Analysis of Atmospheric Aerosols

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Abstract

Aerosols represent an important component of the Earth's atmosphere. Because aerosols are composed of solid and liquid particles of varying chemical complexity, size, and phase, large challenges exist in understanding how they impact climate, health, and the chemistry of the atmosphere. Only through the integration of field, laboratory, and modeling analysis can we begin to unravel the roles atmospheric aerosols play in these global processes. In this article, we provide a brief review of the current state of the science in the analysis of atmospheric aerosols and some important challenges that need to be overcome before they can become fully integrated. It is clear that only when these areas are effectively bridged can we fully understand the impact that atmospheric aerosols have on our environment and the Earth's system at the level of scientific certainty necessary to design and implement sound environmental policies.

1. INTRODUCTION

Atmospheric aerosols: solid or liquid particles suspended in the atmosphere

SOA: secondary organic aerosol

Primary particles: gases or particles emitted directly from a source

Atmospheric aerosols in the troposphere are composed of solid and liquid particles of varying composition and phase (1). Examples include smoke, fog, clouds, and smog (2). Particles play major, yet poorly understood, roles in affecting human health, visibility, air quality, and our overall climate (3). **Figure 1** shows a schematic of the major processes contributing to atmospheric aerosols. Primary particles can be directly emitted into the atmosphere by combustion sources (e.g., coal combustion, biomass burning, and vehicle emissions) or other wind-driven processes such as the resuspension of dust and sea salt. Secondary particles are formed from photochemical reactions of gas-phase species that are emitted directly into the atmosphere, producing more highly oxidized, less volatile species, which can then form new particles or condense on existing particle surfaces. The most common example of this occurs when gas-phase organics undergo oxidation producing less volatile organic species that condense on particle surfaces; these particles are termed secondary organic aerosols

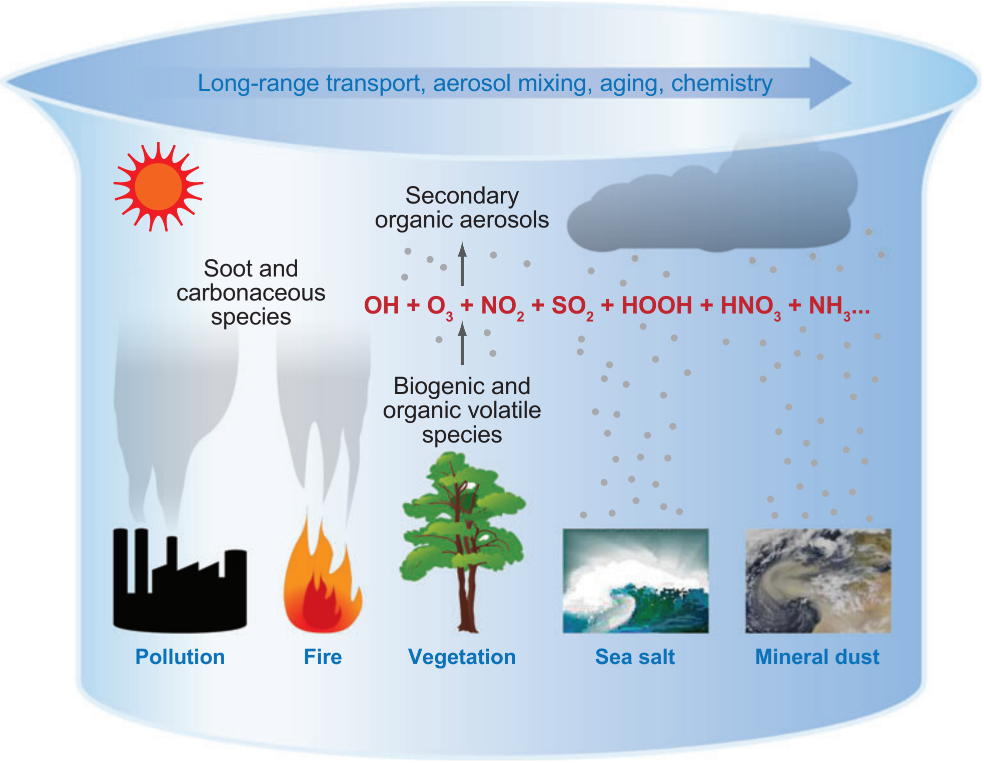

Figure 1

Illustration of the Earth's atmosphere as a chemical reactor. This figure shows examples of the natural and anthropogenic processes producing gases and particles in the atmosphere. Subsequent processes can transform and age these particles as they are transported through the atmosphere.

(SOA). Temperature reduction, as well as reactive uptake via heterogeneous processes and adsorption of chemical species, also shift species from the gas to particle phase.

Details on the variability of chemical species within individual particles remain limited. Additionally, our understanding of chemical speciation within particles is limited by the availability of analytical techniques used to measure them. We understand far more about gas-phase atmospheric components, including ozone, NO_x ($NO + NO_2$), and volatile organic species (4). Analytical methods are typically designed to target a specific molecule or class of molecules in the gas phase. In contrast, each particle is composed of many chemical species, and it is difficult to find a single analytical method that can measure all of them. As discussed below, mass spectrometry (MS) has become the most commonly used method for analyzing the composition of individual particles in recent years as it serves as a universal on-line detector of a broad range of chemical components.

Recent atmospheric chemistry studies have focused much effort on developing new techniques for measuring aerosols. A strong size dependence exists with submicrometer particles comprising primarily carbonaceous species, including elemental carbon (i.e., soot) and organic carbon, as well as inorganic species such as metals, sulfate, nitrate, and ammonium. Supermicrometer particles are made up of inorganic species such as sea salt and dust and thus are composed mostly of transition metals, silicates, and alkali metals (5). Heterogeneous processing adds secondary species to primary particles such as dust and sea salt, resulting in nitrate and sulfate in the particles (6, 7).

Aerosols represent the largest uncertainty in understanding how humans are changing our climate. Thus, more studies are aimed at developing analytical techniques that can be used in laboratory and field studies at the necessary level to better understand and quantify their role in affecting climate. Particles affect climate through several mechanisms: (*a*) scattering and absorbing solar radiation; (*b*) scattering, absorbing, and emitting thermal radiation; and (*c*) acting as cloud condensation nuclei. The first two mechanisms are called the direct climate effect and relate to the optical properties of particles based on their size, shape, and chemistry. The third mechanism is called the indirect climate effect.

Currently, the study of atmospheric aerosols includes three scientific approaches: (*a*) field measurements of aerosol particles; (*b*) laboratory studies of the chemistry and physical properties of model systems representative of atmospheric aerosols; and (*c*) modeling analysis that includes gas-phase chemistry, photochemistry, heterogeneous chemistry, and optical properties so that models can be effectively used to predict important global climate impacts of aerosols. Integration of these three approaches is essential if we are to fully understand the roles of atmospheric aerosols in climate and air pollution.

One complicating factor in the integration of field, laboratory, and modeling studies is the different treatment of aerosol complexity. Field measurements show that nearly every particle differs in size, physical properties, and chemical characteristics. Laboratory studies typically use model systems to decrease the complexity of different particle types. For example, these studies often use NaCl as a surrogate for sea salt, metal oxides to mimic mineral dust, and single-component mixtures as

MS: mass spectrometry

Secondary particles: gases or particles formed by chemical reactions in the atmosphere

Direct climate effect: the manner in which atmospheric particles directly impact climate through the absorption and scattering of solar radiation

Indirect climate effect: the manner in which atmospheric particles indirectly impact climate through their influence on cloud formation and cloud properties

Heterogeneous chemistry: reactions between the gas and particle phases of the aerosol surrogates to study properties of organic aerosols. Many atmospheric chemistry models treat aerosols as a single entity. Even studies that distinguish between aerosol types (e.g., mineral aerosol) treat particles as a single component without considering that different compositions have different reactivities (8, 9). Because the complexity of aerosols is treated so differently, a key question is how to achieve integration of these activities when such different and seemingly disparate approaches to complexity are being taken.

Mixing state: associations of chemical species within individual particles; in internal mixtures, all particles of a given size have the same chemical composition, whereas in external mixtures, they have distinct combinations of chemical species

This review provides some examples of the state of the science in the analysis of atmospheric aerosols. We describe some important results that have emerged when the integration problem has been addressed. Due to space limitations, this is not an exhaustive review of previous studies on aerosols, but instead it provides examples of how analytical chemistry performed in the field and laboratory has shed new light on our understanding of the role aerosols play in air pollution and climate change. The final half of this review provides some key issues and needs in the field of analytical chemistry of atmospheric aerosols.

2. SELECT EXAMPLES OF FIELD MEASUREMENTS AND LABORATORY STUDIES OF ATMOSPHERIC AEROSOLS

Field measurements provide an opportunity to determine the atmospheric species and processes that are indeed driving the chemistry of the atmosphere. Investigators then use field observations to develop laboratory studies that can be conducted under well-controlled conditions in an effort to quantify these atmospheric chemical processes. Additionally, laboratory studies can provide insightful data that can aid the interpretation of field observations. Furthermore, laboratory data can also be expressed in a form that is useful for modeling analysis so that models can predict atmospheric composition. Synergy is thus required between field and laboratory studies to perform the studies required to better understand the atmosphere. In this give-and-take approach, one can more fully understand the important processes and the parameters affecting different measurements. The ultimate goal is to incorporate detailed laboratory mechanistic and kinetic data, acquired in studies motivated by field study findings, into models that can be used to accurately predict and reproduce field measurements. Also, models allow the results to be extrapolated over much larger global scales, giving broad spatial data that would be impossible to obtain in field studies. This closure will allow us to quantify the impact of gases and particles on atmospheric chemistry and climate on global and regional scales.

2.1. Field and Laboratory Measurement Approaches and Questions

Individual field studies are designed to address specific scientific objectives; thus, researchers select the region in which the study is to be conducted in order to best suit these objectives. Some of the questions regarding aerosol chemistry addressed in coupled field-modeling studies are listed below.

1. How does the single-particle mixing state of particles impact the physical, optical, and chemical properties of the particles, as well as the regional climate of specific regions (e.g., marine versus urban, Indo-Asian haze) (10, 11)?

2. How do ocean-atmosphere interactions play a role in cloud formation in marine environments (12)?
3. How does the presence of mineral dust affect the overall resulting chemistry and clouds in the atmosphere?
4. What are the major carbonaceous components in atmospheric aerosols, and are most produced from primary sources, or are they formed through secondary reactions?
5. What is the spatial variability of the chemistry and sources of atmospheric aerosols, and how much does long-range transport of pollutants and aerosols play a role in affecting air pollution and climate on a global scale?

As many laboratory studies typically use simplified model systems to begin to ask fundamental questions about the chemistry and physics of atmospheric aerosols, some key issues and questions in laboratory studies include the following:

1. Which model systems best describe a particular class of atmospheric aerosols?
2. How close can these model systems come to mimicking atmospheric aerosols, and how close do they need to be to provide answers to important scientific issues, such as the impact of aerosol on the chemical balance of the atmosphere, Earth's climate, and the health of humans and ecosystems?
3. As laboratory studies probing aerosol chemistry are often performed using powders, thin films, and isolated particles deposited on substrates as well as suspended particles, questions arise, such as do results from these different model systems agree, and are they applicable to aerosol chemistry?
4. Which combination of analytical techniques is best suited for bridging the results from laboratory studies with field studies of atmospheric aerosols?

Early field studies focused on deriving a better understanding of gas-phase reaction processes, typically measuring ozone and its precursors. More recently, field studies have begun focusing on the particle component of air pollution via platforms such as airplanes, balloons, ships, ground-based sites, unmanned aerial vehicles, and even space shuttles. Advancing an instrument from the laboratory to a field version can be quite challenging. Smaller instruments with lower power requirements and robust operation that can handle extreme temperatures are required. Interestingly, many of the state-of-the-art instruments used in the laboratory are now being developed for the field (13). Field studies serve as an opportunity to intercompare multiple instruments using different approaches for measuring the same, or slightly different, components of the aerosol (14, 15). However, field studies are limited to studying a relatively small spatial scale, and thus models and satellite measurements are important for extrapolating findings to a larger scale.

The ultimate goal of any analytical technique developed for atmospheric studies is to quantitatively identify all species within each individual particle as rapidly as possible to monitor real-time changes in aerosol chemistry. This represents an enormous challenge as particles come in many shapes and sizes and can be quite small and highly complex. Their size range spans from 1 nm up to 10 μm, corresponding to a mass range of 10^{-21} g to 10^{-9} g, respectively. Different instruments are used to measure particle size in various ranges: a scanning mobility particle sizer for particles in the

3- to 600-nm size range and an aerodynamic particle sizer or optical particle counter for larger particles (>500 nm). Size metrics include optical, aerodynamic, geometric, and mobility diameters. [We refer the reader to a review that details the methods used to obtain particle size (16).] In the atmosphere, particle chemistry undergoes dynamic changes owing to heterogeneous reactions, the partitioning of species to and from the gas phase, and aqueous phase processes. Capturing these changes within a minute volume and for such a small mass represents an enormous challenge, requiring high time-resolution measurements, especially for airborne platforms.

ACE-Asia: Aerosol Characterization Experiment–Asia

The sections below provide a brief overview of traditional aerosol chemistry measurements with a focus on the types of questions and techniques used to address them in two rapidly growing areas: (*a*) the characterization of organic species in aerosols and (*b*) single-particle measurements of mixing state. Finally, we describe results from a case study, ACE-Asia, to demonstrate how a combination of laboratory studies, field measurements, and modeling analysis can provide unique insights into atmospheric aerosols.

2.2. Off-Line Aerosol Analysis

Traditionally, field studies use filter-based techniques to collect particles for subsequent analysis. To obtain enough material for quantification and identification by standard analytical methods, researchers collect samples for periods of hours to weeks. Once in the laboratory, multiple traditional analytical techniques, such as gas chromatography/MS and liquid chromatography/MS, are used to analyze major components.

One downside to the off-line approach is sampling artifacts, including the gain or loss of species and reactions that can alter the sample. Thus, questions exist as to how representative the filter samples are of the actual atmospheric aerosol. Also, one goal of field studies is to capture real-time changes in particle chemistry and relate this to other parameters. For these reasons, there has been a major push over the past decade to shift to on-line measurements of aerosol chemistry coupled with other physical and optical properties with high time resolution.

2.3. Characterization of Organic Aerosols

On-line MS analysis has become the method of choice for many environmental studies, including the study of atmospheric aerosols (17). Large research efforts focus on characterizing the organic fraction because it is the most poorly understood component of atmospheric aerosols (18, 19). The organic fraction can account for 50% of the fine particle mass ($PM_{2.5}$) on an annual average, yet only 10%–15% of the organic species have been identified. As a result of photochemical processing, many organic aerosol species are highly oxidized (20). The low-volatility properties that cause substances to exist predominately in the particle phase make it challenging to desorb them into the gas phase for analysis and identification. Additionally, heating the sample to induce vaporization can cause organic species to break down or even polymerize in the presence of an acidic aerosol (21). Thus, electrospray ionization and atmospheric pressure chemical ionization coupled with MS have emerged to identify new organic species in aerosols via off-line analysis (22–24). Water-soluble organic carbon and other inorganic ions can now be analyzed in real time using an ion chromatograph instrument adapted for the field (25, 26). Until recently, the majority of organic species identified in aerosols had molecular weights of less than 300 Da. However, recent smog chamber photochemical studies, as well as field studies, have shown the production of high-mass oligomeric species, which have recently been analyzed using off-line and on-line laser-desorption MS (27–29). Additionally, humic substances similar to those found in aqueous environments have been shown to exist in atmospheric aerosols (30). These complex high-mass species are quite difficult to analyze by conventional analytical methods.

Carbonaceous aerosols: elemental and organic carbon species

2.3.1. Field studies of organic aerosols. High-sensitivity, universal detection of virtually any chemical species and the recent demonstration of smaller, portable, and rugged instruments make MS an ideal choice for field measurements of aerosols. The basic design can be subdivided into those mass spectrometers that measure the chemistry of particle ensembles and those that measure the chemistry of one particle at a time. Different methods of ionization are inherently linked to each class of mass spectrometer (31). One type measures the chemistry of particle ensembles by using a filament to flash vaporize species from the particles and electron impact ionization to form ions. More recently, thermal desorption was coupled with chemical ionization to ionize species evaporated from the particles (32, 33). A commercial version of the electron impact ionization–based mass spectrometer is an aerosol mass spectrometer developed by Aerodyne, Inc. This instrument uses a quadrupole mass spectrometer, and most recently a time-of-flight mass spectrometer, to provide mass concentrations of submicrometer nonrefractory species including ammonium, nitrate, sulfate, and organic carbon with high time resolution (34, 35). The aerosol mass spectrometer has been used in aircraft- and ground-based measurements in a number of field studies around the world as well as in the laboratory. The instrument has been used to distinguish between different forms of nonrefractory carbonaceous species, namely oxidized organic aerosol and hydrocarbon organic aerosol. By examining these basic organic types, investigators have used the aerosol mass spectrometer for extensive studies focusing on the importance of oxidized organic species and SOA formation (36, 37). Recent high-resolution measurements using a newly added time-of-flight mass spectrometer have the potential to delve more deeply into the complexity of the organic fraction (34). Additionally, thermal desorption has been coupled with gas chromatography/MS to separate and identify organic species in atmospheric aerosols (38).

2.3.2. Laboratory studies of organic aerosols. Laboratory studies of the properties of organic aerosols including carbonaceous aerosols (which consist of soot, black and brown carbon, and biomass-burning aerosols) are of particular interest from a global climate perspective as their impact on climate forcing depends on their physiochemical properties, which vary significantly depending on the source. In the

HULIS: humic-like substances

CCN: cloud condensation nuclei

case of carbonaceous aerosols, recent laboratory studies have attempted to determine the most appropriate reference materials for these species (30, 39–41).

Recent studies using a state-of-the-art single-particle analysis technique, scanning transmission X-ray microscopy/near-edge X-ray absorption fine structure spectroscopy, of various laboratory surrogates concluded that carbonaceous aerosols are extremely diverse, and atmospheric aging processes alter their composition (40). Thus, no single standard is available that accurately represents atmospheric carbonaceous aerosols. However, efforts are promising as the International Steering Committee for Black Carbon Reference Materials believes that *n*-hexane soot is the most appropriate standard available (42). Additionally, an inverted methane/air diffusion flame produces soot that appears to be representative of atmospheric black carbon and thus may also be a suitable standard reference material, particularly for light-absorption studies (39, 41). As the physiochemical properties depend strongly on the composition and atmospheric processing, these types of studies are important and should be continued so that appropriate surrogates are identified.

As biomass-burning particles collected in the field show highly complex and heterogeneous particles, it is difficult to study the physiochemical properties of these aerosols because there is currently no appropriate surrogate for laboratory use. Some studies utilize single components observed in biomass plumes (43, 44). Tivanski et al. (40) have shown that biomass-burning particles resemble atmospheric humic-like substances (HULIS) in terms of composition and structural ordering and that they are dissimilar to black carbon standard reference materials. Therefore, atmospheric HULIS may be more representative of biomass-burning aerosol than black carbon standards that have been previously used as surrogates. However, as representative HULIS atmospheric samples are not easily attainable, many laboratory studies substitute atmospheric HULIS with humic and fulvic acids from terrestrial and aquatic sources. Although these surrogates are similar to HULIS as they comprise large-molecular-weight, multifunctional organic molecules and appear to have similar infrared spectral characteristics, there are many differences between terrestrial and atmospheric humic substances (30, 45). For example, water-soluble organic carbon–derived HULIS from fine atmospheric aerosol tend to have higher surface activity, less aromatic functionalities, smaller molecular sizes, and weaker acidity than aquatic fulvic acids. Thus, there remains a need for appropriate surrogates for atmospheric HULIS and biomass-burning aerosols so that we can better understand the properties of carbonaceous aerosols.

Organic aerosols are complex, and many factors play a role in affecting their cloud condensation nuclei (CCN) potential, including surface tension, impurities, contact angle, deliquescence, morphology, age, and volatility (46). Researchers use all these factors when theoretically predicting and interpreting field results for CCN activation. Obviously, deconvoluting the relative impact of each property on CCN activation is more straightforward in well-controlled laboratory experiments. In an effort to better integrate laboratory and modeling studies, Roberts et al. (47) suggested reporting the hygroscopic growth and CCN activity of aerosols studied in the laboratory relative to pure ammonium sulfate, a well-known CCN active aerosol. Additionally, Petters & Kreidenweis (48) theoretically developed a single parameter, κ, related to hygroscopicity that can integrate both laboratory and field CCN properties. As more such systems are developed and utilized, our understanding of atmospheric processing and climate effects of various types of aerosols will strengthen. Thus, laboratory studies are essential for providing necessary information for input into more detailed atmospheric models. However, as many laboratory studies focus on the CCN properties of single-component aerosol, future studies of more complex, multicomponent systems are needed to understand the effects of mixing state on cloud formation.

The poorly understood factors affecting SOA formation are being investigated through careful smog chamber studies (49). However, most early studies used orders of magnitude higher concentrations of reactants/oxidants than are present in the atmosphere to simulate atmospheric aging processes that occur over days in the relatively short time period of a smog chamber experiment (hours). These unrealistic reactant concentrations influence the actual aerosol products that form (50). Smog chamber studies, made feasible by the advent of on-line instruments that provide higher sensitivity, are now being conducted at lower, more realistic oxidant concentrations (51). A question still exists as to how to replicate atmospheric concentrations and timescales, reduce wall losses, and extend the results of smog chamber studies using relatively simplistic aerosols to the real atmosphere. Recently, several research groups have moved in a direction that will better bridge this gap by making aging measurements of aerosols formed under more realistic conditions and emitted from specific sources (29, 52). Although these are still relatively complex chemical mixtures, they are more representative of processes occurring in the atmosphere, and the results are easier to interpret relative to field studies. Smog chambers have been used to study the CCN activation of SOAs, providing insight into how CCN activation changes for slightly more complex organic mixtures (53). These studies represent important steps in bridging field and laboratory studies, and more studies such as these are needed.

2.4. Single-Particle Measurements of Mixing State

An alternative approach for measuring the chemistry of aerosols involves measurements of single particles rather than collections of particles. Such measurements are being used to directly address the diversity of different compositions within the aerosol mix of the atmosphere. A key requirement to answer many climate-related models involves insight into the properties of atmospheric aerosols as a function of chemical mixing state (54, 55). Mixing state refers to the distribution of chemical species within individual particles. The combination of species in a single particle is important in determining the reactivity, water uptake, and optical properties of the particles. Perhaps the most important example of how mixing state can influence the optical properties and radiative forcing of aerosols involves the soot-sulfate mixture (56, 57). Soot is the strongest absorber of tropospheric solar radiation and leads to warming (58, 59). In contrast, sulfate scatters light back to space and leads to cooling. Internally mixed soot-sulfate mixtures are predicted to absorb up to three times more strongly than soot and sulfate in separate particles (57, 60). Soot and sulfate concentrations vary in different regions of the world; thus a better understanding of the spatial variability of the soot-sulfate mixing state is critically needed. If more accurate input on mixing state is provided for models, field observations of aerosols and their radiative properties may be in better agreement with model predictions (61, 62).

LDI: laser desorption/ionization

To obtain single-particle chemical information, investigators use electron microscopy, MS, and laser-induced breakdown spectroscopy (63). Electron microscopy has been used extensively to characterize the size, morphology, water uptake properties, and chemistry of individual particles (64, 65). Techniques such as micro-proton-induced X-ray emission can provide insights on species distribution within individual particles (66). High-resolution scanning electron microscopy/energy dispersive X-ray spectroscopy has been used to estimate the complex refractive index of individual atmospheric particles. One issue with electron microscopy is that most studies examine very few particles; thus statistical questions arise as to whether an atmospherically representative sample was obtained. In addition, other semivolatile components evaporate under vacuum and the intense energy of the electron beam. To overcome losses in vacuum and to study the hygroscopic properties of single particles, a number of researchers use environmental scanning electron microscopy (67).

To establish an understanding of real-time changes in particle size and mixing state, investigators developed single-particle MS. Statistics are not an issue as the size and chemistry of millions of particles can be analyzed. Two recent reviews summarize the different designs of single-particle mass spectrometers and how each provides different types of data (31, 68). **Figure 2*a*** shows a typical mass spectrum obtained via bulk (ensemble) averaging, which analyzes, by necessity, multiple particles. A reasonable interpretation of the spectrum is that all particles are composed of the same average chemical composition. In contrast, mass spectra of single particles (**Figure 2*b***) clearly show that this interpretation is incorrect and that there are distinct particles with different compositions. Thus, the bulk composition analysis predicts incorrect particle properties in this case. The ion fingerprints in the deconvoluted mass spectra show unique combinations of OC, EC, K, and metals (i.e., Zn, Pb, Cr, Ag) that provide unique insight into the specific source of each particle type (**Figure 2*b***). The presence of nitrate and sulfate demonstrates which particle types have undergone atmospheric aging processes. These single-particle mass spectral signatures provide critical insights into the partitioning of species to different particle types, the reactions different particle types undergo in the atmosphere, and the original source that produced each particle.

Friedlander and coworkers (69) developed the original design of these single-particle instruments in the early 1980s. Early mass spectrometers used a filament to desorb the particle and electron impact ionization coupled with a quadrupole mass spectrometer. Today, the majority of single-particle mass spectrometers use time-of-flight technology to obtain the entire mass spectrum of each particle. In fact, many systems now use a dual polarity time-of-flight mass spectrometer, so both positive and negative ions can be obtained from each particle (70). The time-of-flight mass spectrometer is ideally suited for pulsed laser desorption/ionization (LDI), offering the advantage of high-throughput analysis. The particles are under vacuum for less than 1 ms before analysis, and thus minimal artifacts are encountered. The advantage to using a pulsed laser is that all chemical species in each particle can be analyzed.

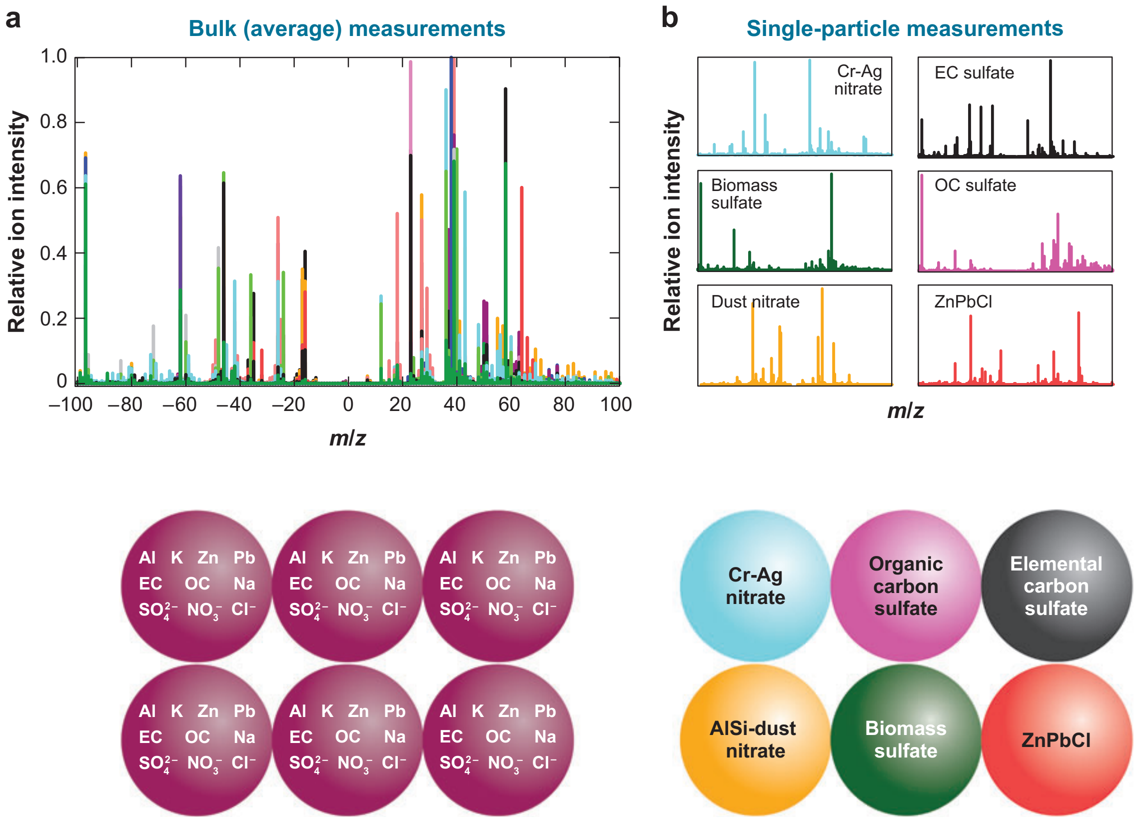

Figure 2

Comparison of mass spectra obtained using (*a*) bulk ensemble analysis versus (*b*) single-particle analysis. The interpretations of the bulk versus single-particle analyses are shown below.

Quantification is more challenging, but various groups are working on this aspect (71–76). One key to improving the quantification step involves homogenizing the LDI laser beam to reduce the shot-to-shot variability of the ion intensity between particles (77).

LDI at the proper wavelengths can produce molecular ions, but the quantification of individual organic species has not been accomplished (78). Two-step LDI shows promise; a pulsed infrared laser heats the particle and rapidly desorbs intact neutral molecules from the particles, and a second, lower-power, ultraviolet laser can ionize the desorbed gas-phase species (79). Investigators have also used extremely high-powered lasers to obtain quantitative results on total elemental composition in individual particles by ablating species from the particles and fragmenting molecules down to elemental forms (80). One recent approach involves desorption with a laser followed by the introduction of low-energy photoelectrons that attach to the desorbed neutrals (81). The Johnston group (82) has shown that vacuum UV photoionization can be used for soft ionization and the characterization of organic species in aerosols.

Details on the surface chemistry and structure of single particles are critical to understanding their reactivity, optical properties, and water uptake potential (83–85). Off-line analysis by time-of-flight secondary ion mass spectrometry has been used to study hydrophobic compounds on the surfaces of atmospheric particles (86). Baer and coworkers (87) demonstrated in laboratory studies that one can study the surface versus core chemistry of individual particles using two-step LDI.

Single-particle mass spectrometers are a relatively new approach for determining the major sources of atmospheric pollution (88, 89). One can use the mass spectral fingerprints (**Figure 2*b***) to identify and determine the relative fractions of particles from different sources (89, 90). Using a combination of unique gas-phase tracers coupled with unique single-particle MS signatures, Guazzotti et al. (91) showed that biomass/biofuel emissions were the most abundant aerosol particle type in the region in shipboard measurements during the Indian Ocean Experiment.

Some promising recent advances in single-particle MS studies couple the instrument with other measurements. Researchers are now using information on particle volatility, hygroscopicity, density, and optical properties to obtain linked chemical-optical or chemical-physical information on individual particles (92–96).

Mineral dust aerosol: soil particles primarily from desert or semiarid regions mobilized by wind currents and entrained in the atmosphere

2.5. Case Study: ACE-Asia

Advances in analytical techniques for aerosol analysis pave the way for a greater understanding of atmospheric aerosols through both field and laboratory studies. However, a complete understanding will only be achieved upon integration of these studies with modeling efforts. Below, we discuss important results and remaining issues that have emerged via integrated efforts during ACE-Asia.

2.5.1. Field studies. Heard (97) reviewed measurements, techniques, and locations for a number of major field campaigns. ACE-Asia represents an excellent example of an intensive field study aimed at quantifying the spatial and vertical distributions of aerosol concentrations, processes controlling aerosol formation and evolution, and the radiative impacts of aerosols in spring 2001. Over 250 publications describe results from this campaign, reflecting how a combination of laboratory, field, and modeling efforts can help unravel the contributions of aerosols to climate change. Three aircraft, two research ships, a lidar network, and many surface sites measured Asian aerosols during the spring dust storm season. A wide range of aerosol models (including microphysical, radiative transfer, chemical transport models, and global climate models) was used to assess how Asian aerosols are influencing pollution and climate in this region. Satellite data provided a larger scale view of the radiative impacts of aerosols over the region under different air mass conditions (98). One major facet of ACE-Asia involved studying the impact of large Asian dust plumes lofted into the free troposphere by dust storms emanating from the desert regions. Mineral dust aerosol represents an important component of the Earth's system that links land, air, and oceans in a unique way, and although it is a naturally occurring aerosol, anthropogenic activities clearly influence the effects of dust in the atmosphere (99). For example, dust serves as a major sink for trace gases in the atmosphere by providing a large surface area upon which heterogeneous chemistry can occur (100).

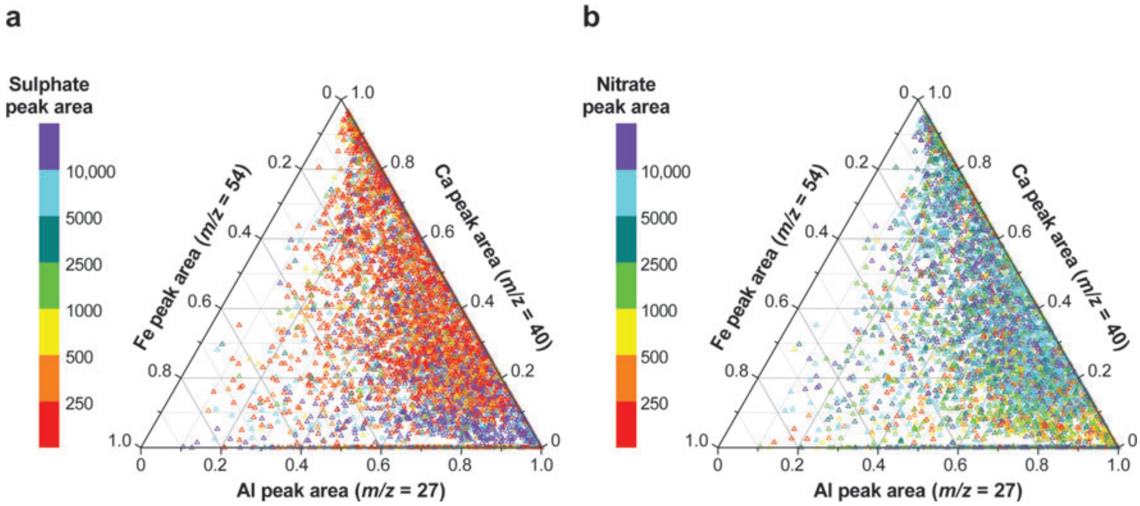

Figure 3

The relative distribution of peak areas for three major mineral dust components sampled during ACE-Asia (Fe, Ca, and Al) mixed with secondary acids (6). Copyright 2007. Reproduced with permission. The same dust particles are displayed in both panels with the symbol color corresponding to (*a*) the sulfate absolute peak area and (*b*) the nitrate absolute peak area. This figure shows that AlSi dust particles have a higher abundance of sulfate, whereas Ca dust particles contain more nitrate.

Arimoto and coworkers' (101) review presents an overview of the findings on the impacts of dust on tropospheric chemistry during ACE-Asia. A unique finding from aerosol time-of-flight mass spectrometry (ATOFMS) measurements made onboard the R/V Ronald H. Brown during ACE-Asia was that, when large amounts of sulfate and nitrate were present, they tended to segregate and partition to dust particles with differing mineralogy (6). The ternary plots in **Figure 3** demonstrate this, displaying the relative ATOFMS single-particle mass spectral ion signals from three major dust mineral components: Al, Ca, and Fe. **Figure 3** shows dramatically different mixing behavior for nitrate versus sulfate and reflects the segregation of nitrate from sulfate in dust particles. The sulfate-rich dust particles lie predominantly near the Al vertex, indicating an association with AlSi dust particles. The nitrate dust particles are mostly located toward the Ca vertex and thus are most likely associated with calcite-rich dust. Notably, this field observation confirmed predictions based on carefully controlled laboratory studies (102). In light of this example, we note that current models treat dust as a single entity that reacts with species such as sulfate and nitrate with one rate constant. Including more kinetic rate data for heterogeneous reactions on dust of differing mineralogy is one specific area in which models can be significantly improved.

ATOFMS: aerosol time-of-flight mass spectrometer

Another interesting observation during ACE-Asia occurred upon the arrival of the dust front: Prior to the dust front, high amounts of nitrate were observed on sea salt particles. When the dust front descended into the boundary layer and mixed with the ground-level pollution, nitrate suddenly shifted from being associated with sea salt to the dust particles (103, 104). This rapid change could result from a variety of factors, including available surface area, the arrival of a new air mass, or the fact that dust reacts faster with NO_y precursors than sea salt. To sort out the possible factors leading to these significant changes, we have begun to design and perform laboratory experiments focusing on heterogeneous chemistry processes observed during ACE-Asia. Ultimately the findings from these laboratory studies will be used as inputs for chemical transport models.

Relative humidity (RH): expressed as a percent, the ratio of the amount of water in air relative to its saturation concentration at a given temperature

2.5.2. Laboratory studies of dust. Laboratory studies of mineral dust typically focus on the common components, including clay, carbonate, and oxide minerals, and therefore can address important issues with respect to dust mineralogy. Recent reviews on heterogeneous reactions of mineral dust describe how the mechanisms for the reaction chemistry of mineral aerosol need to be better understood (105, 106). One important consideration is the need for laboratory studies measuring heterogeneous reaction kinetics of mineral dust as a function of relative humidity (RH). For example, several studies have shown that adsorbed water, which increases as a function of RH, can play an important role in the heterogeneous reactions of nitric acid on Arizona test dust (107), a complex, well-characterized dust mixture; montmorillonite (108), a swellable clay mineral; and calcite (109), a reactive component of mineral dust. Furthermore, laboratory studies analyzing the uptake of other trace gases (such as HCl, CO_2, and SO_2) have also shown that adsorbed water can significantly increase the uptake of these gases on major mineral components (110).

Recently, in addition to the role adsorbed water plays in the heterogeneous chemistry of mineral aerosols, laboratory studies have begun to explore water adsorption over the full dynamic range, including water uptake and hygroscopicity under subsaturated conditions and CCN activity under supersaturated conditions. **Figure 4** shows a schematic of a multianalysis aerosol reaction system developed at the University of Iowa for studying CCN activation and water uptake (111, 112). This instrument has the capability of measuring CCN activity and hygroscopic growth of size-selected aerosol, as well as heterogeneous processing and aerosol infrared extinction over a range of RH values. For example, $CaCO_3$ is highly reactive and can be converted to $Ca(NO_3)_2$ upon heterogeneous reaction with gas-phase HNO_3. The $Ca(NO_3)_2$ reaction product is more soluble and thus takes up significantly more water than the unprocessed $CaCO_3$ aerosol. **Figure 4*c*** shows the hygroscopic growth curves for 100-nm size-selected $CaCO_3$ and the reaction products with HNO_3, $Ca(NO_3)_2$. The CCN activity of $Ca(NO_3)_2$ is significantly greater than that of $CaCO_3$ and is comparable with common CCN such as ammonium sulfate (**Figure 4*d***).

Many recent surface characterization studies have begun to investigate the speciation of adsorbed products on the surfaces of processed mineral aerosol using techniques such as X-ray photoelectron spectroscopy (113, 114). However, more studies are needed to work out details of surface speciation and the role of adsorbed water in the heterogeneous mechanism of atmospheric gas uptake on mineral aerosol.

2.5.3. Model-laboratory-field comparisons. Model analysis was also an important component of the ACE-Asia campaign, both from a forecasting perspective during the

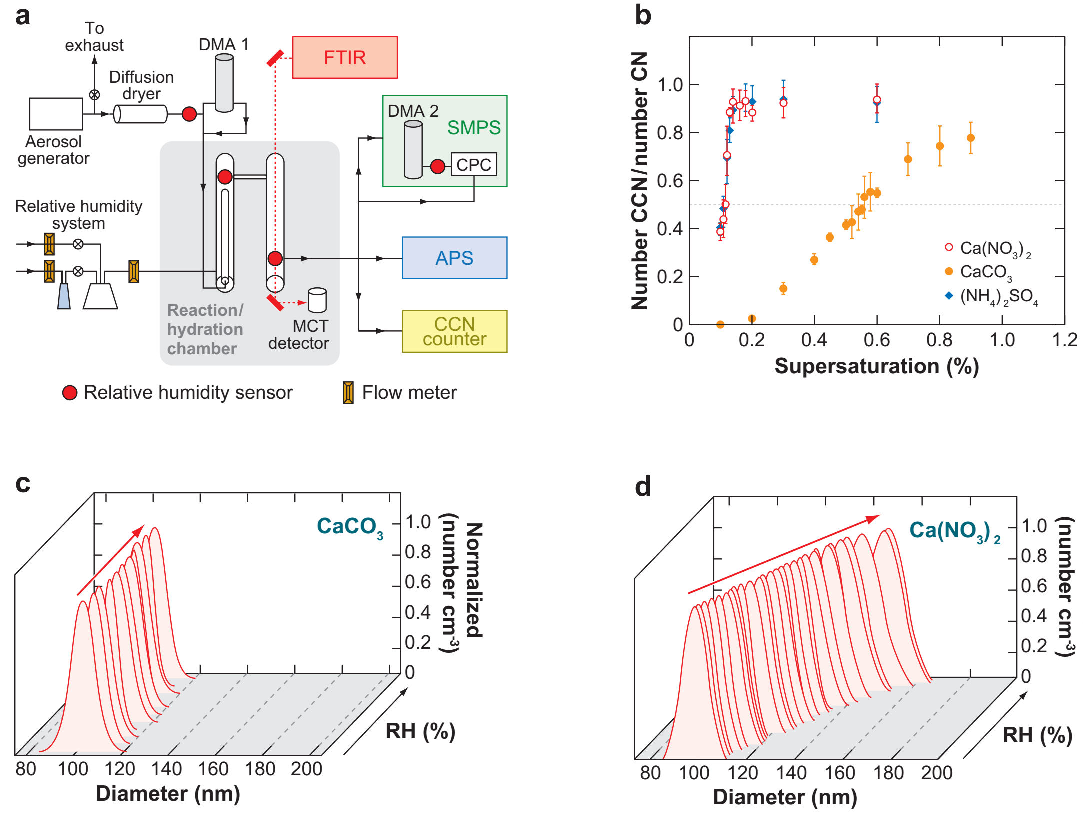

Figure 4

(*a*) A schematic of a laboratory apparatus that measures hygroscopic growth and cloud condensation nuclei (CCN) activity of aerosols representative of mineral dust ($CaCO_3$) and reacted mineral dust [$Ca(NO_3)_2$], as well as the infrared extinction spectra and size distributions of aerosols. $Ca(NO_3)_2$ forms as a result of heterogeneous reactions of $CaCO_3$ with nitrogen oxides in the atmosphere (111). Copyright 2006, American Chemical Society. Reproduced with permission. (*b*) CCN activity plotted as a function of nuclei that are CCN active versus the total number of condensation nuclei as a function of percent supersaturation (112). Copyright 2006, American Geophysical Union. Reproduced with permission. Hygroscopic growth data comparing (*c*) 100-nm $CaCO_3$ (111, 112) and (*d*) 100-nm $Ca(NO_3)_2$ particles (111, 112). Panels *c* and *d* reproduced with permission. Copyright 2006, American Chemical Society; copyright 2006, American Geophysical Union. Abbreviations: APS, aerodynamic particle sizer; CPC, condensation particle counter; FTIR, Fourier transform infrared spectrometer; MCT, mercury cadmium telluride; RH, relative humidity; SMPS, scanning mobility particle sizer.

study and as a tool for understanding observations made during the study. ACE-Asia provided an opportunity to compare the model predictions with atmospheric measurements. **Figure 5** illustrates results from the three-dimensional global sulfur transport and deposition model used to predict the influence of heterogeneous chemistry on some important chemical species, including O_3, NO_2, SO_2, and HNO_3 (115). Each

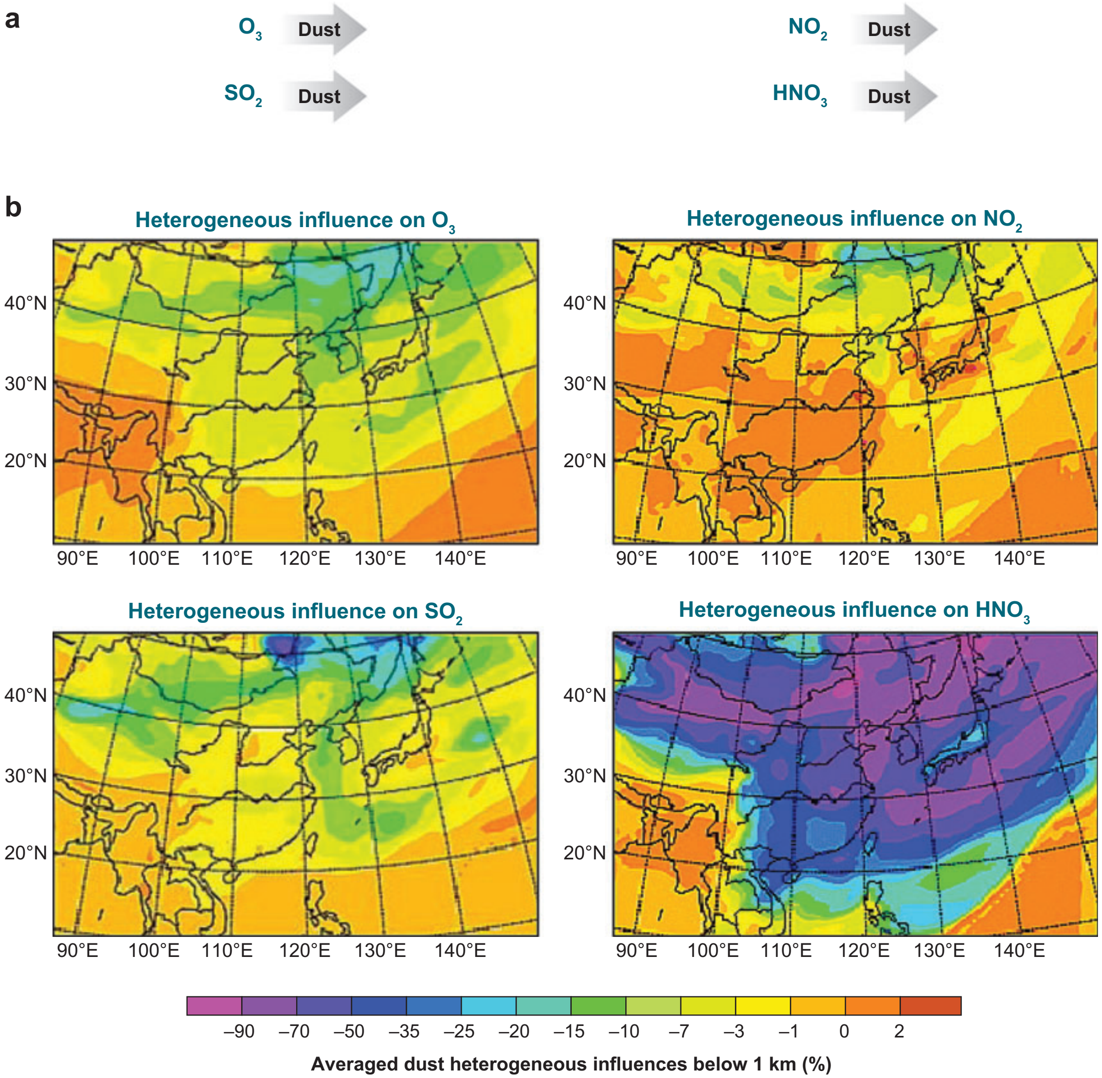

Figure 5

(*a*) The four heterogeneous reactions on mineral dust used by Tang et al. to model dust aerosol chemistry. (*b*) Contour plots showing averaged influences on O_3, NO_2, SO_2, and HNO_3 concentrations due to heterogeneous chemistry on mineral dust aerosol below 1 km (115). Panel *b* reproduced with the permission of the American Geophysical Union. Copyright 2004.

plot represents differences between the gas-phase concentrations of two model runs, one that includes four important heterogeneous reactions on mineral dust and another that includes only gas-phase reactions. The resulting contour plots show that heterogeneous reactions decrease the gas-phase composition of all these species. The greatest influence is on HNO_3 concentrations, which decrease by 90% in some regions.

Finally, new insights were acquired into the partitioning of chloride on atmospheric particles during ACE-Asia. Currently, chloride on filters is used to calculate the amount of unreacted sea salt present in the atmosphere. However, during ACE-Asia a new real-time observation showing the uptake of HCl released from sea salt by dust was measured using single-particle MS (116). This resulted in substantial amounts of Cl on dust rather than sea salt. Model predictions compared with the observations showed poor agreement. Thus, this heterogeneous process is now being studied in the laboratory to obtain kinetic information, which will be added to the model. This example demonstrates how investigators can use field observations, coupled with chemical models, to design laboratory studies to better understand such processes.

The modeling used during ACE-Asia represents a major effort to understand the role of heterogeneous reactions on mineral aerosol, but only four heterogeneous reactions were studied in the model. The incorporation of other species along with the effects of RH and dust composition will significantly improve these efforts in the future. In atmospheric chemistry models, heterogeneous chemistry needs to be treated in a more complex manner if the chemical composition of Earth's atmosphere is to be understood. Ideally, this understanding needs to be at a level that allows models to be used in a predictive fashion for various possible scenarios involving projected future anthropogenic activities and the consequences of these activities.

3. KEY ISSUES AND MEASUREMENT NEEDS

3.1. Marine Aerosols, Oceanic Productivity, and Clouds

As the ocean represents ∼70% of Earth's surface, we need a better understanding of marine aerosol-cloud-climate interactions (117). A strong link exists between the chemical and biological processes in the ocean and the chemistry of the atmosphere above the ocean (118, 119). Thus, field studies focusing on marine environments are vital to furthering our understanding of marine aerosol production and cloud formation.

3.2. Organic Speciation

In the past few years, multidimensional gas chromatography has shown that tens of thousands of different organic species exist in aerosols collected in a single air mass (120). Thus, new methods emphasizing the speciation of organic aerosol are needed. Recent breakthroughs in the areas of near-edge X-ray absorption fine structure spectroscopy, Fourier transform infrared mapping, chemical ionization mass spectrometry, and high-resolution MS are shedding new light on the complexity of the organic fraction of aerosols (121, 122). After identifying a larger fraction of the organics in aerosols, the next step will involve quantifying the actual amounts of these species and better understanding their heterogeneity in particles using real-time measurements. Also, measurements are needed of the interactions between water and organic and mixed organic/inorganic/aqueous particles and the impact of phase changes, hygroscopic growth, cloud activation, and ice nucleation.

3.3. Understanding Cloud Formation and Reducing Uncertainties in the Indirect Effect

CCN formation is an area in which there is a significant disconnect between laboratory findings and field observations (123, 124). Making simplistic aerosols in the laboratory with one or two components has provided a better understanding of the fundamental properties that lead to more effective CCN. Direct measurements of the size-resolved single-particle mixing state of the actual cloud nuclei will improve our understanding of atmospheric CCN (125). For example, recent single-particle MS field measurements yielded new insight into how atmospheric aging affects the number of CCN formed in marine environments (126). Single-particle MS has also been employed to measure the chemistry of individual ice nuclei (95). Currently, it is believed that insoluble materials such as dust and soot play the largest role in ice nucleation (127–129). However, this has been difficult to test in field studies owing to the extremely low number concentrations of ice nuclei that are present. Future aircraft flights will focus on making further direct measurements of the chemistry of ice nuclei (130).

3.4. Linking Size-Resolved Mixing State with Optical Properties

Many field studies have investigated how chemical composition and size influence the radiative forcing in a particular region (10, 131–133). Most commonly, researchers measure particle size, optical properties, and chemistry using three separate techniques. Ideally, coupled size-shape-chemical-optical measurements would be made on the same individual particles. Steps have been taken in this direction in single-particle MS (92, 96). The ultimate measurement involves multiangle light-scattering measurements on the same individual particle, the power of which has been demonstrated for particles of known composition (134). Such direct measurements of the optical properties of a specific mixing state and size of real atmospheric aerosols are required as model inputs to reduce the uncertainties associated with regional and global radiative forcing on climate, as detailed in the recent Intergovernmental Panel on Climate Change report (135). Also, aerosols show strong vertical variability with multiple layers often observed; this vertical structure strongly impacts the overall amount of radiative forcing. To account for this, it is critical that we have a better understanding of how particle chemical mixing state varies as a function of altitude in different regions.

3.5. Nanoparticle Characterization

Particle formation via nucleation occurs in the smallest sized particles ($<$10 nm) on very rapid timescales. The processes involved in nucleation in urban environments are still under debate. Furthermore, with increased interest in the environmental health and safety, including toxicity, of engineered nanoparticles (136), investigators are developing methods that can measure the chemistry of single particles in the 10-nm size range (136, 137). The high sensitivity of MS allows one to detect the contents of an individual particle down to the sub-10-nm size range. However, particles this small cannot be detected using standard optical detection methods, which rely on the particle being larger than ∼80 nm. One could condense water on the particles to grow them to a detectable size range and measure their chemistry via single-particle MS (138). However, charged aerosol detection has been developed as an alternative approach for detecting smaller particles than optical detection allows; it is being used as a universal detector in high-performance liquid chromatography analysis (139).

3.6. Miniaturization of Aerosol Chemistry Instruments

The size of the sampling platform has become very small, with the recent demonstration of using unmanned aerial vehicles to study aerosol-cloud interactions in the Indo-Asian region (140). This study did not obtain aerosol chemical information, but this may be possible in future missions. Time-of-flight mass spectrometers as small as 3 inches are now available (141). Optical spectroscopy techniques do not require pumping systems, and thus single-particle analysis using laser-induced breakdown spectroscopy may be able to meet smaller payload requirements. As is always the case, trade-offs exist between size and performance, but having some chemical information will be a major advance in studies of the spatial variability of aerosols on larger scales.

3.7. Determining the Factors Controlling Gas-Particle Partitioning of Real Atmospheric Aerosols

We need a better understanding of how the seed chemistry of a particle affects the partitioning and reactivity of aerosols (142). A number of recent studies have shown that far more species are associated with the particle phase than predicted from standard models (143). The acidity of the seed has been shown to affect the amount of species partitioned from the gas to particle phase and more recently to induce oligomerization in the particles (21, 143, 144). Because particles are highly concentrated and thus nonideal solutions, the behavior at the surface cannot be approximated, assuming no chemical interactions occur. Techniques that probe interfacial chemistry and interactions and rapid processes occurring at the molecular scale are required (145, 146). Also, we need a better understanding of how chemical mixing state influences the distribution of condensing SOA species.

3.8. Bioaerosols

There is a great deal of interest in the public health issues associated with bioaerosols, which include pollen, viruses, bacteria, and proteins. Issues range from understanding the spread of emerging infectious diseases to concerns over bioterrorism. Conventional analytical methods used for these aerosols include microscopy, protein staining, and microorganism cultivation. However, molecular-based studies have just recently begun and have the potential to provide mechanistic information on the immune response of these reactions (147). Recently, investigators used a single-particle mass spectrometer based on the ATOFMS design for the on-line analysis of single bioaerosols (148). Additionally, bioaerosols are known to undergo nitration when proteins are exposed to parts-per-billion levels of nitrogen dioxide (149). Such heterogeneous reactions may be important triggers for adverse immune reactions, such as allergies and asthma, in humans. However, little is known regarding the effects of the interaction of pollution and bioaerosols. Thus, this remains a largely unexplored area and should be considered in future field measurements and laboratory studies.

4. SUMMARY

As the field of atmospheric analysis moves forward, it is clear that atmospheric aerosols need to be better understood. Over the past decade, there has been a tremendous amount of growth in the number of analytical measurement techniques being developed to measure atmospheric aerosols. These advances are just beginning to unravel the complexity of atmospheric aerosols. Additional instruments that make rapid, real-time measurements of particle interfaces, as well as probe particle heterogeneity and phase, are needed to understand the processes contributing to aerosol formation in the atmosphere. Accurate information will ultimately allow for models to better understand and predict atmospheric aerosol composition and, in turn, to understand the impact these aerosols have on our climate on regional and global scales. In this review, we have highlighted the critical need for synergism between laboratory studies, field measurements, and modeling analysis to achieve the next level of understanding of atmospheric aerosols. Such a combined effort will put us in a much better position for developing sound environmental policies that protect our planet as we move into the future.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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LITERATURE CITED

1. Andreae MO, Crutzen PJ. 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. *Science* 276:1052–58

2. Poschl U. 2005. Atmospheric aerosols: composition, transformation, climate and health effects. *Angew. Chem. Int. Ed. Engl.* 44:7520–40
3. Seinfeld JH. 2004. Air pollution: a half century of progress. *AIChE J.* 50:1096–108
4. Clemitshaw KC. 2004. A review of instrumentation and measurement techniques for ground-based and airborne field studies of gas-phase tropospheric chemistry. *Crit. Rev. Environ. Sci. Technol.* 34:1–108
5. Noble CA, Prather KA. 1996. Real-time measurement of correlated size and composition profiles of individual atmospheric aerosol particles. *Environ. Sci. Technol.* 30:2667–80
6. Sullivan RC, Guazzotti SA, Sodeman DA, Prather KA. 2007. Direct observations of the atmospheric processing of Asian mineral dust. *Atmos. Chem. Phys.* 7:1213–36
7. Gard EE, Kleeman MJ, Gross DS, Hughes LS, Allen JO, et al. 1998. Direct observation of heterogeneous chemistry in the atmosphere. *Science* 279:1184–87
8. Bauer SE, Balkanski Y, Schulz M, Hauglustaine DA, Dentener F. 2004. Global modeling of heterogeneous chemistry on mineral aerosol surfaces: influence on tropospheric ozone chemistry and comparison to observations. *J. Geophys. Res. Atmos.* 109:D02304. DOI:10.1029/2003JD003868
9. Dentener FJ, Carmichael GR, Zhang Y, Lelieveld J, Crutzen PJ. 1996. Role of mineral aerosol as a reactive surface in the global troposphere. *J. Geophys. Res. Atmos.* 101:22869–89
10. Quinn PK, Bates TS. 2003. North American, Asian, and Indian haze: similar regional impacts on climate? *Geophys. Res. Lett.* 30:1555. DOI:10.1029/2003GL016934
11. **Stier P, Seinfeld JH, Kinne S, Boucher O. 2007. Aerosol absorption and radiative forcing. *Atmos. Chem. Phys. Discuss.* 7:7171–233**

11. An excellent overview of modeling the direct effect of aerosols and assumptions regarding mixing state.

12. Cainey JM, Keywood M, Grose MR, Krummel P, Galbally IE, et al. 2007. Precursors to particles (P2P) at Cape Grim 2006: campaign overview. *Environ. Chem.* 4:143–50
13. Sullivan RC, Prather KA. 2005. Recent advances in our understanding of atmospheric chemistry and climate made possible by on-line aerosol analysis instrumentation. *Anal. Chem.* 77:3861–85
14. Ma Y, Weber RJ, Maxwell-Meier K, Orsini DA, Lee YN, et al. 2004. Intercomparisons of airborne measurements of aerosol ionic chemical composition during TRACE-P and ACE-Asia. *J. Geophys. Res. Atmos.* 109:D15S06. DOI:10.1029/2003JD003673
15. Middlebrook AM, Murphy DM, Lee SH, Thomson DS, Prather KA, et al. 2003. A comparison of particle mass spectrometers during the 1999 Atlanta Supersite project. *J. Geophys. Res. Atmos.* 108:8424. DOI:10.1029/2001JD000660
16. **McMurry PH. 2000. A review of atmospheric aerosol measurements. *Atmos. Environ.* 34:1959–99**

16. Excellent review of analytical measurements of aerosol properties.

17. Llamas AM, Ojeda CB, Rojas FS. 2007. Process analytical chemistry—application of mass spectrometry in environmental analysis: an overview. *Appl. Spectrosc. Rev.* 42:345–67

19. Thorough review of organic aerosol with a focus on SOA and its importance for global climate modeling, including highlights of areas that need further study.

18. Fuzzi S, Andreae MO, Huebert BJ, Kulmala M, Bond TC, et al. 2006. Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change. *Atmos. Chem. Phys.* 6:2017–38
19. **Kanakidou M, Seinfeld JH, Pandis SN, Barnes I, Dentener FJ, et al. 2005. Organic aerosol and global climate modeling: a review. *Atmos. Chem. Phys.* 5:1053–123**
20. Claeys M, Graham B, Vas G, Wang W, Vermeylen R, et al. 2004. Formation of secondary organic aerosols through photooxidation of isoprene. *Science* 303:1173–76
21. Denkenberger K, Moffet RC, Holececk J, Rebotier TP, Prather KA. 2007. Real-time, single-particle measurements of oligomers in aged ambient aerosol particles. *Environ. Sci. Technol.* 41:5439–46
22. Grosse S, Letzel T. 2007. Liquid chromatography/atmospheric pressure ionization mass spectrometry with postcolumn liquid mixing for the efficient determination of partially oxidized polycyclic aromatic hydrocarbons. *J. Chromatogr. A* 1139:75–83
23. Muller C, Iinuma Y, Boge O, Herrmann H. 2007. Applications of CE-ESI-MS/MS analysis to structural elucidation of methylenecyclohexane ozonolysis products in the particle phase. *Electrophoresis* 28:1364–70
24. Poulain L, Monod A, Wortham H. 2007. Development of a new on-line mass spectrometer to study the reactivity of soluble organic compounds in the aqueous phase under tropospheric conditions: application to OH-oxidation of *N*-methylpyrrolidone. *J. Photochem. Photobiol. A Chem.* 187:10–23
25. Sullivan AP, Weber RJ, Clements AL, Turner JR, Bae MS, et al. 2004. A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: results from an urban site. *Geophys. Res. Lett.* 31:L13105. DOI:10.1029/2004GL019681
26. Ullah SMR, Takeuchi M, Dasgupta PK. 2006. Versatile gas/particle ion chromatograph. *Environ. Sci. Technol.* 40:962–68
27. Gross DS, Galli ME, Kalberer M, Prevot ASH, Dommen J, et al. 2006. Real-time measurement of oligomeric species in secondary organic aerosol with the aerosol time-of-flight mass spectrometer. *Anal. Chem.* 78:2130–37
28. Kalberer M, Paulsen D, Sax M, Steinbacher M, Dommen J, et al. 2004. Identification of polymers as major components of atmospheric organic aerosols. *Science* 303:1659–62
29. Baltensperger U, Kalberer M, Dommen J, Paulsen D, Alfarra MR, et al. 2005. Secondary organic aerosols from anthropogenic and biogenic precursors. *Faraday Discuss.* 130:265–78
30. Graber ER, Rudich Y. 2006. Atmospheric HULIS: How humic-like are they? A comprehensive and critical review. *Atmos. Chem. Phys.* 6:729–53
31. Hinz KP, Spengler B. 2007. Instrumentation, data evaluation and quantification in on-line aerosol mass spectrometry. *J. Mass Spectrom.* 42:843–60
32. Smith JN, Moore KF, Eisele FL, Voisin D, Ghimire AK, et al. 2005. Chemical composition of atmospheric nanoparticles during nucleation events in Atlanta. *J. Geophys. Res. Atmos.* 110:D22S03. DOI:10.1029/2005JD005912

33. Hearn JD, Smith GD. 2006. Reactions and mass spectra of complex particles using aerosol CIMS. *Int. J. Mass Spectrom.* 258:95–103
34. DeCarlo PF, Kimmel JR, Trimborn A, Northway MJ, Jayne JT, et al. 2006. Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.* 78:8281–89
35. Canagaratna MR, Jayne JT, Jimenez JL, Allan JD, Alfarra MR, et al. 2007. Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrom. Rev.* 26:185–222
36. Kondo Y, Miyazaki Y, Takegawa N, Miyakawa T, Weber RJ, et al. 2007. Oxygenated and water-soluble organic aerosols in Tokyo. *J. Geophys. Res. Atmos.* 112:D01203. DOI:10.1029/2006JD007056
37. Volkamer R, Jimenez JL, San Martini F, Dzepina K, Zhang Q, et al. 2006. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. *Geophys. Res. Lett.* 33:L17811. DOI:10.1029/2006GL026899
38. Williams BJ, Goldstein AH, Millet DB, Holzinger R, Kreisberg NM, et al. 2007. Chemical speciation of organic aerosol during the International Consortium for Atmospheric Research on Transport and Transformation 2004: results from in situ measurements. *J. Geophys. Res. Atmos.* 112:D10S26. DOI:10.1029/2006JD007601
39. Hopkins RJ, Tivanski AV, Marten BD, Gilles MK. 2007. Chemical bonding and structure of black carbon reference materials and individual carbonaceous atmospheric aerosols. *J. Aerosol Sci.* 38:573–91
40. Tivanski AV, Hopkins RJ, Tyliszczak T, Gilles MK. 2007. Oxygenated interface on biomass burn tar balls determined by single particle scanning transmission X-ray microscopy. *J. Phys. Chem. A* 111:5448–58
41. Kirchstetter TW, Novakov T. 2007. Controlled generation of black carbon particles from a diffusion flame and applications in evaluating black carbon measurement methods. *Atmos. Environ.* 41:1874–88
42. Chughtai AR, Kim JM, Smith DM. 2002. The effect of air/fuel ratio on properties and reactivity of combustion soots. *J. Atmos. Chem.* 43:21–43
43. Mochida M, Kawamura K. 2004. Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles. *J. Geophys. Res. Atmos.* 109:D21202. DOI:10.1029/2004JD004962
44. Hedberg E, Johansson C. 2006. Is levoglucosan a suitable quantitative tracer for wood burning? Comparison with receptor modeling on trace elements in Lycksele, Sweden. *J. Air Waste Manag. Assoc.* 56:1669–78
45. Havers N, Burba P, Lambert J, Klockow D. 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. *J. Atmos. Chem.* 29:45–54
46. Rudich Y, Donahue NM, Mentel TF. 2007. Aging of organic aerosol: bridging the gap between laboratory and field studies. *Annu. Rev. Phys. Chem.* 58:321–52
47. Roberts G, Mauger G, Hadley O, Ramanathan V. 2006. North American and Asian aerosols over the eastern Pacific ocean and their role in regulating cloud condensation nuclei. *J. Geophys. Res. Atmos.* 111:D13205. DOI:10.1029/2005JD006661

48. Petters MD, Kreidenweis SM. 2007. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos. Chem. Phys.* 7:1961–71
49. Donahue NM, Hartz KEH, Chuong B, Presto AA, Stanier CO, et al. 2005. Critical factors determining the variation in SOA yields from terpene ozonolysis: a combined experimental and computational study. *Faraday Discuss.* 130:295–309
50. Zhang JY, Hartz KEH, Pandis SN, Donahue NM. 2006. Secondary organic aerosol formation from limonene ozonolysis: homogeneous and heterogeneous influences as a function of NOx. *J. Phys. Chem. A* 110:11053–63
51. Surratt JD, Murphy SM, Kroll JH, Ng NL, Hildebrandt L, et al. 2006. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. *J. Phys. Chem. A* 110:9665–90
52. Weitkamp EA, Sage AM, Pierce JR, Donahue NM, Robinson AL. 2007. Organic aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber. *Environ. Sci. Technol.* 41:6969–75
53. Prenni AJ, Petters MD, Kreidenweis SM, DeMott PJ, Ziemann PJ. 2007. Cloud droplet activation of secondary organic aerosol. *J. Geophys. Res. Atmos.* 112:D10223. DOI:10.1029/2006JD007963
54. Chung SH, Seinfeld JH. 2005. Climate response of direct radiative forcing of anthropogenic black carbon. *J. Geophys. Res. Atmos.* 110:D11102. DOI:10.1029/2004JD005441
55. Stier P, Seinfeld JH, Kinne S, Feichter J, Boucher O. 2006. Impact of nonabsorbing anthropogenic aerosols on clear-sky atmospheric absorption. *J. Geophys. Res. Atmos.* 111:D18201. DOI:10.1029/2006JD007147
56. Bond TC, Bergstrom RW. 2006. Light absorption by carbonaceous particles: an investigative review. *Aerosol Sci. Technol.* 40:27–67
57. Bond TC, Habib G, Bergstrom RW. 2006. Limitations in the enhancement of visible light absorption due to mixing state. *J. Geophys. Res. Atmos.* 111:D20211. DOI:10.1029/2006JD007315
58. Jacobson MZ. 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature* 409:695–97
59. Jacobson MZ. 2000. A physically-based treatment of elemental carbon optics: implications for global direct forcing of aerosols. *Geophys. Res. Lett.* 27:217–20. DOI:10.1029/1999GL010968
60. Chylek P, Videen G, Ngo D, Pinnick RG, Klett JD. 1995. Effect of black carbon on the optical properties and climate forcing of sulfate AEROSOLS. *J. Geophys. Res. Atmos.* 100:16325–32
61. Cheng YF, Eichler H, Wiedensohler A, Heintzenberg J, Zhang YH, et al. 2006. Mixing state of elemental carbon and non-light-absorbing aerosol components derived from in situ particle optical properties at Xinken in Pearl River Delta of China. *J. Geophys. Res. Atmos.* 111:D20204. DOI:10.1029/2005JD006929
62. Chandra S, Satheesh SK, Srinivasan J. 2004. Can the state of mixing of black carbon aerosols explain the mystery of 'excess' atmospheric absorption? *Geophys. Res. Lett.* 31:L19109. DOI:10.1029/2004GL020662

63. Lithgow GA, Robinson AL, Buckley SG. 2004. Ambient measurements of metal-containing PM2.5 in an urban environment using laser-induced breakdown spectroscopy. *Atmos. Environ.* 38:3319–28

64. Laskin A, Cowin JP, Iedema MJ. 2006. Analysis of individual environmental particles using modern methods of electron microscopy and X-ray microanalysis. *J. Electron Spectrosc. Relat. Phenom.* 150:260–74

65. Posfai M, Gelencser A, Simonics R, Arato K, Li J, et al. 2004. Atmospheric tar balls: particles from biomass and biofuel burning. *J. Geophys. Res. Atmos.* 109:D06213. DOI:10.1029/2003JD004169

66. Ma CJ, Choi KC. 2007. A combination of bulk and single particle analyses for Asian dust. *Water Air Soil Pollut.* 183:3–13

67. Semeniuk TA, Wise ME, Martin ST, Russell LM, Buseck PR. 2007. Hygroscopic behavior of aerosol particles from biomass fires using environmental transmission electron microscopy. *J. Atmos. Chem.* 56:259–73

68. Murphy DM. 2007. The design of single particle laser mass spectrometers. *Mass Spectrom. Rev.* 26:150–65

69. Sinha MP, Giffin CE, Norris DD, Estes TJ, Vilker VL, et al. 1982. Particle analysis by mass spectrometry. *J. Colloid Interface Sci.* 87:140–53

70. Gard E, Mayer JE, Morrical BD, Dienes T, Fergenson DP, et al. 1997. Real-time analysis of individual atmospheric aerosol particles: design and performance of a portable ATOFMS. *Anal. Chem.* 69:4083–91

71. Fergenson DP, Song XH, Ramadan Z, Allen JO, Hughes LS, et al. 2001. Quantification of ATOFMS data by multivariate methods. *Anal. Chem.* 73:3535–41

72. Zhao WX, Hopke PK, Qin XY, Prather KA. 2005. Predicting bulk ambient aerosol compositions from ATOFMS data with ART-2a and multivariate analysis. *Anal. Chim. Acta* 549:179–87

73. Qin XY, Bhave PV, Prather KA. 2006. Comparison of two methods for obtaining quantitative mass concentrations from aerosol time-of-flight mass spectrometry measurements. *Anal. Chem.* 78:6169–78

74. Bhave PV, Allen JO, Morrical BD, Fergenson DP, Cass GR, et al. 2002. A field-based approach for determining ATOFMS instrument sensitivities to ammonium and nitrate. *Environ. Sci. Technol.* 36:4868–79

75. Spencer MT, Prather KA. 2006. Using ATOFMS to determine OC/EC mass fractions in particles. *Aerosol Sci. Technol.* 40:585–94

76. Liu DY, Prather KA, Hering SV. 2000. Variations in the size and chemical composition of nitrate-containing particles in Riverside, CA. *Aerosol Sci. Technol.* 33:71–86

77. Wenzel RJ, Prather KA. 2004. Improvements in ion signal reproducibility obtained using a homogeneous laser beam for on-line laser desorption/ionization of single particles. *Rapid Commun. Mass Spectrom.* 18:1525–33

78. Murphy DM, Cziczo DJ, Hudson PK, Thomson DS. 2007. Carbonaceous material in aerosol particles in the lower stratosphere and tropopause region. *J. Geophys. Res. Atmos.* 112:D04203. DOI:10.1029/2006JD007297

79. Morrical BD, Fergenson DP, Prather KA. 1998. Coupling two-step laser desorption/ionization with aerosol time-of-flight mass spectrometry for the analysis of individual organic particles. *J. Am. Soc. Mass Spectrom.* 9:1068–73
80. Zachariah MR, Park K, Rai A, Kittelson DB, Miller A. 2005. Quantitative single particle mass spectrometry characterization of nanoaerosol composition and reactivity. *Abstr. Pap. Am. Chem. Soc.* 230:U1532
81. LaFranchi BW, Petrucci GA. 2006. A comprehensive characterization of photoelectron resonance capture ionization aerosol mass spectrometry for the quantitative and qualitative analysis of organic particulate matter. *Int. J. Mass Spectrom.* 258:120–33
82. Oktem B, Tolocka MP, Johnston MV. 2004. On-line analysis of organic components in fine and ultrafine particles by photoionization aerosol mass spectrometry. *Anal. Chem.* 76:253–61
83. Ellison GB, Tuck AF, Vaida V. 1999. Atmospheric processing of organic aerosols. *J. Geophys. Res. Atmos.* 104:11633–41
84. Semeniuk TA, Wise ME, Martin ST, Russell LM, Buseck PR. 2007. Water uptake characteristics of individual atmospheric particles having coatings. *Atmos. Environ.* 41:6225–35
85. Thornton JA, Abbatt JPD. 2005. N_2O_5 reaction on submicron sea salt aerosol: kinetics, products, and the effect of surface active organics. *J. Phys. Chem. A* 109:10004–12
86. Tervahattu H, Juhanoja J, Vaida V, Tuck AF, Niemi JV, et al. 2005. Fatty acids on continental sulfate aerosol particles. *J. Geophys. Res. Atmos.* 110:D06207. DOI:10.1029/2004JD005400
87. Woods E, Smith GD, Miller RE, Baer T. 2002. Depth profiling of heterogeneously mixed aerosol particles using single-particle mass spectrometry. *Anal. Chem.* 74:1642–49
88. Shields LG, Suess DT, Prather KA. 2007. Determination of single particle mass spectral signatures from heavy-duty diesel vehicle emissions for $PM_{2.5}$ source apportionment. *Atmos. Environ.* 41:3841–52
89. Bhave PV, Fergenson DP, Prather KA, Cass GR. 2001. Source apportionment of fine particulate matter by clustering single-particle data: tests of receptor model accuracy. *Environ. Sci. Technol.* 35:2060–72
90. Murphy DM, Cziczo DJ, Froyd KD, Hudson PK, Matthew BM, et al. 2006. Single-particle mass spectrometry of tropospheric aerosol particles. *J. Geophys. Res. Atmos.* 111:D23S32. DOI:10.1029/2006JD007340
91. Guazzotti SA, Suess DT, Coffee KR, Quinn PK, Bates TS, et al. 2003. Characterization of carbonaceous aerosols outflow from India and Arabia: Biomass/biofuel burning and fossil fuel combustion. *J. Geophys. Res. Atmos.* 108:4485. DOI:10.1029/2002JD003277
92. Moffet RC, Prather KA. 2005. Extending ATOFMS measurements to include refractive index and density. *Anal. Chem.* 77:6535–41
93. Spencer MT, Shields LG, Prather KA. 2007. Simultaneous measurement of the effective density and chemical composition of ambient aerosol particles. *Environ. Sci. Technol.* 41:1303–9

94. Zelenyuk A, Cai Y, Chieffo L, Imre D. 2005. High precision density measurements of single particles: the density of metastable phases. *Aerosol Sci. Technol.* 39:972–86

95. Cziczo DJ, Thomson DS, Thompson TL, DeMott PJ, Murphy DM. 2006. Particle analysis by laser mass spectrometry (PALMS) studies of ice nuclei and other low number density particles. *Int. J. Mass Spectrom.* 258:21–29

96. Murphy DM, Cziczo DJ, Hudson PK, Schein ME, Thomson DS. 2004. Particle density inferred from simultaneous optical and aerodynamic diameters sorted by composition. *J. Aerosol Sci.* 35:135–39

97. Heard DE. 2006. Field measurements of atmospheric composition. In *Analytical Techniques for Atmospheric Measurement*. Oxford, UK: Blackwell, pp. 1–68

98. Kahn R, Anderson J, Anderson TL, Bates T, Brechtel F, et al. 2004. Environmental snapshots from ACE-Asia. *J. Geophys. Res. Atmos.* 109:D19S14. DOI:10.1029/2003JD004339

99. Tegen I, Fung I. 1995. Contribution to the atmospheric mineral aerosol load from land-surface modification. *J. Geophys. Res. Atmos.* 100:18707–26

100. Bian H, Zender CS. 2003. Mineral dust and global tropospheric chemistry: Relative roles of photolysis and heterogeneous uptake. *J. Geophys. Res. Atmos.* 108:4672. DOI:10.1029/2002JD003143

101. Arimoto R, Kim YJ, Kim YP, Quinn PK, Bates TS, et al. 2006. Characterization of Asian dust during ACE-Asia. *Glob. Planet. Change* 52:23–56

102. Krueger BJ, Grassian VH, Cowin JP, Laskin A. 2004. Heterogeneous chemistry of individual mineral dust particles from different dust source regions: the importance of particle mineralogy. *Atmos. Environ.* 38:6253–61

103. Bates TS, Quinn PK, Coffman DJ, Covert DS, Miller TL, et al. 2004. Marine boundary layer dust and pollutant transport associated with the passage of a frontal system over eastern Asia. *J. Geophys. Res. Atmos.* 109:D19S19. DOI:10.1029/2003JD004094

104. Tang YH, Carmichael GR, Seinfeld JH, Dabdub D, Weber RJ, et al. 2004. Three-dimensional simulations of inorganic aerosol distributions in east Asia during spring 2001. *J. Geophys. Res. Atmos.* 109:D19S23. DOI:10.1029/2003JD004201

105. Usher CR, Michel AE, Grassian VH. 2003. Reactions on mineral dust. *Chem. Rev.* 103:4883–939

106. Cwiertny DM, Young MA, Grassian VH. 2007. Heterogeneous chemistry and photochemistry of mineral dust aerosol. *Annu. Rev. Phys. Chem.* 59:27–51

107. Vlasenko A, Sjogren S, Weingartner E, Gaggeler HW, Ammann M. 2005. Generation of submicron Arizona test dust aerosol: chemical and hygroscopic properties. *Aerosol Sci. Technol.* 39:452–60

108. Mashburn CD, Frinak EK, Tolbert MA. 2006. Heterogeneous uptake of nitric acid on Na-montmorillonite clay as a function of relative humidity. *J. Geophys. Res.* 111:D15213. DOI:101029/2005JD006525

97. An excellent book chapter discussing field measurement techniques, goals, and study locations.

105. A review of heterogeneous reactions on mineral dust aerosol.

109. Gibson ER, Cain JP, Wang H, Grassian VH, Laskin A. 2008. Kinetic study of heterogeneous reaction of $CaCO_3$ particles with gaseous HNO_3 using particle-on-substrate stagnation flow reactor approach. *J. Phys. Chem. A.* 112:1561–71

110. Santschi C, Rossi MJ. 2006. Uptake of CO_2, SO_2, HNO_3 and HCl on calcite ($CaCO_3$) at 300 K: mechanism and the role of adsorbed water. *J. Phys. Chem. A* 110:6789–802

111. Gibson ER, Hudson PK, Grassian VH. 2006. Physicochemical properties of nitrate aerosols: implications for the atmosphere. *J. Phys. Chem. A* 110:11785–99

112. Gibson ER, Hudson PK, Grassian VH. 2006. Aerosol chemistry and climate: laboratory studies of the carbonate component of mineral dust and its reaction products. *Geophys. Res. Lett.* 33:L13811. DOI:10.1029/2006GL026386

113. Al-Abadleh H, Grassian VH. 2003. Oxide surfaces as environmental interfaces. *Surf. Sci. Rep.* 52:63–161

114. Baltrusaitis J, Usher CR, Grassian VH. 2007. Reactions of sulfur dioxide on calcium carbonate single crystal and particle surfaces at the adsorbed water carbonate interface. *Phys. Chem. Chem. Phys.* 9:3011–24

115. Tang Y, Carmichael GR, Kurata G, Uno I, Weber RJ, et al. 2004. Impacts of dust on regional tropospheric chemistry during the ACE-Asia experiment: a model study with observations. *J. Geophys. Res.* 109:D19S21. DOI:10.1029/2003JD003806

116. Sullivan RC, Guazzotti SA, Sodeman DA, Tang Y, Carmichael GR, et al. 2007. Mineral dust is a sink for chlorine in the marine boundary layer. *Atmos. Environ.* 41: 7166–79

117. O'Dowd CD, De Leeuw G. 2007. Marine aerosol production: a review of the current knowledge. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 365:1753–74

118. Mahowald NM, Baker AR, Bergametti G, Brooks N, Duce RA, et al. 2005. Atmospheric global dust cycle and iron inputs to the ocean. *Global Biogeochem. Cycles* 19:GB4025. DOI:10.1029/2004GB002402

119. Jickells TD, An ZS, Andersen KK, Baker AR, Bergametti G, et al. 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* 308:67–71

119. An excellent, concise summary of the current understanding of iron-containing aerosols and their roles in global biogeochemical and climate cycles.

120. Adahchour M, Beens J, Vreuls RJJ, Brinkman UAT. 2006. Recent developments in comprehensive two-dimensional gas chromatography (GC × GC) I. Introduction and instrumental set-up. *Trends Anal. Chem.* 25:438–54

121. Gilardoni S, Russell LM, Sorooshian A, Flagan RC, Seinfeld JH, et al. 2007. Regional variation of organic functional groups in aerosol particles on four US East Coast platforms during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign. *J. Geophys. Res. Atmos.* 112:D10S27. DOI:10.1029/2006JD007737

122. Reinhardt A, Emmenegger C, Gerrits B, Panse C, Dommen J, et al. 2007. Ultrahigh mass resolution and accurate mass measurements as a tool to characterize oligomers in secondary organic aerosols. *Anal. Chem.* 79:4074–82

123. Lohmann U, Quaas J, Kinne S, Feichter J. 2007. Different approaches for constraining global climate models of the anthropogenic indirect aerosol effect. *Bull. Am. Meteorol. Soc.* 88:243–49

123. Reviews the status of global models used for predicting the indirect effect and discusses how satellite measurements can be used for validation.

124. Lohmann U, Feichter J. 2005. Global indirect aerosol effects: a review. *Atmos. Chem. Phys.* 5:715–37

125. Medina J, Nenes A, Sotiropoulou REP, Cottrell LD, Ziemba LD, et al. 2007. Cloud condensation nuclei closure during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign: effects of size-resolved composition. *J. Geophys. Res. Atmos.* 112:D10S31. DOI:10.1029/2006JD007588

126. Furutani H, Prather KA. 2007. Assessment of the relative importance of atmospheric aging on CCN activity derived from field observations. *Atmos. Environ.* In press

127. Sassen K, DeMott PJ, Prospero JM, Poellot MR. 2003. Saharan dust storms and indirect aerosol effects on clouds: CRYSTAL-FACE results. *Geophys. Res. Lett.* 30:1633. DOI:10.1029/2003GL017371

128. Richardson MS, DeMott PJ, Kreidenweis SM, Cziczo DJ, Dunlea EJ, et al. 2007. Measurements of heterogeneous ice nuclei in the western United States in springtime and their relation to aerosol characteristics. *J. Geophys. Res. Atmos.* 112:D02209. DOI:10.1029/2006JD007500

129. Cantrell W, Heymsfield A. 2005. Production of ice in tropospheric clouds: a review. *Bull. Am. Meteorol. Soc.* 86:795–807

130. Heymsfield A, Stith J, Rogers D, Field P, DeMott P, et al. 2005. *The Ice in Clouds Experiment: research plan. Scientific overview document.* http://www.eol.ucar.edu/∼dcrogers/Ice-Init/ICE-SOD.pdf

131. Quinn PK, Bates TS. 2005. Regional aerosol properties: comparisons of boundary layer measurements from ACE 1, ACE 2, AEROSOLS99, INDOEX, ACE-Asia, TARFOX, and NEAQS. *J. Geophys. Res. Atmos.* 110:D14202. DOI:10.1029/2004JD004755

132. Bates TS, Anderson TL, Baynard T, Bond T, Boucher O, et al. 2006. Aerosol direct radiative effects over the northwest Atlantic, northwest Pacific and north Indian oceans: estimates based on in-situ chemical and optical measurements and chemical transport modeling. *Atmos. Chem. Phys.* 6:1657–732

133. Carrico CM, Kus P, Rood MJ, Quinn PK, Bates TS. 2003. Mixtures of pollution, dust, sea salt, and volcanic aerosol during ACE-Asia: radiative properties as a function of relative humidity. *J. Geophys. Res. Atmos.* 108:8650. DOI:10.1029/2003JD003405

134. Dick WD, Ziemann PJ, McMurry PH. 2007. Multiangle light-scattering measurements of refractive index of submicron atmospheric particles. *Aerosol Sci. Technol.* 41:549–69

135. Forster P, Ramaswamy V, Artaxo P, Berntsen T, Betts R, et al. 2007. Summary for policymakers. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. S Solomon, D Qin, M Manning, Z Chen, M Marquis, et al. Cambridge, UK: Cambridge Univ. Press, pp. 2–18

136. Smith JN, Moore KF, McMurry PH, Eisele FL. 2004. Atmospheric measurements of sub-20 nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry. *Aerosol Sci. Technol.* 38:100–10

137. Wang SY, Zordan CA, Johnston MV. 2006. Chemical characterization of individual, airborne sub-10-nm particles and molecules. *Anal. Chem.* 78:1750–54

138. Hering SV, Stolzenburg MR. 2005. A method for particle size amplification by water condensation in a laminar, thermally diffusive flow. *Aerosol Sci. Technol.* 39:428–36

139. Dixon RW, Peterson DS. 2002. Development and testing of a detection method for liquid chromatography based on aerosol charging. *Anal. Chem.* 74:2930–37

140. Ramanathan V, Ramana MV, Roberts G, Kim D, Corrigan C, et al. 2007. Warming trends in Asia amplified by brown cloud solar absorption. *Nature* 448:575–78

141. Prieto MC, Kovtoun VV, Cotter RJ. 2002. Miniaturized linear time-of-flight mass spectrometer with pulsed extraction. *J. Mass Spectrom.* 37:1158–62

142. Seinfeld JH, Pankow JF. 2003. Organic atmospheric particulate material. *Annu. Rev. Phys. Chem.* 54:121–40

143. Lee S, Kamens RM, Jang MS. 2005. Gas and particle partitioning behavior of aldehyde in the presence of diesel soot and wood smoke aerosols. *J. Atmos. Chem.* 51:223–34

144. Jang MS, Carroll B, Chandramouli B, Kamens RM. 2003. Particle growth by acid-catalyzed heterogeneous reactions of organic carbonyls on preexisting aerosols. *Environ. Sci. Technol.* 37:3828–37

145. Butler JR, Mitchem L, Hanford KL, Truel L, Reid JP. 2007. In situ comparative measurements of the properties of aerosol droplets of different chemical composition. *Faraday Discuss.* 137:1–16

146. Gilman JB, Tervahattu H, Vaida V. 2006. Interfacial properties of mixed films of long-chain organics at the air-water interface. *Atmos. Environ.* 40:6606–14

147. Despres V, Nowoisky J, Klose M, Conrad R, Andreae MO, et al. 2007. Molecular genetics and diversity of primary biogenic aerosol particles in urban, rural and high-alpine air. *Biogeosci. Discuss.* 4:349–84

148. Tobias HJ, Pitesky ME, Fergenson DP, Steele PT, Horn J, et al. 2006. Following the biochemical and morphological changes of *Bacillus atrophaeus* cells during the sporulation process using bioaerosol mass spectrometry. *J. Microbiol. Methods* 67:56–63

149. Franze T, Weller MG, Niessner R, Poschl U. 2005. Protein nitration by polluted air. *Environ. Sci. Technol.* 39:1673–78

142. An overview of the key models and equations used to predict gas/particle partitioning of organic aerosols.