HUMAN EXPOSURES TO PARTICLE STRONG ACIDITY

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ABSTRACT

This paper reviews the findings of recent research programs and attempts to present an update of our current understanding about human exposures to particle strong acidity (PSA). This review tells of the key steps in our recent progress, such as aerosol chemistry and physics, improvements in samplers and measurement techniques, increases in the databases, and exposure assessments. Remedying an earlier paucity in direct measurements of PSA, there has been a great increase in the database from several recent field studies. These studies have shown that, where appreciable PSA exists, virtually all exposures occur in the warmer months, and the highest PSA levels are specifically associated with summertime, regional stagnation periods. Frequently, PSA episodes are coincident with photochemical smog and high ozone levels, although the converse is not always the case. A number of new studies have shown that the effect of the indoors on human exposures to PSA is entirely protective. That is, there are rarely important sources indoors, and most factors affecting the indoor air quality lead to attenuation of PSA levels. While sulfate aerosol effectively infiltrates from outdoors, the strong acid portion is largely neutralized by ammonia present indoors. The chemical, physical and phenomenological vagaries of PSA in the human environment are such that absolute exposures cannot be predicted by outdoor data alone. Personal (i.e., breathing zone) exposures are found to fall between measured outdoor and indoor values. Because of low indoor PSA concentrations and the higher activity individuals' sustain while outdoors, even for relatively a minor part of the day, time spent outdoors may be the chief determinant of personal dose. Time/activity-weighted models of indoor and outdoor concentrations give better estimates of personal exposures, compared to outdoor concentrations alone. However, they currently fall short of providing accurate predictions of personal exposure. There remains problems in determining the most appropriate exposure metric for epidemiological investigations.

INTRODUCTION

Air pollution epidemiology has been able to clearly demonstrate instances when increases in mortality and/or morbidity were associated with elevated concentrations of airborne particulate matter (PM). At a NIEHS-sponsored symposium in 1987, Professor Morton Lippmann[1] conjectured that the available metrics of particle air pollution were only surrogates for the toxic agents directly responsible for observed health effects, but which were not being directly measured (Lippmann, 1989). Particle strong acidity (PSA) has been hypothesized to be a key agent in the health link, based on episodes in industrial cities of Europe and North America. In the hypothetical relationship Lippmann proposed, the health effects for chronic exposure to PM would improve for the various surrogates, the closer they model this agent (i.e., TSP < PM10 < PM2.5 < sulfate < PSA).

Direct measurements of airborne acidity were limited during the historic air pollution episodes, i.e. prior to the 1960s. However, there have been recent improvements in measurement technology and enhanced focus on PSA. The database on the current exposure concentrations and knowledge of the chemical dynamics have been greatly enhanced from recent, comprehensive monitoring programs. In just the past 5 years, the focus has sharpened on human exposures by measurements on the most relevant microenvironments (in and around residences, workplaces and schools) and the personal breathing zone, to supplement information taken at the central stations traditionally employed in air pollution monitoring. Current programs also include studies of sensitive populations, application of exposure models, and evaluation of accurate surrogate measures for retrospective epidemiological analyses.

This paper reviews the findings of recent research programs and attempts to present an update of our current understanding about human exposures to PSA. This review starts with some of the

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key steps in our recent progress, which have been in the area of aerosol chemistry and physics, and in the improvement in samplers and measurement techniques. To remedy the earlier paucity of PSA data, the completion of several important field studies has provided a substantial increase in available measurements. Their findings regarding spatial and temporal patterns are presented next. We then review several studies which directly investigated PSA levels in important microenvironments, as well as personal exposures. Finally, we review some improvements in statistical and numerical efforts to model or predict exposures in the community, and consider metrics appropriate for PSA exposure assessment in health studies.

AEROSOL CHEMISTRY AND PHYSICS

Airborne acidity can occur as suspended particulate matter (liquid or solid) as well as a gas phase. The concept of airborne acidity includes both the actual acid dissociation and its *potential* when the gas or particle contacts a liquid or solid surface. With respect to pulmonary surfaces and fluids, many components in the air are acidic. Deposition in the airways is greatly affected by whether exposure is to gaseous or particulate acids and according to the size of particles (e.g. Waldman, 1990).

The principal acids found in the atmosphere are related to mineral acids: particulate sulfuric acid (H_2SO_4) and nitric (HNO_3), nitrous (HNO_2), and hydrochloric (HCl) acids, which exist as gases in their pure form (Koutrakis and Mueller, 1989). Organic acids (such as carboxylic and dicarboxylic acids) can also be found in the particulate and gaseous forms. Formic and acetic acids are the most abundant of organic acid compounds. As weak acids, these tend to exist in the non-dissociated form and will often be volatile. In the atmosphere, the magnitude of particle acidity contributed from organic acids is generally found to be minor compared to particle strong acids (Lawrence and

Koutrakis, 1994).

The most prominent particle strong acids (PSA) are derived from sulfuric acid, formed by oxidation of SO_2. When the acid is formed in the gas phase, it immediately condenses to very small particles; these rapidly grow in the atmosphere. When formed by heterogeneous processes, the acidic sulfates are also found to stabilize in accumulation mode particles. Measurements in southern Ontario for aerosols in several size ranges indicated that the vast majority of PSA was in the range of 0.2 to 2 μmad (micron aerodynamic diameter) (Koutrakis et al., 1989). The form of PSA is rarely pure sulfuric acid; H_2SO_4 can be partially neutralized to forms which are still acidic. The few data available indicate aerosol samples have very similar acidic content over the size ranges (Figure 1). This is consistent with internal mixtures of decreasingly acidic sulfate forms: $(NH_4)H_3(SO_4)_2$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $[NH_4]_2SO_4$). Neutralization does not appear to alter the size of the aerosol, although increasing relative humidity does increase particle sizes (Koutrakis et al., 1989). The contribution to PSA from condensation mode (<0.1 μmad) particles, including ultrafine, is not found to be substantial. Particles with acidity of this small size either grow or are neutralized rapidly. The particles larger than 2 μmad contain little sulfate, but include wind-blown materials, in which there is often an abundance of alkaline materials.

Theory predicts a very fast neutralization reaction between PSA and atmospheric ammonia, which limited laboratory experiments with pure compounds appear to confirm (Huntzicker et al., 1980). However, measurements seem to indicate that neutralization is slower under field conditions and that some amount of PSA may persist even with ammonia present (Brauer et al., 1991; Liang and Waldman, 1992; Kitto and Harrison, 1993). The *caveat* to these findings is that simultaneous time-averaged measurements of PSA and ammonia are generally too long to entirely exclude the possibility that non-zero concentrations in different sub-intervals only *appear* as coincident, measurable levels in the whole sample. Recent research has evaluated the possibility that organic compounds retard the rate of neutralization (Daumer et al., 1992).

SAMPLERS AND MEASUREMENT TECHNIQUES

While measurement techniques for sulfate aerosol concentrations are fairly accurate, affordable and robust, determinations of PSA have presented several practical difficulties for widespread use until fairly recently (Stevens, 1986). As stated above, PSA is associated with the finer particles, while alkaline components dominate the constituents found in the coarser particles. Size-selective particulate collection is required, and a fairly sharp size cut at ≈2 μmad is needed to reduce bias in PSA measurements. It is also advisable to collect vapor and particle components separately, because gaseous acids (e.g. nitric acid) or bases (e.g. ammonia) can alter the measured values for particle acidity. However, there is some basis for concern that stripping the gas-phase may alter the equilibria for the particulate compounds, causing artifactual losses of net acidity. Current methods often utilize a correction for this, although it is observed to be only a minor factor when PSA levels are consequential (Koutrakis and Allen, 1994).

There are two principal methods used to measure or infer PSA concentrations: time-averaging filter/denuder samples, and semi-continuous flame-photometric sulfur analyzers (Tanner, 1989). The use of filter/denuder systems is the only method to directly determine PSA and is now widespread. For example, the Harvard-EPA Annular Denuder System (HEADS), and variations of the ADS, have been well characterized in laboratory and field settings (Brauer et al., 1989; Koutrakis et al., 1988). The semi-continuous analyzers directly determine sulfur content in fine aerosol. Adapted with thermal-ramping, these analyzers can speciate various forms of sulfate-containing particles. They can determnine concentrations of sulfuric acid particles (when present) by difference, because this form of sulfate can be separated from the others. The less acidic forms (i.e. NH_4HSO_4 and $[NH_4]_2SO_4$) cannot be separated from one another. However, PSA concentrations can be inferred, using site-specific aerosol data and the assumption of an internal mixture (Allen and Koutrakis, 1992). The available data confirm that short-term peak concentration periods occur within extended intervals of elevated PSA. In sulfate-dominated atmospheres, there is general comparability among the results for the various measurement techniques currently used (Ellestad et al., 1991; Suh et al., 1994a).

AMBIENT LEVELS AND EPISODES

The historical air pollutant events all occurred in the wintertime: e.g. Meuse Valley, Germany (1936), London (1950s), New York City and Pittsburgh (1960s). These and many other severe, localized episodes were induced by the high emissions of sulfur dioxide in industrial and urban centers, and intensified by the same atmospheric conditions (i.e. low elevation temperature inversions, low winds and stagnation) which led to the associated fogs. These conditions produced remarkably high concentrations of SO_2 and sulfate particles. Retrospective analyses indicate these particles were likely to have been in the form of sulfuric acid. The impacts of the "killer fogs" on respiratory health are legend (e.g. Ministry of Health, 1954).

Fortunately, local air pollution controls have dramatically reduced both ground-level emissions of SO_2 and these wintertime episodes. Currently, emissions of SO_2 are largely due to coal burning at power plants and industrial smelters, which use tall stacks to mitigate local impacts. The greatest density of these emissions in the U.S. occurs in the midwest states around the Ohio River Valley. The prevailing winds lead to regional scale transport to the north and east. Much of the sulfate aerosol monitored throughout the eastern U.S. emanates from these sources. Because the rate of sulfate production is sharply increased by photochemical smog conditions occurring during the summer -- due to higher temperatures, relative humidities, and oxidant concentrations -- wintertime sulfate levels are generally minor compared to those during the summer months (Finlayson-Pitts and Pitts, 1986).

Summertime PSA episodes in the eastern U.S. and Canada generally persist for many hours, even for multi-day periods. These periods are fairly obvious to observers, with its characteristic "whitish" haze and often warm, humid conditions. Like elevated sulfate periods, PSA episodes are associated with air trajectories emanating from SO_2 emission regions (e.g. the Ohio River Valley). While correlation is usually found between PSA and sulfate aerosol concentrations, an elevated sulfate level is only a *necessary, but not sufficient* condition for a PSA episode. Meteorology, transport and atmospheric ammonia all affect local PSA-to-sulfate ratios, which are found to be site specific.

Prior to 1985, there were no continuous, yearlong records of PSA concentrations in the U.S. or Canada, and very few coincident, multisite databases. Lioy and Waldman (1989) provide a summary of measurements up to that time, which were mainly limited to research on solitary study sites and relatively narrow study periods. These earlier studies yielded findings which demonstrated the seasonality of exposure levels, but the magnitude (of high-to-low seasonal averages) could not be discerned.

The recent papers by Spengler et al. (1989), Koutrakis and Allen (1994) and Thurston et al. (1992a) have reported data for daily (or alternate day) sampling over the entire year at fixed sites. These have shown that virtually all appreciable PSA exposures occur in the warmer months. The highest levels are specifically associated with summertime, regional stagnation periods. Frequently, PSA episodes are coincident with photochemical smog and high ozone levels, although the converse is not always the case.

Simultaneous measurements on a regional scale have confirmed the spatial homogeneity in PSA levels over large areas (Figure 2). Good correlations for daily PSA concentrations among suburban sites 100+ km apart were observed in New York (Thurston et al., 1992a) and New Jersey (Liang, 1994). Attenuation of regional PSA levels in central city locations has been observed to varying degrees. Very limited data for New York City in 1977 implied that all the PSA might be neutralized in the urban plume (Tanner et al., 1981). However, more complete datasets have shown only 10-30% lower PSA levels in the downtown sites for Toronto (Waldman et al., 1990) and Atlanta (Waldman et al., 1991). A study in Philadelphia showed daily decreases as high as 60%, albeit these were during a summer with notably lower pollution (Allen and Koutrakis, 1994).

People and their activities generate ammonia, and in areas with higher population densities, ambient ammonia concentrations are generally higher. Ammonia emissions can have a local impact on PSA. Differences are observed comparing a central air monitoring site and levels measured directly outside homes, even though sulfate concentrations are generally quite uniform (Suh et al., 1994b).

When measurements are available at greater frequency than one per day (e.g. two 12-h or multiple 3-h intervals per day), diurnal patterns in PSA are consistently observed. PSA peaks usually occur in the afternoon; night-time PSA levels are generally lower, probably because the SO_2 oxidation rate is slower and ammonia concentrations tend to be higher in the relatively shallow, nocturnal mixing layer (Wilson et al., 1991). Noteworthy is the observation that PSA levels are often highest after passage over a body of water and before traversing land, e.g. Great Lake or North Sea. This seems to be due to extended contact with low atmospheric ammonia levels over water bodies (Kitto and Harrison, 1992; Thurston et al., 1994a).

MICROENVIRONMENTAL PATTERNS

The focus of research on human exposure to air pollutants has shifted in the past decade. While virtually all past measurements (and the statutory requirements to make them) were performed at central outdoor monitoring stations, more attention is being paid to air quality in local and microenvironmental settings. This has occurred for several reasons. In some cases, patterns of pollutant release, formation and fate can alter that pollutant's outdoor levels on local scales. Notable examples are organic compounds (release), ozone (formation), and nitric acid (fate), each of which may require greater spatial or temporal measurements.

We know that people do *not* spend nearly as much of their time outdoors as they do *indoors*, whether it be at home, school, work or shopping. Penetration indoors of sulfate aerosols, neutral or acidic, is highly effective. Studies demonstrate that infiltration occurs with 70% to nearly 100% efficiency (Brauer et al., 1991; Liang and Waldman, 1992). The usage of ventilation systems, such as window air conditioners (AC) or central HVAC, tend to reduce the effective penetration, due to losses in the filters. They also lead to greater losses by deposition to room surfaces, by increasing residence times. For this reason, single-family residences may have higher effective penetration values than institutions, such as offices, schools or hospitals.

With respect to PSA, the effect of the indoors on human exposures is entirely protective (Brauer et al., 1991; Waldman and Liang, 1993). That is, there are rarely important sources indoors, and most factors affecting the indoor levels lead to attenuation of the levels (Figure 3). Because people often spend their daytime hours away from home, research has recently focused on PSA exposures in institutional settings, such as schools, hospitals, daycare and elder care facilities (Liang and Waldman, 1992; Waldman et al., 1993). Factors which decrease air penetration lead to lower air exchange rates (AER), e.g. air conditioners, central ventilation systems. These contribute to reductions in indoor acidity levels (Suh et al., 1994b). While sulfate aerosol can effectively infiltrate from outdoors, the strong acid portion is substantially neutralized by ammonia present indoors (or scavenged to surfaces in the case of acid gases). This is because lower AERs lead to both higher indoor ammonia and greater time for neutralization (or surface) reactions. Unfortunately, in the current literature, indoor ammonia concentrations have not yet been adequately correlated with identifiable sources.

PERSONAL EXPOSURES

From the study by Suh et al. (1992), personal (i.e., breathing zone) exposures were found to fall between measured outdoor and indoor values. Time/activity-weighted models of indoor and outdoor concentrations were compared to predict personal exposures. While these models provided improvement compared to outdoor concentrations alone, they currently fall short of providing accurate predictions of personal exposures. Application of the model developed from a study in a semi-rural community in western Pennsylvania did not predict indoor PSA exposures as well when applied to a suburban study in central New Jersey (Zelenka et al., 1993). Notwithstanding the uncertainties, time spent outdoors can be the chief determinant of personal dose, even with relatively minor proportion of outdoor activities (Liang and Waldman, 1992). This is due to the substantially lower levels indoor and the tendency for individuals to maintain higher activity levels (hence higher breathing rates) while outdoors.

A further complication for classification of PSA exposures is the presence of endogenous ammonia in human airways. The ammonia concentrations generated in exhaled breath are extremely high: 100 to 1000 ppb, derived from food particles and plaque in the mouth (Norwood et al., 1992). Even in the absence of other indoor ammonia sources, this may contribute to PSA neutralization in human-occupied microenvironments. The airway ammonia concentrations are sufficiently high to affect PSA doses; however, this may depend upon several person-specific determinants: diet, oral hygiene, and ventilation mode (nose vs. mouth). Calculated by mathematical modeling, neutralization of inhaled PSA in the airways may reduce penetration by 50% or more (Larson, 1989).

EXPOSURE MEASUREMENTS FOR EPIDEMIOLOGICAL USE

Until recently, epidemiological investigations of PSA exposure effects have been limited to a number of small cities, where data are available (e.g. Dockery et al., 1993). Development of databases for PSA in metropolitan settings have only recently been acquired (Koutrakis and Allen, 1994; Thurston et al., 1992b; 1994b; Waldman et al., 1991). Differences can exist in spatial and temporal exposure patterns for PSA compared to other PM components. Detailed study of these phenomena has also only recently been started.

Central site data can often provide a useful index for comparing population exposures, since PSA is a regional pollutant, and exposures are dominated by outdoor levels. However, PSA concentrations for central outdoor monitoring stations are not sufficient to characterize local levels or exposures occurring indoors. Hence, if based on ambient data alone, individual estimates may result in substantial misclassification of individuals' exposure status. Outside of occupational settings and the few studies cited above, there are very limited measurements using personal monitors to directly determine actual personal exposures *vis à vis* estimates based upon ambient and/or indoor data.

The determination of an appropriate metric for correlating air pollution, on a metropolitan area basis, with respiratory health effects will be different for PSA than for PM10, fine particle material (FPM) or sulfate. Since FPM and sulfate aerosol penetrate effectively into buildings, their outdoor measurements may be accurate indicators of indoor exposures, in the absence of indoor sources. The situation is more complicated in the case of PSA, since significant reduction in indoor PSA occurs for all building types. Hence, outdoor PSA is rarely a good indicator of absolute indoor exposure, although relatively high indoor concentrations can occur only in areas with high ambient PSA levels.

One could choose among several available metrics for community exposure: (a) maximum regional concentrations of PSA (i.e. the value for sites on the upwind side of the city), (b) spatial averages, or (c) population-density weighted averages across the city. More information is needed before such decisions can be made. Greater detail on the temporal patterns for PSA is needed. Like ozone, PSA is observed to have its peak values in the afternoon. The data, while limited, suggest the diurnal pattern is not as stable as for ozone. Night-time PSA levels are generally low, because ammonia can reach higher concentrations in the relatively shallow, nocturnal mixing layer. However, regional transport can affect this, and, unlike ozone, PSA episodes occasionally persist through the evening and nighttime. The temporal patterns in ambient PSA levels are important, because most people are indoors at night, as well as for various periods during much of the day. Thus, a mid-day average or a mid-day maximum might be a better indicator of exposure to PSA than the 24-h average.

CONCLUSIONS

The current information base on PSA exposure has improved greatly in the past several years, with recent developments leading to important new insights about aerosol chemistry, temporal patterns, and microenvironmental and personal exposure patterns. However, much of the research relates to suburban eastern U.S. and Canadian sites, and we still lack sufficient data about PSA patterns in urban and metropolitan settings. Based on available information, it seems that a single monitor is probably inadequate for determining the absolute outdoor exposure to PSA across a large metropolitan area. However, it still serve as a useful index of relative PSA exposures, since relatively higher concentrations, locally and indoors, can occur only in areas with high ambient PSA levels. The chemical, physical and phenomenological vagaries of PSA in the human environment are such that individual exposures cannot be predicted by outdoor data alone. At the same time, due to the substantially lower levels indoors and the tendency for individuals to maintain higher activity levels (hence breathing rates) while outdoors, it is clear that PSA doses are dominated by ambient levels. More thought and analysis is required before an improved epidemiological metric for PSA can be determined.

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DISCLAIMER

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FIGURE CAPTIONS

1. Size-fractionated aerosol samples collected using a cascade impactor in Ontario, Canada: (a) PSA and sulfate concentrations in 4 size fractions for eight different samples ($20\ nmol/m^3 = 1 \mu g/m^3$ as H_2SO_4); (b) the PSA/sulfate equivalent ratio for the same samples. Adapted from Koutrakis et al. (1989).

2. Daily PSA concentrations measured at three New York state metropolitan areas. Buffalo is 500 km due W of Albany, which is 200 km due N of White Plains. Adapted from Thurston et al. (1992a).

3. Indoor and outdoor PSA (acidity) and sulfate aerosol concentrations, measured in two 12-h samples daily in Atlanta GA. Adapted from Waldman and Liang (1993).

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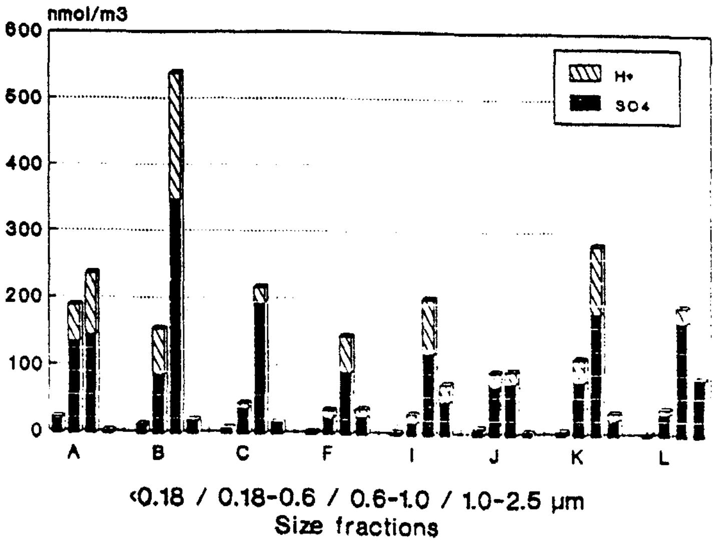
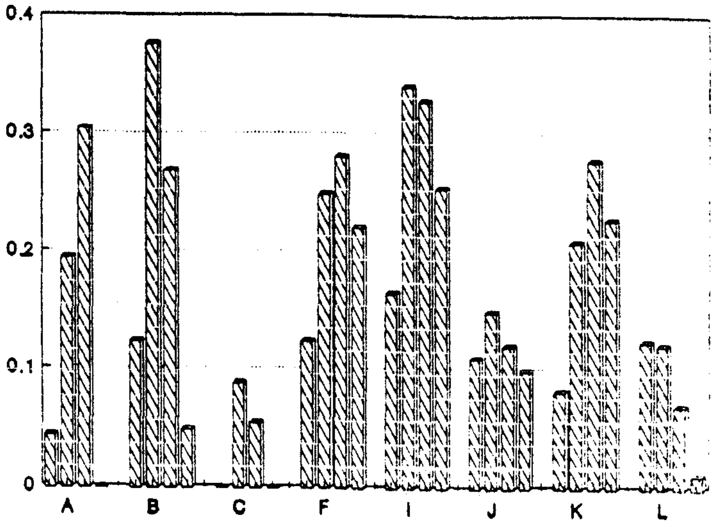
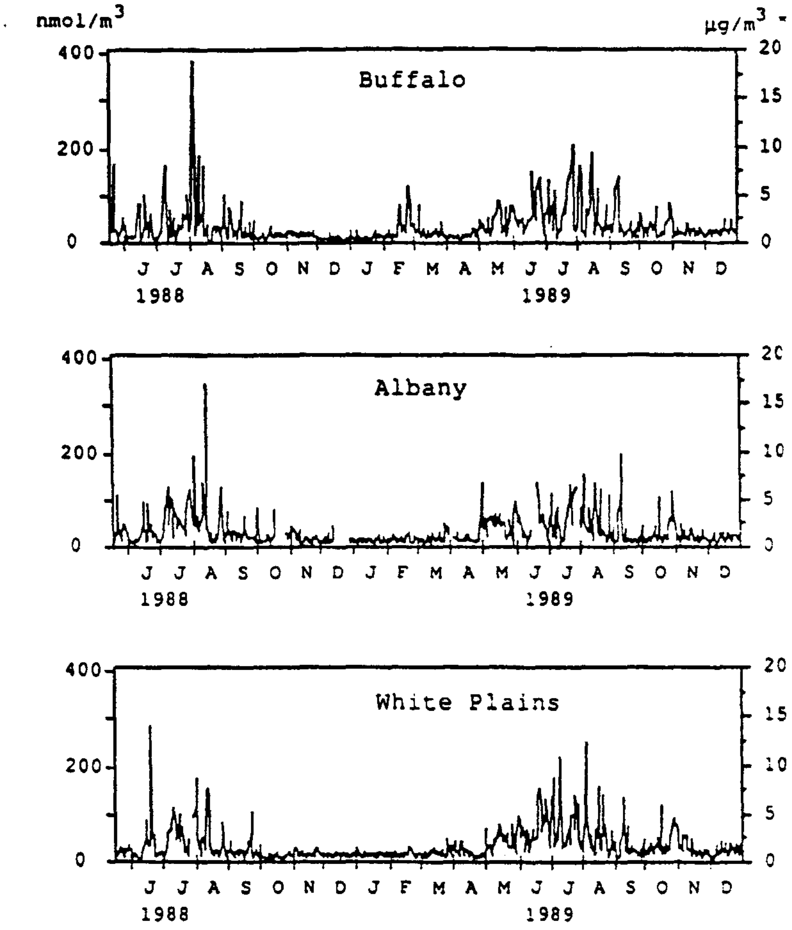
A. Concentration per size fraction



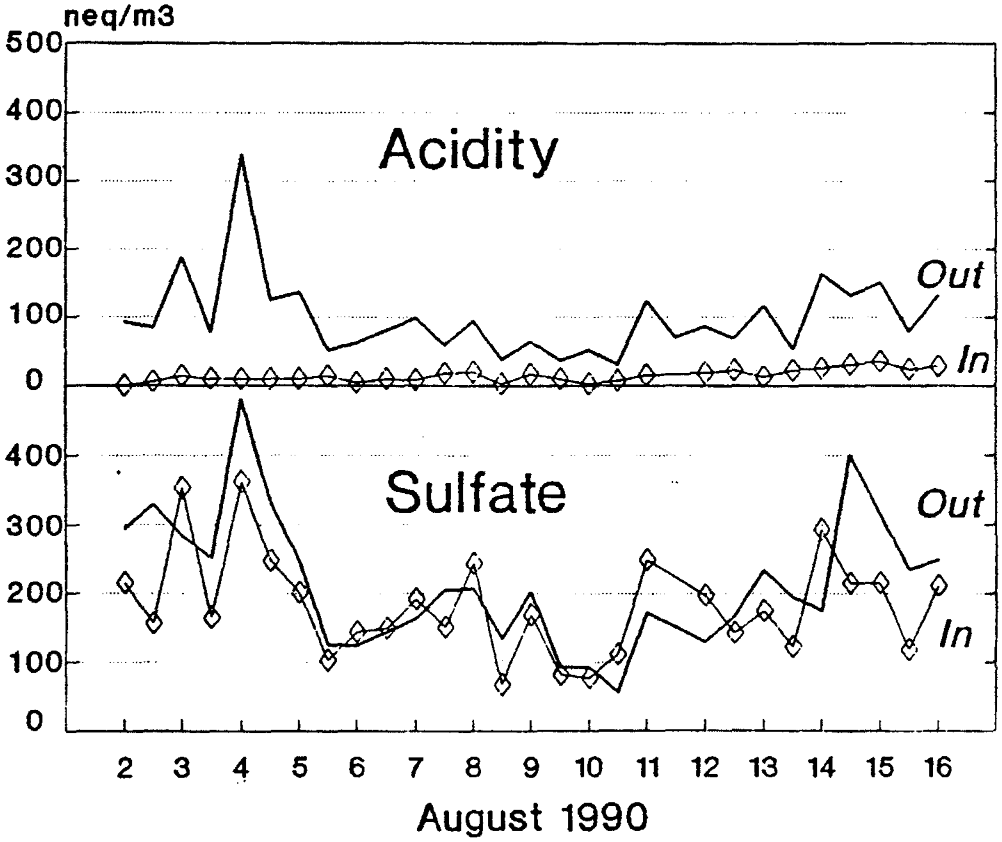
B. H+/SO4 equivalent ratio



1. Size-fractionated aerosol samples collected using a cascade impactor in Ontario, Canada: (a) PSA and sulfate concentrations in 4 size fractions for eight different samples (20 nmol/m^3 = 1 µg/m^3 as H_2SO_4); (b) the PSA/sulfate equivalent ratio for the same samples. Adapted from Koutrakis et al. (1989).



2. Daily PSA concentrations measured at three New York state metropolitan areas. Buffalo is 500 km due W of Albany, which is 200 km due N of White Plains. Adapted from Thurston et al. (1992a).



3. Indoor and outdoor PSA (acidity) and sulfate aerosol concentrations, measured in two 12-h samples daily in Atlanta GA. Adapted from Waldman and Liang (1993).

LOADINGS, SIZE DISTRIBUTIONS AND SOURCES OF COMPOUND CLASSES IN LOS ANGELES AEROSOL

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ABSTRACT

A low pressure impactor, equipped with ZnSe impaction substrates, was used to sample ambient Los Angeles aerosol. This new approach to aerosol characterization provides size resolved data on the loadings of organic and inorganic compound classes. The loadings and size distributions of sulfate, nitrate, aliphatic carbon, carbonyl and organonitrate groups were determined and were used to investigate the sources of these aerosol components. The source resolution studies revealed that secondary aerosol formation processes contribute significantly to the loadings of several aerosol compound classes.

INTRODUCTION

Determining the composition of atmospheric aerosol, as a function of aerosol size, is a challenging problem. The challenge is due in part to the complex nature of atmospheric aerosols, which are mixtures of inorganic salts, organic compounds and water. Additional challenges are provided by the difficulties of size resolved sampling. Despite these difficulties, a number of methods have been developed to determine the loadings of inorganic species in size resolved aerosol. Ion chromatography interfaced with impactors (John et al., 1989a,1989b) proton induced x-ray emission (Cahill et al., 1989) and x-ray fluorescence (Groblicki et al., 1981; Ondov et al., 1990) are just a few of the available methods. In contrast, methods for analysis of organic compounds in size segregated aerosol are limited, and most of the methods that are available rely on organic and elemental carbon analysis (McMurry and Zhang, 1989; Turpin et al., 1989a,b), or on extraction followed by mass spectroscopic analysis, which requires large sample mass (Mazurek et al., 1989; Rogge et al., 1993). This paper will describe a method for the analysis of size segregated aerosol based on infrared spectroscopy. The method described in this work has a number of advantages relative to more traditional methods of aerosol analysis. First, it is non-destructive and requires no extractions. Second, the method accounts for a large fraction of the inorganic and organic aerosol mass. Third, due to the high mass sensitivity of the method, short sampling runs are possible. Finally, in contrast to analysis of carbonaceous aerosol for organic and elemental carbon, infrared methods provide data on the compound classes present in the aerosol, not merely on the total carbon loadings. Balancing these advantages is the fact that individual organic species are not identified, only compound classes. Overall, however, the chemical insight provided by infrared spectroscopy represents a significant advance in the analysis of size segregated aerosol.

This analytical probe of aerosol composition will be used to examine the loadings and size distributions of organic and inorganic compound classes in ambient Los Angeles aerosol. Loadings and size distributions for sulfates, nitrates, aliphatic carbon, carbonyl groups and organonitrates will be reported.and this characterization of Los Angeles aerosol will be used to examine sources of the compound classes.

METHODS

Aerosol samples are collected and size segregated using a Low Pressure Impactor (LPI) (Hering, et al., 1978, 1979) and are analyzed using infrared spectroscopy. The Hering LPI has eight stages, with cutpoints at aerodynamic diameters of 4.0, 2.0, 1.0, 0.5, 0.26, 0.12, 0.075 and 0.05 µm. The first four stages operate at near atmospheric pressure, while the final four stages (0.05-0.26 cutpoint diameters) segregate particles at reduced pressures (50-140 Torr). A critical orifice placed between the fourth and fifth stages controls the volumetric flow rate through the impactor at 1.05 l/min. The LPIs used in this study employ ungreased zinc selenide disks as impaction substrates in stages 2-8. An oiled, sintered stainless steel disk is used in stage 1 to provide a coarse particle precut. The disks in stages 2-8 are uncoated but particle bounce is not believed to be a significant problem (Allen et al., 1994). The ZnSe disks are transparent to infrared radiation in the range of 0.6-17 µm, allowing for direct analysis of the aerosol deposits by infrared spectroscopy. Transmission infrared spectra of each stage are collected using a Digilab FTS-60 (Biorad, Cambridge, Massachusetts) spectrometer with a mercury-cadmium-telluride detector.

Size segregated aerosol samples were collected at Claremont, California during the Southern California Air Quality Study (SCAQS). Samples at Claremont were collected four times per day, at 0600-1000, 1000-1400, 1400-1800, and 1800-0600 PDT. Data were obtained for twelve sampling days, during intense summer photochemical episodes. Samples were also collected in the city of Duarte, California at a site approximately 13 miles west of the Claremont site. Sampling at Duarte occurred during 58 days of varying pollutant and meteorological conditions during the summer of 1987. Each sample at Duarte was collected over a 24 hour period, starting at 0600 PDT.

RESULTS

A typical infrared spectrum of size fractionated ambient aerosol is shown in Figure 1. The spectrum shows a number of strong features, including absorbances due to ammonium sulfate, ammonium nitrate, and a variety of organics. Peak assignments are summarized in Table 1. The absorbance areas associated with the peaks can be used to determine the loadings of sulfate ion, nitrate ion, carbonyl groups, organonitrates, and other functional groups. (Palen, 1991; Palen, et al., 1992; Allen et al., 1994). The estimated loadings are based on an extensive series of calibration studies. For the inorganic ions, field calibrations were performed comparing the loadings and size distributions obtained using Low Pressure Impactor/Fourier Transform Infrared Spectroscopy (LPI/FTIR) to more established field analysis methods. The organic calibrations were based on laboratory studies. All of the calibration studies have been described in detail by Allen et al. (1994). The focus of this paper will be on two of the inorganic and three of the organic groups: sulfate, nitrate, aliphatic carbon, carbonyl groups and organonitrates.

Sulfate size distributions

Daytime ambient sulfate concentrations in Los Angeles during the Southern California Air Quality Study (SCAQS), as determined using Low Pressure Impactor/Fourier Transform Infrared Spectroscopy (LPI-FTIR), ranged from 2 to 13 $\mu g/m^3$. Typical sulfate size distributions are presented in Figure 2. Stage 4 (0.5-1.0 μm) was the dominant size fraction for sulfate, although significant loadings were observed in all size fractions. A secondary mode was frequently observed, peaking in either the 0.075-0.12 μm or the 0.12-0.26 μm ranges, with the latter being more common.

Nitrate size distributions

The ambient nitrate loadings during the SCAQS sampling periods ranged from 1 $\mu g/m^3$ to 19 $\mu g/m^3$. Virtually all ambient nitrate was found in particles having aerodynamic diameters ranging from 0.5 to 4.0 μm, with 50 to 75% of the mass falling between 2.0 and 4.0 μm. Typical nitrate size distributions are presented in Figure 3.

Carbonyl size distributions

Carbonyl group concentrations ranged from 2 $\mu g\ C/m^3$ to 15 $\mu g\ C/m^3$. To interpret these data, it is important to understand the precise definition of the functional group loadings. For the carbonyl group, the bond that is detected in the infrared spectrum is C=O. From the infrared absorbance and model compound calibrations, it is possible to determine the number of moles of C=O bonds that are present in the aerosol sample. Since each mole of C=O bonds represents 12 grams of carbon, the mass of carbon in carbonyl groups can be directly calculated from the loading of C=O bonds. This carbon loading is then reported in units of $\mu g\ C/m^3$. Note that this definition of loading (carbon in carbonyl groups) is quite different than the loading associated with molecules containing C=O bonds. For example, the loading of carbon in carbonyl groups in octanoic acid is one eighth of the total carbon loading. Similar definitions are employed for the organonitrate and aliphatic carbon loadings. The aliphatic carbon loading is the mass of carbon that contains an aliphatic C-H bond (CH, CH_2 and CH_3 groups) and the organonitrate loading is the mass of $-O-NO_2$ bound to carbon. Typical size distributions for carbonyl are presented in Figure 4 (Pickle et al., 1990).

Aliphatic size carbon distributions

The highest aliphatic carbon concentrations observed in Los Angeles were approximately 11 μg C/m^3. The lowest measurements were indistinguishable from zero. The ambient aliphatic concentration typically demonstrated two maxima each day corresponding to the morning and evening rush hours. Aliphatic carbon is predominantly found in the size fractions with aerodynamic diameters below half a micron. Typical aliphatic size distributions are presented in Figures 4 and 5.

Organonitrate size distributions

Loadings of the organonitrate group (C-O-NO_2) during the SCAQS intensive periods ranged between 0.3 and 1.7 μg O-NO_2/m^3. The loading correlated strongly with carbonyl absorbances, indicating that many of the molecules containing the organonitrate group may be difunctional (Mylonas et al., 1991). Smog chamber studies have also indicated that difunctional species containing organonitrates are formed in the atmosphere (O'Brien et al, 1975a,b). Typical size distributions for the organonitrate group are shown in Figure 4. During periods of high photochemical activity, the size distributions show maxima in the 0.05-0.075 μm and the 0.12-0.26 μm size fractions. During periods of low to moderate photochemical activity, the size distributions were shifted to slightly larger sizes, with maxima appearing in the 0.075-0.12 μm and the 0.5-1.0 μm size fractions.

DISCUSSION

The evolution of the size distributions of organic aerosol functional groups during an intense Los Angeles photochemical episode is shown in Figure 4. The aliphatic carbon loadings observed during a more typical episode, shown in Figure 5, peak during morning and evening rush hours, indicating a strong automotive source. Source resolution calculations by Pickle, et al. (1990) confirm an automotive source, but also indicate a secondary component to aliphatic carbon loading in the 0.12-1.0 μm size fractions. Carbonyl loadings peak at mid-day and correlate with ozone, indicating a strong secondary component and organonitrates exhibit similar behavior. Again, principal component analysis confirms and refines these findings. Pickle et al. (1990) found that carbonyl loading was predominantly secondary in nature and Mylonas, et al (1991) came to a similar conclusion for organonitrates.

The source allocation studies reported here, as well as other studies based on SCAQS data (Turpin and Huntzicker, 1991), have revealed a large fraction of the organic aerosol is due to the products of photochemical reactions (secondary organics). If these results are valid, then the organic functionalities observed in the aerosol should be consistent with the reaction products expected from the photooxidation of hydrocarbons emitted into the Southern California Air Basin (SCAB). Grosjean (1992) has used the SCAB emission inventory, the EPA "all-city" inventory and data on photooxidation chemistry to predict the distribution of aliphatic nitrates, aliphatic acids, ketones, aldehydes, phenols and nitroaromatics in secondary components of Los Angeles aerosol. The results reported here are generally consistent with Grosjean's results, although some inconsistencies exist, which will be examined in future work.

CONCLUSIONS

Compound class or functional group analysis of organics present in ambient aerosol represents a compromise between the expensive, yet comprehensive data available through mass spectrometric analyses and the routine, but relatively coarse characterization provided by thermogravimetric analyses. Using infrared spectroscopy, dominant aerosol functionalities can be observed and quantified. The work reported here focussed on determining the loadings, sources and size distributions of sulfate, nitrate, aliphatic carbon, carbonyl groups and organonitrates. Source allocation calculations indicate that a large fraction of the organic loading in Los Angeles aerosol is due to the products of photochemical reactions. Predictions of the chemical nature of these photochemical oxidation products have been made by Grosjean (1992), based on emission inventory and reactivity data, but many uncertainties remain in the analysis. Smog chamber studies now underway have measured aerosol functional group distributions produced by the photooxidation reactions of key species in the SCAB emission inventory. By combining the emission inventory with estimated aerosol yield and composition, predictions of the mass loadings of organic functional groups can be made. For organonitrate and nitroaromatic groups the agreement between predictions and observed ambient loadings are reasonable, however, for aliphatic carbon groups discrepancies arise. As shown in Figure 5, on days with moderate particle concentrations, aliphatic concentrations are substantial, yet during severe multiday episodes the aliphatic carbon disappears, as shown in Figure 4. This may be due to the presence of strong oxidizing agents in the particles during intensive episodes.

ACKNOWLEDGEMENTS

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Table 1. Infrared absorbances observed in spectra of ambient aerosol (Allen et al., 1994).

Functionality	Absorption frequencies (cm^{-1})	Absorbance band chosen for quantification (cm^{-1})	Presence in Los Angeles aerosol sampled in this work	
			supermicron	submicron
INORGANICS				
SO_4^- sulfate ions	612-5, 1103-35	580-635	always	always
HSO_4^- bisulfate ions	580-90,867, 1029, 1180	580-635	occasionally	occasionally
$CaSO_4$ calcium sulfate	671,600,1105, 1135	none	occasionally	never
NO_3^- nitrate ions	830-4, 1318-35	818-838	always	only for d_p>0.5 μm
$NaNO_3$ sodium nitrate	1786	none	occasionally	never
SiO_4^{4-} silicate ions	772-812, 1035	none	always	only for d_p>0.5 μm
SiO_2 silica				
NH_4^+ ammonium ions	1410-35, 3030-52, 3170-3200	none	always	always
H_2O particulate water	1623, 3350-3450	none	always	always
ORGANICS				
Functionality	Absorption frequencies (cm^{-1})	Absorbance band chosen for quantification (cm^{-1})	Presence in Los Angeles aerosol samples in this work	
			supermicron	submicron
C-H aliphatic carbons	1452-5, 2800-3000	2800-3000	rarely	always
C=O carbonyl carbons	1640-1850	1640-1850	only for d_p<2 μm	always
$CONO_2$ organonitrates	856, 1278, 1631	1255-1296	never	always
COH alcohols	3500-3750	none	occasionally	occasionally

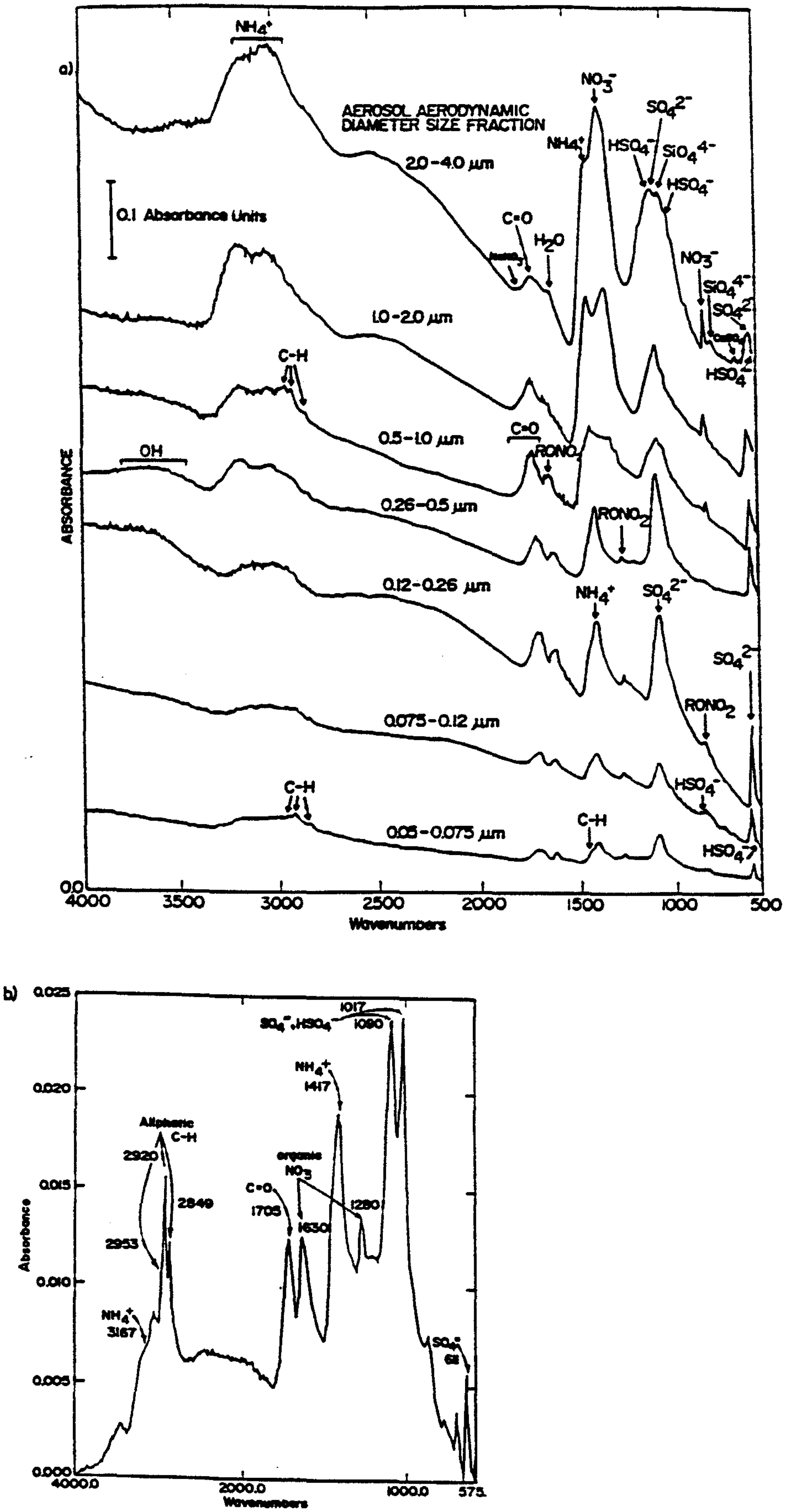


Figure 1. a) Spectra of ambient Los Angeles aerosol (taken at Duarte, California, 8/19/87); each sample consisted of seven size fractions and a spectrum was obtained for each size fraction; all of the spectra are plotted on the same absorbance scale. b) enlarged view of a spectrum of a typical 0.05-0.076 µm size fraction (from Allen et al., 1994, reproduced by permission).

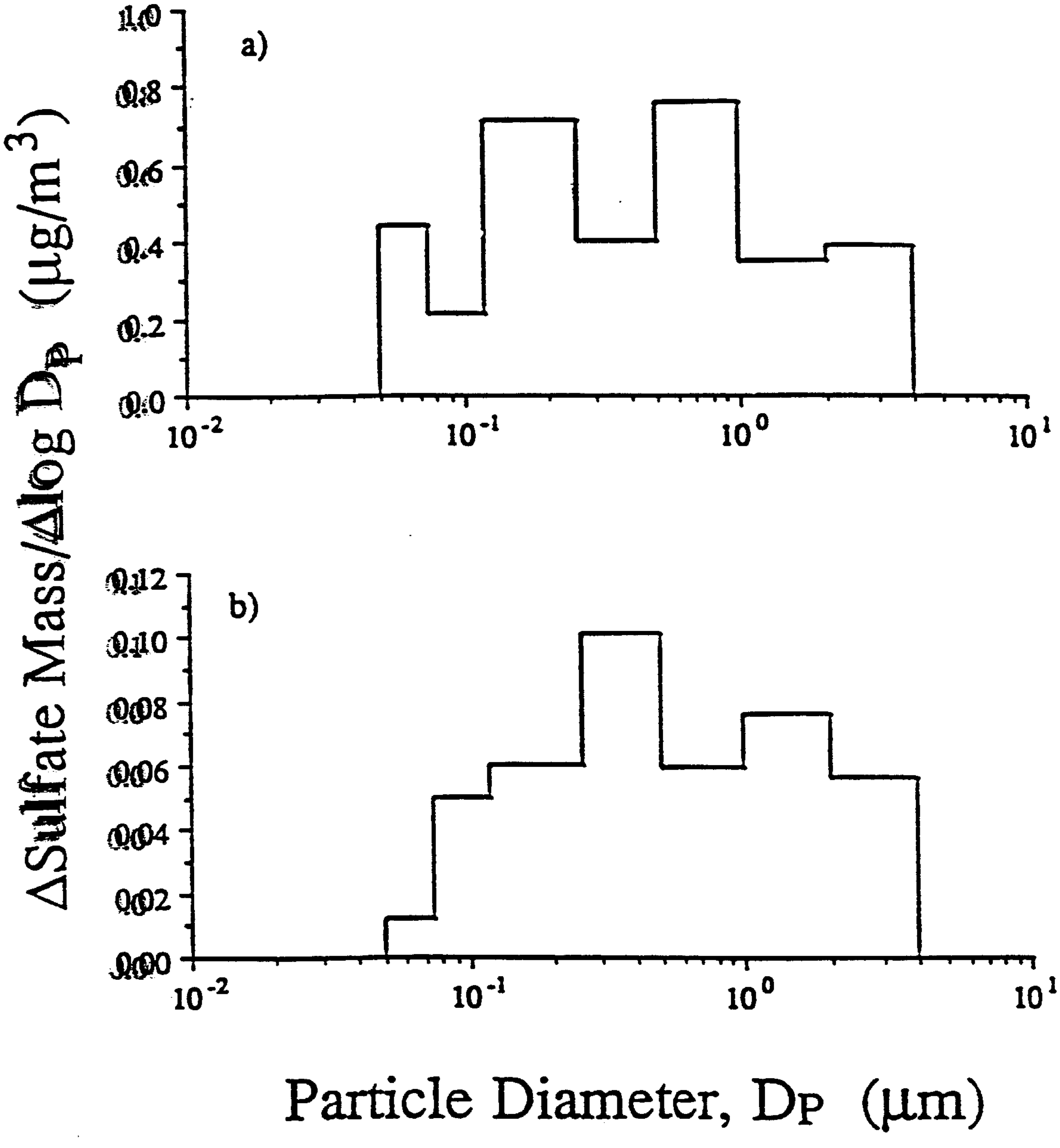


Figure 2. Aerosol sulfate plus bisulfate size distributions determined using the LPI-FTIR method. These data are consistent with data collected using a flame photometric method. a) Data from sample collected on July 27, 1000-1400 hr at Claremont, California. This sample had the highest loading observed during the study. b) Data from sample collected from September 3, 1800 hr to September 4, 0600 hr at Claremont. This sample had the lowest loading observed during the study (from Allen et al., 1994, reproduced by permission).

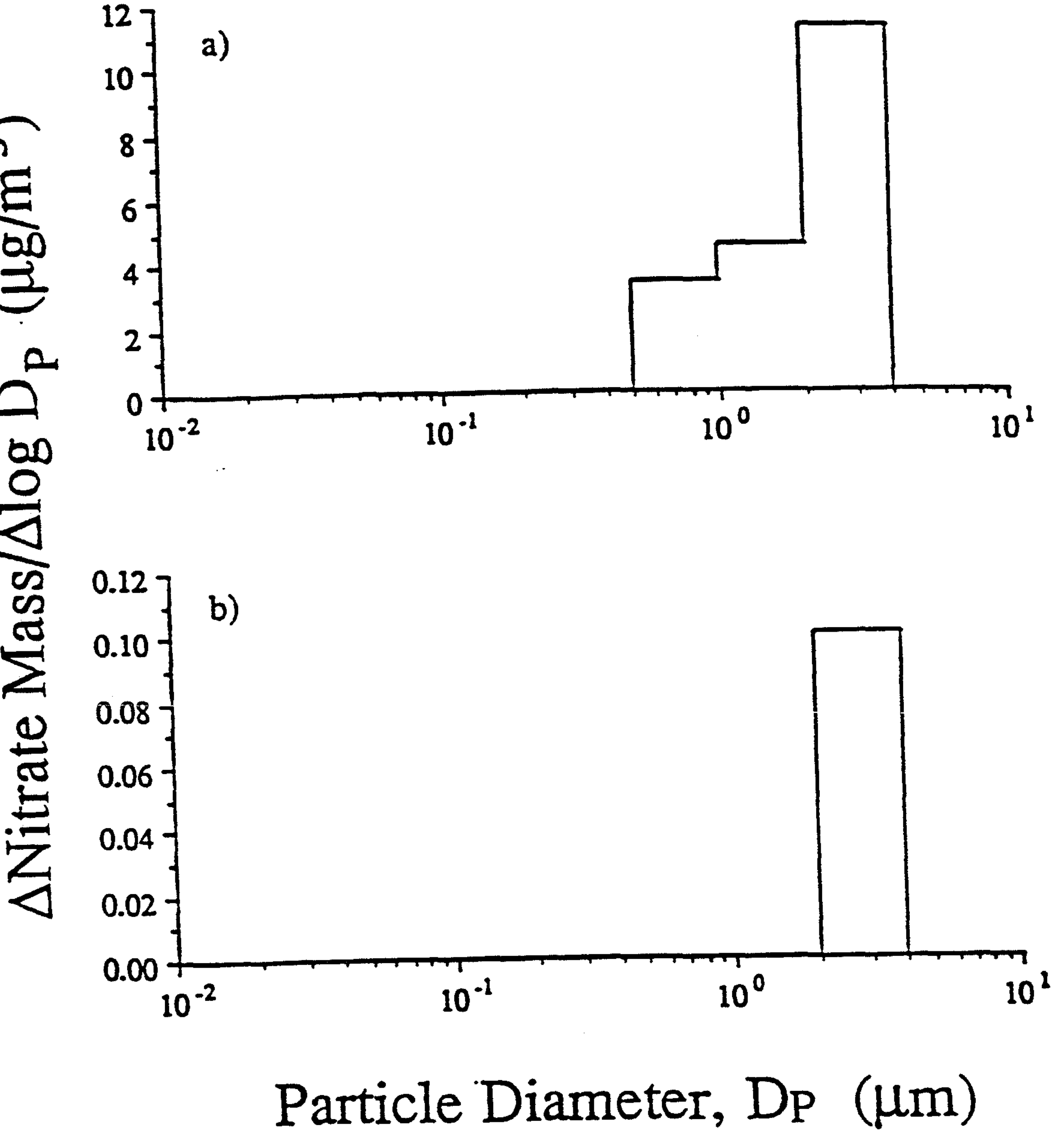
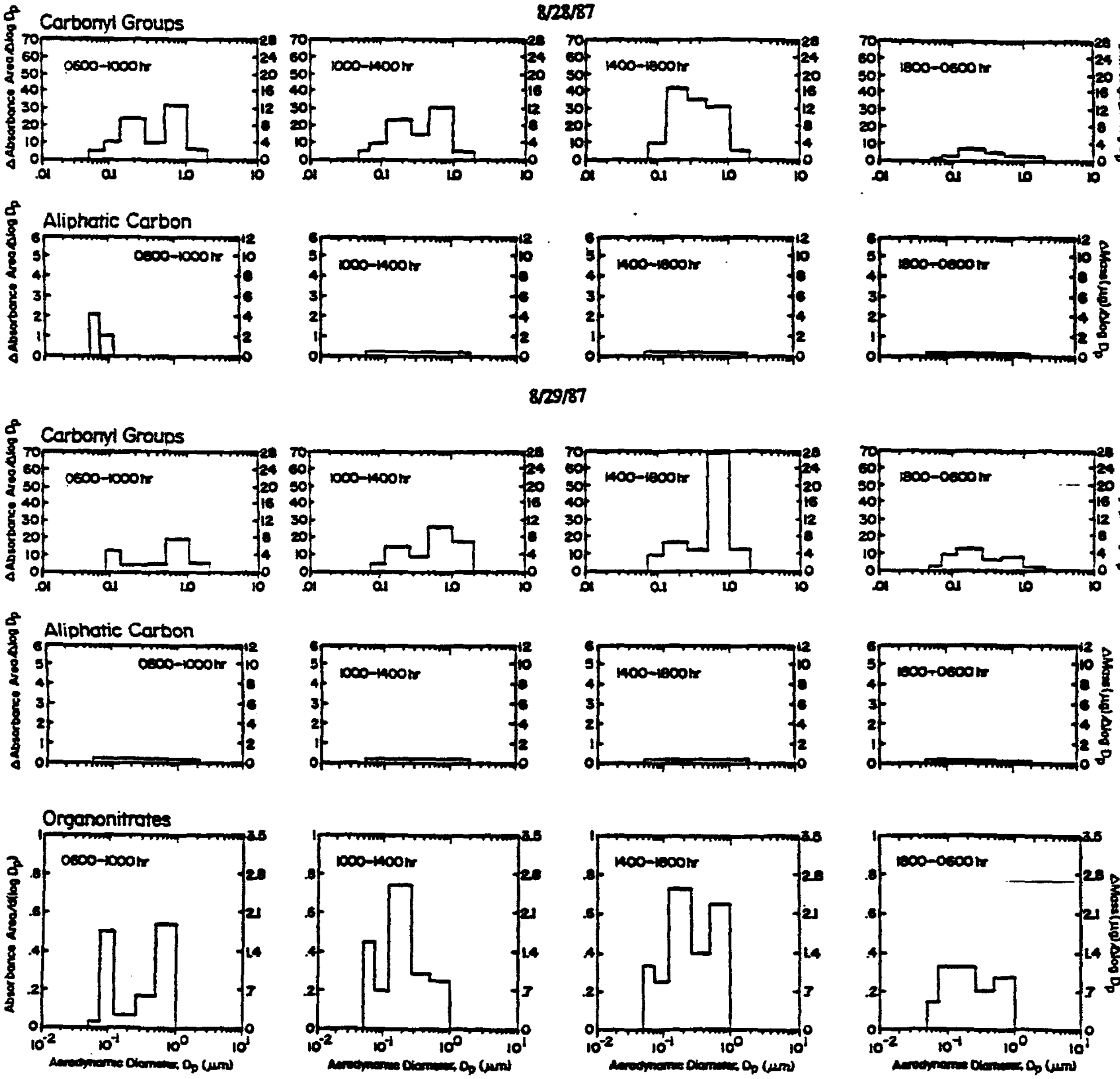


Figure 3. Aerosol nitrate size distributions determined using the LPI-FTIR method. a) Data from sample collected on August 29, 1000-1400 hr at Claremont, California. This sample had the highest loading observed during the study. b) Data from sample collected on September 2, 0600-1000 hr at Claremont. This sample had the lowest loading observed during the study (note that volatilization of nitrate from the sub 0.5 μm stages may be significant) (from Allen et al., 1994, reproduced by permission).

Figure 4. Carbonyl group, aliphatic carbon and organonitrate size distributions determined using the LPI-FTIR method. Loadings are in (μg-C/m^3) for the carbonyl and aliphatic groups; for the organonitrates loadings are in μg-O-NO$_2$/m^3. The size distributions are for August 28 and 29, at Claremont, California, which were the second and third days of an intense photochemical episode (from Allen et al., 1994, reproduced by permission).



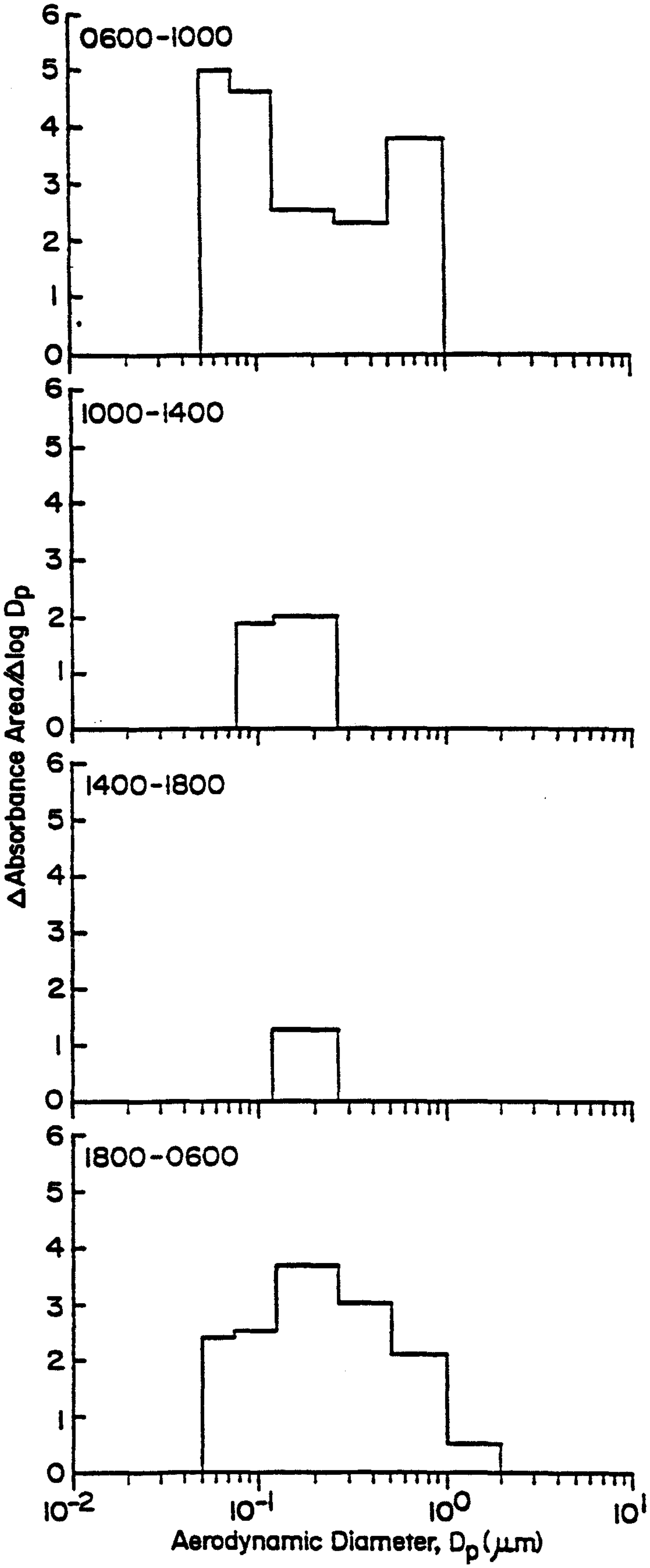


Figure 5. Aliphatic carbon size distributions measured at Claremont, California on June 24, 1987, a day of moderate particulate loadings (Pickle et al., 1990) are substantially different than those reported in Figure 4.

DETERMINATION OF THE SIZE DISTRIBUTION AND CHEMICAL COMPOSITION OF FINE PARTICULATE SEMI-VOLATILE ORGANIC MATERIAL IN URBAN ENVIRONMENTS USING DIFFUSION DENUDER TECHNOLOGY

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Short Title: Particulate Semi-Volatile Organic Material

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ABSTRACT

Collection of particles on a filter results in under-estimation of particulate organic compounds due to losses from the semi-volatile organic fraction during sample collection, i.e. a "negative sampling artifact." This sampling induced change in the phase distribution of semi-volatile organic material resulted in the loss of an average of 35% of the particulate organic material in samples collected at the SCAQMD sampling site at Azusa California in the Los Angeles Basin. These semi-volatile organic compounds lost from particles were measured using two diffusion denuder sampling systems. A multi-channel diffusion denuder sampling system (BOSS) was used to determine the concentrations of fine particulate carbonaceous material, and a multi-system, multi-channel, high-volume diffusion denuder sampler (BIG BOSS) was used for the determination of the particle size distribution and chemical composition of semi-volatile organic compounds in fine particles. Results obtained with the two sampling systems agreed. A smaller artifact associated with the absorption of gas phase organic compounds by the filter during sampling was corrected for using a two tandem quartz filters in the BOSS sampling system. The quartz filter artifact was not present after removal of gas phase compounds by the diffusion denuder. Comparison of the denuder results with those obtained by the SCAQMD using filter pack sampling systems showed that the observed concentration of the quartz filter artifact was dependent on the sample flow rate. However, the denuder sampler results on the concentration of particulate carbonaceous material retained on a quartz filter during sampling, corrected for the quartz filter artifact, were also in agreement with results reported by the SCAQMD. The loss of semi-volatile organic material from

particles during sampling resulted in an underestimation of particulate organic material by collection with tandem quartz filters by an average of 55% of the measured concentration. Semi-volatile particulate organic compounds lost from the particles during sample collection included paraffinic compounds, aromatic compounds, and organic acids and esters. Underestimation of the concentration of semi-volatile organic compounds in particles is a function of molecular weight, chemical compound class and particle size. The majority of the organic compounds in fine particles 0.8 to 2.5 µm in size are semi-volatile organic compounds lost from the particles during sampling onto a filter. The majority of carbonaceous material in particles smaller than 0.4 µm is not lost from the particles during sample collection. The results obtained using the diffusion denuder sampling systems indicate that the fine particulate organic constituents to which an urban population is exposed have not been well characterized or quantified in previous studies.

INTRODUCTION

Correct assessment of the exposure of a population to particulate organic material is in part dependent on accurate determination of the chemical composition as a function of particle size for particles present in the atmosphere. Results obtained from the collection of organic material on a filter indicate that about one-third of the mass of fine particulate matter (diameter < 2.5 µm) collected on filters in remote desert regions of the Southwest U.S. (Macias 1986, Sutherland 1990) and about one-fourth of the fine particulate mass in western urban areas such as the Los Angeles Basin (Hering 1993) is organic compounds and elemental carbon. In the Eastern United States, sulfate is the major component of airborne fine particles. However, based on filter data, organic material also comprises about one-fourth of the fine particulate mass in the east (Gebhart 1993). Collection of particles on a filter results in underestimation of particulate organic material due to losses of the semi-volatile organic fraction from particles during sample collection, i.e. a "negative sampling artifact". This sampling induced change in the phase distribution of semi-volatile organic material results in the loss of about half of the particulate organic material in the Desert Southwest during sampling (Eatough 1993, 1990, 1989, Tang 1994). This "negative sampling artifact" in the desert southwest is an order of magnitude larger than the "positive sampling artifact" resulting from the collection of gas phase organic compounds by a quartz filter (Eatough 1993, Appel 1989, McDow 1990).

The loss of significant amounts of semi-volatile organic material from particles or the collection of gas phase organic material by the sampling media during sampling causes errors in the determination of the aerosol chemical composition. Accurate collection procedures for semi-volatile organic compounds must meet the following two criteria:

1. Organic compounds initially present in the gas phase which can be adsorbed onto particles or the filter during sampling must be distinguished from semi-volatile organic compounds lost from particles and subsequently adsorbed by the filter during sampling.

2. Organic compounds initially present in the particulate phase and lost from particles during sampling must be captured separately from compounds which are present in the gas phase in the atmosphere.

These two criteria cannot be met by any sampling procedure in which the particulate phase organic compounds are collected before the collection or removal of gas phase organic compounds because the gas phase organic compounds and organic compounds volatilized from particles become indistinguishable. Thus, it is necessary to first remove the gas phase organic compounds from the sampled airstream and then to collect the particulate phase organic compounds with a sampler which will collect all organic material, gas and particulate.

This paper describes the results obtained using both a multi-channel diffusion denuder sampling system, BOSS, the Brigham Young University Organic Sampling System (Eatough 1993), and a high-volume, multi-system, multi-channel diffusion denuder sampling system, BIG BOSS (Tang 1994) and associated analytical procedures for the determination of the size distribution and chemical composition of fine particulate organic material. Results obtained using the two sampling systems are compared with each other and with results obtained by the South Coast Air Quality Management District, SCAQMD, using filter pack sampling systems. Details are given on the chemical composition and concentration of semi-volatile organic compounds retained by and lost from particles during sampling at Azusa in the Los Angeles urban area.

METHODS.

The BOSS Sampling System.

The BYU Organic Sampling System, BOSS, has been previously described (Eatough 1993). The sampler is shown schematically in Figure 1. The system requires two separate samplers for the determination of particulate phase organic material. Flow through each sampler is nominally 35 sLpm.

Sampler 1 consists of: a. A multi-parallel plate diffusion denuder with charcoal impregnated filter, CIF, sheets as the denuder surface to collect gas phase organic compounds. b. Two quartz filters, the first to collect particles and the second to correct for the collection of gas phase organic compounds. c. Two charcoal impregnated filters to collect any gas phase organic compounds not collected by the denuder and semi-volatile organic compounds lost from the particles during sampling.

Sampler 2 consists of the same components in a different order: a. A quartz filter to collect particles and an additional quartz filter to correct for collection of gas phase organic compounds. b. A multi-parallel plate denuder to collect gas phase organic compounds. The denuder in this system collects both compounds entering the sampler as gases and semi-volatile organic compounds lost from particles collected on the filter. c. Two charcoal impregnated filters to collect that portion of gas phase organic compounds not collected by the denuder, i.e. denuder breakthrough.

In addition, in the Azusa study a third sampler was used, Sampler 3 in Figure 1. This system contained a quartz filter to collect particles and an additional quartz filter to correct for collection of gas phase organic compounds by the first quartz filter. This part of the system is identical to that normally used in the determination of particulate organic material.

In order to determine the fine particulate organic concentration with proper corrections for any alterations in the phase distribution of organic material due to sampling, the amount of particulate carbon collected directly on a quartz filter, the amount and origin of carbon collected by a second quartz filter (the "quartz artifact"), and the amount of carbon lost from particles during sampling (the "negative artifact") that is not collected by a subsequent quartz filter must all be determined. Details on the determination of each of these quantities using a BOSS have been given (Eatough 1993, Tang 1994). The first two are obtained by analyzing the carbon collected by the respective quartz filters in a filter pack, e.g. Filters $Q_{2,1}$ and $Q_{2,2}$ in Sampler 2 in Figure 1 (Appel 1989, Gebhart 1993, Hering 1993, McDow 1990).

The efficiency of a CIF for the collection of gas phase organic material (nominally 80%, e.g. see Eatough 1990) is calculated as,

$$E_{CIF} = (X_1 - X_2)/X_1 \qquad (1)$$

where X_1 and X_2 are the amounts of gas phase semi-volatile organic material collected by the first and second CIF, respectively, in the filter packs of either Samplers 1 or 2. The negative artifact is calculated by equation 2,

$$\text{SVOC Lost ("Negative Artifact")} = CIF_{1,1}/E_{CIF} - CIF_{2,1}/E_{CIF} \qquad (2)$$

where $CIF_{1,1}$ and $CIF_{2,1}$ are the amounts of organic carbon collected on the first sorbent filters in Samplers 1 and 2, Figure 1, respectively.

The origin of the gas phase organic material collected on a second quartz filter (the "quartz artifact") can be addressed by comparing the amount of carbon found on the second quartz filter in the filter pack preceding the denuder (Sampler 2, Figure 1) with the amount of carbon found on the second quartz filter after a denuder (Sampler 1, Figure 1). I778f in fact the quartz artifact results from the collection of material that was originally present in the gas phase, then after a denuder in which the gas phase organic concentration has been decreased by 95% (Tang 1994), it would be expected that the quartz artifact would be reduced. If the amount of organic material found on the second quartz filter is absent in Sampler 1, but present in Sampler 2, then the artifact would be considered to be a positive artifact.

Using this logic, the total particulate carbon is calculated by equation 3,

$$\text{Total Carbon} = Q_{2,1} \pm Q_{2,2} + \text{CIF}_{1,1}/E_{\text{CIF}} - \text{CIF}_{2,1}/E_{\text{CIF}} \tag{3}$$

where $Q_{2,1}$ is the quartz filter carbon (quartz filter 1 in Sampler 2), $Q_{2,2}$ is the quartz filter artifact (quartz filter 2 in Sampler 2), and the sorbent filters and efficiency are as previously defined (See Figure 1). Whether the plus or the minus sign is used in equation (2) would be dependent on the comparison of the concentration of organic material found on filter $Q_{2,2}$, as compared to filter $Q_{1,2}$. The point to be emphasized here is that the quartz filter artifact may be either a negative or a positive correction. It has been shown in previous studies at Canyonlands (Eatough 1993), where the quartz filter artifact was a negative artifact, that the amount of carbonaceous material collected by the first quartz filters $Q_{1,1}$ and $Q_{2,1}$ are comparable. This indicates that the half-life for the loss of semi-volatile organic material from collected particles is short compared to the sampling time (Eatough 1993). Recent results reported by Kamens et al. (1993) also suggest that the rate of loss of semi-volatile organic compounds from particles during sampling will be of the order of minutes, rather than hours. If this is true then either $Q_{1,1}$ or $Q_{2,1}$ (see Figure 1) appropriately corrected for any positive quartz filter artifact may be used in Equation (3).

The BIG BOSS Sampling System.

The BIG BOSS sampling system has been previously described (Tang 1994). The components of the BIG BOSS are shown schematically in Figure 2. The BIG BOSS uses a variety of size selective high-volume virtual impactor inlets to control the particle size of the particles introduced to the diffusion denuder sampler. Systems 1, 2 and 3 are used to determine total particulate organic material after a diffusion denuder which removes gas phase organic compounds. Total flow through the denuder for each system is nominally 200 L/min. The denuder for these three systems is preceded by a virtual impactor with particle size cuts of 2.5, 0.8 and 0.4 μm, respectively (Tang 1994).

The flow stream after the denuder is split and sampled through two parallel collection systems. The majority of the flow, 150 L/min, is sampled through a quartz filter followed by an XAD-II bed. Particles are collected by the quartz filter. Semi-volatile organic compounds lost from the particles during sampling, and any gas phase organic compounds not collected by the denuder, are collected in the XAD-II bed. The material collected in this part of the sampling system is analyzed by GC and GC-MS to chemically characterize the organic material present in the particles and lost from the particles during sampling.

The remainder of the sample flow, 50 L/min, is sampled through a filter pack with a quartz filter and a charcoal impregnated filter, identical to the filter pack used in Sampler 1 of the BOSS. These filters are used for quantitative determination of total particulate carbonaceous material and semi-volatile compounds lost from the particles during sampling by temperature programmed volatilization, TPV, analysis (Eatough 1993, 1989, Tang 1994). The fourth system in the BIG BOSS, Figure 2, contains a quartz filter in front of the diffusion denuder and is used to correct the data from the other systems for any gas phase organic compounds not collected by the diffusion denuder.

The concentrations of particulate phase organic material collected in Systems 1, 2, or 3 of the BIG BOSS sampler are then calculated from either equation (4) or (5),

$$\text{Total Carbon}_i = Q_{i,1} \pm Q_{i,2} + \text{CIF}_{i,1}/E_{\text{CIF}} - \text{CIF}_{4,1}/E_{\text{CIF}} \tag{4}$$

$$\text{Total Carbon}_i = Q_{i,1} \pm Q_{i,2} + \text{XAD}_{i,1}/E_{\text{XAD}} - \text{XAD}_{4,1}/E_{\text{XAD}} \tag{5}$$

where i = 1, 2 or 3. The various terms in equation (4) have the same meaning as in equation (3), XAD refers to the amount of gas phase organic material collected in the indicated XAD-II sorbent bed and E_{XAD} is the efficiency of an XAD-II sorbent bed for the collection of gas phase organic compounds (nominally about 85%, Tang 1994).

Sampling at Azusa With the BOSS and BIG BOSS.

The BOSS system has been previously used in a year-long study at Canyonlands National Park (Eatough 1993). The BIG BOSS had been field tested in initial experiments conducted in Provo, UT (Tang 1994). The BOSS and BIG BOSS sampling systems were inter-compared in a sampling program completed during May-June 1992 in the Los Angeles Basin at the SCAQMD sampling site in Azusa, CA. Representative results related to the identification of particulate semi-volatile organic compounds in samples collected at Azusa were included in the article describing the BIG BOSS (Tang 1994). Results are reported here for eight-hour samples (10:00 to 20:30 hours with no sample collected from 14:00 to 14:30) collected on 18 consecutive days and four-hour samples collected twice a day (10:00 to 14:00, and 14:30 to 18:30) with the BIG BOSS during the last three days of the sampling program at the SCAQMD Azusa sampling site. These results are compared to four-hour samples collected with the BOSS twice a day (10:00 to 14:00, and 14:30 to 18:30) during each of the 21 sampling days. The collection periods were chosen to coincide with the sampling program of the SCAQMD so that results obtained by the two groups could be compared. Samples were obtained by the SCAQMD using conventional tandem quartz filter sampling systems (Barbosa 1993).

Flow through each of the various parts of the BOSS and BIG BOSS sampling systems was controlled by mass flow controllers or by critical orifices. The flow through each of the minor flow streams in the virtual impactor inlet systems of the BIG BOSS were controlled with orifices and the flow was monitored by measurement of the pressure drop across an orifice in the sample line using a magnehelic gauge (Tang 1994). Flow through the various filter packs containing CIF was controlled using Tylan (Model FC262) mass flow controllers and monitored during sampling with Kurz (Model 1543) mass flow meters. Flow through the various XAD-II sorbent beds and associated filter packs was controlled using Tylan (Model FC262BPV) mass flow controllers and monitored during sampling with Kurz (Model 1544-SP) mass flow meters. The Kurz mass flow meters were both calibrated against dry gas meters. The flow through Samplers 1, 2 or 3 of the BOSS was controlled and measured using Tylan mass flow controllers. Nominal flow was 35 sLpm. The flow through any given sampling system was constant to better than 5% during sample collection with the BOSS or BIG BOSS in the Azusa study.

The charcoal impregnated diffusion denuder surfaces were used as received from the manufacturer. The CIF were cleaned with dichloromethane before use as previously described (Eatough 1990). The quartz filters were found to have acceptable blank concentrations of organic material and were used as received. Both CIF and quartz filters were stored in Millipore petri dishes (No. PD1004700) at -40° C until analyzed. The XAD-II was cleaned by first sonicating 10 times with CH_3OH to remove very small particles and then soxhlet extracting for 24 hours sequentially with methanol, CH_2Cl_2 and $C_2H_5OC_2H_5$. The cleaned XAD-II was stored in clean, dark glass bottles. After sample collection the various filters or XAD-II were stored at -40 °C until analyzed.

Sample Analysis.

The BOSS samples collected during the field sampling program were analyzed to determine artifact-free particulate carbonaceous material for particles smaller than 2.5 μm by quantitative determination of the amount of collected carbonaceous material in each part of the sampling system using temperature programmed volatilization (TPV) analysis (Eatough 1993, 1989). Charcoal impregnated sorbent filters are analyzed in a stream of N_2 while quartz filters are analyzed in a stream of N_2/O_2 (ca 70/30%). The charcoal impregnated sorbent filters are heated from ambient (25° C) to 350° C at a nominal rate of 10° C/min. Desorption of CIF collected organic compounds is done in N_2 to prevent oxidative decomposition of the charcoal absorption surface during the analysis. Organic compounds desorbed from the sorbent filter are catalytically converted to CO_2 and detected by NDIR. The NDIR was calibrated daily against three certified gas standards whose concentrations covered the range used. The instrument calibration is also checked periodically using benzoic acid (NIST Standard Reference Material) spiked quartz filters. Quartz filters are heated to 800° C to determine the sum of particulate organic carbon and elemental carbon. Elemental and organic carbon are generally removed from the filter at temperatures below 700° C by this technique and are well resolved from CO_2 from minerals which may decompose at 800° C (Eatough 1992). The gas phase compounds collected by CIF appear to be revolatilized between about 140 and 280° C (Eatough 1990, 1989).

The quartz filters and the various XAD-II traps in the main flow channel were extracted with organic solvents for organic compound analysis by capillary column gas chromatography and/or gas chromatography/mass spectrometry. The quartz filters were sonicated three times with CH_2Cl_2 (30 minutes each time) and then three times with CH_3OH (30 minutes each time). The combined samples were then concentrated in a K-D tube, the solvent changed to $C_2H_5OC_2H_5$ and the sample esterified with diazomethane. The XAD-II samples were sonicated three times with CH_2Cl_2 (30 minutes each time), concentrated in a K-D tube, solvent changed to $C_2H_5OC_2H_5$ and esterified with diazomethane. The BIG BOSS samples were analyzed to determine carbonaceous material in the particle size ranges of $<0.4\mu m$, $0.4-0.8\mu m$, and $0.8-2.5\mu m$ by both quantitative and qualitative analysis of the collected samples. Quantitative results for total particulate organic material in each of the three size ranges were obtained by TPV analysis (Eatough 1993, 1989). Semi-quantitative chemical characterization results for semi-volatile particulate organic material remaining on the quartz filter and the semi-volatile organic compounds lost from collected particles during sampling as a function of particle size were determined by GC with FID detection (Tang 1994). The specific qualitative identification of the principal organic compounds lost from particles and semi-volatile organic compounds retained by particles during sampling was done by gas chromatography-mass spectroscopy analysis of combined samples.

RESULTS AND DISCUSSION.

Complete results for the Azusa study have been given (Eatough 1994). The precision of the blank data and replicate analyses of a sample give an expected uncertainty of ±1.2 $\mu g/m^3$ and ±0.5$\mu g/m^3$ in the calculated ambient organic carbon concentrations for four-hour CIF or quartz filter samples, respectively, collected with the BOSS samplers or in the side arm of the fine particle stream in each sampling system of the BIG BOSS.

Results for the BOSS Sampler.

The concentrations of carbonaceous material found on the second quartz filter for the filter pack in Sampler 2 and/or Sampler 3, see Figure 1, of the BOSS are shown in Figure 3. These data represent the "quartz filter" artifact as normally determined using a filter pack sampling system. Passage of the mixture of particles and organic gases through the denuder eliminates the quartz filter artifact for these samples, no organic material was collected on filter $Q_{1,2}$ of the BOSS, Figure 1. For the samples collected in Azusa, the quartz filter artifact is a "positive artifact" resulting from the absorption of organic compounds present in the atmosphere in the gas phase by the quartz filters during sampling.

The particulate carbonaceous material retained on the particle collecting quartz filter before a diffusion denuder of Samplers 2 or 3 of the BOSS, Figure 1, is then calculated as:

$$C_{Retained} = Q_{i,1} - Q_{i,2} \qquad (6)$$

where i equals Sampler 2 or Sampler 3. In contrast, since the quartz filter artifact resulting from the absorption of semi-volatile organic material lost from the particles during sampling is negligible, the particulate carbonaceous material retained on the particle collecting quartz filter after the denuder of Sampler 1 of the BOSS, Figure 1, is calculated as:

$$C_{Retained} = Q_{1,1} \tag{7}$$

The $C_{Retained}$ concentrations obtained from the data for Samplers 1, 2 or 3 of the BOSS were in agreement, Figure 4 and Table 1. The agreement in $C_{Retained}$ concentrations for quartz filters placed before or after a diffusion denuder to remove gas phase organic compounds is consistent with the expected rapid loss of semi-volatile particulate compounds during sampling with a loss time of a few minutes (Eatough 1993, Kamens 1993). The average $C_{Retained}$ concentrations for each sampling period obtained with the BOSS are shown in Figure 3. The arithmetic average of the measured concentrations for all samples obtained from these data, 13.8 µg C/m^3, is a factor of five larger than the average concentration of the "positive quartz filter" artifact, 2.8 µg C/m^3.

The concentration of semi-volatile organic material lost from particles during sampling as calculated from the BOSS data using equation 2 are shown in Figure 3. The average concentration of the SVOC lost from particles during sampling, 6.5 µg C/m^3, is 47% of the average concentration of the carbonaceous material retained by the particles, 13.8 µg C/m^3.

The efficiency of the CIF for the collection of semi-volatile gas phase organic material lost from particles obtained using equation 1 was 79.0±1.8%, in agreement with the results of previous studies (Eatough 1990). Even though the efficiency of the denuder of the BOSS for the removal of gas phase organic compounds is greater than 95% (Eatough 1993, Tang 1994), denuder breakthrough is still not negligible relative to the concentration of semi-volatile organic material and must be independently measured to obtain accurate concentrations of particulate organic material using the BOSS sampling system.

The total fine particulate carbonaceous material obtained with the BOSS for each sampling period (equation 3) is given in Figure 3. These concentrations are the sum of the $C_{Retained}$ and SVOC Lost concentrations for each sampling period.

Results for the BIG BOSS Sampler.

Comparison of BOSS and BIG BOSS Sampler Performance.

As demonstrated with the BOSS data, semi-volatile organic material is lost from particles present at Azusa during sample collection on a filter. The amount of particulate organic material on filter $Q_{1,1}$ of the BIG BOSS (the first quartz filter after the 2.5 μm inlet and denuder in the BIG BOSS System 1, Figure 2) agrees with that on filters $Q_{2,1}$ or $Q_{3,1}$ of the BOSS (the first quartz filter in a filter pack, corrected for the quartz filter artifact), Figure 4 and Table 1. This shows that the half-life for the loss of semi-volatile organic material from particles during sampling is much shorter than the sampling time (Kamens 1993) so that the loss is comparable for particles collected on a filter before and after a diffusion denuder for both the BOSS and BIG BOSS. This result also shows that, even at the high flow rates of the BIG BOSS, the positive artifact resulting from the absorption of gas phase organic compounds by the quartz filter is not present after the denuder and, finally, that the gas-particle equilibrium is not significantly perturbed during passage through the denuder. The possible presence of a quartz filter artifact for BIG BOSS samples from adsorption of gas phase compounds not collected by the denuder was also checked by analysis of filters $Q_{4,2}$ of the BIG BOSS, Figure 2. The average concentration of carbon on a quartz filter after a quartz filter and a denuder in System 4 of the BIG BOSS, Figure 2, was -0.03±0.52 μg C/m^3 (total of 12 samples). Negligible concentrations of gas phase organic compounds which can be adsorbed by a quartz filter pass the denuder, even at the high flow rates of the BIG BOSS.

Comparison of the BOSS and BIG BOSS Results.

The data obtained with the BOSS and with Samplers 1 and 4 of the BIG BOSS both give results for particulate carbon in fine (<2.5 μm) particles. The results obtained with the two systems are in agreement within ±10% for the SVOC lost during sampling, and for total fine particulate carbonaceous material, Table 1. The uncertainty in the comparison of the concentrations for the two data sets in all cases is just about a factor of two larger than the expected uncertainties of ±0.9 μg C/m^3 for the SVOC lost during sampling (±1.3 μg C/m^3 uncertainty in the comparison, Table 1), ±1.4 μg C/m^3 for the carbon retained by quartz filters during sampling (±3.1 μg C/m^3 uncertainty in the comparison, Table 1), and ±1.6 μg C/m^3 for total fine particulate carbon (±4.6 μg C/m^3 uncertainty in the comparison, Table 1). For both quartz filter retained carbon and total particulate carbon, the linear regression slope for the comparisons of the BOSS and BIG BOSS results include unity, The BIG BOSS samples gave slightly higher concentrations for the SVOC lost during sampling, with a regression slope with zero intercept for the comparison of the results obtained with the two systems of 1.18±0.05, Table 1.

Comparison of the BOSS and SCAQMD Results

Particulate carbonaceous material was determined by the South Coast Air Quality Management District using collocated sampling equipment during the Azusa study. The SCAQMD study included determination of particulate carbonaceous material with two different sampling systems (Barbosa 1993). SCAQMD System 4 consisted of two sequential quartz filters sampled after at 2.5 μm inlet cut at 15 L/min. Samples were collected with this system over each of the four hour sampling periods. SCAQMD System 7 contained only a single quartz filter after a PM10 inlet. Samples were collected with SCAQMD System 7 over the entire eight hour period each day with a sample flow rate of 35 L/min.

The quartz artifact measured with the SCAQMD System 4 was consistently higher than that obtained with the BOSS system. This difference is probably due to the lower flow rate used in the SCAQMD sampling system. The flow rates in the two sampling systems differed by about a factor of 2.5 - 3. This is also about the average difference between the quartz filter artifact as determined using the two systems (Eatough 1994). This result is consistent with the expected saturation of the adsorption sites on the quartz filters during sampling.

Quartz filter carbonaceous particulate material corrected for the quartz filter artifact (equation 6) determined in the various four hour samples using the BOSS and SCAQMD System 4 samplers were in agreement within ±20% with a possible small positive bias in the SCAQMD, as compared to the BOSS, results, Figure 5 and Table 1. The results obtained using the SCAQMD System 7 sampler were corrected for the quartz filter artifact using the BOSS results since the flows for these two systems were comparable. The resulting calculated concentrations of retained C on the quartz filters of the SCAQMD System 7 were in agreement with the BOSS and BIG BOSS results within ±10%, Figure 5 and Table 1.

Particle Size Distribution of Fine Particulate Carbonaceous Material

The data from the GC analysis of the material collected in the XAD-II beds or the TPV analysis of the charcoal impregnated filters of Systems 1-4 of the BIG BOSS, Figure 2, allow the determination of the particle size distribution of the semi-volatile organic material which was lost from the particles during sampling. The GC analysis of the material extracted from the XAD-II sorbent beds by dichloromethane gives a semi-quantitative measure of the various organic compounds captured by the XAD-II sorbent bed. This is illustrated by the data in Figure 6 where is shown the GC data obtained from analysis of the four XAD-II sorbent beds for the sample collected on 14 June 1992. The amount of material on the XAD-II sorbent bed decreases in going from samples $X_{1,1}$ through $X_{4,1}$, Figure 6. The decreasing amounts seen in going from System 1 through System 3 reflects the decreasing amount of semi-volatile organic material lost from the particles as the inlet particle size cut is decreased from 2.5 μm, to 0.8μm, and finally to 0.4 μm. The small amount of material seen for the $X_{4,1}$ sorbent bed in Sampler 4 results from the incomplete collection of about 5% of the total gas phase organic compounds by the denuder, the denuder breakthrough.

The data for the amount of organic material collected by the XAD-II sorbent beds or the CIF sorbent traps in the first three sampling systems of the BIG BOSS needs to be corrected for the denuder breakthrough measured in the XAD-II sorbent bed or CIF of the fourth sampling system to obtain the semi-volatile artifact as a function of particle size. An estimate of the amount of material present in the GC results, e.g. Figure 6, was obtained by comparison of the GC and TPV analysis (Eatough 1994). This leads to the data shown as SVOC Lost in Figure 7 for the average particle size dependent concentration and composition of the semi-volatile organic material lost during the collection of particles for all of the sampling periods in the Los Angeles Basin study.

The TPV analysis of the corresponding quartz filters in the CIF filter pack for each BIG BOSS system ($Q_{1,2}$, $Q_{2,2}$ and $Q_{3,2}$ in Figure 2) gives the total carbonaceous material remaining on each quartz filter after sampling, Quartz C in Figure 7. The sum of Quartz C and SVOC Lost gives the total particulate C, Particle C in Figure 7. The organic material determined by the GC analysis of the combined dichloromethane/methanol extraction (Tang 1994) of the quartz filters in front of the various XAD-II sorbent beds for BIG BOSS Sampling Systems 1, 2 and 3 ($Q_{1,1}$, $Q_{2,1}$ and $Q_{3,1}$ in Figure 2) is a measure of the semi-volatile organic material not removed from the particles during sampling. The average fraction of the quartz filter artifact corrected particulate carbonaceous material retained by the quartz filter during ampling which can be described as SVOC in each particle size range is given in Figure 7 as Quartz C SVOC. The remaining quartz filter carbonaceous material is non-volatile, Quartz C NVOC in Figure 7.

As indicated in Figure 7, the majority of the organic material in particles 0.8-2.5 μm in size is lost from the particles during collection of the particles on a filter. An average of 67% of the carbonaceous material in the 0.8-2.5 µm particles consists of semi-volatile organic compounds which are stripped from the particles during sampling. The semi-volatile organic material in particles 0.4-0.8 µm in size is also essentially all lost from particles during sampling, Figure 7. However, particles in this size range contain more non-volatile organic material. An average of 55% of the total carbonaceous material in these particles is retained by the particles during sampling, Figure 7. In contrast, the great majority, an average of 78% of the carbonaceous material in the particles smaller than 0.4 µm is retained by the particles during sampling.

The regular trend of decreasing importance of the loss of organic material from particles with decreasing particle size probably results from a combination of two factors: 1. The concentration of elemental carbon increases with decreasing particle size. The increased amounts of "soot" in the <0.4 µm size particles, as compared to larger fine particles, can be expected to result in the retention of some semi-volatile organic material in these particles due to the strong absorption of the semi-volatile organic compounds by the graphitic structure of the soot. 2. The concentration of particulate secondary organic material produced from photochemical processes probably increases with decreasing particle size. This material will be rich in oxygen and nitrogen as a result of the photochemical processes leading to their formation. The resulting organic material will be relatively non-volatile and would be expected to be retained by the particles during sampling.

Chemical Characterization of Fine Particulate Organic Material.

The semi-volatile organic compounds lost from particles during sampling and subsequently collected by an XAD-II trap in System 1 of the BIG BOSS, Figure 2, included significant concentrations of aliphatic, acidic and aromatic organic compounds. Similar compounds were also detected in the GC-MS analysis of the filter extracts. However, the compounds retained by the filter were of higher molecular weight. The distribution of compounds in several classes of the typical semi-volatile organic compounds lost from particles during sampling (the SVOC Lost artifact), and remaining on the particles during sampling is illustrated by the results given in Table 2. It is anticipated that removal of ozone and nitrogen oxides by the denuders minimizes any potential reactions of collected particulate organic material with these species in the BOSS sampling systems. Compounds are present from all major organic compounds classes expected to be present in the atmosphere. Studies currently underway indicate that the classes of compounds given in Table 2 account for about half of the organic material in the semi-volatile organic compounds lost from particles during sampling. The remainder are polar, oxygenated aromatic compounds which have not yet been chemically characterized. Future studies will focus on the characterization of this polar organic material because this fraction of the SVOC lost from particles during sample is potentially toxic because of the OH and NO_2 groups in these compounds.

For those compounds which have been characterized, the envelopes of each class of compounds remaining in the particles and lost from the particles overlap. For each compound class, the more volatile compounds predominate in the material lost from the particles and collected in the XAD-II bed during sampling. In contrast, the higher molecular weight organic compounds are retained by the particles during sampling. For example, particulate n-tetradecane and n-pentadecane are found only in the XAD-II bed and not in the particles after sampling. Hydrocarbons lower in molecular weight than these two compounds are found in comparable concentrations in the XAD-II beds of both Samplers 1 and 4 of the BIG BOSS, indicating they originate mainly from the breakthrough of some fraction of the gas phase component of these species. In contrast, n-tetracosane and higher molecular weight aliphatic hydrocarbons are retained by the particles during sampling and are not found in the XAD-II sorbent beds. Compounds of intermediate molecular weight, e.g. n-decosane, are partially lost and partially retained by the particles. Also illustrated by the GC-MS data is the increased tendency for lower molecular weight semi-volatile organic compounds to be retained by the particles during sample collection as the polarity of a given molecular weight compound increases. For example, n-heptadecane (MW 226) is largely lost from particles during sampling. However, lauric acid (MW 214) and fluoranthene (MW 202) are largely retained by the particles during sampling.

The GC data obtained to the present indicate that the chemical composition of the semi-volatile compounds lost from particles during sampling was similar for all urban areas studied to date. This probably reflects the importance of organic compounds from automotive emissions at each of these sites. Data comparable to those shown in Figure 6 have also been obtained for samples collected in Philadelphia, PA, and Provo, UT. Semi-volatile organic compounds lost from particles during sampling at all of the urban sampling sites studied were comparable, appeared to be dominated by automotive emissions, and included paraffins, aromatic compounds and organic acids and esters.

CONCLUSIONS

An average of 35% of fine particulate carbonaceous material was lost as volatilized semi-volatile organic compounds during the collection of samples at Azusa. This loss results in the under determination of fine particulate organic material unless diffusion denuder sampling systems are used to determine the SVOC Lost fraction. The organic material lost from the particles represents all classes of organic compounds. Studies currently underway suggest that the classes of compounds given in Table 2 account for only about half of the total semi-volatile organic material lost during sampling. Significant concentrations of oxygenated and nitrated aromatic compounds which are potentially toxic and have not yet been chemically characterized constitute the remaining material. It is reasonable to assume that those organic compounds which are easily loss from particles may also be easily assimilated by tissues exposed to fine particles. If these compounds are important with respect to the exacerbation of respiratory health problems in exposed populations, past studies on the health effects of PM10 will have underestimated the concentrations of PM10 organic material of importance in the setting of a suspended particle standard. The fine particulate organic constituents to which an urban population is exposed have not been well characterized or quantified in previous studies.

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Table 1. Linear Regression Analysis of the Results Obtained in the Azusa Study.

System	n	r^2	Slope	Intercept
BOSS $C_{Retained}$ on Collocated Samples	6	0.193	0.973±0.084	±2.9 μg/m^3
BOSS $C_{Retained}$ Before and After a Diffusion Denuder	21	0.629	1.095±0.053	±3.3 μg/m^3
BIG BOSS $Q_{1,1}$ and BOSS $(Q_{2,1}$-$Q_{2,2})$, Quartz Filter Retained Carbon	16	0.733	0.957±0.051	±3.1 μg/m^3
BOSS and BIG BOSS SVOC Lost	15	0.866	1.176±0.051	±1.3 μg/m^3
BOSS and BIG BOSS Total Fine Particulate C	15	0.654	1.023±0.053	±4.6 μg/m^3
BOSS and SCAQMD 4 Hour $C_{Retained}$	18	0.511	1.183±0.069	±4.0 μg/m^3
	18	0.593	0.878±0.182	4.5±3.8 μg/m^3
BOSS and SCAQMD 8 Hour $C_{Retained}$	16	0.643	1.097±0.061	±3.4 μg/m^3
	16	0.654	0.975±0.189	1.8±3.4 μg/m^3

Table 2. Principal Organic Compounds Retained in Particles and Lost From Particles During Sampling with the BIG BOSS Sampling System in Azusa California.

Compound	Molecular Weight	Relative Amount Present on [*] Quartz Filter	XAD-II Bed
Aliphatic Hydrocarbons			
n-Tetradecane	198		++
n-Pentadecane	212		+++
n-Hexadecane	226	+	++++
n-Heptadecane	240	+	++++
n-Octadecane	254	+	++++
n-Nonadecane	268	+	+++
n-Eicosane	282	++	+++
n-Heneicosane	296	++	++
n-Decosane	310	+++	+
n-Tricosane	324	++++	+
n-Tetracosane	338	++++	
n-Pentacosane	352	++++	
n-Hexacosane	366	++++	
n-Heptacosane	380	+++	
n-Octacosane	394	+++	
n-Nonacosane	408	++	
Aliphatic Acids			
Nonanoic Acid	172		+
Decanoic Acid	186		++++
Undecanoic Acid	200		+
Lauric Acid	214	++	++++
Tridecanoic Acid	228	++	++
Myristic Acid	242	++++	++++
Pentadecanoic Acid	256	++	+
Palmitic Acid	270	++++	+++
Margaric Acid	284	++	+
Oleic Acid	298	++++	++
Arachidic Acid	326	+	
Behenic Acid	354	++	
Aromatic Hydrocarbons			
Naphthalene	128		+
2-Methylnaphthalene	142		+
Phenanthrene	178	+	+
Methylphenanthrene	192	+	+
Fluoranthene	202	+	
Pyrene	202	+	
Aromatic Acids			
Isophthalic Acid	194	+	+
Methylphthalic Acid	208	+	

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[*] The number of "+" represents the relative abundance for each compound class.

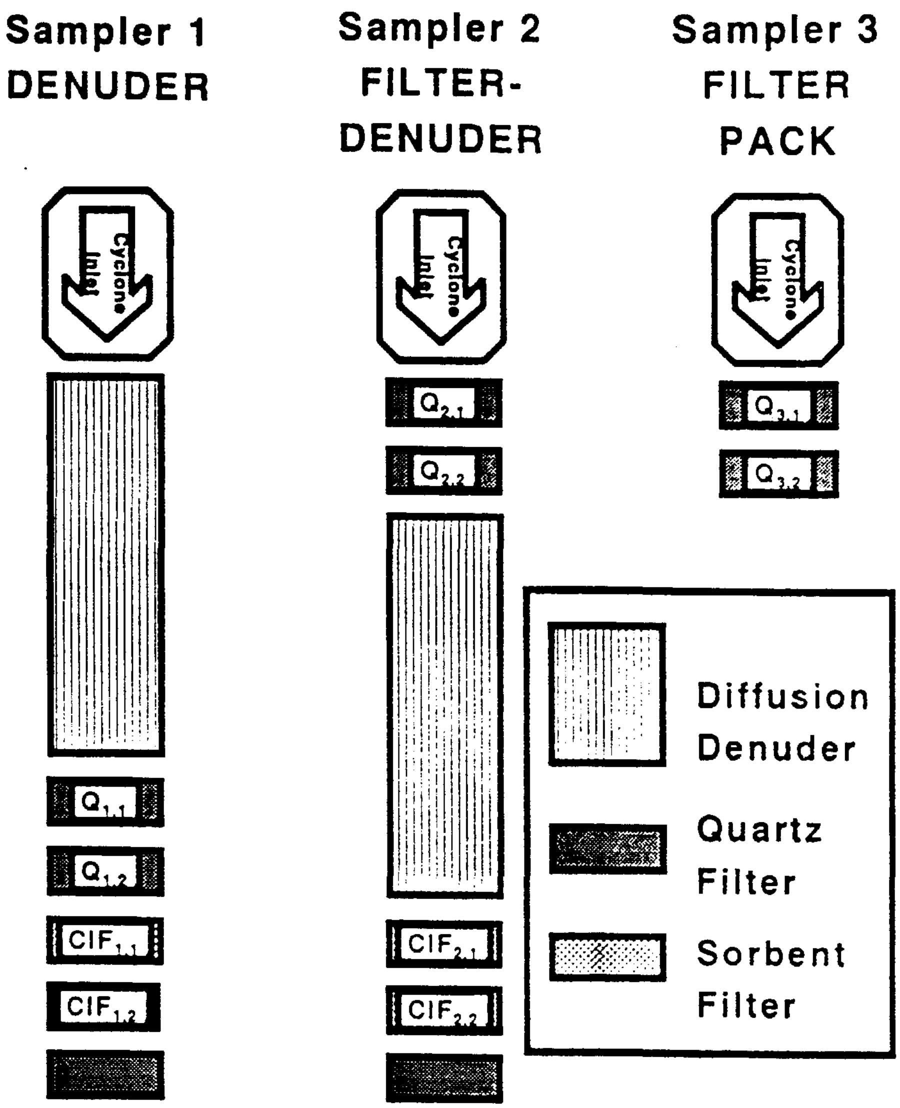

Figure 1. Schematic of the BOSS sampling system.

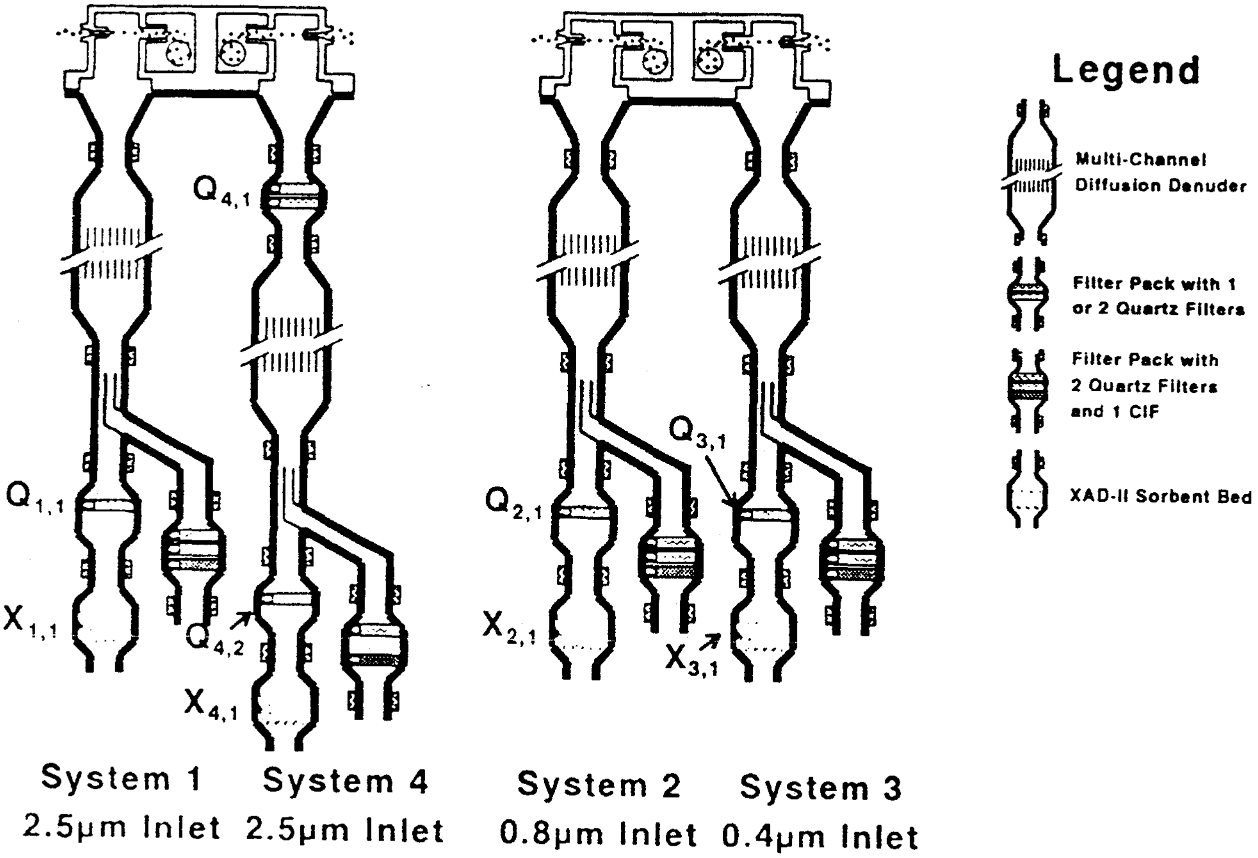

Figure 2. Schematic of the BIG BOSS sampling system, System 1 (denuder, 2.5 μm inlet cut), System 2 (denuder, 0.8 μm inlet cut), System 3 (denuder, 0.4 μm inlet cut), and System 4 (filter/denuder, 2.5 μm inlet cut).

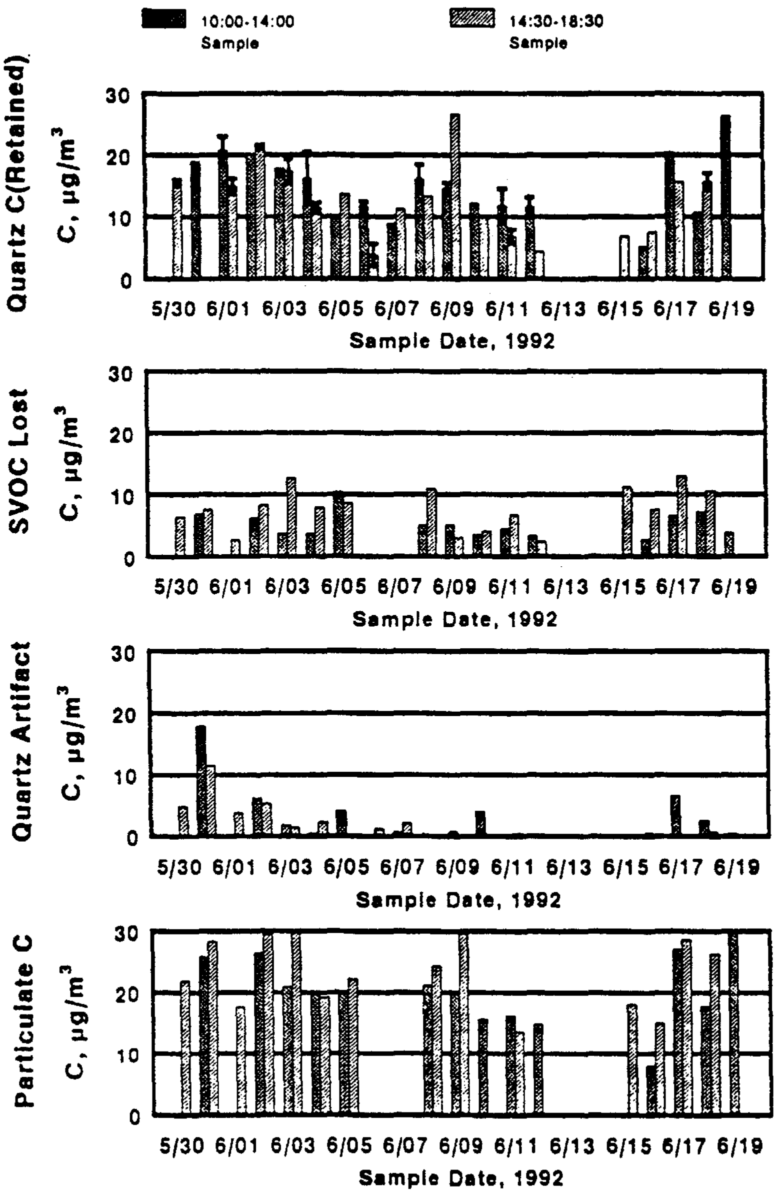

Figure 3. Semi-volatile organic material lost from particles, particulate carbonaceous material retained by particles, the positive quartz filter artifact present during sampling, and the fine particulate carbonaceous material obtained with the BOSS for each sampling period.

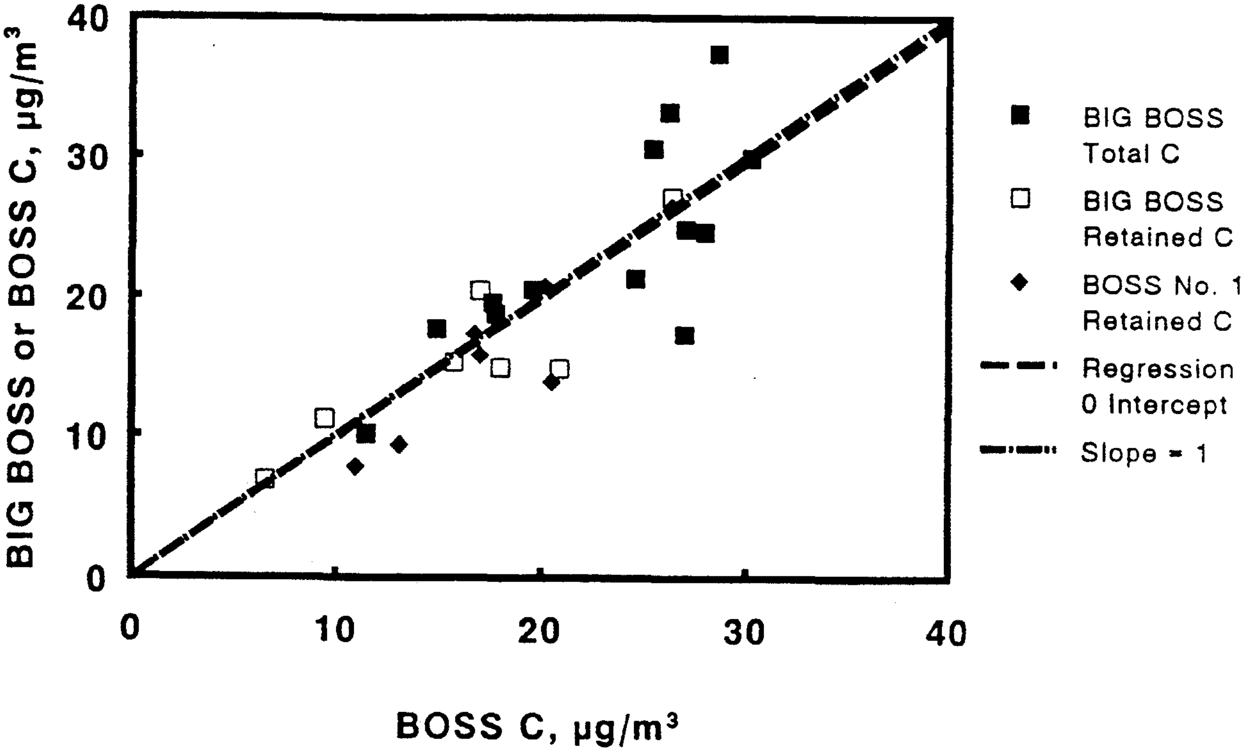

Figure 4. Comparison of $C_{Retained}$ (particulate carbonaceous material collected on a quartz filter corrected for the quartz filter artifact) for Systems 1, 2, or 3 of the BOSS and System 1 of the BIG BOSS, and total fine particulate material determined with the BOSS and BIG BOSS.

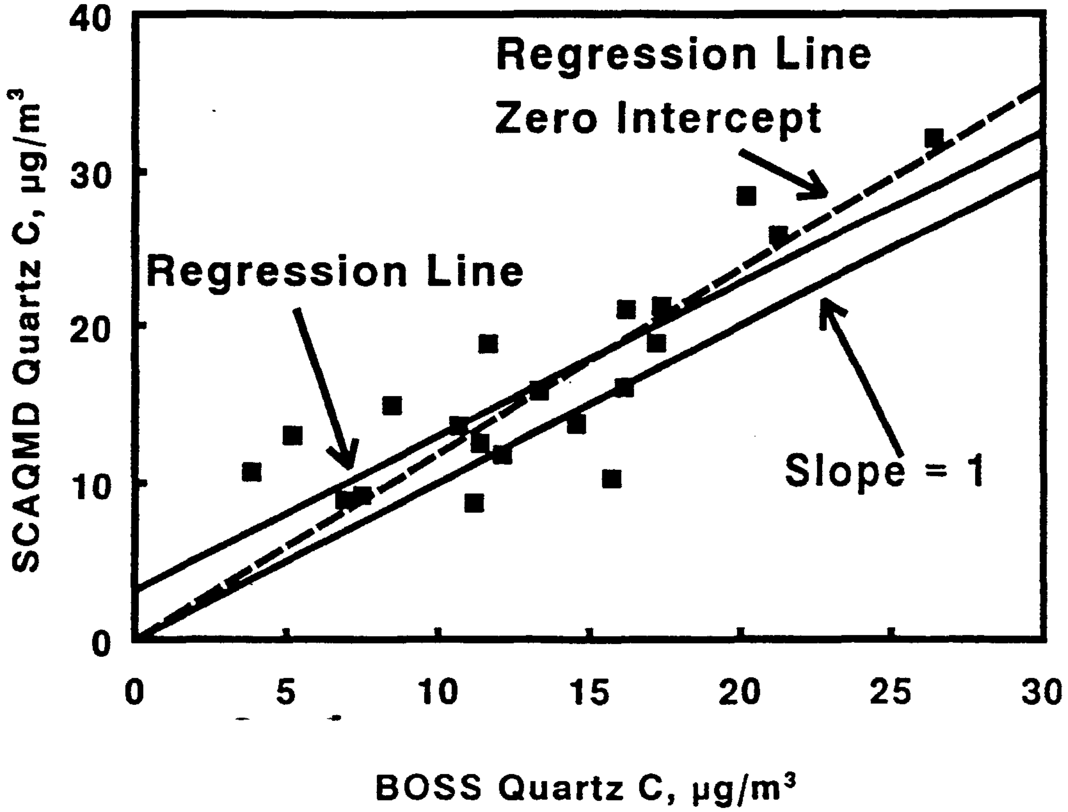

Figure 5. Comparison of BOSS and SCAQMD results for fine particulate carbonaceous material retained by quartz filters during sampling,

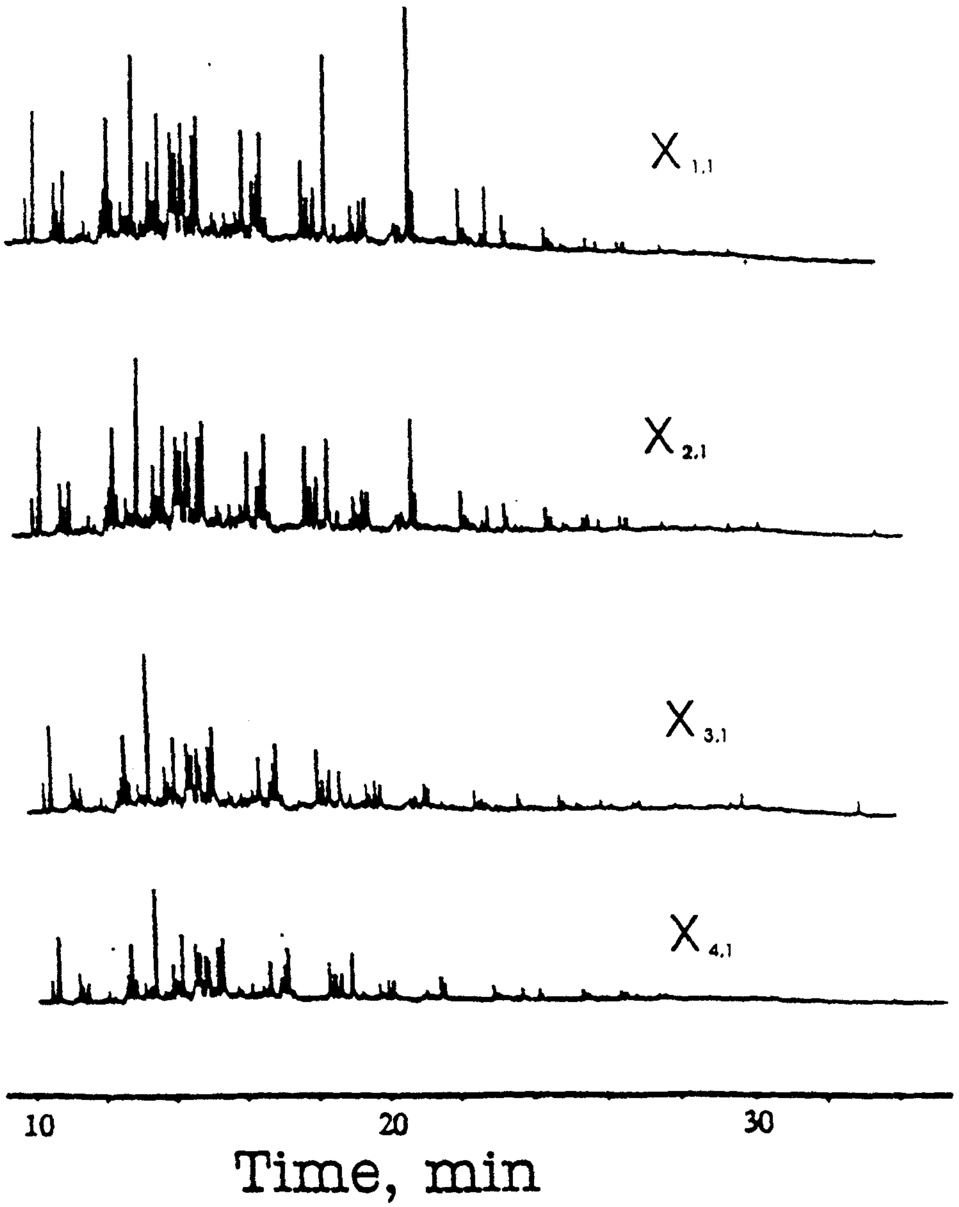

Figure 6. GC data for the organic compounds collected in the XAD-II beds after collection of particles in Samplers 1-4 of the BIG BOSS for samples collected from 10:00 to 18:30 pm June 14 in Los Angeles Basin (Azusa).

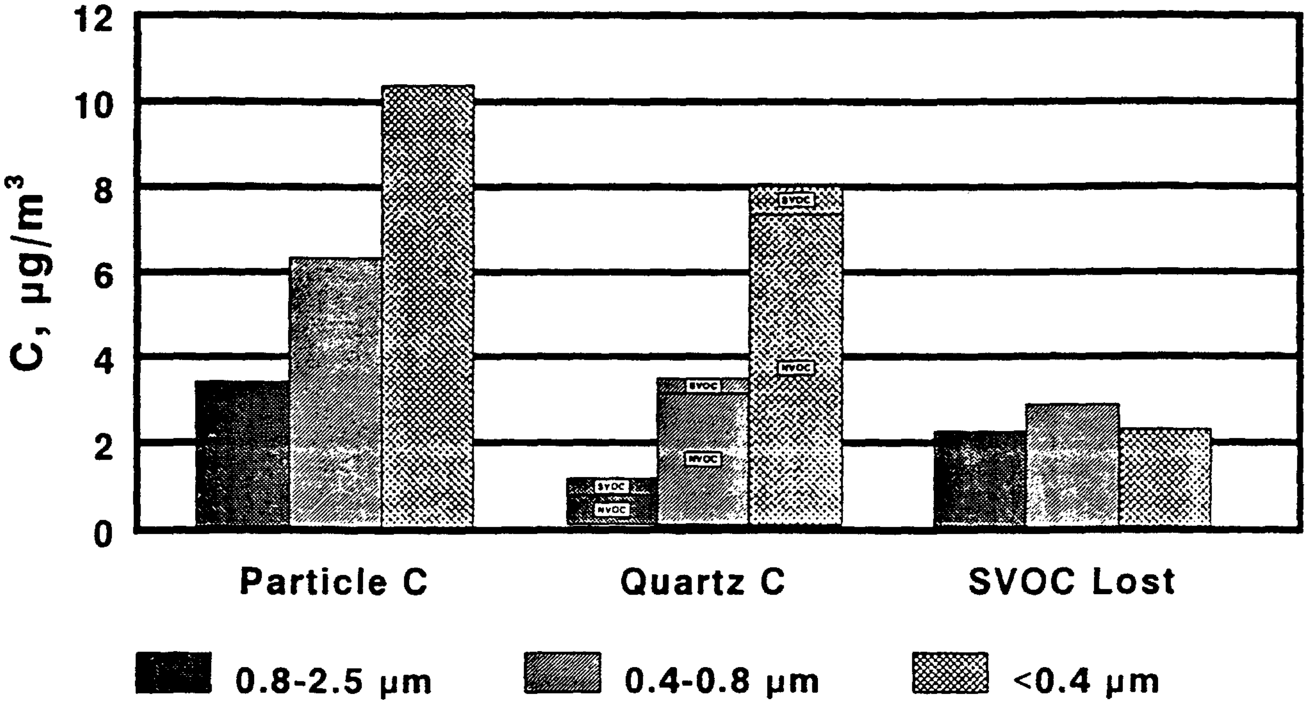

Figure 7. Average fine particulate size distribution of total carbonaceous material (Particle C), total carbonaceous material retained by particles during sampling (Quartz C, expressed as SVOC and NVOC material), and semi-volatile organic material lost from particles during sampling (SVOC Lost) for samples collected with the BIG BOSS at Azusa in the Los Angeles Basin.

THE EFFECT OF PARTICLE SIZE DISTRIBUTION ON THE CUT POINT BETWEEN FINE AND COARSE AMBIENT MASS FRACTIONS

by

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Abbreviated tittle: Cut Point Between Fine and Coarse Mass

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ABSTRACT

A review of recent studies on the size distribution of ambient particles reveals considerable variability, both spatially and temporally, depending on the source of origin, geographical location, meteorological conditions and various other chemical and physical parameters. However, there is generally a clear separation into fine and coarse modes, with a dividing point between 1.0 and 2.5 microns where the mass of the two modes is at a minimum. In the 1970's EPA developed the dichotomous sampler to separate fine and coarse particles and choose a cut point at 2.5 microns. However, recent data collected with new samplers, such as the size fractionating Moudi Impactor, reveal that both aged sulfates and particles associated with aerosol acidity reside in the range below 1.0 micron diameter. Indoor combustion aerosols such as cigarette smoke and kerosene heater emissions have also been found to reside in the submicron range. Before embarking on a new and extensive aerosol characterization study and perhaps establishing separate standards for fine and coarse particles EPA might wish to re-evaluate the choice of a cut size.

This paper discusses the size distribution make up of ambient aerosols from various sources and locations throughout the U.S. The effect of sampler cut points and sampling efficiencies on the accuracy of collection in eastern, combustion-dominated and western, wind-blown-dust-dominated settings will be examined. The advantages and disadvantages of changing the cut point between fine and coarse form 2.5 microns to something nearer 1.0 micron is discussed.

INTRODUCTION

An aerosol is formed by two basic mechanisms: 1) dispersion and 2) condensation. The dispersion mechanism produces an aerosol which, on a mass basis, is almost all within the 1 to 1000 μm diameter size range. This aerosol will be referred to as the coarse particle mode (or supermicron aerosol). Available data on the measured concentration of this coarse particle mode aerosol indicates the atmospheric concentration is often in the range from 10 to 100 $\mu g/m^3$, with most of that mass associated with particles of 2 to 200 μm diameter. Measurement data indicates this aerosol is approximately lognormally distributed with a mass median diameter (MMD) of 10 to 30 μm and distribution geometric standard deviation, σg, (for a best fit lognormal distribution) of about 2. These generalizations are valid if there is no major aerosol generation source near the measurement site and the atmospheric conditions are average (no high winds, no heavy rain, etc). These statements are considered equally valid for natural aerosol, anthropogenic aerosol, or a mixture of the two.

Condensation aerosol is almost always of submicron size (< 1μm diameter), with almost all the mass between 0.01 and 1 μm diameter. This aerosol will be referred to as the submicron mode aerosol or the fine particle mode aerosol. Atmospheric concentration is often in the range from 10 to 100 $\mu g/m^3$, as it is for the supermicron mode aerosol. Concentration can however, be significantly higher or lower for either of the aerosol modes. The submicron mode can usually be approximated with a lognormal distribution having a MMD in the 0.1 to 1 μm range and a σg of 2 to 3 (or greater). These generalizations also assume no major aerosol source adjacent to the measurement site and an aerosol of some reasonable age (perhaps 1 to 100 hours). Again, these statements apply to both natural and anthropogenic aerosols.

An ambient aerosol will normally have a bimodal mass distribution because both dispersion and condensation aerosols will be present. In most large city environments the two modes are present in measurable concentrations. On occasion one mode will overwhelm the other, and a clear separation will not be seen on a simple mass distribution histogram or frequency distribution curve. Because the two modes are formed from different materials and by different mechanisms, the chemical composition of the two modes will be different. Differentiation of the two mass modes is of interest and important for many reasons, including regulatory, health, scientific, etc. Separation of these two modes is the topic of this paper.

BACKGROUND

A wealth of data clearly shows the number distribution of ambient aerosol to be primarily within the 1 nm to 100 nm size range. Calculation of the ambient aerosol surface area distribution (not normally directly measured) clearly shows a surface area distribution within the 10 nm to 1 μm size range. Both distributions normally have a single mode and are approximately of a lognormal shape over the central 90 percent of their distributions.

Ambient mass or volume distributions are normally of bimodal nature. On the average, the mass fractions in each mode (fine vs coarse) are comparable, allowing both to be clearly visible in a mass frequency vs particle diameter plot (or histogram). Conversion of mass frequency data to surface area or number frequency data allows the submicron (or fine) aerosol to mask the supermicron (or coarse) aerosol appearance.

Primary air quality standards are based upon health effects and health effects are assumed to correlate with aerosol mass concentration. This simple correlation is inadequate and both particle size and aerosol composition must be included to obtain a more meaningfull relationship. Detailed and continuous measurements of aerosol composition vs particle size cannot be routinely made across the U.S. because of cost and technical limitations. Therefore; imperfect, but improved, techniques of providing more relevant aerosol data must be selected. This paper study and the comments offered are based upon physical and chemical properties of ambient aerosol and the need for a more relevant aerosol measurement for human health effects considerations.

EARLY MEASUREMENTS OF AEROSOL SIZE DISTRIBUTION

An excellent history of pre 1960 measurements of atmospheric aerosol in contained in Air Chemistry and Radioactivity by Junge (1963). Although the presented particle volume vs size distribution plot (Fig. 24 on page 118) indicated a bimodal (fine and coarse aerosol) volume distribution, this may not have been recognized because a flat "model distribution" was proposed for the general 0.5 to 10 μm diameter size range. Several good and rather complete measurements of the coarse mode aerosol had been made before 1960. These data are discussed and referenced in the Coarse Particle Mode Aerosol section of this paper. Before 1960 the light and electron microscopes were the principal instruments available for obtaining particle number distribution data. The several million fold number concentration differences between 0.1 and 10 μm particles made complete number distribution counts very difficult. Sampling difficulties complicated this further.

During the 1960s automated particle size discriminating counting instruments were available for monitoring of particle number over a two or three decade range of particle size. The optical particle counter had been developed to count particles within the 0.5 to 10 μm range. The condensation nucleus counter had been developed to count particle in the sub 0.01 μm size range. With development of the Whitby Aerosol Analyzer (an early version of the TSI Electrical Aerosol Analyzer or EAA) to cover the 0.005 to 0.5 μm size range, complete measurement of the fine mode (or modes) and the lower half of the coarse mode was possible. Conversion of this number distribution data made apparent the bimodal volume or mass distribution. Early data presented by Clark and Whitby (1967) indicated this bimodal distribution in Minneapolis while latter data from the 1969 Pasadena Smog Aerosol Experiment conclusively demonstrated this bimodal nature of atmospheric aerosols.

A classic set of articles are presented by Whitby and others in the book "Aerosols and Atmospheric Chemistry" (1972) edited by G.M. Hidy. Probably the most significant early data on aerosol size distribution of Los Angeles smog are presented by Whitby, Husar and Liu (1972). This article contains the often reproduced data plot shown as Figure 1. Although these data are now 25 years old, the conclusions drawn in that article are still mostly valid. The inability to accurately sample large particles (~ 10 to 100 μm) made it impossible to accurately assess the coarse particle mode however.

Most old mass and element distribution data did not identify the bimodal distribution. Data were often presented as a cumulative distribution and a single best fitting lognormal distribution used to describe the data. Lundgren (1970), for example, presented a plot of mass and element data which was clearly fine mode for sulfate, nitrate and lead but bimodal (coarse and fine) for iron and total mass. The presented MMD and σg values for mass and iron were therefore, inappropriate. High concentration of fine mode ammonium nitrate aerosol was identified using X-ray diffraction. Other early impactor data was reviewed but was not considered reliable enough to be presented and discussed (because of sampling and analysis difficulties).

COARSE PARTICLE MODE AEROSOL

Early measurements of coarse mode aerosol, often referred to as giant particles, included the size range from 10 to 200 μm diameter. Woodcock and Gifford (1949), Woodcock (1952, 1953) and Moore and Mason (1954) used impactor techniques to study coarse mode aerosol over the ocean. Okita (1955) used sedimentation and web threads to determine a particle size distribution in Japan. Jaenicke and Junge (1967) used a propeller type impactor to collect and measure particles larger than 10 μm. Much of the early work on particle size distribution can be credited to Junge (1955), this is particularly true in the submicron size range. Twomey (1954) conducted early studies of atmospheric hygroscopic particles.

An early study by Noll and Pilat (1971) used a rotary inertial impactor to collect ambient particles from 10 to 200 μm diameter. Number concentration vs size was determined using a microscope and TV camera arrangement. Calculated mass distribution data clearly showed a mass mode peak in the 10 to 100 μm size range (what is now referred to as the coarse mode aerosol).

Whitby, Husar and Liu (1972) calculated volume distributions from optical particle counter and Whitby Aerosol Analyzer (or Electrical Aerosol Analyzer - EAA) number distributions. These data show a mass distribution with a fine mode peak in the 0.1 to 1 μm range, followed by a relative minimum around 1 to 3 μm and then a rather rapid increase which stopped at about 10 μm, the upper size limit of the instrument system. This clearly indicated a coarse mode peak at some size above 5 μm diameter. Aerosol mass above 5 μm appeared to be as great as that below this size.

Lundgren and Paulus (1975) reported on a study designed to obtain size separated samples of the coarse aerosol distribution for direct weight evaluation and microscopic examination. Four, parallel operated, single stage impactors were designed and calibrated to provide size classified aerosol samples at sizes of 54, 26, 13 and 7.5 μm diameter. Enough mass was obtained for accurate weighing by sampling at 60 cfm for 24 hour run times. Lundgren cascade impactors provided additional size-classified samples over the 0.4 to 13 μm diameter range.

The Lundgren data clearly confirmed the atmospheric bimodal mass distribution form suggested by Whitby. Coarse aerosol mode measurements indicated a variable concentration from less than 10 to greater than 100 $\mu g/m^3$. Fine mode concentration varied over the 5 to 50 $\mu g/m^3$ range.

These data show that the coarse aerosol mode could adequately be represented by a near lognormal distribution having a MMD between 10 and 20 μm diameter and a σg of about 2. About 99% of the coarse aerosol mode appeared to be within the 2 to 200 μm diameter size range. Unfortunately, this data only represents one sampling location (a suburb on the north edge of the Minneapolis-St. Paul suburban complex) at one time of the year (July-September).

Lundgren, Hausknecht and Burton (1984) describe a mobile aerosol-sampling system designed and constructed by Lundgren and Rovell-Rixx (1982). This system was used to determine the coarse ambient aerosol size distribution in five cities across the U.S.: Birmingham, AL; Research Triangle Park, NC; Philadelphia, PA; Phoenix, AZ; and Riverside, CA. This mobile system was named the wide range aerosol classifier (WRAC) and was used to obtain size fractionated samples of both the coarse and fine mode aerosol using impactors (as in the earlier fixed site study by Lundgren). Mass distribution measurements were compared with data obtained simultaneously using TSP Hi-Vol and 15 μm cut-size samplers. The presence of a coarse aerosol mass mode was shown at all sites sampled. The concentration and MMD of the coarse aerosol mode varied and was not a simple function of concentration. Representative average coarse mode distributions are shown in Figure 2. Table 1 lists the sites, their acronyms, and the average aerosol concentrations. Table 2 summarizes the approximate average coarse aerosol distribution values for several different cities.

Plots of the total coarse particle grand average distribution and various city average distributions suggest that the coarse particle distribution is approximately lognormal. These data also suggest a minimum value between the coarse and fine modes below 3 μm diameter. Total mass and mass fraction in the coarse particle mode varies from location to location and from day to day.

The large mass concentration difference between the Riverside high-concentration values, noted as RBX-High (255 $\mu g/m^3$) and the Riverside low-concentration values, noted at RBX-Low (90 $\mu g/m^3$), is explained by the respective sampling conditions. During days averaged as the RBX-Low distribution, the winds were predominantly from the east, or off the desert. The aerosol mass was primarily large particles entrained by the wind. The small particle mass mode was low in concentration because automobile and other condensation aerosol sources were located to the west.

During the sampling runs used for RBX-High distribution, the wind was primarily from the west, or from the Los Angeles basin. The wind velocities were, on the average, lower than winds from the east. The air was highly polluted with small particulate matter due to the abundance of condensation aerosol (including photochemical aerosol) being blown in from the Los Angeles basin. The small particle concentration increased by about a factor of eight. An interesting observation is that the large particle mode appeared to change with a downward shift in mean particle size. The Los Angeles basin is a moderate source of large particles, owing to the extensive roadway system and other dispersion sources. However, with low wind speed and long travel time, most of the large particles will settle from the air and produce a downward shift in the mean large particle size.

In contrast to this, the observed distributions in Birmingham were characterized by a more uniform increase in the whole size spectrum. This conditions was usually the result of an air stagnation and resulted in a concentration increase for all particle sizes, although the large particles increased the most.

At the Research Triangle Park site, the low concentrations observed were generally expected because of the lack of pollution sources in the area. The large particle distribution shape was similar to that found in Riverside. These large particles, including pollens, were mainly the result of nature and would exist in relatively clean (air-pollution free) areas around the country.

By normalizing the mass distributions with respect to total aerosol concentration, shapes of the distributions can be compared. The general shapes of the distributions are similar and all distributions show the presence of a large particle mass mode. However, one must be cautious in drawing a conclusion from a single distribution, as the distribution shapes can be quite different even though the concentrations may be very similar. The ambient particulate mass distributions did vary as a function of both location and time.

TABLE 1. Sampling Sites

Location	Data grouping	WRAC total mass	Site acronym
Birmingham:	9-day average	164.9 $\mu g/m^3$	NB-Av
Birmingham:	4 highest days	204.6 $\mu g/m^3$	NB-High
Birmingham:	3 lowest days	113.0 $\mu g/m^3$	NB-Low
Research Triangle Park:	4 days	43.8 $\mu g/m^3$	RTP-Av
Philadelphia:	6-day average	100.1 $\mu g/m^3$	PA-Av
Phoenix:	11-day average	116.5 $\mu g/m^3$	PHX-Av
Riverside:	11-day average	186.8 $\mu g/m^3$	RBX-Av
Riverside:	6 highest days	255.1 $\mu g/m^3$	RBX-High
Riverside:	4 lowest days	89.5 $\mu g/m^3$	RBX-Low
Grand average:	41 days	134.0 $\mu g/m^3$	

TABLE 2. Coarse Particle Mode Distribution Values

City	WRAC	Coarse Particle Mode Measurements			
	Total aerosol µg/m^3	Concentration µg/m^3	Aerosol fraction in Mode–%	Mode MMD µm	Mode spread σg
Birmingham (4 highest days)	204.6	100	50	25	~ 2
Riverside (6 highest days)	255.1	50	20	13	~ 2
Research Triangle Park (4 days)	43.8	12	30	17	~ 2
Phoenix (11-day average)	116.5	50	45	20	~ 2
Philadelphia (6-day average)	100.1	30	40	20	~ 2
Grand average (41 days)	134	50	40	20	~ 2
Minneapolis (1972 data, Lundgren and Paulus, 1975)	71	35	50	15	~ 2

Mamane and Noll (1985) characterized coarse particles at a rural site in western Maryland (Deep Creek Lake) by both mass and by individual particle analysis. Samples were obtained using a modified Noll rotary impactor. Coarse mode aerosol concentration was low (~ 10 $\mu g/m^3$) with a MMD of about 15 μm. Composition was found to be mainly pollen, quartz and calcite for the largest particles (40+ μm), with more clay, fly ash and iron associated with the sub 20 μm particles.

Noll, Draftz and Fang (1986) determined the size and composition of four samples of coarse mode atmospheric aerosol samples obtained in and near Chicago. Particles from the industrial sector of Chicago were represented by limestone, silicates, coal and fly ash. Particles from the commercial sector were mainly limestone, tire rubber and silicates. Two rural site samples were mainly limestone with some silicates and pollens. Aerosol MMD's for the various components were: 20 μm for limestone, 12 μm for silicates, coal, fly ash and iron oxide and 25 μm for tire rubber. Figure 3 shows the mass distribution for the four samples, all of which have a σg of about 2. Chicago samples (C29 and C58) had coarse mode mass concentrations of 121 and 33 $\mu g/m^3$. Urban area samples, from Argonne, Illinois (A15 and A25) had concentrations of 7.8 and 10.5 $\mu g/m^3$.

A study by Lundgren and Rangaraj (1986) on fugitive dust emissions from granular products such as fertilizer, coal, ores and soils reported the dust distributions measured for four materials as having a dust mass median diameter in the 14 to 25 μm range with a σg of about 1.7 to 3 (average of 2).

Lin, Fang, Holsen and Noll (1993) used both a Noll rotary impactor and a cascade impactor to measure both the fine and coarse mode aerosol in Chicago. Total particle mass, lead and calcium were analyzed. Mass concentration of the fine and coarse mode aerosols were both within the 10 to 50 μg/m^3 range. A between mode minimum existed at about 2 or 3 μm diameter. Lead was mainly associated with the fine aerosol and calcium with the coarse aerosol, although both were measured over the entire 0.1 to 100 μm size range.

FINE MODE AEROSOL

Hidy (1975) presented a summary of results from the California Aerosol Characterization Experiment (ACHEX). Data were gathered in 1972 and 1973 in the Los Angeles Basin and several other locations. Submicron (or fine) aerosol components of sulfate, nitrate, noncarbonated carbon, and water were major contributors. These data shown in Figure 4 indicate the fine particles mode to be of submicron size ($< 1\,\mu m$) and the coarse particle mode to peak in the 6 to 10 μm diameter range. A very strong minimum is shown at about 1 μm and data presented supports the report summary statement "The nature of airborne particles less than 1 μm diameter appears to be most relevant to the pollution and visibility problems". An idealized bimodal mass distribution with chemical components was presented as Figure 5.

Wall, John and Ondo (1988) presented size distributions for nitrate and major ionic species. Samples were obtained at Claremont, CA during September 1985 using a Berner nine stage impactor. Nitrate was found to be in both the fine and coarse modes but as different chemical compounds. For all ions measured, a minimum in the fine vs coarse modes appeared at about 1.5 μm diameter, with the fine mode aerosol below 1 μm diameter and the coarse mode aerosol mainly in the 2 μm to 10 μm size range. Similar distribution data was presented for several different ions (ammonium, sulfate, hydrogen ion, sodium and chloride).

Cantrell and Rubow (1990) have presented mass size distribution data for underground coal mine aerosol. Diesel aerosol formed a fine mode and coal dust formed a coarse mode with a clear between mode minimum at about 1 μm. In an all electric mine, only the coarse mode was present but the aerosol tail reached down to about 0.1 μm

diameter. The mass fraction below 1 μm was a small fraction of the total mass however.

Extensive data on size-dependent chemical composition of fine mode aerosol (the submicron size fraction) has been obtained by McMurry (1985, 1986, 1989, 1990, 1993). These data include a 3-day intensive study in Los Angeles (8-10 August, 1984); a study at Hopi Point, Grand Canyon, AZ (9 Sept to 8 Oct, 1985); a Los Angeles area study (eleven days in Claremont and Rubidoux, June-Sept 1989 plus six days in Long Beach and Los Angeles, Nov-Dec 1989); and a Meadview-AZ study (July-Aug, 1992). These data include size-dependent analysis by ion chromatography, X-ray fluorescence (XRF), proton-induced X-ray emission (PIXIE) and thermal-optical carbon analysis. Some mass data was also obtained.

Because the McMurry data is so extensive, data can be selected out to support various conclusions. This author has examined all of the McMurry data and drawn the following conclusions about the submicron or fine particle aerosol.

The 1984 Los Angeles study was stated as a study "to evaluate the utility of new aerosol sampling instrumentation for measuring the size-dependent chemical composition of ambient aerosol." High concentrations of carbon (organic plus elemental) were found within the general 0.1 to 1 μm size range. Sulfate and nitrate, however, were more broadly distributed with much of the nitrate associated with the supermicron (greater than 1.0 μm) size aerosol. These data indicate about one half (50%) of the nitrate aerosol and about one fourth (25%) of the sulfate aerosol is associated with greater than 1 μm diameter particles. A particle cut size of 2.5 μm would be required to contain 90% of the nitrate aerosol. These data are considered less reliable than are the latter data.

Data from the 1985 Grand Canyon study did show that aerosol sulfur was in the fine particle mode and that silicon, aluminum and calcium were mainly associated with the coarse particle mode. Particle bounce was noted as a possible reason for the carry over of crustal materials (Si, Al and Ca) into the submicron size range. The actual mass concentration of these crustal materials, within the submicron size range was very low (~ 0.1 $\mu g/m^3$ for silicon and less for all other crustal elements). Organic and elemental carbon was almost all of submicron size, as was the average gravimetric mass distribution.

The 1989 Los Angeles organic and elemental carbon size distribution measurements indicate a carbon aerosol mass median diameter (MMD) of about 0.5 μm (aerodynamic diameter) with about 90% of this aerosol less than 1 μm diameter and about 95 to 99% less than 2.5 μm diameter. Because the coarse mode aerosol was not measured, conclusions cannot be drawn as to coarse mode carbon or fine to coarse mode ratio, etc. A single mode, lognormal size distribution with a 0.5 μm MMD and a geometric standard deviation (σg) of about 2 would adequately describe the average aerosol carbon fraction.

The 1992 Grand Canyon (MOHAVE) study produced a large volume of data. The data reviewed was not reduced and conclusions were more difficult to draw. Sulfate aerosol was clearly of submicron size and mostly within the 0.1 to 1 μm size range. Nitrate aerosol was normally below the detection limit and no conclusion was drawn. Ammonium was also mainly associated with 0.1 to 1 μm size particles. Element analysis by PIXE provided good measurements for only a few elements. Sulfur was again shown to be within the 0.1 to 1 μm size range. Iron appeared over the entire particle size range. Silicon and calcium were not normally present in measurable concentrations. In general, most of the fine particle mode aerosol was associated with particles less than 1.0 μm diameter.

Zhang et al. (1994) evaluated the contributions of major fine particle species to light scattering in the Grand Canyon area. Impactor classified samples show sulfate to be mostly (~ 95%) in the submicron (fine mode) size range.

Han (1992), Divita (1993) and Dodd, Ondov, Tuncel, Dzubay and Stevens (1991) have conducted several studies of the elemental distribution of ambient fine particulate matter. A 1983 study at Deep Creek Lake, in rural western Maryland, used neutron activation and X-ray fluorescence to analyze samples obtained using a microorifice impactor. Samples for analysis were collected on uncoated Ghia Teflon filters (as impactor substrates). Data was obtained on 44 elements showing peaks at various submicron particle sizes. Although some of the presented data show the elements almost entirely in the submicron range, other data shows a significant fraction of the mass in the 1 to 2.5 μm size range. Certain elements such as Al, Ca and Mn appear to be the tail end of the coarse mode aerosol extending down into the submicron size range. Other elements such as Pb and V were generally all in the submicron range.

A 1990 study in a nonindustrial area of Washington, D.C., looked at the size spectra for vanadium containing particles. Neutron activation analysis was used to analyze samples collected with a microorifice impactor fitted with Teflon impaction substrates. Vanadium containing particles were almost all of submicron size with an average MMD of 0.2 to 0.4μm.

The most receint study of Ondov et. al. was intended to characterize temporal and spatial variations in the elemental size spectra. Two areas, Washington, DC and Philadelphia, were chosen for sample collection using 8-stage, nonrotating micro-orifice impactors. Impactor stage cut-off diameters ranged from 0.055 to 15 μm. Teflon impaction substrates were used with only the first three stages (15, 3.2 and 1.8 μm cut-off) using a grease coating to reduce particle bounce. Up to 44 elements were measured using neutron activation analysis. Data was not presented for size fractions above 1.8 μm and it is assumed that these first three impactor stages were not analyzed.

Although the studies discussed above are unique and of great general interest for a multitude of reasons, they do not clearly suggest a cut point between the fine and coarse mode aerosol. Some of the data for Al, Ca, Ti, Mg and Ba suggest a minimum as low as 0.1 μm diameter. Because impactor samples of 1.8 μm and larger were not analyzed, it is not possible to compare a 1 vs 2 vs 4 μm division between fine and coarse mode aerosol.

BETWEEN MODE AEROSOL

Higher than "expected" concentrations of 1 to 4 μm diameter particles appear to exist in most size distribution data. For convenience this will be referred to as the 2 μm size range. Condensation aerosols do not normally grow above 2 μm and significant concentrations of dispersion aerosols are not normally found in the atmosphere below 2 μm. Neither gravity, coagulation nor rainfall cause a rapid loss of the 2 μm aerosol and most of the concentration change is the result of simple atmospheric dilution. The work of Holden and Noll (1992) and Noll et. al. (1992) on dry deposition suggest a deposition velocity of about 1 x 10^{-2} cm/sec for 2 μm particles. This does account for some removal over a one day time period, but much of the 2 μm aerosol would remain. Although dilution accounts for the immediate concentration reduction, it does not account for the ultimate removal. Available surface area associated with the 2 μm aerosol, rationed to that associated with the fine aerosol mode, would cause and explain transfer of a percent or so of the fine mode aerosol onto the between mode aerosol.

A low but non zero concentration of aged aerosol should be expected within the 1 to 4 μm size range (the 2 μm aerosol discussed above). Available data suggests that about 2 to 20% of the total aerosol mass and certain elements may be contained with this size range. Some data can be found to support either end of the general concentration range values suggested. Very little data was found to support conclusions outside this range except for certain elements which were almost all (99%) in the submicron size range.

IMPACTOR USE AND AEROSOL MEASUREMENT QUALITY

Mass and chemical element size distribution data has most commonly involved use of a cascade impactor to obtain size fractionated samples. Many different impactors have been used starting with the May, and including the Andersen, Lundgren, Berner, Batelle, Hering, Marple, Pilat (U. of Washington), etc. The current impactor of choice appears to be the MOUDI (Micro-Orifice Uniform Deposit Impactor). Which impactor was used in a study may be of secondary importance. All impactors operate on the same fundamental principal and all have some common fundamental operating problems such as wall loss and the bounce-off of particles from the intended collection surface. Bounce-off is often used to refer to the general problem of particles not sticking to a surface, breaking into fragments or dislodging other previously collected particles (often called reentrainment).

The bounce-off problem, in practice, can nearly be eliminated through use of a "soft" collection surface capable of absorbing the kinetic energy of the impacted particle. A fresh, grease-coated surface may prevent bounce-off but may make mass determination difficult and chemical analysis inaccurate. Greased surfaces do become overloaded with particles, resulting in both bounce-off and reentrainment. Detailed studies of these problems have been conducted and discussed in various articles, such as that by Wesolowski, Alcocer and Appel (1980). Most chemical analysis vs particle size studies were conducted using non soft surfaces to prevent contamination. Carry over of particles to smaller cut-size stages of an impactor will result in a bias of mass or composition vs particle size data. Although this problem is often mentioned, it is not normally evaluated. Data is available showing that much of the collected mass in the 1 to 5 μm size range can be associated with the above bounce and reetrainment problem. Simply "greasing" a surface does not necessary solve or eliminate the problem.

Factors affecting aerosol measurement quality are discussed in detail by Baron and Heitbrink (1993) in Aerosol Measurement, Edited by Willeke and Baron. In that same text, methods of size distribution data analysis and presentation is discussed by Cooper (1993) and atmospheric sample analysis and sampling artifacts is discussed by Appel (1993). Each of the above articles contains an extensive reference list clearly indicating the wealth of knowledge which exists concerning aerosol sampling, measurement and data presentation problems. Simple solutions do not exist and all data must be viewed and used with caution.

CONCLUSIONS

Large particle mass distribution data was reviewed. Dispersion aerosol distribution data from industry, industrial materials (rock, sand, grandular products, etc) and from laboratory aerosol generation was also reviewed. Although significant numbers of submicron particles are formed by the dispersion process, the resulting aerosol mass concentration associated with particles less than about 1 μm aerodynamic diameter is normally about 0.1% of the measurable aerosol mass in the 1 to 100 μm size range. Assuming a "dusty roadway" concentration of 1000 μm/m^3, this 0.1% corresponds to only 1 μg/m^3 of submicron aerosol. If, for comparison, a lower size limit of 2.5 μm were selected, the less than aerosol size mass fraction may be as much as 10 μg/m^3. Under more normal coarse mode aerosol concentrations of 100 μg/m^3, the less than 1 μm and less than 2.5 μm aerosol would probably correspond to 0.1 and 1 μg/m^3 concentration values.

The above calculated values were obtained using a very simple model distribution fit to measured dispersion aerosol size distribution data. In all cases in this paper, the equivalent aerodynamic diameter (the diameter of a spherical particle of density one g/cm^3) is used and inferred to be the most relevant measure of particle size.

Three distributions are proposed to represent the coarse mode dispersion aerosol. These aerosols are all presented as having a logarithmic normal (lognormal) distribution. Therefore; the mass concentration, mass median diameter (MMD) and geometric standard deviation (σg) completely describes the proposed distributions shown in Figure 6 and 7. Mass concentration of coarse mode (supermicron) aerosol can range from about 1 to 1000 μg/m^3, but more normal concentrations are 10 to 100 μg/m^3. Aerosol MMD can vary from about 10 to 40 μm with a typical value of about 20 μm. The distribution width is often best represented by a σg of 2, but this can range upward to a value of about 3.

A typical (average) coarse mode aerosol could have a 30 $\mu g/m^3$ concentration, 20 μm MMD and a σg of 2. If this aerosol were evenly distributed over the lower 300 m (1000 ft) of the atmosphere and an average U.S. wind of 5m/sec (10 mph) considered, the transport and loss of particles due only to gravity, using a turbulent mixing model, can be calculated. For the above assumptions, Table 3 listes the average particle residence time ($t_{50\%}$) and maximum transport distance for less than 5% of the aerosol ($L_{5\%}$)

Table 3 calculation values can be used to help explain some differences in the measured aerosol distribution and the simple dispersion aerosol model proposed above. These data also illustrate why a greater than 100 μm diameter aerosol must normally be measured within minutes and kilometers of the generation process, in contrast to a 1 to 10 μm aerosol which can travel for days and thousands of kilometers. Measurement of the 1 to 10 μm aerosol involves measuring particles of all ages which, in general, would have originated from many different dispersion aerosol sources.

A calculation of coarse aerosol surface area distribution shows that most of the dispersion aerosol surface area is within the 2 to 20 μm size range. An integration of surface area and atmospheric residence time vs particle diameter can explain why submicron mode aerosol is often associated with the coarse aerosol tail. Residence time, surface area and diffusive deposition of submicron aerosol help explain the higher concentrations and composition differences within the 1 to 5 μm size range than would be expected from measurement of freshly generated coarse mode aerosol.

Table 3. Residence Time and Transport Distance vs Particle Size.

Particle Diameter μm	**Settling Velocity m/min**	**Residence Time ($t_{50\%}$)**	**Transport Distance ($L_{5\%}$)**
1000	200	1 min	1 km
100	20	10 min	10 km
10	0.2	1 day	1000 km
1	0.002	3 months	100,000 km

General conclusions regarding the generation, measurement and presence of the coarse mode or dispersion aerosol are as follows:

1) For a typical, freshly-generated coarse mode aerosol: a) by mass - about 1% of the aerosol mass is less than 2.5 μm and about 0.1% is less than 1.0 μm; b) by number - about 10 to 50% of the aerosol particles are less than 1.0 μm and 50 to 80% less than 2.5 μm; c) by surface area - most of the particle surface area is within the 2 to 20 μm size range.
2) Atmospheric residence time of near micron size (1 to 3 μm) particles is significant (weeks), causing higher measured concentrations than otherwise expected.
3) Surface area distribution of coarse mode aerosol allows measurable concentrations of submicron mode aerosol to accumulate with the 1 to 10 μm size range.
4) For an aged coarse mode aerosol, the surface area composition and the bulk aerosol composition are expected to be different.
5) Fractionation of ambient aerosol at a 1.0 μm cut point will clearly separate out almost all of the coarse aerosol mass (~99%) from the fine aerosol mass; however, some of the fine aerosol mass will be associated with the greater than 1.0 μm size aerosol in some places at some times.
6) Fractionation of ambient aerosol at a 2.5 μm cut point will, on average, separate the coarse aerosol mass from the fine aerosol mass with, on average, less than 10% of the coarse particles being collected in the fine particle sample.

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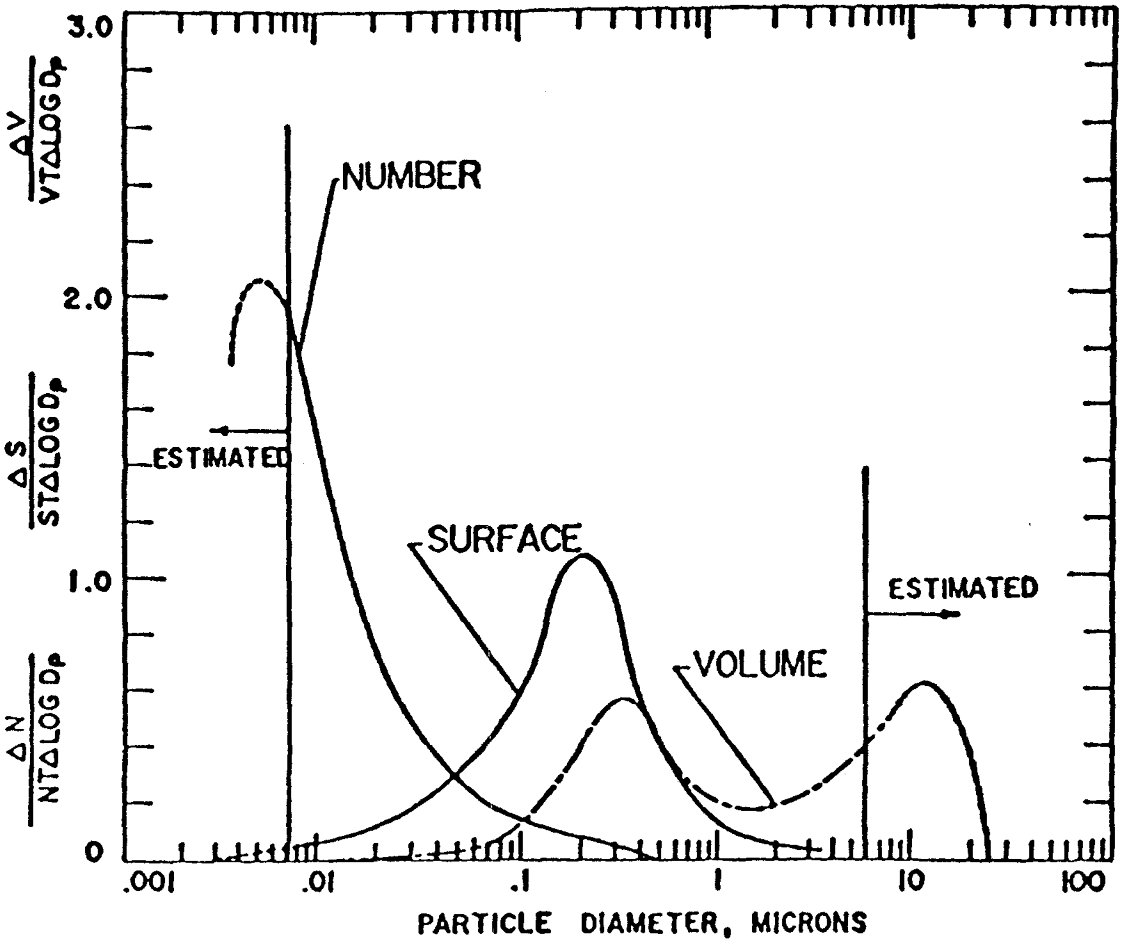

Figure 1. Grand average number, surface area, and volume distribution of Los Angeles smog: From Whitby, Husar and Liu (1972).

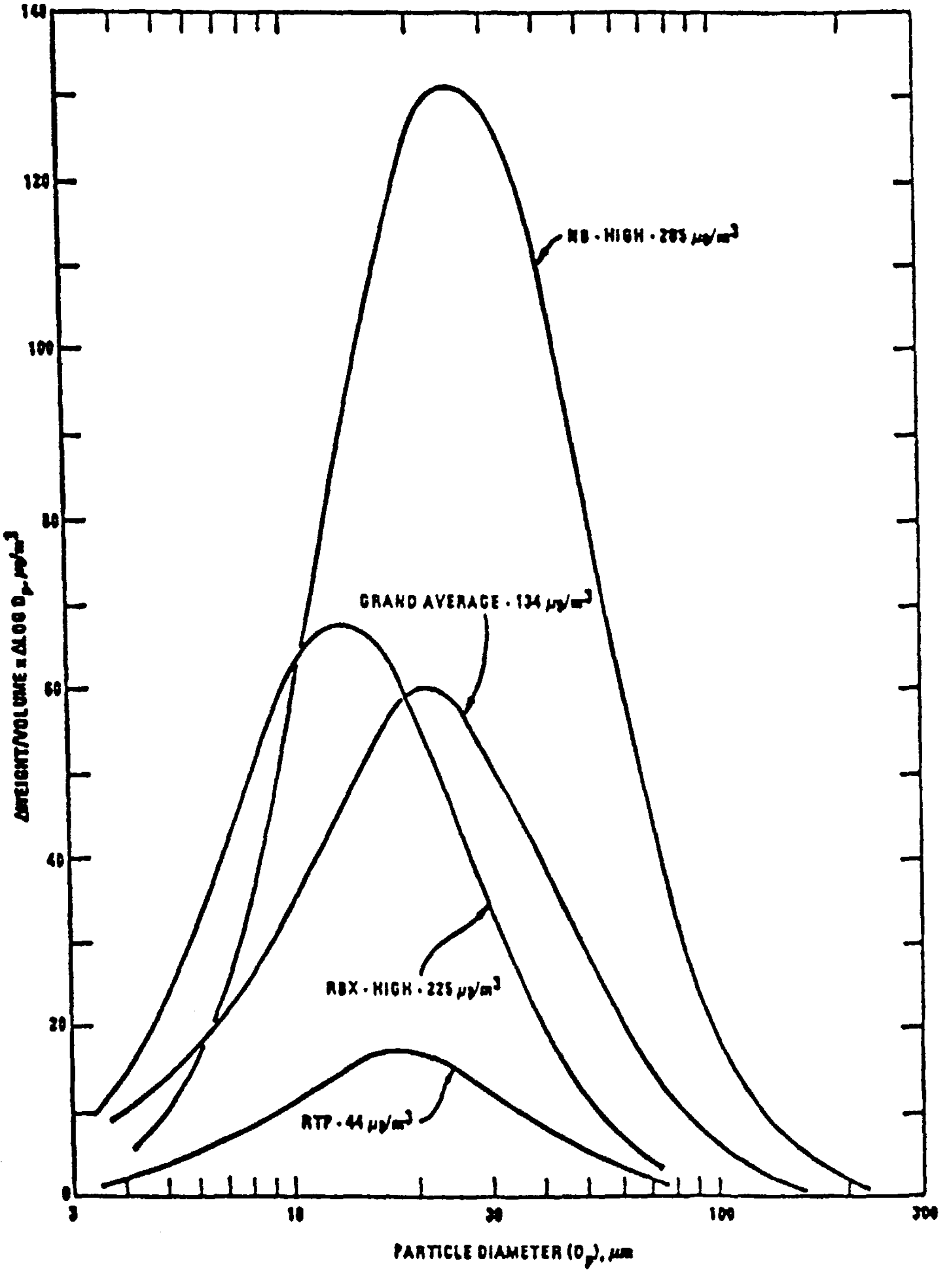

Figure 2. Coarse particle mode distributions: From Lundgren, Hausknecht and Burton (1984).

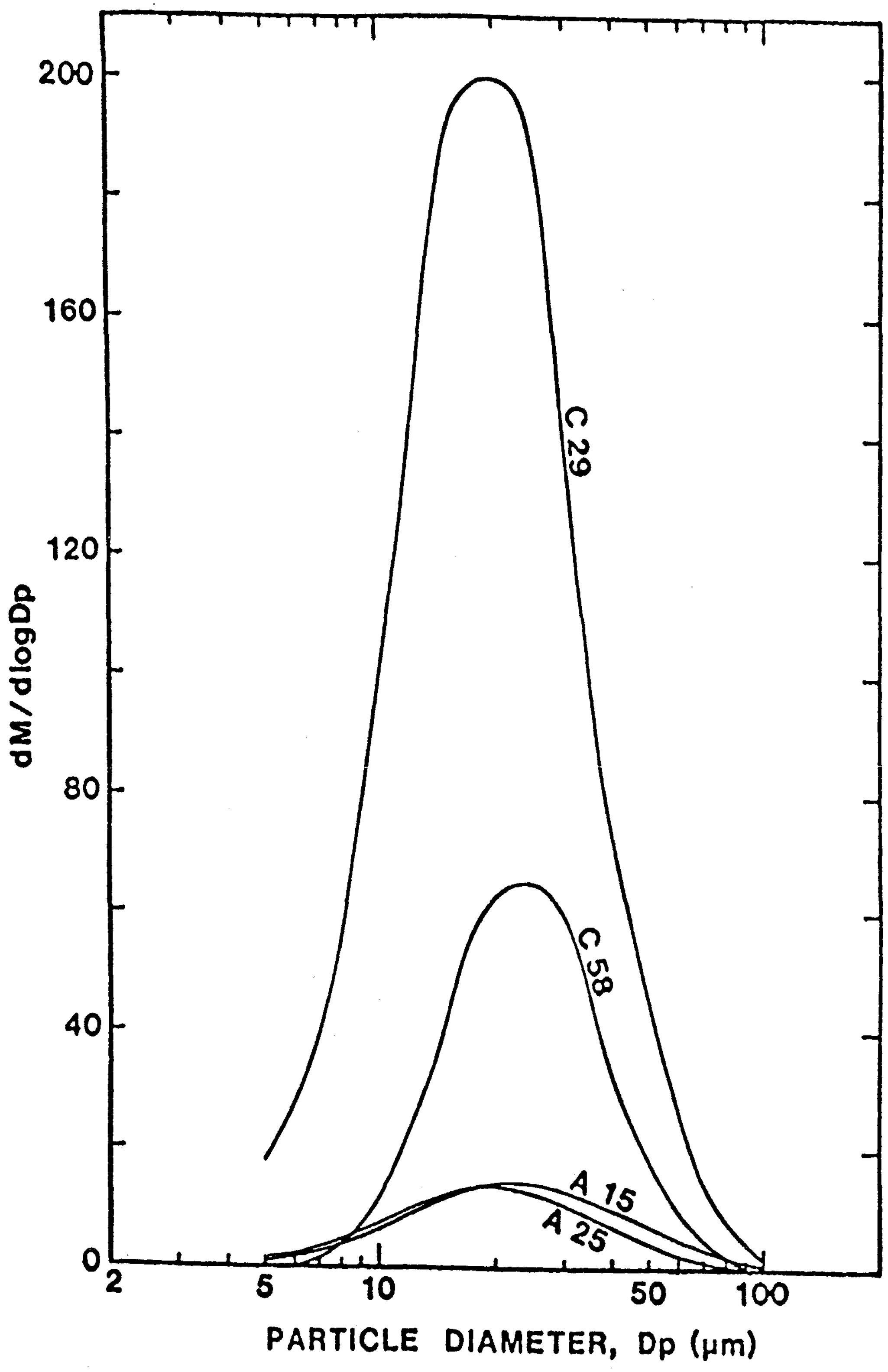

Figure 3. Coarse particle mode distribution: From Noll, Draftz and Fang (1986).

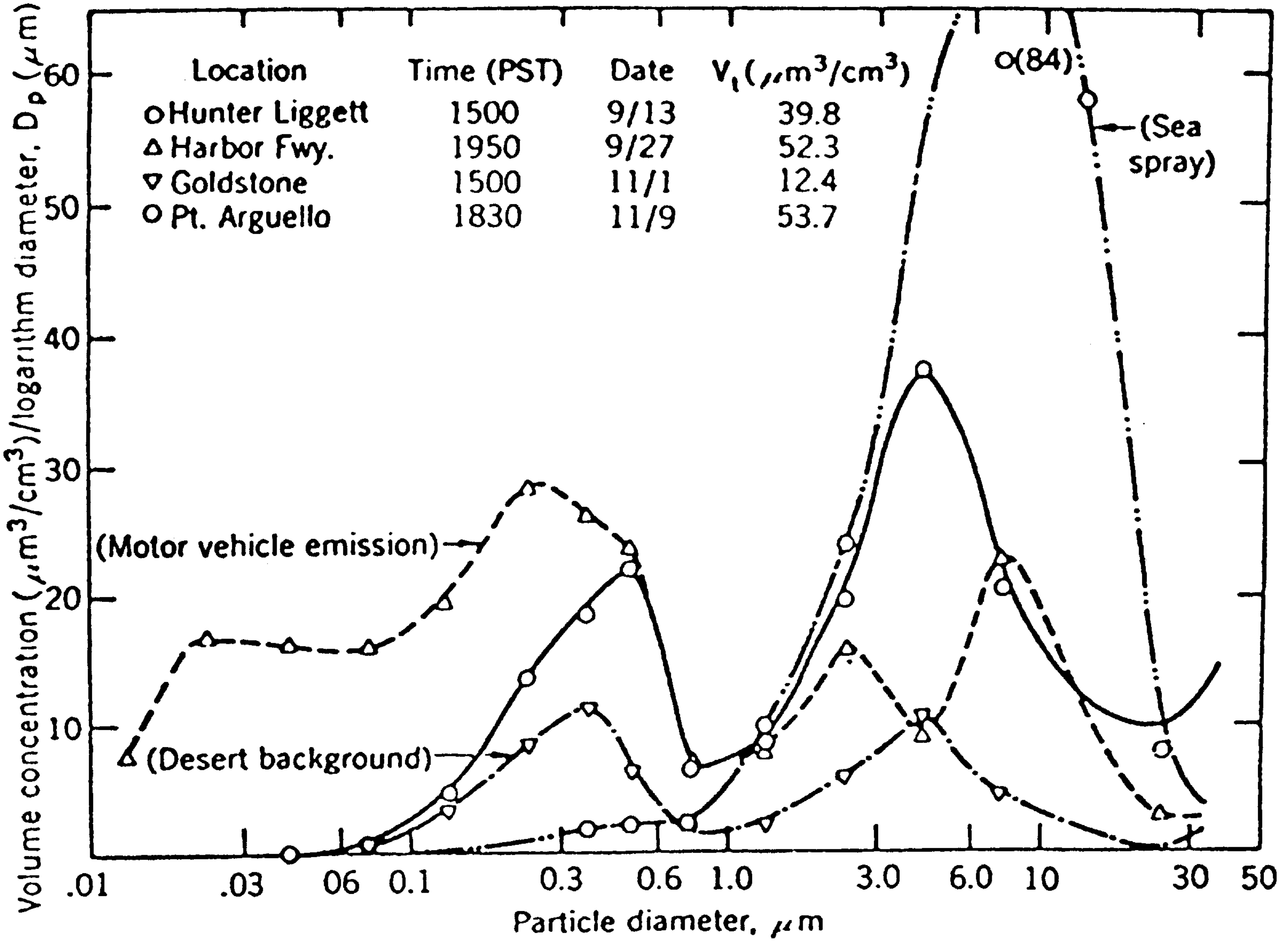

Figure 4. Comparison of volume distributions for background and motor vehicle source enchriched sites: From Hidy (1975).

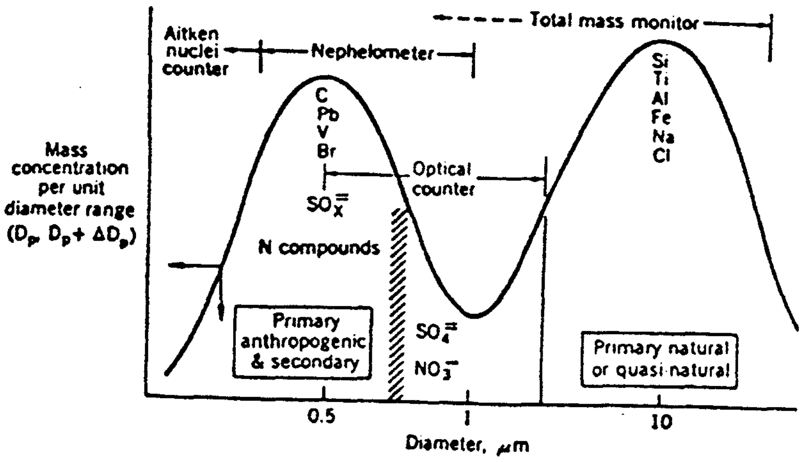

Figure 5. Idealized mass/size distribution for urban aerosols: From Hidy (1975).

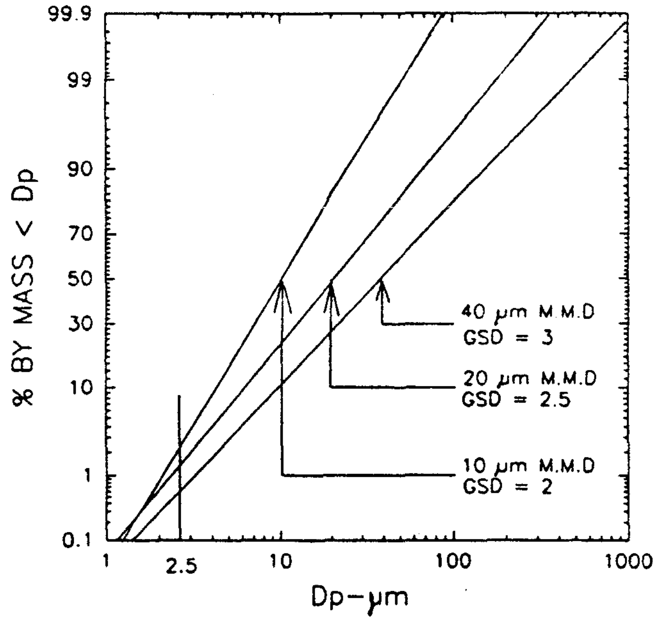

Figure 6. Proposed range of coarse mode dispersion aerosol.

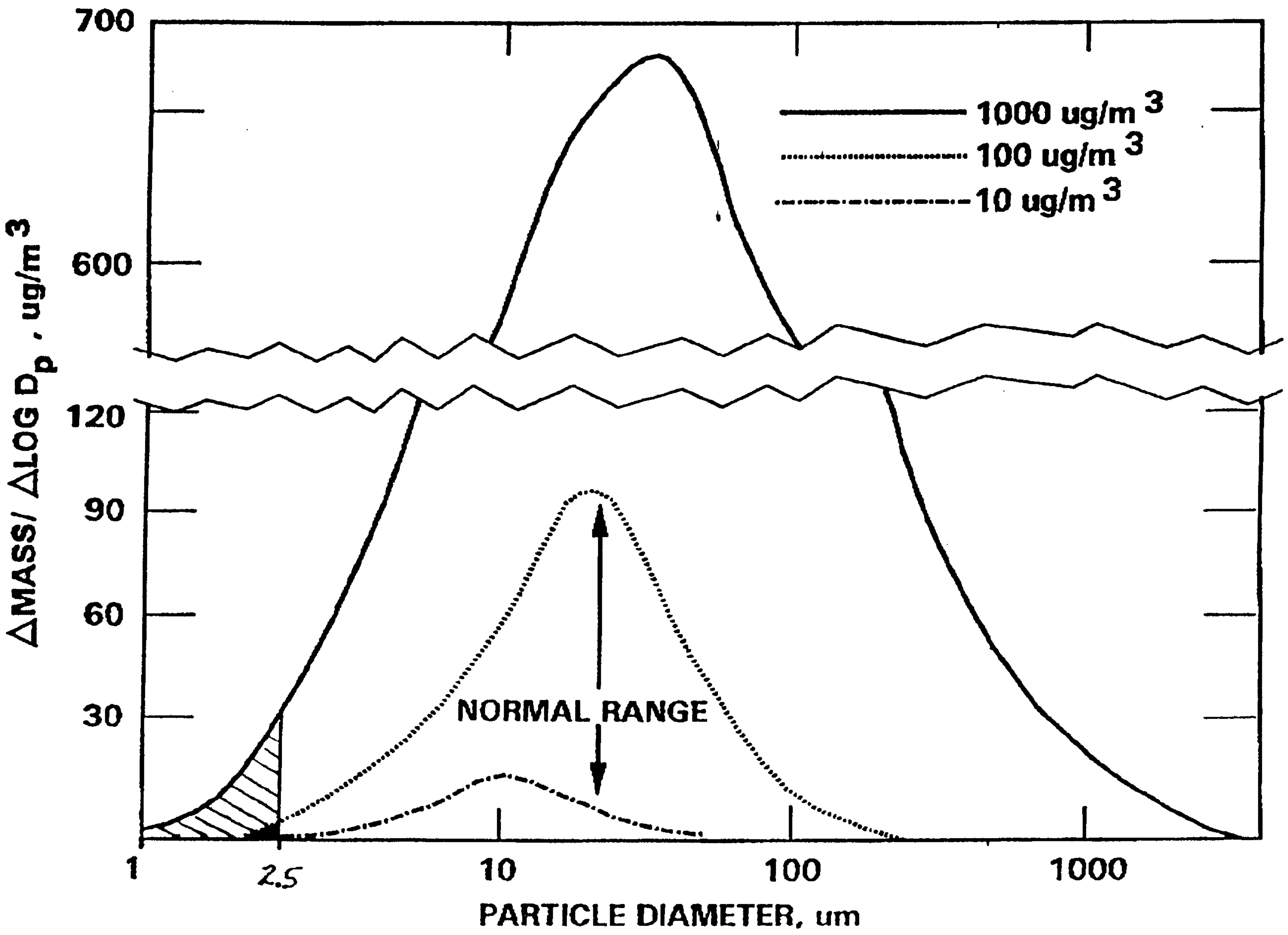

Figure 7. Mass distribution of proposed range for dispersion aerosol.

Temporal Variations of Particulate Air Pollution: A Marker for Free Radical Dosage and Adverse Health Effects?

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ABSTRACT

Statistical associations have been observed between human mortality and fine and sulfate particles. However, significant gaps in our knowledge exist in explaining the observed health effects based on results from controlled exposure studies. It is possible that the causative agent is a species that is correlated with particulate matter, but not measured by routine sampling of atmospheric aerosols. Free radicals, such as hydroxyl radicals, are responsible for the formation of fine and sulfate particles. They are also known to be damaging to lung tissue, as well as playing a role in the pathogenesis of a wide variety of disease states, including inflammation and cancer. These observations suggest that radicals may be at least partly responsible for adverse health effects, and that fine particle mass could serve as a marker for free radical dosage. Applying receptor models to time-series aerosol data to determine the temporal variations of source contributions may provide additional insight regarding mixtures of species that cause a disproportionate fraction of the health effects.

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Introduction

Recent epidemiological studies report increases in human mortality associated with levels of particulate pollution significantly lower than those previously thought to affect human health (Schwartz, 1994; Schwartz, 1991/92). These studies suggest an association between nonaccidental mortality and particulate matter (PM) levels, and have prompted the United States Environmental Protection Agency (USEPA) to review the ambient particulate air quality standard. Since a mechanistic explanation for this link has not yet been established, the USEPA may be forced to revise downward the particulate standard without knowing the causative agent (Friedlander and Lippmann, 1994).

The majority of these studies compare routine measurements of particulate pollution levels (TSP, PM_{10}, $PM_{2.5}$) or surrogates of PM (e.g. coefficient of haze) with daily human mortality. Similar studies have also been carried out comparing PM levels with indicators of morbidity, such as hospital admissions, emergency room visits, and school absences. The mortality data are generally taken from the National Center for Health Statistics mortality tapes or State/County Department of Health records. These studies control to varying degrees for potential confounders, such as age, sex, race, smoking status, weather, epidemics, and other risk factors. The question of coherence among studies is an important issue to consider when determining the validity represented by the growing body of literature on this topic (Bates, 1992).

The use of routine PM measurements for epidemiological studies has proven to be a hindrance in some states, such as California, where PM data are only collected every sixth day. Furthermore, most sampling sites use high-volume aerosol samplers, which are prone to losses of nitrates and organics due to volatilization.

The current particulate standard is based on total PM_{10} mass concentration. If biological plausibility can be established linking a particular chemical component with the observed health effects, the new standard may be based on that component. There have been continuing efforts to identify the role of biologically active chemical species (such as sulfuric acid) that may cause a disproportionate fraction of the health effects. However, significant gaps in our knowledge exist in explaining the observed health effects based on results from controlled exposure studies.

When evaluating the health effects of aerosol chemical components, it is important to realize that the chemical analysis of routinely collected particulate samples is not necessarily an accurate representation of the total composition of the atmosphere. Aerosol samples are usually collected on filters and stored for periods ranging from hours to weeks before being analyzed. Many short-lived chemical species in the gas and/or aerosol phase, such as free radicals, are not present in sampled material at the time of chemical analysis. The collected aerosol is composed of the end products of the atmospheric chemical and physical processes that generated the short-lived components. The unmeasured metastable species may be much more biochemically active than the "dead" components collected on filters, and therefore could be primarily responsible for the adverse health effects. Since inhalation toxicology studies using both human and animal subjects often do not include the potential for metastable species and reactive intermediates to be present, they could greatly underestimate the effects seen in field or epidemiological studies.

Fine Particle Mass and Free Radical Concentrations

One of the most complete studies of the health effects of particulate pollution is the Harvard Six-Cities Study (Dockery et al., 1993). This was an extensive cohort study, involving 8,111 adults over a 14-16 year follow-up period (between 1974 and 1989). The strongest associations were found between human mortality and fine particle mass ($d_P < 2.5$ μm). Significant associations with mortality were also found for sulfates ($SO_4^=$) and, to a lesser extent, total inhalable particulate mass (PM_{15} from 1974-83, PM_{10} from 1984-89).

PM_{10} consists of both coarse ($d_P > 2.5$ μm) and fine particles. Coarse particles are produced by mechanical processes, such as grinding, reentrainment, or erosion, and are usually dominated by crustal/geological sources. Fine particles are emitted from combustion sources and generated by secondary gas-to-particle processes, such as condensation of low volatility vapors and coagulation of smaller particles (Friedlander, 1977).

Solomon et al. (1988; 1989) operated a PM_{10} monitoring network in the California's South Coast Air Basin (SoCAB) during 1986. Twenty-four hour samples of PM_{10} and $PM_{2.2}$ were collected every sixth day in Long Beach (LGB), Hawthorne (HAW), Burbank (BUR), Downtown Los Angeles (DLA), Rubidoux (RUB), Upland (UPL), and Anaheim (ANH).

Samples of ambient PM_{10} were collected on quartz filters using a low volume (1 m^3 hr^{-1}) sampler equipped with a PM_{10} inlet. Simultaneous fine particle samples ($PM_{2.2}$) were collected on quartz filters, preceded by a cyclone separator to remove particles larger than 2.2 μm in diameter. A denuder-difference method was used to collect nitrate samples. Sulfate and nitrate concentrations were measured by ion chromatography.

Fine particles accounted for 52-61% of total PM_{10} mass. The 1986 time-series data also showed that coarse particles vary less with time than fine particles. Values of $\sigma / \bar{x}$ (standard deviation/mean ratio) for coarse particles in the SoCAB ranged from 0.40 to 0.55, while values for fine particles ranged from 0.63 to 1.37 (Kao and Friedlander, 1994a). This suggests that the variability of PM_{10} levels is dominated by the fine particle fraction. This is confirmed by the correlation between $PM_{2.2}$ and PM_{10} mass, shown in Figure 1. Therefore, any associations of human mortality or morbidity with fine particles would also be expected (albeit to a lesser extent) with PM_{10}, as observed by Dockery et al. (1993).

Sulfate particles are generally in the submicron size range, with mass median diameters ranging from 0.1-1.0 μm (Hering and Friedlander, 1982; Milford and Davidson, 1987). Sulfates and other fine particles are able to penetrate indoors, where the majority of total particulate exposure occurs, resulting in strong indoor-outdoor concentration correlations (Dockery and Spengler, 1981).

Sulfate particles can be formed in the atmosphere through gas- and/or aerosol-phase pathways. The dominant sulfate formation pathway is heterogeneous oxidation of SO_2 in the aerosol phase (Hering and Friedlander, 1982; Seinfeld, 1986). In the presence of water vapor, SO_2 is rapidly dissolved:

$$SO_2 + H_2O \rightarrow H_2O \cdot SO_2 \tag{1}$$

Sulfate is subsequently formed within the aqueous droplets by oxidation with hydrogen peroxide:

$$H_2O \cdot SO_2 + H_2O_2 \rightarrow H_2SO_4 + H_2O \tag{2}$$

Homogeneous gas phase oxidation of SO_2 is initiated by reactive free radicals (Stockwell and Calvert, 1983), such as hydroxyl (OH):

$$SO_2 + OH \xrightarrow{M} HSO_3 \xrightarrow{O_2} HO_2 + SO_3 \tag{3}$$

or hydroperoxyl (HO_2) radicals:

$$SO_2 + HO_2 \rightarrow SO_3 + OH \tag{4}$$

followed by the combination of SO_3 with water vapor to produce H_2SO_4:

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{5}$$

Nitrate particles are also typically in the submicron size fraction, ranging from 0.1-1.0 μm in diameter (John et al., 1990). Nitric acid is formed by the gas phase oxidation of NO_2 by hydroxyl radicals:

$$NO_2 + OH \rightarrow HNO_3 \tag{6}$$

In the presence of ammonia, nitric acid is converted to particulate ammonium nitrate:

$$NH_3 + HNO_3 \rightleftarrows NH_4NO_3 \tag{7}$$

The oxidizing agents that drive all of these reactions (OH, HO_2, H_2O_2) are continuously being formed in the atmosphere, especially in the presence of CO, hydrocarbons, and nitrogen oxides. Hydroxyl radical concentrations are approximately an order of magnitude higher in polluted urban regions than in rural or remote areas (Finlayson-Pitts and Pitts, 1986).

Figure 2 shows that the fine particle mass in the SoCAB was significantly associated with sulfates and nitrates. Because the formation of these reactive components involves radicals, the temporal variations of sulfates and nitrates are probably strongly linked with radical concentration. The fluctuating nature of the atmosphere affects the chemical kinetics of the radical forming reactions, which results in highly variable concentrations for the reactive components. Kao and Friedlander (1994b) showed that the additional variability resulting from these reactions was observable by increased geometric standard deviations (GSD) for these reactive aerosol components compared with those of the nonreactive chemical components.

Radicals are known to be damaging to lung tissue, as well as playing a role in the pathogenesis of a wide variety of disease states, including inflammation and cancer (Grisham, 1992; Kensler and Trush, 1984). Free radicals may be present on the surface or inside particles, or in the gas phase before being converted to particulate matter, and could be harmful if inhaled, particularly at high concentrations. Because of the chemical reactivity of SO_2 and NO_x in the presence of oxidizing agents, large quantities of particulate sulfates and nitrates are probably accompanied by high concentrations of free radicals, which may be at least partly responsible for the adverse health effects of particulate air pollution. This secondary particulate matter is the end-product of primarily irreversible reactions, therefore fine particle mass reflects the past integrated history of radical levels. This suggests that fine particle mass concentration could serve as a possible marker for free radical dosage.

When ambient air is inhaled, the removal of this air from the sunlight terminates most of the radical forming reactions, and these transient species will decay. Typical half-lives of hydroxyl radicals in the gas phase are on the order of milliseconds, while HO_2 radicals have halflives of around 5 seconds (Calvert, 1973). This suggests that the reactive intermediates most likely to cause adverse health effects are gaseous HO_2 or dissolved species, such as H_2O_2. Those species associated with the aerosol phase are most likely to penetrate deeply into the lung before decaying.

Temporal Variations of Source Contributions

While most previous efforts have focused on correlating mortality data with total mass or selected components of the aerosol, toxicological and epidemiological studies of mixtures of chemical species have received limited attention. Using mixtures of chemical components would allow the investigation of more realistic exposure scenarios. For example, Kleinman et al. (1985) have examined the health effects associated with various mixtures of ozone, sulfate particles, and nitrogen dioxide. An approach that may offer additional insights on the biological mechanism is to compare the *source contributions* to PM with health effects data. If a particular source category can be identified as being significantly associated with adverse health effects, a combination of chemical species characteristic of this source type should be used for further toxicology studies.

This approach is possible through the application of receptor models to time-series aerosol data. Receptor models are data analysis techniques that use ambient measurements of chemical species to apportion the contributions of various sources. These models assume the emissions from different sources have characteristic chemical profiles. The differences in chemical composition among source emissions allow the contributions from each source type to be inferred.

Given sufficient time-series data for the chemical components of atmospheric aerosols, the source contributions for each sampling day can be determined using a Chemical Mass Balance (CMB) receptor model (Friedlander, 1973). From these calculations, the temporal and spatial variations in the source contributions can be examined. Kao and Friedlander (1994a) recently performed such an analysis for California's SoCAB. It would be of interest to compare these results with health effects data for similar time periods to determine whether correlations exist between human health effects and specific sources of PM_{10}.

Conclusions

The Six-Cities Study found strong associations between fine particle mass and human mortality. Associations were also found to a lesser extent between mortality and PM_{10}. These results add to a growing number of studies reporting similar adverse effects of particulate matter on health.

In efforts to determine a plausible explanation for these observed associations, some researchers are examining correlations between health data and specific chemical components of the aerosol. It is important to realize that routinely collected particulate samples are often stored for a period of time before being analyzed, and that the conditions for the chemical analysis (e.g. relative humidity) are not the same as atmospheric conditions. Therefore, the chemical analysis of these samples is not necessarily an accurate representation of the composition of the atmosphere. Many short-lived chemical species in the gas and/or aerosol phase, such as free radicals, are not present in sampled material at the time of chemical analysis. Those species in the aerosol phase are the most likely to penetrate deeply into the lungs. These unmeasured metastable species may be much more biochemically active than the measured components, and therefore could be responsible for adverse health effects. Fine particle mass concentrations could serve as a possible marker for free radical dosage.

A large portion of atmospheric particulate matter is in the fine particle fraction. Coarse particles are generated by mechanical processes, and are less variable with time than fine particles, which are mostly produced by secondary processes in the atmosphere. The temporal variations of PM_{10} are dominated by the fine fraction, therefore health effects associated with fine particles would also be correlated with PM_{10}. If fine particles are found to be responsible for adverse health effects, or to be a surrogate for the responsible agents, then any meaningful control strategy for PM_{10} must emphasize the fine fraction over the coarse fraction. It would be misleading to propose protection of human health from PM_{10} by controlling the sources of coarse particles if the causative agents are associated with the fine particles.

By applying the CMB receptor model to time-series ambient aerosol data, it is possible to determine the temporal variations of the source contributions to PM_{10}. It would be of interest to compare these results with health effects data for similar time periods to determine whether correlations exist between human health effects and specific sources of PM_{10}. This might offer insight regarding possible mixtures of chemical species to be used for further toxicological and epidemiological studies.

Acknowledgments

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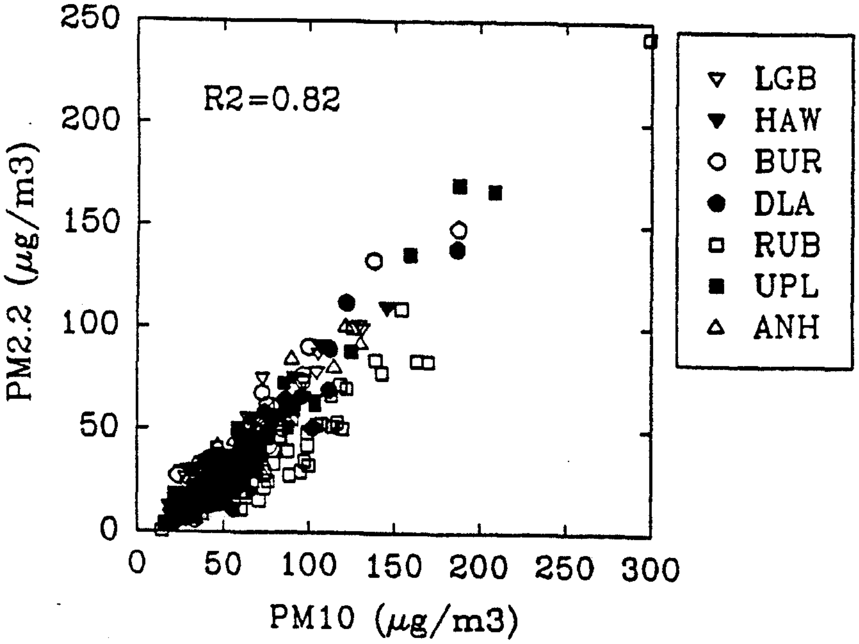

Figure 1. Comparison of PM$_{10}$ and PM$_{2.2}$ mass in South Coast Air Basin, 1986. Coarse particles vary less with time than fine particles. Therefore, fine particles dominate the time variability of PM$_{10}$, and PM$_{10}$ and PM$_{2.2}$ are well correlated (correlation coefficient $r^2=0.82$).

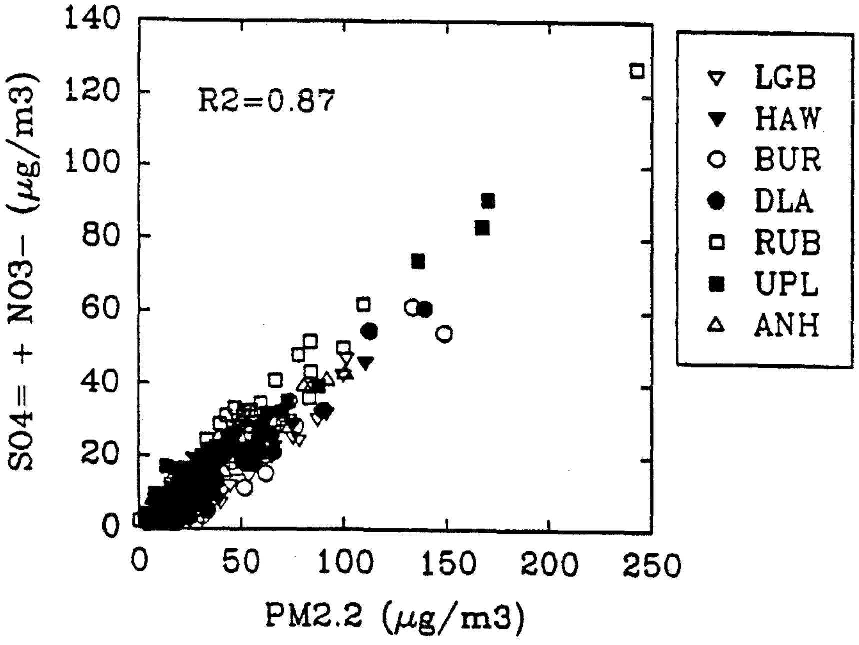

Figure 2. Comparison of PM$_{2.2}$ mass and $SO_4^{=}+NO_3^-$ concentrations in South Coast Air Basin, 1986. Sulfates and nitrates are both secondary in nature and comprise a significant fraction of the fine particle mass. Correlation coefficient $r^2=0.87$.

HUMAN MORTALITY, AIR POLLUTION, AND UNEMPLOYMENT IN SOUTHERN CALIFORNIA

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HUMAN MORTALITY, AIR POLLUTION, AND UNEMPLOYMENT IN SOUTHERN CALIFORNIA

by

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Abstract

Background. *Environmental regulations in the United States are based on the presumption that human mortality is adversely affected by air pollution. Many rules are cast in terms of risks of death per million population. Recent studies published in the* New England Journal of Medicine *and elsewhere have reported associations between air pollution and mortality rates. These studies have not yet persuaded the medical profession to accept a causal relation between smog and human mortality. A new study of 30 cities by Merva and Fowles asserts that mortality is more tightly correlated with unemployment than with air pollution.*

Methods. *In this study we estimated the effects of air pollution on mortality in Southern California, defined as Los Angeles, Orange, San Bernardino and Riverside Counties, while controlling for unemployment. Similarly, we estimated the effects of unemployment on mortality, while controlling for air pollution.*

Results. *Mortality rates in Southern California were most strongly associated with unemployment. After adjusting for unemployment, we observed statistically significant and robust associations between air pollution and mortality.*

Conclusions. *Although there are numerous other factors worthy of separate study, these results suggest that both unemployment and air pollution contribute to excess mortality in Southern California.*

INTRODUCTION AND BACKGROUND

Many air quality regulations are defined in terms of health impacts from impure air. Typical of this logic is Rule 1402 of the South Coast Air Quality Management District, which would prohibit toxic emissions that can be associated with 10 deaths in a population of one million, or a death rate of one per hundred thousand population. Facilities that emit substances that violate this standard would be required to take corrective actions or cease to operate.

A skeptic writing in the New England Journal of Medicine (Schenker, 1993) asks "Can we accept the association between excess mortality and current levels of air pollution in the United States as causal?"

But there appears to be a more virulent cause of mortality. Deaths from heart attacks (specifically acute ischaemic heart disease) or stroke (cerebrovascular disease) have much higher mortality rates.

Deaths from heart attack: 603 per million (1991)
Deaths from stroke: 442 per million (1991)

There is a substantial body of scientific literature that links stress to diseases of the circulatory system, which include heart attack and stroke. Moreover, unemployment or joblessness is widely recognized as a prominent cause of stress in American society. Several articles have been published about the direct correlation between unemployment and mortality. Based on 68 years of data, Brenner concluded that "economic downturns are associated with increased mortality from heart disease and that, conversely, heart disease mortality decreases during economic upturns" (Brenner, 1971).

Other studies explained that unemployment, or simply the threat of being unemployed, affects not only economic stability but the "deeper social roots of the individual." Moreover, the lack of control experienced by the worker in addition to the individual's inability to sell their labor "could be the largest single hazard to their health, outside of physical and environmental factors" (Colledge, 1982). The same study concluded that there was "a strong link between mortality rates and cycles of economic activity."

A longitudinal mortality study of over 450,000 individuals concluded that individuals who were employed between the ages of 25 and 64 had lower risks of death (standardized mortality ratios of 61-74% of the average), as stratified by sex and age (Sorlie/Rogot, 1990). Additionally, deaths due to cancer were closer to the standardized ratio of 100% for all employment classes, while causes of death, cardiovascular disease in particular, were much more susceptible to change in joblessness.

Although increased unemployment and greater mortality appear to be highly correlated, the reasons for this have not been fully analyzed, even though both microeconomic and macroeconomic approaches to the subject yield powerful explanations for this relationship. At the micro level, unemployment may lead to loss of financial resources, social status, or self-esteem. At the macro level, the level of unemployment reflects economic conditions that affect most or all of the population, not simply those that are unemployed. It is this macro approach that suggests intervention by new environmental policies. (Ostfeld/Eaker, 1985).

Still, while all the studies above confirm the relationship between unemployment and mortality, none has adequately explained the reason for the correlation. In 1971 Brenner said "it difficulty, at this point in the study, to ascertain whether the factors linking economic change and heart disease mortality are entirely related to psychophysiologic stress, whether economic factors in the utilization of health services have even a minor impact, or whether the relationship has some other basis"

As late as December, 1993, one medical authority opined, "It is (still) very debatable whether unemployment, per se, leads to higher mortality rates . . ., since unemployed healthy workers may migrate to other regions, while sick unemployed workers may be more likely to stay in the region where they lost their jobs."

Beiying such skepticism however, a recent nationwide study by Mary Merva and Richard. Fowles concluded that a one percentage point change in the unemployment rate increases or decreases deaths due to heart disease by 5.6% deaths due to stroke by 3.1%. The correlation is direct for both positive and negative changes in employment; no bias is evident at the 95% confidence level. The Merva/Fowles Thesis holds for Southern California; heart attacks and strokes are closely tied to unemployment, as shown below:

	1991	6/93
Unemployment Rate:	7.56%	9.70%
Death Rate from Heart Attack	603/million	908/million
Death Rate from Stroke	442/million	590/million

The significant disparity between the 1993 data and observations from 1991 is partially accounted for by the significant increase in the rate of unemployment during the past two years, which increased from 7.5% in 1991 to 9.7% in June, 1993. Additionally, the 1993 death rates do not reflect the fact that as pollution levels have declined in the past 15 years, as have death rates by acute ischaemia and cerebrovascular disease. Pollution levels are obviously a factor in historical mortality data, as we shall see in a moment.

According to the Merva/Fowles national model, a further increase in the unemployment rate in Southern California to 10.7% would increase deaths from heart attacks by 50 per one million people (740 in the region), and deaths from stroke by 18 per one million people (266 in the region).

This paper will test the Merva/Fowles national model against regional death and unemployment rates in Southern California, defined to include Los Angeles, Orange, San Bernardino, and Riverside Counties. Comparisons with mortality associated with air pollution will be made.

UNEMPLOYMENT AND ACUTE HEART ATTACKS

According to the literature of cardiology rates of death due to acute ischaemic heart disease, or acute heart attacks, have been found to be stress-related, more than any other heart illness. Here we are testing the hypothesis that increased stress due to higher unemployment is strongly correlated with increased mortality from acute ischaemic heart disease.

Linear regression of heart attack mortality and lagged variables for unemployment rates from 18 and 30 months yield the following equations: heart attack mortality = 0.11131 +0.00772889 *(U-18) + 0.00703972 *(U-30). The regression is fit with an R-squared statistic of 0.745936 indicating that more than 74% of variation in acute heart mortality can be explained by unemployment rates 18 and 30 months earlier. Coefficients attached to lagged unemployment variables indicate that unemployment 18 months ago is more significant in affecting current changes in heart disease mortality than is unemployment rates 30 months ago.

Cerebrovascular disease can also be classified as a stress-related illness or cause of death. Like acute ischemic heart disease, cerebrovascular disease is found to be directly related to unemployment rates. An increase in the incidence of fatal strokes corresponds to an increase in the unemployment rate.

Linear regression of stroke mortality and unemployment rates, again lagged 18 and 30 months preceding, yields the following equation: stroke mortality - 0.0965244 + 0.00544200 *(U-18) + 0.00199543 *(-30). An R-squared statistic of 0.521200 suggests that more than 52% of the variation in stroke mortality can be explained by changes in unemployment rate changes 18 and 30 months before. Again, coefficients to lagged unemployment rate variables indicate the 18-month lagged variable is the more significant explanatory variable.

SMOG AND DEATHS FROM HEART ATTACKS AND STROKES

Profound interest in possible links between human mortality and air pollution has led to significant meetings and colloquia on the subject. The California Air Resources Board, U.S. Environmental Protection Agency, and several professional associations have sponsored a colloquium at the University of California at Irvine on January 24 and 25, 1994.

Pollution levels, specifically levels of ozone, are also highly correlated with rates of mortality due to acute ischemic heart disease and cerebrovascular disease, according to new study by Dockery and others. (Dockery, 1993). The relationship between photochemical pollutants in the air and resulting sickness is further supported in a 1991 study by Kinney and Ozkaynak of daily mortality rates and air pollution in Los Angeles County. Their article presented results of a multiple regression analysis that evaluated the association between daily mortality counts and levels of five different pollutants. "Using a 10-year record of daily data from Los Angeles County, we have demonstrated associations between short-term variations in total mortality (excluding accidents and suicides) and pollution, controlling for temperature." (Kinney, 1991). Additionally, the study explained that ozone (0_3) was the single pollutant most highly correlated with rates of mortality in the county, and in particular, "ozone is a well-established acute pulmonary toxicant."

The present study concentrates on ozone, (O_3) and the pollution data used covers the number of stages one and stage two episodes of high levels of ozone in the entire South Coast Air Basin from 1977-1991. Pollution levels are highly correlated with variation in deaths due to acute ischemic heart disease and variation in deaths due to cerebrovascular accident. Linear regression of annual heart attack mortality and the number of days in the same year with first or second stage smog alerts is fit with an R-squared statistic of 0.802094, suggesting that 80% of the changes in annual heart attack mortality in Los Angeles County can be explained by increases or decreases in the number of days with poor air quality in the same year. Linear regression of stroke mortality and days in the same year with poor air quality yields a correlation fit by an R-squared statistic of 0.858856.

Deaths due to lung disease (as contrasted to heart attack or stroke) are not analyzed in this paper, but are reserved for a subsequent paper.

CONCLUSIONS

1) Deaths from Heart Attacks and Strokes in the South Coast Air Basin closely match those levels predicted in the national study by Merva and Fowles.

The Merva/Fowles study predicted a 5.6 percent increase in mortality by heart attack and a 3.1 percent increase in mortality by stroke per 1 percent increase in the rate of unemployment. This study concludes that, for an unemployment rate currently at 9.7 percent (13445 deaths from heart attacks), an increase by 1 percent in unemployment will increase deaths by 670, or 5.0 percent. Furthermore, 1% increase in unemployment will increase stroke deaths by 300, or 3.4 percent above the 8738 deaths from stroke at 9.7 percent unemployment. Most of the surge in deaths due to unemployment is likely to fall on the age groups between 40 and 65 years, according to a prominent cardiologist, since persons under forty seldom get heart attacks and those over 65 are probably less affected by unemployment due to retirement. These demographic variations have not been studied here, nor do we have (yet) an analysis by gender, race, or income level.

Our findings closely match those predicted by the Merva/Fowles study which covered 30 metropolitan areas, and support their study (with greater confidence) for the South Coast Air Basin.

The table below summarizes the above text.

CURRENT UNEMPLOYMENT RATE: 9.7% (1993)

Predicted Mortality in Southern California from:

	at 9.7%	1% change	(Average) % of total	(Average) (national) Merva/Fowles
Heart Attack	13445	670	4.98	5.6
Stroke	8738	300	3.43	3.1
TOTAL	22183	970	4.37	4.9

2) Heart attacks and strokes are strongly correlated with unemployment.

As has been documented and previously cited above, acute ischaemic heart disease and cerebrovascular disease are strongly associated with changes in the rate of unemployment. Our studies show, that a 1 percent increase in unemployment corresponds to a 5.0 percent increase in mortality due to acute heart attack and a 3.4 percent increase in mortality due to stroke.

These findings further support the research of previous studies which have documented a strong correlation between joblessness or economic downtums and increased mortality by stress-related illness.

3) Heart attacks and strokes are also strongly correlated with ozone concentrations as measured by first and second stage alerts.

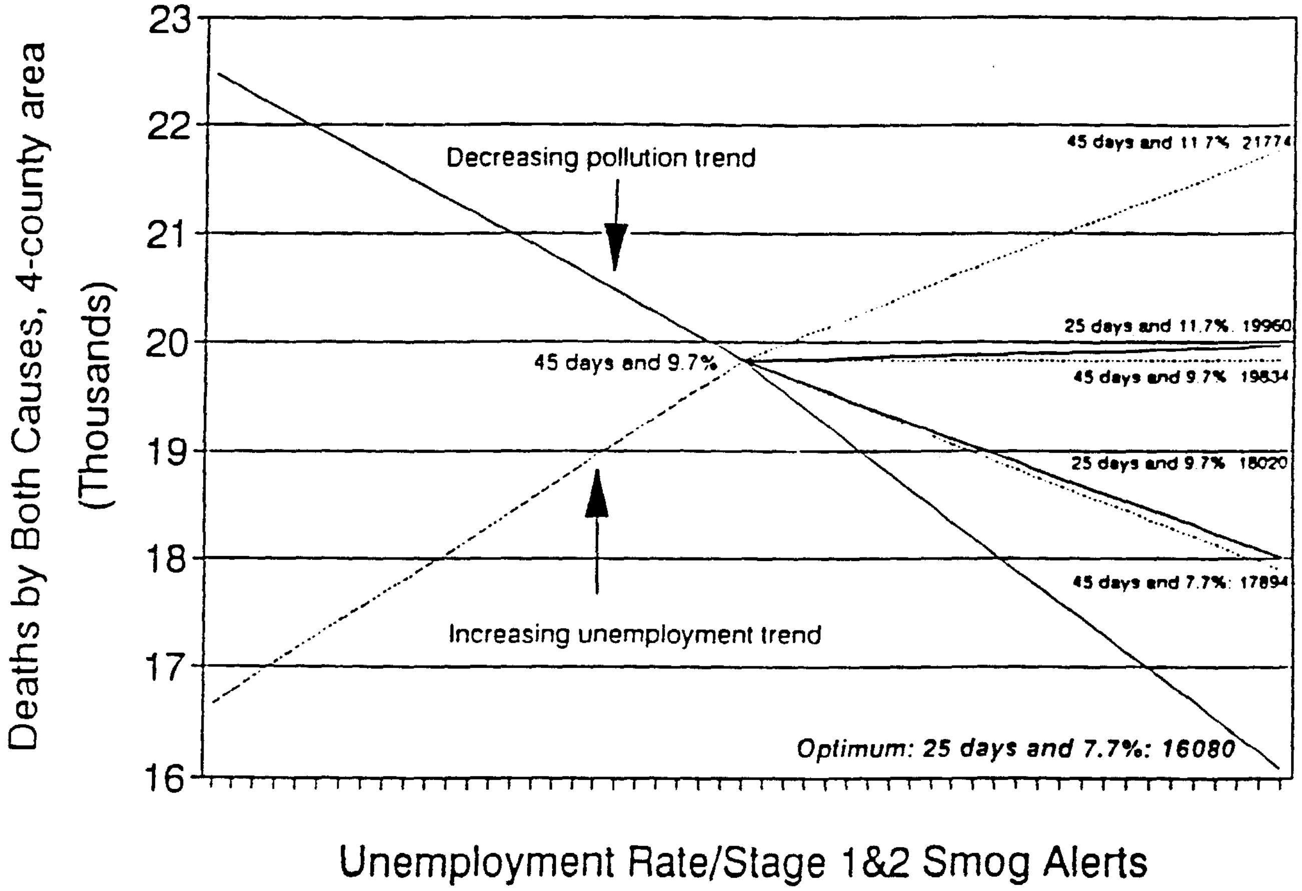
Levels of airborne pollution, particularly ozone, have also been shown in previous studies to be highly associated with mortality rates by cardiovascular diseases. This study specifically examines the correlation between the number of stage one or stage two episodes of ozone in the South Coast Air Basis and corresponding mortality rates of acute heart attacks and strokes on a yearly basis.

Our findings suggest that each additional day with a stage one or stage two episode will result in 50 additional deaths due to acute ischaemic heart disease and 40 additional deaths due to cerebrovascular disease in the four-county area, with a high level of confidence.

These numbers reinforce and support the findings of previous studies, which have concluded that mortality rates, specifically those related to cardiovascular diseases, are linked to pollution levels.

Further testing of these relationships seems warranted. Differential impacts on population sub groups, including ethnic groups, and gender groups are likely to provide more precise factual guidelines for the practice of medicine and refinement of environmental rules.

Projections: Unemployment/Smog/Deaths
Combined Stroke and Heart Attacks



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COMMENTS ON THE CURRENT STATE OF KNOWLEDGE ABOUT THE RELATIONSHIP BETWEEN AIRBORNE PARTICULATE MATTER AND HUMAN MORTALITY AND MORBIDITY AND IMPLICATIONS FOR FUTURE RESEARCH

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and Human Mortality and Morbidity
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The participants in the Colloquium on Particulate Air Pollution and Human Mortality and Morbidity have, in general, oversimplified the interpretation of the estimates derived in epidemiological studies of the statistical correlation between ambient concentrations of particulate matter and various measures of human health. Oversimplified interpretation has resulted from their implicit adoption of a mistaken assumption -- the assumption that, when measurements of ambient concentrations of a single air pollutant are used as an explanatory factor in an epidemiological study, the correlation with human mortality or morbidity that has been estimated for that explanatory factor in the study indicates effects that are attributable to **only** the pollutant whose ambient concentrations have been measured. This assumption is invariably incorrect, and is particularly unsound in urban areas with diverse mixtures of emission sources, such as those with populations large enough to allow performance of a statistically powerful epidemiological study of the health effects of air pollution.

Only a Small Number of Airborne Substances are Routinely Monitored

In any urban area, the agency responsible for monitoring air quality routinely measures the ambient concentrations of only a small number of airborne substances. Substances for which agencies commonly choose to perform regular measurements include: particulate matter [measured variously in terms of such metrics as total suspended particulates (TSP), particulate matter with aerodynamic diameter less than ten microns (PM10), coefficient of haze (CoH), and British Smoke (BS)]; oxides of sulfur (SO_x); oxides of nitrogen (NO_x); ozone (O_3); carbon monoxide (CO); nonmethane volatile organic compounds (VOCs) and lead. In some urban areas, measurements are also made for additional anthropogenic chemicals [e.g., hydrogen sulfide (H_2S), sulfates (SO_4), benzene], and for some airborne substances from natural sources (e.g., pollens, molds, salinity).

There are, however, a multitude of other airborne substances that might affect human health. For example, Title III of the Clean Air Act Amendments of 1990 specifies 189 hazardous air pollutants that scientific research has indicated might be harmful to human health at current ambient concentrations. Few if any of those airborne chemicals are routinely monitored in any urban area. In addition, as Michael Leibowitz has emphasized in his comments in the Monday evening session of the Colloquium, allergic air pollutants from natural sources are strongly implicated as causal agents in asthma attacks. Although ambient concentrations of such pollutants commonly are routinely measured during peak pollen seasons, the measurements are seldom included as explanatory factors in epidemiological studies of the health effects of air pollution.

Ambient Concentrations of Airborne Substances are Mutually Dependent on Meteorological Conditions

Although airborne substances are, to a substantial degree, independently emitted from different types of sources, the day-to-day variations in their ambient concentrations are clearly not independent. The diurnal variations in ambient concentrations are, for the most part, not determined by day-to-day variations in source emissions. Rather, they are driven by day-to-day changes in meteorological conditions.

Changes in meteorological conditions tend to affect the ambient concentrations of substances with similar physical characteristics in similar ways. Ambient concentrations of gases vary inversely with the efficiency of ventilation (the efficiency of horizontal and vertical dispersion) within the airshed; and ambient concentrations of larger particles that are entrained by wind (e.g., fugitive dust, windblown agricultural tillage, pollens) vary directly with wind velocity over a substantial range.

The ambient concentrations of broad classes of airborne substances therefore covary in response to changes in meteorological conditions over time. As a result, in any urban area, the daily ambient concentrations of any airborne substance will be materially correlated with the daily ambient concentrations of any other airborne substance within its class. In fact, over a substantial range of meteorological conditions (esp. whenever vertical dispersion is impeded, as in the case of a thermal inversion), the ambient concentrations of all, or virtually all, airborne substances are appreciably correlated.

Accordingly, at the Colloquium several presenters have displayed matrices presenting the correlation coefficients between the monitored ambient concentrations of all pairwise combinations of the pollutants included in their databases. In those matrices, the measured ambient concentration of particulate matter uniformly is found to be appreciably correlated with that of each of the other pollutants. The smallest correlation coefficient that I recall seeing for particulate matter in any of the matrices is 0.38; many of the reported coefficients have been 0.70 or greater. The weakest correlations with the ambient concentration of particulate matter have tended to be found for ozone (O_3), which is formed through a totally different process (photochemical reaction in the atmosphere) than those that release particulate matter into the outdoor air. Empirical studies nevertheless commonly find sizable correlations between measured ambient concentrations of particulate matter and ozone, despite the notable differences in their sources.

Correlated Explanatory Factors Confound the Interpretation of Effect Estimates in Epidemiological Studies

In epidemiological studies, to the degree that the ambient concentration of an airborne substance that is included in the analysis is correlated with the ambient concentrations of airborne substances that have not been included, the health effects that are estimated to be statistically associated with the included substance will also incorporate effects that are actually attributable to the omitted substances, in addition to indicating the independent effects of the included substance, if any. In such studies, the included substance is acting as an analytic surrogate for the omitted substances whose ambient concentrations covary with that of the included substance.

If two or more substances whose ambient concentrations covary are simultaneously included as explanatory factors in a multivariate statistical analysis of the relationship between air pollution and human health, the variance of the coefficient (e.g., the relative risk or the regression weight) estimated for any of substances will be larger than it would have been if the substance had been the only pollutant included in the analysis as an explanatory factor. Accordingly, the confidence intervals around the estimated values of the coefficients will be broader and their statistical significance levels will generally be lower than they would have been if only one of the covarying pollutant concentrations had been included as an explanatory factor in the analysis.

This is precisely the pattern of results reported by H. Daniel Roth in his presentation at the Colloquium. In particular, Roth has stated that, when the ambient concentrations of individual pollutants have been included as the sole pollution variables in separate multivariate regression analyses, the included pollutants have uniformly been found to be statistically significant. Conversely, he has reported that, when the covarying ambient concentrations of two or more air pollutants have been included simultaneously as explanatory factors in an analysis, the statistical significance of each of the factors has uniformly been found to decrease. In fact, the results presented by Roth indicate that, for particulate matter, not only has the variance of the estimated coefficient increased as additional covarying factors have been introduced into the analysis, but also the value of the estimated coefficient has declined.

Resolution of Epidemiological Ambiguities with Additional Statistical Analysis is Impracticable

Equivocal epidemiological results such as those reported by Roth cannot be resolved by applying more refined statistical methods to databases that contain covarying measurements of ambient concentrations of different pollutants. Statistical techniques are incapable of disentangling the separate influences of the covarying explanatory factors, and thereby deriving reasonably precise estimates of their individual effects. For statistical methods to be able to identify the separate influence of a specific airborne substance on any aspect of human mortality or morbidity, a database must be assembled in which the ambient concentration of that substance is essentially uncorrelated with the ambient concentration of any other airborne substance that might influence that aspect of human health. Because ambient concentrations of airborne substances are mutually dependent on meteorological conditions, however, it is inconceivable that such a database might actually be developable, particularly for an urban area with population large enough to allow performance of an epidemiological study with sufficient statistical power that it would be capable of detecting an effect on human mortality of the magnitude hypothesized to be associated with elevated levels of current ambient concentrations of particulate matter.

Indeed, the development of a database that is capable of isolating health outcomes that are uniquely attributable to a single airborne substance appears especially infeasible for particulate matter. Because particulate matter is a complex mixture of substances with diverse physical and chemical attributes, it quite likely is a more efficient surrogate for all other substances in the outdoor air than is any distinct substance with unique physical and chemical properties. Through their mutual dependence on meteorological conditions, the ambient concentrations of fine particles that are routinely emitted from multiple sources doubtless are substantially correlated over time with the ambient concentrations of gaseous air pollutants; and the ambient concentrations of larger particles that are regularly released or entrained from multiple sources are, within pertinent seasons, substantially correlated over time with the ambient concentrations of airborne pollens.

This is perhaps the principal reason why, in epidemiological studies where different pollutants have been included individually as explanatory factors in separate statistical analyses of the relationship between ambient pollutant concentrations and human health, the coefficients estimated for particulate matter have often appeared more robust than those estimated for distinct airborne chemicals. Such results are particularly common in analyses that have spanned all seasons of the year and broad categories of health outcomes.

The apparent robustness of particulate matter as an explanatory factor accounting for daily variations in human mortality and morbidity often has diminished substantially, however, when analyses have focused on specific seasons of the year and specific health outcomes. In particular, as Suresh Moolgavkar has reported at the Colloquium, when analysis has been restricted to individual seasons of the year, the coefficients estimated for particulate matter have sometimes been found to be less robust than those for other specific individual pollutants. For example, during spring in the Steubenville, Ohio SMSA, the ambient concentration of sulfur dioxide (SO_2) has been found to be associated more statistically significantly with human mortality than is the ambient concentration of particulate matter measured as TSP. Similarly, as reported at the Colloquium by David Abbey, when analysis has been restricted to specific health outcomes, the relative risks estimated for certain individual pollutants have sometimes been found to be greater than those estimated for undifferentiated particulate matter. Abbey and his colleagues have derived such results for sulfates (SO_4) in relation to asthma and for ozone in relation to respiratory cancer. Comparable results have also been described by Neil Roth.

Even in many of those instances, however, the ambient concentration of particulate matter has been found to be statistically significantly correlated with the health outcome studied when it has been the only airborne substance included in the analysis as an explanatory factor. One can only wonder how often similar results would have been derived if similar analyses had been performed for the many airborne substances whose ambient concentrations have never been routinely measured.

So long as the ambient concentrations of different airborne substances are mutually dependent on meteorological conditions, their concentrations will be correlated over time, and statistical analysis will be generally incapable of identifying their separate influences on human health. Under such circumstances, the results derived for the included airborne substance can most realistically be interpreted as estimates of the statistical association between human mortality or morbidity and the ambient concentrations of **all airborne substances in the aggregate.**

Traditional Precepts of Statistical Inference are Inadequate for Identifying Thresholds of Effect

Even if the ambient concentration of a specific air pollutant were totally uncorrelated with the ambient concentration of any other airborne substance, it would not be possible to identify a threshold of effect for that pollutant by applying traditional principles and methods of statistical inference to empirical data on ambient concentrations of the pollutant and human mortality or morbidity. The threshold of effect for an airborne substance is, by definition, the lowest concentration of the substance at which an increase in concentration causes a change in human health, or equivalently -- and more importantly from the perspective of statistical hypothesis testing -- it is the highest concentration of the substance at which a decrease in concentration causes no change in human health.

Thus, to identify a threshold of effect on the basis of statistical analysis of empirical evidence, a test must first be performed to evaluate whether, associated with observed increases of the ambient concentration from a hypothesized threshold level, there are observed differences in the incidence of a specific health outcome that are large enough that they are unlikely to have occurred randomly. In principle, such an evaluation can readily be performed by applying traditional statistical hypothesis testing techniques. Indeed, evaluation of the probable nonrandomness of observed differences in outcomes is the essence of traditional statistical hypothesis testing.

After determining that increases in ambient concentration are, with acceptably high probability, associated with changes in the incidence of a particular health outcome, it is then necessary to evaluate whether, associated with observed decreases in the ambient concentration from its hypothesized threshold level, there are no observed differences in the incidence of that health outcome. Traditional statistical criteria, however, do not sanction the conclusion that there is no difference. Demonstration that, with probability greater than any arbitrarily specified value, the observed differences in incidence might have occurred randomly is not considered sufficient justification for concluding that there is no difference. Rather, traditional principles of statistical inference declare that the absence of demonstrably nonrandom observed differences only justifies reservation of judgment. Thus, even under ideal conditions, traditional statistical methods are incapable of identifying a threshold of effect. Criteria that transcend traditional precepts of statistical inference must be applied when inferring whether and at what concentrations thresholds of effect might exist.

Covarying Concentrations of Airborne Substances Complicate Identification of Thresholds of Effect

The detection of a threshold of effect for an individual air pollutant is even more complex and equivocal when ambient concentrations of airborne substances covary, as they invariably do through their mutual dependence on meteorological conditions. To understand why detection is especially enigmatic under such circumstances, consider the following possible scenario.

First, based on estimated effects on human health that have been statistically associated with prevailing ambient concentrations of particulate matter in epidemiological studies in which particulate matter is the only airborne substance whose ambient concentration has been included as an explanatory factor, the ambient air quality standard for particulate matter is revised to a more stringent level. Additional controls are implemented that reduce emissions of particulate matter, and ambient concentrations of particulate matter decline. The ambient concentrations of other airborne substances do not change, however, because their ambient air quality standards have not been revised and their emissions are not affected by the added particulate matter controls. Moreover, because of their common dependence on meteorological conditions, the ambient concentrations of particulate matter and the other airborne substances continue to covary over time.

Accordingly, if the epidemiological studies are replicated, and if any portion of the previously estimated effects on human health are actually attributable to any of the other airborne substances, the studies will again estimate that effects on human health are statistically associated with prevailing ambient concentrations of particulate matter. Such results will be derived even if the ambient concentration of particulate matter has been decreased to or below its threshold of effect, so long as any portion of the originally estimated effects has actually been caused by another airborne substance whose ambient concentration covaries over time with that of particulate matter.

In addition, if (as is typically posited for dose-response functions) the health effects of airborne particulate matter intensify at an increasing rate as its ambient concentration increases, and if decreases in the ambient concentration of particulate matter do not materially reduce the health effects caused by other airborne substances (i.e., if particulate matter is not a potent cofactor in the health effects caused by other airborne substances), the health effects estimated for airborne particulate matter will decline proportionately less than will its ambient concentration as the ambient concentration descends toward the threshold of effect. As a result, paradoxically, the estimated health effects per unit concentration of particulate matter (i.e., the estimated relative risk or regression weight) will generally increase as its ambient concentration decreases to and below the threshold of effect. This pattern of effect estimates is completely opposite to the statistical results that would be anticipated if the ambient concentration of particulate matter were essentially uncorrelated over time with that of any other airborne substance.

Thus, if conventional statistical criteria for identifying thresholds of effect in epidemiological analyses -- criteria that are totally appropriate in situations where ambient concentrations of airborne substances are essentially uncorrelated over time -- are erroneously applied in situations where ambient concentrations covary, grossly incorrect inferences will be drawn about the effects on human health that are attributable to low ambient concentrations of any substance that has been included in the analyses as an explanatory factor. Interpretation of the pattern of effect estimates described above on the basis of conventional criteria would yield the inference that the substance involves appreciable and increasing risk to human health as its ambient concentration is progressively reduced; whereas, as explained above, the estimates actually indicate that the health risk attributable to the substance has been decreasing, and may have become negligible. It is conceivable that this situation presently prevails in relation to current ambient concentrations of particulate matter.

Ambient Concentrations Are Not Demonstrably Reliable Surrogates for Personal Exposures

The results from epidemiological studies of statistical correlations between ambient concentrations of particulate matter and human mortality or morbidity have conventionally been interpreted as evidence of relationships between people's exposures to respirable particulate matter and their health. That interpretation is predicated on the assumption that measurements of ambient concentrations of particulate matter at stationary outdoor locations during specific time intervals are adequate surrogates for people's actual exposures to respirable particulate matter during those time intervals. The accuracy of this crucial assumption has not been established, however.

During any appreciable time interval, people typically perform a variety of activities at a diversity of indoor and outdoor locations. A person's total exposure to an airborne substance during any time interval is therefore amassed over that interval as, in general, the individual performs varied activities in diverse locations. As a result, measurements of ambient concentrations of particulate matter at stationary outdoor locations will not necessarily be reliable surrogates for people's actual exposures to respirable particulate matter. In fact, the empirical evidence that has been accumulating in the scientific literature throughout the last decade indicates that such surrogation is dubious.

Most recently, as reported by Haluk Ozkaynak at the Colloquium, the pilot study of personal exposures to particulate matter conducted in Riverside, California with the Total Exposure Assessment Methodology (the PTEAM study) has found that the measured concentrations of PM10 to which people are actually exposed generally are about 50 percent higher than contemporaneous measurements of ambient concentrations indoors and outdoors at their homes. The study therefore has concluded that people's personal activities at home generate "personal clouds" of particulate matter that are the sources of substantial portions of their personal exposures.

The reliability of measurements of outdoor concentrations of particulate matter as surrogates in epidemiological studies for measurements of people's actual exposures depends upon the degree to which the sets of measurements covary, however, rather than the observed differences in their absolute magnitudes. In this regard, the PTEAM study has discovered that the measured outdoor PM10 concentrations at people's homes account for only 16 percent of the variance in their measured personal exposures; whereas the measured indoor concentrations in the homes account for 49 percent of that variance. In addition, the study has found that the measured outdoor concentrations at the people's homes account for only 27 percent of the variance in measured indoor concentrations; and the measured outdoor concentrations at a central monitoring location account for only 57 percent of the variance in measured outdoor concentrations at the homes. The collective results from the PTEAM study thus provide scant support for the assumption that, in epidemiological studies of the health effects of air pollution, measurements of ambient concentrations of particulate matter at stationary outdoor locations are adequate surrogates for measurements of people's actual exposures to respirable particulate matter.

It is important to recognize in this regard, however, that the extant studies of the relationship between measurements of outdoor concentrations, indoor concentrations, and personal exposures to airborne particulate matter have not examined the essential issue relating to that crucial assumption. Namely, the assumption concerns covariation between ambient concentrations and personal exposures for a set of **specific individuals** during **different time intervals**, whereas the extant studies have examined covariation between ambient concentrations and personal exposures among **different individuals** during a set of **specific time intervals**.

Thus, it is possible that, in the extant studies, variations in personal exposures among individuals that result from differences in their activity patterns and residence attributes (e.g., location and airtightness) have obscured any consequential covariation that might exist over time between the personal exposures of specific individuals and ambient concentrations of particulate matter at stationary outdoor locations.

To resolve this key issue, it would be necessary to measure actual exposures during several time intervals for each individual included in the study, and then to correlate those measurements with contemporaneous measurements of outdoor concentrations in a statistical analysis that appropriately distinguishes among the personal exposures measured for the different individuals. I am aware of only one study in which personal exposures have been measured on several days for each individual in the study [John D. Spengler, Robert D. Treitman, Tor D. Tosteson, David T. Mage, and Mary Lou Soczek (1985). Personal exposures to respirable particles and implications for air pollution epidemiology. Environmental Science and Technology, 19, 700-707.]. Unfortunately, in that published paper, correlations between outdoor concentrations and personal exposures have only been reported for selected aggregations of the participants. Those correlations relate to measured ambient concentrations at a central outdoor location, and are substantially weaker than the correlation reported in the PTEAM study for outdoor concentrations measured at people's homes. Specifically, the reported correlation coefficient (r) between outdoor concentrations and the personal exposures of all participants is only 0.07, indicating that measured ambient concentrations at the central outdoor location account for less than 0.5 percent of the total variance in personal exposures among individuals and over time. Indeed, for nonemployed participants, the corresponding correlation coefficients are mostly negative, suggesting that increases in outdoor concentrations tend to be accompanied by decreases in personal exposures for such individuals. The available scientific evidence therefore provides meager empirical support for the conventional assumption that measurements of ambient concentrations of particulate matter at stationary outdoor locations represent reliable surrogates for people's actual exposures to respirable particulate matter in epidemiological studies of the relationship between airborne particulate matter and human health.

Additional Epidemiological Research on Health Effects of Ambient Concentrations of Airborne Substances Will Generally Be Uninformative

Because their mutual dependence on meteorological conditions causes the ambient concentrations of airborne substances to covary appreciably over time, additional epidemiological studies of hypothesized associations between the ambient concentrations of specific airborne substances and human mortality or morbidity will generally be uninformative about health effects actually attributable to individual substances. Only in instances where there is valid scientific evidence (e.g., from clinical research, analyses of industrial exposures, or studies of consequential accidental releases) that **distinct** health outcomes have been **uniquely** associated with people's exposures to **specific** airborne substances is it possible that such studies might develop useful information about the practical importance (e.g., incidence and severity) of health effects caused by exposures of the general population to current ambient concentrations of those specific substances.

Under any more equivocal circumstances, as explained above, it would be impossible to infer with any appreciable degree of confidence that health effects detected in an epidemiological study are reliably attributable to any individual airborne substance. Undertaking epidemiological studies in such circumstances would divert scarce research resources from projects with real prospects for producing useful information about important public health problems.

Future Clinical Research on Health Effects of Airborne Substances Should Be Broad-Based Yet Selective

As explained above, the estimated health effects that have been statistically associated with ambient concentrations of particulate matter in epidemiological studies in which particulate matter is the only airborne substance that has been included as an explanatory factor should actually be interpreted as health effects that are statistically associated with ambient concentrations of all airborne substances in the aggregate. Accordingly, clinical research intended to identify the specific airborne substances and associated biological mechanisms that are the bases for the estimated statistical associations should not be restricted to studies of specific physical or chemical components of particulate matter, or to substances that might bind to specific components of particulate matter. Rather, all airborne substances, regardless of their physical relationship to particulate matter, should be considered as possible subjects of clinical research. Selection of specific substances for study should then be based on such considerations as the hazards thought to be involved with human exposure to the substance, and the estimated extent and severity of actual exposure of the general population to the substance.

In this regard, however, it is also important to realize that, when people are exposed to an elevated ambient concentration of one airborne substance, they almost invariably are simultaneously exposed to elevated ambient concentrations of many other airborne substances. Thus, it is conceivable that the estimated health effects that have been statistically associated with ambient concentrations of particulate matter may actually be attributable to people's simultaneous exposures to elevated concentrations of complex mixtures of airborne substances. Moreover, recognizing that there are substantial interpersonal differences in sensitivity to specific substances, it is possible that similar health effects experienced by different people may have resulted from exposures to different specific mixtures of airborne substances to which the people are individually sensitive. Finally, several participants in the Colloquium have speculated that the estimated health effects that have been statistically associated with ambient concentrations of particulate matter may have occurred to people with chronic health problems (such as chronic obstructive pulmonary disease) whose health has been further compromised by acute transitory conditions (such as pneumonia).

If all of the factors discussed above have actually contributed materially to the health effects estimated in the epidemiological studies, clinical research on the health consequences of exposure to specific airborne substances, individually or in combination, may, in practice, be incapable of developing information that will be useful in either isolating the specific causes of the health consequences, or identifying demonstrably effective methods of mitigating the effects. For example, at the extreme, it is conceivable that the estimated health effects relate to people with chronic health problems who are temporarily afflicted with acute transitory conditions and, during only those intervals, are highly sensitive to elevated concentrations of specific mixtures of airborne substances that differ among the individuals. Under those circumstances, it is difficult to comprehend how effective research plans could be established for clinical research projects designed to isolate, with an acceptable degree of confidence, specific mixtures of airborne substances that cause specific health outcomes in subjects with specific chronic and transitory conditions and sensitivities, or even how samples of appropriately susceptible human or animal subjects could be assembled as experimental and control groups for such projects. Even under considerably less extreme circumstances, it doubtless would be more cost-effective to identify the characteristics of potentially susceptible individuals, and then to develop effective therapies for treatment of such individuals on those occasions when they might be critically sensitive to airborne substances.

COMMENTS OF F.W. LIPFERT ON THE FINAL SESSION OF THE "COLLOQUIUM ON PARTICULATE AIR POLLUTION AND HUMAN MORTALITY AND MORBIDITY," IRVINE, CA, JANUARY 25, 1994

These comments are structured as a series of increasingly specific questions, with answers based on the information presented at the Colloquium, supplemented with citations from the literature, as necessary. Citations from the Colloquium are given as (first author). Citations from the literature are identified with the author and publication year and are listed at the end.

1. Does the epidemiological record implicate particulate air pollution in various acute community health studies, including premature mortality and hospitalization?

Yes. Papers by Schwartz, Dockery, Pope, Abbey, Hoek, Ostro, Lyon, Moolgavkar, Li, Kinney, Thurston, Ito, Cook, Delfino, Horstman, Lippmann, Lipsett, Neas, Ozkaynak showed statistically significant ($p < 0.05$) associations for one or more particulate air pollutants with various health endpoints. The existence of these effects has been shown previously by the severe air pollution episodes of the past; current issues should thus be concerned with the shapes of dose-response relationships and with defining the specific pollutants involved.

2. Are other air pollutants also implicated?

Yes. O_3: Ostro, Li, Thurston, Kinney, Ito, Delfino, Ozkaynak
SO_2: Schwartz, Dockery, Moolgavkar, Li, Horstman
CO: Kinney, Ito
NO_2: Kinney

The use of peak hourly rather than 24-h average concentrations in some of these studies may have biased the results for these pollutants downward, because of the implied measurement error (Lipfert); see point # 16, below.

3. How should we interpret a regression result based on entering only one of several collinear pollutants in the regression?

The regression coefficient will reflect the sum of the effects of that pollutant and those of all other pollutants with which it is correlated. If those other pollutants are positively associated with the health endpoint in question, the combined effect and its significance will be enhanced, and vice-versa. (Based on paper by Lipfert and on elementary statistics theory.)

4. What are the effects of errors in exposure measurement on these relationships?

Measurement errors obscure the true degree of collinearity and will bias results towards the null in most cases. In joint (multiple) regressions with correlated independent variables, the variable with the least measurement error will tend to drive out the others (Lipfert). Thus, statistically significant single pollutant regressions are a necessary but insufficient indication of a specific effect, and joint regressions of correlated pollutants are likely to fail the tests of significance, even when a true relationship exists. Nevertheless, the joint regression coefficients are unbiased estimates of the relative magnitudes of effects. Exogenous information must thus be used to make decisions about causality.

5. Which pollutants have been implicated in studies of <u>chronic</u> air pollution effects on community health?

Dockery et al. (Six Cities): $PM_{2.5}$, SO_4^{2-}
Pope et al. (American Cancer Society Study): TSP, SO_4^{2-}
Abbey et al.: TSP, PM_{10}
older studies implicate TSP, SO_4^{2-}, SO_2, NOx, metals (Fe, Mn), ozone.

6. What relationships should we expect between chronic and acute studies?

If positive acute responses are not subsequently canceled by decreases in deaths (the so-called harvesting effect), their annual sums should be reflected in cross-sectional (chronic) studies. Thus, lack of significance in chronic studies may indicate that the acute effects are only transient perturbations. In addition, only cross-sectional effects in excess of the annual sum of acute effects should be considered as actually reflecting chronic responses.

7. Which pollutants have been significantly associated with <u>mortality</u> in both cross-sectional and time-series studies?

TSP and SO_2 (many studies), ozone (several time-series studies, cross-sectional studies by Lipfert (1984, 1992)). $PM_{2.5}$ has not been found to be significant in time-series mortality studies; H^+ has not been implicated in cross-sectional studies and the evidence for SO_4^{2-} in time-series studies is equivocal (Ozkaynak et al. did not evaluate SO_4^{2-} in joint pollutant regressions in Toronto). Iron has been implicated in cross-sectional studies by Lipfert (1978, 1988), but since virtually all particles contain iron, the hypothesis that iron is implicated in time-series studies as well should be confirmed.

8. Why do we need associations in both cross-sectional and time-series mortality studies as a condition for causality?

These two types of study designs are each subject to confounding and to different interpretations, but from quite different perspectives. Daily time-series results differ according to the types of seasonal and weather adjustments used and give no information on the degree of prematurity of death (see point #6 above). Cross-sectional studies of long-term rates (including the prospective studies briefly presented at the Colloquium) suffer from potential confounding from spatial gradients in personal lifestyles and/or socioeconomic status. A pattern of consistent association in both kinds of studies is thus a necessary (but insufficient) requirement for a causal interpretation.

9. Given the inherent indeterminancy of most epidemiological regressions, what criteria, in addition to statistical significance, must be met in order to infer causality for a specific pollutant?

Biological plausibility and actual exposure (which implies the presence of the pollutant indoors, where most people and especially sick people spend the bulk of their time).

10. For which pollutants do we have corroboration from laboratory studies or theory that support biological plausibility (regardless of concentration level)?

Ozone and CO (many studies), ultrafine particles (Oberdorster), iron (Costa), H_2SO_4 (Lippmann).

11. Which pollutants are expected to have a strong indoor-outdoor correlation and thus to relate to actual personal exposures?

Fine particles (but not ultrafines), PM_{10} (including the inhalable portion of TSP), iron (by implication), ozone. Not SO_2, H^+, H_2SO_4 or coarse particles.

12. Which pollutants meet all criteria, based on present information?

Ozone, PM_{10} (including the inhalable portion of TSP), and iron (by implication).

13. Which pollutants may be ruled out as implausible?

H^+, SO_2, ultrafines: based on lack of penetration indoors.
Coarse particles (lower size limit not well defined): based on filtering by the oropharynx and lack of penetration to indoor environments.

14. For which pollutants do we have insufficient information (but which we cannot rule out at this time)?

CO, NO_2, organics, aeroallergens, HCHO, SO_4^{2-}, $PM_{2.5}$, PAN, HONO. We lack direct confirmation of PM_{10} in direct size-specific cross-sectional studies.

15. What is the evidence for a linear dose-response relationship with no threshold?

Some authors have used such linear models and gotten good fits. Most authors have not tested nonlinear models and apparently no one has rigorously tested the superiority of any model form with regard to alternatives. The concept of ambient air quality standards implies that thresholds exist for all criteria pollutants; thus it is incumbent upon investigators to establish the superiority of a given model (say, linear) by comparing it with alternatives. Significant differences due to functional forms of dose-response relationships are unlikely to be apparent from statistics on model fits; residuals or scatter plots must be examined for evidence of heteroscedasticity, for example. In most cases, a systematic investigation will be required, in which different pollutant metrics and dose-response functions are investigated in separate and joint regressions for each pollutant. Since the regression fits for alternative models are often essentially identical, exogenous information may be required to select the most appropriate models.

16. Which pollutant metrics should be used in observational epidemiological studies?

From first principles, 24-h averages are more robust than peak-hour data and often give better statistical performance (Lipfert and Hammerstrom, 1992). When biological responses are to be apportioned among several candidate air pollutants, each pollutant should be given the same averaging treatment, so that errors in exposure estimates are as equivalent as possible (see point #4 above). For example, it would be inappropriate to compare joint regression results for peak-hour ozone with integrated doses (concentration x time) of H^+, for the purpose of partitioning responsibility. When nonlinear responses are suspected, in that peak exposures may be more important than average or total doses, nonlinear models must be used and peak-hour data are more appropriate. This can be performed as a subsequent step in the analysis. Exogenous information on biological responses and defenses may also be helpful in selecting the proper metrics and functional forms.

17. What is the evidence for physiological (i.e., a defined toxicology), as opposed to homeostatic, mortality responses?

Physiological effects imply defined responses by target organs to specific stimuli. The normal respiratory system defenses imply that thresholds should be present, reflecting this defensive capability. Thus, acceptance of a linear dose-response function implies rejection of a physiological response model. In addition, quantitatively similar daily mortality perturbations have been found in response to TSP and PM_{10} in different regions of the country where these particles are likely to have very different characteristics and thus stimuli; this is also inconsistent with the physiological model. (In response to this observation during Colloquium discussion, J. Schwartz offered the opinion that the specific nature of the particle is probably irrelevant, and that particles may act as vectors for some other type of disturbance.) The evidence for homeostatic responses (i.e., death caused by a general upset in the system balance rather than by a specific physiological response) also includes the finding that excess mortality is associated with relatively minor weather perturbations (which do not affect healthy people), including temperature swings well below "heat wave" levels and changes in barometric pressure.

18. Do we have evidence that lives will be extended in the long term if concentrations of particles are reduced?

No. This question can only be addressed by studies of long-term responses to pollution abatement campaigns. Daily time-series studies do not address long-term trends; many of them specifically remove the long-term trends that are of primary interest to policy-makers. Cross-sectional studies analyze spatial gradients only; their derivatives with respect to space provide no information on temporal trends. The Six Cities Study (Dockery et al., 1993) did not analyze changes in survival rates as air quality improved over time in the most polluted city (in which NAAQS were violated). We have evidence from London and Philadelphia that mortality-pollution regression coefficients tend to increase as pollution levels decrease, which implies the presence of surrogate-type effects.

19. What additional research is needed at this time?

<u>Air monitoring</u> must be revamped to provide daily data on population exposures to a full spectrum of environmental agents.

<u>Comprehensive epidemiological studies</u> should be conducted in several cities (including replicates) with different climates and mixes of pollutants. Mortality and morbidity endpoints should be studied simultaneously, using a variety of models and pollutant combinations. Different age groups, lag periods, and causes of death should be studied, using parallel analyses.

<u>A testbed community</u> should be established for long-term studies in the Framingham mode, in which the exposures and outcomes of individuals can be tracked over time. Ideally, such a community should be located in a region of changing air pollutant loading, perhaps in the Ohio Valley. However, the population should be relatively stable. Use of retrospective analysis of existing epidemiological surveillance populations should be investigated.

<u>Animal toxicology</u> should be adapted to the long-term study of susceptible populations, mimicking the (human) daily mortality study. This will probably require use of colonies of aged animals. A "sick human" animal model should be utilized.

<u>A comprehensive analysis of particle size effects</u> should be conducted, including human and animal respiration patterns and respiratory defenses under different stress conditions, physiological effects of deposition within different regions of the respiratory system, particle penetration into indoor spaces (including moving vehicles), and exposure errors entailed by using central (outdoor) monitoring data in various types of epidemiological studies.

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AUTHOR INDEX