as sulfuric or nitric acid, which readily condense onto preexisting particles. If few preexisting particles are present, these acids may form clusters with water vapor to form new particles. Nucleation mode aerosols grow into accumulation mode aerosols via further condensation of gas phase species, coagulation of particles, and processing in clouds. Coarse mode aerosols are result from mechanical aerosol generation processes, including sea spray and bubble bursting, the weathering and erosion of soils, and the ejection of volcanic material.
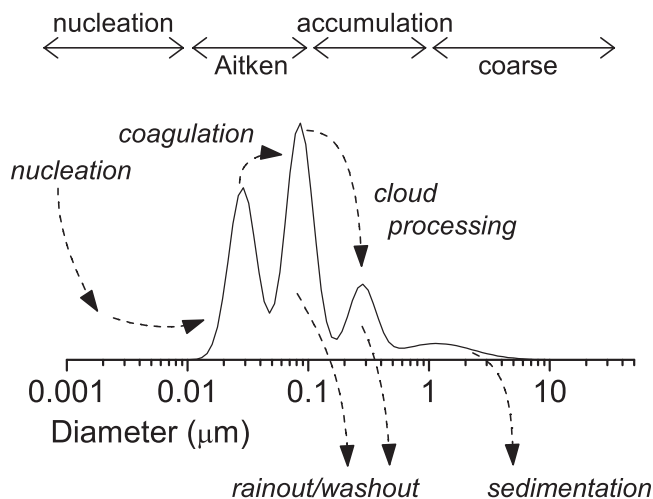

Figure 2. Schematic illustrating particle number in the major aerosol modes as a function of diameter and the relationships to sources, transformation, and removal processes.

In terms of aerosol number and size distribution, marine aerosols differ significantly from continental aerosols. Marine aerosols consist of Aitken particles, accumulation mode particles, and a coarse mode consisting primarily of sea salt. Away from continental sources, marine aerosol numbers (dominated by the nuclei and accumulation modes) are an order of magnitude lower than in typical continental air masses. The database of measurements of the size distribution of marine aerosol has increased greatly in recent years. *Heintzenberg et al.* [2004] compiled more than 10,000 marine aerosol size distributions from several field campaigns (Figure 3). This database provides a statistically robust characterization of the marine aerosol for several regions. One striking aspect of the aggregated data set is that aerosol numbers drop steeply at the low end of the size distribution. This reflects the fact that nucleation mode aerosols are only occasionally observed in the marine boundary layer. In other words, the marine aerosol does not appear to be continuously supplied by the formation of new nucleation mode particles. This differs from many continental aerosol measurements, which show flatter or more "open" distributions at the lowest size ranges. The evidence suggests that nucleation in the marine boundary layer is not a dominant process.

2.3. Removal Processes

Aerosol removal processes exert a major effect on the size distribution and composition of aerosols. Aerosols are removed from the atmosphere by both dry and wet processes.
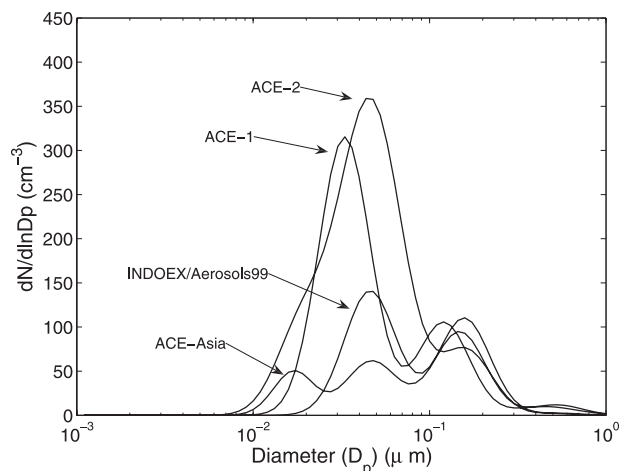
Figure 3. Marine aerosol number distributions as a function of dry particle diameter, derived from several thousand measured aerosol size distributions from four major field campaigns conducted in the Southern Ocean (ACE-1), North Atlantic (ACE-2), Indian Ocean (INDOEX, Aerosols99), and Western Pacific (ACE-Asia). The curves shown represent the median size distribution from each data set, fit to four log-normal modes. From *Heintzenberg et al.* [2004].

The most important physical processes involved in aerosol removal are gravitational settling, impaction, diffusion, and hygroscopic growth with subsequent rainout. The rates of these processes are strong functions of particle size, as illustrated in Figure 4.

The rate at which particles settle out of the atmosphere is a function of their size, shape, and density. All aerosol particles are denser than air, but gravitational settling must compete against the tendency for turbulent motions of the atmosphere to keep particles suspended. As a result, settling is important only for coarse mode particles. These larger particles are also subject to inertial forces, so they tend to impact on surfaces (like the ground or raindrops). Particles of several micrometers in diameter or larger tend to have a short lifetime in the atmosphere. For example, a 10-μm particle has a settling velocity of about 1000 cm h^{-1} or 240 m d^{-1}. So, a large aerosol particle in the boundary layer (lowermost 1–2 km) would have a lifetime of a few days or less.

Particles in air diffuse by Brownian motion, caused by the random collisions with surrounding gas molecules. This motion is important only for smaller particles, while the motion of larger particles is dominated by fluid drag and gravity. Typical diffusion length scales for aerosol particles range from 0.2 cm s^{-1} for a 1-nm particle to 0.0001 cm s^{-1} for a 10-μm particle. As a result, very fine particles tend to collide frequently, and for those particles, coagulation is an important process (Figure 2). This process transfers mass into the larger size range.

Accumulation mode aerosols (0.1–1 μm) are large enough that diffusion is slow, and the collision rate is low. As a result, coagulation is not important for this mode. This size range is small enough that gravitational settling and inertial impaction are not fast removal processes either. As a result, they tend to have a long residence time in the atmosphere and therefore tend to accumulate (hence the name). Wind tunnel studies show that the accumulation mode aerosols lie at the minimum in dry deposition rate, between gravitation settling of larger particles and diffusional loss of smaller particles (Figure 4, right panel).

For accumulation mode particles, cloud scavenging and precipitation is the major removal route. For these particles, removal occurs primarily via hygroscopic activation and growth in the slightly supersaturated conditions occurring in-cloud, followed by rainout. Aerosols of larger and smaller sizes interact with cloud droplets via Brownian diffusion and impaction, both in cloud and below cloud.

2.4. Aerosol Hygroscopicity

Aerosols containing highly soluble ionic constituents, like sulfate or ammonium sulfate salts, interact strongly with atmospheric water. The tendency to absorb moisture from the surrounding atmosphere is known as hygroscopicity. Hygroscopic aerosols grow under conditions of increasing relative humidity (RH) and shrink as RH decreases. The hygroscopic behavior of aerosols means that they are constantly shifting in size, as they adjust to changes in ambient RH. This effect
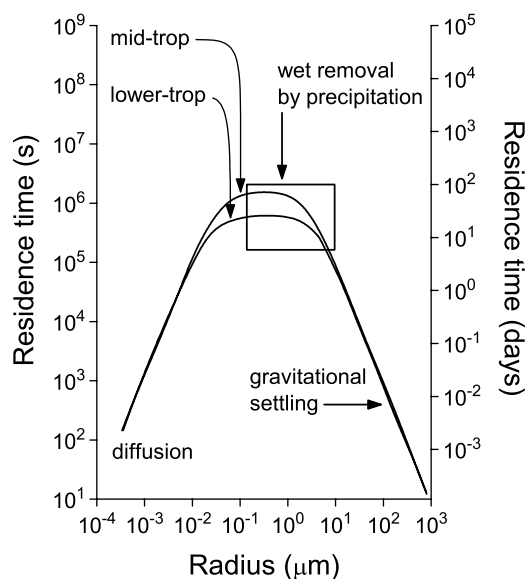

Figure 4. Atmospheric lifetimes of aerosols as a function of particle size [modified from *Kreidenweis et al.*, 1999].

is of considerable importance, in that it affects aerosol size, chemical composition (pH, ionic strength, etc.), light scattering, cloud droplet nucleation, and lifetime. These effects can significantly alter aerosol and cloud properties and their interactions with the climate system.

The hygroscopic growth behavior of pure or mixed salt aerosols can be predicted from thermodynamic properties. The growth curve can be predicted from the solubility of the various salts, their activity coefficients, and RH. In the laboratory, dry salt aerosols exposed to increasing RH exhibit a deliquescence point or threshold at which water is rapidly absorbed by the aerosol, and the dry aerosol becomes an aqueous solution. At relative humidities above the deliquescence point, the aerosol grows to a size which maintains the vapor pressure or activity of water in equilibrium with the surrounding air. For particles of diameter less than about 30 nm, the Kelvin effect of droplet curvature on surface tension exerts a significant effect on the equilibrium particle size at a given RH. The Kelvin effect is discussed further in the chapter by Lohmann, this volume (Marine Boundary Layer Clouds).

Under conditions of decreasing RH, the aqueous aerosol droplet loses water along the same equilibrium vapor pressure curve. However, rather than drying out at the deliquescence point, as one might expect, the aerosols remain hydrated and supersaturated to a much lower RH. Eventually, a second critical RH is reached, called the efflorescence or crystallization point, at which the "excess" water is lost from the particle. This supersaturation reflects the energy barrier involved in nucleation of salt crystals in an aqueous solution with no surfaces or preexisting nuclei. The efflorescence and deliquescence points can be widely separated, leading to hysteresis in particle diameter as RH is cycled. For example, the deliquescence point of pure NaCl occurs around 78% RH, while the efflorescence point is near 45% RH. An example of sea salt aerosol behavior during hydration/dehydration is shown in Figure 5. Sea salt aerosol behavior is slightly different from that of pure NaCl. Sea salt deliquesces and effloresces at slightly lower RH than pure NaCl. In fact, sea salt does not dry out completely even at very low RH. These differences in behavior are attributable to the presence of other salts, particularly $MgSO_4$ and $MgCl_2$ [*Tang et al.*, 1997]. Sulfuric acid solutions do not crystallize as they dry, and as a result, they exhibit symmetrical behavior during growth and drying.

Atmospheric aerosol particles are complex mixtures of ionic, organic, and insoluble species, and they exhibit behavior which may be difficult to model based on laboratory studies of pure compounds. A very useful resource for information on aerosol thermodyamics is the Aerosol Inorganic Model developed by S.L. Clegg, P. Brimblecombe, and
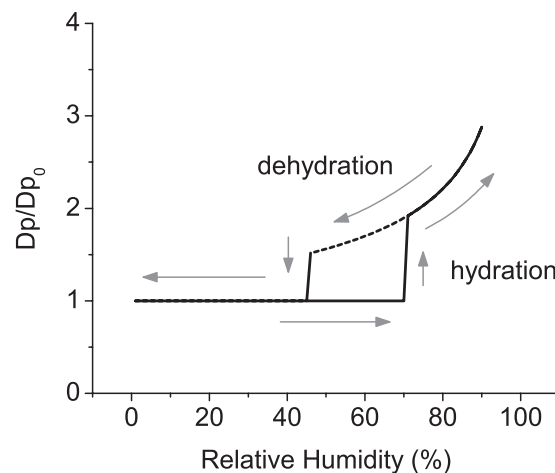

Figure 5. Change in diameter of a sea-salt particle with increasing and decreasing relative humidity. Note that the particle follows different paths during hydration and dehydration [after *Tang et al.*, 1997].

A.S. Wexler (http://www.aim.env.uea.ac.uk/aim/aim.php). In general, aerosols composed primarily of ionic solutions exhibit larger hygroscopic growth factors, and the presence of neutral and insoluble compounds such as soot or mineral dust tends to reduce their hygroscopicity.

In the marine boundary layer, RH levels generally range from 70% to 90%, well above the efflorescence point of most sulfate and sea-salt aerosols, so they remain in the aqueous state. The hygroscopicity of ambient aerosols is usually reported as a *hygroscopic growth factor*, defined as the ratio of aerosol diameter at a given RH to that at a lower reference RH (e.g., Dp (90% RH)/Dp(dry)). Accumulation mode aerosols in clean marine air masses typically exhibit growth factors at 90% RH ranging from about 1.6 to 2.0. Sea-salt aerosols have larger growth factors, typically greater than 2. Anthropogenically influenced air masses over the oceans typically exhibit lower growth factors, in the range of 1.2 to 1.5 [*Berg et al.*, 1998; *Massling et al.*, 2003]. Even lower growth factors are associated with freshly polluted air containing very high levels of elemental carbon, recently advected over the ocean. These differences point to the importance of polluted air mass "aging" in which the aerosols increase their hygroscopicity with time. This can occur via the heterogeneous oxidation of sulfur dioxide, leading to an increase in aerosol sulfate or via the oxidation of less polar organic compounds to more soluble organic acids.

2.5. Cloud Processing

Cloud processing plays an important role in the evolution of marine aerosols [*Hoppel et al.*, 1986, 1990]. Cloud drop-
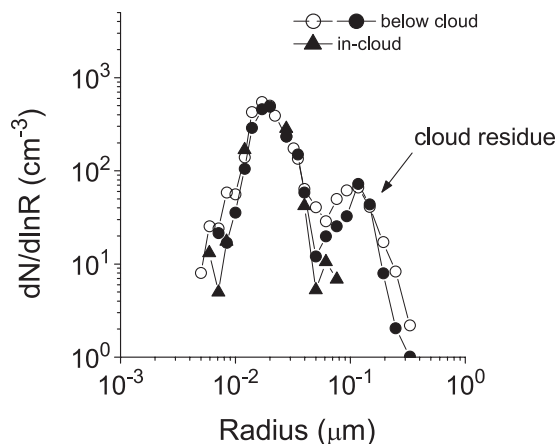
Figure 6. Cloud droplet and aerosol size spectra off the Oregon coast, illustrating the effect of processing on the marine aerosol size distribution [*Hoppel et al.*, 1994]. ▲, in-cloud, nonactivated aerosols; ●,○, below cloud aerosols.

lets are formed from aerosols above a critical size threshold that are activated as they enter a region of elevated RH (see chapter by Lohmann, this volume). Most cloud droplets ultimately re-evaporate, regenerating the aerosol from which they formed. Some fall as raindrops, either reaching the ground or re-evaporating below cloud. Cloud droplets can absorb not only water, but also soluble gases such as sulfur dioxide, which oxidizes in the droplet to sulfate. When these cloud droplets evaporate, they generate aerosols that are larger than the original cloud condensation nuclei. These appear as a new, larger aerosol mode with a distinct minimum between it and the original precursor aerosol. The mass of aerosol in this "cloud residue" mode greatly exceeds that in the precursor aerosol. Field observations of aerosols in marine clouds typically show an aerosol mode that is identical within the cloud (interstitial aerosols) and below cloud representing the population of nonactivating aerosols (Figure 6). A larger mode observed below cloud is interpreted as the "cloud residue." The two modes are sometimes referred to as the *condensation mode* and *droplet modes*. This process constitutes a major global pathway for the production of sulfate aerosol in the accumulation mode [*Hegg*, 1985].

2.6. Chemical Properties

The chemical properties of the marine aerosol reflect: (1) the original composition of particles injected into or formed in the atmosphere, and (2) chemical modification of particles during transport through the atmosphere, via chemical reactions within the particle or with the surrounding gas phase. Figure 7 shows electron micrographs of a few types of in-

dividual aerosol particles associated with the major aerosol size modes. The Aitken and accumulation mode particles shown consist of sulfuric acid, soot, and various organics. The larger particles include sea salt, pollen, and terrestrial dust. Since larger particles make up the majority of aerosol mass (see Figure 1), they tend to dominate the average aerosol composition. However, differences in chemical composition as a function of particle size can greatly affect the climate and health impacts of the aerosol.

The fine particles of the Aitken and accumulation modes include sulfate aerosols (either sulfuric acid or partially or fully neutralized ammonium sulfate), and organic carbon-rich particles, which may be biogenic or derived from combustion processes. There is also a sea salt contribution to the submicron aerosol fraction.

Aerosols are highly variable, complex chemical mixtures. A single aerosol particle may consist of a single mineral species or contain dozens or even hundreds of distinct chemical compounds. The complete chemical characterization of aerosols is therefore an enormous and challenging undertaking and one which we do not yet have the tools to carry out. Many of the molecules present in aerosols are highly reactive and many are present at only trace levels. Fortunately, for many types of aerosol particles, the majority of the mass is contained in only a few compounds, making it possible
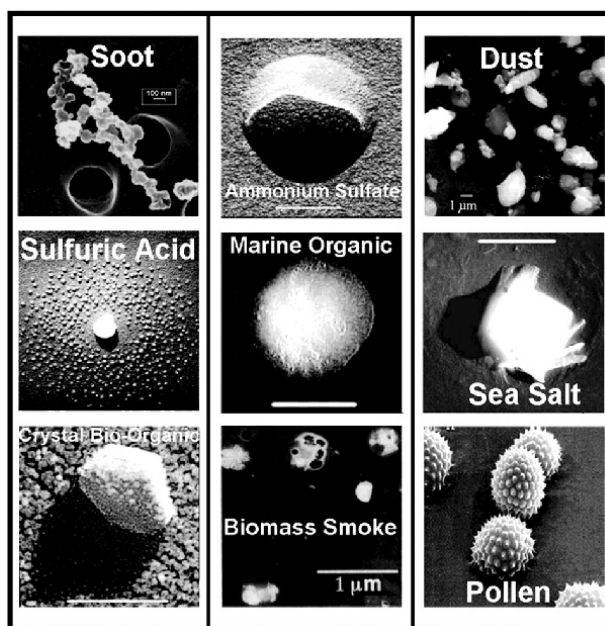

Figure 7. Electron micrographs of aerosol particles found in the three major aerosol modes: (left) Aitken mode, (middle) accumulation mode, (right) coarse mode [*Brasseur et al.*, 2003].

to chemically characterize them in a meaningful way with relatively few measurements.

Size-based chemical information is obtained from a number of techniques. Electron micrographs and X-ray probe techniques are an important tool for characterizing individual aerosol particles and understanding their origin. However, some aerosol particles containing semivolatile constituents do not survive the high vacuum environment needed to obtain such images. In those cases, the particle size, geometry, and composition may be altered from its original state in the atmosphere. Bulk aerosols are collected using filters, and size segregated bulk aerosols are collected using a variety of aerodynamic impactors. Impactors utilize the differences in aerodynamic properties of different size aerosols to separate them for collection and subsequent analysis. Filter and impactor samples are commonly extracted with water or other solvent and analyzed for inorganic ions using ion chromatography, for organics using GC/MS or combustion

techniques, and for trace elements using X-ray fluorescence, neutron activation, or ICP-MS techniques. Impactors are the most commonly used technique for obtaining aerosol chemical size distributions. An example of a chemical size distribution from impactor measurements is shown in Figure 8. Impactor-based chemical analyses provide quantitative chemical information, but do not differentiate between internally and externally mixed aerosols. A number of single particle mass spectrometers have been developed in recent years, with the capability to provide elemental and molecular information about the composition of individual aerosol particles.

Plate 1 is a cartoon illustrating some of the properties typical of aerosol chemical size distributions. Chemical size distributions look different from the aerosol number distributions. The Aitken mode, which is often prominent in the aerosol number distribution, is dwarfed by the accumulation mode aerosols. That is because the chemical distribution reflects aerosol *mass*, rather than aerosol *number*. Aitken mode particles may be numerous, but they are small, and contain relatively little mass.

Sulfate is a major component of the accumulation mode. This is typical of many environments, both polluted and marine. Sulfur is greatly enriched in marine aerosols relative to the composition of bulk seawater. Both the enrichment and the size distribution of sulfur are clues that the oxidation of sulfur gases to sulfuric acid is an important mechanism of aerosol formation. In continental air, these sulfates are usually associated with ammonium (NH_4^+), which is formed by the absorption of gas phase ammonia (NH_3) onto the sulfate aerosols. In marine air, there is usually an excess of sulfate relative to ammonium, so the aerosol is acidic. Iodine is a minor element that is greatly enriched in marine aerosols and resides primarily in the fine aerosol fraction. Like sulfur, iodine is transported from sea to air primarily in the form of organic gases (such as CH_3I, CH_2I_2, etc.), which undergo subsequent oxidation to inorganic iodine compounds.

Organic compounds have also been detected in the accumulation mode. We know there can be a great deal of organic matter in aerosols, which can consist of hundreds or thousands of different compounds. Identifying and quantifying them is beyond the capability of any single analytical technique. Organic acids can be analyzed by ion chromatography and nonpolar organics by gas chromatography. Partially oxidized, highly polar organic molecules are usually analyzed using gas chromatography, often after a derivatization process such as esterification. High-performance liquid chromatography is also used, and the relatively new technique of electrospray mass spectrometry has considerable potential for studying polar organics in aerosols.

The coarse mode aerosol contains primarily sea salt and/or mineral dust derived from mechanical erosion of soils and
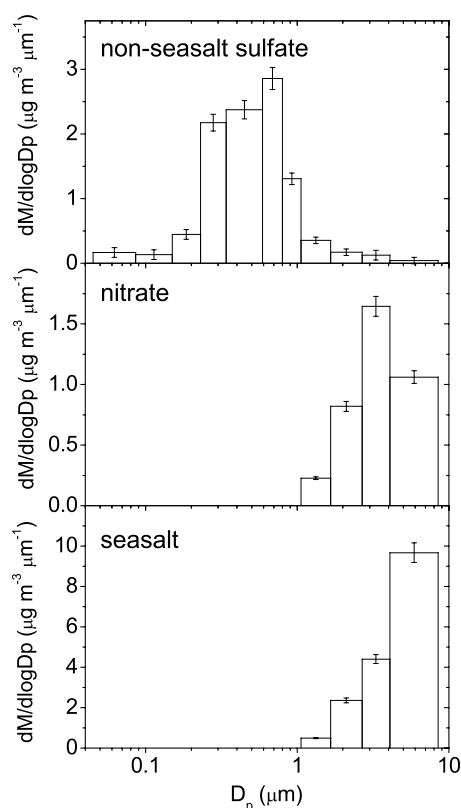

Figure 8. Atlantic ocean aerosol sample from *Virkkula et al.* [2006]. Chemical size (mass) distributions of three major components inferred from impactor measurements of anions and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and $CH_3SO_3^-$). The columns show the size bins of the individual impactor stages.

desert sands. Coarse mode mineral dust aerosols are rich in crustal elements like Ca, Si, Al, Fe, while sea-salt aerosols are enriched in Na, Mg, Cl, and SO$_4$. The coarse mode can also exhibit a peak in nitrate (NO$_3^-$), if the sea salt has reacted with nitric acid from continental or ship emissions.

The uptake of nitric acid by a sea-salt particle is an example of how gas phase molecules can dissolve into preexisting aerosols. If this uptake is irreversible, one would expect the absorbed species to exhibit a size distribution related to the surface area of the aerosol particles. If the molecule is volatile (i.e., it can leave one aerosol and diffuse into another one), then it will migrate in an attempt to reach a thermodynamically stable distribution. Of course, "equilibrium" is a moving target, as the aerosol continuously changes composition via generation, gas/aerosol interactions, and deposition. For example, a nonionic, semivolatile organic compound would most likely acquire a size distribution similar to that of aerosol mass or volume.

The cartoon in Plate 1 also includes an unknown category, to emphasize that the mass of aerosols in either the fine or coarse modes may not be fully accounted for by the sum of all the chemicals measured by the commonly used analytical techniques. This is known by comparing the total of the measured constituents to a gravimetric measurement of aerosol mass. The difference can be attributed to analytical uncertainty in the measured quantities, to loss/gain of volatile constituents such as ammonium and water, or to uncertainty in the conversion of measured total organic carbon to particulate organic mass (including oxygen, nitrogen, etc.).

3. TYPES OF MARINE AEROSOLS

3.1. Sea Salt

The ejection of seawater droplets from the sea surface into the atmosphere is a major global source of primary aerosols [*Woodcock*, 1948]. These aerosols account for much of the mass and surface area of marine aerosols, and a significant fraction of the aerosol optical depth of the marine atmosphere [*Quinn and Coffman*, 1999]. The mass flux associated with sea spray is predominantly carried by a small number of large (supermicron) particles. Much effort has gone into determining the relationship between wind speed, sea state, and sea-salt aerosol production. This is a challenging research topic because of the difficulties inherent in measuring particle fluxes in the field, reproducing field conditions in the laboratory, and developing a theoretical framework for describing turbulent fluxes at the interface of two fluids with very different densities. *Lewis and Schwartz* [2004] recently published an extensive compilation of the literature on sea-salt aerosols.

Sea-salt aerosol generation is caused primarily by the action of wind on the sea surface, which generates waves. At sufficiently high wind speeds (typically >5 m s^{-1}), wave breaking occurs, generating bubbles which are entrained into the water, then rise to the surface and burst. The onset of this process is evidenced by the development of whitecaps. Two distinct types of aerosols are produced by bursting bubbles: *film* drops and *jet* drops [*Blanchard*, 1963; *Foulk*, 1932]. Film drops are formed from the shattering of the thin upper surface of the bubble, and they are ejected with a wide angular distribution (Figure 9). Several hundred film drops can be generated from a single bubble. Film drop sizes vary over a wide size range from 0.01 to >10 μm in diameter. Jet drops are formed from the column of water expelled vertically as water fills a bubble after bursting. Typically only a few jet drops are produced from a single bubble. Jet drops produce large aerosols whose sizes are roughly 10% that of the precursor bubble diameter. Typically, jet drop diameters range from 1 to >100 μm. At very high wind speeds, *spume* drops can be sheared off wave crests directly [*Monahan et al.*, 1983]. This process generates extremely large sea-salt droplets with diameters of several hundred micrometers. The residence time of these droplets is short, and they do not contribute significantly to the marine aerosol. It is generally believed that film droplets are responsible for the fine (<1 μm) fraction of sea-salt aerosols, while jet drops generate the coarse mode sea-salt aerosols.

Developing algorithms for sea-salt aerosol production over the oceans is an extremely challenging task. It involves understanding and parameterizing wave breaking, bubble formation, bubble bursting, aerosol ejection, deposition, and entrainment into the boundary layer. Sea-salt aerosol production rates have been estimated from laboratory studies using artificially (nonwind-driven) generated whitecaps [*Gong et al.*, 1997; *Monahan et al.*, 1982; *Monahan and Omuircheartaigh*, 1986; *Monahan et al.*, 1986]. These studies yield an estimate of the interfacial flux of particles as a function of whitecap area, which can be extrapolated to oceanic conditions using observed or modeled fractional whitecap coverage. Whitecap coverage is a highly nonlinear function of wind speed, varying over many orders of magnitude over the range of ambient wind speeds. Sea-salt aerosol production parameterizations typically have cubic or higher wind speed dependencies. Not surprisingly, therefore, observations of sea-salt particle number over the ocean show wide variations as a function of wind speed. Despite the importance of wind speed as a controlling parameter for sea-salt aerosol production, there are few field observations of this process at wind speeds above 15 m s^{-1}. It is important to remember that most of the models currently used to describe sea-salt generation are essentially empirical, rather than physically based.
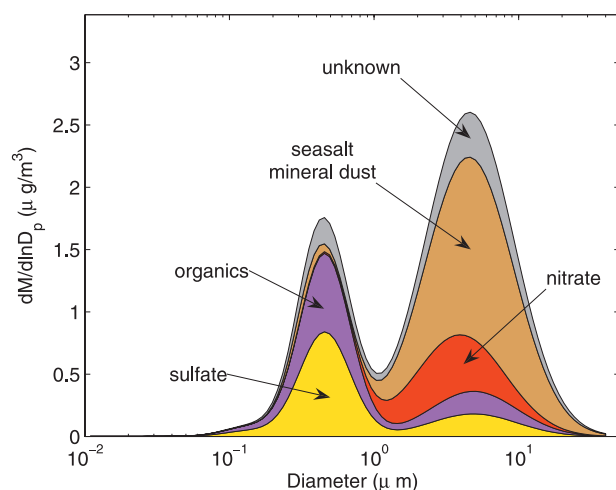
Plate 1. Idealized illustration of marine aerosol illustrating the size distribution of the mass of various aerosol components.

There have been many field observations of the size distribution of sea-salt aerosols in marine air and reasonable agreement regarding its major features. *Lewis and Schwartz* [2004] derived a "canonical size distribution" capturing the features common to many published studies, over the size range r_{80} = 0.1–25 μm (droplet radius at 80% RH) and wind speed range of 5–20 m s^{-1} (at 10 m height). This distribution consists of a single lognormal mode describing the sea-salt aerosol. As expected, the distribution shows strong dependence of particle number on wind speed. Perhaps unexpectedly, the compiled data suggest a modal radius of 0.3 μm, independent of wind speed. This suggests that while wind speed markedly alters bubble production, whitecap coverage, and the amount of aerosol produced, it does not appear to dramatically change the energetics of bubble bursting and resulting aerosol production. Note that this is simply a reasonable fit, not a parameterization based on underlying physical principles, and the field data exhibit scatter of roughly an order of magnitude about the distribution.

In contrast to the *Lewis and Schwartz* [2004] canonical size distribution, many individual field studies have noted multimodal sea-salt distributions, and a variety of expressions have been proposed to describe the dependence of the sea-salt aerosol number distribution on local wind speed. An example is the North Atlantic shipboard study by *O'Dowd* [1993] who utilized a thermal volatility technique to distinguish between sea salt and other particles. The data from that study was fit to a model consisting of three modes (film, jet, and spume), with wind speed-based fits for each mode. The literature on sea-salt distributions contains many contradic-

tions with regard to the nature of the dependence of sea-salt aerosol size distribution on local wind speed. A number of studies show little dependence of sea-salt aerosol properties on local wind speed [for example, *Bates et al.*, 1998; *Covert et al.*, 1998]. In some respects, these contradictions in the literature are not surprising. It is easy to imagine that the sea-salt aerosol properties at any specific location reflect both local wind conditions and air mass history, and the influence of each might vary as a function of particle size and atmospheric residence time.

The wind-speed dependence of sea-salt particle number and size is important in terms of understanding climate feedbacks. Changes in wind speed may alter sea-salt aerosol concentration and size distributions, leading to changes in both the direct radiative effect of sea-salt aerosol and indirect effects related to its role as cloud condensation nuclei. Model-based estimates of the strength of such feedbacks suggest that they may be significant, but these are based on various assumed wind speed dependencies, which are highly uncertain at present [*Dobbie et al.*, 2003; *Latham and Smith*, 1990].

In terms of major ion chemistry, fresh sea-salt aerosols are composed largely of unaltered bulk seawater. To a first approximation, seawater is a sodium chloride, magnesium sulfate brine, with a pH of about 8.1. This applies primarily to the larger size sea-salt aerosol particles, which dominate the sea-salt mass distribution. The composition of the fine particle marine aerosols is more difficult to assess because in the atmosphere they are mixed with non-sea-salt and organic-containing particles of different origins.

Organic compounds from the sea surface microlayer can also be incorporated into the sea-salt aerosol. This process can result in enrichment of organics in sea-salt aerosols relative to bulk seawater. Under low wind speeds, the sea surface accumulates an organic film, composed of surfactant materials thought to be derived from algal exudates and other biological or photochemical sources. These compounds reside at the sea surface because they contain both hydrophilic groups, such as alcohols or acids, along with hydrophobic groups, such as long chain hydrocarbons. These surfactants can increase surface tension, inhibit wave breaking, and change the relationship between wind speed and the turbulent state of the sea surface. These surfactants and other near-surface organic colloids and particles may also be transferred to droplets during sea spray formation, affecting the physical and chemical properties of the resulting sea-salt aerosol.

3.2. Sulfate Aerosols

Sulfates are among the most important aerosol-forming compounds in the marine atmosphere. In terms of aerosol
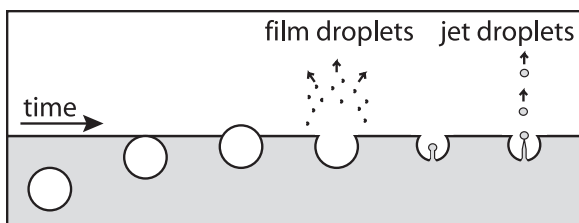
Figure 9. Conceptual model of sea-salt aerosol formation from a bubble rising to the sea surface and bursting. Adapted from *Lewis and Schwartz* [2004].

number, sulfate aerosols are probably the most abundant particles in the marine atmosphere. Over the oceans, there are typically 10^2–10^3 cm^{-3} sulfate aerosol particles, residing largely in the accumulation mode (Figure 5). Sulfate aerosols contribute to the aerosol optical depth of the marine atmosphere and are a significant source of cloud condensation nuclei.

The major precursors for sulfate aerosols over the oceans are sulfur dioxide (SO_2) emitted from fossil fuel combustion and volcanoes, and oceanic emissions of biogenic dimethylsulfide (DMS). DMS is produced biologically in the surface ocean and emitted via air/sea gas transfer. Once emitted, DMS is subsequently oxidized by OH and, to a lesser extent, NO_3, and perhaps halogen atoms and halogen oxide radicals. The oxidation of DMS can produce a variety of products, such as sulfur dioxide (SO_2), dimethylsulfoxide, dimethylsulfone, and methanesulfonic acid. These reaction products have different physical/chemical properties, and hence, different implications for the production of marine aerosol. In particular, the yield of SO_2 from DMS is an important question. All of the DMS reaction products have the potential to contribute mass to the marine aerosol, but of these products, only SO_2 has the potential for oxidation directly to gas phase sulfuric acid, which can create new particles.

The term non-sea-salt sulfate is used to distinguish between aerosol sulfate derived from seawater and that derived from gaseous precursors. Sea-salt sulfate and non-sea-salt sulfate are somewhat distinguishable by their size distribution, with the sea-salt component typically in the coarse mode aerosols and non-sea-salt sulfate in the Aitken and accumulation mode aerosols. However, some sea-salt aerosols contribute sulfate to the submicron fraction, and sea-salt uptake of sulfur dioxide contributes to the coarse mode aerosols. The sea-salt sulfate and non-sea-salt sulfate components of an aerosol sample are commonly determined using one of the major cations in seawater (commonly Na$^+$) as a conservative tracer for seawater input. Sea-salt sulfate is calculated by multiplyi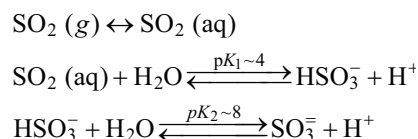ng the aerosol Na+ concentration by the seawater sulfate to Na+ ratio. Non-sea-salt sulfate is obtained from the difference between the measured total sulfate and the calculated seawater sulfate.

SO_2 can undergo gas phase oxidation by OH via the following reactions:

$$SO_2 + OH \xrightarrow{M} HOSO_2$$
$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$$
$$SO_3 + H_2O + H_2O \rightarrow H_2SO_4 + H_2O$$
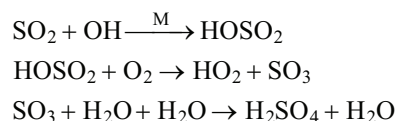
where M denotes the involvement of a third body (air) in the reaction. As discussed earlier, at sufficiently high concentrations, sulfuric acid can cluster with water and can generate new particles via nucleation. This process of binary nucleation (i.e., $H_2SO_4 + H_2O$) will occur in marine air only if it is sufficiently free of preexisting particles. New particles formed in this way rapidly grow into the Aitken mode and ultimately into the accumulation mode via condensation, coagulation, and cloud processing. If particles are already present, newly formed sulfuric acid will deposit on the preexisting particles, resulting in aerosol growth, rather than new particle formation.

The gas phase oxidation of SO_2 by OH, also referred to as *homogeneous oxidation*, is rather slow. Under typical conditions, the lifetime of SO_2 with respect to this process is on the order of several days. SO_2 can also be absorbed into preexisting marine aerosol particles or cloud droplets. SO_2 is a weak acid, and undergoes the following acid/base equilibria:

$$SO_2\,(g) \leftrightarrow SO_2\,(aq)$$
$$SO_2\,(aq) + H_2O \underset{}{\overset{pK_1\sim4}{\rightleftharpoons}} HSO_3^- + H^+$$
$$HSO_3^- + H_2O \underset{}{\overset{pK_2\sim8}{\rightleftharpoons}} SO_3^= + H^+$$

Collectively, $SO_{2\,aq}$, HSO_3^-, and $SO_3^=$ species are referred to as S(IV) or ΣS(IV) denoting the fact that sulfur is in the +4 oxidation state in all these compounds. This differentiates these species from sulfate ($SO_4^=$) and its protonated form, bisulfate (HSO_4^-). In these stable S(VI) compounds, sulfur is present in the +6 oxidation state. The bisulfite ion (HSO_3^-) is the dominant form of S(IV) at the pH typical of marine cloud droplets and sea-salt aerosols. It is highly reactive in aqueous solution, and is rapidly oxidized to sulfate by a variety of reaction mechanisms. This process is generally referred to as *heterogeneous oxidation*, as it involves the transfer of material between the gas and aqueous phases. This process is interesting because the oxidation of S(IV) generates sulfuric acid, which in turn lowers the aerosol pH, reducing the effective solubility of SO_2, shifting its speciation in solution

and altering various reaction rates. At high pH (>7), ozone is a very effective oxidant for dissolved S(IV). Oxidation by hydrogen peroxide (H_2O_2) and aqueous free radicals such as OH is much slower, but less pH dependent. Free radicals may either be produced photochemically in cloud/aerosol droplets or scavenged from the gas phase.

SO$_2$ oxidation proceeds somewhat differently in cloud droplets and sea-salt aerosols. Newly formed cloud droplets are slightly acidic (pH of 5.7 or less, due to equilibrium with atmospheric CO_2 and the presence of organic acids) and are weakly buffered. As a result, pH drops rapidly as dissolved S(IV) oxidizes, and the reaction rate slows. In cloud droplets, reaction with H_2O_2 is responsible for most sulfate production. In contrast, fresh sea-salt aerosols are strongly buffered by the carbonate system in seawater, with a pH near 8. The pH of these aerosols remains high, and the reaction of ozone with dissolved S(IV) remains rapid until sufficient sulfuric acid is generated to overcome the carbonate buffer. This process occurs rapidly over the course of a few hours. Once the buffer is neutralized, aerosol pH begins to fall, SO$_2$ becomes less soluble, and the oxidation of S(IV) slows. The buffering of sea-salt aerosol is a major factor controlling the uptake of sulfur into sea-salt aerosols and plays a major role in the global sulfur cycle [*Chameides and Stelson*, 1993; *Sievering et al.*, 1999]. There is also some evidence that aerosol-borne biogenic $CaCO_3$ derived from phytoplankton skeletal fragments may play a similar role, leading to the production of coarse mode sulfate in marine air [*Sievering et al.*, 1999].

The relative importance of homogeneous and heterogeneous oxidation of SO$_2$ is relevant to understanding aerosol/climate interactions. Sulfur undergoing oxidation on coarse sea-salt aerosols contributes to aerosol mass, but does not increase the number of cloud condensation nuclei in marine air. Homogeneous oxidation, on the other hand, contributes to the growth of nuclei mode aerosols into the cloud condensation size range and, under the right conditions, has the potential to contribute to new particle formation. The interaction of sea salt with the sulfur cycle is a good example of the degree to which various components of marine aerosols are interrelated.

3.3. Nitrate Aerosols

Nitric acid is formed photochemically in the atmosphere from the gas phase reaction:

$$OH + NO_2 \xrightarrow{\text{M}} HNO_3$$
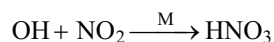
NOx, which consists of NO and NO$_2$, originates from lightning, fossil fuel combustion, biomass burning, soil emissions, and stratospheric input. The formation of nitric acid, its incorporation into aerosols, and the deposition of those aerosols constitutes the main removal mechanism of NOx from the atmosphere. Nitrate is one of the major limiting nutrients in the oceans. The deposition of aerosol nitrate (and other aerosol-borne nitrogen-containing compounds) can have a significant impact on ocean productivity, particularly in oligotrophic regions which have limited upwelling or riverine inputs.

Although nitric acid is formed largely in the gas phase, it is found in the coarse mode of the marine aerosol, rather than in the fine particle mode as one might expect. This unusual size distribution results from the fact that although nitric acid is a strong acid, it is significantly weaker than sulfuric acid and is fairly volatile. Nitric acid deposited on a highly acidic sulfate aerosol is revolatilized and migrates to the coarser, less acidic sea salt or mineral dust particles. An example of the typical size distribution of nitrate in marine aerosol is shown in Figure 5. Typically, the peak in the nitrate size distribution resembles the sea-salt aerosol surface area distribution.

The revolatilization of nitric acid is referred to as acid displacement. This process occurs as follows:

$$NO_3^- + H_2SO_4 \rightarrow HNO_3 \text{ (g)} + HSO_4^-$$
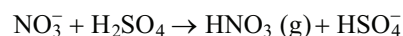
In similar fashion, nitric acid or sulfuric acid can displace HCl from marine aerosols, resulting in a "chloride deficit" relative to sodium or other conservative cations.

$$Cl^- + H_2SO_4 \rightarrow HCl \text{ (g)} + HSO_4^-$$
$$Cl^- + HNO_3 \rightarrow HCl \text{ (g)} + NO_3^-$$
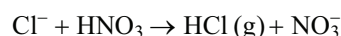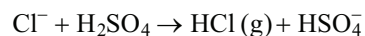
H_2SO_4 is the strongest acid in the atmosphere. It cannot be displaced and is only revolatilized from aerosols by drying them out completely at very low RH. Acids can also react with calcium carbonate in sea salt or mineral dust aerosol, causing release of CO_2.

The redistribution of nitrate onto the coarse mode aerosols has a major impact on its role in the climate system. If nitrate were deposited in the fine particle fraction, it would influence aerosol and cloud radiative properties in the same way as sulfate aerosols do, i.e., enhance the scattering of incoming shortwave solar radiation and increase the number of CCN. On coarse mode aerosols, however, nitrate has much less radiative impact. The coarse size distribution of nitrate also means that its atmospheric residence time is shorter than sulfate aerosols, leading to more rapid removal from the atmosphere via gravitational settling.

3.4. Carbon-Containing Aerosols

Carbon-containing aerosols over the oceans are derived from a wide range of natural and anthropogenic processes

and originate from both marine and continental environments. Such processes include the direct production of primary organic aerosols from the combustion of fossil fuels or natural wildfires and the mechanical production of organic-rich aerosols by the erosion of soils or the formation of sea spray. Secondary organic aerosols can also be formed in the atmosphere by the condensation or polymerization of reaction products of organic gases emitted naturally from the sea surface, from terrestrial plants, or from anthropogenic processes. In general, the carbon-containing components are the least well characterized and understood component of the marine aerosol.

The terminology used for organic aerosols in the literature is sometimes inconsistent, containing a variety of terms like soot, black carbon, carbonaceous aerosols, and brown carbon. Generally, soot is used identically with the terms "black carbon" or "elemental carbon." Soot consists almost exclusively of carbon and is formed in flames during the combustion phase of fuel burning, from diesel, gasoline, wood burning, and coal. Biomass burning (wildfires or controlled burns for agriculture) are another major source of elemental carbon aerosols. Soot is the major light-absorbing component in fossil fuel emissions, and its absorption properties have little or no spectral dependence (hence the term "black carbon").

In addition to soot, there are a wide range of other aerosols consisting of or containing organic carbon. These carbonaceous or "brown" aerosols can have a wide range of composition and are chemically much more complex than elemental carbon. In biomass burning, for example, organics are formed by pyrolysis during the smouldering phase of combustion.

A wide range of oxygenated organic compounds in aerosols are associated with biomass burning of forests and grasslands. The nature of the organic compounds produced is related to the chemistry of the fuel. Anhydrous sugars are among the most abundant compounds produced because they are formed directly from the pyrolysis of cellulose and lignin. Levoglucosan (anhydrous glucose) typically makes up a significant fraction of the total carbon in biomass burning aerosol, sometimes accounting for as much as 50% of the total carbon. Lignin pyrolysis gives rise to a wide range of compounds. There are three basic types of lignin structures, based on conifryl, sinapyl, and paracoumaryl alcohols. Upon pyrolysis, these give rise to the analogous aromatic methoxy phenols, carboxylic acids, and various dimers. As one might expect, the chemically more complex "brown" aerosols are also optically more complex than elemental carbon. They exhibit light absorption and scattering properties that vary as a function of wavelength.

The marine aerosol also contains organic compounds emitted from the sea surface, both directly in the form of sea spray with its microlayer coating, and indirectly, in the form of volatile or semivolatile organics, which may condense once in the atmosphere. Presumably, the properties of the organics in aerosols over the oceans are related to the nature of the physical state and biogeochemistry of the underlying waters. Surprisingly little is known about these processes and the extent to which they influence the properties of marine aerosol.

It has been known for decades that organic matter constitutes a significant fraction of the mass of marine aerosols. Studies from the SEAREX program during the 1970s showed that the majority of the carbonaceous mass in subtropical aerosols resided in the fine particle fraction [*Hoffman and Duce*, 1977]. This fine particle carbon was found to be isotopically light (i.e., depleted in ^{13}C, δ^{13}C ~-26 per mil), which is characteristic of continental sources including plant emissions, biomass burning, and fossil fuel combustion [*Chesselet et al.*, 1981]. Coarse mode aerosols exhibited heavier ^{13}C isotopic ratios (δ^{13}C ~-18–23 per mil), which are associated with carbon of marine origin. This fine particle continental material is clearly capable of undergoing long distance transport and undoubtedly undergoes considerable photochemical aging in the atmosphere. The coarse mode marine-derived organics are most likely shorter-lived and more local in origin simply because they reside on aerosols with much shorter atmospheric residence times. In the atmosphere, these locally derived aerosols probably undergo less photochemical ageing because of their short residence times. Presumably, this material is derived from the sea surface microlayer. Photochemical modification of surfactant material could occur prior to emission, via interaction with ozone and reactive free radicals at the sea surface.

The origin of organic carbon in marine aerosols is not a settled issue. For example, [*O'Dowd et al.*, 2004] observed a strong seasonal variability in the fine particle fraction of the organic aerosols at Mace Head, Ireland with highest levels during summertime. This summertime, increase in aerosol carbon coincided with the summertime North Atlantic phytoplankton bloom. These researchers proposed that increased levels of biological activity enriched the sea surface with surface active organic compounds, which were emitted as fine particle aerosols during bubble bursting. This interpretation of the data appears to conflict with the earlier δ^{13}C evidence. The existing data base characterizing the chemical and isotopic composition of marine aerosol organic matter is not large, and this is an important issue on which further work is needed.

3.5. Mineral Dust

Mineral dust is one of the major components of the global atmospheric aerosol in terms of mass fluxes, radiative and

climate impact, and nutrient deposition to the oceans. See chapters by Ridgwell and Boyd (this volume) for additional information about dust and its oceanic impacts. Mineral dust is generated in arid regions from the action of wind on surface soils. The major dust source regions lie in the northern hemisphere subtropics in North Africa, the Middle East, Central and South Asia [*Prospero et al.*, 2002]. The source soil is aerosolized as a result of two processes: *saltation*, the net horizontal motion of particles near the surface and *sandblasting*, the generation of new dust particles from the impact of saltated particles with particles on the surface. The size distribution of the resulting mineral dust aerosol depends to a large extent on the size distribution of the precursor soil, but also on the wind speed and wind speed variability in a highly nonlinear way [*Grini and Zender*, 2004]. The dust generation process results in formation of two principle modes: giant particles, with mass median diameters of >40 μm and a saltation mode with mass median diameters of 3–6 μm. The saltation mode constitutes the majority of the dust mass transported over and deposited onto the oceans. Measuring the size distribution of dust is challenging because of the difficulties in collecting or analyzing large particles without losses due to impaction in inlets and sampling tubes. These particles have highly nonspherical shapes and complex chemical composition, leading to large apparent differences between size distributions inferred from aerodynamic measurements and those from optical light scattering techniques [*Reid et al.*, 2003].

At the source, mineral dust typically consists of various insoluble soil minerals including various clays (kaolinite, chlorite, illite, smectite, etc.), gypsum, calcite, and quartz. The mineralogy and chemistry of dust reflects the nature of the weathered source material and the climate of the source region. Although dust production is not itself related to air pollution, there is a strong association between the long distance transport of mineral dust and polluted air masses over the oceans. For example, the air masses associated with Saharan dust outbreaks over the tropical Atlantic Ocean frequently originate over Western Europe and contain high levels of pollutants, which interact with the dust during transport [*Savoie and Prospero*, 1989]. During transport, through the atmosphere, mineral dust aerosols can absorb nitric and sulfuric acid from the atmosphere and act as sites for heterogeneous reactions of ozone and nitrogen oxides. These processes result in the formation of soluble sulfate and nitrate coatings on mineral dust aerosols, which alter hygroscopic and optical properties in relation to the original insoluble aerosol. In highly polluted dust generation regions, such as China, the mineral emitted from the eroded surface may be completely reacted in the atmosphere, and the composition of the aerosol may differ significantly from the underlying soil. For example, calcite particles may be completely converted to $CaSO_4$. The acidification of airborne dust by reaction with SO_2, sulfates, and nitrates may also have a significant effect on the bioavailability of aerosol iron after deposition to the surface oceans (see chapter by Boyd, this volume).

4. NUCLEATION AND THE FORMATION OF NEW PARTICLES IN MARINE AIR

The size distribution of marine aerosols and the discussion in section 3.2 may give the impression that there is a continuous supply of new particles to marine air via nucleation of gas phase precursors. For example, DMS oxidation leads to the production of sulfur dioxide and sulfuric acid in marine air. One might expect that binary (two-component) nucleation of sulfuric acid, water vapor, and sulfuric acid-water vapor clusters generates new nuclei mode aerosols. In fact, this is not the case under typical marine boundary layer conditions. There always exists a competition for newly formed sulfuric acid between nucleation of new particles and uptake onto preexisting aerosol particles. Under most conditions, the preexisting aerosol surface area is sufficiently high that sulfuric acid levels remain well below the threshold for formation of new particles. Ternary nucleation involving sulfuric acid, water, and ammonia has been proposed as a way to lower the threshold for new particle formation, but ammonia levels are generally too low over the oceans for this to be a significant process. This situation leads to something of a chicken-and-egg paradox, in the sense that new particles are needed in order to create the existing size distribution, but they cannot be created because of the existing size distribution.

Observational evidence of active nucleation is obtained from the detection of newly formed, nanometer-sized, nucleation mode particles, also referred to as ultrafine particles. Such particles are believed to be on the order of 1 nm diameter when first formed, but current instrumentation can only detect particles greater than about 3 nm [*Stolzenburg and McMurry*, 1991]. Consequently, nucleation mode particles are operationally defined as ranging in size from 3 to 10 nm. Recent progress has permitted the detection of particles as small as 1.5 nm [*Kulmala et al.*, 2007]. Once formed, these particles grow rapidly beyond 10 nm, on timescales of roughly an hour, so their presence indicates recent nucleation. In the marine boundary layer, nucleation mode particles are rarely observed. However, bursts of nucleation mode particles have been observed in association with outflow from clouds or in air that has recently experienced precipitation [*Clarke and Kapustin*, 2002; *Hegg et al.*, 1990]. Typically, active nucleation is evidenced in marine air by particle concentrations of $1–5 \times 10^3$ particles cm^{-3}. Calculations suggest that such levels are equivalent to a nucleation

rate on the order of 1 particle cm^{-3} s^{-1}. Sulfuric acid-water nucleation has also been observed in the tropical upper troposphere, where air masses typically have lower preexisting surface area due to washout in convective clouds. Nucleation mode particle concentrations of up to 5×10^4 cm^{-3} have been observed in those regions [*Brock et al.*, 1995]. This process is thought to play a major role in controlling upper troposphere/lower stratospheric aerosol populations.

Ion-induced nucleation has also been proposed as a significant mechanism for nucleation of new particles. Ions are formed in the atmosphere primarily from galactic cosmic rays and radioactive decay of radon. Sulfuric acid is highly electronegative and readily forms negatively charged ions and water clusters. Tropospheric ion production rates increase strongly with altitude and typically range from 1 to 10^2 cm^{-3} s^{-1}. Although ion-mediated nucleation is not likely to be responsible for the nucleation events observed in field studies, it may be a significant background contributor to the global production of new aerosol particles [*Kazil et al.*, 2006].

The picture that emerges from many field, laboratory, and modeling studies is that in the marine boundary layer, new particles are not generated everywhere, at all times. Most new particles appear to be generated aloft in association with cloud outflow. The marine boundary layer also exports aerosol precursors, like dimethylsulfide to the upper troposphere, where new particle formation occurs. Subsidence of air from above therefore probably plays a major role in sustaining the observed Aitken mode in marine aerosols.

Aerosol nucleation in coastal air has been observed to occur in association with iodine (I$_2$) emissions from kelp beds [*McFiggans et al.*, 2004; *O'Dowd et al.*, 2002]. Iodine
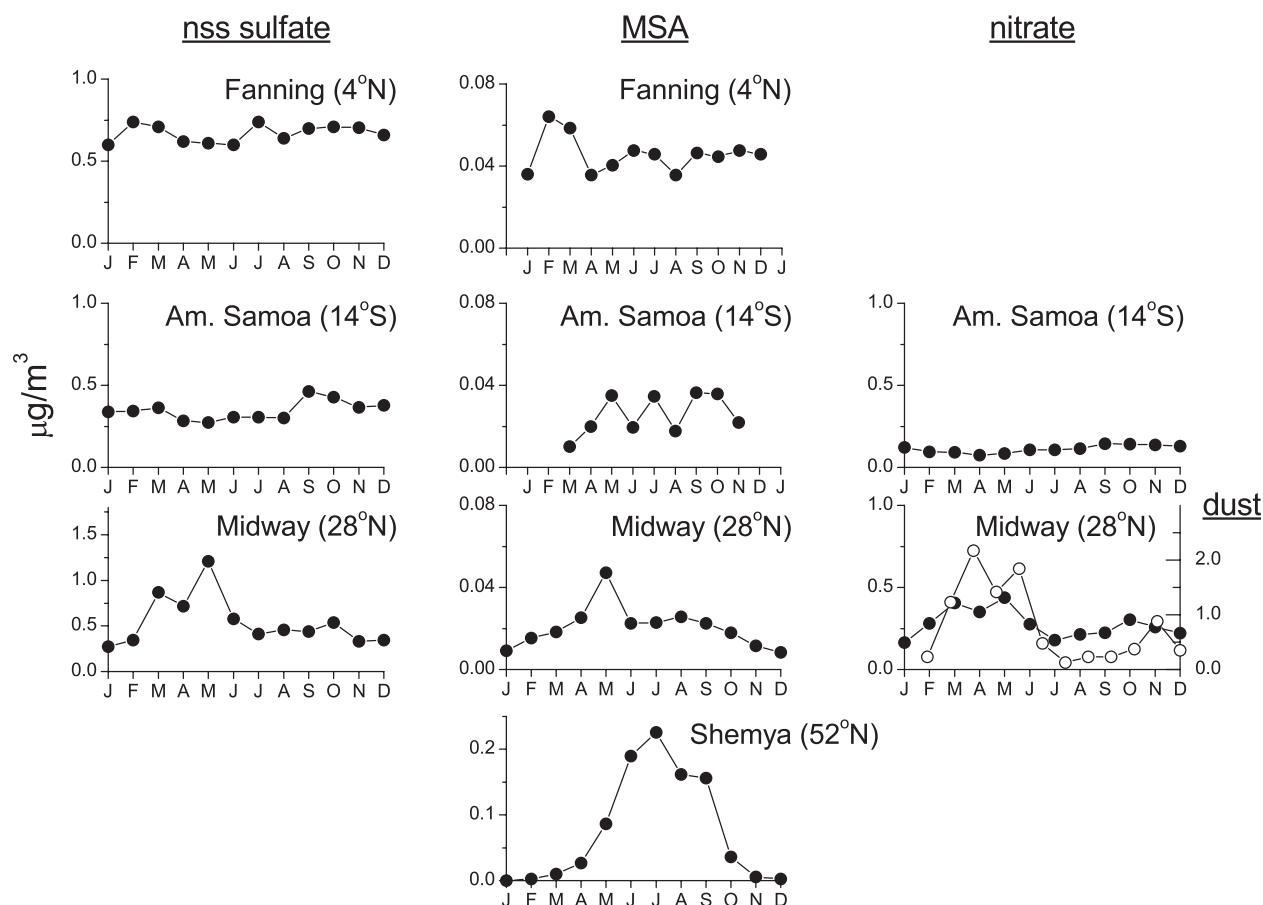

Figure 10. Multiyear averaged monthly aerosol records from the SEAREX program from Pacific islands in tropical (Fanning and American Samoa), midlatitude (Midway), and high latitude (Shemya) locations. Data shown for (left) nonsea-salt sulfate, (center) methanesulfonate, (right) nitrate. Mineral dust shown for Midway only (open circles). All data are in units of μg/m^3. Data from *Savoie and Prospero* [1989] and *Prospero and Savoie* [1989].

emissions lead to the rapid photochemical production of iodine oxides IO and OIO, which in turn lead to production of higher oxides in the form of I_2O_y, where y ranges from 2 to 5. These oxides nucleate rapidly, and nucleation mode particle concentrations of 10^4–10^5 cm^{-3} have been observed. This process can potentially generate significant numbers of Aitken mode aerosols and cloud condensation nuclei [*Saiz-Lopez et al.*, 2006]. Because kelp beds are restricted to coastal regions, this process is likely of limited importance to marine air over the open oceans. Active iodine chemistry has also recently been observed in coastal Antarctica and over sea ice-covered regions of the Southern Ocean [*Saiz-Lopez et al.*, 2007a, 2007b]. This iodine production is presumably related to biological activity in sea ice, and it appears to be a large-scale phenomenon, which may be important to the large-scale properties of the aerosol in that region.

Is iodine-based nucleation important globally to the marine aerosol? Short-lived, highly reactive iodine-containing halocarbons, such as CH_2I_2, CH_2ClI, and CH_2BrI have been detected in both coastal and open ocean seawater [*Carpenter et al.*, 1999; *Class and Ballschmiter*, 1988; *Dobbie et al.*, 2003]. The concentrations and fluxes of such gases are probably too low to result in significant particle production under typical open ocean conditions, but the observational data base is limited, and this remains an open question.

Is there a role for organics in the formation of new particles in marine air? In terrestrial environments, the reaction of terpenes and other biogenic organic compounds leads to the formation of organic aerosols. Such compounds are present in seawater, but at such low levels that nucleation is not likely. *Leck and Bigg* [2005] proposed an entirely different mechanism of new particle formation via ejection of marine microcolloids from the sea surface into the marine boundary layer. They demonstrated that this is an important mechanism for particle formation in the Arctic and suggest it is important throughout the open ocean. This mechanism has the potential to produce new particles directly into the nuclei mode without requiring gas to particle conversion. Further observations are needed to determine the global significance of this mechanism.

5. LARGE-SCALE CHARACTERIZATION OF THE MARINE AEROSOL

Large-scale, regional and global pictures of aerosol distributions, properties, and variability is needed in order to assess aerosol (and gas phase precursor) sources, transport patterns, climate impacts, and biogeochemical fluxes. Knowledge about the large-scale distribution of aerosols over the oceans is derived from a combination of intensive

field campaigns, time series of measurements from island and coastal stations, satellite observations, and numerical models simulating aerosol production, transport, and deposition. Each of these approaches provides different types of information, and all of them are needed to characterize global aerosol properties. For example, only in situ intensive measurements can provide accurate chemical and physical properties of aerosols and the basic calibration/validation for satellite or other remote sensing observations. Multistation in situ time series observations generally provide long-term records of a less detailed set of parameters and provide a basis for evaluating seasonal and interannual variability. Finally, numerical models test our ability to explain the observed distributions in terms of the known aerosol generation, transformation, and removal mechanisms.

The climatology of sulfate aerosols over the oceans illustrates the coupling between ocean biology and the production of sulfur gases, and the overlying aerosol chemistry. During the SEAREX program in the 1980s, weekly bulk aerosol samples were collected at a number of Pacific islands for several years. The sulfate and methanesulfonate data shown in Figure 10 indicate that biogenic sulfur dominates as a source of sulfate aerosol in the south and equatorial Pacific [*Prospero and Savoie*, 1989]. Midlatitude Pacific sites, like Midway Island, show evidence of the seasonality in the biogenic source. Midway Island also shows the impact of long distance transport of both terrestrial-derived sulfate associated
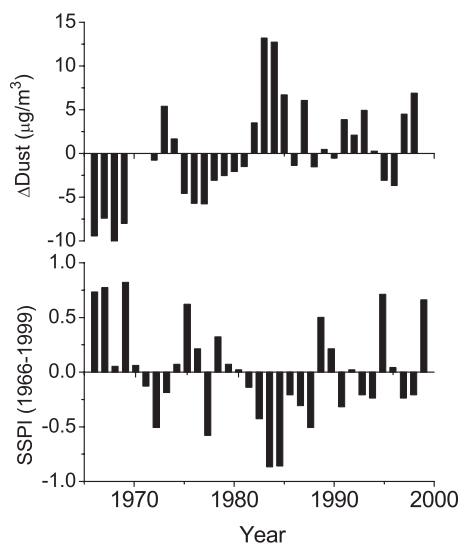

Figure 11. Mineral dust and climate. The upper panel shows dust levels at Barbados, West Indies, between April and September for the years 1966–1999, expressed as a deviation from the mean. The lower panel shows the sub-Saharan Precipitation Index (SSPI) over the same period [data from *Prospero and Lamb*, 2003].
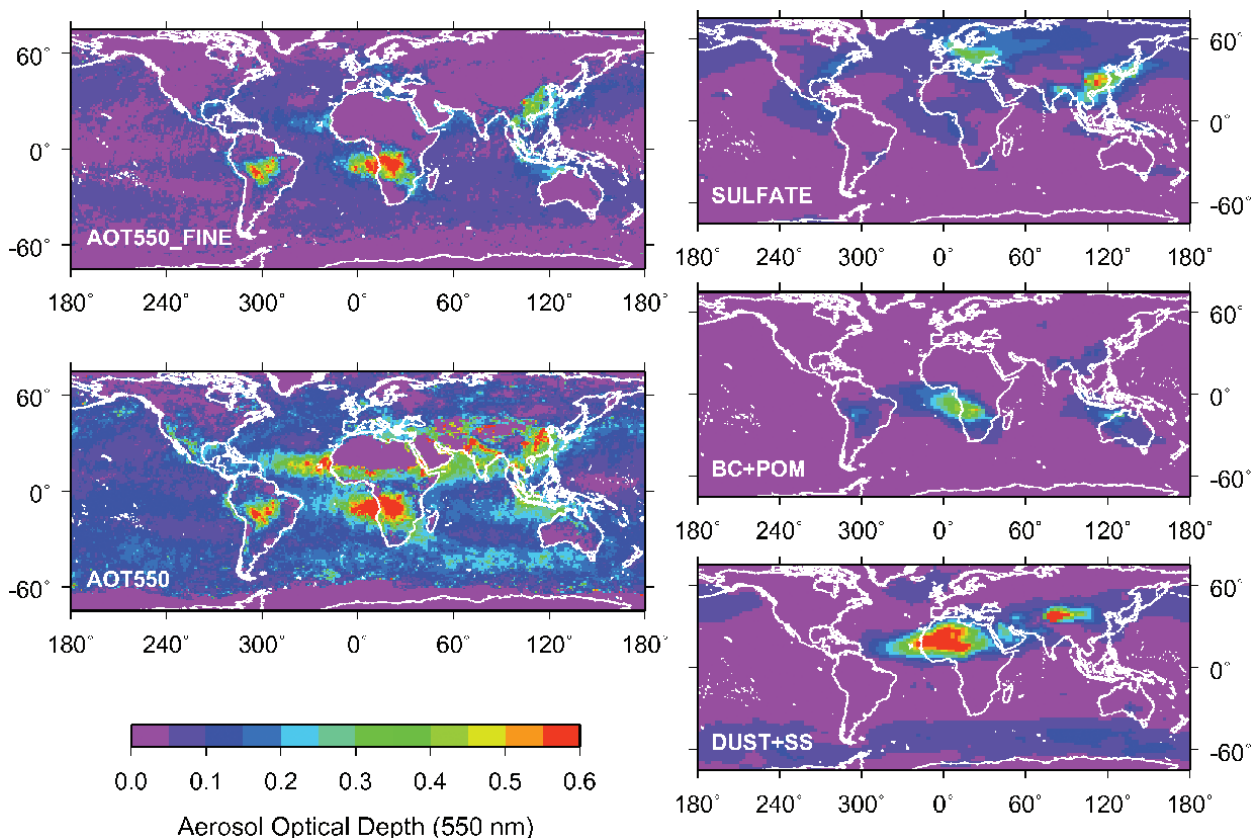
Plate 2. Satellite observations and model simulations of global aerosol optical thickness (at 0.55 μm) for September, 2000. Left, NASA Moderate Resolution Imaging Spectroradiometer (on EOS) satellite observations of (upper left) fine aerosols and (lower left) total aerosols. Right, results from the GOCART model simulating sources, transport, and deposition of (upper right) anthropogenic sulfate, (middle right) black carbon and particulate organic matter, and (lower right) dust and sea salt. Data obtained from the NASA Giovanni online data system (http://disc.sci.gsfc.nasa.gov/giovanni). See *Kaufman et al.* [2002] and *Chin et al.* [2002] for further information.

with Asian outflow and of biogenic sulfur transported from the Bering Sea and other northerly waters with very high DMS emissions. The impact of continental outflow also has a strong impact on aerosol nitrate [*Prospero and Savoie*, 1989; *Savoie and Prospero*, 1989]. The long-term records clearly show the seasonality of Asian dust outflow, and the correlation between dust loading and elevated nitrate levels.

Atmospheric dust records from the tropical Atlantic illustrate the value of time series measurements. Multidecadal monthly measurements of atmospheric dust levels at several sites clearly show that dust transport over the Atlantic is a large-scale phenomenon, with significant interannual variability [*Ginoux et al.*, 2004]. Time series data reveal a relationship between atmospheric dust loading and climate. For example, there is a strong inverse correlation between the levels of atmospheric mineral dust at Barbados, West Indies and rainfall anomalies in sub-Saharan North Africa (Figure 11) [*Prospero

and Lamb, 2003]. Such a relationship is related to large-scale modes of variability in regional climate, such as the El Niño-Southern Oscillation and North Atlantic Oscillation.

Satellite observations of aerosols are based on detection and analysis of outgoing reflected and emitted radiation at the top of the atmosphere (see chapter by Loisel, Jamet, and Riedi, this volume). A number of different satellite platforms have been used as aerosol detectors, employing a variety of techniques [*Kaufman et al.*, 2002]. Single-wavelength, single-angle sensors, such as the AVHRR, METEOSAT, and GOES instruments, detect sulfates and other highly reflective aerosols. The TOMS instruments use dual-channel UV sensors to detect highly absorbing smoke and dust aerosols. POLDER is a multiwavelength, multiview angle instrument that measures light polarization. MODIS, MISR, and ASTR instruments utilize various combinations of wide spectral range, and multiple viewing angles, to characterize aerosol

abundance and type. All of these instruments provide a measure of the aerosol optical thickness of the atmosphere, typically reported for a wavelength of 0.55 μm.

Satellite observations provide a unique global view of the marine aerosol. The combination of satellite observations and regional/global aerosol modeling is particularly powerful. As illustrated in Plate 2, current satellites and models are capable of capturing some of the major climatological features of the atmospheric aerosol. These images and model simulations clearly show the outflow of pollutant aerosols from North America, Europe, and Asia, dust transport from Africa and Asia, and biomass burning aerosols from Africa and South America. A strong sea-salt signal appears over the Southern Ocean, but it is recognized that optical remote sensing of aerosol properties in cloudy regions of the atmosphere is particularly challenging. One of the most striking features of this global view is the extent to which continental regions dominate the fine particle aerosol optical thickness. The influence of biogenic marine aerosols is less evident because the optical depths are low in the regions dominated by marine gaseous emissions. For coarse particles, both continental and marine sources are evident.

6. CONCLUDING REMARKS

It should be evident from this brief survey that understanding the origin and evolution of marine aerosols is a challenging subject that requires expertise from a wide range of disciplines. The driving force for this research is the pressing need to assess the climate impact of marine aerosols, in terms of radiative forcing from aerosols, aerosol indirect effects on cloud properties, and aerosol impacts on biogeochemical processes, which impact the carbon cycle. Parameterizing marine aerosols in global climate models is a complex task because the processes involved occur on subnanometer to micron size scales with many chemical components. The challenges of understanding and parameterizing aerosol processes will continue to motivate research for many years to come. Progress will continue to come from a combination of in situ observations, remote sensing, and simulations that integrate real-world observations with our understanding of fundamental physical and chemical processes.

ADDITIONAL READING

For additional reading, see the following texts and reviews.

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