

# PM Exposure Assessment Research: Supplement to *Accomplishments of the Particulate Matter (PM) Centers (1999-2005)*

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This document summarizes the progress made by the EPA Particulate Matter (PM) Centers during their first 6 years in identifying and understanding human exposures to PM air pollution since the mid-course report prepared in 2002 (Lippmann et al., 2003). When the PM Centers were designated in 1999, the primary body of evidence for personal and population-based exposures to ambient air PM consisted, in large measure, of research conducted as part of the Harvard Six Cities Study and the U.S. EPA Particle Total Exposure Assessment Methodology Study (Clayton et al., 1993), and we concluded that the pre-existing PM exposure database was inadequate for investigating associations between personal exposures and outdoor concentration data from compliance based monitoring sites. In the first phase of the PM Centers program there was substantial work to understand and assess potential flaws and weaknesses in this body of evidence, and to develop an understanding of the spatial and temporal aspects of exposures to PM of ambient air origin. In the more recent work, the PM Centers research has substantially expanded the range of PM mass and PM component concentration variations in community air for PM<sub>10</sub>, PM<sub>2.5</sub>, PM<sub>1.0</sub>, and for PM<sub>0.1</sub> (ultrafine PM, or UFP).

## ***FROM SOURCES TO EXPOSURE***

### ***Outdoor Exposure***

#### ***PM<sub>10</sub> and PM<sub>2.5</sub>***

Ito et al. (2001) showed that monitor-to-monitor correlations of ambient air concentrations of criteria pollutants are relatively high (~0.6) over a scale of 100 miles in the North-Central region of the United States (US) for PM<sub>10</sub>, O<sub>3</sub>, and NO<sub>2</sub>, but only ~0.3 for CO and SO<sub>2</sub> using a nationwide database (Ito et al., 2005a). The overall rank in monitor-to-monitor correlation, on the average, was: O<sub>3</sub>, NO<sub>2</sub>, PM<sub>10</sub>, (0.7~0.8) > CO (~0.6) > SO<sub>2</sub> (~0.4). Both the separation distance and regional variation were important predictors of the correlation. For PM<sub>10</sub>, for example, the correlation for the monitors along the East Coast was higher by ~0.2 than for monitors in western regions.

Some previous research suggested a relationship between coarse mode (>2.5µm), accumulation mode (0.1 to 1.0µm) and inter-modal (1-2.5 µm) PM. For coarse, inter-

modal, and fine PM collected across four sites in the Los Angeles (LA) Basin, the studies showed that the inter-modal PM consists of a significant portion of particles that are similar in chemical composition to PM<sub>1</sub>. These results indicated that a PM<sub>1</sub> standard would not constitute an unambiguous separation of coarse and fine mode PM in this urban air shed (Geller et al., 2004).

### *PM<sub>2.5</sub> Components*

Spatial variability of PM components was examined using a mobile lab at 6 locations within an area of New York City (NYC), the South Bronx, where high concentrations of diesel trucks and waste transfer facilities are located (Maciejczyk et al., 2004), as well as at the Hunter College School of Health Sciences on the east side of midtown Manhattan. PM<sub>2.5</sub>, black carbon (BC), and gaseous pollutants were measured at 6 locations for three four-week intervals each during the period of April 2001–February 2003. Although the median daily PM<sub>2.5</sub> concentrations agreed within 20%, the median hourly BC concentrations were higher at all South Bronx sites, ranging from 2.2 to 3.8 µg/m<sup>3</sup>, compared to 1.0–2.6 µg/m<sup>3</sup> at Hunter College. Continuous Aethalometer BC measurements at additional 27 sampling sites in the South Bronx along major highways indicated that the BC concentrations varied within each site, depending on time-of-day, with a large spatial variability from site-to-site.

Ito et al. (2004) used EPA's PM<sub>2.5</sub> speciation data for NYC to evaluate the potential exposure error associated with each source type, and found the strongest temporal correlations across the three monitors for the individual PM components related to secondary aerosols (e.g., S, NH<sub>4</sub><sup>+</sup>). Source-apportionment of these data identified four major source/pollution types: 1) secondary (largely regional) aerosols; 2) soil; 3) traffic-related; and 4) residual oil burning/incineration, at each of three monitoring sites. The estimated source-apportioned PM<sub>2.5</sub> mass generally showed the highest monitor-to-monitor correlation for the secondary aerosol factor (r range = 0.72 to 0.93). The correlation for the more localized traffic-related factor was more variable (r range = 0.26 to 0.95).

PM size and chemical composition were extensively characterized in the LA Basin, showing that the PM physical and chemical properties depend greatly on locations and season. UFP concentrations were found to be the highest at the source sites, characterized as being near fresh vehicular emission sources. Mass concentrations in the accumulation mode (0.1 < d<sub>p</sub> < 2.5 µm) were lower in winter than in summer, especially at the receptor sites. PM concentrations in the coarse thoracic particulate matter (CTPM) range (2.5 < d<sub>p</sub> < 10 µm) were lower in winter, and were composed mostly of nitrate (NO<sub>3</sub><sup>-</sup>) and crustal elements (Fe, Ca, K, Si, and Al). In the accumulation mode, NO<sub>3</sub><sup>-</sup> and organic carbon (OC) were predominant, with higher NO<sub>3</sub><sup>-</sup> levels found at the receptor sites. The UFP consisted of mostly OC, with higher wintertime levels at the source sites, due to the enhanced condensation of organic vapor from motor vehicles at lower temperatures. Conversely, higher UFP OC levels at the receptor areas were due to secondary organic aerosol formation by photochemical reactions, as well as increased advection of polluted air masses from upwind areas (Sardar et al., 2005a).

The effects of atmospheric transport on the size distribution of PM-bound species, such as polynuclear aromatic hydrocarbons (PAHs), elemental carbon (EC), OC, SO<sub>4</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> were also reported in the LA Basin. For October - February, the size

distributions of PAHs were similar, but were drastically different from those in March to July. A significant fraction of the PAH and the  $\text{NO}_3^-$  mass was in the coarse mode, as compared with the previous period. The correlation of temperature with the concentration of PAHs in the less volatile or PM-phase group was negative, consistent with increased partitioning from the vapor-phase with decreasing temperature. During all seasons, the form and shape of the EC size distributions did not vary much, and were distinguished by prominent mass in the UFP and accumulation modes. For the individual modes of the major species measured, the highest correlations were found in the UFP for  $\text{SO}_4^{2-}$  and EC, suggesting increased atmospheric transport of vehicular emissions from the urban downtown LA region (Miguel et al., 2004).

Measurements of daily size-fractionated ambient  $\text{PM}_{10}$  metals were conducted at source (Downey) and receptor (Riverside) sites within the LA Basin. All crustal species were predominantly in particles  $> 1 \mu\text{m}$ . At the source site, potentially toxic metals (e.g., Pb, Sn, Ni, Cr, V, and Ba) were predominantly partitioned (70–85%, by mass) in the particles  $< 1 \mu\text{m}$ . The receptor site exhibited coarser distributions for almost all particle-bound metals.  $\text{PM}_{2.5}$  metal concentrations at that site were due to a few local emission sources and transport from urban LA. CTPM metal concentration trends were governed by variations in the wind speeds in each location, whereas the diurnal trends in the  $\text{PM}_{2.5}$  metal concentrations were a function of prevailing meteorological conditions and upwind sources (Singh et al., 2002).

A nationwide cross-sectional source apportionment used the 2000 to 2003 EPA  $\text{PM}_{2.5}$  speciation quarterly average concentrations for over 200 US locations. The eight largest pollution source categories were: traffic, coal combustion, secondary sulfates, soil, salt, residual oil combustion, metals, and steel production. Of these, traffic was a major contributor to the total  $\text{PM}_{2.5}$  throughout the US, with the highest levels observed along the West Coast, especially in California. However, other components were often more regional, or limited in scope; for example, coal combustion effluents and secondary sulfates appeared to affect most of the Northeast US, while the soil levels were most elevated in the southwest of the country. The residual oil combustion component was found to be associated mainly with the deep US seaports, where electric power plants burn residual oil, and containerized cargo ships burn extremely polluting "bunker" fuel oil. Wood burning was a major component of  $\text{PM}_{2.5}$  in selected cities in the Pacific Northwest (Kim et al., 2003, 2004; Maykut et al., 2003; Larson et al., 2004).

Reactive oxygen species (ROS), a term used to collectively describe oxygen-containing species with strong oxidizing ability, include molecules like hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ions like the hypochlorite ion ( $\text{OCl}^-$ ), hydroxyl (OH) radical, and the superoxide anion ( $\text{O}_2^-$ ). One hypothesis for the adverse health effects of airborne PM is that ROS, formed by metals acting as catalysts for Fenton reactions, at concentrations that cause inflammation, lead to systemic dysfunctions (Stohs and Bagchi, 1995). Docherty et al. (2005) investigated the role of organic peroxides in secondary organic aerosol (SOA) formation from biogenic monoterpenes such as  $\alpha$ -pinene, and concluded that SOA was predominantly organic peroxides, which contributed anywhere between 47% and 85% of the total SOA mass. Venkatachari *et al.* (2005; 2006) determined diurnal concentrations of particle-bound ROS for various size fractions of the aerosol, ranging from 10 nm to 18  $\mu\text{m}$  in Rubidoux, CA in July 2003, and in Flushing, NY during the period of January and early February 2004, using a MOUDI™ cascade impactor. In

Rubidoux, California, ROS concentrations correlated moderately with the ambient O<sub>3</sub> concentrations, smaller particles were observed to have higher ROS concentrations, and the general magnitude of ROS concentrations were found to be at least an order of magnitude higher than those observed in studies in Taipei (Hung and Wang, 2001). In NYC, correlations of the PM ROS concentrations with the intensity of photochemical reactions and gas phase radical concentrations were found to moderate factors affecting PM ROS concentrations. Lower concentrations of ROS were found in NYC than those in Rubidoux, CA.

### *Ultrafine Particles (UFP)*

Increasing epidemiological and toxicological evidence links cardiopulmonary health effects with UFP exposures. The method of Dillner et al. (2005) was used to measure the composition of UFP at two sites in Houston, TX; one surrounded by refineries, chemical plants, and vehicular and commercial shipping traffic, and the other, 25 miles inland, which was surrounded by residences, light industrial facilities, and vehicular traffic. Twenty-four hour size-segregated ( $0.056 < D_p < 1.8 \mu\text{m}$ ) PM samples were collected. Inductively coupled plasma/mass spectroscopy (ICP/MS) was used to quantify 32 elements with concentrations as low as a few picograms per cubic meter ( $\text{pg}/\text{m}^3$ ). Concentrations of PM mass,  $\text{SO}_4^{2-}$  and OC were often not significantly different from each other, and had smooth uni-modal size distributions, indicating the regional nature of these chemical species. Concentrations varied widely, and often showed sharp peaks for diameters between 0.1 and 0.3  $\mu\text{m}$  and in UFP, suggesting that the sources were local, high-temperature processes. The clustered elements were generally attributed to different sources (such as automobile catalysts, fluid catalytic cracking unit catalysts, fuel oil burning, a coal-fired power plant, and high-temperature metal working) at the two sites during each sampling day, indicating the diversity of local sources that impact metals concentrations in the region.

Motor vehicles may be the primary direct emission sources of UFP to urban atmospheres, especially in the LA Basin. It is important to understand how UFP behave after being emitted and transported. Understanding the characteristics of UFP volatility and UFP penetration into indoor environments is also a vital information need.

Utilizing a mobile particle concentrator, the physical and chemical PM characteristics and volatility on/near freeways, the impact of mobile sources on indoor environments, and PM characteristics and emission factors in roadway tunnels with light-duty or heavy-duty vehicles were determined. Relative concentrations of CO, EC and UFP number decreased exponentially and tracked each other well with distance from a freeway (Zhu et al., 2002a; 2002b; 2004). In-vehicle measurements showed a 5-fold higher particle numbers and EC concentrations compared to those measured in typical urban background areas (Westerdahl et al., 2005), and that PM emissions from vehicles are externally mixed; i.e., different particles of the same size can have different chemical compositions (Kuhn et al., 2005a). Between 70-90% of the particles, and 10-30% by mass consisted of semi-volatile material originating from condensation of organic vapors from fuel and lubricating oil (Kuhn et al., 2005a). The non-volatile portion consists primarily of EC, which is often coated with more volatile organic species. The volatility of the surface coatings explains the more rapid decay in their concentration with respect to distance from a roadway, as compared to that of non-labile PM species (such as EC) or

gaseous co-pollutants, such as CO and NO<sub>x</sub>, the concentrations most affected by atmospheric dilution (Zhang et al., 2004; 2005). These studies also showed that the volatile components of PM may be present in its gaseous phase in indoor environments, causing particle shrinkage and/or complete evaporation as they infiltrate indoors (Zhu et al., 2004 b; Kuhn et al., 2005b). In future research, given that the majority of people's exposure during commuting will be dominated by these particles, it would be useful to know whether the non-volatile or semi-volatile material is more toxic.

A better understanding of UFP characteristics and their volatility would allow for a narrowing of the search for the most toxic PM components. Current particle traps for Diesel engines remove non-volatile soot particles, but not the precursors of the smaller semi-volatile particles. An unintended result of any reduction of the larger, non-volatile particles from the exhaust may be a potential increase in the formation/emission of the smaller, semi-volatile PM, as seen in experiments performed at the Caldecott tunnel, in which size fractionated emission factors were determined for heavy and light duty vehicles and compared to those of previous studies in the same location (Geller et al., 2005).

Studies in Southern California showed that UFP size distributions at source sites were generally unimodal, with a mode diameter of 30–40 nm, and without significant monthly variations, but were bimodal at receptor sites, with a significant increase in the accumulation mode sizes in summer. Afternoon periods in the warmer months were characterized by high number counts, while mass and EC remained low, suggesting the formation of new particles by photochemistry. Particle mode diameters ranged from 30 nm up to above 100 nm, a result not seen in other urban or rural areas where mode diameters are generally less than 50 nm. UFP concentrations and size distributions were influenced by long-range advection and photochemical processes, as well as by vehicular emissions, which have previously been assumed to dominate day-to-day UFP levels (Fine et al., 2004a).

The very small mass of UFP has posed a great challenge in determining their size-dependent chemical composition using conventional aerosol sampling technologies. The use of two technologies in series, the USC Ultrafine Concentrator described by Kim et al. (2001a, b), and the MSP NanoMOUDI, made it possible to overcome these problems. UFP were measured at source and receptor sites during three consecutive 3-hour time intervals (i.e., morning, midday and afternoon). A distinct mode in the 32-56 nm size range was most pronounced in the morning. While the mass concentrations at the source site decreased with time, the levels measured at Riverside, CA (a "receptor" site) were highest in the afternoon, with a minimum at midday. At that site, UFP EC and OC concentrations were highly correlated during the morning period, but collapsed later in the day in this area (Geller et al., 2002).

The PM Center exposure research was coupled with toxicological and health effects studies that demonstrated increased toxicity in terms of the oxidative potential of UFP, compared to other PM size fractions on a mass basis, as measured by a variety of *in vitro* bioassays (Li et al., 2003; Xia et al., 2004; Cho et al., 2005) as well as by *in vivo* concentrated ambient particle studies (CAPs) conducted in the vicinity of freeways (Campbell et al., 2005; Kleinman et al., 2005), as described in the health effects section.

Since UFP originates from vehicular emissions the concentrations of gases such as CO, NO, or NO<sub>2</sub> that also originate from traffic sources have been used as surrogate

measures of UFP. The validity of that assumption was tested at five sites in the LA Basin. There was an overall lack of significant associations between hourly and 24-hr particle number (PN) versus gaseous co-pollutant concentrations, which may be attributable to the differences in the sources and formation mechanisms responsible for generating these pollutants in the LA Basin. These findings also imply that potential confounding effects of co-pollutants will not affect epidemiologic analysis seeking to link UFP to health effects because of the general lack of associations between PN and co-pollutant concentrations (Sardar et al., 2005b).

Improved characterization of individual UFP became possible through improvements in the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) described by Su et al. (2004). They use a more efficient ATOFMS, for the on-line detection and determination of the size and chemical composition of single fine (100-300 nm) and UFP (<100 nm) particles. Polystyrene latex spheres (PSL) were used to characterize: the particle sizing efficiency, particle detection efficiency, and particle beam profile, and to perform instrument calibration. At PN concentrations of <20 particles/cm<sup>3</sup>, the particle sizing efficiencies were ~0.5% for 95 nm, and ~47% for 290-nm PSL particles, while the particle detection efficiencies were ~0.3% for 95 nm, and 44% for 290-nm PSL. This represents an increase by 3 orders of magnitude in detection efficiencies for smaller particles over the conventional ATOFMS. In addition, the beam profiles for PSL followed a Gaussian distribution, with a full width at half-maximum of ~0.35  $\mu\text{m}$ . The resulting higher detection efficiencies allow the ATOFMS to obtain higher temporal resolution measurements of the composition of individual fine and UFP, as demonstrated in initial ambient measurements in La Jolla, CA. At typical ambient PN concentrations of 102-103 particles/cm<sup>3</sup>, ~30 000 particles with aerodynamic diameters of <300 nm were detected with average 24-h hit rates of 30% for PM between 50 and 300 nm. This advancement allows high temporal resolution measurements of the composition of smaller particles with higher efficiency in order to chemically characterize individual fine and UFP.

### *Source Apportionment*

The PM Centers sponsored a Workshop on Source Apportionment for Particulate Matter Health Effects in May 2003 to evaluate the consistency of the various source apportionment methods for assessing source contributions to daily PM<sub>2.5</sub> mass-mortality associations. Seven groups of investigators, using various methods, estimated source apportionments of PM<sub>2.5</sub> mass samples collected in Washington, DC and Phoenix, AZ. Apportionments were evaluated for their respective associations with mortality using Poisson regressions, allowing a comparative assessment of the extent to which variations in the apportionments contributed to variability in the source-specific mortality results. Analyses indicated that source types were significant predictors of relative risks, whereas apportionment group differences were not, adding only ~15% to the mortality regression uncertainties (Thurston et al., 2005). Other Workshop results investigations of inter-method variability in the associations for Washington (Ito et al., 2005b) and in Phoenix (Mar et al., 2006).

Hopke et al. (2006) presented the results of the source apportionment inter-comparison, and reported that there was good agreement among the major resolved source types. Crustal (soil), sulfate, oil combustion, and salt were the sources that were

most unambiguously identified (generally highest correlation across the sites). Traffic and vegetative burning showed considerable variability among the sites, and there was variability in the ability of the methods to partition the motor vehicle contributions between gasoline and diesel vehicles. However, when the total motor vehicle contributions were estimated, good correspondence was obtained among the results. The source impacts were especially similar across various analyses for the larger mass contributors (e.g., the standard error (SE) for Washington, DC, for secondary sulfate, was 7%, and for traffic it was 11%; in Phoenix, the secondary sulfate SE was 17%, and was 7% for traffic). Especially important for time-series health effects assessment, the source-specific impacts were found to be highly correlated across analysis methods/researchers for the major components (e.g., mean analysis to analysis correlation,  $r > 0.9$  for traffic and secondary sulfates in Phoenix, and for traffic and secondary nitrates in Washington. The mean sulfate  $r$ -value was  $> 0.75$  for Washington. Overall, although this inter-comparison suggested areas where further research is needed (e.g., better division of traffic emissions between diesel and gasoline vehicles), they provided support for the contention that  $PM_{2.5}$  mass source apportionment results are consistent across users and methods, and that today's source apportionment methods are sufficiently robust for application to  $PM_{2.5}$  health effects assessments.

By examining the seasonal, temporal, spatial, size-fractionation, and inter-correlations of individual organic compounds, the sources and atmospheric fate of these tracers can be better understood and their utility as molecular markers can be assessed. Southern California PM Center investigators used a high-flow rate, low pressure-drop UFP separator to collect sufficient mass for organic speciation of UFP and accumulation mode aerosol on a diurnal basis. Sampling was conducted at two sites (source and receptor oriented) over two seasons (summer and winter). Hopanes, used as organic markers for vehicular emissions, were found to exist primarily in the UFP mode. Levoglucosan, an indicator of wood combustion, was quantified in both size ranges, but more was present in the accumulation mode particles. An indicator of photochemical secondary organic aerosol formation, 1,2 benzenedicarboxylic acids, was found primarily in the accumulation mode and varied with site, season, and time of day, as one would expect for a photochemical reaction product. These data will be used to assess the concentration of specific PM sources to personal exposure and ultimately to health effects in upcoming epidemiological and toxicological studies in the LA Basin (Fine et al., 2004b).

## ***FROM EXPOSURE TO HEALTH EFFECTS***

### **Personal Exposure**

#### *PM<sub>2.5</sub>*

A number of PM Center studies were conducted to obtain a better understanding of the relationship of personal exposures to ambient and indoor concentrations of  $PM_{2.5}$ . A large panel study of Seattle residents (Liu et al., 2003) provided important information about daily average exposures of at-risk groups to  $PM_{2.5}$  and also about the relationship between personal exposures to  $PM_{2.5}$  and simultaneous measurements at fixed-site community monitors. This 3-year study involved 108 individuals with and without

chronic obstructive pulmonary disease (COPD), coronary heart disease (CHD), and asthma. Overall, the elderly healthy, COPD and CHD subjects had similar exposures. All three groups had lower PM<sub>2.5</sub> exposures than the asthmatic children. Within a given group, the PM<sub>2.5</sub> exposure varied with the subject's residences, due to the different particle infiltration efficiencies of different buildings. Although a wide range of longitudinal correlations between central site and personal PM<sub>2.5</sub> measurements were found, the longitudinal correlation for any given subject was closely related to the particle infiltration efficiency,  $F_{inf}$ , of their residence.

Allen et al. (2003) used a recursive mass balance model to estimate the 10-day average  $F_{inf}$  for individual residences of panel subjects. The average  $F_{inf}$  was  $0.65 \pm 0.21$  for 44 residences.  $F_{inf}$  differed significantly by season, being higher in the non-heating season. For the 44 study residences, outdoor-generated particles accounted for an average of  $79 \pm 17\%$  of the indoor PM<sub>2.5</sub> concentration, with a range of 40 to 100% at individual residences. In a subsequent analysis of 62 residences of panel subjects,  $F_{inf}$  was found to vary by: residence type (group homes > private residences); the presence of an air cleaner; and meteorological conditions (temperature and rainfall) (Koenig et al., 2005). The Seattle studies found that total personal exposure was poorly predicted by stationary outdoor monitors among persons whose PM<sub>2.5</sub> exposure was dominated by non-ambient sources, for example, those living in tightly sealed homes, those who cook, and active children (Allen et al., 2003).

Using a similar approach, Wu et al. (2004, 2005) studied children living in Alpine, CA. The contributions to the children's hourly, personal PM<sub>2.5</sub> exposure from outdoor sources, indoor sources and personal activity were 11.1, 5.5, and 10.0  $\mu\text{g}/\text{m}^3$ , respectively, when the modeling error was minimized. The high PM<sub>2.5</sub> exposure to personal activities was attributed to the children's more active lifestyle as compared with those of older adult subjects in previous studies.

Sheppard et al. (2005a, b) conducted a series of simulated acute health effects studies to examine the consequences of using the ambient concentrations measured at fixed sites in place of personal exposures measurements. They included important model parameters based upon the Seattle panel study results (Liu et al., 2003; Allen et al., 2003, 2004), including the distributions of  $C_0$ ,  $C_i$ ,  $\phi$ , and  $E_{ig}$ . Assuming that  $\phi$  (ambient PM<sub>2.5</sub> contribution fraction) does not vary with individual over time, they found no noticeable impact on the estimation of the effect estimate from the time-series model, even under the most restrictive condition that  $E_{ig}$  is independent of  $E_{ag}$ . However, when the value of  $\phi$  for each individual was allowed to vary with season, the time-series health effect estimates changed. They concluded that understanding the temporal variability in  $\phi$  is important to interpreting the results of time-series studies. They also concluded that the suggestion of using total personal exposure as the exposure metric of interest for acute time-series studies (NRC, 1998; Zeger et al., 2000) is not realistic, because daily personal measurements are needed for the entire study population. Using only a few individuals to estimate the daily average population exposure results in a highly attenuated health effect estimate, but it is possible to correct for this measurement bias using a measurement error model.

The relationship between ambient concentrations and personal exposures to PM<sub>2.5</sub> and gases was examined using data from Boston, MA and Steubenville, OH. These studies used similar methods and study designs to measure, over 24 hr periods, indoor,



outdoor, and personal PM<sub>2.5</sub> and gaseous levels (PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, EC, O<sub>3</sub>, NO<sub>2</sub>, and SO<sub>2</sub>) In Boston, study participants included 20 healthy senior citizens and 23 schoolchildren, while in Steubenville, study participants included 10 senior citizens. In both studies, personal exposure and ambient concentration data were analyzed using correlation and mixed model regression analyses to examine relationships between ambient and personal PM<sub>2.5</sub> and gaseous exposures.

Similar results were observed in Boston and Steubenville. In Boston, substantial correlations were found between ambient PM<sub>2.5</sub> concentrations and corresponding personal exposures over time. Additionally, these results supported the earlier finding that summertime gaseous pollutant concentrations may be better surrogates of personal PM<sub>2.5</sub> exposures, especially personal exposures to PM<sub>2.5</sub> of ambient origin, than surrogates of personal exposures to the gases themselves. PM<sub>2.5</sub> health effects studies that include both ambient PM<sub>2.5</sub> and gaseous concentrations as independent variables must be analyzed carefully and interpreted cautiously, since both parameters may be serving as surrogates for PM<sub>2.5</sub> exposures (Sarnat et al., 2006).

Similarly, in Steubenville, strong associations were found between ambient PM<sub>2.5</sub> concentrations and corresponding personal exposures as well as between ambient O<sub>3</sub> and NO<sub>2</sub> and their corresponding exposures. These associations, in particular those for O<sub>3</sub>, were highest for individuals spending the majority of their time in highly, as compared to poorly, ventilated environments. In cross-pollutant models, significant associations between ambient PM<sub>2.5</sub> concentrations and personal gas exposures were found, with particularly strong associations between ambient SO<sub>4</sub><sup>2-</sup> and personal O<sub>3</sub>, and between ambient EC and personal NO<sub>2</sub>. Findings that ambient gas concentrations reflect corresponding personal exposures have implications for air pollution epidemiology, suggesting that confounding of PM-associated health effects by gaseous pollutants may occur given the often strong correlations among the ambient pollutants. Furthermore, findings that ambient PM<sub>2.5</sub> may represent exposures to both PM<sub>2.5</sub> and gases, suggest that time-series health studies based on 24-hour ambient concentrations may not be able to separate the independent effects of PM<sub>2.5</sub> and gases.

### *PM<sub>2.5</sub> Components*

In addition to particle mass, a subset of the Seattle panel filters were analyzed for selected chemical species and positive matrix factorization was then used to identify five contributing sources: vegetative burning, mobile emissions, secondary sulfate, a source rich in chlorine, and a source of crustal-derived material. Vegetative burning contributed the majority of mass and BC in all samples. The indoor/outdoor ratios for vegetative burning and secondary source contributions varied significantly by residence, in agreement with the infiltration efficiencies derived using the recursive mass balance model approach (Allen et al., 2003). Personal exposure to the combustion-derived particles was correlated with outdoor sources, whereas exposure to the crustal and Cl-rich particles was not. Personal exposures to crustal source particles were strongly associated with personal activities, especially time spent at school among children, in agreement with a follow-up panel in Seattle (Jansen et al., 2005) that measured indoor, outdoor and personal levels of BC on a daily basis in adult subjects with asthma and/or COPD. There were good correlations between daily measures of indoor, outdoor and personal BC, but poor correlations between outdoor and personal PM<sub>10</sub>.

Lippmann et al. (2005) measured personal PM<sub>10</sub> exposures for a cohort of elderly COPD patients in New York City for twelve days in both summer and winter, and compared them with levels of PM<sub>2.5</sub> and PM<sub>10</sub> measured indoors, outdoors, and at a community air quality monitor. For all pollutant measures, personal concentrations tended to be higher and more variable than corresponding indoor and ambient concentrations in both seasons, and the mean indoor concentrations tended to be higher than co-located outdoor concentrations. Particle concentrations showed some degree of seasonal variation, and had larger variability in summer months compared to winter months. Indoor and personal concentrations were higher in the summer as compared to winter for each of the measured pollutants. In contrast, summer and winter outdoor measurements (residential outdoor and central site) tended to be comparable.

Data from Boston were analyzed to characterize the relationships between personal, home indoor, home outdoor and ambient levels of SO<sub>4</sub><sup>2-</sup>, EC, and PM<sub>2.5</sub> for a panel of sensitive individuals with either chronic CVD or COPD. Four main factors that were likely to affect personal exposures were investigated: time spent in key microenvironments, such as the home; infiltration into the home; spatial variability in home outdoor concentrations; and measurement error. This investigation was based on simultaneous 24-hour integrated personal, home indoor, and home outdoor PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, EC, O<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub> concentrations that were measured in 25 single-family homes in the Boston, MA area (Brown, 2006).

Ambient SO<sub>4</sub><sup>2-</sup> was strongly correlated with personal and home indoor SO<sub>4</sub><sup>2-</sup> for all individuals without an indoor source of SO<sub>4</sub><sup>2-</sup>. Associations were not as strong for EC and PM<sub>2.5</sub>, likely due to local and indoor sources of these pollutants. While the strength of the associations for SO<sub>4</sub><sup>2-</sup> varied between subjects and by season, outdoor or ambient SO<sub>4</sub><sup>2-</sup> accounted for approximately 80% or more of the variability in personal and indoor SO<sub>4</sub><sup>2-</sup> concentrations. Housing conditions, as indicated by the high indoor-outdoor SO<sub>4</sub><sup>2-</sup> correlations, tended to be quite similar day-to-day, indicating that home indoor and home outdoor levels correspond consistently regardless of the differences in the absolute levels in the two microenvironments. While ambient levels and indoor source contributions of

PM<sub>2.5</sub> can vary by day, the infiltration into homes appears to be relatively constant, at least during a one-week monitoring period (Brown, 2006).

Contrary to the results for SO<sub>4</sub><sup>2-</sup>, EC showed relatively weak associations between personal/indoor EC levels and outdoor/ambient levels. This result was likely due to indoor and local source generation of EC. Indoor EC concentrations explained only 50% of the variation in corresponding personal exposures, likely the result of exposures to EC that occurred outside the home, or of greater imprecision in the EC measurement method as compared to those for SO<sub>4</sub><sup>2-</sup> and PM<sub>2.5</sub>. Additionally, indoor-outdoor ratios were higher and more variable for EC than SO<sub>4</sub><sup>2-</sup>. This difference in ratios could include different infiltration rates, or a greater contribution of indoor sources of EC as compared to SO<sub>4</sub><sup>2-</sup>. Since relatively few homes had indoor-outdoor EC ratios greater than 1, indicating few indoor EC sources, the results suggest that differences in SO<sub>4</sub><sup>2-</sup> and EC infiltration was the more important factor. Differences in their infiltration may be related to corresponding differences in their particle size distributions (Seinfeld and Pandis, 1998). The results also indicate greater spatial variability in EC-related PM than for PM<sub>2.5</sub> or SO<sub>4</sub><sup>2-</sup>, for which outdoor concentrations were relatively uniform (Brown, 2006).

Particle infiltration is a key determinant of the indoor concentrations of ambient air PM. To address the issue of the influence of PM<sub>2.5</sub> composition on infiltration, a comprehensive indoor air monitoring study was conducted in 17 Los Angeles area homes (Sarnat, 2006). In this study, indoor/outdoor concentration ratios during overnight (non-indoor source) periods were used to estimate the fraction of ambient PM<sub>2.5</sub> remaining airborne indoors, or the particle infiltration factor ( $F_{INF}$ ), for PM<sub>2.5</sub>, its non-volatile (i.e., BC) and volatile (i.e., NO<sub>3</sub><sup>-</sup>) components, and particle sizes ranging between 0.02 and 10 μm.  $F_{INF}$  was found to be highest for BC (median = 0.84) and lowest for NO<sub>3</sub><sup>-</sup> (median = 0.18). The low  $F_{INF}$  for NO<sub>3</sub><sup>-</sup> was likely due to volatilization of NO<sub>3</sub><sup>-</sup> particles once indoors, in addition to depositional losses upon building entry. In addition, it was found that the  $F_{INF}$  for PM<sub>2.5</sub> (median = 0.48) fell between those for BC and NO<sub>3</sub><sup>-</sup>, reflecting the contributions of both particle components to PM<sub>2.5</sub>.  $F_{INF}$  varied with particle size, air exchange rate and outdoor NO<sub>3</sub><sup>-</sup> concentrations. The  $F_{INF}$  for particles between 0.7-2.0 μm in size was significantly lower during periods of high, as compared to low, outdoor NO<sub>3</sub><sup>-</sup> concentrations, suggesting that outdoor NO<sub>3</sub><sup>-</sup> particles fall in this size range, and that its volatilization influenced the size distribution of indoor particles. This study demonstrated that infiltration of PM<sub>2.5</sub> varies by component, and is lowest for volatile species such as NH<sub>4</sub>NO<sub>3</sub>. Thus, indoor PM<sub>2.5</sub> of ambient origin may differ from that outdoors with respect to composition and size distribution, especially when the outdoor concentration of volatile particle components is high. In addition, based on these results, SO<sub>4</sub><sup>2-</sup> particles may not be suitable proxies of particles of outdoor origin in areas with high concentrations of volatile PM<sub>2.5</sub>. Particle composition, therefore, may influence the ability for outdoor PM<sub>2.5</sub> concentrations to represent indoor and thus personal PM<sub>2.5</sub> exposures, and can ultimately influence observed epidemiologic relationships based on ambient monitoring data.

A study to evaluate contributions of vehicle generated UFP to indoor environments in close proximity to freeways in the absence of known indoor aerosol sources found that PN concentration I/O ratios showed a strong dependence on particle sizes, and was influenced by different ventilation mechanisms. Highest I/O ratios (0.6–0.9) were usually observed for larger UFP (70–100 nm), while the lowest I/O ratios (0.1–

0.4) occurred typically around 10–20 nm. The size distributions of indoor aerosols showed less variability than those of outdoor freeway aerosols. The penetration factors and deposition rates also varied significantly, depending on particle size, and agreed with literature data and theories for particles greater than 20 nm. For particles less than 20 nm, I/O ratios, penetration factors, and deposition rates did not follow the expected trend based on theoretical prediction, as a result of the unique, semi-volatile, nature of freeway UFP. Sub-50 nm particles from mobile sources are semivolatile, thus shrink to a smaller size (or evaporate completely) as they infiltrate indoors (Zhu et al., 2005).

## ***GENERATION AND CHARACTERIZATION OF PM FOR LABORATORY EXPOSURES***

### **Model Particles**

To perform human/animal exposure studies, there is a need for methods that can be used to generate high number concentrations of UFP with controllable compositions. The Palas spark discharge generator (Palas GFG 1000) generates “soot-like” particles for such studies. It is important to assess the chemical variability and reproducibility of the UFP produced using such techniques. Su et al. (2005) performed an on-line assessment of the chemical variability of individual UFP and fine (50–300 nm) particles produced by a Palas generator. The aerodynamic size and chemical composition of  $^{12}\text{C}$  and  $^{13}\text{C}$  elemental carbon (EC), composite iron–carbon ( $\text{Fe-}^{12}\text{C}$ ), and welding particles were analyzed using an ATOFMS. When using  $^{12}\text{C}$  electrodes, EC particles were produced with sizes peaking in the UFP mode and 96% of the mass spectra containing distinct  $\text{C}_n^+$  ( $n = 1\text{--}3$ ) envelopes at  $m/z$  12, 24, and 36. In contrast, the mass spectra of the particles generated from  $^{13}\text{C}$  labeled graphite electrodes showed 73% of the particles producing EC carbon ion cluster patterns at  $m/z$  13 ( $^{13}\text{C}^+$ ), 26 ( $^{13}\text{C}_2^+$ ), and 39 ( $^{13}\text{C}_3^+$ ), with additional OC species. Observed differences between the  $^{12}\text{C}$  and  $^{13}\text{C}$  particle spectra are most likely due to their different surface properties, with  $^{13}\text{C}$  particles more effectively adsorbing semivolatile organic species originating in the particle-free dilution air. Homogeneous metal particles were also generated from  $\text{Fe-}^{12}\text{C}$  and welding rods with almost all (92% and 97%, respectively) of the spectra showing reproducible Fe/Mn/Cr and  $\text{Fe}/^{12}\text{C}$  ion ratios.

### *Particle Concentrators*

The size, concentration enrichment, and chemical composition of coarse-mode ( $> 2.5 \mu\text{m}$ ) and fine-mode ( $< 2.5 \mu\text{m}$ ) particles within the non-concentrated and concentrated flows of a coarse particle concentrator used for human exposure studies have been characterized using an ATOFMS (Moffett et al., 2004) for fixed time intervals over the course of three days. The coarse particle concentrator was intended to concentrate ambient particles in the  $\text{PM}_{10-2.5}$  size range before sending them into a human exposure chamber. Based on the ATOFMS results, it was found that there was no change in the composition of the ten major particle types observed in the upstream and downstream flows of the concentrator under normal operating conditions. Furthermore, no new particle types were detected downstream that were not detected upstream. A characterization of the aerosol chemical composition and its dependence on sampling

conditions was also discussed. Aerosol size distributions were measured with three aerodynamic particle-sizing (APS) instruments sampling simultaneously from different regions of the concentrator. The APS size distributions were used to scale ATOFMS data and measure the ambient concentration factors for the coarse particle concentrator and the exposure chamber. The average concentration factor (ratio of inlet number concentration to the outlet number concentration) for the particle concentrator was  $60 \pm 17$  for the 2.5–7.2  $\mu\text{m}$  size range before dilution and transport to the exposure chamber. It was observed that not only were coarse particles being concentrated, but PM<sub>2.5</sub> was being concentrated as well, with concentration factors ranging from 2–46 for aerodynamic particle sizes from 0.54–2.5  $\mu\text{m}$ .

UFP concentrators have also been used in PM health effects studies in an effort to control exposure levels to ambient aerosols over a broad enough concentration range. An ATOFMS was used to characterize individual concentrated UFP and fine (100–300 nm in aerodynamic diameter) PM from several UFP concentrators (Su et al., 2005). Experimental results showed that particles undergo chemical changes during the enrichment processes at super-saturation ratios of 3.0 or lower. Comparing the relative fractions of particle types in concentrated versus non-concentrated ambient airstreams, a decrease was observed in nominally fresh EC particles relative to EC particles coated with OC after undergoing the concentration process. An increase in the number fraction of aromatic- and polycyclic aromatic hydrocarbon-containing particles was also observed in both the UFP and the fine mode. Such changes are attributable to gas-to-particle partitioning (e.g. water-soluble organic compounds) onto pre-existing UFP and fine particles during the particle enrichment process, which involves super-saturation, condensation, desolvation, and evaporation for particle growth and size restoration. In addition, during the morning hours in Rochester, NY, aqueous phase sulfur chemistry occurred in the concentrated particles, as indicated by the presence of hydroxymethanesulfonate (HMS), an indicator commonly used to indicate fog processing in ambient aerosols.

Two different particle mass spectrometers, the Aerodyne (AMS) and the UC Davis RSMS-3, were used to evaluate the performance of the Versatile Aerosol Concentration Enrichment System (VACES) developed by USC. The Rapid Single-particle Mass Spectrometer (RSMS-3) experiments were conducted as part of the EPA Supersite program in Pittsburgh during March 2002. RSMS-3 hit rate increases were measured, and possible particle composition changes introduced by the VACES were examined in the single particle mass spectra. Both ambient and concentrated carbonaceous and ammonium nitrate composition distributions were indistinguishable with RSMS-3, suggesting that VACES introduces an insignificant artifact for those particles (Zhao et al., 2005). The effect of concentrating semi-volatile aerosols using the VACES and the AMS during measurements of ambient aerosol in Pittsburgh, PA was also investigated. It was found that the shape of the  $\text{SO}_4^{2-}$  mass-weighted size distribution was approximately preserved during passage through the concentrator for all the experiments performed, with a mass enhancement factor of about 10 to 20 depending on the experiment. The size distributions of OC, ammonium and  $\text{NO}_3^-$  were preserved on a relatively clean day ( $\text{SO}_4^{2-}$  concentration around  $7 \mu\text{g}/\text{m}^3$ ), while during more polluted conditions the concentration of these compounds, especially  $\text{NO}_3^-$ , was increased at small sizes after passage through the concentrator. The amount of the extra material, however,

was found to be rather small: between 2.4% and 7.5% of the final concentrated PM<sub>2.5</sub> mass is due to “artifact” condensation (Khlystov et al., 2005).

A subchronic animal inhalation study using an ambient particle concentrator addressed the issues of composition and sources of ambient PM<sub>2.5</sub>, as well as the relationship of these PM<sub>2.5</sub> characteristics to the cellular response of human bronchial epithelial cells (Maciejczyk and Chen, 2005). An *in vitro* exposure technique was used to compare the daily variations of the responses of cells to fine CAPs collected from a rural area upwind of New York City for the period of 9 a.m. to 3 p.m. on weekdays only, March–September 2003. Chemical composition data for CAPs were modeled using factor analysis, with Varimax orthogonal rotation, to determine four particle source categories contributing significant amount of mass to CAPs at Sterling Forest (Tuxedo, NY). These source categories are: (1) regional secondary sulfate characterized by high S, Si, and OC; (2) resuspended soil characterized by high concentrations of Ca, Fe, Al, and Si; (3) oil-fired power plants emissions of the eastern United States identified by presence of V, Ni, and Se; and (4) unknown other sources. To estimate the mass contributions of each individual source category, the CAPs mass concentration was regressed against the factor scores. Regional SO<sub>4</sub><sup>2-</sup> was the largest contributor to mass (65%), followed by soil (20%), residual oil combustion (2%), and the other sources contributing 13%.

## **CONCLUSIONS**

The research conducted at the EPA PM Centers on exposures has provided a substantial body of new data indicating that:

- Spatial correlations over large metropolitan areas are relatively high (~0.6) for O<sub>3</sub>, NO<sub>2</sub>, PM<sub>10</sub> and PM<sub>2.5</sub>
- Spatial correlations over large metropolitan areas are relatively low (~0.6) for CO and SO<sub>2</sub>.
- Spatial correlations over short distances can be very low for black carbon and for UFP
- Semi-volatile components in ambient air can move from fine PM to coarse PM over time, especially in warm months
- Reactive oxygen species (ROS) are found in particles ranging in size from UFP to coarse PM, and are found in larger concentrations influenced by photochemical reactions
- PM source categories were shown to be significant predictors of relative risks in epidemiological studies
- PM<sub>2.5</sub> exposures of asthmatic children were higher than those of healthy people, and subjects with coronary heart disease and chronic obstructive pulmonary disease.

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