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Secondary Particulate Matter in the United States: Insights from the Particulate Matter Supersites Program and Related Studies

Philip M. Fine and Constantinos Sioutas
Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA

Paul A. Solomon
U.S. Environmental Protection Agency, Office of Research and Development, Las Vegas, NV

ABSTRACT

Secondary aerosols comprise a major fraction of fine particulate matter ($PM_{2.5}$) in all parts of the country, during all seasons, and times of day. The most abundant secondary species include sulfate, nitrate, ammonium, and secondary organic aerosols (SOAs). The relative abundance of each species varies in space and time as a function of meteorology, source emissions strength and type, thermodynamics, and atmospheric processing. Transport of secondary aerosols from upwind locations can contribute significantly at downwind receptor sites, especially regionally in the eastern United States, and across a given urbanized area, such as in Los Angeles. Processes governing the formation of the inorganic secondary species (sulfate, nitrate, and ammonium) are fairly well understood, although the occurrence of nucleation bursts initiated with the formation of ultrafine sulfuric acid particles observed regionally on clean days in the eastern United States was unexpected. Because of the complex nature of organic material in air, much is still to be learned about the sources, formation, and even spatial and temporal distributions of SOAs. For example, a considerable fraction of ambient organic PM is oxidized organic species, many of which still need to be identified, quantified, and their sources and formation mechanisms determined. Furthermore, significant uncertainty (approaching 50% or more) is associated with estimating the SOA fraction of organic material in air with current methods. This review summarizes the findings of the Supersites Program and related studies addressing secondary particulate matter (PM), including spatial and temporal variations of secondary PM and its precursor species, data and methods for determining the primary and secondary fractions of PM mass, and findings on the anthropogenic and natural fractions of secondary PM.

IMPLICATIONS

Secondary aerosols comprise a significant fraction of the $PM_{2.5}$ mass in virtually all locations and seasons. The sources, formation, composition, and spatial and temporal variability of the inorganic fraction are generally well understood. However, for SOAs, considerable uncertainties in these areas remain. As primary PM emissions and inorganic precursor species are reduced through emissions control programs, the SOA will become a more important fraction of the secondary aerosol associated with $PM_{2.5}$. The potential health effect implications of SOAs are also not well understood. Thus, a better understanding of the SOA fraction of ambient PM is needed to develop more cost-effective and efficient strategies for reducing PM to meet the National Ambient Air Quality Standards and to protect public health and ecosystems from the adverse effects of PM.

INTRODUCTION

Suspended particles in the atmosphere, measured as ambient particulate matter (PM) mass, have been repeatedly associated with significant adverse human health outcomes.[1] Toxicologists have also found similar effects of PM exposure in both in vivo and in vitro studies.[1] Understanding the relationship between PM and health effects is complicated by the fact that ambient PM consists of a complex mixture of particles of different sizes, shapes, and chemical compositions derived from a wide range of sources and formation mechanisms.[2] However, a lack of consistent evidence as to which sources, components, or characteristics of PM are most responsible for the observed health effects as well as non-PM confounding factors, such as, socioeconomic status and lifestyle, have limited most regulatory efforts to the control of emissions and ambient levels of PM mass.[3]

In the regulatory arena, ambient PM mass is segregated by size on the basis of differing respiratory tract deposition efficiencies and the potential health effects. Size ranges of interest include thoracic particulate, PM_{10} (particles with aerodynamic diameters, d_p, less than 10 μm), fine particles or $PM_{2.5}$ ($d_p < 2.5$ μm), coarse particles or $PM_{2.5-10}$ (2.5 μm $< d_p <$ 10 μm), and ultrafine particles or UF PM ($d_p < 0.1$ μm).[2] As a U.S. Environmental Protection Agency (EPA) criteria pollutant, atmospheric levels of PM mass (PM_{10} and $PM_{2.5}$) are targeted for reduction through current National Ambient Air Quality Standards (NAAQS).[4,5] A fraction of ambient PM is considered primary—particles emitted directly from sources such as vehicles, fires, industrial smoke stacks, road dust,

cooking, etc. The remaining portion is considered secondary PM—particle mass formed in the atmosphere through the chemical reactions of gaseous precursors, producing low-volatility condensable material that ends up mainly in the fine particle fraction. Both primary and secondary precursor species are emitted from a range of anthropogenic and natural sources. If current and future NAAQS are to be achieved, it is likely that continued reductions in the anthropogenic emissions of both primary PM and the precursor gases that form secondary PM will be necessary.

A succinct review of secondary PM and its regulatory implications can be found in a PM assessment created by NARSTO.[2] Secondary PM is composed of both inorganic and organic compounds. The most abundant inorganic components of secondary PM are sulfate, nitrate, and ammonium. The precursor gas SO_2, emitted by combustion sources with sulfur in the fuel, is oxidized in the atmosphere to form sulfate.[6] This can occur via gas-phase reactions with the hydroxyl radical (OH), and thus occurs mostly during daylight hours when photochemistry results in higher OH concentrations. Sulfur dioxide (SO_2) to sulfate oxidation also can occur through aqueous-phase chemistry in clouds, rainwater, or within the water fraction of ambient aerosols. The produced sulfate, in the form of sulfuric acid (H_2SO_4), reacts quickly with ammonia to form nonvolatile ammonium sulfate ($(NH_4)_2SO_4$). The precursor gas ammonia is emitted by several sources such as livestock[7] and motor vehicles.[8] If there is not enough ammonia available to fully neutralize the H_2SO_4, then ammonium bisulfate (NH_4HSO_4) forms and the particles remain acidic.

The precursor gases nitric oxide (NO) and nitrogen oxides (NO_x) are emitted mainly from combustion sources and similar to SO_2, they are oxidized by OH during daylight hours to form nitric acid. There are other nighttime and aqueous-phase pathways, such as formation of the nitrate (NO_3) radical from the reaction of NO_2 and ozone, which leads to nitric acid. The latter dominates at night because the NO_3 radical is rapidly photolyzed during the day. In the gas phase, nitric acid vapor reacts with gaseous ammonia to form condensable ammonium nitrate (NH_4NO_3), mostly found in fine particles. Ammonium nitrate is semi-volatile and, in general, considered to be in equilibrium with its gas-phase precursor species, nitric acid and ammonia. The particle phase is favored by low temperatures and high relative humidity (RH). Nitric acid also can react with other particle-phase species, such as sea-salt and soil dust resulting in coarse-mode NO_3 (e.g., sodium nitrate [$NaNO_3$] from reaction with sea-salt).[9] The major processes by which inorganic secondary PM is formed are fairly well understood.

More complex and less understood are the pathways leading to the formation of the organic portion of secondary PM, also known as secondary organic aerosol (SOA, throughout this paper referring to the particle-phase portion of the aerosol). SOA actually consists of hundreds or thousands of individual organic species, only a small fraction (10–20%) of which is routinely identified or measured in ambient samples.[10] Volatile organic compound (VOC) gas-phase precursors are emitted from a variety of sources, including natural biogenic emissions from vegetation, as well as anthropogenic combustion and fugitive (by evaporation) sources. Some of the higher molecular weight VOC species react with atmospheric oxidants such as OH, ozone, and NO_3 radicals to produce low-volatility products, such as organic acids, nitro-polycyclic aromatic hydrocarbons (nitro-PAH), etc., which subsequently condense onto the existing atmospheric aerosol.[6] Most SOA is formed during the day and is more abundant during summer when the concentrations of photochemical atmospheric oxidants are higher. VOCs such as toluene, xylene, and other aromatics are the most important anthropogenic SOA precursors. Terpenes and sesquiterpenes emitted from trees are significant biogenic SOA precursors, especially in rural areas with substantial vegetation cover (e.g., Southeast United States and the area north of Houston[11]).

Many of the suspected SOA formation reactions have been reproduced in smog chamber experiments, designed to measure reaction rates and aerosol yields for input into air quality models. However, many of these models appear to underestimate SOA formation.[12] In addition to gas-phase reactions, particle phase heterogeneous reactions also can produce additional SOA material. This has been observed in laboratory studies of acid-catalyzed organic reactions that form SOA,[13–18] and isoprene oxidation to form SOA in clouds has been modeled successfully.[19] However, recent work in Pittsburgh observed little impact of acid-catalyzed organic reactions in ambient air.[20] The uncertainties in the mechanisms of formation, as well as the difficulties in apportioning PM organic species between secondary and primary with routine measurements, has made SOA one of the most active areas of PM research over the past several years.

In 1997, EPA issued NAAQS[4] for $PM_{2.5}$ on the basis of mounting epidemiological evidence of adverse health effects.[1] But given the uncertainties as to which sources or characteristics of PM were most responsible for these observations, improved ambient measurements of PM composition, size, source contributions, and spatial and temporal variability were considered essential. To this end, EPA established the Particulate Matter Supersites Program (Supersites, http://www.epa.gov/ttn/amtic/supersites.html). The primary goals were (1) to fully characterize ambient PM at several locations throughout the United States to elucidate the sources and formation mechanisms of PM, and thus, inform modeling efforts; (2) to support health effects and exposure research with advances in atmospheric PM measurements; and (3) to conduct methods development and testing and validation of emerging and routine PM measurement techniques. Two initial Supersites Projects were chosen in Atlanta, GA,[24] and Fresno, CA,[25] and operated in 1999 (Phase I). Subsequently, seven additional projects were competitively awarded cooperative agreements with EPA for 5 yr in duration (Phase II). The locations were Fresno (continued from Phase 1); Baltimore, MD; Houston, TX; Los Angeles, CA; New York, NY; Pittsburgh, PA[26]; and St. Louis, MO. Most of the monitoring activities associated with the Supersites concluded by the end of 2004. The findings have been and continue to be reported in over 400 articles in peer-reviewed journals, with a significant number in dedicated Supersites Program

journal issues[24,27–29] or journal issues associated with the 2005 American Association for Aerosol Research (AAAR) PM Supersites Program and Related Studies International Conference, February 7–11, 2005, Atlanta, GA.[30–33]

This review aims to summarize the findings of the Supersites Program relating to secondary PM. It includes results quantifying the spatial and temporal variations of secondary PM and its precursor species (both organic and inorganic). It reports on data and methods that elucidate what fraction of PM mass is secondary and what fraction of secondary PM is anthropogenic versus natural. The Supersites Program addressed many of these issues and this review focuses primarily on Supersites Program-related research. However, important results from other related and unrelated studies over the past 6 yr also are included where informative and appropriate. Included in the review are results of secondary PM reaction studies carried out in laboratory environments and novel ambient measurements of secondary PM components and precursors.

LABORATORY STUDIES OF SECONDARY PM FORMATION

Most of the known reaction mechanisms for secondary PM formation have been established via smog chamber or reaction tube experiments in the laboratory. Although it is almost impossible to re-create the complex mixture of particle and gas-phase species found in outdoor environments, these studies have provided great insight into the types of atmospheric processes that may be occurring. Because the inorganic formation pathways are better understood, most recent work has focused on both gas-phase and heterogeneous SOA production.

Although the Supersites focused primarily on ambient and not laboratory measurements, some Supersites investigators and other researchers have conducted several important laboratory-scale experiments of SOA formation over the past several years. Only a few examples are given here. In Los Angeles, Reisen et al.[34] showed in chamber experiments that dimethylnitronaphthalenes and/or ethylnitronaphthalenes can be formed by gas-phase photooxidation of precursor alkyl-polycyclic aromatic hydrocarbons found in diesel fuel. OH-initiated reactions form these nitro-polyaromatic hydrocarbons, which are known mutagens. The study also showed that the same set of reaction products are found in ambient samples. Previously, the reaction products had only been observed for the methylnaphthalene conversion to methylnitronaphthalenes. It was noted that although the ambient dimethyl- and ethylnaphthalene precursor concentrations were lower than those of naphthalene and the methylnaphthalenes, the relative abundances of the product nitro-derivatives were similar. The precursors as well as the products of these reactions are semi-volatile species, and thus can potentially partition to the particle phase and contribute to SOA mass.

The standard view of SOA formation is that gas-phase oxidation of organic precursors leads to low-volatility products, and that the amount of SOA depends only on gas-to-particle partitioning. However, recent evidence suggests that once the oxidation products condense into the particle phase, heterogeneous particle-phase reactions may occur leading to even lower volatility organics, and thus, increasing SOA levels in the atmosphere.[35] As mentioned in the introduction, one of the most interesting developments concerning heterogeneous SOA formation is the demonstration of acid-catalyzed organic reactions leading to increased SOA production in the laboratory,[13–18] although the influence of acid-catalyzed SOA formation was not observed in ambient air in Pittsburgh.[20] For a variety of organic precursors, including biogenics and aldehydes, the presence of an acidified seed aerosol led to multifold increases in SOA production compared with a nonacidic seed. Another development has been observations of heterogeneous oligomer formation from low-molecular weight precursors. Laboratory studies have measured oligomeric species with molecular weights between 200 and 900 from the reaction of biogenic and anthropogenic gaseous precursors.[17,35] For instance, Gao et al.[35] estimated that over 50% of the total SOA mass formed by α-pinene ozonolysis is comprised of oligomers. It also has been observed that an acidic seed aerosol increases, but is not necessary for, oligomer production.[36] Although the exact processes have not yet been confirmed in the atmosphere, some of the reaction products have been measured in ambient particles.[37] In any case, the occurrence of such heterogeneous reactions has significant implications for ambient SOA formation, concentrations, and analysis methods for organic species, as well as organic carbon (OC) and elemental carbon (EC) by thermal-optical methods. Appropriate temperature protocols designed to volatilize these high-molecular weight species need to be included in the analysis to ensure the most accurate measurements.

AMBIENT MEASUREMENTS OF GASEOUS PRECURSORS TO SECONDARY PM

The inorganic precursors SO_2 and NO_x are routinely monitored extensively by regional and local regulatory agencies. The spatial and temporal coverage of these measurements overshadow the few localized measurements made at Supersites locations. Hourly SO_2 and NO_x data demonstrate predictable diurnal patterns, with a strong NO_x peak in the morning hours, and a less prominent SO_2 peak midday.[38,39]

Long-term spatial and temporal trends of SO_2 and NO_x concentrations and emissions are described in the EPA National Air Quality and Emissions Trends Report–2003 Special Studies ed.[39] Briefly, ambient annual NO_2 levels have dropped by an average of 21% between 1983 and 2002, and estimated NO_x emissions have dropped 15% over the same period. Most emissions are from transportation sources, and thus the spatial distribution of emissions across the United States tends to correspond to population density. Even greater reductions in SO_2 have been achieved, with a 54% decrease in average annual concentrations and a 33% decrease in estimated emissions over the same 20-yr time frame. Most SO_2 is emitted from fuel combustion, including high emissions from coal and oil combustion in midwestern U.S. industries and power plants. This leads to the much higher particulate sulfate levels in the eastern United States than those found in the western states.

The Supersites Program focused primarily on ambient measurements of particles, their spatial and temporal

variation, and their characteristics. However, to varying degrees, the Supersites Program also made measurements of gas-phase species to help elucidate particle formation mechanisms and sources. More specialized inorganic precursor data were collected at several of the Supersites. During July 1999 in Atlanta, GA, nitric acid (HNO_3) and nitrous acid (HONO) concentrations were measured with 10- to 15-min time resolution with two different measurement systems.[40] HONO readily undergoes photolysis during the day to from OH and NO, and is therefore expected to have nighttime maxima and daytime minima, as was observed in Atlanta. But two distinct HONO peaks were often distinguishable. The first peak occurred between evening and a few hours past midnight, whereas the second peak occurred between sunrise and approximately 8:00 a.m. Vehicular emissions are known sources of HONO,[41] and given that the nature of the morning peak differed between weekends and weekdays, it was thought to be mostly primary emissions from vehicles. The evening through midnight peak arises from evening traffic as well as secondary nighttime atmospheric reactions that form HONO. Nitric acid measurements revealed a strong correlation between HNO_3 and light intensity during the day. Like HONO, nitric acid levels reacted to changes in radiation levels (in the opposite direction, but with a slight lag time). In the evening, nitric acid lingers beyond sunset due to formation from nighttime chemical reactions. Minimum HNO_3 levels occur in the early morning when NO_3 is shifted to the particle phase because of the semi-volatile nature of NH_3NO_3, with the particle phase being favored under cool, humid conditions.

Another set of instruments in Atlanta measured gas-phase ammonia (NH_3), hydrochloric acid (HCl), HNO_3, HONO, SO_2, and acetic, formic, and oxalic acids over 10- to 24-hr integrated periods.[42] The study was conducted during stagnant periods with high temperatures, RH, and ultraviolet (UV) radiation, conditions conducive to photochemical production of ozone and secondary PM. The diurnal measurements suggested photochemical sources of HNO_3, HONO, acetic, and formic acids. During an ozone episode, HNO_3, the organic acids, and $PM_{2.5}$ levels all showed high levels. All these photochemical products were highly dependent on meteorological conditions, dropping to low levels during rain as well as after wind shifts that brought relatively clean air to the area (seen as low NO_2 levels).

Primary and secondary contributions to ambient levels of VOCs were determined in Pittsburgh, PA, during winter and summer periods of 2002.[43] Results indicated that some of the quantified VOCs might participate in or be indicative of SOA formation reactions. Primary emission ratios for gas species were defined by correlation with species of known origin, and then contributions from primary, secondary/biogenic, and regional background sources were determined. Primary anthropogenic contributions to ambient levels of acetone, methylethylketone, and acetaldehyde were found to be 12–23% in winter and 2–10% in summer. Secondary production and biogenic emissions accounted for 12–27% of the total mixing ratios for these compounds in winter and 26–34% in summer. The remainder was due to regional background levels. Factor analyses of the VOC as well as aerosol data were used to determine the dominant source types affecting the site in both seasons. The factor attributed to local automotive emissions was the strongest contributor to the variability in VOC concentrations.

A model was used to predict sesquiterpene emissions, important biogenic SOA precursors, in the Houston-Galveston area.[11] On the basis of a land cover database and emission factors taken from literature, average sesquiterpene emissions were estimated to be between 0.07 and 0.65 kg carbon/km^2-h. These emissions factors resulted in estimated modeled mean ambient SOA concentrations of 11.7 μg/m^3 (range 5.8–23.2 μg/m^3). The range depended on the different uncertainty estimates for sesquiterpene emissions in the literature. After adjusting oak emissions factors to more realistic values for Houston on the basis of the species present, SOA from sesquiterpene emissions resulted in mean SOA concentrations of approximately 2.4 μg/m^3, which corresponded closely with experimentally determined SOA concentrations based on ^{14}C measurements in Houston.[44] Modeled spatial distribution showed that north and southwest of Houston, SOA formation is dominated by biogenic emissions sources. This also agrees with results by Lemire et al.,[44] in which biogenic SOA accounted for up to 80% of SOA north of Houston during the summer, whereas at urban sites the fraction is much less and at times not detectable. Another study in Houston applied a novel factor analysis that included meteorological data and weekend/weekday effects to identify and apportion VOC sources.[45] Many of the heavier VOCs measured, such as toluene and xylene, photochemically react to produce SOA. Nine sources were identified, including several industrial point sources and vehicular emissions, and time series for individual VOC species concentrations as well as the source contributions are provided. The wind direction results were consistent with known point sources of VOCs in the surrounding area.

AMBIENT MEASUREMENTS OF INORGANIC SECONDARY PM

Seasonal Variations

Time-integrated, filter-based measurements of the main inorganic components of secondary PM (sulfate, NO_3, and ammonium) have become routine for several national and regional PM monitoring networks.[46,47] As was the case for the inorganic precursor gases, better spatial and temporal coverage of these ionic species concentrations can be found in the data and publications from those networks. For instance, Chu[48] looked at all $PM_{2.5}$ episodes (95th percentile) over 2.5 yr and approximately 200 monitoring sites. The analysis revealed that $PM_{2.5}$ episodes in the summer are dominated by high concentrations of acidic particles with higher levels of sulfate and organics. Because some of the episodes occurred on days when the solar radiation was not at its highest, the analysis suggests that acid-catalyzed heterogeneous reactions might be enhancing SOA production beyond what is formed through gas-phase photochemistry. During cold seasons, NO_3 and organic particles are the major contributors to the episodes, and it is suggested that organics are mostly primary. Chu et al.[49] also looked at 2000–2002 speciation trends network (STN) data from Fresno and Atlanta, both corresponding to Supersites locations. The

seasonal variability of the major $PM_{2.5}$ species were reported, as well as differences between eastern and western U.S. locations and relationships with meteorology. During summers in Atlanta, $PM_{2.5}$ sulfate and ammonium were high when temperatures, humidity, and ozone levels were high. OC concentrations showed much less seasonal variation. In Fresno, sulfate levels were very low year round. $PM_{2.5}$ mass was much higher in the winter, dominated by organic material and nitrate, and accompanied by much lower mixing heights and stagnant conditions.

The Supersites Program and related studies also made relatively routine measurements of the major ionic components of $PM_{2.5}$. Butler et al.[50] found that there was little variation of $PM_{2.5}$ components in Atlanta between sites located 5–20 mi apart, thus demonstrating the representative nature of the Atlanta Supersites Project location. On average, they found that 45% of the $PM_{2.5}$ mass consisted of sulfate, NO_3, and ammonium. Nitrate peaked in winter when lower temperatures favor partitioning to the particle phase and mixing heights were lower. In Pittsburgh, similar uniformity was observed among three urban (~3 km separation) and three rural (50–270 km separation) sampling sites.[51] The secondary PM components sulfate, ammonium, and NO_3 were all highly correlated between all six sites. Like Atlanta, $PM_{2.5}$ mass, sulfate, and ammonium peak in the summer, whereas NO_3 peaks in the winter. In New York, levels of ionic PM species were highly correlated at three sampling sites separated by hundreds of kilometers, suggesting upwind regional sources.[52] Backward air trajectories showed that the highest sulfate levels occurred for air masses passing through the Ohio River Valley and around the Great Lakes Basin. It was estimated that annually, 44–60% of the sulfate measured at the three sampling sites derived from long-range transport. Another analysis at six sites in New York indicated similar results for sulfate and ammonium, with higher summer levels and correlated seasonal trends among sites.[53] Nitrate was much higher in winter, especially at the urban sites. An ion balance revealed a consistently acidic aerosol, with more acidity at the rural locations, which may have implications for heterogeneous SOA formation.

Size-Resolved Measurements

In addition to the typical 24-hr measurements of ionic composition, the Supersites deployed more advanced instrumentation that measured the major ionic components on a size-resolved basis. The Pittsburgh and Los Angeles Supersites used micro-orifice uniform-deposit impactors (MOUDI) to collect PM on several impaction stages that were subsequently analyzed for inorganic ions. Size distributions for the major chemical components for summer and winter intensive monitoring periods in Pittsburgh are shown in Figure 1, a and b,[54] respectively. During the summer, both ammonium and sulfate ions showed similar bimodal size distributions. A condensation mode occurred around 0.2 μm, formed by the gas-phase oxidation of sulfate, and a larger droplet mode is seen at approximately 0.7 μm, formed by heterogeneous reaction in clouds and accumulation of material from the condensation mode. NO_3 levels were very low in the summer, with small peaks in the droplet mode as well as the coarse mode (1–2.5 μm). The same bimodal distributions were seen for sulfate and ammonium in the winter as the summer, but the concentrations were lower and the droplet mode was less pronounced relative to the condensation mode. Significantly more NO_3 was observed in winter with the same bimodal distribution as was observed for ammonium and sulfate, suggesting particle growth by cloud processing NH_4NO_3 as well. Ultrafine particles (<100 nm) were 50% inorganic in the summer (mainly sulfate and ammonium), and only 30% inorganic in the winter. The remainder is mostly carbonaceous material with little NO_3 observed in ultrafine particles.

Different patterns were observed in Los Angeles, where sulfate and NO_3 in the ultrafine (<100 nm), accumulation (100 nm to 2.5 μm), and coarse (2.5–10 μm) modes were reported[55] at four different locations sampled consecutively. The four locations included two urban source sites (Downey and University of Southern California [USC]) and two inland receptor sites (Claremont and Riverside). As opposed to Pittsburgh and most sites in the eastern United States, $PM_{2.5}$ nitrate levels were comparable to or higher than sulfate in every season and location. This is due to the lack of significant SO_2 emissions within and upwind of Los Angeles. Significant NO_3 levels were seen in the coarse PM, (likely $NaNO_3$ from reaction of HNO_3 and sea salt[56]), but most nitrate (as NH_4NO_3) is found in the accumulation mode. Similar to Pittsburgh, more sulfate is generally measured in the ultrafine mode than NO_3, although organic material (OM; OC mass adjusted for the presence of other elements, such as oxygen, nitrogen) is the major species in both locations in the ultrafine mode. Although the eastern U.S. cities show very low NO_3 levels in the summer, Los Angeles PM can exhibit very high summer NO_3 levels (e.g., monthly average values exceeded 25 $\mu g/m^3$), especially at the inland receptor sites where high NO_x levels react under intense solar radiation to form HNO_3 during transport from west to east with subsequent reaction with NH_3 emitted from dairy farms in the eastern basin. The tendency of NH_4NO_3 to partition to the gas phase under the prevailing high temperatures and low humidity is apparently overcome by higher gas-phase concentrations of NH_3 (because of less available sulfuric acid) and HNO_3. Also in Los Angeles, a study looked at size-resolved chemistry within the ultrafine mode using NanoMOUDI impactors in two locations.[57] Results revealed a consistent submode of both sulfate and NO_3 in particles between 32 and 56 nm in diameter, and diurnal and spatial patterns (higher during daytime hours and at eastern Basin sites) suggested a photochemical origin.

Under certain conditions, atmospheric reactions result in homogeneous nucleation of new particles resulting in a sharp increase in number concentration of very small particles (<10 nm) over 1–2 hr. Such nucleation events have been observed in rural areas, near forests, in the upper troposphere, regionally in the eastern United States, and in major urban areas.[21,58] The regional nature of events in the United States was unexpected before its observation during the Supersites Program and has been studied in some detail.[22,58–61] In the Pittsburgh area, nucleation events occurred on 50% of the measurement days, and were observed regionally on approximately 30% of the measurement days. The events occur during

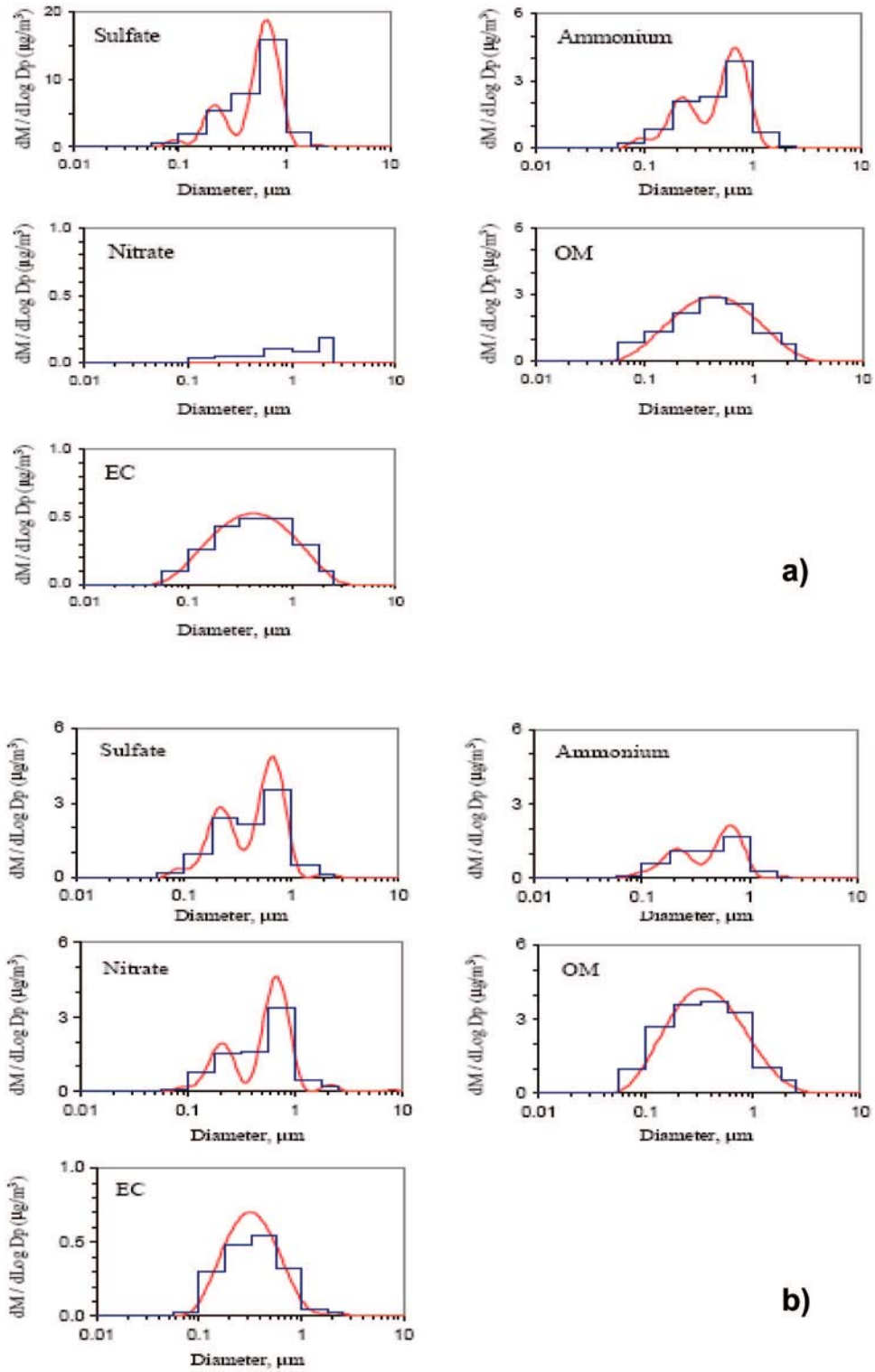

Figure 1. (a) Summer intensive size-resolved chemical composition during PAQS, for the major components of the $PM_{2.5}$. Also shown are the MICRON inverted size distributions (smooth lines). (b) Winter intensive (January 2002) size-resolved chemical composition during PAQS, for the major components of the $PM_{2.5}$. Reprinted with permission from Cabada et al.[54] Copyright 2004 Elsevier.

low pollution periods, on clear sunny days, initiating sometime after sunrise, and remaining for several hours.[58] Gaydos et al.[22] modeled the process for regional nucleation bursts in the eastern United States (Figure 2). Ambient data and modeling results are illustrated with excellent agreement between the two. The mechanism in this case appears to be a sulfuric acid-water-NH_3 ternary reaction. Sulfuric acid initially forms and is neutralized by available NH_3 during the first hour. Subsequently, the particles grow by condensation due to additional reactions with sulfate, NO_3, and organic species. If the NH_3 was insufficient to neutralize the initial aerosol, then the aerosol remains acidic, and this may

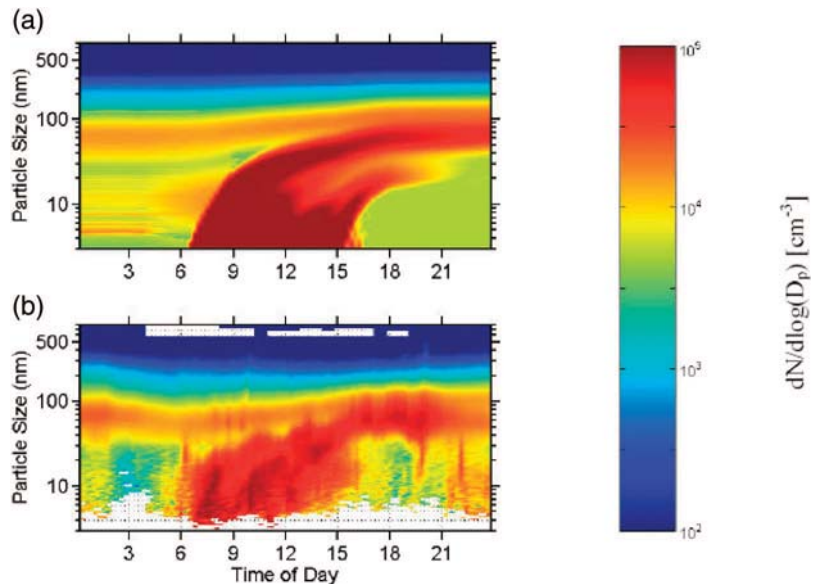

Figure 2. Comparison of (a) modeled and (b) measured size distributions as a function of time for one day with nucleation activity (July 27, 2001). Particle number (z-axis) is plotted against time of day (x-axis) and particle size (y-axis). The increased number concentrations observed between 6:00 and 7:00 a.m. Eastern Standard Time (EST) and after 9:00 p.m. are due to local emissions of ultrafine particles. The observed onset of nucleation at approximately 7:00 a.m. EST is captured in the model, and the qualitative features of particle growth are also captured by the model. Reproduced/modified with permission from Gaydos et al.[22] Copyright 2005 American Geophysical Union.

enhance SOA formation. However, during nucleation events in Pittsburgh, it was observed that although fresh particles were acidic, organic species did not condense on them; organic condensation occurred primarily on neutral larger particles.[61] Although nucleation events can dominate ambient particle number concentrations, the new particles are too small to significantly affect ambient $PM_{2.5}$ or PM_{10} mass. However, recent data suggesting that ultrafine particle mass or particle number concentrations may increase health risks,[23] which might make homogeneous nucleation an important regulatory issue in the future, especially with regards to the large regional bursts that may be acidic and remain at relatively high levels for several hours, as observed in the east.

Diurnal Variations

The Supersites also evaluated and ran several newly developed PM NO_3 and sulfate monitors that collect data on a semicontinuous 10-min to 1-hr basis, with some instruments also providing size-fractionated data. The data provided by these instruments are useful in determining short-term fluctuations, diurnal patterns, and sources of these important secondary PM components. In Baltimore, 10-min resolution NO_3 data were collected for most of the year in 2002.[62] Over the entire study period, NO_3 levels of 1.7 ± 1.6 $\mu g/m^3$ accounted for 11.4% of the $PM_{2.5}$ mass. As was the case with the filter-based measurements, monthly average NO_3 levels were much lower in summer, ranging from 4.7% of $PM_{2.5}$ mass in August (0.8 $\mu g/m^3$) to 17.3% of $PM_{2.5}$ mass in November (2.9 $\mu g/m^3$). The hourly NO_3 concentrations, however, were often larger with a maximum contribution to $PM_{2.5}$ mass of 58.5%. Most of these short-term NO_3 excursions, where NO_3 levels exceeded 5 $\mu g/m^3$, occurred in the colder months and often were accompanied by elevated NO_x and ultrafine particles during the morning commute hours (Figure 3). Another less prevalent and less elevated type of NO_3 event occurred in the afternoon because of photochemical activity. A third type of transient event occurred at night, typically between 8:00 p.m. and 2:00 a.m. Multiple linear regression analyses between the NO_3 events and volume size distributions showed that the morning excursions were associated with smaller sized particles (0.1–0.2 μm). The nighttime excursions were more associated with droplet modes (0.5–1 μm) and coarse modes (1–2.5 μm), suggesting that processes governing particulate NO_3 formation depend on time of day.

The NO_3 particle events in Baltimore were further observed with a real-time single particle mass spectrometer (RSMS-III).[63] Two types of NO_3 events were observed with this instrument corresponding to those mentioned above. The more frequent nighttime events consisted of a fast increase in small NO_3-rich particles (50–90 nm), whereas the less frequent daytime events showed moderate production of nitrate-rich particles followed by growth to larger sizes (100–200 nm) within a few hours. Condensation onto existing particles occurred during both of these event types. The measurements showed that when ambient conditions are cold and humid, NH_4NO_3 partitions to the particle phase, which then dominates the particle number concentrations as well as the chemical composition.[63]

In Los Angeles, the Integrated Collection and Vaporization System (ICVS) was applied to a modified cascade impactor resulting in a method capable of measuring semicontinuous NO_3 in three distinct size ranges (0.1–0.45 μm, 0.45–1 μm, and 1–2.5 μm).[64] An example of a time-series of hourly averaged NO_3 data for two selected consecutive days in August 2001 at the inland Rubidoux sampling site is given in Figure 4. On August 7, a single $PM_{2.5}$ NO_3 maximum was observed between 10:00 a.m. and 12:00 p.m. The size-segregated data suggest that the NO_3 peak initially contained a higher contribution from

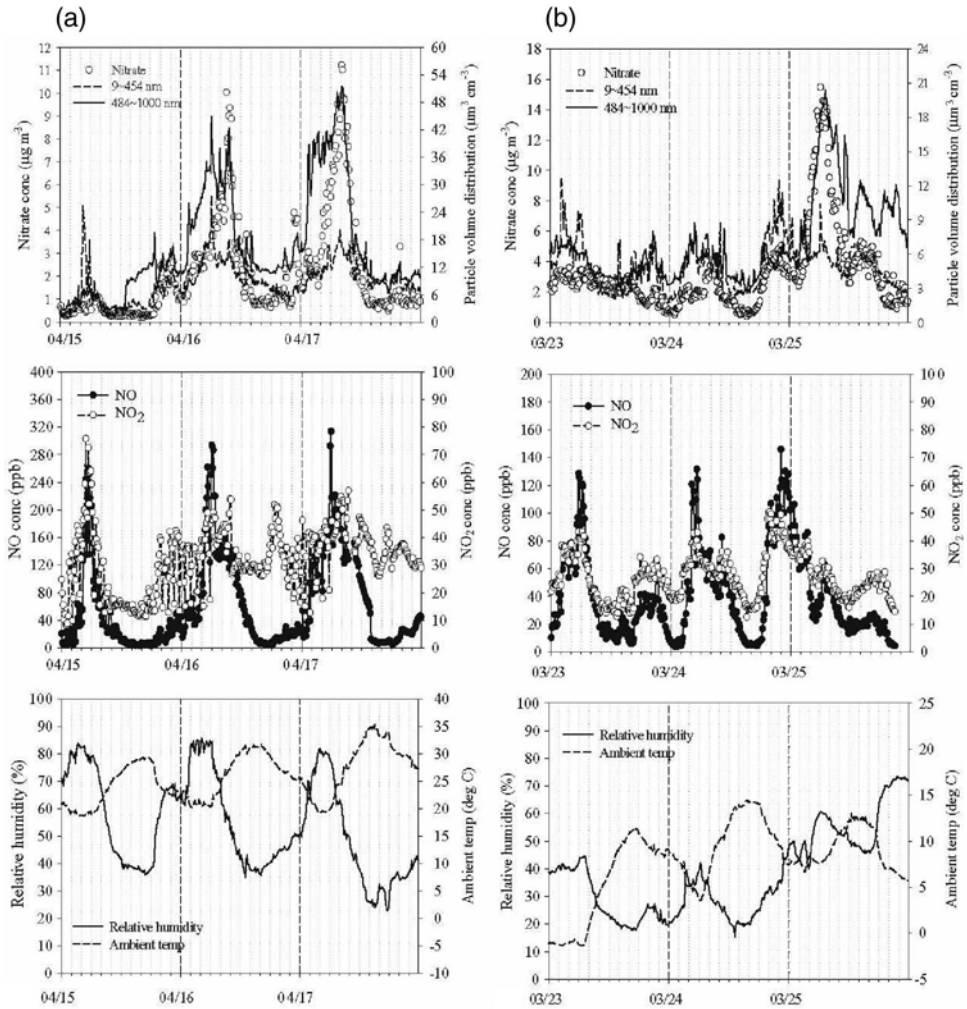

Figure 3. Temporal profiles of NO_3 and NO_x for three morning transient events in Baltimore in (a) April 2002 and (b) March 2002. Reprinted with permission from Park et al.[62] Copyright 2005 Elsevier.

the smaller particles, and then, in the next hour was caused by an increase in NO_3 in the middle size range. The following day exhibits the same general pattern. A second NO_3 maximum occurred around 5:00 p.m. on the second day with a relatively large contribution from the largest particle size fraction. As was the case in Baltimore, the diurnal fluctuations of NO_3 in the different size modes suggest different mechanisms of NO_3 formation at different times of day.

Methods for 10-min $PM_{2.5}$ NO_3 and sulfate measurements were evaluated as part of the Pittsburgh Supersites Project.[65] The calibrated semicontinuous results were used together with temporally resolved gas-phase measurements and meteorological data to investigate short-term inorganic secondary PM phenomena. It was observed that NO_3 followed a consistent diurnal pattern, with maximum NO_3 levels in the early morning and minimum NO_3 in the late afternoon. The timing of the NO_3 maxima and minima shifted according to seasonal changes in ambient temperature and UV radiation. The gas-to-particle partitioning of NO_3 also varied daily and seasonally with temperature, humidity, and solar radiation. A majority of the NO_3 partitioned to the particle phase at night and during the winter months. Summer sulfate levels showed diurnal patterns consistent with gas-phase photochemical production during daylight, peaking a couple of hours before sunset. Fall, winter, and spring sulfate concentrations showed little variation over the course of a day.

An Aerodyne aerosol mass spectrometer (AMS) also was deployed during the Pittsburgh Supersites Project from September 7–22, 2002, to measure nonrefractory components of PM_1 ($d_p < 1$ μm).[60] Sulfate and organics were found to be the major constituents, whereas the concentrations of NO_3 and chloride were generally low. The size distributions of sulfate, ammonium, and NO_3 varied on timescales of hours to days, showing unimodal, bimodal, and even trimodal distributions. The accumulation mode (peaking around 350–600 nm in vacuum d_p) and the ultrafine mode (<100 nm) were observed most frequently. The accumulation mode (d_p 0.1–1 μm) was dominated by sulfate internally mixed with oxidized organic components. Sulfate was often estimated to be fully neutralized by ammonium ($(NH_4)_2SO_4$), but at times, when insufficient NH_3 was available the aerosol was acidic and more than 50% of the sulfate was estimated to be as NH_4HSO_4. On the other hand, the main component of ultrafine particles appeared to be composed of combustion-emitted organic species (likely traffic related), except during nucleation events. In the latter, sulfate (H_2SO_4) initially

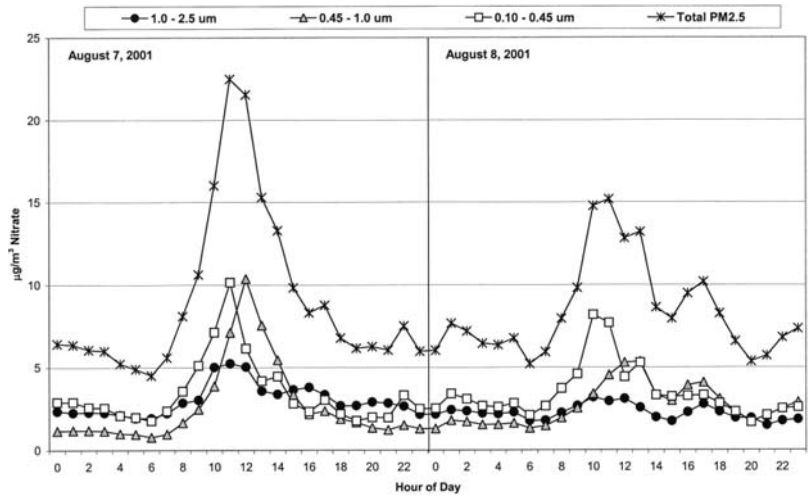

Figure 4. Size-fractionated hourly-averaged nitrate measurements from the Aerosol Dynamics Inc. monitor for August 7–8, 2001, at Rubidoux, CA. Reprinted with permission from Fine et al.[64] Copyright 2003 American Association for Aerosol Research.

dominated the ultrafine mode with neutralization by NH_3 within about 1 hr and growth by condensation of organics (likely with a significant fraction being oxygenated), NO_3, and additional sulfate, both with associated ammonium, later in the day.[61] The diurnal patterns match those previously described in Pittsburgh,[61] with a morning NO_3 peak, a NO_3 minimum during the day, and a less dramatic afternoon sulfate maxima.

During the summer of 1999 in Atlanta, instruments for measuring semicontinuous sulfate, NO_3, and ammonium showed very short-term transients in $PM_{2.5}$ inorganic secondary PM concentrations.[66] Like Pittsburgh, average diurnal patterns in the summer showed a NO_3 peak in the morning and a sulfate peak in the late afternoon. On any given day, $PM_{2.5}$ mass concentrations could vary by a factor of 2 or 3 over only a few hours. These events were typically characterized either by a sudden increase of primary EC and OC in the early morning or the increase in sulfate in the late afternoon from photochemical oxidation of regional SO_2.

At the New York Supersites Project, several semicontinuous instruments measuring $PM_{2.5}$ sulfate and NO_3 were compared during intensive summer field campaigns in Queens, NY, (2001) and in rural upstate New York (2002).[67] The array of instruments provided data that allowed for the study of particulate sulfate and NO_3 diurnal patterns and short-term events. The average diurnal pattern of sulfate showed a late afternoon peak as was observed in other eastern cities. The rural location did not show this diurnal pattern. The diurnal pattern of NO_3 measured in the urban location showed the expected morning peak and afternoon minimum, as well as a smaller maximum near midnight. Again the rural site showed much less diurnal variation but with slightly higher levels throughout the night. Several NO_3 events were observed at the urban site, and they were found to coincide with sulfate events. Continuous size-resolved measurements during the summer of 2001 in Queens, NY, with the Aerodyne AMS showed that sulfate and NO_3 size distributions were similar, being broad, with a single mode maximum at approximately 400 nm, which changed little during the day.[68] Furthermore the NO_3 mode diameter seemed to be related to sulfate mass concentrations. This suggests that these aerosol components were internally mixed and that NH_4NO_3 partitions to pre-existing sulfate-containing particles. The fact that there was little change in these size distributions over the course of the day points to long-range transport of these particles from distant sources.

Receptor modeling by factorization and principal component methods statistically analyzes multiple speciated measurements at a single site, resulting in independent factors contributing to the chemical profiles measured at the site. The factors can then be roughly assigned to particle sources, both secondary and primary. The recent inclusion of wind direction data, different OC fractions, and particle size data in these analyses has aided in the assignment of factors to real-world sources. Several studies were carried out using Supersites Programs and other ambient datasets.[69–75] Results of these studies often only apportion sulfate, NO_3, and ammonium to factors identified as secondary PM, but they do not provide links to the sources that emitted the precursor species, SO_2, NO_x, and NH_3. Therefore, the use of receptor models provides limited information with respect to secondary inorganic aerosols and a simple examination of the ambient data provides similar information on the spatial and temporal variability of these species.

AMBIENT MEASUREMENTS OF ORGANIC SECONDARY PM

EC/OC Tracer Method

The measurement of the inorganic fraction of secondary PM is relatively straightforward, given that essentially all sulfate, NO_3, and ammonium measured is secondary in nature. However, determining the SOA fraction of ambient PM is more challenging, and considerable uncertainty remains regarding its source, formation, and accumulation in air. Most particulate OC analysis techniques measure total OC, and thus cannot readily distinguish between primary and secondary OC sources. The most commonly applied method to estimate the fraction of OC that is secondary versus primary was first introduced by Turpin et al.[76] and requires concurrent measurements of

EC (often provided by the same analysis instrument used for OC measurements). The method is often referred to as the OC/EC ratio technique or the EC tracer method. In its simplest form, the following equations are used to estimate the secondary OC concentration in ambient PM samples:

$$OC_{secondary} = OC_{total} - OC_{primary}, \quad (1)$$

where

$$OC_{primary} = EC^{*}(OC/EC)_{primary}. \quad (2)$$

Secondary OC (or SOA) as defined in eq 1 is calculated as the difference between the total OC and an estimate of the primary OC. The estimate of primary OC is based on the assumption that, for a given location, sampling method, carbon analysis method, and season, there is a linear relationship between primary OC and EC (all EC is primary) for the given mix of primary combustion and noncombustion sources in the area. The method can be further refined to separate combustion and noncombustion primary sources[77] using

$$OC_{primary} = A + B^{*}EC = OC_{non\text{-}combustion} + OC_{combustion} \quad (3)$$

where B is the OC/EC ratio from sources emitting EC (combustion) and A is $OC_{non\text{-}combustion}$. Noncombustion primary sources of OC (the A term) are mostly biogenic, and often contribute greater than 0.5 $\mu g/m^3$ in many areas of the United States. However, many studies ignore the A term and just assume primary OC is a fixed multiple of EC. The primary OC/EC ratio can be determined by examining a large OC and EC dataset for a particular location. A linear fit to data collected during periods when secondary OC is expected to be negligible (i.e. night, winter, overcast, clean background, no long range transport, etc.) can yield an estimate of the ratio. Minimum observed values for OC/EC ratios also are used, as well as emissions inventories and emission factors of sources in the area. Note that the OC/EC ratio is not a constant, varying with sampling method, carbon analysis method, surrounding area and sources, season, and perhaps time of day. The use of denuders during sampling reduces the positive OC adsorption artifact, giving smaller OC/EC ratios. Different carbon analysis techniques give different OC-EC splits, affecting the ratio. Thus, primary OC/EC ratios are very specific to the particular conditions of a given set of samples.

Several variations on this method were used in the studies described below. But in general, estimates of SOA using this simple method include a considerable degree of uncertainty, up to 50% or more. Uncertainty in the method results from the fact that the primary OC/EC ratio varies significantly in emissions from different combustion source types, as well as changes in source strengths and emissions characteristics with time of day and season. For example, examination of Table 1, which provides a summary of the methods and results used here, indicates differences by a factor of 2 to 3 in the primary OC/EC ratio between summer and winter seasons in several fairly different locations across the United States. Results from St. Louis,[78] using hourly data, also indicate significant variations in the ratio within the course of a given day, as well as location and season. Thus, EC tracer studies[78–81] using daily average or highly time-resolved EC and OC data that do not account for this diurnal variation may be biased.

Also, the carbon analysis method used to obtain OC and EC can exhibit biases in the split between EC and OC determinations.[82] These differences can result in a factor of two difference in reported EC concentration and 10–20% in reported OC concentrations. Another source of uncertainty in estimated SOA contributions to total aerosol mass is the factor used to convert OC mass to organic compound mass. Estimates indicate this factor can vary from 1.4 to 2.1, with oxidized secondary organics generally at the higher end of the range.[83] However, the OC/EC ratio method is currently the primary approach used to estimate secondary OC contributions to PM mass.

Table 1 summarizes the results, including seasonally adjusted primary OC/EC ratios for the studies described below. All estimates of the primary OC/EC ratio were similar, with higher ratios in the winter than summer, ranging from approximately 1 to 3, except for Houston in the winter, with most estimates between 5 and 7. The seasonal and spatial differences in the primary OC/EC ratio are likely due to seasonal and spatial differences in emissions. For example, the presence of wood smoke and/or seasonal variations in the primary emissions from motor vehicle traffic (e.g., less efficient combustion in vehicles during colder months), or potentially other EC-generating sources with temporal emission profiles tracking with rush hours can influence the primary OC/EC ratio during different seasons.

Annual and seasonal estimates of SOA were obtained using data collected in Pittsburgh, PA, during 1995, July 2001, and winter and summer 2002. All three Pittsburgh studies used the OC/EC ratio method; however, different assumptions were used to estimate primary OC. For the 1995 dataset, background and seasonally adjusted primary OC/EC ratios were estimated using emissions inventory, emissions factors, and activity levels for a series of combustion source types.[84] Monthly average OC data were then used to calculate SOA. During the July 2001 study,[79] the primary OC/EC ratio was estimated based on periods dominated only by primary emissions, such as low ozone concentrations, minimal transport, and during rain. Millet et al.[43] estimated primary OC/EC ratios by applying a new method using a range of markers for primary (toluene, etc.) and secondary processes (acetaldehyde, etc.) provided by the VOC dataset, which then defined the primary OC/EC ratio for summer and winter periods in Pittsburgh. The methods described above to estimate the primary OC/EC ratio, the key to the OC/EC ratio method, each have their own assumptions that bound the uncertainty of the estimate and these assumptions are described within the cited papers.

SOA results for the three studies in Pittsburgh are summarized in Table 1. Overall, SOA varied from near zero in the winter to greater than 50% in the summer.[43,79,84] Annual average results ranged between 10 and

Table 1. Estimates of SOA in Pittsburgh, PA; Atlanta, GA; and Houston, TX, on the basis of application of the OC/EC tracer method.

Location, Date of Study	Primary OC/EC Assumption	Primary OC/EC Winter (W): Summer (S):	SOA (Percent of OC) Winter (W): Summer (S): Annual (A):	Comments
Pittsburgh, 1995 (Cabada et al.)[84]	Monthly average primary OC and EC based on calculated emissions inventory (emission factor x activity); background adjusted	W: 2.4 S: 1.0	W: near zero–18% S: 25 to >50% A: 10–35%	Uncertainty in SOA estimate is about 50%
Pittsburgh, July 2001, (Cabada et al.)[79]	Periods dominated only by primary emissions	S: 2.3 (bare quartz filter) (ratio for other methods ranged from 0.9 to 3.1)	W: near zero–18% S: 25 to >50% A: 35% (range 20–50%)	Several configurations were used to collect OC, each providing different estimates of OC artifact on quartz filters. Uncertainty estimate is about 20%
Pittsburgh, January–February 2002, July–August 2002 (Millet et al.)[43]	VOC emissions ratios	W: 1.85 S: 1.36	W: 16% S: 37%	
Atlanta, August 1999 (A) (Lim and Turpin);[10] (B) (Butler et al.)[50]	Periods dominated only by primary emissions	S: (A) 2.1 (B) –	S: (A) 46% (B) 50–60% during peak episode day (August 4, 1999)	(A) Used semicontinuous method; SOA peaked in the afternoon with ozone, with a smaller peak between 2 and 4 a.m., likely due to condensation
Houston, TX, August 2000–2002 (Russell and Allen)[85]	Periods dominated only by primary emissions	March–October: ~1–3 November–February: ~5–7 (Channelview 1.9)	Percent of $PM_{2.5}$: 5–10% on average over the 2-yr study at all sites	The OC/EC ratio varied by time of day and season. Primary OC > SOA at all locations. SOA peaks in September when ozone concentrations are highest. Urban areas tended to have both higher SOA and primary OC than rural areas
Baltimore, MD, February 15–November 30, 2002 (Park et al.)[80]	Periods dominated only by primary emissions, most likely motor vehicle emissions	April: 1.7 Nov: 2.8	Selected days in June/August: 62%, hourly maximum–82%	The OC/EC ratio tracked or lagged a few hours behind ozone. SOA contributions were similar daytime vs. nighttime.
United States (IMPROVE and SEARCH Networks), June 15–August 31, 1999 (Yu et al.)[81]	Primary OC/EC ratios from an emission/transport-model	Northeast United States: 1.16 West Pacific: 3.49 Range in Southeast among sites 1–5	Range of SOA was ~48% in the West to >60% in the eastern United States	Emissions inventory estimates dominate the uncertainty

35% depending on the assumptions associated with estimates of background OC.[84] A strong seasonal dependence also was observed for the SOA contribution to total $PM_{2.5}$ OC, as shown in Figure 5 and as expected from the variations in the primary OC/EC ratio. Use of highly time-resolved measurements during July 2001 resulted in SOA estimates that were 5–10% higher than those using either daily or monthly averages.[79] Authors indicated this was because of the strong dependence of SOA formation on photochemistry, with higher values during the day. Figure 6 illustrates the calculated diurnal patterns of SOA production and correspondence to high ozone and solar radiation, as expected.

Lim and Turpin[10] obtained hourly average OC and EC data in Atlanta during August 1999. Butler et al.[50] obtained 24-hr average data at three representative sites located in Atlanta. Both groups used the EC tracer method[77] (eq 3) estimating the primary OC/EC ratio using periods dominated only by primary emissions. The peak day (August 4, 2005) spatial average indicated over 50% SOA. Using hourly data, the SOA at the Atlanta Supersites location was estimated to contribute 46% of

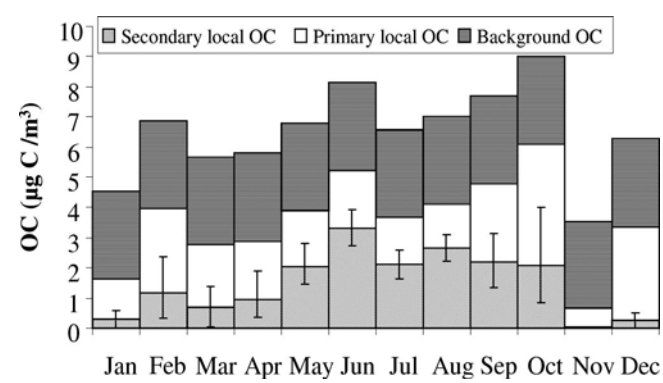

Figure 5. Contribution of SOA, primary emissions, and background to total OC $PM_{2.5}$ in Pittsburgh in 1995 on the basis of results from the OC/EC ratio method,[77] assuming average background concentrations of 2.9 μg C/m^3 for OC and 0.5 μg/m^3 for EC. Uncertainties are based on the uncertainties of the OC/EC. Reprinted with permission from Cabada et al.[84] Copyright 2003 Air & Waste Management Association.

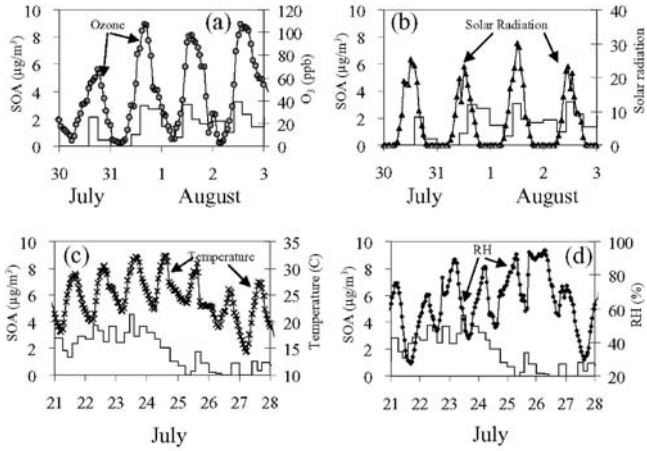

Figure 6. Hourly SOA production patterns for various periods during the summer intensive 2001 at PAQS. SOA concentrations calculated from the undenuded front quartz-fiber (QF) filter. (a) Ozone concentration and SOA production. (b) Solar radiation (UV) and SOA production. (c) Ambient temperature influences over the SOA production in Pittsburgh. (d) RH has a minor role in the production of SOA. Reprinted with permission from Cabada et al.[79] Copyright 2004 American Association for Aerosol Research.

measured particulate OC overall, with 1-hr average contributions reaching as high as 88%. Figure 7 shows the average diurnal profile of secondary OC with an afternoon peak corresponding to high ozone levels. Peaks in secondary OC and ozone also were observed on several nights of the study period. The most likely explanations were the partitioning of semi-volatile organic compounds to the particulate phase, with lower temperatures and higher RH as well as the possible vertical transport of regional pollutants from above to ground level. This research suggests that secondary OC concentrations in Atlanta were influenced by both "fresh" SOA formed by local photochemical reactions in the early afternoon and "aged" SOA transported from upwind regions or formed on previous days.

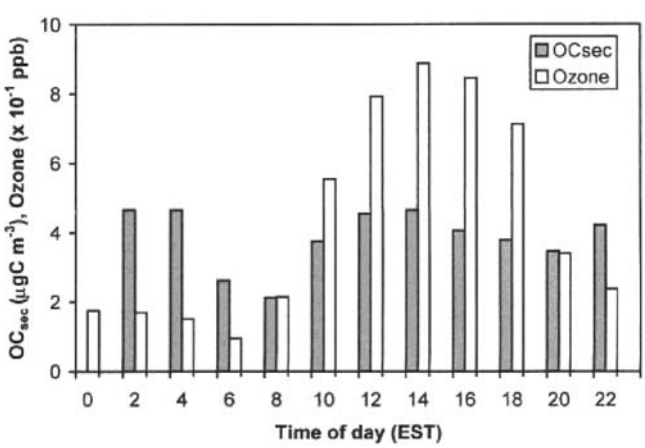

Figure 7. Study-average concentrations of secondary OC (OC_{sec}) and ozone in Atlanta, August 7–31, 1999. Secondary OC and ozone concentrations are in units of μg of C·m^{-3} and 10 ppb (value $\times 10$ = ppb) by time of day, respectively. Reprinted with permission from Lim and Turpin.[10] Copyright 2002 American Chemical Society.

In Houston, site and season specific primary $OC_{combustion}$/EC ratios and $OC_{noncombustion}$ concentrations were determined by linear regression applied to 24-hr integrated samples (see eqs 1–3).[85] The primary OC/EC ratio was determined from the EC versus OC slope during periods when primary OC dominates. The relationship between primary OC and EC varied by site and season. Using the results of the regression, secondary OC was estimated to be 5% (Galveston) to 10% (Deer Park) of $PM_{2.5}$ mass in southeast Texas. SOA may have been 1.2–2.1 times higher than these estimates and is therefore a fairly significant fraction of $PM_{2.5}$ in southeast Texas. Secondary OC concentrations varied from site-to-site and with season as seen in Figure 8. The highest SOA levels were seen in late summer and early fall at most sites. The more urban and industrial sites generally had higher primary and SOA concentrations, but one rural site (Conroe) also showed relatively high SOA levels. This suggests that gas-phase emissions from urban, industrial, and biogenic sources are all important SOA precursors.

In Baltimore, the EC tracer method was applied to 1-hr EC and OC data to determine the concentrations of SOA.[80] Primary OC/EC ratios were determined from periods of low photochemical activity. Although the range varied considerably, regression results indicated values of 1.7 in April and 2.8 in November with an overall average

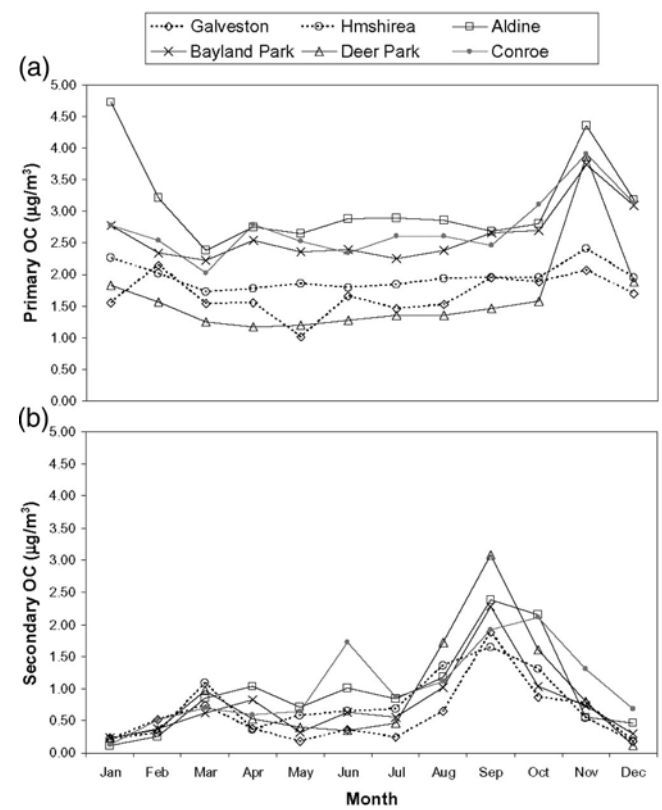

Figure 8. Mean monthly (a) primary and (b) secondary OC concentrations for the six sites in Southeast Texas with 2 full-years of valid data. Means were calculated from the regression data. Note that the regression for Conroe was significant at the 80% confidence level for March–October; regressions for all other sites were significant at the 90% confidence level or greater.[85] Reprinted with permission from Russell and Allen.[85] Copyright 2004 Elsevier.

of 2.7. From June 10–13, 2002, the estimated hourly SOA concentrations varied between 0.6 and 9.8 μg C/m^3 with a mean value of 5.4 μg C/m^3. This represented 17.3–80.9% of the measured OC, with an average value of 63.8%. Similar results were observed during an ozone episode (August 11–14, 2002) when an average of 59.4% of the measured total OC was secondary. In general, the nighttime levels of secondary OC were similar to daytime levels, which was suggested to be a result of transport from upwind sources and/or SOA produced the previous day.

The temporal and spatial distributions of both primary and secondary organic aerosols were examined over the continental United States between June 15 and August 31, 1999.[81] The 24-hr ambient OC and EC data from the IMPROVE (Interagency Monitoring of Protected Visual Environments—vista.cira.colostate.edu/improve/) and SEARCH (Southeastern Aerosol Research and Characterization Study—www.atmospheric-research.com/studies/SEARCH/) networks were combined with estimated primary OC/EC ratios from an emission/transport model. The mean values of modeled primary OC/EC ratios ranged from 1.16 ± 0.13 over the northeast to 3.49 ± 1.22 in the West Pacific region. Figure 9 shows the estimated primary and secondary OC concentrations at all the sites considered. Regional analysis indicates that for the study period, primary and secondary OC contribute about equally to total OC in the western United States, whereas, secondary OC is dominant (>60%) in the Southeast and Northeast. Average secondary OC concentrations in the Northeast, Southeast, Central, West ,and West Pacific were 1.27 ± 0.15, 1.52 ± 0.59, 0.90 ± 0.51, 0.51 ± 0.29, and 0.94 ± 0.52 μg C/m^3, respectively. The relatively large uncertainties in the estimates likely result from uncertainties in the emissions inventories. Differences in OC/EC sampling methods were not an issue because all samples were analyzed by thermal/optical reflectance.[82] It was further found that modeled OC/EC primary ratios could vary significantly on a daily basis, even at a single sampling site (ranging at urban sites from ~2 to >4) and between similar site types (e.g., among rural sites in SEARCH ranging from ~1 to 4). The results indicate that the use of a constant value for the primary OC/EC ratio at a location is not appropriate over longer time periods.

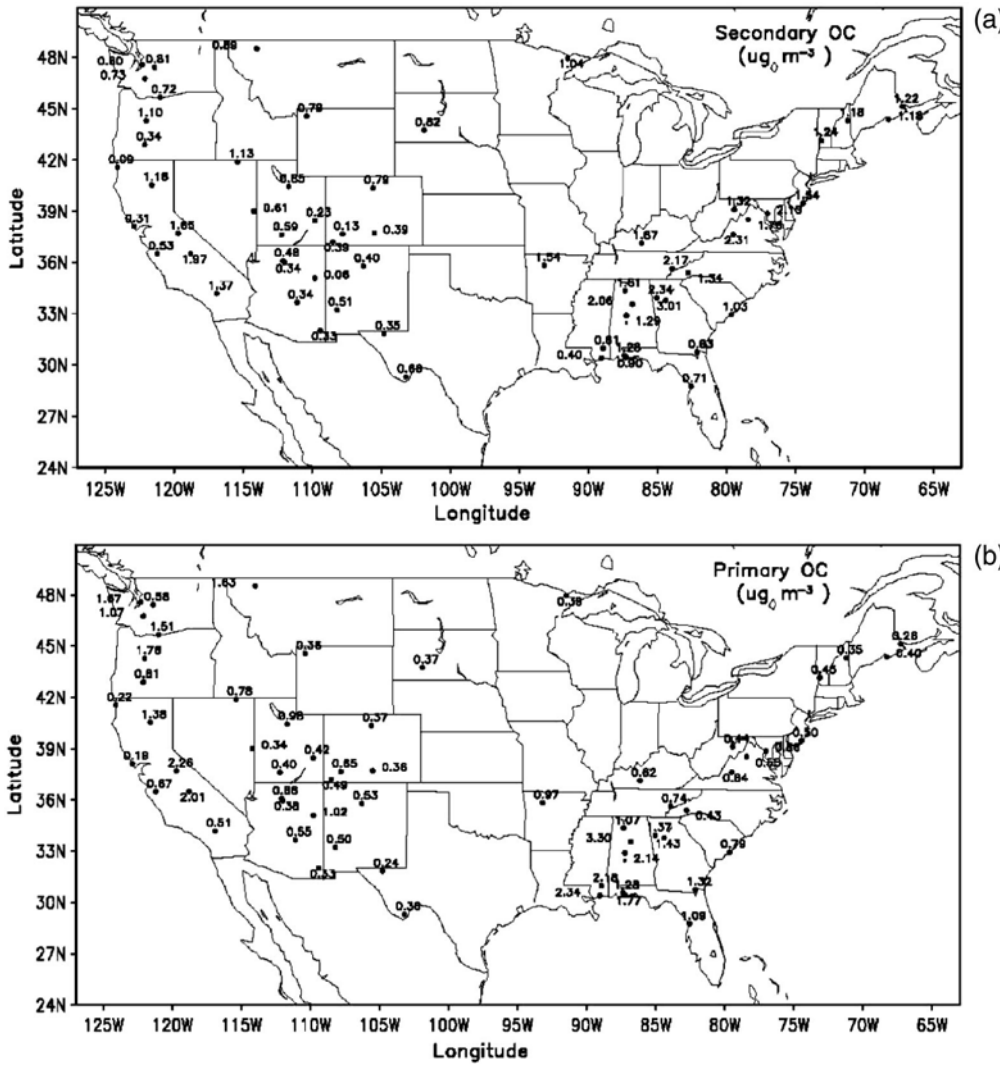

Figure 9. Spatial distribution of mean values of estimated (a) secondary and (b) primary OC concentrations over the United States.[81] Reprinted with permission from Yu et al.[81] Copyright 2004 Elsevier.

Speciated SOA Indicator Measurements

More detailed organic speciation analysis techniques have identified many compounds in ambient PM that are likely components of SOA. The types of SOA species measured may help to elucidate the reaction pathways and ultimately the source of the precursor VOCs. Furthermore, although the hundreds or thousands of SOA species cannot all be realistically quantified in ambient samples, certain compounds may serve as tracers of SOA contributions to PM. For example, a study in the southeastern United States determined that the $PM_{2.5}$ levels of phthalic acid (1,2-benzenedicarboxylic acid) were correlated with the sum of sulfate, NO_3, and ammonium.[86] Another study in the South Coast Air Basin, Los Angeles, CA, found that phthalic acid was correlated with the "other" mass in a chemical mass balance (CMB) apportionment model.[87] The main contributor to this other mass is thought to be secondary organics, providing further support for the idea that this compound may be an indicator of SOA formation. Similar conclusions were reached by Yu et al.[81] on the basis of their transport modeling of SOA across the United States. In Los Angeles, diurnal measurements of phthalic acid also were made at two locations over two seasons (winter and summer) in two particle size fractions ($d_p < 0.18$, ultrafine mode; $d_p = 0.18–2.5$ μm, accumulation mode).[88] The locations were downtown Los Angeles (USC) a source site and at Riverside, an inland receptor location. As seen in Figure 10, phthalic acid was found primarily in the accumulation mode, peaked in the daytime, and was more prevalent in the summer. These observations are what one would expect for a SOA component. Somewhat surprising were the higher levels found at the urban location relative to the downwind, inland location where more photochemical activity is expected. It is possible that the oxidation reaction forming this compound, which is not yet known, may occur relatively quickly in urban air sheds and/or the degradation or further reaction of phthalic acid may occur on time scales shorter than the transport time across the Los Angeles Air Basin.

Gas- and particle-phase measurements of nitropolyaromatic hydrocarbons, known to be both mutagenic and to be secondary reaction products, also were obtained during the above mentioned Los Angeles field study.[89] Particulate-phase polyaromatic hydrocarbon (PAH) concentrations were highest in Los Angeles (USC) in the winter, a result of traffic at this source site under winter atmospheric inversions and condensation of semi-volatile species because of cooler temperatures, whereas nitro-PAH levels were highest in Riverside in August, a result of enhanced summer photochemistry. Although it was determined that hydroxyl radical-initiated reactions produced nitro-PAHs in both seasons, little evidence for NO_3 radical chemistry was seen in winter. In the summer, NO_3 radical-initiated formation of nitro-PAHs is suggested by nitro-PAH isomer profiles at both the downwind and urban locations, consistent with the observations of phthalic acid given above. Figure 11 gives the diurnal, seasonal, and spatial variations of the nitro-PAH relative to corresponding PAH precursor. Although the Riverside samples show higher ratios relative to Los Angeles, the general diurnal and seasonal patterns look very similar to those found for phthalic acid in Figure 10. Such ratios or compounds may therefore also serve as indicators of SOA formation.

Measurements at a remote location in northern Michigan revealed relatively high levels of organic di-, tri-, and tetracarboxylic acids, all thought to be indicators of secondary organic aerosol.[90] The authors compared time periods when the site was not impacted by primary anthropogenic sources to time periods when it was impacted by such sources, which allowed for a better understanding of which organic species are not from primary anthropogenic sources, and thus, may represent either primary biogenic sources or secondary aerosol products. Concentrations of aromatic and aliphatic dicarboxylic acids peaked in July with lower concentrations in the fall, coinciding with trends in total $PM_{2.5}$ OC. The distribution of aliphatic diacids and the aromatic di- and triacids appeared to vary with different atmospheric conditions, suggesting different precursor gases and/or reaction mechanisms for the formation of these SOA components. Results also indicated that multiple organic species must be measured to account for anthropogenic and biogenic fractions of SOA.

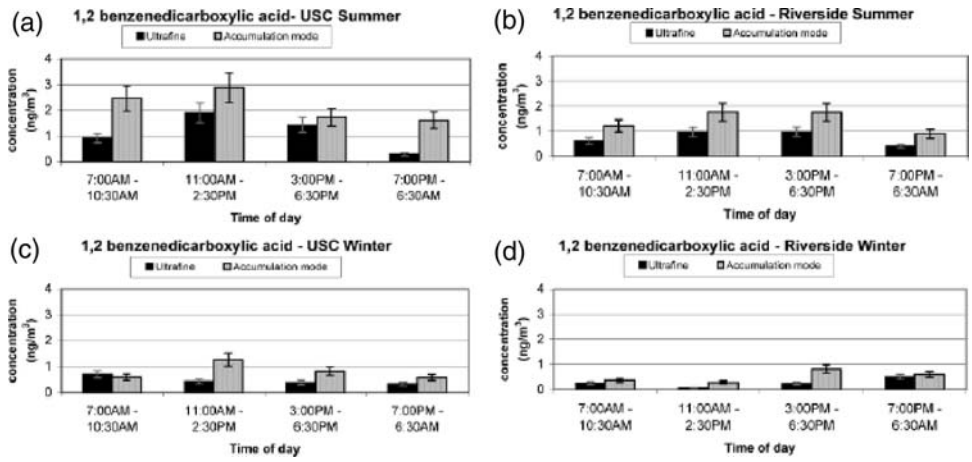

Figure 10. Atmospheric concentrations of phthalic acid, a secondary organic compound, in the Los Angeles Basin during (a and b) summer and (c and d) winter.[88] Reprinted with permission from Fine et al.[88] Copyright 2004 American Chemical Society.

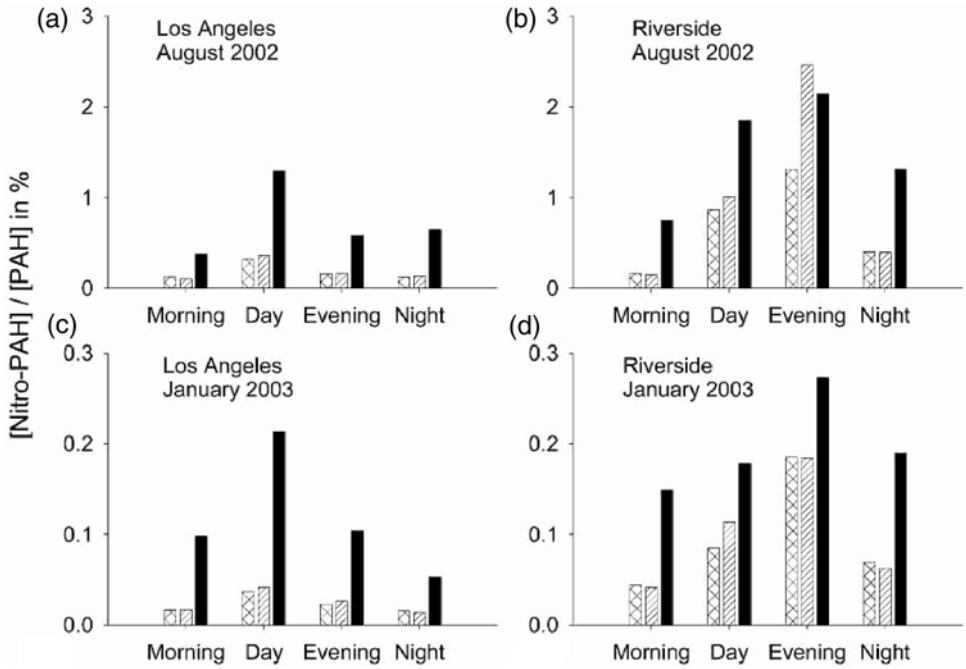

Figure 11. Diurnal, seasonal and spatial variations of the ratios of [NPAH]/[PAH] (in %) for NNs/Naph (bars with X), MNNs/MNs (hatched bars) and (DMNNs + ENNs)/(DMNs + ENs) (solid bars) for (a and c) Los Angeles and (b and d) Riverside.[89] PAH = polycyclic aromatic hydrocarbons; NPAH = nitro-polyaromatic hydrocarbon; NN = nitronaphthalene; Naph = MNN, methylnitronaphthalene; MN = methylnaphthalene; DMNN = dimethylnitronaphthalene; ENN = ethylnitronaphthalene; DMN = dimethylnaphthalene; EN = ethylnaphthalene. Reprinted with permission from Reisen and Arey.[89] Copyright 2005 American Chemical Society.

Ambient $PM_{2.5}$ filter samples collected in North Carolina were analyzed by Fourier transform infrared spectroscopy (FTIR) to identify compound classes containing –C=O and –OH functional groups as well as by derivatization/mass spectrometry to confirm the presence of the oxygenated species.[91] Several classes of oxygenated compounds were identified, including a number that appeared to be similar to those observed by irradiation of an α-pinene/NO_x/air mixture in a smog chamber. Classes of compounds identified included: oxo-monocarboxylic acids, trihydroxy-monocarboxylic acids, dihydroxy-dicarboxylic acids, hydroxyl-dicarboxylic acids, normal dicarboxylic acids, oxo-dicarboxylic acids, methoxy-dicarboxylic acids, tricarboxylic acids, triols, as well as photooxidation products of α-pinene and toluene. Many of these oxygenated species are believed to be biogenic SOA products.

The size distributions of aliphatic carbon, carbonyl, and organonitrate functional groups in ambient PM were measured at the three Houston Supersites Project sampling sites during intensive monitoring from August 1 to September 15, 2000.[92] Samples were collected using the Hering low-pressure impactor and analyzed by FTIR for the three functional groups of interest. Carbonyls and organonitrates showed modes in the 0.05- to 0.26-μm and 0.5- to 1-μm size ranges and appear to be primarily due to SOA formation. The submicron aliphatic carbon had similar maxima, but weak correlations to ozone indicated the species associated with aliphatic carbon are likely primary in origin. The FTIR analysis techniques used in this study, although not specific to individual organic species, may prove useful in quantifying SOA contributions to ambient PM. Another set of samples collected during the same study in Houston were analyzed by derivatization/gas chromatograph–mass spectrometry (GC-MS) for a series of polar organic compounds many of which are thought to be SOA components.[93] A comparison of the unapportioned organic mass from a CMB source apportionment with the sum of propanedioic and butanedioic acids yielded reasonable correlation. This further supports the idea that certain dicarboxylic acid concentrations as well as the unapportioned CMB mass may serve as indicators of SOA.

Havers et al.[94] suggested that humic-like substances (HULIS) are important constituents of the OC associated with airborne PM. Kunit and Puxbaum[95] and Puxbaum and Tenze-Kunit[96] have reported on the presence of cellulose as a particulate organic component. Thus, these studies support the hypothesis that a large fraction of the organic aerosol is polymeric and oligomeric substances that are water-soluble with unknown potential toxicity. It is uncertain whether these materials are primary or secondary in nature. However, there has been recent increasing evidence for polymerization reactions that build oligomers from monomeric species in the atmosphere. Kalberer et al.[97] examined the organic components in smog-chamber experiments and found polymeric material with molecular weights up to the order of 1000 Da. Tolocka et al.[17] found oligomeric products between 200 and 900 Da. The masses and dissociation products of these ions were consistent with various combinations of

the known primary products of reactions of "monomers" with and/or without the expected acid-catalyzed decomposition products of the monomers. Gao et al.[36] examined seven hydrocarbon systems (i.e., R-pinene, cyclohexene, 1-methyl cyclopentene, cycloheptene, 1-methyl cyclohexene, cyclooctene, and terpinolene) and observed oligomers with MW from 250 to 1600 in the SOA formed, both in the absence and presence of seed particles and regardless of the seed particle acidity. Thus, there is a need to better understand the presence of HULIS and related materials in actual atmospheric aerosols to ascertain how much of this material is likely to be degraded primary biological material and how much of it is secondary reaction product polymers.

Continuous Mass Spectrometer Signals for SOA

Particle mass spectrometers, which measure real-time particle size and composition information, have the potential of providing signals indicative of secondary organic PM mass. For example, AMS spectra with prominent peaks at $m/z = 44$ amu (from CO_2^+) are thought to derive from photochemically generated oxidized organic aerosol species. Other peaks are more indicative of vehicular primary, unoxygenated species. Using these associations in New York during a summer intensive monitoring program in 2001, a major fraction of the organic PM measured was shown to have both traffic and secondary sources.[98] The fractions of the total mass spectral ion signal due to traffic-related aerosol and photochemically generated aerosol have clear diurnal patterns as seen in Figure 12. As expected, the fraction of traffic-related particles shows maxima during the high-traffic periods, and the fraction of photochemically generated particle peaks between noon and evening hours. Although precise quantification of particle types is still not possible, the results support the idea that certain ion signatures may help to differentiate primary and secondary organic PM.

A different particle mass spectrometer (Particle Analysis by Laser Mass Spectrometry—PALMS), was operated in Atlanta during August 1999.[99] The chemical components of individual particles between 0.35 and 2.5 μm in diameter were measured. Their results indicated that approximately 45% of the negative spectra contained ions representative of oxidized organic compounds and they were more pronounced in particles with higher light scattering intensities. It appeared that RH drove much of the diurnal variation of these semi-volatile oxidized organic species with apparent condensation to the particle phase during cooler, higher RH conditions and minima during the afternoon, resulting in diurnal patterns similar to NO_3. A small afternoon maximum of oxidized organic species was likely attributable to photochemical production as the oxidized organics appeared to be associated with organic/sulfate particles. Heterogeneous aqueous chemistry is suggested for some of the oxidized organic formation given the coexistence with hydroxymethanesulfonate (HMS) in the same spectra. HMS is known to be created by SO_2 reacting with formaldehyde in clouds or fogs.[100]

Other Indicators of SOA

In Los Angeles, the diurnal variations of ultrafine particle chemical composition were measured in several particle size modes less than 180 nm.[57] OC and EC were the primary constituents of UF PM below 32 nm. NO_3 and sulfate were not observed in this size range at any of the four sites or seasons with the exception of Riverside in the fall, where NO_3 reached just over 10 ng/m^3. Another interesting result was the presence of a small submode of organics between 32 and 56 nm. The organic submode also was observed in 2-wk time-integrated samples collected during another Los Angeles study.[101] The submode is either caused by condensation of semi-volatile vapors emitted by motor vehicles at sites influences by traffic, or perhaps by photochemical organic reaction products, which also may condense to this size range. Seasonal and spatial patterns observed in both studies, as well as EC and OC correlations, suggest that secondary photochemical reactions are playing a role in forming this ultrafine organic material.

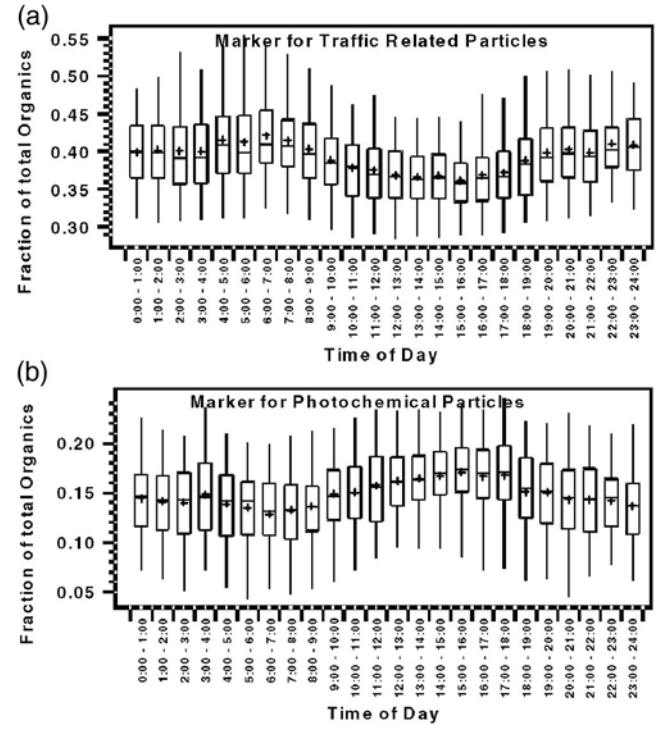

Figure 12. Average diurnal patterns of the fraction of organic particles relative to total particles that have been identified as markers for (a) traffic aerosol and for (b) photochemical aerosol in Queens, New York. Unlike the diurnal pattern of the total organic mass concentration, these fractions both show a distinct diurnal pattern. Reprinted with permission from Drewnick et al.[98] Copyright 2004 American Association for Aerosol Research.

Because much of the SOA material is highly oxidized, it is more likely to be water-soluble than many primary emissions. Thus the water-soluble OC (WSOC) component of aerosol particles may be a general indicator of the presence of SOA. In St. Louis, a particle-into-liquid sampler (PILS) measured WSOC on a 6-min basis, whereas another carbon monitor measured EC and OC on an hourly basis.[102] Summer and fall measurements showed WSOC/OC ratios typically ranging from 0.40 to 0.80. In June, the diurnal variation of WSOC/OC correlated modestly with ozone, suggesting a photochemical origin for WSOC. However, the relationship was not observed in August. The results suggest that WSOC is composed of a

complex mixture of compounds, a significant fraction of which may be secondary.

Many components of SOA are semi-volatile and measurements of particulate-phase semi-volatile organic matter (SVOM) were made in Pittsburgh and a second suburban location during a 2001 intensive study.[103] SVOM levels coincided with high ozone concentrations during midday, possibly indicating that much of SVOM was secondary. SVOM was not associated with the morning commute. Although it is expected that a fraction of SVOM is also primary, measurements of semi-volatile organics also may serve as a general indicator of SOA formation.

Sources of SOA Precursors

Both natural and anthropogenic sources emit gas phase organic precursors that form SOA. The biogenic contributions can be estimated based on ^{14}C measurements to separate out modern carbon from fossil carbon. Although fossil carbon is primarily anthropogenic, modern carbon can have both natural (e.g., vegetative VOC emissions) and anthropogenic sources (e.g., controlled burning or residential wood combustion). In Houston, a limited set of samples were analyzed for modern carbon and compared with observed OC/EC ratios.[44] As the OC/EC ratio increased, indicating higher SOA contributions, so did the percentage of modern OC in the samples, indicating that SOA has a large biogenic component in southeast Texas, accounting for up to 80% of the SOA north of Houston during the summer. At or near urban sites, the fraction is significantly less and at times not detectable. Similar observations and conclusions based on modern carbon measurements have been made in both urban and rural locations in Tennessee.[104,105] But in other locations, such as Los Angeles, modeling efforts have estimated that more than 90% of SOA is from anthropogenic precursors.[106]

SOA formation due to anthropogenic precursor emissions from sources in the Houston-Galveston area were estimated by multiplying the anthropogenic emissions of SOA precursors by fractional aerosol coefficients (FACs) describing how much of the precursor is expected to react and form SOA.[107] The analysis showed that area and nonroad mobile sources contributed 56% of the aerosol precursor emissions, mobile sources contributed 27%, and point sources contributed only 16%. However, point source emissions resulted in 53% of the projected SOA because of the high SOA yields from point source precursors, especially terpenes from pulp and paper processing and aromatics. Comparison of the FAC method to a gas/particle partitioning model[108] indicated that the FAC method may be high by a factor of 2, although the relative order of importance of SOA from specific precursors was generally consistent between the two approaches. Considerable uncertainty still exists with emissions estimates of both the biogenic and anthropogenic precursors that form SOA. In addition, statistical approaches (e.g., OC/EC tracer method) also have considerable uncertainty in their estimates. Therefore, significant uncertainty still exists in estimating SOA, especially in comparison to estimates of inorganic secondary aerosols, which are measured directly.

Another important recent discovery by Claeys et al.[109] suggests that isoprene can be a significant contributor to SOA concentrations. They have identified 2-methyl tetrols and suggest that the 2-methyl tetrols represent a SOA source strength of approximately 2 Tg per year. Kleindeinst et al.[110] reported finding particulate 2-methyl tetrols in studies in New York City and Baltimore. Xia and Hopke[111] also measured concentrations of 2-methyltetrols (2-methylthreitol and 2-methylerythritol) in Potsdam, NY, from June through December 2005. The 2-methyltetrols peaked during the summer and contributed approximately 2.8% to the total OC mass.

CONCLUSIONS

It is clear that particles formed in the atmosphere comprise a major portion of ambient $PM_{2.5}$. The main secondary species include sulfate, NO_3, ammonium, and SOA; many of the latter are likely oxygenated organic compounds of either biogenic or anthropogenic origin. The three inorganic species typically account for more than 50% of the $PM_{2.5}$ mass and, during summer episodes in the eastern United States, may account for more than 70% of the mass, whereas in the western United States they may account for 70% of the mass in the wintertime. In the eastern United States, sulfate and OM usually dominate, with sulfate being higher than OM, especially during peak $PM_{2.5}$ periods. NO_3 is usually a minor component in the summer (<10%). In the winter, sulfate is lower and NO_3 is higher and both species are of about equal proportions. OM only has a slight seasonal trend, and therefore becomes the dominant component during the winter. In the western United States in the winter, sulfate is a minor component and NO_3 is often the most abundant species, although OM can at times be greater than NO_3 because of the impact of primary OC from local sources (e.g., residential wood burning). In the summer, OM is often the most important species, although NO_3 can be significant, with sulfate likely comprising less than 20% of the mass. OM typically is the major component of UF PM, with growth due to condensation of other OM (e.g., SOA), sulfate, and NO_3. The noted exception is during nucleation bursts, which are initiated by the formation of sulfuric acid through a tertiary reaction. The sulfuric acid is neutralized by NH_3, either partially or fully, with subsequent growth by typical processes.

In the eastern United States, sulfate and associated cations appear to have only a modest diurnal pattern with a slight peak in the afternoon during the summer due to local photochemical production of sulfate from SO_2. The modest diurnal pattern likely is due to transport of sulfate from upwind locations that may be 1000 km or more away. Conversely, NO_3 has a strong diurnal pattern driven by thermodynamics, with the aerosol phase favored in the early morning when temperatures are lowest and RH highest. OM can have a varied diurnal pattern based on the sources impacting the site, although as noted above, OM has only a slight seasonal pattern. For example, OM may peak in the morning with rush hour traffic, with another peak in the afternoon due to photochemical production of SOA, followed perhaps by a late evening peak if the area is impacted by residential wood burning. On the other hand, OM can peak at night with

a minimum in the daytime driven by changes in the mixing height. At times, SOA can be a significant portion of the total OC. SOA is believed to be composed of oxygenated organic species, including a series of dicarboxylic acids and nitro-organic species, such as nitro-PAH compounds. This has been tentatively confirmed though atmospheric sampling, smog chamber experiments and source apportionment modeling. Very high–molecular-weight compounds (oligomers) also have been identified and are likely secondary in origin. HULIS also has been measured in $PM_{2.5}$, although the fraction that is primary versus secondary still needs to be determined.

SOA is difficult to quantify and several methods are described in this review. One of the most widely used methods is the OC/EC ratio method, also referred to as the EC tracer method. Here the primary OC/EC ratio is estimated and used along with ambient EC concentrations to estimate SOA. High time-resolution measurements indicate that the primary OC/EC ratio can have considerable temporal variation, even on a few hourly basis adding to the uncertainty associated with the EC tracer method. Several variations of the EC tracer method are discussed along with associated uncertainties. Source apportionment also is used to estimate SOA by using ambient species believed to be tracers of SOAs. This approach requires the measurement of specific organic species or functional groups. Nonetheless, there is a large uncertainty associated with the estimate of SOA in air.

In summary, EPA's PM Supersites Program has significantly pushed forward our knowledge of the spatial and temporal behavior of secondary aerosols, particularly SOA. Results from the Supersites Program also reaffirm our past knowledge, now in multiple locations, and over one or several years that secondary aerosols comprise a significant portion of $PM_{2.5}$ and although the inorganic fraction is easy to measure, there is still considerable difficulty with quantifying secondary organic contributions with significant uncertainty approaching 50% or more. Areas of important future research include the further elucidation of the chemical pathways and aerosol yields for SOA formation, especially heterogeneous and acid-catalyzed processes. Results from these studies will allow the refinement of models to better predict the SOA content of PM, and these data provide a rich dataset for model performance evaluation. Concurrently, advances in ambient measurement techniques and secondary PM estimation methods will be needed to validate new models and help determine the sources of secondary PM precursors, especially organic aerosol precursors. Determining the SOA fraction of PM is an active and ongoing research area at this time, and considerable progress is expected over the next several years.

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About the Authors

Philip M. Fine is a research assistant professor and Constantinos Sioutas is a professor with the Department of Civil and Environmental Engineering at USC. Paul A. Solomon is a senior environmental scientist with EPA's Office of Research and Development in Las Vegas, NV. Please address correspondence to: Philip M. Fine, University of Southern California, Department of Civil and Environmental Engineering, KAP-210, 3620 South Vermont Avenue, Los Angeles, CA 90089; phone: +1-213-740-0560; fax: +1-213-744-1426; e-mail: pmfine@usc.edu.