

ORGANIC ATMOSPHERIC AEROSOLS: REVIEW AND STATE OF THE SCIENCE

M. C. Jacobson,¹ H.-C. Hansson,
K. J. Noone, and R. J. Charlson²
*Department of Meteorology
Stockholm University
Stockholm, Sweden*

Abstract. Atmospheric aerosol particles are known to contain organic carbon material in variable amounts, depending on their location. In some parts of the world, organic compounds make up the majority of the total suspended particle mass. This class of particulate matter is important in a wide range of geophysical and environmental problems, ranging from local issues (e.g., pollution toxicity) to the global scale (e.g., climate change). Unfortunately, the richness of organic chemistry and the highly variable physical properties associated with both natural and anthropogenic organic particles lead to great difficulties in sampling and obtaining complete chemical information on these materials. These obstacles result in an incomplete picture of a potentially significant part of atmospheric chemistry and a corre-

spondingly poor understanding of the geophysical and environmental effects of this aerosol. Given the paucity of quantitative molecular data, the purpose of this paper is not to quantitatively describe the importance of organic aerosols in environmental issues, but rather to present a basis for defining what data are needed. With this goal in mind, we begin with an overview of the major environmental issues known to be affected by organic aerosols, followed by a description of the distribution, sources, and chemical and physical properties of organic aerosols as they are currently understood. Methods used to collect and study organic aerosols are provided, followed by a list of outstanding scientific questions and suggestions for future research priorities.

1. INTRODUCTION

1.1. Overview

Particulate matter in the lower atmosphere is composed of highly water soluble inorganic salts, insoluble mineral dust, and carbonaceous material; this last fraction includes organic compounds ranging from very soluble to insoluble, plus elemental carbon. Fine particles (diameter $\leq 2.0 \mu\text{m}$) are identified as a separate component of the total aerosol because they are usually chemically different from coarse particles ($> 2 \mu\text{m}$) and have different sources, much longer atmospheric lifetimes, and very different effects. For the purposes of this paper, unless otherwise stated, "aerosol" refers to fine particulate matter, since the majority of the environmental effects of aerosols are due to material in the smallest particle sizes. The water-soluble inorganic fraction of fine-particle aerosol is mostly a mixture of various sulfate compounds [Heintzenberg, 1989; Intergovernmental Panel on Climate Change (IPCC), 1995; U.S. Environ-

mental Protection Agency (U.S. EPA), 1996]. This fraction has been studied extensively, and several models of the geographical distribution and climatic effects of this group of compounds in the aerosol have appeared [IPCC, 1995]. While somewhat less studied, the insoluble inorganic fraction has been analyzed, for example, with nuclear methods, and generally consists of metal oxides, silicates, and clay minerals derived from soil dust. Unlike the salt and soil dust fractions, the organic compounds cover a very wide range of molecular forms, solubilities, reactivities, and physical properties, which makes a complete characterization extremely difficult. The so-called "elemental" carbon (EC) aerosol has been studied extensively, but it is still not clear to what degree it is indeed elemental [graphitic, C(0)] material or high molecular weight refractory organic species or a combination of both. Consequently, there is still no complete inventory of the chemical compounds that compose the fine-particle organic aerosol from any site in the world, and there is only a limited understanding of the sources, sinks, transport, and transformation processes of these particles and their effects. Since organic compounds are usually the second most abundant component of fine aerosol after sulfates [Heintzenberg, 1989; White, 1990; U.S. EPA, 1996], our understanding of the numerous

¹Presently at Department of Laboratory Medicine, University of Washington, Seattle.

²Also at Departments of Atmospheric Sciences and Chemistry, University of Washington, Seattle.

public health, climatic, and environmental issues surrounding atmospheric aerosols remains seriously hindered without more information on this fraction.

1.2. Purposes of This Paper

This paper attempts to define the current “state of the science” regarding atmospheric carbonaceous (especially organic) aerosols. More specific goals are as follows:

One goal is to provide a survey of recent literature illustrating the current state of knowledge about organic aerosols. The intention with our literature survey is not to be completely comprehensive, but rather to be illustrative. Several comprehensive literature reviews have been produced [Hahn, 1979; Saxena and Hildemann, 1996]. The latter is particularly extensive and contains references to a large body of recent literature. We have selected references that illustrate where the limitations are in our knowledge of the composition and cycling of atmospheric organic aerosols, as well as how our knowledge base is influenced (and to a large extent defined) by the techniques that are used to sample, extract, and analyze organic aerosols.

A second goal is to describe the importance of organic aerosols to issues such as atmospheric chemistry and physics, climate, health effects, and other topics of importance. The environmental and geophysical effects of organic aerosols that are listed in the next section span disciplines ranging from civil engineering to medicine to atmospheric chemistry. A good deal of what we presently know about atmospheric organic aerosols has arisen from isolated research groups looking for specific compounds (or classes of compounds) for specific reasons, for example, carcinogenic compounds to study human health effects. In presenting a broad list of the reasons one would study organic aerosols, we hope to show that obtaining a more complete chemical characterization of organic aerosols would benefit a wide range of disciplines. Cross-discipline awareness may also lead to more comprehensive approaches in this characterization and therefore a greater understanding the cycling of organic compounds in the atmospheric aerosol.

A third goal is to explore how the sampling, extraction, and analysis techniques currently in use influence what we know about atmospheric organic aerosols. Perhaps to a larger extent than for any other component of the atmospheric aerosol, what we find in the organic fraction is to a large extent determined by how we look. Different types of compounds have widely different properties and require very different sampling, extraction, and analysis techniques to be used for the compounds to be detected. Another limitation is that most of the analysis techniques need a certain minimum amount (mass) of a particular compound in a sample, which often necessitates sampling times longer than typical residence times for aerosol particles. The limitations of the analytical methods used up to now have in some cases stagnated forward movement in research by plac-

ing emphasis only on molecular forms that are easily measured.

A fourth goal is to determine the important gaps in our knowledge of atmospheric organic aerosols to suggest future avenues of research. We begin with a “big picture” perspective, taking into consideration many of the environmental effects listed below simultaneously in order to identify the topics or questions we first need to make advances. We have accordingly made recommendations on what research should be prioritized.

1.3. Environmental Effects of Organic Aerosols

While the organic fraction of the atmospheric aerosol is not well characterized, there are a few outstanding examples of its environmental ramifications that illustrate its potential importance. From the connection of these effects of organic aerosols to the molecular forms of the organic species, it is clear that acquisition of a much fuller understanding of carbonaceous aerosols, in general, is necessary.

1.3.1. Physiological response: Toxicity. There are several types of highly toxic organic compounds found in the environment, but polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and other organochlorine compounds have received the most attention as pollutants that occur in the aerosol phase. Man-made PCBs and organochlorines especially have been found in a very wide range of environments and matrices throughout the world, including Arctic snows, seawater, and myriad types of biological tissues [Tanabe et al., 1984; Tanabe and Tatsukawa, 1986; Hinckley et al., 1991]. Generally used as pesticides, these compounds are subject to long-range atmospheric transport as both gases and particles [Patton et al., 1991] and are particularly damaging to Arctic ecosystems, which have very few species in the food chain. Arctic animals bioconcentrate these hydrophobic compounds because of the large amount of lipids in their tissues. PAHs are produced industrially and in biomass burning and are some of the most toxic and carcinogenic compounds known, even at extremely low concentrations [Payne, 1982; Stanley et al., 1990]. Bushby et al. [1993] presented measurements of these and similar classes of compounds from wet and dry atmospheric deposition. The effectiveness of organic aerosols for physiological action is evident from the fact that aerosol forms are often selected for efficient delivery of medications on the one hand and are used as chemical warfare agents on the other. It is unclear how the interaction of these compounds with water and other organic compounds affects their toxicological action.

1.3.2. Direct climate forcing (reflection of sunlight by aerosol particles). Aerosol particles in the atmosphere can directly influence climate by filtering incoming solar radiation. The current IPCC estimate of total direct climate forcing from aerosol particles is -0.5 W m^{-2} , averaged over the entire planet [IPCC, 1995]. This figure represents the contribution of mostly sulfate aero-

sols. Given the ubiquity of carbonaceous aerosols, our understanding of the “direct effect” of aerosols on climate is certainly incomplete. Penner *et al.* [1992] have estimated that the global contribution of organic aerosols to radiative forcing is -2.0 W m^{-2} , but this estimate is highly uncertain. Clearly, additional data on organic aerosols must be provided to better estimate changes in the Earth’s radiative balance.

1.3.3. Cloud nucleation and indirect climate forcing (changes in cloud reflectance). Although standard cloud-nucleation theory is based on an assumption that cloud condensation nuclei (CCN) are composed of highly soluble inorganic salts, there are many highly and slightly soluble organic compounds that also can be cloud active [Kulmala *et al.*, 1996]. Besides the essential role of providing solute for vapor-pressure depression, organics have often been mentioned to cause delays in droplet formation [Bigg, 1986] or evaporation [Gill *et al.*, 1983]. Such effects have long been suggested to result from organic films or coatings on incipient cloud droplets, although both the physical and chemical data to support such ideas are meager to nonexistent. Novakov and Penner [1993] and Rivera-Carpio *et al.* [1996] showed that organic aerosols can significantly contribute to the mass of CCN particles, and Novakov and Corrigan [1996] report that pure organic smoke from cellulose containing no salt component is able to form CCN without being associated with sulfates or other inorganic compounds. This indicates that organic compounds in smoke from biomass burning may be a significant source of CCN and therefore indirect climate forcing [Penner *et al.*, 1996]. For an in-depth discussion of the mechanism of indirect climate forcing, see Schwartz and Slingo [1996].

1.3.4. Rainwater chemistry and acidification. Organic acids from $\text{C}_1\text{--C}_{34}$ have been found in precipitation samples around the world, with formic and acetic acids generally predominating [Galloway *et al.*, 1976; Lunde *et al.*, 1977; Matsumoto and Hanya, 1980; Galloway *et al.*, 1982; Kawamura and Kaplan, 1983; Likens *et al.*, 1983; Guiang *et al.*, 1984; Munger *et al.*, 1989]. Although rainwater acidification is generally caused by sulfuric and nitric acid in areas affected by anthropogenic emissions, organic compounds found in aerosol particles (e.g., C_2 and higher diacids and formic and acetic acids) may be major contributors to the free acidity of rainwater in more remote regions, where strong inorganic acids are scarce [Chameides and Davis, 1983; Keene and Galloway, 1984; Weathers *et al.*, 1988]. The larger molecular weight acids are found in the dry atmosphere as aerosol particles and are removed via nucleation scavenging in clouds.

1.3.5. Tropospheric ozone and photochemical smog. The only significant source of tropospheric ozone (O_3) is from the photolysis of NO_2 , which produces atomic oxygen, leading to ozone after reaction with molecular oxygen (O_2). Organic compounds (both natural and anthropogenic) are involved in ozone pro-

duction because organic peroxy radicals (RO_2) react with NO , converting it to NO_2 . Peroxy radicals are intermediate products resulting from initial reaction of organic compounds with hydroxyl radicals (OH). Thus ozone production is sensitive to the amount of organic material with respect to the amount of NO_x ($\text{NO} + \text{NO}_2$). Although discussion and research into this organic component have traditionally been linked to volatile (gaseous) compounds (VOCs), there is speculation that organic particulate matter is also involved in ozone production [National Research Council, 1991].

Since organic aerosols are also a product of VOC oxidation by ozone, photochemical smog episodes have nearly always been associated with organic aerosols. This association has often been qualitative or even conjectural, since the chemical data sets are sparse for smog outside of Los Angeles, an area that is particularly rich in organic materials [Cronn, 1975; Hidy *et al.*, 1980; Rogge *et al.*, 1993a; Hildemann *et al.*, 1994a]. Both primary aerosols (produced directly from sources) and secondary aerosols (produced from oxidation of gaseous species) are elevated in such episodes [Husar and Shu, 1975; Hidy *et al.*, 1980; Gray *et al.*, 1986]. Important effects of the organic aerosol are visibility degradation (see below) and eye irritation, where organic aerosols have often been alleged as the cause.

1.3.6. Biogeochemical cycling. There is evidence that organic aerosols are produced in significant quantities from the large amount of volatile organic compounds emitted naturally by vegetation [Graedel, 1979; Duce *et al.*, 1983; Fehsenfeld *et al.*, 1992]. The cycling of natural organic compounds plays a large role in balancing the global carbon cycle and also in the formation of oxidants (see description of tropospheric ozone above). Zimmerman *et al.* [1978] estimated that roughly 480 Tg of terpenes are emitted as gases every year from natural sources. This figure is actually larger than the estimate of the total anthropogenic nonmethane hydrocarbon emission rate of 60 Tg yr^{-1} by Duce [1978]. Terpenes are combinations of two units of isoprene, C_5H_8 , which are joined together in either cyclic or acyclic ways. The double bonds in these compounds leave the molecule susceptible to oxidation by both ozone and the hydroxyl radical, yielding oxidized products that have very low vapor pressures compared with the parent compounds, and thus are usually found in the aerosol phase. Terpenes have been measured in the gas phase at many forested sites around the world, including Scandinavia [Janson, 1992, 1993] and the rest of Europe [Simpson *et al.*, 1995]. The effect of terpenes on tropospheric ozone has also been modeled for a Swedish forest [Johansson and Janson, 1993]. It was found that terpenes are a significant sink for ozone during nighttime hours and during periods of high organic emission. The products of these reactions are highly oxidized organic compounds that are likely to have low vapor pressures and therefore appear as aerosols. Went [1960] first postulated that terpenoid compounds are responsible for the blue haze

often associated with forested hilly areas, due to oxidative particle formation. Although it is clear that terpenes have a tendency to form particles when oxidized, this effect has not been investigated thoroughly in the natural atmosphere, and it is unclear to what extent this contributes to the total organic aerosol burden.

Incorporation of both natural and anthropogenic organic compounds into the particle phase is a principle mechanism of extraction from the atmosphere into other reservoirs. This cycling may take place by sorption to large particles that are dry deposited, by sorption onto fine particles followed by wet deposition, or by dissolution into solution droplets in clouds. The specific cycling process for any compound depends on properties governed by molecular form (vapor pressure, water solubility, etc.). *Ballschmiter* [1992] provides a thorough review of biogeochemical cycling and fates of known organic compounds in the environment.

1.3.7. Visibility degradation. Aerosol particles, particularly those with sizes comparable to the wavelengths of visible light, scatter and absorb light and thereby control the transmission of light through the atmosphere. Both primary and secondary aerosols are effective in this regard. *White* [1990] has summarized calculations for apportionment of fine-particle scattering and reports that organics are sometimes responsible for as much as 60% of this scattering, especially in the urban areas of the western United States. The average for the eastern United States is 30%, while we are unaware of similar evaluations for Europe.

Colored (blue, yellow, brown, and black) smoke plumes from combustion sources utilizing fossil or biomass fuels are a traditional target for air pollution regulations. All such smokes have a significant organic content and can absorb light due to the presence of a variety of light-absorbing chromophores in the carbon-containing molecules. Some of the absorption is due to impure elemental carbon in graphitic form [*Rosen et al.*, 1978], although currently available analytical methods are not adequate for unambiguously apportioning light absorption to the organic/elemental fractions. Wavelength-dependent scattering, usually causing a smoke plume to appear blue, white, or gray (when scattered light is observed) or yellow to brown (when light transmitted through the plume is observed), is common with organic smokes due to the propensity of the molecular species that are involved to form submicrometer particles via condensation at elevated temperatures.

2. DESCRIPTION OF ORGANIC AEROSOL

2.1. Spatial Distribution of Carbonaceous Aerosol

Carbon-based aerosols may contain organic compounds, elemental carbon, or carbonate minerals. The latter are almost exclusively found as a remnant of soil dust in supermicrometer particles and will not be discussed further. Because of its resistance to high-temper-

ature decomposition, elemental (black) carbon is also sometimes referred to as refractory carbon. In the atmosphere this fraction is generally coated with organic compounds, and therefore a complete conceptual separation of the two chemical classes is not possible; that is, elemental carbon is nearly always linked to organics, but organic aerosols may exist independently of elemental carbon. The worldwide distributions of these aerosols are not well known because data are sparse, and what data do exist have usually been collected for short sampling durations. *Lioussse et al.* [1996] reviewed the available measurements and developed a model to describe the global distribution of carbonaceous aerosol. Their model relies on emission inventories of fuel usage and natural combustion, as well as on natural sources of organic particulate matter. They report calculated average organic submicrometer particle concentrations of $1\text{--}2\ \mu\text{g m}^{-3}$ for the eastern United States, $0.5\text{--}1.0\ \mu\text{g m}^{-3}$ for the southwestern United States, and as high as over $10\text{--}12\ \mu\text{g m}^{-3}$ in central Europe, the Amazon basin, west central Africa, eastern China, and northern Australia. Marine estimates for organic aerosols are mostly in the range $0.1\text{--}2.0\ \mu\text{g m}^{-3}$. These estimates appear to correlate well with the data that are available, although there are large uncertainties in both the emission factors and ambient measurements, which are in themselves difficult to quantify. It has been shown that different types of biomass fuel sources lead to different ratios of black carbon to total carbon in the product aerosol [*Cachier et al.*, 1989]. This complicates the problem of estimating the production of black versus organic carbon. *White* [1990] has also surveyed the composition of fine particles in the United States and showed that organic compounds compose approximately 30% of fine particulate mass in the eastern United States (both in urban and rural locations), between 20% and 40% mass in the rural western United States, and between 30% and 80% mass in urban areas of the western United States. Similar results are reported by *Heintzenberg* [1989], who reviewed studies that included measurements of both total suspended particle (TSP) mass and chemical analysis from sites around the world. Reported averages of percentages of TSP that is organic are 31% in urban areas, 24% in nonurban continental areas, and 11% in remote regions. Although these studies do not report the variability of organic contribution to fine-particle mass, they do show that organic material is a ubiquitous and significant constituent of fine aerosol.

2.2. Sources

The source of particles determines both the chemical composition of the aerosol and the size distribution. Organic particles may be either directly emitted into the atmosphere (primary sources) or developed in situ by chemical reactions of gas phase compounds (secondary sources). The relative contributions of these two source processes depend on the local types of emissions as well as on the meteorological and atmospheric chemical con-

TABLE 1. Yearly Emissions of Submicrometer Carbonaceous Particles

Source	Organic Particulate, Tg yr ⁻¹	Black Carbon Particulate, Tg yr ⁻¹
Biomass burning	44.6	5.63
Fossil fuel	28.5	6.64
Natural sources	7.8	0
Total	81	12.3

Data compiled from *Lioussé et al.* [1996].

ditions in the area. Both primary and secondary aerosols can be of either anthropogenic or natural origin. Depending on the type of formation, aerosols may be limited to the geographic region where they entered the atmosphere or possibly transported over very long distances before they become their final forms and are removed from the atmosphere.

Although the source strength of organic and black carbon atmospheric particles is very uncertain, *Lioussé et al.* [1996] have estimated the following inventory of yearly emissions of submicrometer carbonaceous particles. Their data are summarized in Table 1. Biomass burning sources include burning of savannas, tropical forests, agricultural fires, and the burning of domestic fuels such as wood, charcoal, and dung. Although forest fires may be started by natural causes, all biomass burning sources are listed together here. Determination of emissions and amount of biomass burned is extremely difficult, and these figures are subject to future revision. Fossil fuel sources are better defined because of record keeping of amount of fuel sold and studies on emissions from different sources. The only significant natural source of organic aerosol considered in this estimate is photochemical oxidation of gaseous terpene emissions from vegetation. Direct emission of particles from plants was not included.

2.2.1. Primary sources. One form of natural primary organic aerosol results from the disintegration and dispersion of bulk plant material. Particles from this source are generally in the supermicrometer size range and have a distinctive *n*-alkane signature that has a predominance of compounds with an odd number of carbons from C₂₇ to C₃₃ [*Simoneit et al.*, 1977; *Gagosian et al.*, 1982; *Sicre et al.*, 1990; *Hildemann et al.*, 1996]. Long-range transport of this aerosol has been described by *Folger* [1970] and *Simoneit et al.* [1977], especially as part of aeolian dust in the Atlantic, downwind of Africa. *Hildemann et al.* [1996] have recently determined the *n*-alkane profile of the waxes found on leaves in the Los Angeles area and correlated this profile with ambient samples. It was found that primary vegetation-derived aerosols account for less than 3% of the total fine aerosol burden in this urban area, but other studies have indicated that in remote locations this source may be relatively more important [*Mazurek et al.*, 1991]. *Marty and Salot* [1982] studied the odd-even carbon number

preference as a function of particle size in the western equatorial Atlantic and reported that terrestrial sources were the dominant source of *n*-alkanes for particles larger than 1 μm. Smaller particles appeared to have an oceanic source. In other work, *Schneider et al.* [1983] and *Schneider and Gagosian* [1985] found that *n*-alkanes with an odd carbon number preference (land plant wax or soil origin) were predominant for all particle sizes off the coast of Peru but that this trend was more pronounced for the largest particle size fractions. For smaller particles, *n*-alkanes containing an even number of carbons became increasingly important. These compounds were listed as anthropogenic, but the authors do state the possibility of marine phytoplankton and bacteria as potential sources.

Primary production is responsible for the presence of viable biological microbes such as bacteria, viruses, and fungal spores, which are ubiquitous in the atmosphere and cover a very large size range from viruses (about 1 nm diameter) to pollen (up to 300 μm diameter) [*Duce et al.*, 1983]. These particles are mostly produced on the surface of plants and may be transported over very long distances [*Edmonds*, 1979]; however, *Fuzzi et al.* [1997] recently measured biological particle populations in fogs and hypothesized that fog droplets themselves are favorable growth media for bacteria and yeasts.

By collecting particles on impactor plates that are coated with dyes that react with proteins in biological particles, larger biological particles (>2 μm) can be identified and counted using a light microscope, while smaller particles can be identified as biological on the basis of their morphology and elemental composition using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX) [*Matthias-Maser and Jaenicke*, 1991, 1994]. Air masses that are influenced by rural areas generally have a large amount of giant biological particles such as pollen spores, whereas in urban and industrial air there is a higher concentration of smaller biological particles such as bacteria [*Matthias-Maser and Jaenicke*, 1995].

It has long been known that primary production over the oceans is caused at least in part by the ejection and dispersion of saltwater droplets from bursting bubbles at the sea surface [*Woodcock*, 1953]. The sea-salt aerosol that results may have an organic coating resulting from scavenging of surface active material from seawater, although the importance of this process as a source of marine organic aerosol remains speculative. *Duce* [1978] estimated that 1.4 Mt yr⁻¹ of fine mode particulate carbon is injected into the atmosphere from the ocean, which compares with about 10% of the estimated global anthropogenic source. *Hoffman and Duce* [1976] investigated the factors that affect the amount of organic material that is deposited on particles emitted during bubble bursting and found that the distance an air bubble travels in seawater before breaking at the surface, as well as the quantity and type of organic and surfactant material present in the seawater, is important. The bub-

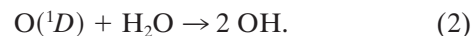
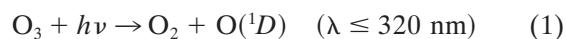
ble-breaking mechanism is very complicated from both a physical and chemical point of view, which makes it difficult to generalize. A recent experiment performed in Cape Grim, Tasmania, utilized single particle analysis by laser mass spectroscopy (see section 4.6) to study clean marine aerosol [Middlebrook *et al.*, 1998]. This study showed a positive trend between organic material and iodine concentrations in recently formed particles, which suggested bubble bursting releasing surface-layer material as the probable source.

There may be other mechanisms at work in producing marine organic aerosol. Noone *et al.* [1996] analyzed single particles using an electron probe X-ray microanalysis/scanning electron microscope technique [Jambers *et al.*, 1995] and observed particles in marine aerosol that contained both carbon and chlorine but no sodium. Sodium would be expected if the particles were sea-salt derived, and the authors suggest that its absence may be the result of a natural marine source of organohalogenes. Indeed, several halogenated terpene compounds and other organohalogen compounds with low vapor pressures have been identified as having biological marine sources [Gribble, 1992]. These compounds may be an underestimated marine organic aerosol.

Biomass and fossil fuel burning are the two most important sources of primary organic particles globally, and combustion processes are, in general, the sole source of black carbon in the atmosphere [Andreae, 1991; Lioussé *et al.*, 1996]. The amount of organic material compared with black carbon produced seems to depend on the type of material burned and the temperature of combustion [Cachier *et al.*, 1989]. Most of the work in identifying compounds originating from biomass burning sources has concentrated on polycyclic aromatic hydrocarbons (PAHs), which are toxic. These types of compounds exist in both the gas and particle phase [Ligocki and Pankow, 1989]. The concentrations and sizes of PAH molecules emitted during burning episodes depend highly on the efficiency of burning and do not seem to be affected by the type of plant being burned [Jenkins *et al.*, 1996]. Oxygenated organic compounds also are produced by high-temperature oxidation in biomass burning, some of which have vapor pressures that are sufficiently low that they may be found in the particle phase. Novakov and Corrigan [1996] reported that the burning of cellulose, the molecule common to all wood species, produces smoke particles that are nearly 100% water soluble, which they have analyzed to be mostly carboxylic acids. Andreae *et al.* [1988] analyzed particles produced in biomass burning plumes in Brazil for monocarboxylic acids and methanesulfonic acid and found that all of the organic acid ions they searched for were significantly enriched. Very little additional work, however, has gone into sampling of ambient fires to determine the quantity and molecular forms of oxygenated, water-soluble organics produced in biomass burning. Particles derived from fossil fuel combustion have not been examined at all in this respect.

In urban areas, motor vehicle emissions account for a significant amount of primary fine organic particles. Rogge *et al.* [1993b] estimated that this figure is 21% in Los Angeles. Car engine emissions of particles depend on a wide range of parameters relating to the type, size, and age of the engine, as well as on the fuel and lubrication used. In the gas chromatography/mass spectrometry (GC/MS) performed by Rogge *et al.* [1993b] on samples from automobile exhaust, a great variety of chemical species was found, including *n*-alkanes, *n*-alkanoic acids, benzoic acids, and a host of other cyclic, polycyclic, and aromatic compounds. It is important to remember that this represents only the 20% of the total amount of organics that could be resolved in the GC spectrum. Other unresolved fractions probably contained branched alkane and cyclic alkane compounds, which are difficult to chromatograph. Besides motor vehicles, other major sources of organic fine aerosol in Los Angeles have been investigated by the same research group and include 21% from meat cooking [Rogge *et al.*, 1991], up to 30% from fireplaces, depending on the season [Rogge *et al.*, 1998], and 16% from road dust, tire debris, and brake dust [Rogge *et al.*, 1993c].

2.2.2. Secondary organic aerosols: Aerosol formation from the gas phase. Organic aerosols that are formed from the reactions of gases in the atmosphere are thought to result from oxidation of gaseous species by one of three electrophilic gases present in trace amounts in the atmosphere: the hydroxyl radical (OH), ozone (O₃), and the nitrate radical (NO₃). These oxidizers are produced photochemically and are active as reactants during limited times of the day. O₃ is active during both daytime and nighttime hours, but OH is produced in large quantities only during daylight hours from the photolysis of O₃. This produces singlet-D oxygen (an excited state of oxygen) that reacts with water:



NO₃ is only active during nighttime hours because it photolyzes readily in the presence of sunlight. The oxidized forms of gaseous organic compounds generally have vapor pressures much lower than the reduced compound. This is illustrated in Figure 1, which shows that vapor pressure is dependent both on the number of carbon atoms in the molecule and on the number and type of polar functional groups.

In order for secondary aerosol formation to occur, the gas phase products of oxidation reactions must be produced in high enough concentrations to either condense onto existing particles or nucleate into a condensed form. The thermodynamics governing the gas-particle partitioning of organic compounds is covered in the next section, but generally speaking, particle production will not occur if either the oxidation reaction is too slow or the vapor pressure of the product is higher than that of the reduced form [Grosjean *et al.*, 1976].

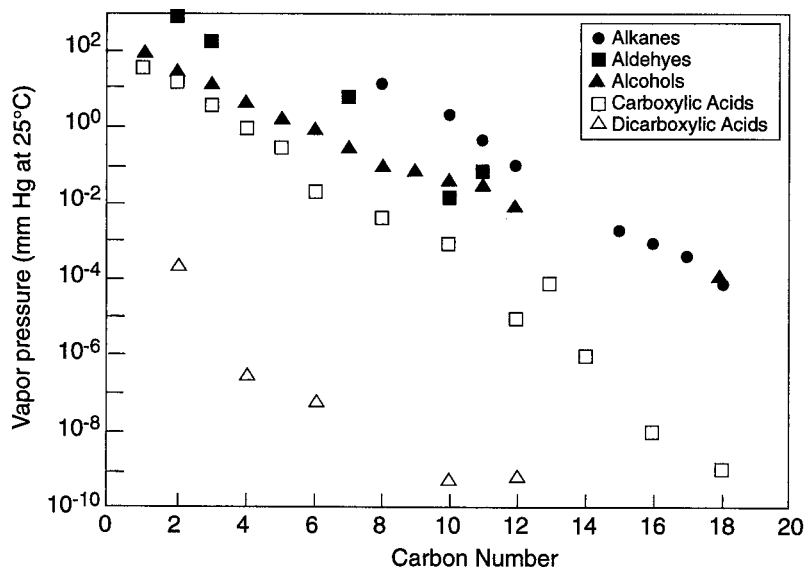


Figure 1. Vapor pressures of organic compounds as a function of carbon number and functionality. Data from Grosjean [1978].

Most of the information on sources of secondary organics comes from controlled laboratory smog-chamber experiments, where gases that have been measured in the atmosphere are introduced into a chamber and allowed to react with an oxidant. Usually, a set of seed particles is provided in these experiments as surfaces for heterogeneous nucleation of the oxidized organics. The resultant aerosol is then examined using a variety of methods including gravimetric analysis to determine aerosol yield, nephelometry to examine light scattering properties, differential mobility analysis and optical particle counting as sizing techniques, and carbon analysis to determine the amount of carbon transferred to the particle phase. On the basis of a literature search of studies using reaction chambers, Grosjean and Seinfeld [1989] have put together a remarkably short list of reactive organic gases (ROGs) that have been measured in the ambient atmosphere and have significant aerosol-producing potential (i.e., those that have over a 10%

conversion to aerosol in the presence of realistic atmospheric oxidant concentrations). These gaseous compounds are listed in Table 2. Although the chemistry of available precursor ROGs may be quite simple, dozens of aerosol and oxidized gas products can result from a single ROG because of differences in possible reaction pathways [Grosjean, 1978; McMurray and Grosjean, 1985]. Additionally, there is now empirical evidence that organic secondary particles become associated with inorganic secondary materials [Murphy and Thomson, 1997; Noble and Prather, 1996]. This is consistent with the theory that fine particles inevitably mix due to Brownian motion. The anthropogenic gases listed in Table 2 are found mostly in automobile exhaust [Grosjean and Seinfeld, 1989], whereas the terpenes are emitted naturally by trees [Zimmerman et al., 1978].

One of the more studied product groups of ROG oxidation is dicarboxylic acids. These compounds are abundant in photochemical smog [Cronn, 1975;

TABLE 2. Reactive Organic Gases That Have Been Measured in the Ambient Atmosphere and Have at Least 10% Conversion to Aerosol in the Presence of Realistic Atmospheric Oxidant Concentrations

<i>Anthropogenic Reactive Organic Gases</i>	<i>Molecular Forms</i>	<i>References</i>
Phenols	ortho cresol 4-hydroxy-2-nitrotoluene	McMurray and Grosjean [1985]
Diolefins	1,5-hexadiene 1,6-heptadiene 2-methyl-1,5-hexadiene 1,7-octadiene cyclopentadiene	Prager et al. [1960]; O'Brien et al. [1975] Prager et al. [1960]; O'Brien et al. [1975]; Grosjean and Friedlander [1979] O'Brien et al. [1975]; Zhang et al. [1992] Schuetzle and Rasmussen [1978]
Natural reactive organic gases (terpenes)	α -pinene limonene	

Originally compiled by Grosjean and Seinfeld [1989].

Grosjean, 1978; Appel et al., 1980] and appear to be the products of the oxidation of cyclic and aliphatic diolephins, especially by reaction with ozone [Grosjean, 1977, 1978; Grosjean and Friedlander, 1979; Hatakeyama et al., 1985, 1987]. There is strong evidence that the gaseous precursors of these aerosols can travel long distances and photochemically produce particles at locations very far away from the sources. This has been seen in several studies in Japan [Satsumabayashi et al., 1989; Satsumabayashi and Kurita, 1990], where there is a clear diurnal variation in the concentration of these species. These compounds have even been measured in the Arctic atmosphere at polar sunrise [Kawamura et al., 1995]. The presence of these aerosols affects visibility and climate through scattering of solar radiation and also influences cloud droplet processes, which are discussed in section 2.4.

A goal in using information on the formation and transport of secondary aerosols is to be able to make models that predict the spatial distribution of particles and their chemistry, based on knowledge of gaseous emissions, weather patterns, and oxidant levels. Pandis et al. [1992] made the first attempt to create such a model and applied the calculations to sites in California where concurrent measurements were being made of organic and elemental carbon particles [Turpin and Huntzicker, 1991]. Although the contribution of secondary organic aerosol to total carbonaceous aerosol can be roughly estimated by examining the correlation between the diurnal variations of organic carbon and elemental carbon [Turpin and Huntzicker, 1991], the lack of complete chemical analysis techniques for organic aerosols prevents any reliable method of apportioning carbonaceous material to primary or secondary emissions; thus it is difficult to utilize the model results for comparison with a parameter directly measured in the atmosphere. The model inputs, such as gas phase emission rates and aerosol yields, have high uncertainties, as do the physical processes (discussed in the next section) that control the formation of the secondary aerosol. These shortcomings, pointed out by Pandis et al. [1992], currently limit the usefulness of such models.

2.3. Phase Characteristics of Organic Aerosols

Since atmospheric organic compounds are found in both the gas and condensed phases, it is imperative to consider a compound's partitioning characteristics in order to understand its distribution, lifetime, and removal mechanisms and the effects the compound has on light scattering, cloud drop formation, and public health. Indeed, the very existence of most organic aerosol depends on the complicated dynamic state of all of the condensable species present. For secondary aerosols and some of the products of combustion, the gas-particle partitioning determines the yield of aerosol mass that forms from the gaseous products of atmospheric reactions. Partitioning is also an important consideration when sampling organic aerosol because positive and

negative artifacts are inherent when collecting semivolatile material. In general, partitioning of a compound toward particles depends on its vapor pressure (controlled by the molecular form) as well as on the amount and chemical nature of particles available as condensation sites, and temperature. This means that understanding a trace substance such as PAH necessarily requires information on the other organic and inorganic substances present and the amount of liquid water.

In a scenario for the formation of aerosol from the gas phase, a semivolatile organic compound (SOC) is either produced through photochemical oxidation in the atmosphere or emitted by a combustion source. Traditionally, it has been assumed that the SOC remains in the gas phase until its concentration reaches a point that it sorbs onto available seed particles or homogeneously nucleates. This process continues until there is thermodynamic equilibrium between the gas and particle phases. An equation that parameterizes the partitioning is [Yamasaki et al., 1982; Pankow, 1987, 1993, 1994]

$$K_p = \frac{c_p}{c_g(\text{TSP})}, \quad (3)$$

where K_p ($\text{m}^3 \mu\text{g}^{-1}$) is the temperature-dependent equilibrium partitioning constant; c_p and c_g are the concentrations of the SOC in the particle and gas phases, respectively; and TSP ($\mu\text{g m}^{-3}$) is the concentration of total suspended particulate. The distribution c_p/c_g can be measured by collecting particles on a filter with an adsorbent such as Tenax downstream to catch the gas phase portion. This technique has mostly been used in cities to measure partitioning of polycyclic aromatic hydrocarbons (PAHs), alkanes, phthalate esters, fatty acids, and organohalogens [Cautreels and Van Cauwenbergh, 1977; Yamasaki et al., 1982; Ligocki and Pankow, 1989]. It has more recently been applied to the partitioning of PAH products of biomass burning [Jenkins et al., 1996]. Vapor phase information has also been acquired using gas chromatographic retention data for PCB compounds [Falconer and Bidleman, 1994] in order to predict gas-particle distributions. We are unaware of studies of this type pertaining to secondary aerosol species, which are more highly oxidized and more difficult to analyze than these nonpolar compounds listed. Interestingly, it appears that K_p values for a single SOC in the urban atmosphere are very similar even when measured from city to city [Falconer and Bidleman, 1994].

One of the goals of using gas-particle partitioning theory is to develop realistic models for the production of a secondary aerosol and to predict which reactive gas emissions are most important in the production of particulate pollution. These models rely on inputs of the emission rates of ROGs, concentrations of oxidant species, and the fractional aerosol yield for each ROG, Y , calculated as

$$Y = \frac{\Delta M_o}{\Delta \text{ROG}}, \quad (4)$$

where ΔM_o is the organic aerosol mass concentration ($\mu\text{g m}^{-3}$) produced from ΔROG , the amount of ROG reacted ($\mu\text{g m}^{-3}$). These aerosol yields usually come from smog-chamber measurements, but traditionally it has been difficult to obtain a single value for aerosol yield from a single ROG with low uncertainty. As pointed out by *Pandis et al.* [1992], reported aerosol yields may differ by more than an order of magnitude. It may be that a factor causing these discrepancies is a poor assumption on how the products of the oxidation reactions partition between the gas and particle phases. *Odum et al.* [1996] investigated gas-particle partitioning assumptions to see how they affect Y .

Odum et al. [1996] rely on an analysis by *Pankow* [1994], who points out that although K_p is constant for a single compound at a single temperature, it does not state anything about the mechanism involved in the sorption of the gas to the existing particles. Traditionally, this problem has been treated according to a simple Langmuir isotherm, so that the gas is assumed to simply physically adsorb to the surface of the particles [*Junge*, 1977; *Yamasaki et al.*, 1982; *Pankow*, 1987]. In this case, K_p would be predicted by theory to be [*Pankow*, 1987]

$$K_p = \frac{N_s a_{\text{tsp}} T e^{(Q_1 - Q_v)/RT}}{1600 p_L^o}, \quad (5)$$

where N_s (sites cm^{-2}) is the surface concentration of sorption sites; a_{tsp} ($\text{m}^2 \text{g}^{-1}$) is the specific surface area of the existing particulate matter; T is temperature (kelvins); Q_1 (kJ mol^{-1}) is the enthalpy of desorption from the particle surface; Q_v (kJ mol^{-1}) is the enthalpy of vaporization of the adsorbing compound from the liquid phase (subcooled if necessary); R is the universal gas constant; and p_L^o is the vapor pressure of the adsorbing compound as a liquid (subcooled, if necessary). Note that this equation predicts that the degree of sorption is independent of the amount of material already sorbed to the particles. However, *Pandis et al.* [1992] and *Pankow* [1994] suggest that the partitioning process for organic compounds may have an absorption, or chemisorption, component, which may even dominate the sorption process. This would happen if there were liquid or amorphous organic material present in particles for organic gases to dissolve into, and thus as more organic material is added to particles, the partitioning characteristics would change. If this absorption were the only mechanism for partitioning, with no adsorption component, then theory would predict that [*Pankow*, 1994]

$$K_{p,i} = \frac{f_{om} 760RT}{MW_{om} \zeta_i 10^6 p_{L,i}^o}, \quad (6)$$

where f_{om} is the weight fraction that is the absorbing organic material in the particles; R is the universal gas constant; T is temperature (kelvins); MW_{om} is the mean molecular weight of the absorbing organic material (g mol^{-1}); ζ_i is the activity coefficient of compound i in the organic material; and $p_{L,i}^o$ is the vapor pressure (torr) of

the absorbing compound as a liquid at the temperature of interest.

Odum et al. [1996] take *Pankow's* work one step further, pointing out that the expression for $K_{p,i}$ in (6) changes as more organic is dissolved into the particles. They define instead a partitioning coefficient for species i in terms of both the fraction of compound i dissolved into the particles ($F_{i,om}$) and the total organic mass concentration in the particles (M_o). The term $c_{g,i}$ refers to the gas phase concentration of species i .

$$K_{om,i} = \frac{F_{i,om}}{c_{g,i} M_o} = \frac{K_{p,i}}{f_{om}}. \quad (7)$$

This equilibrium partitioning coefficient will be constant as long as the total mass of absorbing organic (M_o) increases as $F_{i,om}$ increases. *Odum et al.* [1996] go on to define an expression for overall semivolatile organic aerosol yield that is equivalent to the expression in (4) but based on the partitioning coefficient given in (7):

$$Y = M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \right), \quad (8)$$

where α_i is a proportionality constant relating the concentration of the ROG that reacts to the total concentration of product i that is formed. It depends on both the molecular form of the ROG and the temperature:

$$1000 \alpha_i \Delta\text{ROG} = C_i. \quad (9)$$

By comparing yields predicted by (8) and data from a variety of smog-chamber experiments, *Odum et al.* [1996] show that the absorption model for partitioning seems to fit. Furthermore, experiments performed by other groups were rationalized by analysis using the absorption model.

A picture of gas-particle partitioning as it stands now is that a combination of adsorption and absorption may drive partitioning of trace species, so that the partitioning coefficient can be written as [*Pankow*, 1994]

$$K_{p,i} = \frac{1}{p_{L,i}^o} \left[\frac{N_s a_{\text{tsp}} T e^{(Q_1 - Q_v)/RT}}{1600} + \frac{f_{om} 760RT}{MW_{om} \zeta_i 10^6} \right]. \quad (10)$$

Current work seems to indicate that the second term in the brackets (the absorption term) may be more important, as was suggested by *Odum et al.* [1996]. *Storey et al.* [1995] also evaluated the relative importance of the two terms. They performed experiments using model semivolatile organic compounds (alkanes and PAHs) in the gas phase to determine the degree to which they adsorb onto the surface of clean quartz, as a model for adsorption to mineral dust in the atmosphere. Their results show that their model compounds adsorb less to quartz than the attachment that is seen in the ambient atmosphere. They suggest that absorption to the organic component of urban particles is probably a more important mechanism in the partitioning of these compounds but that in a rural environment where there is a consid-

erable amount of soil and nonorganic continental mineral dust, adsorption still may be important. These hypotheses have not yet been tested on more polar compounds found in atmospheric particulate matter. Unfortunately, phase relationship data are absent for nearly all of the other organic species found in atmospheric aerosol.

The most ubiquitous condensable gas in the atmosphere is water vapor, which is responsible for the formation of fog and cloud droplets by condensation onto aerosol particles. The question of how water vapor affects the gas-particle partitioning of organics has not been studied in depth. There is evidence that relative humidity (RH) affects the adsorption of organic vapors to aerosol particles. SOC partial pressure has been observed to increase over particles as relative humidity increases, indicating that water molecules may compete with the SOC for the same sorption sites [Spencer et al., 1982; Chiou et al., 1988]. Thibodeaux et al. [1991] drew upon the aerosol/vapor adsorption partitioning equations of Junge [1977] to develop a competition model of both water vapor and organic vapors adsorbing to the same particle. They suggest that at low RH, organic adsorption should decrease with increasing RH due to competition with water for sites on the particle surface. At some intermediate “damp” humidity the water molecules on the particle begin to touch, forming a liquid layer at the surface. This represents maximum crowding of water molecules and is the point when the smallest amount of SOC would be expected to occupy the particle surface. After the liquid water layer forms, the organic can sorb to or into the water film, and thus at this point adsorption increases with increasing RH. This scenario implies that aerosol particles associated with the most SOC are either completely dry or completely covered by a film of liquid water.

Although competition with water vapor may affect condensation of organic species, the opposite question arises of how organic compounds affect the condensation of water vapor to the surface of aerosol particles. This complementary issue is covered in the next section and has ramifications for the removal processes of organic particulate matter, the hydrologic cycle, and the “indirect climate forcing” effect of organic aerosols, as discussed briefly in section 1.2.

2.4. Hygroscopic Growth

It appears that numerous organic compounds may be present in cloud condensation nuclei [Novakov and Penner, 1993; Noone et al., 1996]. A major question is how these particles grow into droplets when exposed to water vapor. Although it had previously been assumed that organic compounds would need to be associated with inorganic salt compounds in order to nucleate cloud droplets, some organic compounds found in wood smoke are hygroscopic enough by themselves to cause cloud droplet growth [Novakov and Corrigan, 1996]. Another possibility is that surface active organics are

present on a small droplet or dry particle as a film. The topic of surface organic films has been discussed in detail by Gill et al. [1983]. Depending on the molecular structure of the organic coating and the type of particle it resides on, a film could conceivably help or hinder hygroscopic growth, affect evaporation of water vapor from the droplet, or simply change the equilibrium size to which a droplet might grow at a certain relative humidity. Some evidence that organic surface films exist on aerosol droplets in the ambient atmosphere is from electron micrographs, such as those taken by Husar and Shu [1975]. These pictures show particles that are wrinkled in appearance, thought to be because a volatile inner core (H_2O) evaporated, leaving behind a relatively nonvolatile organic coating.

The growth of droplets from organic-coated dry particles has been studied in the laboratory both using a tandem-differential mobility analyzer method (TDMA) [Hansson et al., 1990, 1998] and using suspended single particles in an electrodynamic balance [Rubel and Gentry, 1985; Andrews and Larson, 1993]. These studies have generally shown that the growth of normally hygroscopic particles such as NaCl and $(\text{NH}_4)_2\text{SO}_4$ is hindered by the presence of a coating of an organic compound, although the work by Hansson et al. [1998] showed that NaCl particles must be coated with very large amounts of hydrophobic organic material in order to significantly affect water uptake. This is probably because even hydrophobic organic coatings are susceptible to cracks where the hygroscopic salt is exposed. On the other hand, particles that are normally hydrophobic (e.g., soot) may experience increased affinity for water if certain organic coating types are present [Andrews and Larson, 1993]. This behavior has also been seen in ambient aerosols [Saxena et al., 1995]. In a nonurban location (the Grand Canyon) the presence of organic compounds enhanced water absorption by particles, accounting for 25–40% of total water uptake on average. In an urban area (Los Angeles), water uptake was inhibited by the presence of organic compounds by 25–35%. It is possible, however, that the TDMA may not have allowed sufficient time for equilibrium of water uptake, which could have increased the apparent effect in the urban locations.

Experiments dealing with organic coatings and their effects raise the question of the type of mixing present in atmospheric particles and how much of the organic material in a set of particles is associated with inorganic materials. Junge [1950] first described the concept of two limiting cases of aerosol particle mixing: internal mixtures, in which each particle is a uniform combination of several chemical species, and external mixtures, where individual particles are composed of a single chemical compound that is different from particle to particle. Realistically, most atmospheric aerosols are probably between these two extremes, so that each particle contains a different mixture of chemical compounds. Identifying the type of mixing in an aerosol sample requires

either examining individual particles by single particle analysis (e.g., electron microscopy or single particle laser spectroscopy) [Noble and Prather, 1996; Murphy and Thomson, 1997] or conditioning ambient aerosol in a certain way so as to cause a change to only one type of particle. An example of a conditioning technique is using a TDMA and humidifying the monodisperse aerosol between the two DMA classifiers. Using a combination of electron microscopy analysis, TDMA analysis, and chemical analysis on size fractionated samples, Zhang et al. [1993] found that aerosols collected in Los Angeles and at the Grand Canyon were externally mixed as a nonhygroscopic fraction with a fraction that was more hygroscopic. This behavior has also been seen in other locations [Svenningsson et al., 1994]. It appeared that in Los Angeles and at the Grand Canyon, the fraction of particles that was found to be less hygroscopic was too small to account for all of the carbon measured by chemical analysis, indicating that organic compounds were in both modes. This was confirmed by single particle analysis by a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX). There appeared to be particles that contained carbon or carbon and oxygen only, particles that contained sulfur, and particles that contained sulfur and carbon together. Because of their different chemical compositions, these particles would be expected to also have different hygroscopic properties consistent with the TDMA measurements. The concept that organic material could be associated with either hygroscopic or hydrophobic particles is consistent with the rich and varied chemistry of organic compounds.

The exact mechanism for differences in the apparent hygroscopic properties of a particle as seen by TDMA at this point remains unclear. TDMA experiments such as those discussed above could be affected by the amount of time aerosol particles are exposed to humid air, in which case particles that do not appear hygroscopic might not have had time to interact with the water vapor in order to dissolve fully. Lowering of the surface tension of the droplet solution, which would change droplet growth characteristics [see, e.g., Shulman et al., 1996], is another mechanism that needs to be explored. Such a change in surface tension arises from the presence at the particle-air interface of molecules having one or more polar functional groups on the end of a long carbon chain. The molecules are lined up so that the polar ends are in the water while the nonpolar (hydrophobic) ends are repelled into the air, away from the surface of the droplet. The amount of surface tension lowering varies according to the organic's molecular structure, the amount of surfactant present, and the degree to which the organic molecule partitions to the aerosol droplet surface, as opposed to being dissolved in the liquid. Shulman et al. [1996] showed that this last parameter is related in some cases to the solubility of the organic compound.

Shulman et al. [1996] measured surface tension for

five straight-chain organic diacids, phthalic acid, and *cis*-pinonic acid, all of which have been measured in the ambient atmosphere and are probably the products of secondary aerosol formation (see section 2.2.2). It was found that there is a general decrease in surface tension with increasing organic concentration and that the decrease in surface tension is greater for organic compounds with higher carbon number. The solubilities of these compounds were also measured in various concentrations of ammonium sulfate solutions. It was found that in many realistic cases, these compounds would experience complete dissolution only after droplet growth had taken place past deliquescence. The effects of surface tension and slight solubility of organic compounds on the growth of aqueous droplets can be calculated using the Köhler equation [Köhler, 1936; Shulman et al., 1996], which gives the relationship between supersaturation of water vapor and droplet size at equilibrium:

$$\frac{e'}{e_s} = 1 + \frac{2\sigma M_w}{kT\rho r^3} - \frac{3M_w\Phi}{4\pi\rho r^3} \left(\frac{\nu_{\text{org}} X_{\text{org}} m_{\text{org}}}{M_{\text{org}}} + \frac{\nu_{\text{sulf}} m_{\text{sulf}}}{M_{\text{sulf}}} \right), \quad (11)$$

where e' is the equilibrium vapor pressure of water over a solution droplet of a given radius (r) relative to the water vapor pressure over a plane surface of water (e_s); σ is the surface tension; M_w is the molecular weight of water; k is the Boltzmann constant; T is the temperature; ρ is the solution density; Φ is the osmotic coefficient of the aqueous solution; ν_{org} is the number of ions into which the organic dissociates when dissolved; X_{org} is the mole fraction of organic material present that is dissolved; m_{org} is the total mass of organic compound; m_{sulf} is the mass of the sulfate salt in the dry particle; M_{org} is the molecular weight of the organic; and M_{sulf} is the molecular weight of ammonium sulfate.

When the Köhler equation is plotted as supersaturation versus droplet size as shown in Figure 2, there is a radius that corresponds to a maximum supersaturation on the curve. These values are the critical radius and critical supersaturation. This is the level of supersaturation and droplet size the droplet must experience in order to grow spontaneously, without any increase in supersaturation of water vapor. These values depend on the dry particle size and the chemical and physical properties of the particle, especially the solubility. The shape of the curve is also affected by the solubility of the individual constituents of the particle. Figure 2 shows Köhler curves for droplets nucleated on pure ammonium sulfate, 90% succinic acid + 10% ammonium sulfate, and 50% *cis*-pinonic acid + 50% ammonium sulfate, all with a 0.03- μm dry particle radius. Succinic and *cis*-pinonic acids are both organic compounds with slight solubility in water. *Cis*-pinonic acid is less soluble (about 0.02 mol L⁻¹ in water) than succinic acid (about 0.25 mol L⁻¹ in water).

The curve for the pure salt exhibits a single maximum,

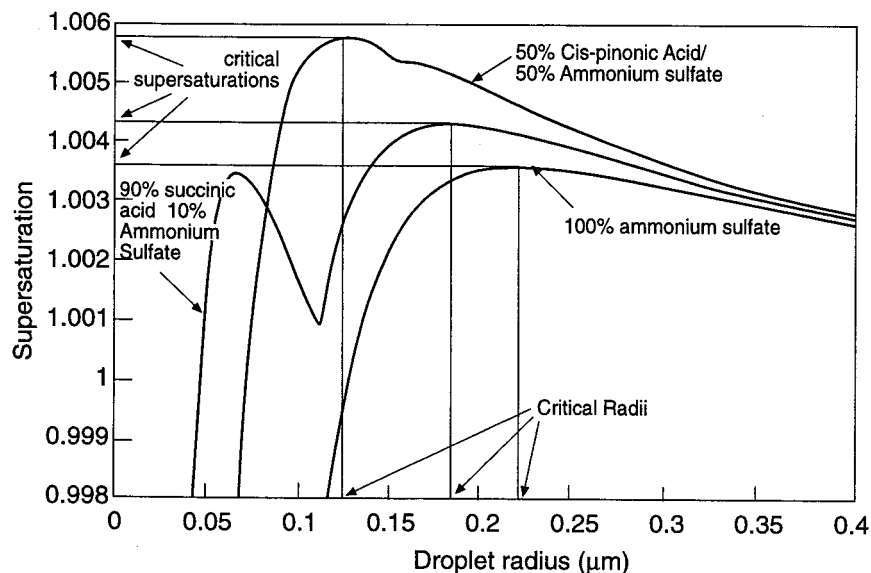


Figure 2. Köhler curves (equilibrium water vapor supersaturation versus droplet size) for droplets nucleated on particles containing organic material in varying amounts and solubility. The three examples shown are (1) for a pure salt (pure ammonium sulfate), (2) for a relatively high proportion (90% of particle mass) of a relatively soluble dicarboxylic acid (succinic acid), and (3) for a relatively low proportion (50% of particle mass) of a relatively insoluble oxygenated organic acid (*cis-pinonic acid*). The critical radius and critical supersaturation corresponding to the point of activation for each droplet are indicated. Dry particle radius for all three cases is 0.03 μm . Adapted from *Shulman et al.* [1996].

while the curves for droplets containing organic material have a cusp and/or double peak, caused by the gradual dissolution of the organic material into the droplet as it grows. The magnitude of this effect is governed by both the solubility of the organic and the amount the organic material contributes to the mass of the dry particle. The critical supersaturation is increased with lower compound solubility and with higher mass fraction of organic. However, this effect may be diminished if the organic compound is surface active; lowering the surface tension lowers the critical supersaturation, as depicted in (11). In general, the lower the solubility, the more surface active an organic will be.

The form of the Köhler equation given in (11) can be used to model the effects that slightly soluble compounds present in CCN would have on the size distribution of cloud droplets [Jacobson *et al.*, 1996]. Figure 3 shows the number size distributions of modeled cloud droplets grown from a chemically homogeneous, lognormal dry aerosol distribution with the chemistry indicated. These distributions were determined by using an adiabatic parcel model to calculate the water vapor supersaturation that a particle would experience by being lifted at a constant rate from an initial saturation of vapor pressure of 99%. Equation (11) was then used to calculate the resulting droplet size that each dry particle in the lognormal distribution would attain at each height. The cloud droplet size distribution in Figure 3 is a snapshot of the distribution of droplets in the parcel at a specific height above cloud base (1250 m), at a certain updraft speed (1 m s^{-1}).

In each case, the distributions containing organics are shifted to a smaller number of droplets with larger sizes than is the case with the droplet distribution nucleated from a pure inorganic. The size shift is dependent on both the molecular form (solubility) and the mass fraction of organic in the dry particles. This is due to the effect of the organic material on the Köhler curve, as shown in Figure 2. The critical supersaturation increases with lower compound solubility and with higher mass fraction of organic. The higher the supersaturation, the more difficult it is for the smallest particles in the distribution to nucleate, so only the largest particles take on appreciable water. Succinic acid shows less effect than *cis-pinonic acid* because it is more soluble. In general, the more mass the organic contributes, the size distribution shifts to a fewer number of larger droplets. Such a change in the size distribution of cloud droplets also causes changes in cloud optical properties, which could have an effect on climate if compounds with solubility lower than inorganic salts were widely distributed in the Earth's atmosphere and contributed significantly to CCN mass. At the moment it is unclear how much organics and other slightly soluble compounds contribute to the CCN population.

2.5. Chemical Transformations

Since the majority of organic aerosol mass remains poorly characterized, the study of chemical reactions involving organics in the condensed phase is sparse, especially in the ambient atmosphere. However, since the typical water content of particles in the lower atmo-

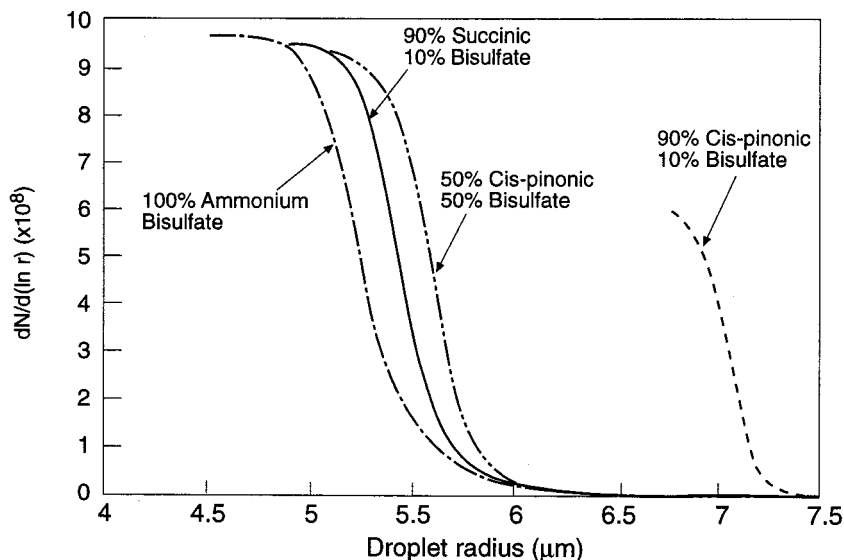


Figure 3. The effect of organic mass fraction and solubility on the size distribution of cloud droplets. The example shown is for a single height (1250 m above cloud base), with a single updraft speed (1 m s^{-1}). An adiabatic cloud model has been used to calculate the water vapor supersaturation at these conditions, and the Köhler relationship like the one shown in Figure 2 was used to calculate the resulting droplet sizes grown from dry particles in a lognormal size distribution. Four examples are shown, with the chemistry of the dry particles indicated. The initial dry size distribution was identical for all of the examples. Differences in the wet distributions are caused entirely by differences in particle chemistry. Adapted from *Jacobson et al.* [1996].

sphere is about 30–50% by mass, theoretical and laboratory study of reaction chemistry in the atmospheric condensed phase can be approximated, in part, as taking place in aqueous solutions, assuming that organic compounds have dissolved into the solution [*Graedel and Weschler, 1981*]. Under these idealized conditions the most reactive atmospheric species are oxidants, such as the hydroxyl radical, atomic oxygen, ozone, and molecular oxygen. In general, if organic compounds are reactive, they become smaller and more polar through oxidative cleavage and the addition of oxygen. Additionally, if nonpolar coatings or organic gases become associated with cloud droplets, oxidation reactions can take place in the aqueous phase that change the chemical composition of the organic material. If the water subsequently evaporates from these droplets, the modified organic becomes “new” organic aerosol. This is a plausible mechanism because clouds form and evaporate on the same CCN several times before precipitating. This process may be responsible for a large fraction of low molecular weight, polar organics in the atmosphere.

Dicarboxylic acids are once again a good example of a class of compounds that illustrate reactivity trends of organic material in the atmosphere. As was mentioned in section 2.2.2, laboratory experiments show that larger dicarboxylic acids ($>C_6$) are formed by photochemical oxidation of alkenes, especially cyclic alkenes [*Grosjean, 1978; Hatakeyama et al., 1985, 1987*]. Their vapor pressures are low, even at low carbon number, which causes them to partition into the aerosol phase (Figure 1). Numerous studies have shown that the most abundant

dicarboxylic acid is oxalic acid, the smallest (C_2) diacid species, followed by malonic (C_3) and succinic (C_4) acids [*Kawamura et al., 1995, 1996; Sempere and Kawamura, 1996*]. These three species account for more than 80% of the diacids found in Arctic regions, which are far away from the source of reactive gases. This distribution suggests that when the longer-chain dicarboxylic acids form, they remain photochemically labile, continuing to cleave to successively smaller carbon chains.

An additional area in which condensed phase organic compounds may play an important role is the oxidation and reduction of transition metals in cloud and fog droplets. The oxidation of aldehydes to carboxylic acids takes place, in part, through the reduction of Fe (III) to Fe (II) [*Cunningham et al., 1985; Faust and Hoffmann, 1986; Erel et al., 1993; Pehkonen et al., 1993*]. Ions such as oxalate can also act as ligands, forming transition metal complexes, and appear to also be involved in the oxidation/reduction chemistry of iron. Although the studies involving metals have focused on the oxidation state of the metal, the interaction with organic compounds may be an important parameter in controlling the acidity of the solution droplets. Reactions such as these can also affect solubility of gas phase atmospheric components, which could further affect droplet growth. One example is the influence of highly or somewhat soluble gases on the Raoult term in (11). It is now clear that molecules such as formic and acetic acids in the gas phase will dissolve into growing cloud droplets and cause depression of the water vapor pressure of the nucleating droplet [*Laaksonen et al., 1998*].

3. SAMPLING

The collection of clean, analyzable atmospheric samples is crucial for further understanding of organic aerosol particles. Unfortunately, the varied and sometimes unpredictable physical properties of organic material make meaningful sampling very difficult to carry out. There are two general complicating issues that must be kept in mind during most investigations of atmospheric organic compounds. The first issue is sampling time. Organic compounds are by far the most numerous class of chemical compounds, and in the atmosphere each individual species generally is a small proportion of the sample compared with the total amount of organic carbon. In some regions with very low particle concentrations, long sampling times, of the order of days or weeks, may be necessary to collect enough sample to satisfy detection limits of the analytical method. Sampling for a period that is too short will cause relevant material to be missed in analysis, while sampling too long may increase sampling artifacts and be less useful if concentrations are meant to be followed over time. The second issue is positive and negative artifacts. Since organic compounds are ubiquitous in the atmosphere as gases and particles, and on surfaces such as skin and laboratory benches, contamination is a primary concern, especially for non-specific analyses, such as for total organic carbon. The lower the concentration of the target atmospheric material, the more important the questions of contamination are. During sampling, gas phase organic material may adsorb to particles already collected or to the sampling substrate itself, appearing as particulate matter in analysis. Negative artifacts arise from the inherent volatility of most organic material. A comprehensive literature review on these subjects is presented by *McDow and Huntzicker* [1990]. This combination of positive and negative artifacts due to condensibility and volatility of organic compounds may skew results in ways that are difficult, if not currently impossible, to trace or detect in most situations. A greater understanding of gas-particle partitioning theory will eventually help make these artifacts more predictable, since vapor adsorption onto filters can be approached by considering the filter acting as a model aerosol [*Turpin et al.*, 1994]. There have been a few studies that investigate sampling artifacts, which are discussed in section 3.2 on filter sampling. These artifacts are relevant for any study involving the gravimetric analysis of aerosol mass concentration. Depending on the measurement method, the loss or gain of organics could be larger than all other errors, especially in cases when filter samples are heated to drive off water.

3.1. Size Segregation

An issue common to all collection of aerosol for subsequent chemical analysis is the size of aerosol collected. As mentioned in the introduction, fine particles are usually chemically different from coarse particles (diameter $> 2 \mu\text{m}$) because they have different sources

and much longer atmospheric residence times. These chemical differences cause differences in physical properties such as index of refraction, water solubility, and surfactant properties, all of which help determine the environmental effects. The size of the aerosol alone causes differences between the coarse and fine modes in light scattering efficiency [*Waggoner and Charlson*, 1976], breathability, and deposition rates. The fine mode aerosol is generally much more abundant on a per-particle basis, contributing over 99% of the total particle number. The fine mode, however, may contribute less total mass than larger particles. Although aerosol particles have been called “breathable” at sizes up to $15 \mu\text{m}$ [*Miller et al.*, 1979], optical and cloud effects of aerosols tend to be a function of particle number rather than mass. Thus chemical analysis techniques performed on samples of mixed coarse and fine mode particles will not yield meaningful predictions of many of the environmental effects of the aerosol and will skew the apparent sources, favoring the less numerous coarse particles. Many studies have been, and continue to be, performed with high-volume, non-size-segregated sampling for the sake of equipment convenience and cost and to satisfy mass requirements for analytical detection limits. It has also been the standard reference method for measuring total suspended particulate levels. It is not clear that these studies provide interpretable data on the ramifications of the presence of the aerosols. Even in certain health studies that require chemical knowledge of particles up to $15 \mu\text{m}$, it is important to segregate the aerosol by size and also ensure that particles at the largest sizes are collected quantitatively without wall or inlet losses. The relevant cutoff sizes depend on the type of study. For example, for a study examining the effect of different chemical species on visibility, an appropriate cutoff would be around $1\text{--}2 \mu\text{m}$ since light scattering efficiency drops off significantly at this size. The major methods of collecting size-segregated aerosol are outlined in Table 3. For a more detailed description of aerosol sampling and sizing methods, see *Liu and Pui* [1981], *Hinds* [1982], and *Finlayson-Pitts and Pitts* [1986].

3.2. Filter Sampling

Particles are collected onto filters in most sampling campaigns. The main issue in choosing a filter type is the type of analysis that will be run on the sample later (discussed in section 4). A basic analysis run on most samples of organic aerosols is total organic and elemental carbon, which is measured by combustion of the sample and measuring the CO_2 that is evolved from the carbon. For this method it is important to use a filter substance that can withstand the heat used in the analysis and will not contaminate the sample with carbon. Traditionally, the solution has been to use woven quartz fiber filters, which have an approximate melting point of 1000°C , contain no carbon, and are easy to cut into several sections. In order to reduce blank levels, standard procedure is to heat the filters in a furnace over-

TABLE 3. Comparison of Size-Segregating Equipment for Collecting Aerosol Particles

<i>Sizing Method</i>	<i>Principle of Operation</i>	<i>Advantages</i>	<i>Disadvantages</i>
Cyclone	large particles removed by centrifugal force; smaller particles collected on back filter	inexpensive and simple to install; high flow rates possible	size cut somewhat difficult to characterize and calibrate
Impactor	particles with sizes above cut size impact onto a surface (stage) due to higher momentum; smaller particles do not impact and pass through onto another stage or back filter	very sharp cutoff diameter with very small contamination by larger particles; several different cut sizes can be collected simultaneously; flow rates up to 80 L min ⁻¹ possible, depending on equipment	many parts that are time consuming to assemble in the field; many analyses necessary for each sample; O-rings and grease used to collect largest particles may contaminate samples; without grease, particle bounce may be a problem; may bias partitioning of some submicron semivolatile organic compounds due to pressure drops
Dichotomous sampler (virtual impactor)	particles in stream impact against a mass of slowly moving air rather than a plate; this mass is drawn through a filter	no grease or surfaces that contaminate sample; commercially available with cut sizes at 2.5 and 10 μm (pm2.5 and pm10)	not generally available at different cut sizes, and 2.5 μm may not be the best choice; other size cuts are difficult to design

night at about 600°C, which should remove all organic compounds. However, a serious problem with this type of filter is adsorption of organic and CO₂ vapors. This causes a positive sampling artifact when only the particulate carbon is of interest. As stated above in the introduction to section 3, a related problem is volatilization of organic material from sample filters. These two problems have been investigated by *McDow and Huntzicker [1990]* and *Turpin et al. [1994]*. These authors present experiments that show that the concentration of organic material on quartz filters is dependent on the face velocity (the volumetric flow rate divided by the exposed area of the filter). As face velocity increases, the amount of organic material found on the filter decreases. Collection of elemental carbon (soot) is unaffected by face velocity. This effect is also seen when two quartz filters are sampled in tandem. There is always much more organic material found on a quartz backup filter when it is placed behind a Teflon filter instead of another quartz filter. After a series of calculations and laboratory experiments, both *McDow and Huntzicker [1990]* and *Turpin et al. [1994]* concluded that (1) quartz filters significantly adsorb organic vapors; (2) Teflon, which is inert and has a much lower surface area than quartz, does not significantly adsorb organic vapors; and (3) the face velocity dependence of organic material collected on quartz front filters can be eliminated by subtracting the organic carbon load on a backup quartz filter, sampled behind a Teflon filter at the same face velocity. These conclusions led to the recommendation of the type of sampling design shown in Figure 4.

Since the Teflon filter has been found not to adsorb vapor phase organics, it traps particles and allows vapors to pass through to the quartz filter (Q2 in Figure 4). Q1 receives both particles and vapor phase material. Thus a

measure of carbon just from particles is found by subtracting the organic carbon present on Q2 from that of Q1, or

$$(\text{particles} + \text{vapors}) - (\text{vapors}) = \text{particles.}$$

When sampling in this way, it is convenient to use the Teflon filter for other analytical methods, especially those that involve extraction with a solvent since the Teflon membrane is a fairly strong matrix, and the material extracted from this filter should represent mostly particulate phase material. This method works well when sampling in areas with large concentrations of gas phase organics compared with organic material in the particle phase, but it must be emphasized that it does not correct for volatilization artifacts. In pristine locations, where secondary aerosols make up a larger percentage of the total organic particle mass, volatilization

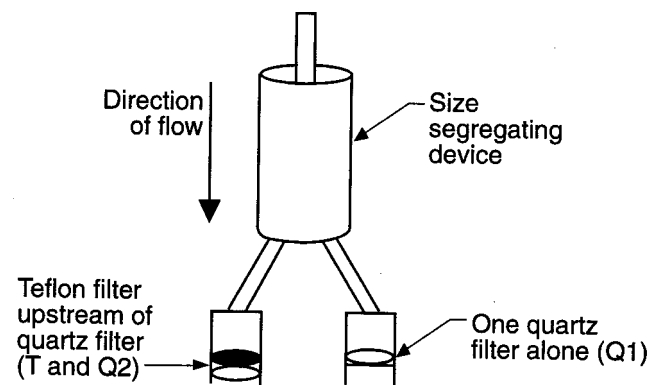


Figure 4. Scheme for sampling organic aerosols to minimize positive artifacts, as recommended by *McDow and Huntzicker [1990]* and *Turpin et al. [1994]*.

may be a larger artifact than adsorption. Volatilization from the Teflon filter preferentially adsorbs onto the quartz back filter and appears to register as an overcorrection for adsorption when sampling in such areas [Chow *et al.*, 1996].

It is important to point out that the majority of sampling campaigns through the 1980s were performed with filters without any attempts to correct for artifact. Depending on the location, the resultant errors associated with sampling alone can become extremely large. There are relatively little data available to suggest what the uncertainty might be. The Chow *et al.* [1996] study used several methods of aerosol collection in parallel, including the method shown in Figure 4, plus multistage impactors. The two methods gave different estimates of the sampling uncertainty. They found that in their remote locations, the organic carbon adsorbed onto quartz back filters was about 70% of the total apparent organic material collected on quartz front filters sampled in parallel, meaning that as little as 30% of the "organic carbon" analyzed on quartz front filters may have been truly particulate organic material and not adsorbed gases. The organic carbon/elemental carbon ratio measured on the impactor samples (not prone to adsorption artifacts) suggested that there should be less of a correction, with only 40% of the organic carbon on front quartz filters estimated being due to particulate material. Neither of these estimates takes into account the negative artifacts due to loss of semivolatile organics after particle deposition.

Other groups have used sampling methods for organics using denuders to remove gas phase material both upstream and downstream of the aerosol sampler [Appel *et al.*, 1983, 1989; Eatough *et al.*, 1993, 1996]. However, after a comparison study of denuded and undenuded filter sampling using all of the size segregation methods listed in Table 3, it was concluded that the methods employing denuders were not particularly consistent with one other in the amount of organic material they collect [Hering *et al.*, 1990]. This may be explained, at least in part, by a recent set of experiments that showed that certain semivolatile organics evaporate very quickly from the particle phase when passed through a denuder system [Kamens and Coe, 1997]. This implies that denuding the sample flow prior to filter collection may introduce large partitioning biases from ambient values. These problems with denuder sampling make it especially difficult to estimate the negative artifact due to volatilization for most studies. Eatough *et al.* [1996] suggest that perhaps 40% of aerosol carbon is volatilized during sampling, corresponding to a 67% positive correction that would have to be added for nondenuded samples. Thus the true amount of particle carbon on a noncorrected filter may only be accurate to within roughly a factor of 2 in either direction. Older data in particular must be reviewed critically with respect to these potentially large uncertainties due to artifacts. These high uncertainties are also problematic for

projects such as filter sampling from airplanes, which was considered recently [Novakov *et al.*, 1997]. In such studies, it is extremely difficult to make any corrections at all because of the small sampling times.

4. CHEMICAL ANALYSIS

Several methods are currently available to process and chemically analyze organic atmospheric aerosol samples. It is important to realize that the analysis conditions used with each of these methods will determine the chemical range of organic species analyzed. Thus, although certain methods are more appropriate for certain families of organic compounds, a given method should not automatically be associated with any particular fraction of organic aerosol. We have attempted to point out useful variations in each technique when possible and include cautionary notes where artifacts are commonly introduced. Appropriate applications of these methods for investigating specific environmental effects of organic aerosols are listed in Table 4.

4.1. Extraction

If chemical analysis is performed using a chromatographic method, aerosols collected on filters or impactor plates are subjected to an extraction procedure. In the case of analyzing rain, fog, or cloud water, the sampling strategy provides a natural extraction process where atmospheric water is the solvent. The selection of solvents and the method in which the sample is extracted is the critical first step that largely determines what is seen in the chemical analysis. Saxena and Hildemann [1996] provide a thorough review of the extraction characteristics of atmospheric organic carbon, pointing out that a significant fraction of material examined in most organic solubility studies is water soluble (one fifth to two thirds). Not all of this water-soluble material will dissolve into nonpolar solvents that are traditionally used in gas chromatography/mass spectrometry (GC/MS) analysis [Grosjean, 1975]. Thus, for a complete characterization, a more polar extraction fraction needs to be used alongside a nonpolar solvent. This may necessitate using different types of chemical analysis (e.g., liquid chromatography).

The physical nature of the extraction process may also be important to the chemical composition reported. Ultrasonic irradiation, which is very commonly used, works by creating cavitating gas bubbles in the solution. The interior of the collapsing bubbles may have temperatures near 5000 K and pressures of several hundred atmospheres [Suslick *et al.*, 1986; Shutilov, 1988]. These extreme conditions have led to the detection of hydroxyl radicals in water, which is the principle oxidant in the atmosphere. Also, a large variety of chemical reactions have been shown to be catalyzed or induced by ultrasound passing through solutions [Suslick, 1988]. It is evident that such harsh conditions could also induce

TABLE 4. Compilation of Suggested Measurements for Studying the Various Environmental Effects of Organic Aerosols

<i>Environmental Effect</i>	<i>Controlling Aerosol Property</i>	<i>Required Chemical Information</i>	<i>Candidate Analytical Methods</i>	<i>Ancillary Physical Measurements</i>
Photochemical smog	mass as a function of radius water content as a function of RH surface area distribution for adsorption of gases	gaseous emissions oxidant levels product molecular forms	GC/MS ion chromatography reverse-phase chromatography/MS	particle size distribution
Visibility, smoke plumes, direct climate forcing	complex index of refraction shape mass as a function of radius water content as a function of RH	molecular forms state of mixing total amounts of organic and inorganic carbon	TOCA GC/MS ion chromatography reverse-phase chromatography/MS single particle analysis	$f(\text{RH})$ light scattering light absorption size distribution
Indirect climate forcing	size distribution soluble mass Van't Hoff factor surface tension insoluble fraction solubility of slightly soluble matter	molecular forms of solutes as a function of size state of mixing	ion chromatography reverse-phase liquid chromatography/MS GC/MS single particle analysis	size distribution solubility surface tension as a function of concentration
Effects on rainwater chemistry	soluble mass Van't Hoff factor surface tension insoluble fraction solubility of slightly soluble matter pK_a of acidic species presence of metallic ions	molecular forms of solutes solution pH conductivity	ion chromatography reverse-phase liquid chromatography/MS GC/MS UV/visible spectrometry oxidation of soluble fraction	total solute mass
Physiological response: Toxicity and carcinogenicity	size distribution (breathability) solubility	molecular forms total carbon	ion chromatography reverse-phase liquid chromatography/MS GC/MS TOCA	size distribution
Biogeochemical cycling	size distribution (affects removal) gas-particle partitioning reactivity with oxidant molecules age of aerosol (older aerosol tends to be smaller, more polar molecules) solubility geographical placement	molecular forms state of mixing	ion chromatography reverse-phase liquid chromatography/MS GC/MS	source strengths

RH, relative humidity; GC/MS, gas chromatography/mass spectrometry; TOCA, thermal/optical carbon analysis.

changes in the chemistry of material collected in the atmosphere prior to analysis. The standard use of this extraction method should be reevaluated. Additionally, Soxhlet extraction, which is an extraction procedure that involves heating and refluxing the solvent, may cause thermal degradation of certain analytes.

Supercritical fluid CO_2 has been used to extract organic material from filters for subsequent separation and analysis by GC/MS [e.g., Hansen et al., 1995]. The method is extremely sensitive for detecting volatile compounds such as PAHs. Drawbacks are the cost of purchasing and maintaining such a system and the limitations of analyte polarity similar to conventional GC/MS.

4.2. Thermal/Optical Carbon Analysis

Thermal/optical carbon analysis (TOCA) is a technique for separating and measuring the total amount of organic and elemental carbon, generally from quartz filter samples. The technique was first reported by Cadle et al. [1980] but has been updated to correct for uncertainties in the distinction between the two types of carbon [Huntzicker et al., 1982; Chow et al., 1993]. This measurement is important in any study that involves extraction of material from filters because it allows measurement of the extraction efficiency. The first step in this type of analysis is to heat the sample under a stream of helium gas. This process liberates volatile organic

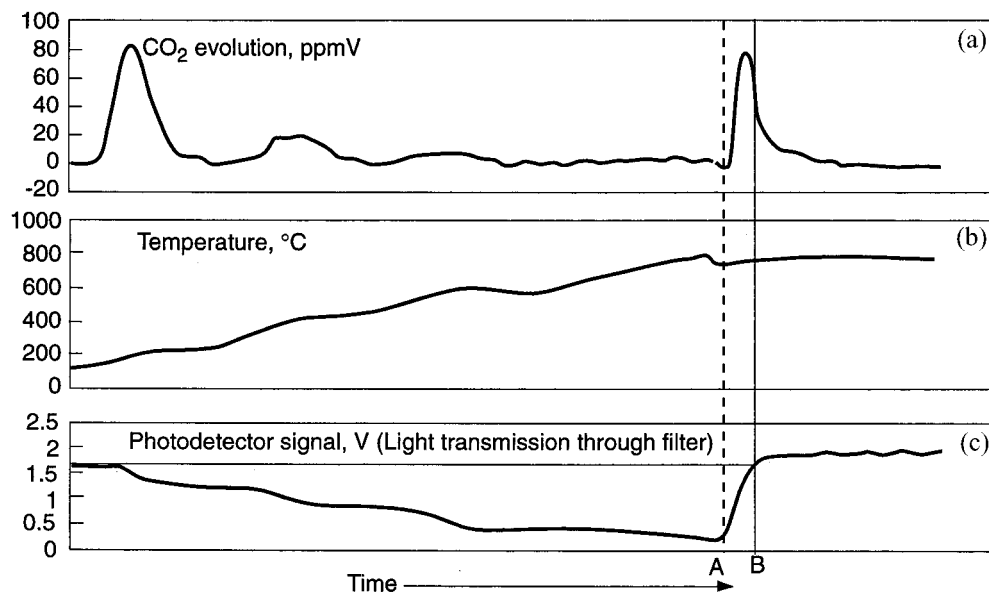


Figure 5. Carbon analysis output: (a) CO₂ evolution, (b) temperature, and (c) filter reflectance (all versus time). The large peak in the CO₂ trace at the end of the run is due to the oxidation of elemental carbon when oxygen is introduced into the carrier gas (at the point labeled A). This point coincides with the sharp rise in transmission of light through the filter. Evolved carbon is counted as elemental at the point when the transmission as measured with the photodetector returns to the preanalysis value (at the point labeled B). All of the carbon evolved prior to this point is assumed to be organic. The carbon evolved between points A and B is the amount charred during analysis, turning it into black carbon rather than being detected as organic compounds. Thus there is considerably less black carbon than the apparent quantity based on the CO₂ evolution curve.

compounds. These vapors pass over a catalyst and are mixed with a small amount of oxygen, which oxidizes the organic vapors to CO₂. The CO₂ is then either measured directly by nondispersive infrared spectrometry (NDIR) or in some cases passed through a methanator, which reduces the carbon to CH₄, which is then measured by flame ionization detection (FID). The temperature of the filter sample is raised slowly over the course of the experiment so that organic compounds of different volatility are released at different times from the filter. A typical temperature range is from 200°C to 800°C. Once the maximum temperature has been reached and organic compounds cease to be liberated from the sample, a small amount of oxygen is added to the gas mixture over the sample, still held at about 800°C. This causes combustion of any elemental carbon present on the filter. The vapors released in this process are also passed through the catalyst-O₂ mixture and analyzed in the same way as the CO₂ from the organic part of the analysis. Some groups [e.g., Chow *et al.*, 1993] only heat to 600°C during organic carbon analysis and continue to heat to 800°C after oxygen is added to the gas mixture.

A problem with this type of carbon analysis is that some organic compounds char during the initial heating stages, turning into elemental carbon. This leads to underestimation of organic carbon and overestimation of elemental carbon [Huntzicker *et al.*, 1982; Cadle *et al.*, 1983]. To correct for this problem, the reflection or

transmission of a helium/neon laser beam through the quartz filter is measured. Initially, light absorbed by the filter is due to elemental carbon present from sampling. During the organic volatilization step, light reflection and transmission drop as the filter becomes darker due to charring. During the elemental carbon combustion step, transmission increases as graphitic carbon is liberated from the filter. The cutoff between organic and elemental carbon can be given the operational definition as the point at which light absorption is equal to what it was on the filter initially [Huntzicker *et al.*, 1982; Chow *et al.*, 1993]. Typical output for this type of analysis is shown in Figure 5 (M. C. Jacobson, unpublished data, 1997). There are peaks for the concentration of carbon released at different temperatures. These signals are integrated to give the total mass of carbon on the analyzed section of filter, which is multiplied by the area of the filter and divided by the volume of air sampled to get the mass concentration ($\mu\text{g m}^{-3}$) of carbon in the atmosphere. For organic compounds this concentration is generally multiplied by values ranging from 1.2 to 1.8 to give the mass concentration of organic material because of carbon to organic compound mass ratio [Chow *et al.*, 1993]. This factor is a source of uncertainty in the measurement, and the best value to use may depend on the location. Calibration is generally carried out by injection and combustion of a known mass of methane, which is the most difficult organic compound to oxidize.

Although this is a useful method in combination with other measurements, it provides very little insight into the types or sources of organic compounds present. The limit of detection using this method is approximately $1.0 \mu\text{g C cm}^{-2}$ of quartz filter. This figure includes both organic and elemental carbon. The uncertainty is approximately $\pm 0.1 \mu\text{g}$.

4.3. Carbon Isotope Analysis

The ratios of the carbon isotopes ^{13}C and ^{14}C to the most common carbon isotope, ^{12}C , have been used with some success to demonstrate the sources of carbonaceous aerosols. Differences in the $^{13}\text{C}/^{12}\text{C}$ ($\delta^{13}\text{C}$) ratio are caused by chemical fractionation processes (e.g., during photosynthesis or atmospheric oxidation). Carbon 14, on the other hand, is radioactive, so its presence is a function of age. This isotope is generated in the upper atmosphere by cosmic radiation and is subsequently mixed into the troposphere. Contemporary sources of carbon (i.e., non-fossil-fuel carbon, plants and trees) have a ^{14}C content that is comparable to the atmospheric concentration at the time it was formed; thus ^{14}C is a unique tracer for vegetative emissions (natural emissions and biomass burning). Carbon released in fossil fuel emissions has almost no ^{14}C because it is much older than the half-life of ^{14}C (5726 years).

The $\delta^{13}\text{C}$ ratio is expressed in parts per thousand (‰) compared with a standard, generally a sample of Cretaceous belemnite from the Pee Dee formation in North Carolina called PDB-1 such that

$$\delta^{13}\text{C} = \left[\left(\frac{^{13}\text{C}_{\text{sample}}}{^{12}\text{C}_{\text{sample}}} \bigg/ \frac{^{13}\text{C}_{\text{std}}}{^{12}\text{C}_{\text{std}}} \right) - 1 \right] \times 1000. \quad (12)$$

Measuring $\delta^{13}\text{C}$ from an aerosol sample starts with a procedure similar to that used in TOCA. Samples are collected on quartz fiber filters and are dry combusted to about 1000°C to release organic and elemental carbon and oxidize it to CO_2 . After removal of water and other contaminants using a series of cold traps, the CO_2 is passed into an isotope ratio mass spectrometer [Chesselet et al., 1981; Cachier, 1989]. Other studies have examined the $\delta^{13}\text{C}$ ratio of individual compounds, for example, from rainwater by initial separation with liquid chromatography. After collecting individual fractions and drying, the residue is oxidized to CO_2 and analyzed in the same way [Sakugawa and Kaplan, 1995]. The value of $\delta^{13}\text{C}$ obtained for a mixture can be considered as the weighted average of the individual $\delta^{13}\text{C}$ values of the components making up the mixture [Chesselet et al., 1981; Cachier, 1987]. Marine sources are generally enriched in ^{13}C with $\delta^{13}\text{C}$ of $-20\text{‰} \pm 2\text{‰}$ [Fontugne and Duplessy, 1981], which is the isotopic composition of the seawater surface in most temperate parts of the ocean. Continental source carbonaceous aerosol is about $-26\text{‰} \pm 2\text{‰}$, which has also been found in fine aerosol samples in marine locations [Cachier et al., 1986]. The coarser particles in this study seemed to come from

sea-salt particles, whereas the fine particles were interpreted to have continental sources.

There are two methods of determining ^{14}C . The simpler method is to oxidize the sample to CO_2 followed by purification and direct counting of β particles by low-level gas proportional counters [Cooper et al., 1981]. This method requires about 100 mg of sample. The second method is accelerator mass spectrometry [Klouta et al., 1984]. In this technique the sample is oxidized to CO_2 and purified, followed by transition into graphite. The sample is introduced into an ion accelerator and bombarded by cesium ions. This releases C^- ions, which are extracted and stripped of four electrons to produce $^{14}\text{C}^{+3}$ and $^{13}\text{C}^{+3}$. The ratio of these ions is then measured by a $\Delta E/E$ nuclear detector and a Faraday cup, respectively. Although this method is much more complex, it can be used to analyze submilligram quantities of sample. This method was used recently to help apportion sources of carbonaceous aerosol in the Los Angeles area [Hildemann et al., 1994a]. Recent work has allowed analysis of individual compounds separated by GC followed by off-line accelerator mass spectrometry [Currie et al., 1997].

4.4. Gas Chromatography/Mass Spectrometry (GC/MS) and High-Resolution GC (HRGC)

GC/MS has by far been the most common means of identifying organic compounds in atmospheric aerosol. The reason is that GC can be used to separate a very wide range of compounds on a single column, and the simple on-line coupling to mass spectrometry (generally electron-impact quadrupole) makes compound identification relatively straightforward. This method has been invaluable in showing that organic particulate matter contains large numbers of different chemical compounds. There are, however, limitations associated with this technique that prevent a complete characterization of the organic fraction if it is used alone.

The number of authors using GC/MS for aerosol characterization is too numerous to list here, but some representative works are those by Mazurek et al. [1987], who describe sample preparation and transfer practices that have become standard in this area, and Rogge et al. [1993a], who were the first to examine in-depth the abilities and limitations of current GC/MS technology as applied to atmospheric organic particles. Saxena and Hildemann [1996] also present a thorough discussion of some problems in using GC/MS alone for identifying atmospheric organic compounds. A few of these problems are related to gas chromatography itself: Polar solvents, especially aqueous solutions, cannot be introduced onto the GC column, which prevents the most polar constituents from entering the extract. Furthermore, even polar compounds such as carboxylic acids which do dissolve into certain nonpolar media may bind so strongly to the GC column that they will not elute or may not be sufficiently volatile. These compounds must first be derivitized to less polar forms. Diazomethane is

commonly used for this purpose, but it may not effectively react with many polar compounds present. The result of these two limitations is that only a fraction of the organic carbon is extracted, and that which is extracted may only partially elute. Of the compounds that elute, only a fraction may be separated into individual compounds such that they are unambiguously identified by the mass spectrometric method, which is appropriate for compounds having molecular weight up to about 600 amu.

As an alternative to measurements of individual compounds, high-resolution GC (HRGC) alone has been investigated to determine if it is appropriate for measuring total organic mass as well as for separating organic material into different compound classes on the basis of retention time alone [Hildemann et al., 1994b]. The method is much faster than GC/MS and appears to be able to account for between 56% and 91% of fine organic aerosol in the Los Angeles area. However, it carries with it some of the same problems described above for GC/MS in terms of extraction and elution of polar compounds.

Finally, one of the first sets of studies on organic aerosols utilized direct injection of material into a high-resolution mass spectrometer [Schuetzle, 1972; Cronn, 1975]. The absence of the GC step removes the problems associated with extraction and elution of material from the column. Organic material that was collected on gold impactor plates was thermally desorbed directly into the mass spectrometer. Some separation was possible by ramping the temperature of the sample. Although the separation achieved using this method was not as complete as what is possible with GC, a very wide range of chemical compounds were identified, including a large number of polar dicarboxylic acids in several urban areas. A perturbation of this technique has recently been used with addition of the GC step to make measurements of organic aerosol [Velikamp et al., 1996]. In that study, aerosol was collected directly into an apparatus that was also used to thermally desorb and inject material directly into a GC/MS. This method requires no solvent extraction, but the disadvantage is that polar compounds are still lost to the GC column. Other less polar material is efficiently separated, and short sampling times are possible.

4.5. Liquid Chromatography (LC) and LC/MS

Compared with GC and GC/MS methods, liquid chromatography (LC) has seldom been used for the study of organic aerosols. This is probably because of the convenience of GC methods in using a single column and only needing to change the temperature in order to analyze for different compound classes. LC methods employ a very wide range of different types of columns, many designed to separate analytes within a narrow compound class. Given the current need to identify large numbers of unknown compounds, this has not been the most convenient route to take, but since GC/MS appears

capable of accounting for only about 25% of carbonaceous mass in most locations, other methods such as LC should be considered in order to fill in the gaps.

There are two distinct advantages in using LC methods, especially for polar compounds: First, aqueous solutions can be injected onto many columns, and second, polar compounds do not need to go through a derivitization step in order to elute from most LC columns. This combination of being able to introduce relevant extract solutions directly into the system reduces the analysis time and losses substantially. The main disadvantage, besides the targeting of specific compound classes, is that LC methods are not easily coupled to mass spectrometer systems.

Most of the atmospheric work involving LC with organic compounds has been for the analysis of organic acids in aqueous solution using ion exchange chromatography [Weathers et al., 1988; Munger et al., 1989; Li and Winchester, 1993]. Other uses have been mainly preparatory, for separating compounds with wide ranges of polarity for eventual injection into a GC system [Ip et al., 1984; Bushby et al., 1993].

The use of liquid chromatography coupled to mass spectrometry is promising in this research area. There are two types of interfaces available between the LC and MS systems: electrospray and particle beam. With the electrospray interface, solvent from the LC system enters a charged metal needle. The charge causes the liquid passing through it to break up into very small droplets. The solutes present in the liquid also become ionized in the process. The droplets are evaporated, and the ions produced are electrically introduced into a quadrupole mass spectrometer. This method generally produces only parent ions but is sensitive for masses corresponding to proteins, which may be useful for some areas of atmospheric research, especially the investigation of large biomolecules such as humic substances. Certain eluent conditions must be met in order to maintain a good spray and ionization, including a certain minimum amount of organic solvent and a certain maximum amount of sodium or potassium, both of which could be problematic depending on the type of LC separation chosen. Electrospray LC/MS has been used for measurement of hydroxymethanesulfonate in rain [Chapman et al., 1990].

The particle beam interface creates an aerosol out of the eluent emerging from the LC column by using an inert gas nebulizer. The particles are heated to evaporate the liquid and are introduced into an electron impact chamber, where ionization takes place, followed by mass selection in the mass spectrometer. The advantage of this technique is that electron impact is used in GC/MS and produces many mass fragments in spectra that are predictable and are found in search libraries. Behymer et al. [1990] investigated this technique for analyzing a variety of environmentally relevant organic compounds that are problematic in a GC/MS setup.

Their study, however, did not include atmospheric compounds.

4.6. Single Particle Analysis (Electron Microscopy and Laser Methods)

Electron microscopy in combination with electron probe X-ray microanalysis (EPXMA) has been valuable in analyzing single particles for size, morphology, and chemical composition [Jambers *et al.*, 1995]. This technique can be performed on particles on porous filters or impactor plates. Other types of single particle analysis are currently in the development stages and involve laser ablation of particles as they enter a sampling inlet, followed by time-of-flight mass spectroscopy [Johnston and Wexler, 1995; Murphy and Thompson, 1995]. These methods can determine the presence of carbon in a sample but cannot yet identify individual compounds.

5. SUGGESTIONS FOR FURTHER RESEARCH

On the basis of the environmental issues listed in section 1.3, a number of basic scientific questions arise that point the direction for further research on organic atmospheric aerosols. We suggest the following, in approximate order of importance: (1) What is the spatial distribution of carbonaceous aerosol globally and locally? (2) What is the fraction of organic versus elemental carbon? (3) What fraction of this aerosol is water soluble? (4) What is the size distribution of this aerosol? (5) What are the principle sources and fluxes of this aerosol? (6) What chemical compounds are present in the organic fraction? (7) What physical properties do these compounds have (index of refraction, water solubility, toxicity)? (8) What is the time variability of these properties? (9) What radiative forcings can be apportioned to this aerosol (scattering, absorption, and effects on cloud droplet growth and droplet size)?

To begin to answer these questions more fully, we suggest the following series of recommendations. The first recommendations are those that can be initiated directly that will make data collected more useful to a wide range of research questions and involve measurements that can be implemented with existing technology. We suggest additional projects and measurements in our later recommendations that require equipment or measurements that require improvements over our current range of technical capabilities. The purposes of these recommendations are to indicate the strategy we believe should be taken in the long term toward answering these questions and to start a dialog in the scientific community about the technology needed to develop these projects.

5.1. Parameterized Sampling

One of the major challenges in sampling carbonaceous particles is collecting sufficient amounts of material to be analyzed while still sampling on timescales that

are shorter than the meteorological processes that carry material from the source to the point of collection. This problem is not unique to sampling organic aerosols, but the challenge may be more acute because of the large number of individual compounds possibly making up the sample, low concentrations in remote locations, and the demands of the various analytical methods for a certain minimum amount of mass. Our first recommendation is to parameterize all sampling that is performed away from sources according to additional measurements that indicate changes in air mass or sources to avoid contamination by spurious pollution episodes. The additional parameters used to govern sampling will vary by location, but an example of such an approach would be changing or stopping sampling when there is a wind change out of a specified sector or during large changes in particle concentrations. Up to this point the majority of investigations and monitoring projects involving carbonaceous aerosols have not utilized this type of sampling strategy.

5.2. Total Organic and Elemental Carbon Concentration

Total carbon and the fraction that is organic are relevant to all of the environmental issues listed in the introduction. This measurement is possible with existing technology (e.g., TOCA; see section 4) and could be implemented immediately. As evidenced by Lioussé *et al.* [1996] and Penner *et al.* [1996], a detailed, comparable set of measurements from a wide range of locations around the world would be very helpful for modeling both the biogeochemical transport and climatic effects of carbonaceous aerosols. The current models described in these references utilize data that have very large uncertainties, especially in remote locations. To be useful in such studies, individual measurements must be collected and analyzed according to similar protocol, so planning for measurements should include input from the modeling community.

5.3. Water-Soluble Fraction of Total Carbon

Measurement of the water-soluble fraction is a relatively simple extension of the total carbon measurement and supplies valuable clues regarding the chemistry of organic aerosol and its interaction with water vapor as described in section 2.4. The simplest way of determining this fraction is to measure total carbon before and after treatment with water. We suggest that this measurement be done twice per sample: one measurement with a large excess of water and one measurement with approximately the same amount of liquid water available in atmospheric clouds. The excess water experiment provides an analytical estimate of the fraction that is difficult to characterize using traditional GC/MS. This can be compared with the “unanalyzed fraction” always present in such experiments to attempt mass balance of the type of compounds making up this unknown fraction. The experiment with atmospherically realistic

amounts of water roughly gives the mass of organic carbon likely to enter aqueous solution in cloud droplets. The amount of water available is calculated from the average liquid water content (g m^{-3}) divided by the mass concentration of carbon ($\mu\text{g m}^{-3}$). The amount of water to use in the soaking experiment is then calculated by multiplying this figure by the amount of organic carbon (in micrograms) on the filter section to be analyzed. Although this is a very simple procedure, it may be difficult or impossible to make this measurement with low mass concentration of carbon, since it would require using extremely small volumes of water. Thus the ability to make this measurement will vary from location to location and will also depend on sampling time. Also, other physical and chemical variables, such as the amount of agitation, exposure to ultrasonic treatment, solution pH, and ionic strength, become important in determining the amount of carbon that enters the solution when there is a low ratio of water to carbon mass.

5.4. Composition of Water-Soluble Carbon

Organic compounds have successfully been analyzed in rainwater using the wet chemical methods outlined by *Likens et al.* [1983]. In their study, more than 80% of dissolved organic carbon could be identified as carboxylic acids, aldehydes, carbohydrates, tannin/lignin, primary amines, or phenols in rainwater collected in up-state New York. Although they do not in most cases yield actual molecular form information, these methods can be applied to water extracts from filter samples and give major organic functionality of the water-soluble fraction. Since it is the more polar fractions that are most difficult to analyze using GC/MS, a combination of water extraction and this type of wet chemical analysis followed by organic extraction and GC/MS on the same filter would provide significant improvement over the traditional protocol, which generally calls for organic extraction–GC/MS alone.

5.5. Characterization of Major Sources

Although it is very difficult to collect and analyze organic aerosol, especially in clean and remote locations, there are many obvious primary sources of organic and black carbon aerosols that have not been thoroughly characterized chemically or isotopically. Biomass burning (especially savanna fires) and fossil fuel combustion are thought to be the major sources of primary organic aerosol and the only sources of black carbon aerosol, as discussed in section 2.2.1. Sampling of enough material to analyze from these sources would be comparably simple, and chemical information (especially on the water-soluble fraction) is severely lacking yet possible to obtain with existing technology. We recommend that these sources be sampled and analyzed using the methods outlined above for ambient aerosol: determination of organic/elemental carbon ratio, determination of soluble/insoluble fraction with excess and nonexcess of water, determination of major functionality of water-

soluble fraction, GC/MS analysis of nonsoluble fraction, and isotopic analysis (as discussed in the next section).

5.6. Isotope Analysis

Analysis of $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ was discussed in section 4. These methods remain some of the most powerful tools available for source determination. The $^{13}\text{C}/^{12}\text{C}$ ratio of ambient aerosol is especially useful when compared with measurements of suspected sources. Several source regions have been characterized isotopically by *Cachier* [1987, 1989]. This work should be expanded and continued with isotopic measurement of the sources listed in section 2.2.1 and coordinated with isotopic measurements and the other measurements listed above for ambient aerosol. The $^{14}\text{C}/^{12}\text{C}$ ratio is less convenient to measure but is very helpful in determining whether a sample is composed of fossil or contemporary carbon. We recommend that this measurement be done on a more regular basis with concurrent chemical measurements of ambient aerosol as listed above in sections 5.1–5.4.

5.7. General Aerosol Information

Along with the chemical measurements listed, certain physical measurements of ambient aerosol allow a more complete understanding of the aerosol's environmental effects when collected simultaneously with filter samples for chemical analysis. These measurements can generally be performed with commercially available instrumentation and have been included under "ancillary measurements" in Table 4. The two most important sets of measurements relevant to these environmental effects are size distribution and optical extinctions (i.e., scattering and absorption coefficients). Size distribution is the primary physical parameter controlling removal rates, optical properties, cloud droplet growth properties, and breathability. Measurement is relatively straightforward with commercially available instruments such as scanning differential mobility analyzers (DMA) combined with a condensation particle counter (CPC) for fine particles and optical particle counters for larger sizes. Routine size distribution measurements will allow correlation of the composition and size distribution for determining particle formation mechanisms and also will allow determination of the degree of internal consistency in a mass determination via size distribution and chemical analysis. However, before recommending that this be done routinely, it is imperative to establish a protocol by which the chemical and physical data sets will be integrated, which is seldom done and is not always easy. Nonetheless, calculation of sensitivities (i.e., the partial derivative of some property or effect x with respect to chemical variable y) requires the integration of such data sets. The problem is less complex for scattering and absorption coefficients measured optically. Coefficient averages from multiple least squares regression analyses can be directly compared with chemical measurements over the aerosol sampling time to

determine the dependence of these optical properties on whatever chemical concentration data are available. Scattering efficiency varies between the various atmospheric aerosol components, so for realistic estimations of climate impact, complete chemical analysis and multivariate statistics from a variety of regions and seasons are needed [Charlson et al., 1999].

5.8. Chemical Analysis

It would appear that the most difficult problem facing the scientific community in the study of carbonaceous aerosols is the lack of reliable forms of chemical analysis to elucidate the hundreds of compounds that may compose a single aerosol sample. Along with the above recommendations, additional work must go into development of analytical methods that will yield a complete mass balance of organic carbon. Chromatographic and mass spectrometric methods, especially LC/MS and direct mass spectrometry of individual aerosol particles, hold great promise in helping to elucidate the balance of the unidentified organic mass fraction. These analytical developments must continue along with the suggestions listed above that can be implemented right away.

6. CONCLUSION

There are important environmental effects of carbonaceous aerosols that depend on their physical and chemical properties, such as size, water solubility, and index of refraction. These properties are determined by their sources and the conditions to which the particles have been subjected. The wide range of properties associated with organic aerosols requires that an integrated approach be used for their meaningful study. Although a great deal of knowledge has been gained in seeing the potential ramifications of carbonaceous particles in the environment, our understanding remains limited without reliable methods to completely characterize this fraction. By presenting the various aspects of carbonaceous aerosols in a single paper, we hope to encourage cooperation between research groups with seemingly large differences in research interests. This philosophy will help elucidate this ubiquitous and complicated aerosol fraction.

ACKNOWLEDGMENTS. The authors acknowledge the United States Fulbright Program and the Fulbright Commission in Stockholm, who funded a great deal of the work in this paper.

Michael Coffey was the Editor responsible for this paper. He thanks Dan Murphy and an anonymous reviewer for the technical reviews and Barb Dutrow for the cross-disciplinary review.

REFERENCES

- Andreae, M. O., Biomass burning: Its history, use, and distribution and its impact on environmental quality and global climate, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 3–21, MIT Press, Cambridge, Mass., 1991.
- Andreae, M. O., et al., Biomass-burning emissions and associated haze layers over Amazonia, *J. Geophys. Res.*, 93(D2), 1509–1527, 1988.
- Andrews, E., and S. M. Larson, Effect of surfactant layers on the size change of aerosol particles as a function of relative humidity, *Environ. Sci. Technol.*, 27, 857–865, 1993.
- Appel, B. R., S. M. Wall, and R. S. Knights, Characterization of carbonaceous materials in atmospheric aerosols by high-resolution mass spectrometric thermal analysis, *Adv. Environ. Sci. Technol.*, 9, 353–365, 1980.
- Appel, B. R., Y. Tokiwa, and E. L. Kothny, Sampling of carbonaceous particles in the atmosphere, *Atmos. Environ.*, 17, 1787–1796, 1983.
- Appel, B. R., W. Cheng, and F. Salaymeh, Sampling of carbonaceous particles in the atmosphere, II, *Atmos. Environ.*, 23, 2167–2175, 1989.
- Ballschmiter, K., Transport and fate of organic compounds in the global environment, *Angew. Chem. Int. Ed. Engl.*, 31(5), 487–515, 1992.
- Behymer, T. D., T. A. Bellar, and W. L. Budde, Liquid chromatography/particle beam/mass spectrometry of polar compounds of environmental interest, *Anal. Chem.*, 62, 1686–1690, 1990.
- Bigg, E. K., Discrepancy between observation and prediction of concentrations of cloud condensation nuclei, *Atmos. Res.*, 20, 82–86, 1986.
- Bushby, B., A. Fernandes, D. Wallace, and M. Kibblewhite, Determination of trace organic micropollutants in atmospheric deposition, *Sci. Total Environ.*, 135, 81–94, 1993.
- Cachier, H., Atmospheric particulate carbon cycle: Evidence from isotopic measurements, Ph.D. dissertation, Univ. de Paris, Paris, 1987.
- Cachier, H., Isotopic characterization of carbonaceous aerosols, *Aerosol Sci. Technol.*, 10, 379–385, 1989.
- Cachier, H., P. Buat-Menard, M. Fontugne, and R. Chesselet, Long-range transport of continentally-derived particulate carbon in the marine atmosphere: Evidence from stable carbon isotope studies, *Tellus, Ser. B*, 38, 161–177, 1986.
- Cachier, H., M.-P. Bremond, and P. Buat-Menard, Carbonaceous aerosols from different tropical biomass burning sources, *Nature*, 340, 371–373, 1989.
- Cadle, S., P. J. Groblicki, and D. P. Stroup, Automated carbon analyzer for particulate samples, *Anal. Chem.*, 52, 2201–2206, 1980.
- Cadle, S. M., P. J. Groblicki, and P. A. Mulawa, *Problems in the Sampling and Analysis of Carbon Particulate*, Gen. Motors, Warren, Mich., 1983.
- Cautreels, W., and K. Van Cauwenberghe, Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase, *Atmos. Environ.*, 12, 1133–1141, 1977.
- Chameides, W. L., and D. D. Davis, Aqueous-phase source of formic acid in clouds, *Nature*, 304, 427–429, 1983.
- Chapman, E. G., C. J. Borinaga, and H. R. Udseth, Confirmation and quantitation of hydroxymethanesulfonate in precipitation by electrospray ionization-tandem mass spectrometry, *Atmos. Environ.*, 24, 2951–2957, 1990.
- Charlson, R. J., T. L. Anderson, and H. Rodhe, Direct climate forcing by anthropogenic aerosols: Quantifying the link between atmospheric sulfate and radiation, *Contrib. Atmos. Phys.*, 72(1), 79–94, 1999.
- Chesselet, R., M. Fontugne, P. Buat-Menard, U. Ezat, and

- C. E. Lambert, The origin of particulate organic carbon in the marine atmosphere as indicated by its stable carbon isotopic composition, *Geophys. Res. Lett.*, 8(4), 345–348, 1981.
- Chiou, C. T., D. E. Kile, and R. L. Malcolm, Sorption of vapors of some organic liquids on soil humic acid and its relation to partitioning of organic compounds in soil organic matter, *Environ. Sci. Technol.*, 22, 298–303, 1988.
- Chow, J. C., J. G. Watson, L. C. Pritchett, W. R. Pierson, C. A. Frazier, and R. G. Purcell, The DRI thermal/optical reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies, *Atmos. Environ., Part A*, 27, 1185–1201, 1993.
- Chow, J. C., J. G. Watson, Z. Lu, D. H. Lowenthal, C. A. Frazier, P. A. Solomon, R. H. Thuillier, and K. Magliano, Descriptive analysis of PM_{2.5} and PM₁₀ at regionally representative locations during SJVAQS/AUSPEX, *Atmos. Environ.*, 30, 2079–2112, 1996.
- Cooper, J. A., L. A. Currie, and G. A. Klouda, Assessment of contemporary carbon combustion source contributions to urban air particulate levels using carbon-14 measurements, *Environ. Sci. Technol.*, 15, 1045–1050, 1981.
- Cronn, D. R., Analysis of atmospheric aerosols by high resolution mass spectrometry, Ph.D. dissertation, Univ. of Wash., Seattle, 1975.
- Cunningham, K. M., M. C. Goldberg, and E. R. Weiner, The aqueous photolysis of ethylene glycol adsorbed on goethite, *Photochem. Photobiol.*, 41, 409–416, 1985.
- Currie, L. A., T. I. Eglinton, B. A. Benner, and A. Pearson, Radiocarbon “dating” of individual chemical compounds in atmospheric aerosol: First results comparing direct isotopic and multivariate statistical apportionment of specific polycyclic aromatic hydrocarbons, *Nucl. Instrum. Methods, Sect. B*, 233(2), 265–271, 1997.
- Duce, R. A., Speculations on the budget of particulate and vapor phase nonmethane organic carbon in the global troposphere, *Pure Appl. Geophys.*, 116, 244–273, 1978.
- Duce, R. A., V. A. Mohnen, P. R. Zimmerman, D. Grosjean, W. Cautreels, R. Chatfield, R. Jaenicke, J. A. Ogren, E. D. Pellizzari, and G. T. Wallace, Organic material in the global troposphere, *Rev. Geophys.*, 21(4), 921–952, 1983.
- Eatough, D. J., A. Wadsworth, D. A. Eatough, J. W. Crawford, L. D. Hansen, and E. L. Lewis, A multiple-system, multichannel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere, *Atmos. Environ.*, 27, 1213–1219, 1993.
- Eatough, D. J., D. A. Eatough, L. Lewis, and E. L. Lewis, Fine particulate chemical composition and light extinction at Canyonlands National Park using organic particulate material concentrations obtained with a multisystem, multichannel diffusion denuder sampler, *J. Geophys. Res.*, 101(D14), 19,515–19,531, 1996.
- Edmonds, R. L. (Ed.), *Aerobiology: The Ecological Systems Approach*, Van Nostrand Reinhold, New York, 1979.
- Erel, Y., S. O. Pehkonen, and M. R. Hoffmann, Redox chemistry of iron in fog and stratus clouds, *J. Geophys. Res.*, 98(D10), 18,423–18,434, 1993.
- Falconer, R. L., and T. F. Bidleman, Vapor pressures and predicted particle/gas distributions of polychlorinated biphenyl congeners as functions of temperature and ortho-chlorine substitution, *Atmos. Environ.*, 28, 547–554, 1994.
- Faust, B. C., and M. R. Hoffmann, Photoinduced reductive dissolution of hematite by bisulfite, *Environ. Sci. Technol.*, 20, 943–948, 1986.
- Fehsenfeld, F., J. Calvert, R. Fall, P. Goldman, A. B. Guenther, C. N. Hewitt, B. Lamb, S. Liu, M. Trainer, H. Westberg, and P. Zimmerman, Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Global Biogeochem. Cycles*, 6(4), 389–430, 1992.
- Finlayson-Pitts, B. J., and J. N. J. Pitts, *Atmospheric Chemistry*, John Wiley, New York, 1986.
- Folger, D. W., Wind transport of land-derived mineral, biogenic and industrial matter over the North Atlantic, *Deep Sea Res.*, 17, 337–352, 1970.
- Fontugne, M., and J. C. Duplessy, Organic isotopic fractionation by marine plankton in the temperature range –1 to 31 degrees C, *Oceanol. Acta*, 4, 85–90, 1981.
- Fuzzi, S., P. Mandrioli, and A. Peretto, Fog droplets—An atmospheric source of secondary biological aerosol particles, *Atmos. Environ.*, 31, 287–290, 1997.
- Gagosian, R. B., O. C. Zafriou, E. T. Peltzer, and J. B. Alford, Lipids in aerosols from the tropical North Pacific: Temporal variability, *J. Geophys. Res.*, 87(C13), 11,133–11,144, 1982.
- Galloway, J. N., G. E. Likens, and E. S. Edgerton, Acid precipitation in the northeastern United States: pH and acidity, *Science*, 194, 722–724, 1976.
- Galloway, J. N., G. E. Likens, W. C. Keene, and J. N. Miller, The composition of precipitation in remote areas of the world, *J. Geophys. Res.*, 87(11), 8771–8786, 1982.
- Gill, P. S., T. E. Graedel, and C. J. Weschler, Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes, *Rev. Geophys.*, 21(4), 903–920, 1983.
- Graedel, T. E., Terpenoids in the atmosphere, *Rev. Geophys.*, 17(5), 937–947, 1979.
- Graedel, T. E., and C. J. Weschler, Chemistry within aqueous atmospheric aerosols and raindrops, *Rev. Geophys.*, 19(4), 505–539, 1981.
- Gray, H. A., G. R. Cass, J. J. Huntzicker, E. K. Heyerdahl, and J. A. Rau, Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles, *Environ. Sci. Technol.*, 20, 580–589, 1986.
- Gribble, G. W., Naturally occurring organohalogen compounds—A survey, *J. Nat. Prod.*, 55(10), 1353–1395, 1992.
- Grosjean, D., Solvent extraction and organic carbon determination in atmospheric particulate matter: The organic extraction–organic carbon analyzer (OE–OCA) technique, *Anal. Chem.*, 57, 797–805, 1975.
- Grosjean, D., Aerosols, in *Ozone and Other Photochemical Oxidants*, chap. 3, pp. 42–125, Natl. Acad. of Sci., Washington, D. C., 1977.
- Grosjean, D., Secondary organic aerosol: Identification and mechanisms of formation, paper presented at the Carbonaceous Particles in the Atmosphere Conference, Natl. Sci. Found., Berkeley, Calif., March 20–22, 1978.
- Grosjean, D., and S. K. Friedlander, Formation of organic aerosols from cyclic olefins and diolefins, in *The Character and Origins of Smog Aerosols*, edited by G. Hidy, pp. 435–476, John Wiley, New York, 1979.
- Grosjean, D., and J. H. Seinfeld, Parameterization of the formation potential of secondary organic aerosols, *Atmos. Environ.*, 23, 1733–1747, 1989.
- Grosjean, D., J. P. Smith, T. M. Mischke, and J. N. Pitts Jr., Chemical and physical transformations in urban-suburban transport of air pollutants, in *Atmospheric Pollution*, edited by M. M. Benarie, pp. 549–563, Elsevier Sci., New York, 1976.
- Guiang, S. F., III, S. V. Krupa, and G. C. Pratt, Measurements of S(IV) and organic anions in Minnesota rain, *Atmos. Environ.*, 18, 1677–1682, 1984.
- Hahn, J., Organic constituents of natural aerosols, in *Aerosols: Anthropogenic and Natural, Sources and Transport*, pp. 359–376, N. Y. Acad. of Sci., New York, 1979.
- Hansen, K. J., B. N. Nansen, E. Cravens, and R. E. Sievers, Supercritical-fluid extraction gas-chromatographic analysis

- of organic compounds in atmospheric aerosols, *Anal. Chem.*, *67*, 3541–3549, 1995.
- Hansson, H.-C., A. Wiedensohler, M. J. Rood, and D. S. Covert, Experimental determination of the hygroscopic properties of organically coated aerosol particles, *J. Aerosol Sci.*, *21S*, S241–S244, 1990.
- Hansson, H.-C., M. J. Rood, S. Koloutsou-Vakakis, K. Hameri, D. Orsini, and A. Wiedensohler, NaCl aerosol particle hygroscopicity dependence on mixing with organic compounds, *J. Atmos. Chem.*, *31*, 321–346, 1998.
- Hatakeyama, S., T. Tanonaka, J. Weng, H. Bandow, H. Takagi, and H. Akimoto, Ozone-cyclohexene reaction in air: Quantitative analysis of particulate products and the reaction mechanism, *Environ. Sci. Technol.*, *19*, 935–942, 1985.
- Hatakeyama, S., M. Ohno, J. Weng, H. Takagi, and H. Akimoto, Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, *Environ. Sci. Technol.*, *21*, 52–57, 1987.
- Heintzenberg, J., Fine particles in the global troposphere: A review, *Tellus, Ser. B*, *41*, 149–160, 1989.
- Hering, S. V., et al., Comparison of sampling methods for carbonaceous aerosols in ambient air, *Aerosol Sci. Technol.*, *12*, 200–213, 1990.
- Hidy, G. M., P. K. Mueller, D. Grosjean, B. R. Appel, and J. J. Wesolowski (Eds.), *The Character and Origins of Smog Aerosols: A Digest of Results From the California Aerosol Characterization Experiment (ACHEX)*, 776 pp., John Wiley, New York, 1980.
- Hildemann, L. M., D. B. Klinedinst, G. A. Klouda, L. A. Currie, and G. R. Cass, Sources of urban contemporary carbon aerosol, *Environ. Sci. Technol.*, *28*, 1565–1576, 1994a.
- Hildemann, L. M., M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Seasonal trends in Los Angeles ambient organic aerosol observed by high-resolution gas chromatography, *Aerosol Sci. Technol.*, *20*, 303–317, 1994b.
- Hildemann, L. M., W. F. Rogge, G. R. Cass, M. A. Mazurek, and B. R. T. Simoneit, Contribution of primary aerosol emissions from vegetation-derived sources to fine particle concentrations in Los Angeles, *J. Geophys. Res.*, *101*(D14), 19,541–19,549, 1996.
- Hinckley, D. A., T. F. Bidleman, and C. P. Rice, Atmospheric organochlorine pollutants and air-sea exchange of hexachlorocyclohexane in the Bering and Chukchi Seas, *J. Geophys. Res.*, *96*(C4), 7201–7213, 1991.
- Hinds, W. C., *Aerosol Technology*, John Wiley, New York, 1982.
- Hoffman, E. J., and R. A. Duce, Factors influencing the organic carbon content of marine aerosols: A laboratory study, *J. Geophys. Res.*, *81*(21), 3667–3670, 1976.
- Huntzicker, J. J., R. L. Johnson, J. J. Shah, and R. A. Cary, Analysis of organic and elemental carbon in ambient aerosols by a thermal-optical method, in *Particulate Carbon: Atmospheric Life Cycle*, edited by G. T. Wolff and R. L. Klimisch, pp. 79–88, Plenum, New York, 1982.
- Husar, R. B., and W. R. Shu, Thermal analysis of the Los Angeles smog aerosol, *J. Appl. Meteorol.*, *14*, 1558–1565, 1975.
- Intergovernmental Panel on Climate Change (IPCC), *Climate Change*, Cambridge Univ. Press, New York, 1995.
- Ip, W. M., R. J. Gordon, and E. C. Ellis, Characterization of organics in aerosol samples from a Los Angeles receptor site using extraction and liquid chromatography methodology, *Sci. Total Environ.*, *36*, 203–208, 1984.
- Jacobson, M. C., M. L. Shulman, R. J. Charlson, and G.-J. Roelofs, Sensitivity of droplet size distributions to organic cloud condensation nuclei constituents, in *Proceedings of the Fourteenth International Conference on Nucleation and Atmospheric Aerosols*, pp. 953–955, Pergamon, Tarrytown, N. Y., 1996.
- Jambers, W., L. de Bock, and R. Van Grieken, Recent advances in the analysis of individual environmental particles, *Analyst*, *120*, 681–692, 1995.
- Janson, R., Monoterpene concentrations in and above a forest of Scots pine, *J. Atmos. Chem.*, *14*, 385–394, 1992.
- Janson, R., Monoterpene emissions from Scots pine and Norwegian spruce, *J. Geophys. Res.*, *98*(D2), 2839–2850, 1993.
- Jenkins, B. M., A. D. Jones, S. Q. Turn, and R. B. Williams, Particle concentrations, gas-particle partitioning, and species intercorrelations for polycyclic aromatic hydrocarbons (PAH) emitted during biomass burning, *Atmos. Environ.*, *30*, 3825–3835, 1996.
- Johansson, C., and R. W. Janson, Diurnal cycle of O₃ and monoterpenes in a coniferous forest: Importance of atmospheric stability, surface exchange, and chemistry, *J. Geophys. Res.*, *98*(D3), 5121–5133, 1993.
- Johnston, M. V., and A. S. Wexler, MS of individual aerosol particles, *Anal. Chem.*, *67*, 721A–726A, 1995.
- Junge, C., Das Wachstum der Kondensationskerne mit der relativen Feuchtigkeit, *Ann. Meteorol.*, *3*, 129–135, 1950.
- Junge, C. E., Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants, part 1, in *Fate of Pollutants in the Air and Water Environments*, edited by I. H. Suffet, pp. 7–25, John Wiley, New York, 1977.
- Kamens, R. M., and D. L. Coe, A large gas-phase stripping device to investigate rates of PAH evaporation from airborne diesel soot particles, *Environ. Sci. Technol.*, *31*, 1830–1833, 1997.
- Kawamura, K., and I. R. Kaplan, Organic compounds in the rainwater of Los Angeles, *Environ. Sci. Technol.*, *17*, 497–501, 1983.
- Kawamura, K., H. Kasukabe, O. Yasui, and L. A. Barrie, Production of dicarboxylic acids in the arctic atmosphere at polar sunrise, *Geophys. Res. Lett.*, *22*(10), 1253–1256, 1995.
- Kawamura, K., S. Steinberg, and I. R. Kaplan, Concentrations of monocarboxylic and dicarboxylic acids and aldehydes in southern California wet precipitations: Comparison of urban and nonurban samples and compositional changes during scavenging, *Atmos. Environ.*, *30*, 1035–1052, 1996.
- Keene, W. C., and J. N. Galloway, Organic acidity in precipitation of North America, *Atmos. Environ.*, *18*, 2491–2497, 1984.
- Klouda, G. A., L. A. Currie, D. J. Donahue, A. J. T. Jull, and T. H. Zabel, Accelerator mass-spectrometry sample preparation—Methods for C-14 in 50–1000 microgram samples, *Nucl. Instrum. Methods, Sect. B*, *233*(2), 265–271, 1984.
- Köhler, H., The nucleus in the growth of hygroscopic droplets, *Trans. Faraday Soc.*, *32*, 1152–1161, 1936.
- Kulmala, M., P. Korhonen, T. Vesala, H.-C. Hansson, K. Noone, and B. Svenningsson, The effect of hygroscopicity on cloud droplet formation, *Tellus, Ser. B*, *48*, 347–360, 1996.
- Laaksonen, A., P. Korhonen, M. Kulmala, and R. J. Charlson, Modification of the Köhler equation to include soluble trace gases and slightly soluble substances, *J. Atmos. Sci.*, *55*, 853–862, 1998.
- Li, S., and J. W. Winchester, Water soluble organic constituents in arctic aerosols and snowpack, *Geophys. Res. Lett.*, *20*(1), 45–48, 1993.
- Ligocki, M. P., and J. F. Pankow, Measurements of the gas/particle distributions of atmospheric organic compounds, *Environ. Sci. Technol.*, *23*, 75–83, 1989.
- Likens, G. E., E. S. Edgerton, and J. N. Galloway, The composition and deposition of organic carbon in precipitation, *Tellus, Ser. B*, *35*, 16–24, 1983.
- Liousse, C., J. E. Penner, C. Chuang, J. J. Walton, H. Eddle-

- man, and H. Cachier, A global three-dimensional model study of carbonaceous aerosols, *J. Geophys. Res.*, 101(D14), 19,411–19,432, 1996.
- Liu, B. Y. H., and D. Y. H. Pui, Aerosol sampling inlets and inhalable particles, *Atmos. Environ.*, 15, 589–600, 1981.
- Lunde, G., J. Gether, N. Gjøs, and M. B. S. Lande, Organic micropollutants in precipitation in Norway, *Atmos. Environ.*, 11, 1007–1014, 1977.
- Marty, J.-C., and A. Saliot, Aerosols in equatorial Atlantic air: *n*-Alkanes as a function of particle size, *Nature*, 298, 144–147, 1982.
- Matsumoto, G., and T. Hanya, Organic constituents in atmospheric fallout in the Tokyo area, *Atmos. Environ.*, 14, 1409–1419, 1980.
- Matthias-Maser, S., and R. Jaenicke, A method to identify biological aerosol particles with radius > 0.3 μm for the determination of their size distribution, *J. Aerosol Sci.*, 22, suppl. 1, S849–S852, 1991.
- Matthias-Maser, S., and R. Jaenicke, Examination of atmospheric bioaerosol particles with radii > 0.2 μm , *J. Aerosol Sci.*, 25, 1605–1613, 1994.
- Matthias-Maser, S., and R. Jaenicke, The size distribution of primary biological aerosol particles with radii > 0.2 μm in an urban/rural influenced region, *Atmos. Res.*, 39, 279–286, 1995.
- Mazurek, M. A., B. R. T. Simoneit, G. R. Cass, and H. A. Gray, Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analyses of carbonaceous fine aerosol particles, *Int. J. Environ. Anal. Chem.*, 29, 119–139, 1987.
- Mazurek, M. A., G. R. Cass, and B. R. T. Simoneit, Biological input to visibility-reducing aerosol particles in the remote arid southwestern United States, *Environ. Sci. Technol.*, 25, 684–694, 1991.
- McDow, S. R., and J. J. Huntzicker, Vapor adsorption artifact in the sampling of organic aerosol: Face velocity effects, *Atmos. Environ., Part A*, 24, 2563–2571, 1990.
- McMurray, P. H., and D. Grosjean, Photochemical formation of organic aerosols: Growth laws and mechanisms, *Atmos. Environ.*, 19, 1445–1451, 1985.
- Middlebrook, A. M., D. M. Murphy, and D. S. Thomson, Observations of organic material in individual marine particles at Cape Grim during the First Aerosol Characterization Experiment (ACE I), *J. Geophys. Res.*, 103(D13), 16,475–16,483, 1998.
- Miller, F. J., D. E. Gardner, J. A. Graham, R. E. Lee Jr., W. E. Wilson, and J. D. Bachman, Size considerations for establishing a standard for inhalable particles, *J. Air Pollut. Control Assoc.*, 29, 610–615, 1979.
- Munger, J. W., J. J. Collett, B. C. J. Daube, and M. R. Hoffmann, Carboxylic acids and carbonyl compounds in southern California clouds and fogs, *Tellus, Ser. B*, 41, 230–242, 1989.
- Murphy, D. M., and D. S. Thomson, Laser ionization mass spectroscopy of single aerosol particles, *Aerosol Sci. Technol.*, 22, 237–249, 1995.
- Murphy, D. M., and D. S. Thomson, Chemical composition of single aerosol particles at Idaho Hill: Negative ion measurements, *J. Geophys. Res.*, 102(D5), 6353–6368, 1997.
- National Research Council, *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, Natl. Acad. Press, Washington, D. C., 1991.
- Noble, C. A., and K. A. Prather, Real-time measurement of correlated size and composition profiles of individual atmospheric aerosol particles, *Environ. Sci. Technol.*, 30, 2667–2680, 1996.
- Noone, K. J., E. Öström, R. A. Pockalny, L. de Bock, and R. Van Grieken, The size distribution and chemical composition of cloud droplet residual particles in marine stratocumulus clouds observed during the MAST experiment, in *Nucleation and Atmospheric Aerosols 1996, Proceedings of the Fourteenth International Conference of Nucleation and Atmospheric Aerosols*, edited by M. Kulmala and P. E. Wagner, pp. 868–871, Pergamon, Tarrytown, N. Y., 1996.
- Novakov, T., and C. E. Corrigan, Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, 23(16), 2141–2144, 1996.
- Novakov, T., and J. E. Penner, Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, 365, 823–826, 1993.
- Novakov, T., D. A. Hegg, and P. V. Hobbs, Airborne measurements of carbonaceous aerosols on the east coast of the United States, *J. Geophys. Res.*, 102(D25), 30,023–30,030, 1997.
- O'Brien, R. J., J. R. Holmes, and A. H. Bockian, Formation of photochemical aerosol from hydrocarbons—Chemical reactivity and products, *Environ. Sci. Technol.*, 9, 568–576, 1975.
- Odum, J. R., T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan, and J. G. Seinfeld, Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol.*, 30, 2580–2585, 1996.
- Pandis, S. N., R. A. Harley, G. R. Cass, and J. H. Seinfeld, Secondary organic aerosol formation and transport, *Atmos. Environ., Part A*, 26, 2269–2282, 1992.
- Pankow, J. F., Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere, *Atmos. Environ.*, 21, 2275–2283, 1987.
- Pankow, J. F., A simple box model for the annual cycle of partitioning of semi-volatile organic compounds between the atmosphere and the Earth's surface, *Atmos. Environ., Part A*, 27, 1139–1152, 1993.
- Pankow, J. F., An absorption model of gas/particle partitioning of organic compounds in the atmosphere, *Atmos. Environ.*, 28, 185–188, 1994.
- Patton, G. W., M. D. Walla, T. F. Bidleman, and L. A. Barrie, Polycyclic aromatic and organochlorine compounds in the atmosphere of northern Ellesmere Island, Canada, *J. Geophys. Res.*, 96(D6), 10,867–10,877, 1991.
- Payne, K., Chemistry and toxicology of PCDDs, *Chem. Ind.*, 9, 298–300, 1982.
- Pehkonen, S. O., R. L. Siefert, Y. Erel, S. Webb, and M. R. Hoffmann, Photoreduction of iron oxyhydroxides in the presence of important atmospheric organic compounds, *Environ. Sci. Technol.*, 27, 2056–2062, 1993.
- Penner, J. E., R. E. Dickenson, and C. A. O'Neill, Effects of aerosol from biomass burning on the global radiation budget, *Science*, 256, 1432–1434, 1992.
- Penner, J. E., C. C. Chuang, and C. Liousse, The contribution of carbonaceous aerosols to climate change, in *Proceedings of the Fourteenth International Conference of Nucleation and Atmospheric Aerosols*, edited by M. Kulmala and P. E. Wagner, pp. 759–769, Pergamon, Tarrytown, N. Y., 1996.
- Prager, M. J., E. R. Stephens, and W. E. Scott, Aerosol formation from gaseous air pollutants, *Ind. Eng. Chem.*, 52, 521–524, 1960.
- Rivera-Carpio, C. A., C. E. Corrigan, T. Novakov, J. E. Penner, C. F. Rogers, and J. C. Chow, Derivation of contributions of sulfate and carbonaceous aerosols to cloud condensation nuclei from mass size distributions, *J. Geophys. Res.*, 101(D14), 19,483–19,493, 1996.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol, 1, Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, 25, 1112–1125, 1991.
- Rogge, W. F., M. A. Mazurek, L. M. Hildemann, G. R. Cass,

- and B. R. T. Simoneit, Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ., Part A*, 27, 1308–1330, 1993a.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol, 2, Nuncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, *Environ. Sci. Technol.*, 27, 636–651, 1993b.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol, 3, Road dust, tire debris, and organometallic brake lining dust—Roads as sources and sinks, *Environ. Sci. Technol.*, 27, 1892–1904, 1993c.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol, 9, Pine, oak and synthetic log combustion in residential fireplaces, *Environ. Sci. Technol.*, 32, 13–22, 1998.
- Rosen, H., A. D. A. Hansen, L. Gundel, and T. Novakov, Identification of the optically absorbing component in urban aerosols, *Appl. Opt.*, 17(24), 3858–3859, 1978.
- Rubel, G. O., and J. W. Gentry, Measurement of water and ammonia accommodation coefficients at surfaces with adsorbed monolayers of hexadecanol, *J. Aerosol Sci.*, 16, 571–574, 1985.
- Sakugawa, H., and I. R. Kaplan, Stable carbon isotope measurements of atmospheric organic acids in Los Angeles, California, *Geophys. Res. Lett.*, 22(12), 1509–1512, 1995.
- Satsumabayashi, H., and H. Kurita, Photochemical formation of particulate dicarboxylic acids under long-range transport in central Japan, *Atmos. Environ., Part A*, 24, 1443–1450, 1990.
- Satsumabayashi, H., H. Kurita, Y. Yokouchi, and H. Ueda, Mono- and di-carboxylic acids under long-range transport of air pollution in central Japan, *Tellus, Ser. B*, 41, 219–229, 1989.
- Saxena, P., and L. M. Hildemann, Water-organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57–109, 1996.
- Saxena, P., L. M. Hildemann, P. H. McMurry, and J. H. Seinfeld, Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, 100(D9), 18,755–18,770, 1995.
- Schneider, J. K., and R. B. Gagosian, Particle size distribution of lipids in aerosols off the coast of Peru, *J. Geophys. Res.*, 90(D5), 7889–7898, 1985.
- Schneider, J. K., R. B. Gagosian, J. K. Cochran, and T. W. Trull, Particle size distributions of *n*-alkanes and 210-Pb in aerosols off the coast of Peru, *Nature*, 304, 429–432, 1983.
- Schuetzle, D., Computer controlled high-resolution mass spectrometric analysis of air pollutants, Ph.D. dissertation, Univ. of Wash., Seattle, 1972.
- Schuetzle, D., and R. A. Rasmussen, The molecular composition of secondary aerosol particles formed from terpenes, *J. Air Pollut. Control Assoc.*, 28, 236–240, 1978.
- Schwartz, S. E., and A. Slingo, Enhanced shortwave cloud radiative forcing due to anthropogenic aerosols, in *Clouds, Chemistry and Climate*, edited by P. Crutzen and V. Ramanathan, pp. 191–236, Springer-Verlag, New York, 1996.
- Sempere, R., and K. Kawamura, Low molecular weight dicarboxylic acids and related polar compounds in the remote marine rain samples collected from the western Pacific, *Atmos. Environ.*, 30, 1609–1619, 1996.
- Shulman, M. L., M. C. Jacobson, R. J. Charlson, R. E. Synovec, and T. E. Young, Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, *Geophys. Res. Lett.*, 23(3), 277–280, 1996.
- Shutilov, V. A., *Fundamental Physics of Ultrasound*, Gordon and Breach, Newark, N. J., 1988.
- Sicre, M.-A., J.-C. Marty, and A. Saliot, *n*-Alkanes, fatty acid esters, and fatty acid salts in size fractionated aerosols collected over the Mediterranean sea, *J. Geophys. Res.*, 95(D4), 3649–3657, 1990.
- Simoneit, B. R. T., R. Chester, and G. Eglinton, Biogenic lipids in particulates from the lower atmosphere over the eastern Atlantic, *Nature*, 267, 682–685, 1977.
- Simpson, D., A. Guenther, C. N. Hewitt, and R. Steinbrecher, Biogenic emissions in Europe, 1, Estimates and uncertainties, *J. Geophys. Res.*, 100(D11), 22,875–22,890, 1995.
- Spencer, W. F., W. J. Farmer, and W. A. Jury, Review: Behavior of organic chemicals at soil, air, water interfaces as related to predicting the transport and volatilization of organic pollutants, *Environ. Toxicol. Chem.*, 1, 17–26, 1982.
- Stanley, J., R. Ayling, P. Cramer, K. Thornburg, J. Remmus, J. Breen, J. Schwemberger, H. Keng, and K. Watanabe, PCDD and PCDF levels in human adipose tissue in the continental U.S. collected between 1971 and 1987, *Chemosphere*, 20(7–9), 895–903, 1990.
- Storey, J. M. E., W. Luo, L. M. Isabelle, and J. F. Pankow, Gas/solid partitioning of semivolatile organic compounds to model atmospheric solid surfaces as a function of relative humidity, 1, Clean quartz, *Environ. Sci. Technol.*, 29, 2420–2428, 1995.
- Suslick, K. S., *Ultrasound: Its Chemical, Physical and Biological Effects*, edited by K. S. Suslick, VCH, New York, 1988.
- Suslick, K. S., D. A. Hammerton, and D. E. Cline Jr., The sonochemical hot spot, *J. Am. Chem. Soc.*, 108(18), 5641–5642, 1986.
- Svenningsson, B., H.-C. Hansson, A. Wiedensohler, K. J. Noone, J. Ogren, A. Hallberg, and R. Colville, Hygroscopic growth of aerosol particles and its influence on nucleation scavenging in cloud: Experimental results from Kleiner Feldberg, *J. Atmos. Chem.*, 19, 129–152, 1994.
- Tanabe, S., and R. Tatsukawa, Distribution, behavior, and load of PCBs in the oceans, in *PCBs and the Environment*, vol. 1, edited by J. S. Waid, chap. 8, pp. 143–161, CRC Press, Boca Raton, Fla., 1986.
- Tanabe, S., H. Tanaka, and R. Tatsukawa, Bioaccumulation of PCBs, DDT and HCH isomers in the North Pacific ecosystem, *Arch. Environ. Contam. Toxicol.*, 13, 731–738, 1984.
- Thibodeaux, L. J., K. C. Nadler, K. T. Valsaraj, and D. D. Reible, The effect of moisture on volatile organic chemical gas-to-particle partitioning with atmospheric aerosols—Competitive adsorption theory predictions, *Atmos. Environ., Part A*, 25, 1649–1656, 1991.
- Turpin, B. J., and J. J. Huntzicker, Secondary formation of organic aerosol in the Los Angeles Basin: A descriptive analysis of organic and elemental carbon concentrations, *Atmos. Environ., Part A*, 25, 207–215, 1991.
- Turpin, B. J., J. J. Huntzicker, and S. V. Hering, Investigation of organic aerosol sampling artifacts in the Los Angeles basin, *Atmos. Environ.*, 28, 3061–3071, 1994.
- U.S. Environmental Protection Agency, Criteria document on fine particles, *EPA/600/P-95/001CF*, Washington, D. C., April 1996.
- Veltkamp, P. R., K. J. Hansen, R. M. Barkley, and R. E. Sievers, Principal component analysis of summertime organic aerosols at Niwot Ridge, Colorado, *J. Geophys. Res.*, 101(D14), 19,495–19,504, 1996.
- Waggoner, A. P., and R. J. Charlson, Measurements of aerosol optical parameters, in *Fine Particles: Aerosol Generation, Measurement, Sampling, and Analysis*, edited by B. Y. H. Liu, pp. 511–533, Academic, San Diego, Calif., 1976.
- Weathers, K. C., et al., Cloud water chemistry from ten sites in North America, *Environ. Sci. Technol.*, 22, 1018–1026, 1988.

- Went, F. W., Blue hazes in the atmosphere, *Nature*, 187, 641–643, 1960.
- White, W., Contributions to light extinction, section 4 of Visibility: Existing and historic conditions—Causes and effects, edited by J. C. Trijonis, report 24 in *Acid Deposition: State of Science and Technology*, edited by P. M. Irving, pp. 24-85–24-102, U.S. Natl. Acid Precip. Assess. Program, Washington, D. C., 1990.
- Woodcock, A. H., Salt nuclei in marine air as a function of altitude and wind force, *J. Meteorol.*, 10, 362–371, 1953.
- Yamasaki, H., K. Kuwata, and H. Miyamoto, Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, 16, 189–194, 1982.
- Zhang, S.-H., M. Shaw, J. H. Seinfeld, and R. C. Flagan, Photochemical aerosol formation from α -pinene and β -pinene, *J. Geophys. Res.*, 97(D18), 20,717–20,729, 1992.
- Zhang, X. Q., P. H. McMurry, S. V. Hering, and G. S. Casuccio, Mixing characteristics and water content of submicron aerosols measured in Los Angeles and at the Grand Canyon, *Atmos. Environ., Part A*, 27, 1593–1607, 1993.
- Zimmerman, P. R., R. B. Chatfield, J. Fishman, P. Crutzen, and P. L. Hanst, Estimates of the production of CO and H₂ from the oxidation of hydrocarbon emissions from vegetation, *Geophys. Res. Lett.*, 5(8), 679–682, 1978.
-
- R. J. Charlson (corresponding author), H.-C. Hansson, and K. J. Noone, Department of Meteorology, Stockholm University, 106 91 Stockholm, Sweden.
- M. C. Jacobson, Department of Laboratory Medicine, University of Washington, Seattle, WA 98195.