CHARACTERIZATION OF THE COMPOSITION OF PERSONAL, INDOOR, AND OUTDOOR PARTICULATE EXPOSURES

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DISCLAIMER

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ABSTRACT

A study entitled "Characterization of the Composition of Personal, Indoor, and Outdoor Particulate Exposures" was conducted to characterize the chemical composition of personal, indoor, and outdoor fine particulate ($PM_{2.5}$) exposures for individuals with chronic obstructive pulmonary disease (COPD) living in the Los Angeles, CA region. This study was conducted in conjunction with a study funded by the U.S. Environmental Protection Agency (EPA).

In the first study phase, mini-speciation samplers to measure fine particle nitrate (NO_3^-) and EC were validated in field experiments, which showed that both mini-samplers performed well. These mini-samplers were subsequently used with our multi-pollutant sampler to characterize fine particulate exposures for 22 individuals with COPD. For each individual, 24-hr personal, indoor and outdoor PM_{10}, $PM_{2.5}$, and fine particle NO_3^-, elemental carbon (EC) and elemental concentrations were measured. [O_3, SO_2, and NO_2 were measured as well as part of our companion EPA study as were PM_{10} and $PM_{2.5}$.] Measurements were made for each individual over seven days during either or both summer of 1999 and winter of 2000.

Personal, indoor, and outdoor $PM_{2.5}$, NO_3^- and EC concentrations varied by season, with the exception of outdoor NO_3^- concentrations for which no seasonal difference was observed. Personal $PM_{2.5}$ exposures were higher than corresponding indoor and outdoor concentrations in both seasons. In contrast, outdoor NO_3^- and EC concentrations were in general higher than indoor and personal levels in both seasons, which may be due to the fact that motor vehicles are their major source and the high reactivity of NO_3^-, which may result in losses of NO_3^- indoors. Indoor concentrations for all three particulate measures were more strongly associated with personal exposures as compared to outdoor concentrations, which may be attributed to the facts that individuals spent most of their time indoors at home. Correlations among personal, indoor, and outdoor concentrations, however, generally varied by season and by particulate measure. In addition, the individual-specific correlations and longitudinal relationships were consistent with those observed in other studies conducted in Western U.S. and Canada. For $PM_{2.5}$ and EC, for example, the effective penetration efficiency and the indoor source contribution varied by season, with a greater effective penetration efficiency in the summer and a greater indoor pollutant source contribution in the winter. The average contribution of NO_3^- and EC to $PM_{2.5}$ varied by season and by sample type. For personal, indoor, and outdoor samples, both NO_3^- and EC comprised a relatively small proportion of the overall $PM_{2.5}$ mass, demonstrating the need to measure concentrations of other particle components to account for more of the $PM_{2.5}$ mass.

Analysis of the $PM_{2.5}$ filters showed limited ability of ICP-MS to detect elemental concentrations at the low sampling flow volumes used in our study. Of the detectable elements (Al, B, Ba, Cr, Mn, Ni, Pb, Zn), personal, indoor, and outdoor concentrations varied seasonally. Except for Al, significant and positive correlations between personal exposures and corresponding indoor and outdoor concentrations were observed in both seasons. Of the elements, Ba and Ni displayed the strongest associations between personal exposures and indoor and outdoor concentrations, and Al the weakest associations. The magnitude and strength of the associations generally differed by element and also differed from those observed for $PM_{2.5}$. Despite this, significant positive correlations between mass and elemental concentrations were found, with associations strongest in both seasons for indoor and outdoor samples as compared to personal samples.

EXECUTIVE SUMMARY

Background. A study was conducted to characterize the chemical composition of personal, indoor, and outdoor fine particulate ($PM_{2.5}$) exposures for a cohort of individuals with chronic obstructive pulmonary disease (COPD) living in metropolitan Los Angeles, California. This study was specifically intended to test three hypotheses: (1) that the composition of personal and indoor $PM_{2.5}$ exhibits significant inter- and intra-personal variation; (2) the relationship between personal and outdoor concentrations differs for each particulate component; and (3) the composition of personal and indoor $PM_{2.5}$ and its relationship to that outdoors differs for individuals with COPD living in Los Angeles as compared to those living in other cities. By testing these hypotheses, our study addresses a critical research question concerning the use of stationary ambient monitoring (SAM) site measurements to estimate exposures in epidemiological studies. The use of these SAM site measurements is known to estimate exposures for study populations imperfectly; however, the impact of this exposure error on the exposure-effect associations in epidemiological studies is not well understood, especially for specific $PM_{2.5}$ components and for Western U.S. populations. To address these research needs, our study characterized the relationship among indoor, outdoor, and personal concentrations of $PM_{2.5}$ – and most importantly its chemical components – for a cohort of sensitive individuals. It was the first study to characterize these relationships in the Western U.S. and among the first to focus on sensitive individuals. Results from this study provide information that improves (1) our understanding of exposures to fine particulate NO_3^-, EC and the elements, (2) our ability to assess the impacts of exposure error in epidemiological studies conducted in the Western U.S., and (3) our knowledge about the contribution of indoor and outdoor sources to $PM_{2.5}$ exposures.

Methods. Recently developed mini-samplers to measure fine particle NO_3^- and fine particle EC concentrations were validated in field experiments. Once validated, mini-samplers were used to modify our multi-pollutant sampler to allow $PM_{2.5}$ components, NO_3^-, EC, and the elements to be measured simultaneously with PM_{10}, $PM_{2.5}$, and gaseous pollutants that were measured as part of our EPA-sponsored study. In total, 24-h indoor, outdoor, and personal PM_{10}, $PM_{2.5}$, fine particle NO_3^-, EC, and elements, SO_2, NO_2, and O_3 concentrations were measured for 22 individuals with COPD living in the Los Angeles, CA area. Measurements were made for each individual for seven 24-hr periods in either or both Summer 1999 and Winter 2000. Activity, housing characteristics and air exchange rate data were also collected for each home and monitoring day. Data were analyzed statistically using a variety of techniques, including descriptive summaries, correlation coefficients, generalized linear models, and micro-environmental exposure models. Statistical methods were selected based on the research question and the underlying structure of the data. Note that summer PM_{10} and gaseous pollutant data were not included in these analyses due to filter contamination and data unavailability issues, respectively.

Results. The NO_3^- and EC fine particle mini-samplers performed well. For NO_3^-, when mini-PEM concentrations were regressed on the reference HI concentrations, an R^2 of 1.0, a slope of 1.04 (±0.02), and a non-significant intercept was observed. Regression of the mini-sampler EC on the reference ChemComb concentrations resulted in a slope of 1.08 (±0.05), a non-significant intercept, and an R^2 of 0.62. The relatively low R^2 value may be due to the fact that samples were collected over a narrow range in ambient EC levels. In the exposure study, when EC concentrations were more varied, the accuracy of the EC mini-sampler was substantially higher.

Personal, indoor, and outdoor $PM_{2.5}$, NO_3^- and EC concentrations varied by season, with the exception of outdoor NO_3^-, for which no seasonal difference was found. Mean (19.6, 25.1 ug/m^3) and maximum (63.5, 137.8 ug/m^3) personal $PM_{2.5}$ exposures were higher than mean (16.9, 18.1 ug/m^3) and maximum (49.5, 94.8 ug/m^3) indoor and outdoor (mean=13.5, 19.3; max=56.5, 53.5 ug/m^3) levels in winter and summer, respectively. For NO_3^- and EC, higher outdoor (2.8-3.1 ug/m^3), as compared to indoor (1.1-1.7 ug/m^3) and personal (1.2-1.6 ug/m^3) levels, were found in both seasons, reflecting the fact that motor vehicles are their major source and that loss of NO_3^- may occur indoors due to its high reactivity. NO_3^- and EC comprised a small fraction of personal, indoor, and outdoor $PM_{2.5}$ (max. 28.5% and 17%, respectively), demonstrating the need to measure additional $PM_{2.5}$ components to account for more of its mass.

Personal exposures to $PM_{2.5}$, NO_3^- and EC were significantly correlated with indoor and outdoor levels in both seasons. Similarly, indoor-outdoor associations for all three particulate measures were significant and varied by season. For $PM_{2.5}$ and EC, the effective penetration efficiency was greater in the summer, with a higher indoor source contribution in the winter. The opposite seasonal pattern was observed for NO_3^-. Personal $PM_{2.5}$, NO_3^- and EC exposures were more strongly associated with indoor as compared to outdoor levels, which may be attributed to the facts that individuals spent most of their time indoors at home. Of the measurable fine particle elements (Al, B, Ba, Cr, Mn, Ni, Pb, Zn), Al had the highest personal, indoor and outdoor levels. Personal exposures to Al, however, were not significantly correlated to indoor and outdoor concentrations. Personal exposures for the other detected elements were positively correlated to indoor and outdoor concentrations in both seasons, with patterns generally differing from those observed for $PM_{2.5}$. In both seasons, associations between mass and elemental levels tended to be weakest for personal exposures as compared to indoor and outdoor concentrations.

Conclusions. EC and NO_3^- comprised small fractions of total $PM_{2.5}$ in personal, indoor, and outdoor environments. Personal $PM_{2.5}$ and EC exposures were significantly associated with indoor and outdoor levels, with the associations strongest in the summer when air exchanges rates are high. These findings suggest that the relationships among personal, indoor, and outdoor concentrations for EC are similar to those for $PM_{2.5}$, which may result from the fact that the major sources for both pollutants are outdoors. NO_3^- associations, while also significant, showed an opposite seasonal pattern for personal-outdoor comparisons and no seasonal pattern for indoor-outdoor comparisons, which may be related to the reactivity of NO_3^- in indoor and personal environments. Similarly, the relationship among personal, indoor, and outdoor elemental concentrations differed by element and season and from that observed for $PM_{2.5}$. Results suggest that $PM_{2.5}$ components may behave differently from total $PM_{2.5}$, with these differences greatest for reactive pollutants such as NO_3^-.

Recommendations. Further research should be conducted to (1) develop methods to detect elemental concentrations at the low sampling air volumes used in this and other exposure studies, (2) characterize personal $PM_{2.5}$, EC, and NO_3^- exposures in other cities and for other sensitive populations, and (3) identify factors affecting personal-outdoor $PM_{2.5}$ associations to explain why associations in Los Angeles are lower than those in the eastern U.S, including possible loss of NO_3^- and other semi-volatile particles from the $PM_{2.5}$ filters. Additional research should also be conducted to quantify the contribution of various sources to $PM_{2.5}$, EC, and NO_3^- exposures; however, such research should be conducted using more active study populations.

BODY OF REPORT

INTRODUCTION

Epidemiological studies have consistently found an association between currently observed ambient particle concentrations with daily mortality, as well as with a range of morbidity indicators, including hospital admissions, emergency room visits, symptom exacerbation in asthmatics, and lung function decrements (Dockery *et al.*, 1993; Pope, 1991; Pope *et al.*, 1995; Schwartz *et al.*, 1992). These associations have been demonstrated primarily with total suspended particles and PM_{10}, in large part because concentration data for these particles have been historically available. Recent time-series studies support these findings and further suggest that fine particles ($PM_{2.5}$) are the particle component responsible for the observed increases in mortality and morbidity (Schwartz *et al.*, 1997).

Nonetheless, results from these health studies have been the subject of considerable controversy. Much of the controversy surrounding these studies is focused on the use of outdoor concentrations measured at a single stationary ambient monitoring (SAM) site to estimate exposures. The use of these SAM site measurements is known to impact the exposure-effect associations observed in epidemiological studies; however, there is wide disagreement about the magnitude and the direction of its impact. This disagreement has been difficult to resolve, since the relationship between personal PM_{10} and $PM_{2.5}$ exposures and outdoor concentrations is not well understood (Janssen, 1998). Even less is known about the chemical composition of $PM_{2.5}$ in indoor and personal environments.

Research indicates that personal PM_{10} and $PM_{2.5}$ exposures differ from corresponding outdoor concentrations. Results from the Particle Total Exposure Assessment Methodology (PTEAM) study, for example, showed 12-hr daytime personal PM_{10} exposures to be on average 50% higher than corresponding ambient levels (Thomas *et al.*, 1993; Clayton *et al.*, 1993), while the Six City study found mean personal PM_{10} exposures to be more than 100% greater than mean ambient levels (Spengler *et al.*, 1985). Personal PM_{10} and $PM_{2.5}$ exposures were also higher than outdoor levels in our previous studies of individuals with chronic obstructive pulmonary disease (COPD) (Bahadori *et al.*, 1996), a cohort identified by epidemiological studies to be at risk from particulate exposures (Bascom *et al.*, 1996). Findings from our follow-up Boston study further showed that the relationship between personal exposures and outdoor concentrations varied substantially by individual. Linear regressions of personal $PM_{2.5}$ exposures on outdoor concentrations by individual yielded coefficients of determination that ranged from 0.01 to 0.87 (Rojas *et al.*, 2000), with only about half (10 of 17) of the monitored individuals showing statistically significant associations between personal exposures and outdoor concentrations. Slopes of the regression lines of personal on outdoor concentrations also varied substantially, ranging from 0.5 to 1.6 for individuals with significant associations. The observed inter- and intra-personal differences in the relationship between personal and outdoor concentrations are consistent with findings from other studies conducted in the eastern U.S. (Lioy *et al.*, 1990). In each of these studies, the inter- and intra-personal variability was attributed to the importance of indoor particulate exposures and the presence of a personal particulate cloud. The importance of both factors is likely to differ substantially by particulate components and by activity patterns. However, the relative influence of these factors has been explored in only a few studies to date.

Based on the findings and our experiences from these and other studies, EPA provided funds to our group to continue researches examining the relationship between personal particulate and gaseous exposures and corresponding outdoor concentrations. This EPA-sponsored study built upon findings from our earlier studies and expanded this investigation to other areas of the U.S. and to other sensitive subgroups. As part of our EPA-sponsored study, personal particulate and gaseous exposures were characterized for individuals with COPD living in Atlanta, GA and Los Angeles, CA – cities characterized by diverse climates and air pollutant profiles. Individuals with COPD were chosen as the population of interest based on findings from epidemiological studies that have consistently shown associations between ambient $PM_{2.5}$ and exacerbation and incidence of existing chronic obstructive pulmonary disease (COPD) (including chronic bronchitis and emphysema) (Schwartz and Dockery, 1992; Schwartz et al., 1996; Pope et al., 2000; Sunyer, 2001). Personal particulate and gaseous exposures were also characterized for asthmatics and for individuals with myocardial infarctions living in Boston, MA. The Atlanta field studies took place during the fall of 1999 and the spring of 2000, while field data collection for both of the Los Angeles and Boston field studies were completed during winter of 1999-2000 and summer of 2000.

In each of these cities and for each sensitive subgroup, repeated 24-hr outdoor, indoor, and personal particulate mass (PM_{10} and $PM_{2.5}$) and gaseous (CO, SO_2, NO_2, O_3) measurements were made for 15 individuals using our multi-pollutant sampler (Table 1). Each of these individuals was monitored for seven days in both the summer and winter months, with three individuals monitored each week. Air exchange rates were measured in these homes over 24-hr periods, as were corresponding time-activity and housing characteristics information.

Our CARB-sponsored study supplements measurements made as part of our EPA-sponsored study by including personal, indoor, and outdoor measurements of the major components of $PM_{2.5}$, including fine particle nitrate (NO_3^-), elemental carbon (EC), organic carbon (OC), and the elements. NO_3^-, EC, OC, and the elemental concentrations were measured using mini-samplers with a $PM_{2.5}$ size-selective inlet that were recently developed by our group and that were validated as part of this study. These mini-samplers were added to our previously developed multi-pollutant sampler (Chang *et al.*, 1999), and are small in size and operate at low flow rate. As a result, the modified multi-pollutant samplers provided not only simultaneous measurements of PM_{10}, $PM_{2.5}$, and several criteria gases, but also of the major personal $PM_{2.5}$ components (EC, OC, NO_3^-, elements) as well.

These measurements for particle components were used to characterize the chemical composition of personal, indoor, and outdoor $PM_{2.5}$ and to examine the inter- and intra-personal variability in the relationship between personal exposures and indoor and outdoor concentrations for these fine particle components. Specifically, the study addressed the following hypotheses that the:

- composition of personal and indoor $PM_{2.5}$ exhibits significant inter- and intra-personal variation;
- relationship between personal exposures and corresponding outdoor concentrations differs for each particulate component; and
- composition of personal and indoor $PM_{2.5}$ and its relationship to that outdoors differs for individuals with COPD living in Los Angeles as compared to those living in other cities.

Table 1. EPA-sponsored and CARB-sponsored Study Measurements

Measurement	**Study Sponsor**	
	EPA	**CARB**
Personal (24-hr):		
PM_{10}, $PM_{2.5}$	✓	
O_3, SO_2, NO_2[1]	✓	
EC, OC		✓
NO_3^-		✓
Elements		✓
Time-activity diaries	✓	
Indoors (24-hr): Homes		
PM_{10}, $PM_{2.5}$	✓	
O_3, SO_2, NO_2[1]	✓	
EC, OC		✓
NO_3^-		✓
Elements		✓
Integrated air exchange rates	✓	✓
Housing characteristics	✓	
Outdoors (24-hr): Home sites		
PM_{10}, $PM_{2.5}$	✓	
O_3, SO_2, NO_2[1]	✓	
EC, OC		✓
NO_3^-		✓
Elements		✓
Outdoors (24-hr): SAM Site		
PM_{10}, $PM_{2.5}$	✓	
O_3, SO_2, NO_2[1]	✓	
EC, OC	✓	
NO_3^-	✓	
Elements	✓	

[1] Personal, indoor, and outdoor gas data are the responsibility of co-investigators at Rutgers University, as specified in our EPA Cooperative Agreement. As a result, gas data are not currently available for inclusion in this report.

The study addressed these hypotheses, by:

- validating small speciation monitors to measure fine particle nitrate and elemental and organic carbon concentrations in a field study conducted in Los Angeles, CA,
- characterizing the chemical composition of personal $PM_{2.5}$ exposures,
- examining the inter- and intra-personal variability in the relationship between outdoor concentrations and personal exposures for each of the measured particulate species,
- characterizing the magnitude and variability in
    - personal exposures and indoor concentrations for each of the measured particulate species,
    - the relationship among personal, indoor and outdoor concentrations for each particulate measure,
- identifying factors, including personal activities and housing characteristics, that are important predictors of personal exposures and their relationship with ambient concentrations for each of the particulate species, and
- qualitatively comparing the PM mass measurements to those obtained in other particulate exposure studies conducted in Baltimore, MD, Boston, MA, and Fresno, CA.

Note that as originally proposed, results from this study were to be compared to results obtained from our companion EPA-funded studies conducted in Boston, MA and Atlanta, GA. Data from these studies are, however, not yet available. As a result, qualitative comparisons were made using data obtained in earlier exposure studies conducted in Baltimore, MD and in Boston, MA by our group and in Fresno, CA by EPA.

MATERIALS AND METHODS

The primary objective of the study was to characterize the composition of personal, indoor, and outdoor $PM_{2.5}$ for a panel of individuals with COPD. To achieve its objective, the study was performed in two phases, with the first phase to validate the performance of two new $PM_{2.5}$ speciation mini-samplers and the second phase to use the validated speciation samplers to determine the composition of personal, indoor, and outdoor $PM_{2.5}$ for individuals with COPD living in metropolitan Los Angeles, CA. The second phase of the study was performed in conjunction with our EPA-sponsored exposure study of these same individuals.

Personal, indoor, and outdoor air pollutant concentrations for individuals with COPD were measured using a modified multi-pollutant sampler, which was originally developed to measure $PM_{2.5}$, PM_{10}, and the gases O_3, SO_2, and NO_2 concentrations simultaneously (Chang *et al.*, 1999; Sarnat *et al.*, 2000). The multi-pollutant monitor was modified as part of this study to include two recently developed mini-speciation samplers to measure fine particle nitrate, EC and OC. In addition, the $PM_{2.5}$ filters were acid washed to allow elemental analysis of the collected $PM_{2.5}$ filters by ICP-MS for this study.

The two new mini-samplers measure fine particle nitrate and EC and OC using the multi-pollutant sampler pump. Both mini-samplers operate at flow rates of 0.8 liter per minute (LPM). To maintain high sensitivity at these low sampling flow rates, the samplers use small diameter filters (12 mm) to collect fine particles. To allow flow through these mini-samplers, the flow from the pump is split into four-ways: 1.8 LPM through each of the $PM_{2.5}$ and PM_{10} samplers and 0.8 LPM through the two mini-samplers. Impaction plates of both mini-samplers are greased to improve particle collection efficiency and to provide a sharp particle cut-point.

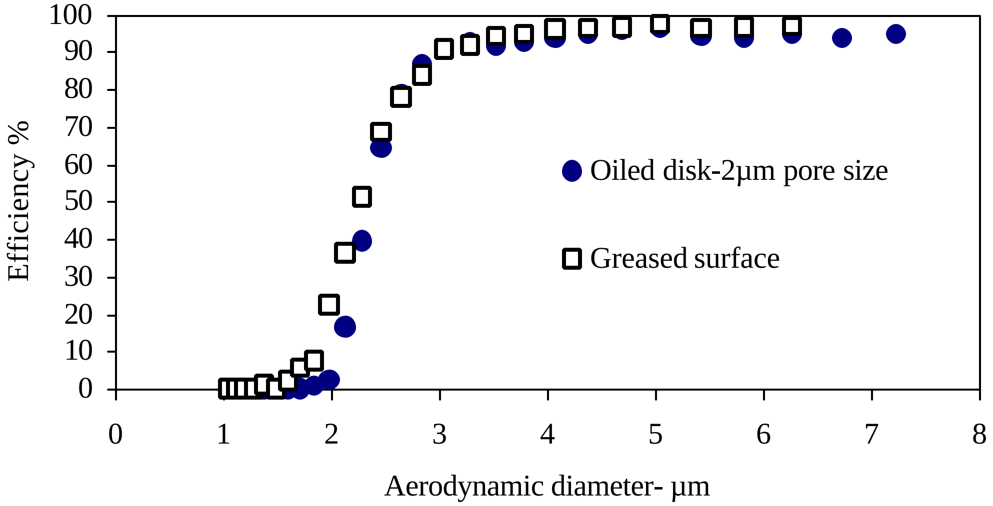
Phase I: Validation of Inorganic Ion and EC/OC Samplers

In Phase I of the study, the performance of the fine particle NO_3^- and elemental/organic carbon mini-samplers was evaluated in a series of validation tests.

Mini-samplers. Both samplers are miniaturized versions of commonly used methods. The NO_3^- mini-sampler is comparable to the honeycomb denuder/filter pack system (HDS) (Koutrakis *et al.*, 1988; Koutrakis *et al.*, 1994). Like HDS, the NO_3^- mini-sampler consists of an inlet-impactor section to remove coarse particles followed by a sodium carbonate (Na_2CO_3)-coated glass honeycomb denuder to collect acidic gases – nitric acid, nitrous acid, and SO_2.
A 12 mm, Na_2CO_3-coated glass fiber filter located downstream of the denuder collects NO_3^-. After sampling, filters are extracted in 1.0 ml of solution. Extracts are analyzed for NO_3^- using ion chromatography.

The EC/OC mini-sampler consists of an inlet-impactor section to remove coarse particles followed by a single quartz fiber filter. After sampling, the filter is analyzed by thermal optical reflectance (TOR). This design follows the recommendations of the EPA Expert Panel on Speciation (U.S. EPA, 1998), which concluded that the impact of a denuder or a second quartz fiber filter on method performance is unknown.

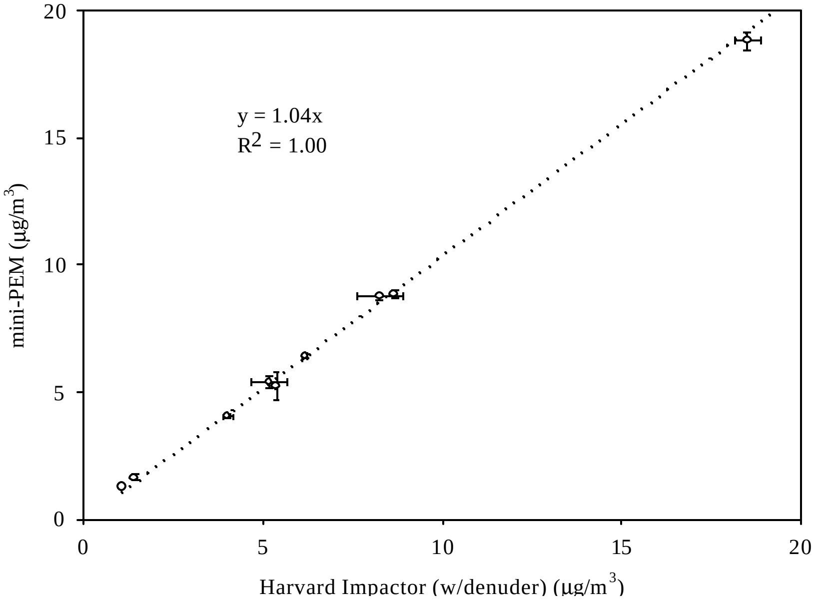
Figure 1. Particle Impaction Efficiencies for the Mini-Speciation Samplers



Laboratory Performance. The performance of the mini-samplers was shown to be high in a series of laboratory studies conducted by our group (Demokritou *et al.*, 2001a). Results from these laboratory tests show a collection efficiency of almost 100% for particles with aerodynamic diameters greater than 2.5µm (Figure 1), indicating that the sampler collects only those particles with size under 2.5 µm. Greased and oil impaction surfaces were used in these analyses to examine their effect on particle bounce. Although not shown on this figure, later tests showed that greased impaction surfaces performed better, with minimal particle bounce (Demokritou et al., 2001a,b). The 50% cut-point of the sampler was determined experimentally to have a geometric mean of 2.4 (±0.1) µm. Particle nozzle and wall losses for particles smaller than 2.5 µm were small, equaling approximately 10%.

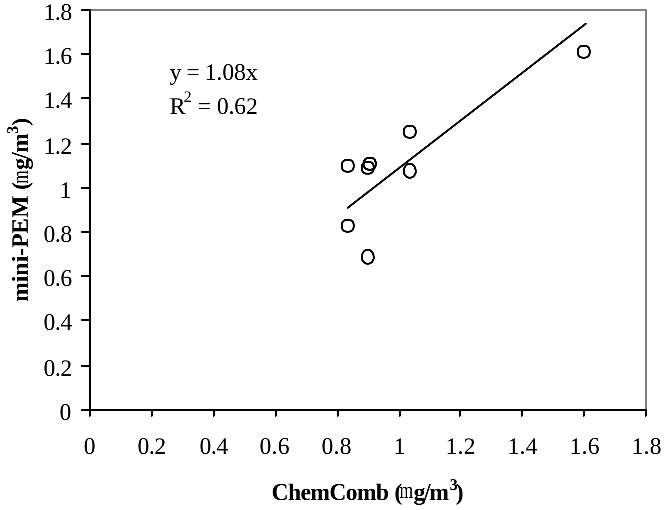
Field Validation. Prior to the start of the field study, the performance of the nitrate mini-sampler was further evaluated. Field validation tests were performed in the backyard of a home located in Irvine, CA, in December 1999. In these tests, nitrate concentrations were measured using mini-samplers and reference Harvard Impactors (HI), which were comprised of an inlet-impaction section to remove particles larger than 2.5 um, a coated honeycomb denuder to remove acidic gases, and a Na_2CO_3-coated glass fiber filter to collect nitrate. Nitrate concentrations were measured with each of these systems for ten 24-hr sampling periods under two distinct weather patterns: (1) mild and clear and (2) cool and rainy. During each sampling period, three mini-sampler and two HI reference nitrate samples were collected. Results from the nitrate field tests showed that the mini-samplers performed excellently (Figure 2), with an R^2 of 1.0, a slope of 1.04 (±0.02), and a non-significant intercept when mini-PEM were regressed on HI concentrations.

Figure 2. Mini-PEM vs. HI Nitrate Concentrations: December 1999



The performance of the EC/OC mini-sampler was evaluated in Boston, MA in January 2000. 24-hr EC/OC concentrations measured by the mini-sampler were compared to those measured using the reference ChemComb, which consists of a cartridge that contains a $PM_{2.5}$ inlet with impactor, two honeycomb denuders for the removal of selected gases, and a four-stage 47mm diameter filter pack for the collection of particle-related components (Demokritou *et al.*, 2001b). Although the sample size was small (n=9), results of the EC comparison tests showed that the mini-sampler performed well, with a slope of 1.08 (±0.05), a non-significant intercept, and an R^2 of 0.62 (Figure 3). The relatively low R^2 value may be attributed to the fact that samples were collected over a relatively narrow range in ambient EC levels.

Figure 3. Mini-PEM vs. ChemComb EC Concentrations: January 2000



Phase II: Multi-Pollutant Exposure Characterization for Panel of Individuals with COPD

Phase II of the study was conducted jointly with our EPA-sponsored study characterizing the particulate and gaseous exposures of 15 individuals with COPD living in metropolitan Los Angeles in each of the two sampling seasons. For these individuals, indoor, outdoor home, and personal $PM_{2.5}$, PM_{10}, NO_3^-, EC, and OC samples were collected over multiple 24-hour monitoring periods. Elemental levels were also determined in this study by analyzing each of the collected $PM_{2.5}$ filters by ICP-MS. As part of the EPA-sponsored study, corresponding 24-h indoor, outdoor, and personal O_3, SO_2, and NO_2 measurements also were made during each monitoring period at the participants' homes. In addition, 24-h $PM_{2.5}$, PM_{10}, fine particle NO_3^-, fine particle EC, fine particle OC, O_3, SO_2, and NO_2 measurements were also made at a stationary ambient monitoring (SAM) site located on the rooftop of a South Coast Air Quality Management District monitoring site in Hawthorne, CA. These measurements were made at the Hawthorne SAM site specifically for this study and were made to correspond to each monitoring day of the study. Information about housing characteristics, time-activity patterns, and air exchange rates also were collected for each home and monitoring day. Samples were collected in the winter (February 11–March 22) and summer (June 12–July 24) of 2000.

Samples were collected over five weeks in each season, with three individuals measured each week, for a total of 30 personal-week sampling sessions. Multi-pollutant samples were collected for seven days for each subject, except for one subject (LPD-01A) who was monitored for only 5 sampling days. In total, 105 $PM_{2.5}$, fine particle EC/OC, and fine particle NO_3^- samples were collected for each of the personal, indoor, and outdoor home measurements in each season. Field blanks were collected for approximately 10% of the total samples. These field blanks accompanied actual samples to the field and were stored and analyzed with study samples. Field blank concentrations were used to determine detection limits. Independent standards, not used for calibration, were analyzed to examine analytical accuracy. In addition, a blind, inter-laboratory audit was conducted to evaluate the ability of the laboratories to conduct ion chromatography, gravimetric, and elemental analyses. Replicates were collected for each measured particulate species to determine sampler precision, with the number of replicates for each species equaling approximately 10% of the total number of samples. Multi-pollutant samplers were also co-located with reference monitors (used specifically for this study) at the Hawthorne SAM to determine sampler accuracy and precision.

Study participant recruitment and profile. A total of 22 individuals with COPD were monitored as part of this study (Table 2), with eight of these individuals participating in both the winter and summer seasons. Although women were not preferentially targeted for participation in the study, the participants were predominantly female, with 19 of the 22 people being women. As mentioned above, individuals with COPD were selected for the study participation based on the fact that they may be particularly sensitive to $PM_{2.5}$ exposures. Participants lived in several communities within metropolitan Los Angeles. Most of the participants lived in coastal communities, located southwest of downtown Los Angeles. Four individuals lived in inland areas (Figure 4). In general, inland participants lived in areas with higher population densities and closer to major roads and were preferentially recruited due to the historically higher air pollutant levels found in these inland communities. Although age information was not available for each participant, participants were older, ranging in age from 55 to 84 years old. [Study questionnaires and diaries were administered as part of the EPA-sponsored study, and as a result, were approved by the U.S. Office of Management and Budget (OMB). To obtain this approval, the number of questions asked on the questionnaires and diaries were limited to minimize the burden to study participants.] Participants were reimbursed $150 for each 7-day monitoring period to compensate them for their time and also for any electricity used during the course of the study.

Participants were recruited based on their self-reported status of moderate-to-severe physician-diagnosed COPD. Some with less severe COPD worked part-time, and others used supplemental oxygen. Participants were recruited mainly through Little Company of Mary Hospital and an exercise and rehabilitation center, both of which were located in Torrance, CA. At both facilities, field coordinators attended a luncheon, which was attended by approximately 30 and 5 individuals at the Hospital and rehabilitation center, respectively. At these luncheons, introductions were made, the study was described, and informational flyers were given to attendees. The personal sampler was also shown to give potential participants a clear indication of study requirements. Persons who were interested in participating completed contact information sheets and were later contacted to arrange individual meetings. At these individual meetings, study details, requirements, and consent forms were reviewed with the potential participants. If the individual agreed to participate, a seven-day sampling period was scheduled.

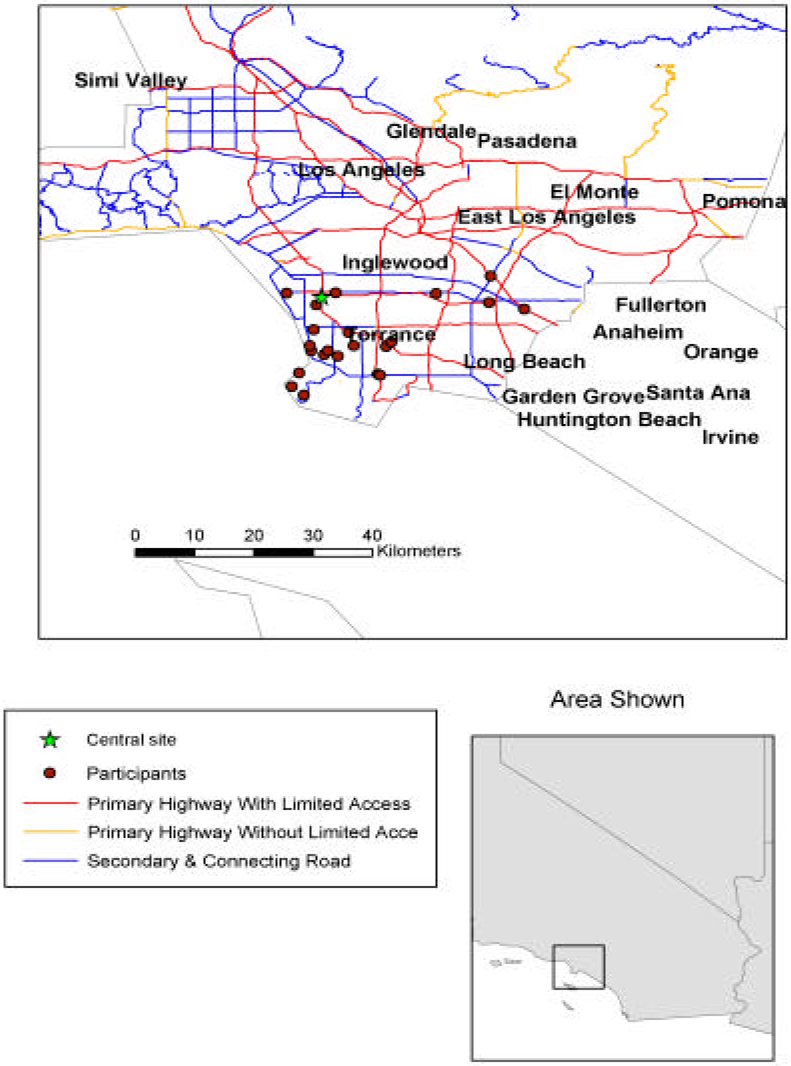
Table 2. Participant Profile

Participant ID	**Age**	**Sex**	**City**	**Zip Code**	**Location**	**Population Density (#/km^2)***	**Distance to Major Roads (m)****	**Season**	
								Winter	**Summer**
LPD-01A	73	F	Palos Verdes Estates	90274	Coastal	173	2029	v	v
LPD-02	84	F	El Segundo	90245	Coastal	4108	252	v	v
LPD-03	69	F	Hawthorne	90205	Coastal	3568	696	v	v
LPD-04	60	M	Wilmington	90744	Coastal	4504	146	v	
LPD-05	NA	F	Torrance	90504	Coastal	3417	256	v	
LPD-06	68	F	Hawthorne	90250	Coastal	9693	89	v	v
LPD-07	NA	F	Torrance	90505	Coastal	2588	1196	v	
LPD-08	NA	F	Redondo Beach	90278	Coastal	5118	598	v	v
LPD-09	73	F	Redondo Beach	90277	Coastal	5441	228	v	v
LPD-10	68	F	Bellflower	90706	Inland	3911	65	v	
LPD-11	NA	F	Downey	90240	Inland	3466	76	v	v
LPD-12	63	F	Lynwood	90262	Inland	4647	401	v	v
LPD-13	NA	F	Torrance	90501	Coastal	660	1045	v	
LPD-14	62	F	Redondo Beach	90277	Coastal	450	93	v	
LPD-15	61	F	Carson	90745	Coastal	2226	604	v	
LPD-20	NA	M	Torrance	90503	Coastal	3737	683		v
LPD-21	NA	F	Carson	90745	Coastal	292	425		v
LPD-22	NA	F	Norwalk	90650	Inland	5587	26		v
LPD-27	NA	F	Torrance	90505	Coastal	4588	470		v
LPD-28	NA	F	Wilmington	90744	Coastal	2855	0		v
LPD-29	75	M	Palos Verdes Estates	90274	Coastal	49	2098		v
LPD-30	55	F	Rancho Palos Verdes	90275	Coastal	522	191		v

* Population densities were obtained using 1990 Census Data.
** Major roads were defined as highways and secondary & connecting roads as defined by US Census TIGER/Line Files.

Participants were also recruited via other study participants or “word of mouth”. To recruit participants living inland, field coordinators also tried to recruit participants from a small COPD exercise group in Downey, CA using notices in their member newsletter and using direct contacts for individuals identified by the group coordinator as “likely to participate”. Recruitment from this group was less successful as compared to the Torrance group, primarily due to lack of interest in the study. Finally, for the summer sampling period, all of the winter participants were re-contacted and were asked to participate again in the summer period. Two of these individuals declined to re-participate due to lack of interest, while five individuals could not re-participate in the summer portion of the study due to their declining health. The same recruitment methods as discussed above were followed to replace these seven individuals with new participants. In total, 22 individuals participated in the study.

Figure 4. Map of Participant Residences



Housing characteristics. The characteristics of the participants' residences were determined using technician administered questionnaires (Appendix), which asked for detailed information about home size, type, age, ventilation characteristics, heater use, cooking fuels, carpeting, and occupants (participant data included in Appendix). Data were subsequently summarized into broad categories (Tables 3a and 3b) for presentation and for incorporation into subsequent data analyses. Approximately half of the participants lived in single family, detached houses, with all but one of the remaining participants living in apartments or multi-family homes. One participant lived in a trailer home. Particulate data for individuals living in the non-single family dwellings represent some of the first data of this type collected in California. Three and four of participants used air conditioners at home in the winter and summer, respectively, while more than 73% of the participants reported that they lived in homes near a busy road. Information about daily use of air conditioners, stoves, and other housing factors was obtained using daily housing questionnaires (see below).

Table 3a. Housing Characteristics (Number of Homes)

Characteristic	**Winter**		**Summer**	
	Yes	**No**	**Yes**	**No**
Air Conditioner Usage	3	12	4	11
Location Near Busy Road	11	4	13	2
Attached Garage	8	7	7	8
Storm Windows	1	14	1	14
Stove Fan	13	2	14	1
Clothes Dryer	11	4	6	9

Table 3b. Housing Characteristics

Housing Characteristic	**Number of Houses**	
	Summer	**Winter**
Dwelling		
Detached house	9	7
Low rise apartment	4	6
Trailer	1	0
Townhouse/Multi-family	1	2
Heater		
Forced air	9	9
Gas furnace	2	1
Gas wall heater	2	2
Electric wall unit	1	2
Other	1	1
Cooking Fuel		
Electric	7	9
Gas	8	6
Vacuum Filter		
Standard	10	9
Micro filter bags	1	1
High efficiency filters	4	5
No vacuum filters	0	1

Time-activity (TADs) and housing activity diaries. Monitored subjects recorded their daily activities for each 24-hr sampling period using time-activity diaries (Appendix). This information was collected in order to obtain information on possible sources of exposures and to help interpret measured exposures, with questions determined by EPA and approved by the Office of Management and Budget, which resulted in a limited number of information that could be collected, since OMB-approval required that the participant burden to be minimized. Subjects were asked to record their activities in 15-minute increments throughout the sampling period and to update the diaries every time they changed their activity. All diaries followed an identical format, in which pre-designated checkboxes were used as descriptors of the subject's activities. The TADs had a space for the subjects to fill out their primary activity during each 15-minute interval. In addition, there were check boxes in which the subject recorded their location during that period, to ascertain whether they were indoors or outdoors, at home or away from home, or in transit (via car, bus, or other means). Diaries also included checkboxes to indicate the participant's proximity to particle generating sources, such as whether the subject was near a smoker or was cooking or cleaning or was near someone cooking or cleaning. Technicians collected the time-activity diaries during each visit at the end of each 24-hr monitoring period. The diaries were then reviewed with the subject. At this time, any vague or illegible items could be clarified, and any questions could be asked of the subject.

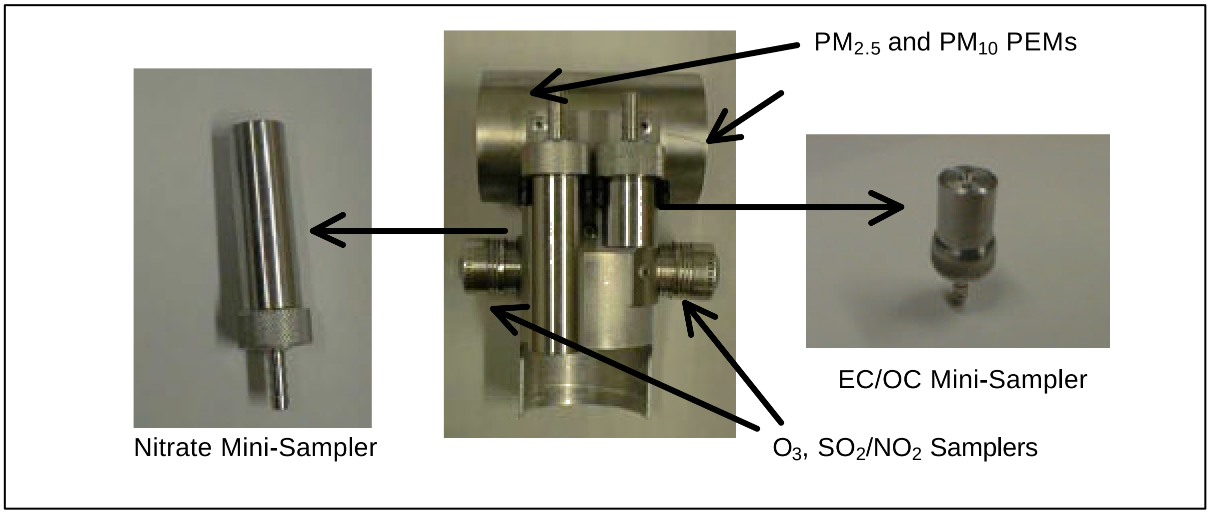
Also during each morning visit, a field technician administered a separate housing questionnaire (Appendix), which was intended to provide information on potential indoor particulate sources, as well as information on the home ventilation status by obtaining data for the number of open windows and doors in the home, the number of inches each was open, and the amount of time each was opened. The daily questionnaire also collected additional information on the use of air cleaners, ventilation fans, humidifiers, space heaters, sources of indoor combustion other than a stove (candles, incense), and the presence of pets. Again, questions were determined by EPA and were limited to minimize the burden to participants.

In total, 208 person-days of time-activity and housing data were collected. Time-activity data were analyzed as 15-minute intervals and also were aggregated over 24 hours to correspond to the 24-hr air pollutant samples. The data were analyzed by season and by individual. For the data analyses, the six original location variables were reduced to four categories, since the amount of time spent inside at home dominated that spent in all other locations. The four resultant categories were: indoors at home, indoors away from home, outdoors, and in transit. In addition, data for one subject (LPD-20) was excluded from the summer database, because the subject was admitted to the hospital and consequently spent little time at or near home. As a result, a total of 201 person-days were included in the data analysis.

Air pollution measurements. All air pollutant concentrations were measured in the study using an integrated multi-pollutant monitor that was recently developed by our group to measure the simultaneous particulate and gaseous exposures. This sampler is essentially several individual samplers that have been joined together to form a simple, compact, and relatively lightweight personal monitor (Figure 5). The entire monitor (plus pump and battery pack) weighs approximately six pounds. Participants were able to wear the monitor successfully throughout the monitoring period. Participants were allowed to remove the monitor and place it nearby when they would be stationary for long periods of time, such as when they were sleeping or reading. For participants using oxygen, monitors were strapped to their oxygen tanks to ease the sampling burden. Although not specifically cited by any participant, it is possible that winter participants that declined to participant again in the summer did so in part due to the burden of carrying the monitor with them for seven days.

For indoor, outdoor home, and SAM monitoring, the monitors were placed on a tripod, with the inlets approximately one meter above the ground. Both indoor and outdoor monitors were placed away from any objects (e.g., trees, houses, vents) to minimize interference with pollutant measurements. Outdoor monitors were placed under a rain cap to protect the samplers from precipitation. For personal monitoring, the monitor was attached by Velcro to the shoulder strap of a padded backpack at breathing level. If the participant was mobility-restricted or otherwise hampered, the samplers were attached to fixed objects near the participant's body, with the inlet protruding into the breathing zone.

Figure 5. Multi-Pollutant Sampler



The multi-pollutant sampler measured PM_{10} and $PM_{2.5}$ concentrations using Personal Exposure Monitors (PEMs), small inertial impactors designed specifically for personal and micro-environmental monitoring (Marple *et al.*, 1987; Thomas *et al.*, 1993; Chang *et al.*, 1999; Demokritou *et al.*, 2001). Impactor plates in all samplers were greased to minimize particle bounce (Demokritou et al., 2001a; Demokritou et al., 2001b). In both seasons, indoor and outdoor PM_{10} and $PM_{2.5}$ measurements were made using Harvard PEMs operated at flow rates of 4 LPM. In the winter, personal PM_{10} and $PM_{2.5}$ concentrations were measured using PEMs manufactured by SKC. Since these samplers were designed to operate at flow rates of 4 LPM, the SKC PEMs were modified to allow their use at flow rates of 1.6 and 2 LPM for PM_{10} and $PM_{2.5}$ sampling, respectively (Rojas *et al.*, 1998). Because the cut-point of the impactors are a function of flow rate, the number of nozzle holes was reduced from ten to four for the PM_{10} PEM and to five for the $PM_{2.5}$ PEM to maintain the same size cut-offs as originally designed. In the summer, personal PM_{10} and $PM_{2.5}$ concentrations were measured using PEMs designed by Harvard to operate at 1.8 LPM, since these samplers were lighter, could be used without modification, and would be comparable to the Harvard PEM samplers used to sample indoors and outdoors. As discussed in the *Quality Assurance and Quality Control* section of the report below, measurements obtained using the SKC and Harvard PEMs were comparable.

Both the SKC and Harvard PEMs used Teflon filters as the particle collection media and included drain disk rings to prevent metal contamination for future ICP-MS analysis. The $PM_{2.5}$ and PM_{10} PEMs were attached to either side of the monitor using a 10 cm long elutriator (Figure 5). Nitrate and EC/OC mini-samplers were attached to the front of the elutriator using clips. The passive O_3 and SO_2/NO_2 badges were placed in the side of the elutriator, with their face exposed to the sample air stream to allow for constant sampler collection rates.

Home ventilation conditions. As part of both the EPA- and CARB-sponsored studies, air exchange rates (AER) were measured over 24-hr periods. Since air exchange rates can be measured accurately only for detached homes, air exchange rate data are available only for 9 and 7 single family detached homes in the winter and summer, respectively. Six of these homes were monitored in both the winter and summer. In the winter and summer, respectively, two and one homes were located in inland Los Angeles. All homes were asked on the following day for information about open windows in the home during the previous sampling day (as described above in *Time Activity and Housing Activity Diaries*).

Air exchange rates were measured using a tracer gas source (perfluorocarbon, PFT) and passive samplers (capillary adsorption tubes, CATs). PFT gas was released at a controlled rate from multiple sources within a home; where the sources were placed inside the home approximately 24 hours prior to sampling to allow for equilibrium (Dietz *et al.,* 1986). CATs were used for sample collection and were normally placed in the living room, bedroom, and kitchen. In general 3 to 4 CATs were collected for each house. Additionally, collocated and field blank CATs samples were collected for quality assurance. After sampling, CATs were analyzed by gas chromatograph with electron capture detector (GC/ECD). Air exchange rates were calculated using average collected PFT concentrations, house volume, sample durations, and source emission and collection rates. The detection limit (LOD) for air exchange measurements was calculated using the 90th percentile concentrations of the valid field blanks (5 picoliters), which then was converted to the LOD (the highest air exchange rate that can be measured) using 24-hr sampling duration and related house characteristics.

Elemental analysis. All personal, indoor, and outdoor $PM_{2.5}$ filters were analyzed for elemental concentrations using ICP-MS techniques at RTI International (Research Triangle Park, NC). Prior to these analyses, a series of validation tests were conducted in conjunction with CONSOL Energy, Inc. (Pittsburgh, PA) to evaluate the ability of ICP-MS to analyze elemental concentrations for the low-flow rate $PM_{2.5}$ samples used in this study. The ability of ICP-MS to determine elemental concentrations was assessed both in terms of the accuracy and precision of the ICP-MS method and its performance relative to XRF analysis. Detailed descriptions and results from these tests are included in the Appendix.

Table 4. Comparison of XRF and Two ICP-MS Methods using NIST Urban Particulate SRM 1648 and Four Ambient $PM_{2.5}$ Samples

Element	XRF	ICP-MS (CONSOL High Res.)	ICP-MS (DRC)
Ca	Generally 20-30% lower than ICP-MS	Results are in good agreement with each other and with NIST 1648	
K	XRF, H. Res. ICP-MS agree well with each other and with NIST 1648.		Biased high by 50-100%
Al	Generally 80-100% lower than ICP-MS	Fair agreement for 4 of 6 samples. DRC ICP-MS results high for two samples. Good agreement for 1 sample of NIST 1648.	
Cr	Poor precision	3x higher than DRC ICP-MS for both NIST 1648 and the filter samples	Good results for NIST 1648
Mn	No general trend. Results could be higher, lower, or comparable with ICP-MS.	ICP-MS results are in better agreement with each other than with XRF. Good agreement with NIST 1648.	
Se	Good agreement with DRC ICP-MS, except one filter sample seemed high	--	Good agreement with XRF (except one sample) and with NIST 1648.
Fe	Often 10-20% lower than ICP-MS	Good agreement except that DRC ICP-MS appeared high for one filter sample. Good agreement with NIST 1648.	
Na	Poor precision	Both ICP-MS techniques were biased high by as much as 100% when compared to NIST 1648. Fair agreement between ICP-MS techniques for PM filters.	
Mg	Very poor precision	DRC ICP-MS generally 25-30% higher than High Res. ICP-MS. Both were biased high compared to NIST 1648.	
Si	Generally 5-10 times lower than DRC ICP-MS. No measure of accuracy.	Background was too high to determine Si.	Generally 5-10 times higher than XRF. Good agreement with NIST 1648.
Ti	Poor precision	Results are in good agreement with each other and with NIST 1648	
V	Poor precision	Results are in good agreement with each other and with NIST 1648	
Cu	Poor multi-pollutant, improved FRM precision. Unknown accuracy.	Both ICP-MS techniques are biased high compared to NIST 1648.	
Co	Poor precision	Results are in good agreement with each other and with NIST 1648	
Ni	Results generally lower than those by ICP-MS. Precision generally >30%.	ICP-MS techniques agree but are biased high for both NIST 1648 samples, suggesting that the results for filter samples may be biased high. Results are generally higher than XRF but the discrepancy is less than that for NIST 1648.	
Zn	Generally 20-60% lower than ICP-MS.	ICP-MS agree well with each other. Both biased ~20% higher as compared to NIST 1648.	
As	Poor precision	Both ICP-MS techniques produce acceptable results for NIST 1648 but when agree with each other only within 50-100% for filter samples	
Cd	Poor precision	Results are in good agreement with each other and with NIST 1648	
Sn	Poor precision	Results are in good agreement with each other and with NIST 1648	
Ba	Poor precision	Results are in good agreement with each other and with NIST 1648	
Pb	X-ray and both ICP-MS techniques agree well		

Key: shaded: unacceptable; unshaded: acceptable; DRC method most similar to that used by RTI.

Briefly, ICP-MS was chosen as the analysis method for elemental concentrations based on its known high sensitivity. Elemental analysis by XRF, the method that has historically been used in air pollution exposure studies to determine elemental concentrations, was not a viable option for our study, due to its low sensitivity, which would prevent the detection of many elements at the low sampling volumes used in our study. ICP-MS was performed on the $PM_{2.5}$ Teflon filters, after $PM_{2.5}$ concentrations were determined and validated. The ICP-MS technique used in our study determines elemental concentrations using a mass spectrometer of ~1 amu resolution and a reaction cell to minimize polyatomic interferences (e.g., ArO^+ on Fe^{56}). Interferences are minimized in the reaction cell through the introduction of reaction gases, which change the interfering species to a charged species of different mass than the analyte or to a neutral species.

The performance of this ICP-MS method was examined in a series of laboratory and field tests. These tests were conducted using NIST samples, repeated analyses, and comparisons with high resolution ICP-MS (as determined by Columbia University) and XRF (as determined by Desert Research Institute). Results from these tests showed that the ICP-MS method was able to measure many elements of concern reliably and with sufficient sensitivity, accuracy and precision (Table 4). Specifically, results showed that the ICP-MS method provided accurate and precise measurements of vanadium, a marker of oil combustion, and Ca and Si, markers of crustal sources. Other elements, including chromium, iron, manganese, cadmium, and lead, were also measured with a high degree of accuracy and precision. These elements, together with EC, nitrate, and the criteria gas concentrations, can serve as appropriate markers of important particulate sources, and can be used to apportion the contribution of particles of outdoor and indoor origin to personal and indoor $PM_{2.5}$ levels.

Note that validation of the ICP-MS method was not included as a specific task in the study as originally proposed to CARB, since validation of this technique was thought to be relatively straightforward and thus was thought to be more comparable to a quality control task. However, the validation of this technique proved to be more difficult than anticipated, requiring a series of laboratory and field tests to be conducted and a variety of elemental analyses to be performed using multiple methods, further requiring the participation and cooperation of several different laboratories. As a result, validation of the ICP-MS technique was completed by CONSOL later than expected, delaying the elemental analysis of the $PM_{2.5}$ filters from the field study. Based on results of this validation and time consideration, $PM_{2.5}$ filters were analyzed for elements using ICP-MS by RTI.

Quality assurance and quality control. Standard QA/QC procedures were followed for this study as stipulated in our QA/QC plan. Briefly, the Teflon filters used to collect PM were weighed in a temperature and humidity controlled weighing room (temperature, 18-24^{o}C; RH, 40±5%). Filters were left to equilibrate 24 hours before the initial weighing and 48 hours prior to post-sampling weighing. In order to eliminate the effects of static charge, the Teflon filters were passed over Po^{210} sources (alpha rays) just before each weighing. Each filter was weighed in duplicate both before and after sampling using a Mettler Model MT5 microbalance. Filter weights were also corrected for barometric pressure during weighing. The average of the two weights was used as the filter weight. When the two filter weights differed by more than five micrograms, the filter was weighed a third time, with the final value being the average of the two closest weights. All of the filters were stored and shipped post-sampling in refrigerated environments to reduce potential volatilization from the filters. Detailed shipping and sample and data custody protocols were followed to ensure the integrity of the samples and subsequent data.

Table 5a. Mean Blank Corrections for $PM_{2.5}$, NO_3^-, EC, and PM_{10}

Pollutant	Sample Type	Season	N	Mean Blank (μg)	Std. Dev. of Blanks (μg)
$PM_{2.5}$	Outdoor	Winter	13	12.1	5.58
		Summer	13	5.47	5.19
	Indoor	Winter	8	7.33	7.87
		Summer	15	10.7	6.74
	Personal	Winter	7	8.25	5.25
		Summer	18	6.52	9.16
NO_3^-	All	Winter	29	0.28	0.11
		Summer	44	0.11	0.10
EC	All	Winter	32	0.36	0.31
		Summer	41	2.53	0.77
PM_{10}	Indoor, Outdoor	Winter	19	7.43	5.75
	Personal		10	14.2	8.48

Table 5b. Geometric Mean Blank Corrections for Elements

Element[1]	Geo. Mean Blank (ng)		Geo. Std. Dev. (ng)	
	Winter (n=27)	Summer (n=46)	Winter (n=27)	Summer (n=46)
Ni	1.48	1.51	2.60	2.69
Cu	13.75	17.07	2.45	2.51
Zn	52.95	56.44	2.29	1.77
B	1.90	1.26	2.23	1.84
Pb	2.23	2.02	2.22	2.10
Mn	2.40	2.32	2.03	2.09
Al	101.84	105.88	1.68	1.64
Fe	15.25	16.33	1.56	1.30
Cr	76.45	80.46	1.25	1.23
Ca	ND	3.48	ND	12.88

ND: not detected

[1] Blanks were also analyzed for Be, Co, Se, Rb, Sr, Zr Mo Pd, Cd, Sn, Sb, Ba, Eu, Au, Tl, and Th, but were not detected.

Blank filters were used to correct concentrations of all measured species. For $PM_{2.5}$, NO_3^-, EC, OC, and PM_{10}, concentrations were corrected using the mean filter blank level for the respective pollutant, when mean blank levels differed significantly from zero (Table 5a). Corrections were generally made by season and by sample type. Corrections by sample batch or sample date were unnecessary, as blank values did not differ significantly by either of these parameters. For both nitrate and EC, mean blank levels did not vary statistically by sample type; as a result, corrections were made using the mean blank value for all sample types in each season. Elemental concentrations were corrected using the geometric mean of the elemental field blanks, since their blank levels were log-normally distributed (Table 5b). Blank corrections were made by season, as significant seasonal differences in the blank levels were found. The blank levels did not differ significantly by sample type.

Data points were voided due to sampling (e.g., pump or battery failures, tube disconnection) or laboratory (e.g., contamination) problems. Where possible, data for samples with negative levels or with concentrations below the method limit of detection (LOD) were flagged, but were left in the data set and subsequent data analyses. Samples with elemental concentrations below the LOD were assumed to equal ½ the limit of detection, since the laboratory, which performed the analysis, did not provide sample values for data below the LOD. Data handling approaches for PM, gas and elemental samples were determined to be the most appropriate as they would minimize potential distortions of pollutant means, standard deviations and other descriptive parameters, particularly for those pollutants for which concentrations were frequently below their LOD. Organic carbon concentrations were not included in this report due to errors associated with the collection of gaseous organic carbon and the volatilization of particulate organic carbon from the filter. These errors are typical of all of the current filter-based collection methods, including the EPA-recommended method used in this study. Since gaseous organic carbon concentrations tend to be high indoors, these errors are generally highest for personal and indoor OC samples. Summertime PM_{10} filters were contaminated by the downstream drain disks.

Completeness, LODs, precision, and accuracy. Field data were assessed for completeness, the detection limit, precision, and accuracy (if the reference measurements were available) for each pollutant. Percent data completeness was calculated as the total number of valid samples divided by the number of collected samples (105 and 103 for summer and winter samples, respectively). As shown in Table 6, samples were successfully collected and analyzed in both seasons of the study, as the percentage of valid samples relative to the total number of planned samples was generally high. While still relatively high (<83%), the percent data completeness of personal samples, however, was lower as compared to those of indoor and outdoor samples. In addition, the percent data completeness for the personal samples was below our previously specified target completion rate and was below typical values observed in our previous personal exposure studies. Reasons for this low percentage are due primarily to the problem with battery failure that occurred in the field during the study. This problem was resolved during the study with the purchase of new batteries. Note that for outdoor and indoor sampling, pumps were plugged directly into home electrical outlets. Consequently, outdoor and indoor samples were not affected by battery failure problems as shown by percent data completeness values mostly greater than 90%.

Method LODs were estimated as three times the standard deviation of the field blanks. Note that since elemental field blanks were log-normally distributed, LODs were estimated based on the geometric standard deviation of the field blanks. Elemental blanks with values below the laboratory detection limits were assumed to equal one half of the laboratory detection limit, since the laboratory that performed the analysis did not provide actual values below the LOD. Blanks that were statistical outliers (defined as more than two standard deviations outside of the mean blank value) were excluded from the LOD calculation. A total of two winter $PM_{2.5}$, three summer $PM_{2.5}$, three PM_{10} blanks, one NO_3^- winter and one NO_3^- summer blank, one winter EC blank, four winter elemental, and five summer elemental blanks were not included in the LOD calculations, which comprises only a small fraction of the total number of blank values.

Table 6. Data Completeness: Valid Percentage (%) as Compared to Total Collected Samples

Sample Type/Pollutant	Winter	Summer	Total
Outdoor			
$PM_{2.5}$	89	98	94
NO_3^-	89	97	93
EC	91	97	94
Element*	88	91	90
PM_{10}	91	NA	91
Indoor			
$PM_{2.5}$	89	99	94
NO_3^-	91	98	95
EC	87	96	92
Element*	89	91	90
PM_{10}	92	NA	92
Personal			
$PM_{2.5}$	84	92	88
NO_3^-	95	99	97
EC	88	84	86
Element*	83	85	84
PM_{10}	86	NA	86

NA: not available; *Aluminum data were used to calculate the completeness for the elemental samples.

Precision of the multi-pollutant sampler methods were calculated by collocating replicated, fully configured sampling backpacks at the SAM site. In addition to the multi-pollutant samplers, this site was equipped with reference samplers for accuracy comparison: HIs to measure for PM_{10} and $PM_{2.5}$, a ChemComb (without an upstream denuder) to measure EC/OC, a $PM_{2.5}$ HI with denuder to measure NO_3^-, and passive O_3 and SO_2/NO_2 badges. The samplers were operated for 24 hours (±10%). For a given pollutant, precision was estimated as the standard deviation of the absolute difference between the collocated multi-pollutant samplers, divided by the square root of two. Accuracy for a given method was determined using the ratio between the mean multi-pollutant sampler concentrations and the mean corresponding reference method concentrations. Three $PM_{2.5}$ sample pairs were contaminated in the summer and were thus excluded from the precision and accuracy determinations. Similarly, 1 sample pair for aluminum in the summer was excluded from the analysis also due to contamination problems. These contaminated filters may be indicative of less-optimal field sample collection during the summertime.

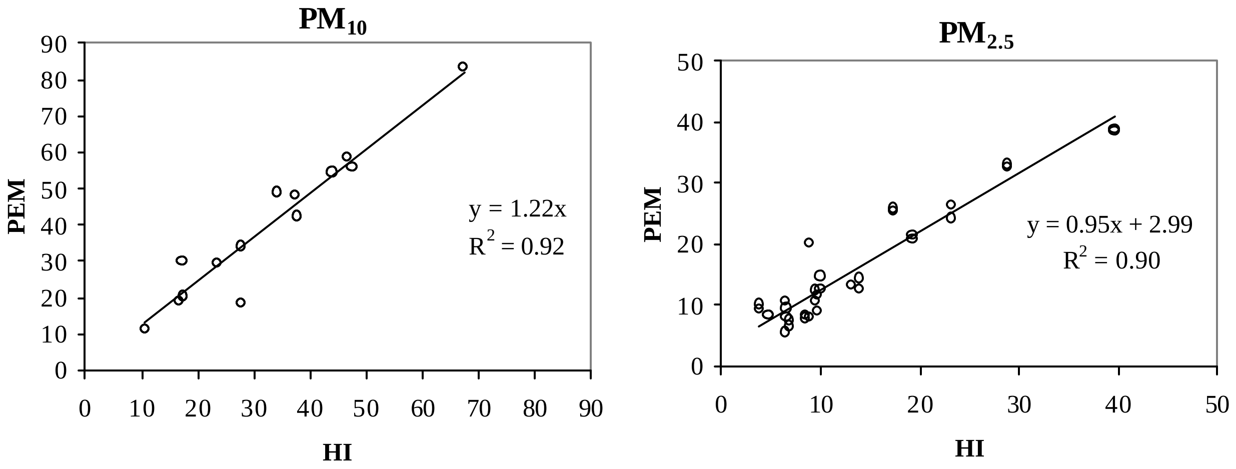
Table 7a. $PM_{2.5}$, Nitrate, Elemental Carbon, and PM_{10} Detection Limits

Pollutant	Sample Type	Season	LOD (μg)	LOD (μg/m^3)	% <LOD
$PM_{2.5}$	Outdoor	Winter	16.74	2.91	11.7
		Summer	15.57	2.70	0
	Indoor	Winter	23.61	4.10	14.6
		Summer	20.22	3.51	0
	Personal	Winter	15.75	5.47	21.4
		Summer	27.48	10.60	0
NO_3^-	Outdoor	Winter	0.30	0.26	10.7
	Indoor	Winter	0.30	0.26	20.4
	Personal	Winter	0.30	0.26	10.7
	All	Summer	0.29	0.25	0
EC	Outdoor	Winter	0.92	0.80	15.5
	Indoor	Winter	0.92	0.80	23.3
	Personal	Winter	0.92	0.80	16.5
	All	Summer	2.32	2.01	0
PM_{10}	Outdoor	Winter	17.25	2.99	8.7
	Indoor		17.25	2.99	7.8
	Personal		25.44	11.04	18.5

$PM_{2.5}$ and PM_{10}. For $PM_{2.5}$, a total of 74 blanks were collected in the study, with 28 blanks collected in the winter and 46 in the summer. LOD, accuracy, and precision for personal samples were calculated using SKC PEMs in the winter and Harvard PEMs in the summer. For indoor and outdoor samples, all QA/QC parameters were determined using Harvard PEMs. The limits of detection for the $PM_{2.5}$ measurements ranged between approximately 15 and 27 μg for the personal, indoor, and outdoor samples, which correspond to concentration LODs ranging between 2.70 μg/m^3 and 10.60 μg/m^3 for 24-hr sampling. The LOD for personal $PM_{2.5}$ samples in the summer were almost twice that in the winter, which may be indicative of poorer measurement quality in the summer. Despite this, none of the personal, indoor or outdoor $PM_{2.5}$ samples were below the LOD in the summer. In contrast, in the winter 21.4%, 14.6%, and 11.7% of the personal, indoor and outdoor $PM_{2.5}$ samples were below their corresponding LOD, respectively. As mentioned above, similar, albeit more severe, problems were found for PM_{10} in the summer as well. For PM_{10}, a total of 29 blank samples were collected during the winter. The limits of detection for PM_{10} samples were comparable to those for $PM_{2.5}$, ranging between 2.99 and 11.04 μg/m^3 for 24-hr samples. The percentage of PM_{10} samples below the LOD were slightly lower than corresponding values for $PM_{2.5}$.

The accuracy and precision of the low-flow $PM_{2.5}$ and PM_{10} samplers were determined using collocated PEMs as configured in the multi-pollutant samplers. The relative precision was found to equal 6.5% and 9.7% for $PM_{2.5}$ in the winter and summer, respectively. For PM_{10}, for which data are only available in the winter, the precision of the wintertime measurements was found to equal 5.3%. Using HI as the reference method, the accuracy of the $PM_{2.5}$ PEM was high, especially in the winter, with the ratios of the mean PEM to the reference HI concentrations equaling 1.16 and 1.26, respectively. For PM_{10}, the ratio of the PEM to HI measurements equaled 1.20 in the winter (Figure 6). The association between the PEM and the HI measurements was high for both particle cut-sizes and for $PM_{2.5}$ in both seasons, with R^2 values greater than 0.90 for all PEM-HI comparisons. Results indicate that the PEM consistently overestimates particulate concentrations. Despite this slight positive bias in PEM measurements, the strong associations between the PEM and HI measurements and the high precision of the PEM measurements show that the PEM is able to provide accurate and precise measurements of $PM_{2.5}$ and PM_{10} concentrations at the low flow rates used in our study. These results are consistent with those from our previous studies (Chang, *et al.*, 1999).

Figure 6. Winter PM_{10} and Winter and Summer $PM_{2.5}$ Measurements: PEM vs. HI



NO_3^-. For NO_3^-, a total of 29 and 44 blanks were used to calculate the winter and summer detection limits, respectively. The LODs in both seasons were 0.26 μg/m^3 for 24-hr sampling. No exposure samples were below the LOD in the summer, while between 10.7-20.4% were below the LOD in the winter. The relative precision of the nitrate mini-PEM sampler was high, equaling 14.6% and 11.3% in the winter and summer, respectively. In addition, NO_3^- concentrations measured using the mini-PEM were strongly associated with those measured using the reference HI with denuders, with R^2 values at least 0.78 in both sampling seasons (Figure 7). However, in the winter, the mini-PEM NO_3^- measurements were substantially higher than those measured using the HI system, resulting in a slope of the regression line of 1.68. In the summer, the mini-PEM measurements were comparable with the reference levels, with a slope 0.98. The observed higher mini-PEM measurements in the winter may be due to

inaccuracies in the reference measurements, as NO_3^- may have volatilized from the uncoated Teflon filter used in the HI system. Additional explanations include seasonal changes in temperature, relative humidity, and aerosol composition (Hering and Cass, 1999), and to higher flow rates in the HI sampler. Despite the observed bias in the winter, the mini-PEM were found to be an appropriate NO_3^- measurement method for our study, since (1) the association between the two measurement methods was strong and (2) the precision of the method was high, as a result any biases introduced by the sampling method were uniform across sampling locations.

Figure 7. NO_3^- Measurements: Mini-PEM vs. HI with Denuder

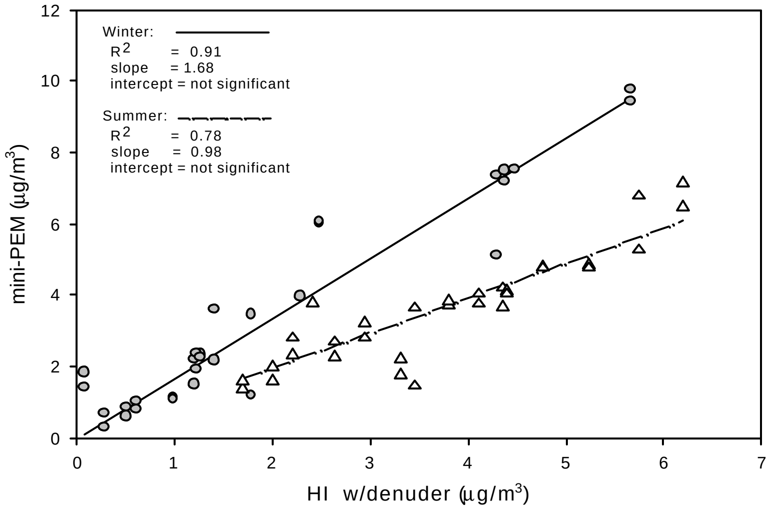
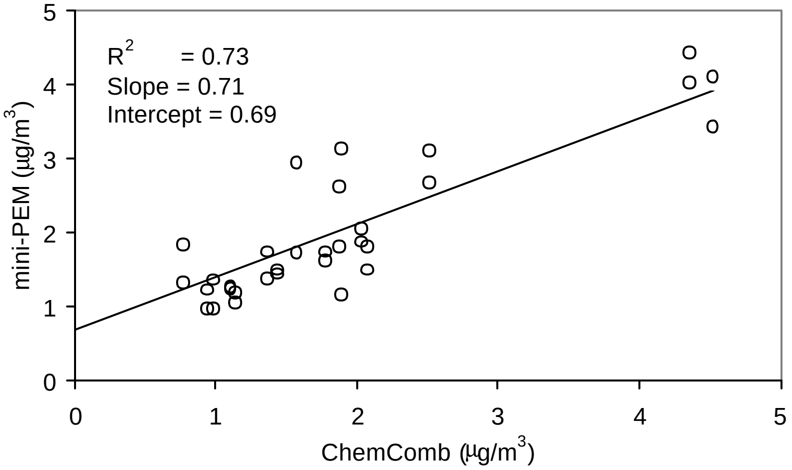


Figure 8. EC Measurements: Mini-PEM vs. ChemComb



Elemental Carbon. 24-h LODs for EC were calculated to equal 0.80 µg/m^3 in the winter and 2.01 µg/m^3 in the summer using 32 and 41 blanks, respectively. No EC exposure samples were below the LOD in the summer. Between 15.5% and 23.3% of the exposure samples were below the LOD in the winter. The relative precision of the elemental carbon measurements was determined to equal 17.8% using collocated mini-PEM samplers. The accuracy of the EC mini-sampler, which was determined only in the winter, was also good, with a ratio of the mean mini-PEM to the reference ChemComb measurements of 1.10. These results indicate that the mini-sampler overestimated EC concentrations slightly, by an average of 10%. EC concentrations obtained by the mini-PEM and the reference sampler were strongly associated, as the mini-PEM measurements explained 73% of the variability in the corresponding reference measurements (Figure 8). Results demonstrate that the mini-PEM is an appropriate method to measure EC in our study.

Table 7b. Elemental Detection Limits and Precisions

Element	**Limit of Detection (ng/m^3)**		**Precision (ng/m^3)**	
	Winter	**Summer**	**Winter**	**Summer**
Al	1.84	1.69	13.24	14.13**
B	4.25	2.41	0.67	0.77
Ba	0.73*		0.78	0.23
Cr	2.49*		2.16	3.37
Mn	3.23	3.53	0.18	0.80
Ni	6.80	7.47	0.86	1.47
Pb	4.24	3.56	0.25	1.56
Zn	4.63	2.12	11.09	11.35
Au	0.85*		NA***	
Be	0.54*			
Ca	99.34*	825.05		
Cd	0.60*			
Co	0.75*			
Cu	5.66	6.10		
Eu	0.79*			
Fe	1.48	0.84		
Mo	1.04*			
Pd	1.14*			
Rb	0.95*			
Sb	0.98*			
Se	1.18*			
Sn	0.96*			
Sr	0.93*			
Th	0.54*			
Tl	0.54*			
Zr	0.68*			

* Levels represent one half of the laboratory detection limit.
** Two outliers were excluded from the calculation
*** NA represents data whose concentrations were below the detection limit.

Elements. Since small sampling volumes were used in the study, only eight elements (Al, B, Ba, Cr, Mn, Ni, Pb, and Zn) were detected with sufficient frequency and were included in subsequent descriptive data analyses. [Other elements were either not detected (e.g., Cd) or were detected at concentrations well below the method LOD (e.g., Fe).] Due to the overall poor performance of ICP-MS at our low sampling volumes, however, data for the eight detected elements were not included in multivariate and micro-environmental models. For the eight detected elements, a total of 27 and 46 blanks were used to calculate the winter and summer detection limits, respectively (Table 7b). The LODs in both seasons were generally comparable for each element (except for Ca), with the levels of less than 7.5 ng/m^3 for 24-hr sampling using the Harvard PEMs operating at 1.8 LPM. For six of the eight elements, summer indoor, outdoor and personal levels were all above the LOD; however, winter samples values of all elements had many values that were below their corresponding LOD (Table 7c). Precision was determined using collocated PM$_{2.5}$ PEMs as configured in the multi-pollutant samplers. In general, the precision for each measured element was comparable in both seasons, with a range varying between approximately 0.7 ng/m^3 (e.g., B) to 14 ng/m^3 (e.g., Al) (Table 7b). Also, the precision in the summer was generally worse than that in the winter for each element, which again may suggest less-optimal field sample collection during the summertime.

Table 7c. Percent of Sample Values below the LOD

Element / Sample Type	**% <LOD**	
	Winter[1]	**Summer**[2]
Outdoor: Al	31.1	0
B	69.9	0
Ba	46.6	13.3
Cr	80.6	58.2
Mn	68.9	0
Ni	77.7	0
Pb	81.6	0
Zn	35.9	0
Indoor: Al	20.4	0
B	67.0	0
Ba	54.4	11.2
Cr	82.5	51.0
Mn	87.4	0
Ni	81.6	0
Pb	89.3	0
Zn	35.9	0
Personal: Al	31.1	0
B	73.8	0
Ba	67.0	26.5
Cr	78.6	53.1
Mn	81.6	0
Ni	70.9	0
Pb	95.2	0
Zn	50.5	0

[1] For all sample types, total number of samples=103;
[2] For all sample types, total number of samples=98

Air Exchange Rates. The precision of air exchange rate measurements was reasonable, with an intra-class correlation coefficient of reliability for duplicate CAT measurements of 0.83 (one-side 95% confidence interval = 0.78). [Intra-class correlation coefficients of reliability assesses both the association and agreement between the two air exchange rate measurements, with a value of one indicating perfect agreement and a value of zero indicating no agreement (Fleiss, 1986).] The LODs for 24-hr AER measurements varied widely, ranging between 3.3 and 10 exchanges/hr^{-1} due to the corresponding wide variation in the volumes of the sampled homes. Only 2 wintertime AER measurements had values below the calculated detection limit.

Data analysis. Units for pollutant concentrations and exposures are reported in $\mu g/m^3$, except for the elements, where the data are presented in ng/m^3. Coarse particle ($PM_{2.5-10}$) concentrations were calculated as the difference between PM_{10} and $PM_{2.5}$ measurements. Summer PM_{10} and $PM_{2.5-10}$ concentrations were included in the descriptive data summaries, but were not included in subsequent data analyses, due to the limited number of valid summer PM_{10} values. All data manipulations and statistical analyses were performed in SAS (SAS Institute, Cary, NC). Unless otherwise specified, statistical significance is reported at the 0.05 level.

Data were characterized using descriptive statistics, graphical displays, t-statistics, Spearman correlation coefficients, general linear regressions and general mixed models. Individual-specific Spearman correlation coefficients were calculated only for those individuals with four or more repeated measurements. The relationship between outdoor concentrations measured at the home and SAM sites and between personal, indoor, and outdoor concentrations was examined using general mixed models, in which subjects were modeled as random variables to account for between subject variability (Diggle *et al.*, 1994). Autocorrelation between pollutant concentrations over time was modeled using either an autoregressive or compound symmetry covariance structure. Since mixed models do not have a single measure of goodness-of-fit, crude R^2 values between the measured and estimated exposures (which was generated based on the results of mixed models) were calculated. Simple linear regression techniques were applied to obtain crude R^2 values to give a rough indication of the data scatter around the estimated regression lines. Models comparing indoor and personal levels with outdoor concentrations were based on outdoor levels measured at the home sites and not the SAM site, since outdoor home concentrations were generally more significant predictors.

Statistical and/or physical modeling techniques were used to investigate the effects of geographic location, particle-generating activities, including cooking, cleaning, and tobacco smoking, building type, and time-activity patterns on the exposure levels. The impacts of distance from road, population density, and geographical location (coastal vs. inland) on outdoor concentrations were examined using generalized mixed models with outdoor home concentrations as the dependent variable. Fixed effects included the outdoor (or SAM site) concentrations and the covariate of interest. Population density and distance from road information were determined using GIS methods and were included in the models as either categorical or continuous variables. Categorical classifications of “high” and “low” were made based on the median values for the measured homes, which for “population density” was less or greater than 3500 persons per square mile and for “distance from road” was less or greater than 250 meters from a major road. For “distance from road”, a second categorical variable was also created, in which “high” and “low” were classified as less or greater than 100 meters from a major road, since this distance was found to be important in earlier studies (Zhu et al., 2002). Since they were strongly correlated, separate models to examine the effects of distance from road, population density, and geographic location were created.

For indoor and personal pollutant levels, pollutant-specific models were also constructed to identify factors affecting their concentrations. These models followed the general format:

$$[C_i]_{ij} = [C_o]_{ij} + \mathrm{Ventilation}_{ij} + [C_o]_{ij}\mathrm{Ventilation}_{ij} + X_i \quad (1)$$

where C_i is the pollutant concentration measured indoors, C_o the measured outdoor concentration, *Ventilation* the home ventilation condition, and X a covariate that may influence indoor pollutant concentrations. Home ventilation conditions were determined using either the measured air exchange rates (hour^{-1}) or the recorded open window frequencies. Both air exchange rates and open window frequencies were included in the models as either continuous or categorical variables. As categorical variables, air exchange rates and open window frequency were classified as either “high” or “low” based on their respective median values. Since air exchange rates were only valid for detached houses, median air exchange rates were calculated using data only for the 9 winter and 7 summer participants that lived in detached homes. In addition, indoor concentrations models that included air exchange rates were constructed using data only for these participants. Models based on open window frequency, in contrast, were constructed using data for all homes. Covariates were selected based on previous studies showing their importance as PM sources and based on whether there was sufficient variability in their values to warrant their inclusion in the models. The covariates X considered in our analyses included presence of tobacco smoke, cooking, and cleaning, with these variables also included as either continuous or categorical variables. As categorical variables, smoking, cooking, and cleaning were assigned a value of 1 if it was present or performed anytime during the 24-hour monitoring period. As continuous variables, smoking, cooking, and cleaning were expressed as exposure duration per hour. Other variables considered but not evaluated included number of occupants and/or pets, presence of carpeting, humidifier use, and heater use, as their values generally varied little by participant or by monitoring day.

Factors influencing personal exposures were identified based on time-weighted microenvironmental exposure models (Duan, 1982). Personal exposures were estimated using time-weighted microenvironmental exposures from two microenvironments, indoor and outdoor, plus a covariate X to account for the contribution from other potential sources:

$$C_p = F_iC_i + F_oC_o + X \quad (2)$$

where C_p, C_i, and C_o are the measured personal exposures, indoor, and outdoor concentrations, respectively. F_i is the fraction of time spent indoors in a given day, and F_o is the fraction of time spent outdoors. Several factors were included as covariate X in the model, including ETS, cooking, and cleaning. As before, the impact of ETS, cooking, and cleaning were assessed as continuous and categorical variables. Concentrations for all indoor and outdoor environments were assumed to equal those measured inside and outside the subject’s home, respectively.

RESULTS AND DISCUSSION

Data were analyzed to test the three hypotheses from the study, that (1) the composition of personal and indoor $PM_{2.5}$ exhibits significant inter- and intra-personal variation, (2) the relationship between personal exposures and corresponding outdoor concentrations differs for each particulate component, and (3) the composition of personal and indoor $PM_{2.5}$ and its relationship to that outdoors differs for individuals with COPD living in Los Angeles as compared to those living in other cities. Prior to testing these hypotheses, activity pattern, housing characteristics, and air pollution data were characterized to ensure that the results were interpreted properly. Since the results of the study address additional issues, results associated with study hypothesis testing are specifically mentioned in relation to their corresponding hypothesis for clarity.

Table 8. Time-Activity Patterns: Fraction of Time (over 24-h period) Spent in Each Microenvironment by Season

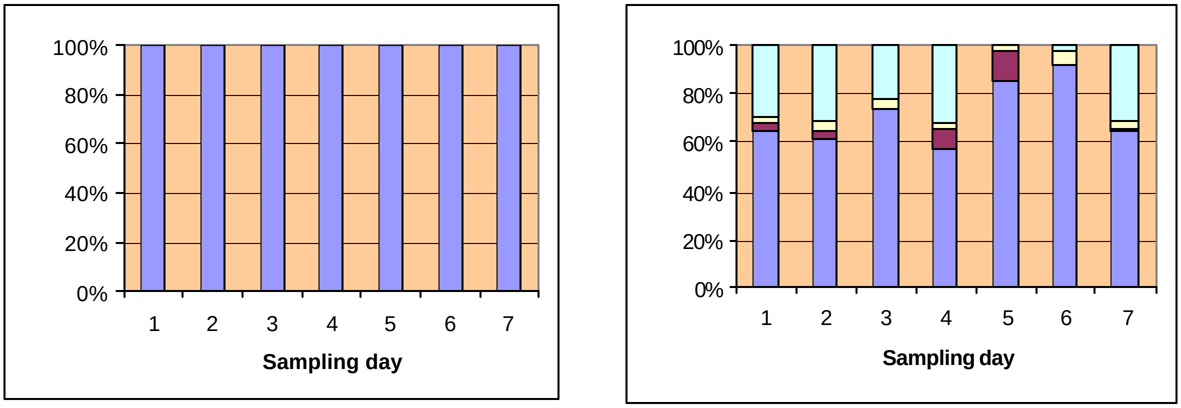
Microenvironment	N	Mean ± Std. Dev.	Median	Minimum	Maximum
Indoors – Home					
Winter	103	0.87 ± 0.11	0.89	0.53	1.00
Summer	98	0.88 ± 0.11	0.90	0.56	1.00
Outdoors					
Winter	103	0.01 ± 0.02	0.0	0.0	0.12
Summer	98	0.03 ± 0.05	0.0	0.0	0.25
Indoors – Others					
Winter	103	0.08 ± 0.09	0.06	0.0	0.34
Summer	98	0.06 ± 0.07	0.04	0.0	0.28
In Transit					
Winter	103	0.03 ± 0.04	0.03	0.0	0.17
Summer	98	0.03 ± 0.04	0.02	0.0	0.16

Time-activity Patterns

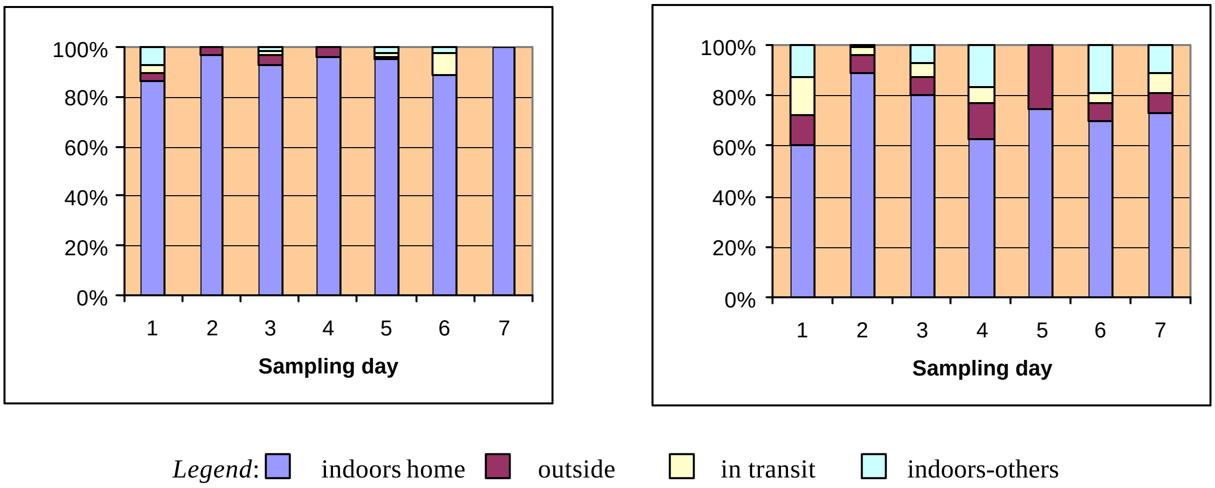
In both seasons, subjects spent the overwhelming majority of their time indoors at their homes (Table 8), with subjects spending on average approximately 90% of their time inside their homes. Subjects only spent on average less than 5% of their time in all other microenvironments, with the exception of indoor, non-home microenvironments in which subjects spent an approximate average of 6% of their time in both seasons. The activity patterns of the subjects, however, did exhibit substantial inter-personal and intra-personal variability, as illustrated by Figures 9a-d, which show time-activity patterns by season for subjects exhibiting the least and most day-to-day variability, and by Figure 10, which shows the fraction of time spent outdoors by season for individuals participating in both sampling seasons. The time spent in each of microenvironment varied substantially. For example, the fraction of time spent outdoors ranged anywhere from 0% to 25% in the summer and from 0% to 12% in the winter, while the time spent in non-residential indoor environments ranged between 0% and 28% and 0% and 34% in the summer and winter, respectively.

Figure 9. Time-Activity Patterns for Four Subjects by Season

a. Subject 11- Least Active – Winter *b. Subject 14 – Most Active – Winter*

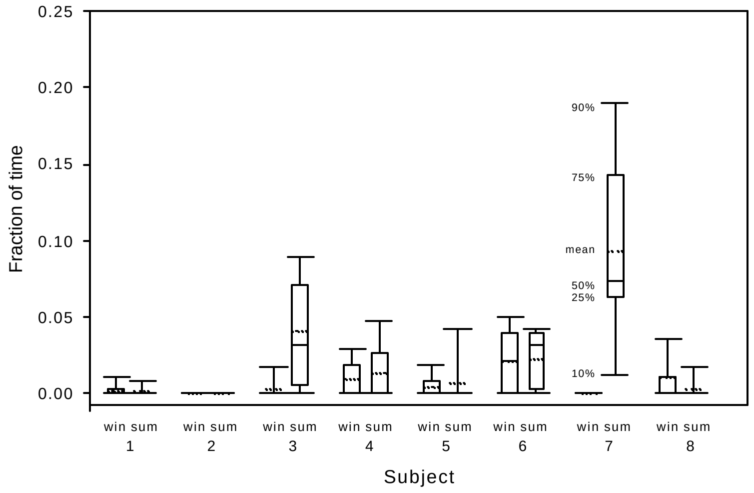


c. Subject 17 – Least Active – Summer *d. Subject 22 – Most Active – Summer*



Seasonal variation in time-activity patterns and in time spent performing particle-generating activities was examined using non-parametric Wilcoxon ranked sum tests, which were performed using data for all subjects (201 sample-days), and using only those data for individuals participating in both sampling sessions (110 sample-days). Results from these tests showed that time spent outside did not differ significantly by season (p=0.53 for all data, p=0.27 for paired data). Nonetheless, as shown on Figure 10, subject-specific seasonal differences in the fraction of time spent outdoors did exist. Especially in the summer, many of the participants exhibited substantial variation in the amount of time they spent outdoors over the seven-day monitoring period. This daily variability, however, was not consistent across seasons or individuals.

Figure 10. Fraction of Time Spent Outdoors for Subjects Participating Two Seasons*



* Distribution of values (in percentiles) shown for Subject 7 in the summer.

Table 9. Time-Activity Patterns: Fraction of Time (over 24-h Period) Spent Performing or Near Particle Generating Activities by Season

Activity[1]	N	Mean ± Std. Dev.	Median	Minimum	Maximum
Smoking					
Winter	103	0.004 ± 0.02	0.0	0.0	0.22
Summer	98	0.001 ± 0.003	0.0	0.0	0.02
Cooking					
Winter	103	0.04 ± 0.03	0.03	0.0	0.14
Summer	98	0.03 ± 0.04	0.02	0.0	0.30
Cleaning					
Winter	103	0.02 ± 0.03	0.0	0.0	0.21
Summer	98	0.01 ± 0.03	0.0	0.0	0.18

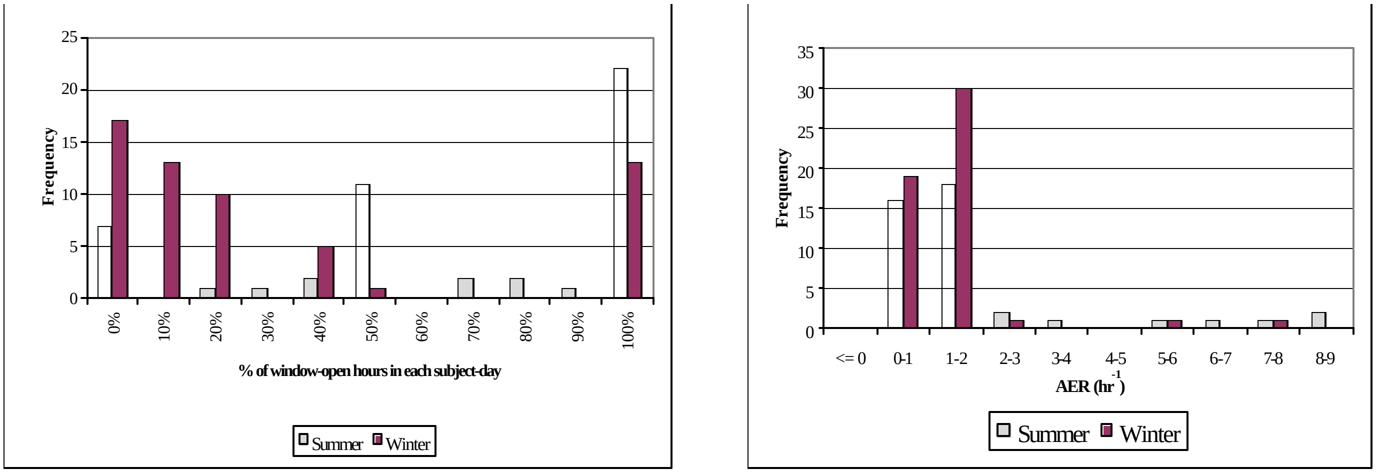
[1] Activity includes time in which the participant was engaging in the activity and when the participant was near someone else performing the activity.

Participants spent minimal but varying amounts of time performing or being in the proximity of particle-generating activities, such as smoking, cooking, and cleaning (including vacuuming, dusting, and mopping). The time participants spent performing these particle-generating activities did not differ significantly by season (Table 9), suggesting that on average, particle-generating activities are uniform across seasons. Nevertheless, the amount of time spent performing any particle generating task was minimal, as the median values for time spent in these activities were zero or close to zero. In addition, the fraction of time spent near smoking was zero or near zero in all cases except for two of the total 201 subject-days. This was expected, as all participants were non-smokers (as required for study participation) and had COPD, a pulmonary condition that may cause them to avoid environments with tobacco smoke.

Home Ventilation Conditions

Seasonal variation in home ventilation conditions was examined using both the recorded number of hours with open windows or the measured air exchange rates (Figure 11a, b). However, as mentioned previously, air exchange rates could not be measured for all homes, making open window usage the only measure of home ventilation that was available for all homes in the study. These measures are not necessarily equivalent, as the correlation between air exchange rates and open window usage for the single detached homes was insignificant in the summer and weak in the winter, with Spearman correlation coefficients of 0.20 (p=0.22) and 0.30 (p=0.08), respectively. Since open window information was obtained via a recall questionnaire and since various factors are known to affect home ventilation conditions, including window-open time and duration, house volume, house tightness, and indoor/outdoor temperature differences, AER measurements were considered to be the better indictor for home ventilation conditions as compared to open window usage.

Figure 11. Home Ventilation Conditions in Both Seasons


a. Window-open Percentage

b. Air Exchange Rates

Results from two-sample t-tests showed that AERs measured in the detached, single-family homes did not differ statistically between the two seasons (p=0.12), as mean values for the winter and summer were comparable. Open window frequency, however, did differ significantly by season (p<0.0001), with open windows open on average 76% and 34% of the time in the summer and winter, respectively. This seasonal variation in open window frequency remained statistically significant when the analysis was performed separately for detached and other home types. Although statistically different, observed seasonal variation in the air exchange rates and open window frequency are consistent with one another, as mean air exchange rates equaled 2.0 hr^{-1} in the summer and 1.4 hr^{-1} in the winter. Regardless, air exchange rates and window-open hours in both the summer and winter in the Los Angeles were higher than those observed in eastern U.S. areas, as air exchange rates in the eastern U.S. are generally less than one exchange per hour. These higher air exchange rates and open window hours reflect the temperate climate of the Los Angeles area. In the summer, air exchange rates were significantly higher in homes located along the coast as compared to in those located inland using 2-sample t-tests, with mean air exchange rates for coastal homes equaling 2.6 exchanges/hour (std.dev.=2.1) and for inland homes equaling 1.6 exchanges/hour (std. dev.=1.0). The air exchange rates of the inland and coastal homes were comparable, however, in the winter (p-value=0.71). Similar geographical variation was found for open window frequency.

Table 10. Air Exchange Rates and Open Window Frequency by Home and Season

		Air Exchange Rates (exchanges/hour)					Open Window Frequency				
Season	**Subject**	**N**	**Mean**	**Std. Dev.**	**Min.**	**Max.**	**N**	**Mean**	**Std. Dev.**	**Min.**	**Max.**
Winter	LPD-01A	4	1.53	0.18	1.39	1.76	5	0.00	0.00	0.00	0.00
	LPD-02	7	1.14	0.20	0.97	1.51	7	0.10	0.06	0.00	0.17
	LPD-03	7	1.76	0.27	1.24	2.12	7	0.93	0.19	0.50	1.00
	LPD-04	7	1.19	0.41	0.76	1.93	7	0.10	0.05	0.04	0.21
	LPD-05	7	1.36	0.28	0.97	1.79	7	0.29	0.09	0.17	0.38
	LPD-06	7	0.78	0.23	0.51	1.17	7	0.10	0.07	0.00	0.17
	LPD-07	7	1.15	0.24	0.71	1.38	7	1.00	0.00	1.00	1.00
	LPD-08	7	0.96	0.26	0.69	1.32	7	0.00	0.00	0.00	0.00
	LPD-09	7	3.45	2.12	1.56	7.99	5	1.00	0.00	1.00	1.00
	LPD-10	4	0.61	0.17	0.36	0.77	6	0.05	0.04	0.00	0.08
	LPD-11	7	0.60	0.38	0.30	1.41	7	0.72	0.35	0.33	1.00
	LPD-12	2	6.65	1.36	5.68	7.61	6	0.04	0.02	0.00	0.06
	LPD-13	5	0.47	0.08	0.36	0.55	7	0.36	0.12	0.17	0.51
	LPD-14	5	0.35	0.04	0.32	0.42	7	0.18	0.36	0.04	1.00
	LPD-15	5	1.50	0.28	1.07	1.80	7	0.26	0.27	0.00	0.67
Summer	LPD-16	5	0.70	0.09	0.62	0.84	7	0.67	0.28	0.11	1.00
	LPD-17	4	6.34	1.03	5.07	7.58	7	1.00	0.00	1.00	1.00
	LPD-18	5	2.00	0.37	1.69	2.51	7	0.86	0.24	0.50	1.00
	LPD-19	6	6.82	2.13	3.30	8.87	7	0.81	0.33	0.25	1.00
	LPD-21	7	2.81	2.27	0.82	7.05	7	0.93	0.19	0.50	1.00
	LPD-22	7	2.32	0.95	0.94	3.74	7	0.68	0.24	0.50	1.00
	LPD-23	0	.	.	.	.	7	0.85	0.25	0.46	1.00
	LPD-24	7	0.95	0.10	0.85	1.16	7	0.00	0.00	0.00	0.00
	LPD-25	5	1.20	0.26	1.00	1.62	7	1.00	0.00	1.00	1.00
	LPD-26	7	1.06	0.41	0.64	1.82	7	0.43	0.06	0.33	0.50
	LPD-27	7	2.96	0.87	1.96	4.68	7	1.00	0.00	1.00	1.00
	LPD-28	7	1.85	1.12	0.52	3.40	7	0.74	0.30	0.21	1.00
	LPD-29	7	1.12	0.20	0.90	1.44	7	0.77	0.28	0.42	1.00
	LPD-30	7	2.34	0.66	1.41	3.25	7	0.93	0.19	0.50	1.00

When examined by home, air exchange rates and open window frequency were shown to differ substantially by home (Table 10), with many but not all homes exhibiting variability in ventilation conditions across the seven-day monitoring period. Due to the relatively small number of homes in the study, especially when stratified by season, statistical analysis of home ventilation by different home types could not be performed. As discussed later, however, these daily and home-specific variations in home ventilation conditions will be examined in longitudinal analyses of personal, indoor, and outdoor pollutant relationships.

Pollutant Levels

Summary statistics for the various particulate measures stratified by season and sample type are presented in Tables 11a and 11b. In general, outdoor pollutant levels measured at the homes were strongly associated with those measured at the SAM site. At both home and SAM sites, outdoor $PM_{2.5}$ levels were higher during the summer as compared to the winter, which may be due to the enhanced photochemical formation of secondary pollutants (Burton *et al.*, 1996; Suh *et al.*, 1997). The same seasonal pattern was also observed for indoor and personal exposures; however, the pattern was less distinct. During both seasons, personal $PM_{2.5}$ exposures were significantly higher than corresponding outdoor and indoor levels, while indoor and outdoor concentrations were comparable. For all microenvironments, $PM_{2.5}$ levels were consistently higher for individuals living in inland locations as compared to those living in coastal locations (Figure 12). Higher personal exposures relative to indoor and outdoor concentrations are consistent with results from our previous Boston COPD study (Rojas *et al.*, 2000), but differed from the results from the Fresno study of older adults (Evans et al., 2000). In the Fresno study, mean winter outdoor $PM_{2.5}$ concentrations were approximately 50% higher than winter concentrations measured in our study. In addition, mean winter outdoor concentrations in Fresno were 50% and 100% higher than corresponding personal exposures and indoor concentrations.

Figure 12. $PM_{2.5}$ Concentrations by Sample Type, Season, and Location

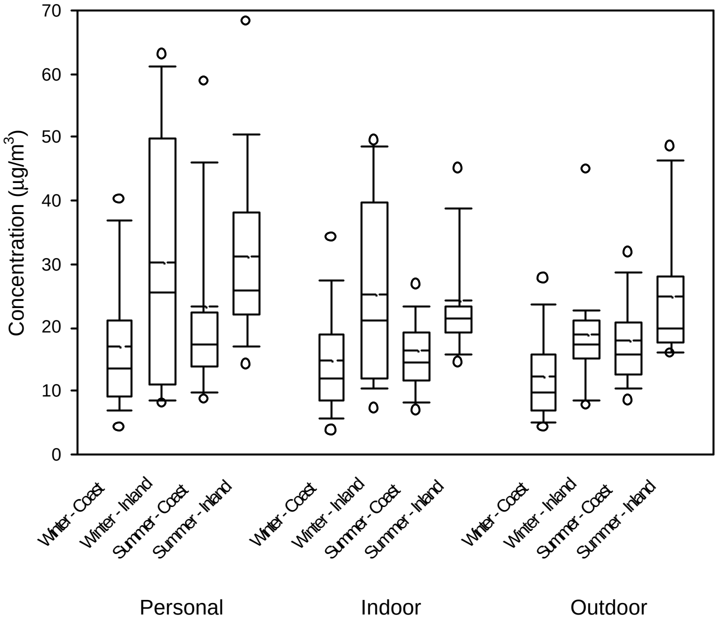


Table 11a. Descriptive Statistics for Outdoor, Indoor, and Personal Samples

Pollutant/Season/Type	**N**	**Mean ± Std. Dev.**	**Median[1]**	**Maximum**	**Minimum[1]**
$PM_{2.5}$ ($\mu g/m^3$)					
Winter					
Outdoor	92	13.51 ± 8.46	11.20	56.53	2.75
Indoor	92	16.87 ± 11.69	12.84	49.51	2.94
Personal	87	19.59 ± 14.49	14.43	63.45	2.60
Summer					
Outdoor	96	19.33 ± 9.00	17.36	53.45	5.46
Indoor	97	18.12 ± 11.09	16.97	94.81	4.34
Personal	92	25.07 ± 20.79	18.77	137.77	2.08
NO_3^- ($\mu g/m^3$)					
Winter					
Outdoor	92	3.12 ± 2.57	2.23	11.77	0.36
Indoor	94	1.13 ± 1.01	0.87	4.71	ND
Personal	98	1.23 ± 1.14	0.81	6.38	0.13
Summer					
Outdoor	95	2.76 ± 1.51	2.53	7.14	0.14
Indoor	96	1.65 ± 0.82	1.48	4.20	0.47
Personal	97	1.63 ± 0.93	1.40	4.96	0.04
EC ($\mu g/m^3$)					
Winter					
Outdoor	94	1.90 ± 1.06	1.69	5.54	ND
Indoor	90	1.59 ± 0.86	1.42	5.20	0.12
Personal	91	1.92 ± 0.98	1.68	4.88	0.50
Summer					
Outdoor	95	0.07 ± 0.74	ND	2.74	ND
Indoor	95	0.16 ± 0.71	0.15	2.06	ND
Personal	85	0.28 ± 0.75	0.15	3.32	ND
PM_{10} ($\mu g/m^3$)[2]					
Winter					
Outdoor	94	36.05 ± 13.17	33.68	86.12	5.91
Indoor	95	30.63 ± 21.75	23.25	148.15	6.47
Personal	89	35.04 ± 22.00	27.52	114.69	6.82
Summer					
Outdoor	21	15.16 ± 8.64	12.45	34.22	6.06
Indoor	21	28.96 ± 14.66	25.50	62.84	12.50
Personal	19	29.06 ± 12.80	23.98	62.82	13.49
$PM_{2.5\text{-}10}$ ($\mu g/m^3$)					
Winter					
Outdoor	92	22.84 ± 10.75	22.53	62.71	2.84
Indoor	91	12.86 ± 10.16	10.29	63.14	0.11
Personal	85	15.35 ± 12.24	13.46	76.37	0.09
Summer					
Outdoor	21	-3.91 ± 5.15	-3.21	3.28	ND
Indoor	21	11.86 ± 7.68	10.61	35.03	0.85
Personal	18	9.99 ± 7.99	8.11	31.97	ND

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[1] "ND" indicates that the concentrations were negative and therefore not detected.

[2] PM_{10} blank data in the summer showed that contamination of the filters occurred. As a result, summer PM_{10} are suspect and were excluded from subsequent analyses.

Table 11b. Descriptive Statistics for Outdoor, Indoor, and Personal Elemental Concentrations (ng/m^3)

Summer

Element	Indoor						Outdoor						Personal					
	N	Med.	Mean	STD	MAX	MIN	N	Med.	Mean	STD	MAX	MIN	N	Med.	Mean	STD	MAX	MIN
Al	96	16.5	37.4	98.8	687.0	ND	96	13.1	43.9	135.0	858.7	ND	89	19.1	47.3	100.6	727.3	ND
B	96	5.69	6.59	4.99	35.8	0.00	96	5.41	5.65	3.44	16.1	0.00	89	6.08	6.75	5.13	33.9	0.00
Ba	94	1.81	5.24	8.80	51.9	0.00	93	2.19	6.41	10.6	53.3	0.00	87	2.35	5.54	8.56	45.2	0.00
Cr	96	2.32	3.06	6.70	19.1	ND	96	1.61	1.77	6.66	21.2	ND	89	3.21	3.58	12.1	30.0	ND
Mn	96	0.75	0.92	1.04	6.5	0.00	96	0.75	1.20	1.71	9.51	0.00	89	1.24	1.16	1.17	5.44	0.00
Ni	96	3.33	3.69	2.37	11.6	0.00	96	3.34	3.83	2.32	12.9	0.00	89	3.96	3.83	3.76	13.3	0.00
Pb	94	1.01	1.85	2.46	13.5	0.00	93	1.14	2.11	2.97	19.4	0.00	87	0.71	1.54	2.31	11.5	ND
Zn	91	3.46	6.91	11.5	72.9	ND	96	4.56	8.45	14.4	74.8	ND	88	4.49	19.9	80.2	650.0	ND

Winter

Element	Indoor						Outdoor						Personal					
	N	Med.	Mean	STD	MAX	MIN	N	Med.	Mean	STD	MAX	MIN	N	Med.	Mean	STD	MAX	MIN
Al	92	19.5	31.4	36.4	171.8	ND	91	21.4	47.6	126.0	909.7	ND	86	35.9	52.6	67.3	317.1	ND
B	92	2.58	7.73	14.1	65.0	0.00	91	2.52	4.11	6.12	43.6	0.00	86	1.63	5.88	11.3	50.22	0.00
Ba	92	1.65	2.60	3.27	13.8	0.00	91	4.18	6.91	11.4	76.2	0.00	86	0.00	2.80	4.72	29.73	0.00
Cr	92	ND	0.60	11.1	66.1	ND	91	ND	1.48	14.0	78.2	ND	86	ND	1.56	23.2	152.3	ND
Mn	92	1.54	1.76	1.27	5.60	0.00	90	2.16	2.68	2.13	11.8	0.00	86	1.87	2.02	2.05	10.13	0.00
Ni	91	3.40	3.67	3.61	15.4	0.00	91	3.23	4.19	4.84	32.3	0.00	86	4.14	5.37	5.90	18.95	0.00
Pb	92	0.78	1.47	1.98	8.73	0.00	90	1.72	2.59	3.37	15.4	0.00	86	0.00	0.87	2.25	13.34	0.00
Zn	92	14.3	17.9	19.2	109.4	ND	91	16.1	26.6	38.8	271.9	ND	86	7.03	24.2	47.5	292.7	ND

“ND” indicates that the concentrations were negative and therefore not detected.

The wintertime micro-environmental and geographical patterns for $PM_{2.5-10}$ (Figure 13) and PM_{10} (Figure 14) differed from those observed for $PM_{2.5}$. In general, outdoor $PM_{2.5-10}$ and PM_{10} concentrations were higher than their corresponding indoor and personal exposures, except for inland PM_{10}, for which personal exposures tended to be higher than corresponding indoor and outdoor concentrations. These findings are consistent with those from the Fresno study, even though mean wintertime outdoor and especially indoor concentrations in Fresno were much lower than those in Los Angeles. Findings, however, differ from those from our Boston study of individuals with COPD (Rojas *et al.*, 2000), in which higher personal particulate exposures were found for all particle measures. These differences may be due to the fact that the Los Angeles cohort participated if a limited number of particle generating activities and that outdoor $PM_{2.5-10}$ and PM_{10} concentrations were higher in Los Angeles as compared to Boston, which may obscure any contribution of particle generating activities to personal exposures.

Figure 13. Wintertime $PM_{2.5-10}$ Concentrations by Sample Type and Location

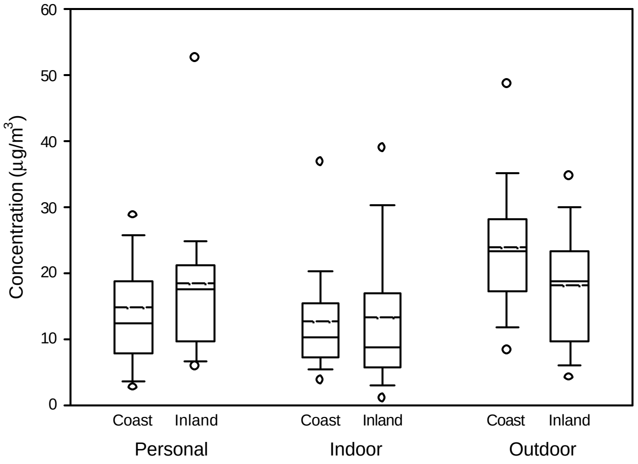
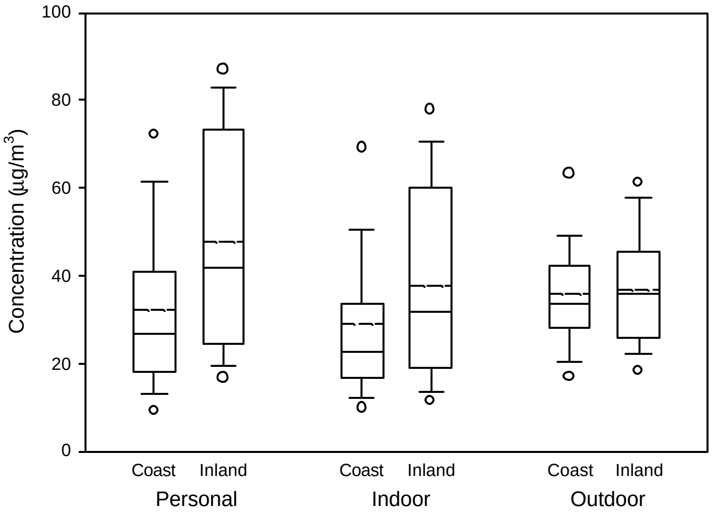


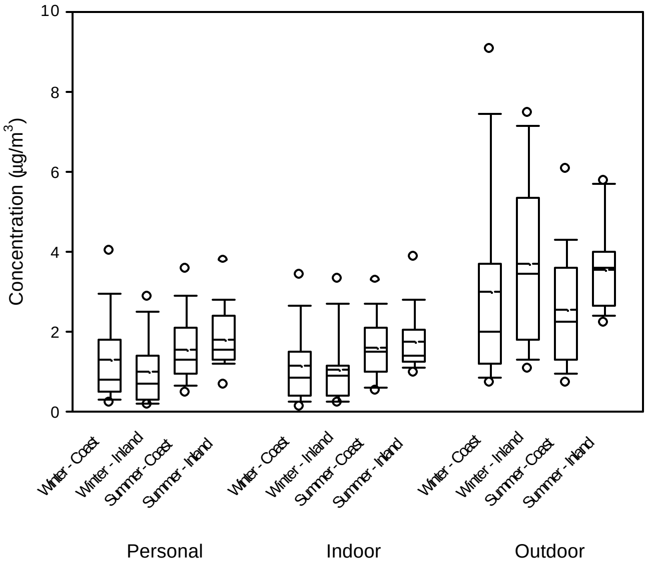
Figure 14. Wintertime PM_{10} Concentrations by Sample Type and Location



As with $PM_{2.5}$, inland PM_{10} levels were slightly higher than those measured for individuals living in coastal areas in the winter, with the differences most pronounced among personal exposures and indoor concentrations. For $PM_{2.5-10}$, in contrast, the wintertime concentration distributions were comparable for indoor concentrations and personal exposures. Outdoors, wintertime concentrations were significantly higher in coastal as compared to inland areas, which may result from greater contributions from wind blown dust and sea spray to coarse particle levels in these coastal areas.

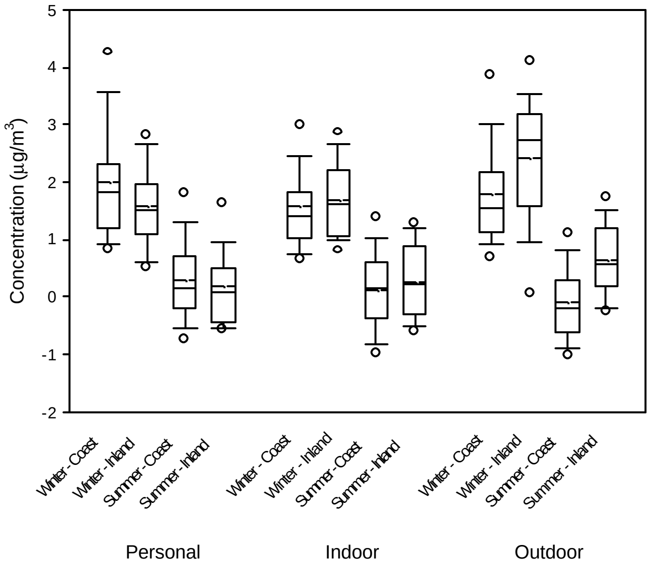
Outdoor NO_3^- concentrations were significantly higher than corresponding indoor and personal levels in both seasons (Figure 15), which is consistent with the fact that motor vehicles are the major source of NO_3^-. In indoor and personal microenvironments, summertime levels were statistically higher than wintertime levels. This seasonal difference may actually be even more pronounced than was observed, as NO_3^- measurements were shown to be high in the winter as compared to the standard methods. Outdoor NO_3^- concentrations were statistically similar across seasons, but again based on results from the accuracy tests may be more indicative of higher summer as compared to winter concentrations. The location of the homes relative to the coast was again found to impact observed outdoor concentrations, where outdoor NO_3^- concentrations were significantly higher in the inland areas as compared to those along the coast. The effects of location on personal and indoor levels were less pronounced and less consistent.

Figure 15. NO_3^- Concentrations by Sample Type, Season, and Location



For elemental carbon, strong seasonal differences in the concentration relationships were observed, as elemental carbon concentrations in the summer were very low (Figure 16). Outdoor EC levels were higher in the inland as compared to the coastal areas in both seasons. Indoor and personal levels were, in contrast, comparable across geographical locations. In the inland areas, outdoor concentrations tended to be higher than the corresponding personal and indoor levels in both seasons, with a pattern similar to that for inland nitrate concentrations but less distinct. On the other hand, personal EC exposures in the coastal areas were generally higher than corresponding indoor and outdoor levels, which may reflect differences in the inland and coastal study participants in terms of their activities and housing characteristics.

Figure 16. EC Concentrations by Sample Type, Season, and Location



As mentioned previously, eight elements were detected with sufficient frequency to allow their values to be summarized and included in subsequent data analyses. These eight elements represent a range of source types. Al is thought to originate primarily from crustal material, Ni and Ba from fuel oil combustion (residual oil) (Wongphatarakul *et al.*, 1998), B from coal combustion (Zevenhoven and Kilpinen, 2001), and Mn, B, Cr, Zn, and Pb from various industrial processes (Spengler and Thurston, 1983; Lyons *et al*., 1993; Lee *et al*., 1994). Ba may also be associated with motor vehicles, as Ba is a known component of brakewear (Garg et al., 2000; Torre et al., 2002). Similarly, Pb may also be associated with motor vehicles, even though it is no longer added to gasoline, as several source apportionment studies still show Pb to be related to other motor vehicle tracers. The contribution of sea spray to $PM_{2.5}$ concentrations could unfortunately not be determined due to unreliable detection of sodium by ICP-MS.

Various seasonal patterns were found for the eight measurable elements (Al, B, Ba, Cr, Mn, Ni, Pb, and Zn) in the personal, indoor, and outdoor samples. Aluminum (Al), a crustal-related element was present at the highest concentrations, with a median level of at least 13 ng/m^3 across different sample types and both seasons (Table 11b). In personal, indoor, and outdoor microenvironments, Al, B, Cr, and Zn varied seasonally, with the higher summer median levels for B and Cr and higher Zn and Al levels during wintertime. In both seasons, personal Al exposures were higher than corresponding outdoor and indoor levels, while for indoor and outdoor Al concentrations were comparable. For Ba, Mn, and Pb, seasonal differences were dependent on sample type, with wintertime outdoor concentrations consistently highest. Finally, neither seasonal nor sample type differences were found for Ni concentrations.

$PM_{2.5}$ Percent Composition

The composition of personal, indoor, and outdoor $PM_{2.5}$ was examined to test the first hypothesis that the composition of personal and indoor $PM_{2.5}$ exhibits significant inter- and intra-personal variation.

The average contribution of NO_3^- and EC to $PM_{2.5}$ differed by season and by sample type (Table 12). [The contribution of the elements to $PM_{2.5}$ concentrations could not be determined due to uncertainty about the oxidation states and chemical forms of the elements.] In both seasons, NO_3^- comprised a greater fraction of outdoor $PM_{2.5}$ on average as compared to indoor and personal $PM_{2.5}$. In addition, the percent contribution of outdoor, but not indoor nor personal, NO_3^- varied by seasons. For EC, the percent contributions were generally similar for outdoor, indoor, and personal samples in a given season. In the summer, this contribution was extremely low, where EC contributed essentially nothing to the corresponding $PM_{2.5}$ levels. For all three sample locations, both NO_3^- and EC comprised a relatively small fraction of the overall $PM_{2.5}$ mass, especially for summertime personal and indoor $PM_{2.5}$ samples for which NO_3^- and elemental carbon comprised less than 14% of the measured mass. Similar contributions of NO_3^- and EC to both personal and indoor $PM_{2.5}$ concentrations across seasons may be indicative of the importance of indoor particle sources to indoor and personal $PM_{2.5}$ exposures.

Table 12. Percent Composition of $PM_{2.5}$ Mass Concentrations by Season (%)

Pollutant	Summer			Winter		
	Indoor	Outdoor	Personal	Indoor	Outdoor	Personal
NH_4NO_3[*]	13.09	17.95	10.62	9.59	28.46	9.86
EC	0.23	0.00	0.78	12.99	17.00	14.19
Others	86.68	82.05	88.60	77.42	54.54	75.95

[*] NO_3^- mass contributions were determined assuming that all NO_3^- was in the form of NH_4NO_3.

The mean percent contribution of elemental carbon to $PM_{2.5}$ did not differ by sample type in either season using ANOVA techniques, which may be due to the fact the elemental carbon comprised a small fraction of $PM_{2.5}$, especially in the summer. In contrast, the mean percent contribution of nitrate differed by sample type in both seasons, where nitrate comprised a greater fraction of outdoor

Particulate Pollutant Relationships

For outdoor, indoor, and personal samples, correlations among $PM_{2.5}$ and its components (EC, and NO_3^-) varied from weak to relatively strong, although most of them were statistically significant (Table 13a). In both seasons, correlations among these pollutants tended to be strongest among outdoor concentrations followed by personal exposures and indoor concentrations. Stronger associations among the pollutants outdoors as compared to indoors may reflect the fact that the sources of NO_3^-, EC, and to a lesser degree $PM_{2.5}$ are located primarily outdoors, including traffic and other motor vehicle-related pollution. The weaker associations among personal exposures as compared to outdoor concentrations likely reflects the fact that individuals spent time both outdoors and indoors. For all 3 sampling types, associations were strongest between $PM_{2.5}$ and NO_3^-, especially in outdoor environments, while the correlations between NO_3^- and elemental carbon and between $PM_{2.5}$ and elemental carbon were weak. Correlations between NO_3^- and elemental carbon were higher in outdoor and personal environments, but were still only moderately correlated, with the strongest associations observed in the summer months.

In the winter, for personal, indoor, and outdoor samples, the associations between $PM_{2.5-10}$ and PM_{10} were relatively strong and comparable to those between PM_{10} and $PM_{2.5}$. Personal and indoor $PM_{2.5}$ were only weakly correlated with corresponding $PM_{2.5-10}$ levels, and outdoor $PM_{2.5}$ was insignificantly associated with $PM_{2.5-10}$ outdoors. Additionally, $PM_{2.5-10}$ was poorly correlated with NO_3^- and EC. These results are consistent with the fact that sources of $PM_{2.5-10}$ differ from those of $PM_{2.5}$ and its components NO_3^- and EC. These results also suggest that the variability of PM_{10} in greater Los Angeles reflects the sum of the fine and coarse particle variability. Although this finding differs from that in our Boston COPD study, in which the correlations between PM_{10} and $PM_{2.5}$ were stronger than those between PM_{10} and $PM_{2.5-10}$, they were not unexpected as $PM_{2.5-10}$ concentrations in Los Angeles were higher than that observed in Boston (Table 11a).

Table 13a. Spearman Correlations (r_s) among $PM_{2.5}$, NO_3^-, EC, PM_{10}, and $PM_{2.5-10}$ Levels

Season	Type	Pollutant	NO_3^-	EC	PM_{10}	$PM_{2.5-10}$
Summer	**Indoor**	**$PM_{2.5}$**	***0.43***	***0.28***		
		NO_3^-		***0.31***		
Summer	**Outdoor**	**$PM_{2.5}$**	***0.82***	***0.43***		
		NO_3^-		***0.44***		
Summer	**Personal**	**$PM_{2.5}$**	***0.58***	***0.27***		
		NO_3^-		***0.44***		
Winter	**Indoor**	**$PM_{2.5}$**	***0.51***	***0.41***	***0.84***	***0.38***
		NO_3^-		0.17	***0.54***	***0.31***
		EC			***0.29***	0.06
		PM_{10}				***0.75***
Winter	**Outdoor**	**$PM_{2.5}$**	***0.80***	***0.51***	***0.60***	-0.06
		NO_3^-		***0.36***	***0.59***	0.03
		EC			0.18*	-0.14
		PM_{10}				***0.70***
Winter	**Personal**	**$PM_{2.5}$**	***0.49***	0.18	***0.78***	***0.34***
		NO_3^-		***0.30***	***0.41***	0.16
		EC			0.10	0.01
		PM_{10}				***0.82***

Italic bold indicates $p<0.05$; * p-value<0.10

Table 13b. Spearman Correlations (r_s) between $PM_{2.5}$ and Elemental Concentrations

Season	Type	Pollutant	B	Al	Cr	Mn	Ni	Zn	Ba	Pb
Summer	**Indoor**	**$PM_{2.5}$**	***0.35***	***0.35***	0.17	***0.21***	***0.32***	***0.45***	***0.58***	***0.61***
		B		0.10	***-0.21***	-0.16	-0.09	0.03	***0.38***	***0.36***
		Al			-0.05	***0.36***	***0.23***	***0.49***	***0.20***	***0.27***
		Cr				0.17	***0.23***	0.12	0.10	0.18
		Mn					***0.29***	***0.56***	***0.26***	***0.24***
		Ni						***0.23***	0.16	***0.24***
		Zn							***0.51***	***0.48***
		Ba								***0.80***
Summer	**Outdoor**	**$PM_{2.5}$**	***0.42***	***0.58***	***0.21***	***0.34***	***0.45***	***0.51***	***0.54***	***0.54***
		B		***0.23***	-0.19	-0.20	-0.05	0.03	***0.41***	***0.49***
		Al			0.14	***0.45***	***0.32***	***0.59***	***0.42***	***0.46***
		Cr				0.10	***0.25***	0.15	0.10	0.16
		Mn					***0.35***	***0.62***	***0.33***	***0.27***
		Ni						***0.29***	0.20	***0.26***
		Zn							***0.48***	***0.50***
		Ba								***0.87***
Summer	**Personal**	**$PM_{2.5}$**	***0.29***	***0.26***	0.12	0.01	***0.32***	***0.33***	***0.47***	***0.39***
		B		-0.11	***-0.25***	***-0.32***	-0.06	0.11	***0.40***	***0.44***
		Al			-0.02	***0.34***	***0.27***	***0.40***	0.12	0.10
		Cr				-0.12	0.15	-0.03	0.02	0.04
		Mn					0.16	***0.27***	-0.17	-0.21
		Ni						***0.33***	***0.31***	***0.33***
		Zn							***0.53***	***0.51***
		Ba								***0.87***
Winter	**Indoor**	**$PM_{2.5}$**	***0.71***	0.17	***0.24***	***0.45***	***0.58***	***0.49***	***0.63***	***0.59***
		B		***0.29***	0.05	***0.44***	***0.76***	***0.46***	***0.72***	***0.63***
		Al			***0.28***	***0.27***	***0.21***	***0.29***	***0.35***	***0.22***
		Cr				***0.34***	0.06	0.19	***0.32***	***0.34***
		Mn					***0.43***	***0.66***	***0.65***	***0.56***
		Ni						***0.53***	***0.68***	***0.63***
		Zn							***0.64***	***0.71***
		Ba								***0.81***
Winter	**Outdoor**	**$PM_{2.5}$**	***0.70***	0.12	0.20	***0.29***	***0.51***	***0.34***	***0.47***	***0.56***
		B		***0.34***	-0.03	***0.33***	***0.68***	***0.47***	***0.63***	***0.66***
		Al			***0.34***	***0.46***	***0.33***	***0.40***	***0.46***	***0.37***
		Cr				***0.32***	0.02	0.07	0.13	0.08
		Mn					***0.34***	***0.56***	***0.65***	***0.58***
		Ni						***0.45***	***0.69***	***0.63***
		Zn							***0.63***	***0.70***
		Ba								***0.86***
Winter	**Personal**	**$PM_{2.5}$**	***0.67***	***0.43***	0.10	***0.36***	***0.48***	***0.40***	***0.35***	0.18
		B		***0.40***	0.06	***0.28***	***0.67***	***0.36***	***0.49***	***0.27***
		Al			***0.28***	***0.39***	***0.24***	***0.34***	***0.33***	0.15
		Cr				***0.35***	-0.04	0.09	***0.37***	0.12
		Mn					0.10	***0.31***	***0.51***	***0.38***
		Ni						***0.32***	***0.50***	***0.33***
		Zn							***0.27***	***0.34***
		Ba								***0.53***

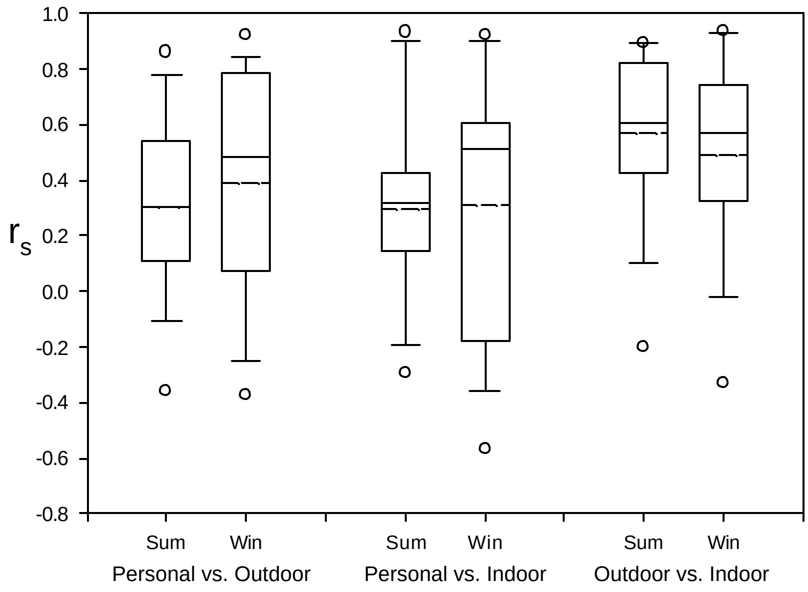
Italic bold indicates $p<0.05$.

For most elements, positive correlations between $PM_{2.5}$ and elemental concentrations were found, with correlations ranging from insignificant to relatively strong ($0.01<r_s<0.71$) (Table 13b). In both seasons, $PM_{2.5}$ and elemental levels tended to be more weakly correlated in personal microenvironments as compared to inside and outside the homes. Lead and barium were generally more strongly correlated with $PM_{2.5}$ as compared to other elements, especially in the summer. Furthermore, in both seasons and in all three microenvironments, lead and barium were strongly correlated with one another. Since both lead and barium are associated with motor vehicles, these significant correlations suggest that motor vehicles are an important source of fine particles in personal, indoor, and outdoor microenvironments. In the winter, $PM_{2.5}$ was most strongly correlated with boron in all three microenvironments. The observed strong correlations might be attributed to local boron sources, as boron is produced domestically in the State of California, with four major companies centered in southern California (U.S. Geological Survey, 2000). Lastly, for personal, indoor, and outdoor samples, chromium, aluminum, and manganese were insignificantly or weakly correlated with $PM_{2.5}$ in both summer and winter seasons. This lack of correlation may be to actual lack of correlation and/or to due to the uncertainty in the elemental concentration measurements, especially when the analytical uncertainty associated with elemental analysis was high in relationship to the measured concentrations.

Personal Exposures and Outdoor and Indoor Concentration Relationships

The relationship between personal exposures and indoor and outdoor concentrations was examined to test the second hypothesis that the relationship between personal exposures and corresponding outdoor concentrations differs for each particulate component. To test this hypothesis, the personal, indoor, and outdoor relationships were examined initially by pollutant, with results compared across pollutants.

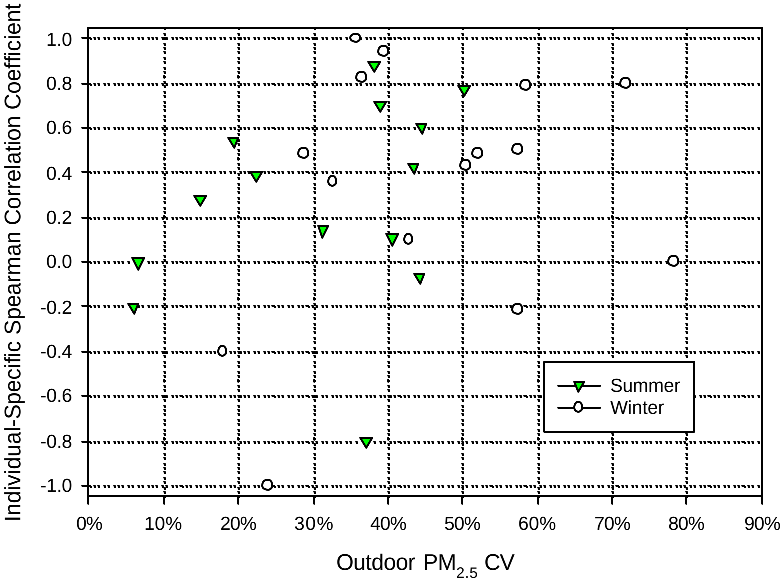
Figure 17. Individual-specific Spearman Correlation Coefficients for $PM_{2.5}$



$PM_{2.5}$. The associations between personal $PM_{2.5}$ exposures and corresponding outdoor home concentrations varied widely by individual (Figure 17), with the personal $PM_{2.5}$ exposures for some but not all individuals being significantly associated with outdoor concentrations. Median correlation coefficients were found to equal 0.49 in the winter and 0.30 in the summer. The relatively weak associations between personal and outdoor $PM_{2.5}$ concentrations in the summer were surprising, as these associations are typically strong due to increased ventilation during these months, as evidenced by the higher air exchange rates in the monitored Los Angeles homes and by results from similar studies conducted in Boston, MA (Rojas *et al.*, 2000), and Baltimore, MD (Sarnat *et al.*, 2000; Williams *et al.*, 2000). Although not directly comparable, the observed personal-ambient associations in our study are also lower than that found in Fresno, CA in the spring (Evans et al., 2000), during which an R^2 value of 0.70 for personal-ambient associations was found. These stronger associations in Fresno may be due to the fact that the Fresno participants, unlike those in our study, lived in a single retirement facility, thus minimizing individual-specific differences in indoor and outdoor exposures. The summer and winter median values in our study were, however, comparable to those in exposure studies conducted in the Western U.S. and Canada, including the study of individuals with COPD conducted in Vancouver, Canada (Ebelt *et al.*, 2000) and in Seattle, WA (Liu *et al.*, 2003).

Individual-specific indoor-outdoor associations for $PM_{2.5}$ followed a more commonly observed pattern, where associations were stronger in the summer as compared to winter months. Despite this, median correlation coefficients also tended to be low as compared to those from previous studies, especially in summer months. Perhaps most surprising, however, was the fact that individual-specific correlations for personal and indoor comparisons were weak, which was unexpected since participants spent the majority of their time indoors at home. Reasons for these weak correlations are unknown but may be due in part of higher sampler error in the summer.

Figure 18. Individual-Specific Correlation Coefficients for Personal-Outdoor $PM_{2.5}$ Comparisons vs. the Coefficient of Variation in Outdoor Concentrations



It is possible that the observed lower individual-specific correlation coefficients were due to the low variability in outdoor concentrations during the seven-day monitoring periods for some individuals. However, as shown on Figure 18, the individual-specific correlation coefficients were not related to the variability in outdoor concentrations, suggesting that other factors impact the ability of outdoor concentrations to reflect personal $PM_{2.5}$ exposures.

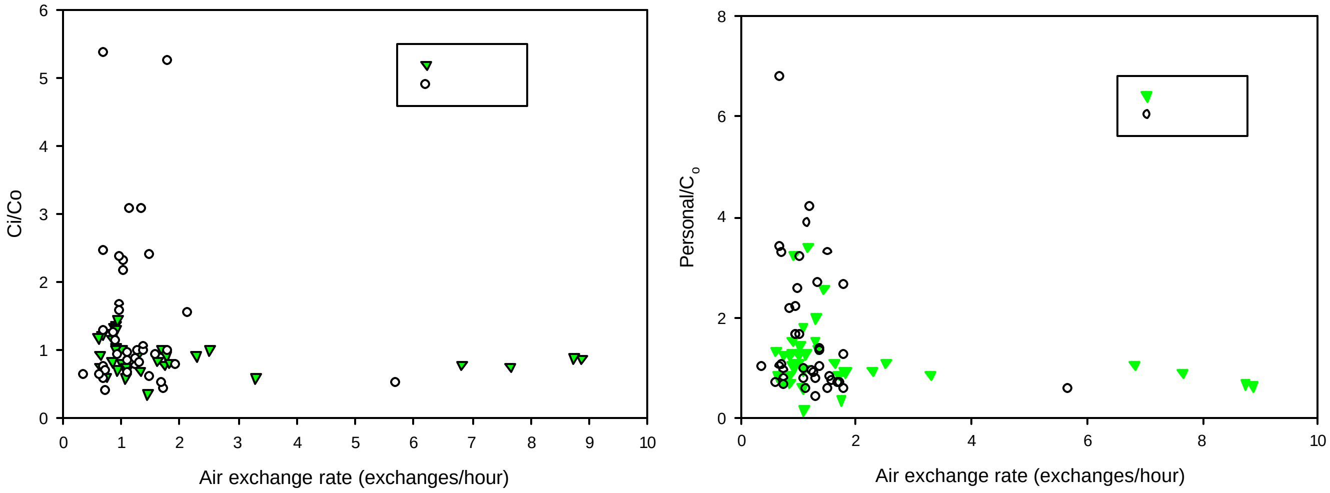
Table 14. Results of Longitudinal Analysis for Comparisons of Outdoor, Home Indoor and Personal Particulate Levels

Pollutant	**Comparison**	**Season**	**N**	**Slope**	**Std. Error**	**Intercept**	**Std. Error**	**Crude R^2**
$PM_{2.5}$	Personal vs. Outdoor	Winter	82	***0.51***	0.13	***13.2***	3.51	0.19
		Summer	90	***1.25***	0.22	1.01	4.70	0.30
	Personal vs. Indoor	Winter	80	***0.98***	0.08	2.51	1.75	0.63
		Summer	91	***0.56***	0.19	***15.0***	4.35	0.14
	Indoor vs. Outdoor	Winter	83	***0.42***	0.08	***11.3***	2.78	0.21
		Summer	95	***0.70***	0.11	4.48*	2.29	0.34
NO_3^-	Personal vs. Outdoor	Winter	89	***0.35***	0.03	0.12	0.14	0.61
		Summer	94	***0.24***	0.06	***0.97***	0.22	0.28
	Personal vs. Indoor	Winter	90	***0.91***	0.07	0.22*	0.11	0.65
		Summer	95	***0.66***	0.09	***0.53***	0.19	0.46
	Indoor vs. Outdoor	Winter	84	***0.25***	0.02	0.34*	0.16	0.60
		Summer	93	***0.27***	0.05	***0.89***	0.20	0.23
EC	Personal vs. Outdoor	Winter	84	***0.32***	0.08	***1.30***	0.23	0.17
		Summer	82	***0.60***	0.08	0.23*	0.12	0.38
	Personal vs. Indoor	Winter	80	***0.71***	0.11	***0.70***	0.22	0.36
		Summer	83	***0.69***	0.09	0.13	0.08	0.55
	Indoor vs. Outdoor	Winter	82	***0.38***	0.06	***0.87***	0.19	0.45
		Summer	92	***0.61***	0.08	0.12	0.09	0.42
PM_{10}	Personal vs. Outdoor	Winter	84	0.15	0.15	***29.6***	7.16	0.00
	Personal vs. Indoor	Winter	84	***0.65***	0.09	***14.8***	3.71	0.49
	Indoor vs. Outdoor	Winter	87	0.13	0.13	***26.8***	6.84	0.01
$PM_{2.5-10}$	Personal vs. Outdoor	Winter	80	-0.02	0.11	***15.0***	3.10	0.01
	Personal vs. Indoor	Winter	78	0.24*	0.14	***12.5***	2.63	0.06
	Indoor vs. Outdoor	Winter	82	0.08	0.10	***11.3***	3.06	0.00

Significant values ($p < 0.05$) in bold
* p value < 0.10

When data were analyzed using repeated measures regression models, the relationships between personal exposures and indoor and outdoor home concentrations were found to follow similar patterns as has been observed in previous studies (Table 14). For personal-outdoor and indoor-outdoor comparisons for $PM_{2.5}$, for example, the wintertime slope of the regression lines was substantially lower than one with a significant intercept, which is consistent with a low effective penetration efficiency and a significant contribution of indoor (or personal) pollutant sources, respectively. Both the low effective penetration efficiency and the higher indoor (or personal) source contribution are consistent with the lower air exchange rates found in the winter (Figure 11). At these lower air exchange rates, particles penetrate less efficiently from outdoor to indoor environments, as reflected by the lower wintertime slopes for personal and outdoor $PM_{2.5}$ and for indoor and outdoor $PM_{2.5}$ comparisons (Sarnat et al., 2000). In addition, particles emitted from indoor sources have more time to accumulate when air exchange rates are low. Consequently, the contribution of indoor particulate sources to indoor $PM_{2.5}$ concentrations – and thus personal exposures – is generally higher in poorly ventilated environments, resulting in higher wintertime intercepts (Sarnat et al., 2000).

Figure 19a. Indoor (C_i)/Outdoor (C_o) and Personal/Outdoor $PM_{2.5}$ Ratios vs. Air Exchange



Rates**

*includes data only for detached homes

The effect of air exchange rates on indoor concentrations is also illustrated in Figure 19a, in which the ratio of indoor-to-outdoor and personal-to-outdoor $PM_{2.5}$ concentrations is plotted against air exchange rates. At relatively high air exchange rates of around 1.5 exchanges/hour and above, the indoor-outdoor and personal-outdoor ratios were generally close to one, which is consistent with indoor-outdoor penetration efficiencies close to one and a reduced influence of indoor sources. In contrast, at air exchange rates below 1 exchange/hour, indoor-outdoor and personal-outdoor ratios ranged widely with many values substantially greater than one, suggesting that indoor $PM_{2.5}$ sources can impact indoor concentrations at these lower air exchange rates. Consistent with these findings, indoor/outdoor $PM_{2.5}$ ratios for detached homes are shown to be near one when open windows are open more than 40% of the time (Figure 19b).

For attached homes, however, the results are less clear, with no relationship between indoor/outdoor ratios and home ventilation (Figure 19c). Reasons for this discrepancy are unknown but may be due to differences in the movement of particles from outdoor to indoor environments in apartments and other attached homes. Home ventilation was found to have a similar effect on the association between personal exposures and outdoor concentrations for individuals living in detached homes. Again, for other individuals, home ventilation had little or no effect on personal-outdoor associations.

Figure 19b. Indoor-Outdoor $PM_{2.5}$ Ratios vs. Open Window Frequency: Detached Homes

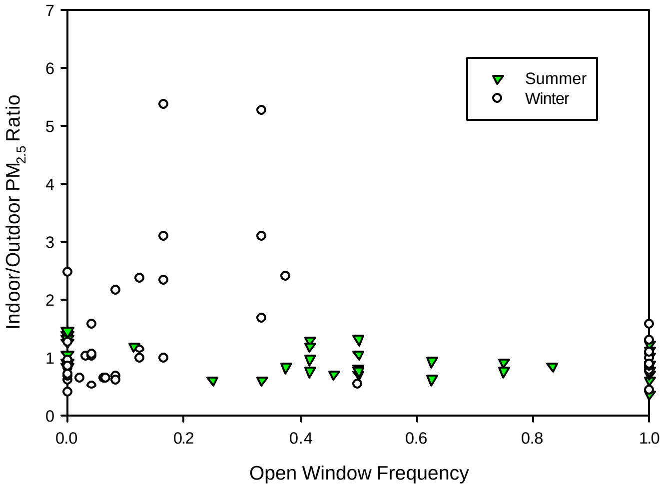
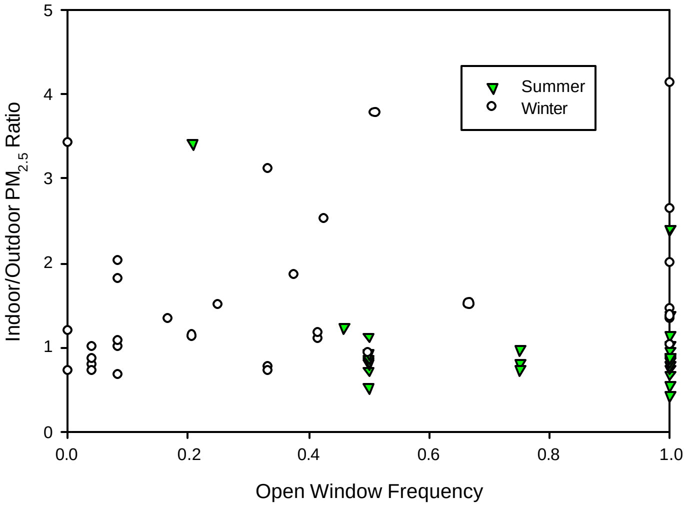


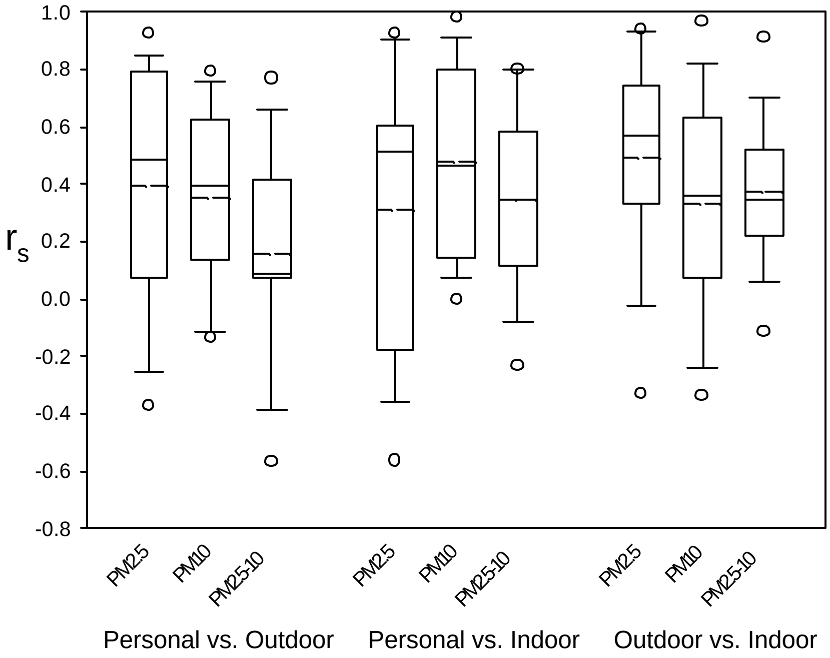
Figure 19c. Indoor-Outdoor $PM_{2.5}$ Ratios vs. Open Window Frequency: Attached Homes



$PM_{2.5\text{-}10}$ and PM_{10}. Individual specific associations between personal exposures and corresponding outdoor concentrations were weak for $PM_{2.5\text{-}10}$, with individual-specific correlations much weaker than those observed for $PM_{2.5}$ (Figure 20). The individual-specific correlations for PM_{10} generally fell between those for $PM_{2.5}$ and $PM_{2.5\text{-}10}$, which is expected since PM_{10} is the compilation of the two particulate measures. These associations are similar to the winter results from previous studies in Boston (Rojas-Bracho et al., 2001) and Baltimore (Sarnat et al., 2000). Since no information on the individual-specific associations are available for the summer months, the overall comparability of the PM_{10} and $PM_{2.5\text{-}10}$ to earlier studies is not known.

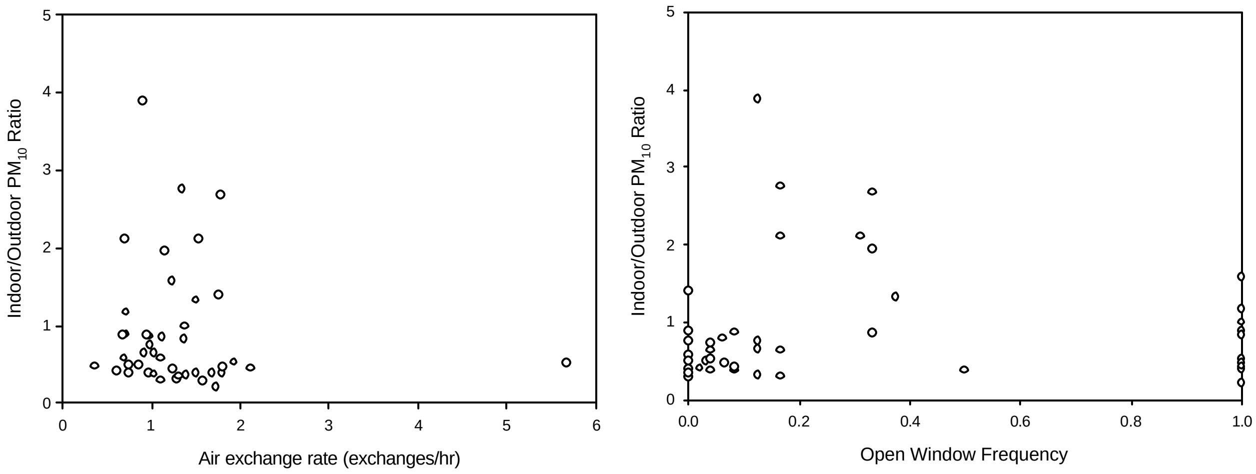
When data were analyzed longitudinally across participants, the relationships among the winter outdoor, indoor, and personal $PM_{2.5\text{-}10}$ concentrations were weak, as shown by insignificant slopes and the near zero crude R^2 values (Table 14). For PM_{10}, winter personal-outdoor and indoor-outdoor associations were similarly insignificant; however, personal exposures and indoor concentrations were significantly associated, with a slope of 0.65, an intercept of approximately 15 ug/m^3, and a crude R^2 of 0.49 when personal exposures were regressed on indoor concentrations. Significant personal-indoor associations for PM_{10} in the winter may be due to the fact that $PM_{2.5}$ comprises a significant fraction of PM_{10} and that individuals spent most of their time indoors. These associations did not change when analyses were conducted by inland or coastal location, which may be due to small number of inland homes.

Figure 20. Individual-specific Spearman Correlation Coefficients for $PM_{2.5}$, $PM_{2.5\text{-}10}$, and PM_{10} during Wintertime



The impact of air exchange rates and open window use on indoor/outdoor ratios were difficult to examine due to the fact that PM_{10} concentrations were available only for the winter season. As shown on Figures 21a and b, however, the relationship between indoor/outdoor concentration ratios and home ventilation for PM_{10} was similar to that observed for $PM_{2.5}$ for single family, detached homes. Indoor/outdoor concentrations ratios were generally below or near one at high ventilation conditions and were only above one when air exchange rates or open window frequencies were low, again illustrating that the contribution of indoor sources is only evident when ventilation is poor. Indoor/outdoor ratios lower than one and lower than that found for $PM_{2.5}$ are consistent with the higher deposition rates for PM_{10} as compared to $PM_{2.5}$. For attached homes, ventilation conditions appeared to have no effect on indoor/outdoor concentration ratios (figure not shown). As mentioned previously, this lack of association may result from inaccurate reporting of open window frequency or to differences in the movement of particles from outdoor to indoor environments in apartments and other attached homes.

Figure 21. Winter Indoor/Outdoor PM_{10} Ratios vs. Home Ventilation: Detached Homes

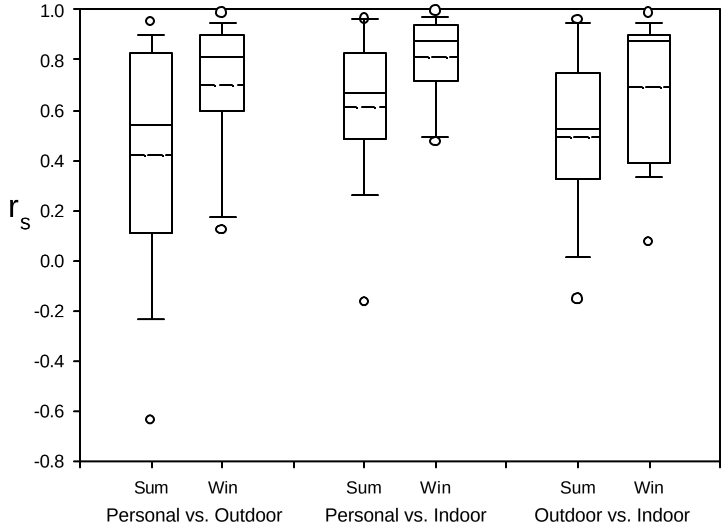


a. Air exchange rates

b. Open window frequency

NO_3^-. For NO_3^-, individual-specific correlation coefficients for all pair-wise comparisons were higher and less variable in the winter as compared to the summer (Figure 22a). The variability was lower in both seasons for the personal-indoor associations as compared to the personal-outdoor and indoor-outdoor associations; nonetheless, the season-specific median coefficients were similar for all pair-wise comparisons. Stronger winter- as compared to summer-time associations were somewhat unexpected, as sources of NO_3^- are located primarily outdoors (as reflected by the higher outdoor concentrations) and infiltration of NO_3^- and other particles of outdoor origin is traditionally greatest in the summer months when air exchange rates are highest.

Figure 22a. Individual-specific Spearman Correlation Coefficients for NO_3^-



When data were analyzed longitudinally across participants, similar results were found (Table 14). For comparisons of personal NO_3^- exposures with outdoor and indoor concentrations, slopes and crude R^2 values were generally higher in the winter as compared to summer, while the slopes of the regression of indoor on outdoor concentrations did not vary by season. These results are inconsistent with those for $PM_{2.5}$ and with those from previous studies, which have found the slopes for personal-outdoor and indoor-outdoor associations to be greatest in the summer when homes tend to be well ventilated (Sarnat et al., 2000; Suh et al., 1994). Results suggest that ventilation had little effect on the effective penetration efficiency of NO_3^-. Correspondingly, home ventilation conditions, measured as either air exchange rates or open window frequency, had generally no effect on the associations between indoor and outdoor and between personal and outdoor levels (Figures 22b and c). Several factors may contribute to these findings. Seasonal differences in the accuracy of the mini-sampler, for example, may contribute to observed higher winter associations, as the mini-PEM concentrations were higher than the reference sampler in the winter months (Figure 7). Since the mini-PEM was used to measure personal, indoor, and outdoor NO_3^- concentrations, this factor alone is insufficient to explain the observed results. Alternative explanations include greater volatilization or loss of NO_3^- in indoor environments or during the hotter summer months or different NO_3^- formation and removal processes in outdoor and indoor microenvironments (Riley *et al.*, 2002), as seasonal and micro-environmental changes in temperature, relative humidity, sunlight, and aerosol and pollutant composition may affect the volatility of NO_3^- (Hering and Cass, 1999).

Intercepts for each of the pair-wise comparisons were generally insignificant in the winter and significant during the summer. These results indicate that the contributions of indoor and personal NO_3^- sources were important only during the summer. Again, this could reflect greater formation of NO_3^- indoors in the summer months or greater loss of NO_3^- indoors in the winter months. In both seasons, indoor concentrations were consistently shown to be better indicators of personal exposures as compared to outdoor levels, which is not surprising given that individuals spent the majority of their time indoors at home. Similar results were found in both the coastal and inland areas. The generalizability of these results to other studies and communities is not currently possible, as no other studies have been performed to date characterizing the relationship between personal, indoor, outdoor NO_3^- concentrations.

Figure 22b. Indoor/Outdoor NO_3^- Ratios vs. Home Ventilation: Detached Homes

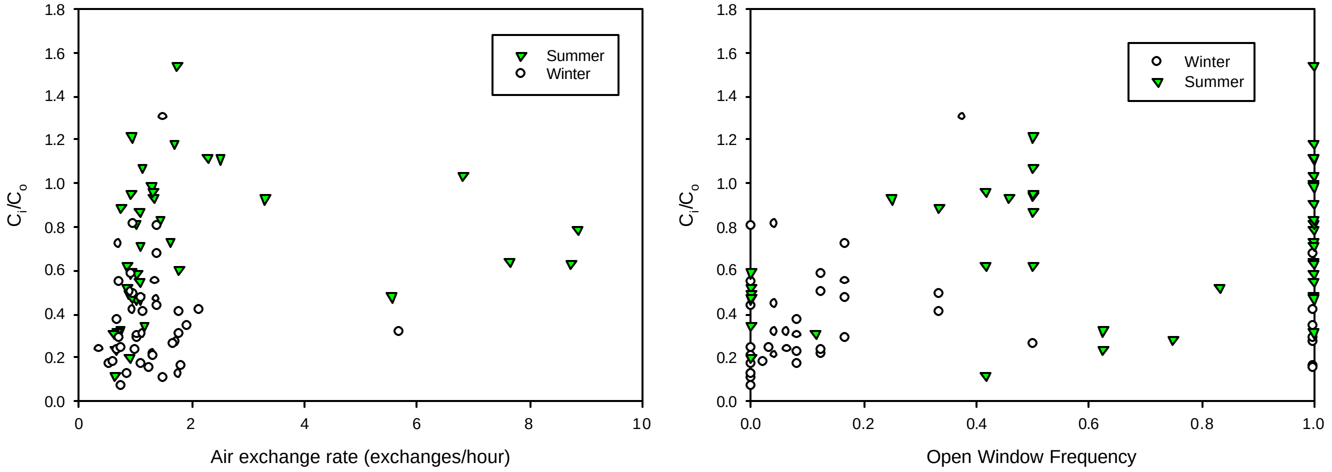
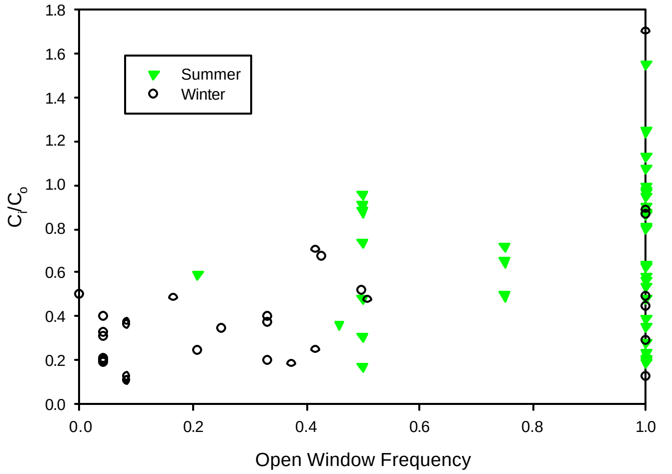
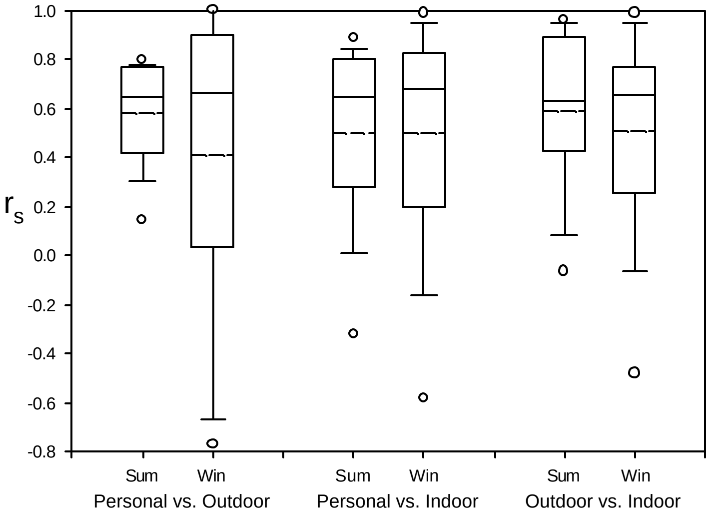


Figure 22c. Indoor/Outdoor NO_3^- Ratios vs. Home Ventilation: Attached Homes



Elemental carbon. For elemental carbon, individual correlation coefficients were generally less variable in the summer as compared to winter (Figure 23), with season-specific median coefficients comparable for all pair-wise comparisons. This lack of variability in the correlation coefficients in the summer may be due to the fact that summertime elemental carbon concentrations were extremely low in all three microenvironments, with the lowest concentrations measured outdoors. For elemental carbon in the winter, the association between personal exposures and outdoor concentrations exhibited the greatest variability, suggesting that the variability in the contribution of indoor elemental carbon sources to corresponding personal exposures was greater in the wintertime as well.

Figure 23. Individual-specific Spearman Correlation Coefficients for EC



The longitudinal associations between personal exposures and indoor levels on corresponding outdoor concentrations were similar to those for $PM_{2.5}$, where slopes were lower and intercepts were greater during the winter as compared to the summer (Table 14). Again, the seasonal differences may be attributed to seasonal differences in home ventilation conditions, where poorer ventilation conditions would result in lower effective penetration efficiencies and higher indoor source contributions in the winter. Consistent with this theory, significant intercepts were found for all of the wintertime associations, suggesting the greater influence of indoor EC sources in the winter. When examined explicitly, however, neither air exchange rates nor open window frequency (as continuous or categorical variables) were found to affect the association between indoor and outdoor elemental carbon concentrations or the association between personal exposures and outdoor elemental carbon concentrations. Reasons for this are unclear but may be related to measurement or reporting error of air exchange rates and open window frequency, respectively. Observed indoor-outdoor and personal-outdoor associations did not differ when data were analyzed by geographic location, although the observed relationships – as shown by the crude R^2 values – were stronger in homes located in coastal as compared to inland areas. The generalizability of these results to other studies and communities is not currently possible, as studies characterizing the relationship between personal, indoor, outdoor EC concentrations are currently underway and have not yet been published in the peer-reviewed literature.

Source Contributions

Due to the limited number of elements that were detected, traditional source apportionment and mass reconstruction methods could not be used to apportion $PM_{2.5}$ into source types (Andrews, *et al.*, 2000; Malm, *et al.*, 1994; Yakovleva, *et al.*, 1999). As a result, other statistical tests were used to determine the source contributions to $PM_{2.5}$. These tests included single- and multivariate regression, longitudinal analysis, and the investigation of the enrichment factors.

Unfortunately, results from these tests were difficult to interpret. For example, multiple regression techniques that allowed for repeated measures were used to estimate the contribution of various components to $PM_{2.5}$ by season. As shown on Table 15, the meaning of the model coefficients were especially difficult to interpret, due in part to the uncertainty about the oxidation state and chemical form of the elements. For the elements, the slopes could not be used to infer information about possible chemical forms of the elements. For nitrate and elemental carbon, the slopes were likely affected by correlations among the different particulate components, since nitrate and elemental carbon slopes should otherwise have been close to one. Other tests yielded similarly confusing results. Possible explanations for the failure of these tests may include the small sample volumes used during sampling, the low number of detectable elements, and the narrow range of observed concentrations for some elements.

Table 15. Compositional Regression Models for $PM_{2.5}$

	Summer			**Winter**		
	Indoor	**Outdoor**	**Personal**	**Indoor**	**Outdoor**	**Personal**
$NH_4NO_3^{-*}$	**1.94**	**2.32**	**3.70**	**2.16**	**0.92**	**1.74**
EC				**2.97**	**1.08**	
Al	**19.0**	**33.0**				
B	**683.2**	**578.6**	**699.1**	**536.1**	**894.2**	**735.7**
Mn	**1829.9**					**1117.6**
Ni						**476.3**
Intercept	**6.46**	**6.62**	**9.79**	**4.50**	**4.26**	**6.75**
RMSE**	5.47	5.32	12.45	7.42	3.78	8.22
R^2	0.54	0.67	0.21	0.62	0.81	0.67

* NO_3^- mass contributions were determined assuming that all NO_3^- was in the form of NH_4NO_3.
** RMSE = root mean square of error
Bold indicates $p < 0.05$

Indoor Concentration and Personal Exposure Factors

Analysis of Variance (ANOVA) procedures and longitudinal regression analyses were performed to examine the effects of potential particle-emitting activities, geographical location, traffic, and population density on the exposure levels.

Factors affecting outdoor concentrations. The geographic location of the homes were generally found to be important predictors of their outdoor $PM_{2.5}$ and NO_3^- concentrations (Table 16a). Outdoor $PM_{2.5}$ concentrations at homes located along the coast were approximately 6.5 and 5.6 ug/m^3 lower than those measured outside homes located in inland locations during the summer and winter, respectively. For NO_3^-, outdoor concentrations were approximately 1.5 ug/m^3 lower for coastal homes in both seasons. As either continuous or categorical variables, population density and distance from road were not found to impact winter outdoor $PM_{2.5-10}$ or EC concentrations at the home in either season. Homes located in high population density areas were found to have 0.38 ug/m^3 on average lower wintertime outdoor EC levels as compared to other homes. This result was surprising, since data from previous studies suggests the opposite to be true (Burton et al., 1996; Kinney et al., 2000). In addition, population density was an insignificant predictor of outdoor home concentrations for all other fine particulate parameters, suggesting that this effect may have no real physical meaning. Traffic was shown to contribute to outdoor summer $PM_{2.5}$, winter PM_{10}, and summer NO_3^- concentrations; however, the effect of traffic was dependent on the definition of "high" traffic. For $PM_{2.5}$ and NO_3^-, the effect was present for individuals living within 100 meters of a major road, but disappeared when the definition was expanded to include homes located within 250 meters of the major roads. These findings are somewhat consistent with those from a study of fine and ultra-fine particle concentrations by a southern California highway, which showed that the effect of traffic on ultra-fine particle concentrations dropped 100 meters from the highway (Zhu et al., 2002). In contrast, traffic was a significant predictor of winter PM_{10} concentrations only when the effect was seen for individuals living within 250 meters of the major road, but not present when the analysis was restricted to homes within 100 meters of the road. Reasons for this discrepancy are not clear, but may be related to the fact that few homes were located within 100 meters of a busy road, which provided limited power to examine the effect of road distance on fine particle concentrations.

Table 16a. Factors Affecting Outdoor Particulate Concentrations

Pollutant	Summer					Winter				
	N	Factor[1]	Estimate	SE	t-stat	N	Factor[1]	Estimate	SE	t-stat
$PM_{2.5}$	86	**Geography**	**-6.46**	**2.54**	**-2.54**	83	**Geography**	**-5.64**	**1.36**	**-4.15**
		Traffic-250	3.44	2.42	0.18		Traffic-250	0.33	1.71	0.85
		Traffic-100	**5.86**	**2.19**	**2.68**		Traffic-100	1.04	1.91	0.54
		Pop. Dens.	3.73	2.54	1.47		Pop. Dens.	-0.58	1.74	-0.34
$PM_{2.5-10}$						80	Geography	4.61	4.33	1.06
							Traffic-250	4.34	3.43	1.27
							Traffic-100	-1.41	4.14	-0.34
							Pop. Dens.	-4.74	3.49	-1.36
PM_{10}						85	Geography	-1.82	3.60	-0.51
							Traffic-250	**5.85**	**2.39**	**2.45**
							Traffic-100	1.81	3.29	0.36
							Pop. Dens.	-5.09	2.78	-1.83
NO_3^-	85	**Geography**	**-1.49**	**0.54**	**-2.78**	88	**Geography**	**-1.53**	**0.44**	**-3.48**
		Traffic-250	0.76	0.52	1.45		Traffic-250	0.00	0.50	0.01
		Traffic-100	**1.46**	**0.43**	**3.36**		Traffic-100	0.46	0.54	0.85
		Pop. Dens.	0.31	0.59	0.53		Pop. Dens.	-0.13	0.50	-0.26
EC^2						91	Geography	**-0.36**	0.22	-1.66
							Traffic-250	0.22	0.18	1.27
							Traffic-100	0.18	0.20	0.90
							Pop. Dens.	**-0.38**	**0.14**	**-2.72**

[1] All factors are categorical. Estimates for "geography" show concentration difference between coastal and inland homes. "Traffic-250" and "traffic-150" indicate concentration differences for homes with "high" and "low" traffic, with definitions of "high" traffic being those homes located less than 250 and 100 meters from busy roads,

respectively. “Population density” indicates concentration differences for homes located in areas with high (>3500 persons/sq.mile) and low (<3500 persons/sq.mile) population densities. Significant factors in bold.

[2] EC concentrations were not available from the SAM site during the summer season.

Factors affecting indoor concentrations. Particle-generating activities were not found to be important contributors to indoor particulate concentrations, as cooking, cleaning and ETS were statistically insignificant predictors of indoor concentrations (Table 16b). This result was no doubt due to the fact that participants were relatively inactive, with little time spent participating in these activities. For indoor NO_3^-, air exchange rates were found to be an important effect modifier, with its penetration efficiency increasing and the indoor source contribution decreasing with air exchange rates. For other particulate species, air exchange rates were neither a significant covariate nor an important effect modifier. These results may be due to the non-linear effect of air exchange rates on indoor concentrations. When air exchange rates are greater than one exchange/hour, as was the case in the monitored homes of our study, large changes in the measured air exchange rate correspond to only small changes in the home ventilation conditions and thus to only minimal effects on indoor concentrations.

Other factors that were identified were important to specific particulate species during certain seasons. In the summer, few factors were important other than outdoor concentrations. For $PM_{2.5}$, geographic location was found to be important in the summer, as indoor $PM_{2.5}$ concentrations were on average 9.6 (±1.3) $\mu g/m^3$ lower in coastal residences as compared to those located inland. Population density, on the other hand, was an important determinant of wintertime indoor EC concentrations, where the indoor levels increased by 0.21 (±0.05) $\mu g/m^3$ with every 1000 persons per km^2. For $PM_{2.5-10}$ in the winter, no factor, including outdoor concentrations, were important predictors of indoor concentrations. This finding is consistent with the fact that sources of $PM_{2.5-10}$ are located primarily indoors.

Table 16b. Factors Affecting Indoor Particulate Concentrations[1]

Pollutant	Summer					Winter				
	N	Factor	Estimate	SE	R^{2+}	N	Factor	Estimate	SE	R^{2+}
$PM_{2.5}$	48	Intercept Outdoor Location	**14.3** **0.56** **-9.6**	1.9 0.06 1.3	0.72	45	Intercept Outdoor	**10.1** **0.30**	3.1 0.09	0.12
$PM_{2.5-10}$						45	Intercept Outdoor	**11.5** 0.004	3.5 0.12	0.01
PM_{10}						50	Intercept Outdoor	**22.6** 0.15	8.9 0.19	0.00
NO_3^-	40	Intercept Outdoor AER[2] Co*AER[4]	**1.21** 0.04 -0.07 **0.05**	0.27 0.07 0.08 0.02	0.39	42	Intercept Outdoor AER[2] Co*AER[4]	**0.88** 0.06 -0.49 0.14*	0.36 0.07 0.30 0.07	0.42
EC	46	Outdoor	**0.63**	0.13	0.37	48	Outdoor PopDens[1]	**0.45** **0.21**	0.10 0.05	0.69

[1] Significant factors in bold. [2] AER: air exchange rate [3] per 1000 persons/sq.mile [4] Interaction between outdoor concentration and air exchange rates, indicates influence of air exchange rates on penetration efficiency of outdoor particles

Table 16c. Factors affecting Personal Particulate Exposures*

Pollutant	Summer					Winter				
	N	Factor	Estimate	SE	R^{2+}	N	Factor	Estimate	SE	R^{2+}
$PM_{2.5}$	74	Intercept	*10.16*	5.57	0.17	74	Intercept	1.36	2.29	0.70
		F_iC_i	**0.71**	**0.27**			**F_iC_i**	**1.05**	**0.09**	
		F_oC_o	1.19	1.51			F_oC_o	1.33	1.33	
		F_{smoke}	-5.91	29.45			**F_{smoke}**	**2.82**	**1.44**	
		F_{clean}	3.30	2.87			F_{clean}	-1.18	1.03	
		F_{cook}	-0.72	2.20			F_{cook}	0.78	1.36	
$PM_{2.5-10}$						73	**Intercept**	**10.57**	**3.45**	0.09
							F_iC_i	*0.23*	*0.13*	
							F_oC_o	0.78	1.09	
							F_{smoke}	0.31	1.90	
							F_{clean}	-1.76	1.88	
							F_{cook}	1.39	1.38	
PM_{10}						79	**Intercept**	**11.92**	**4.50**	0.50
							F_iC_i	**0.66**	**0.09**	
							F_oC_o	0.94	1.0	
							F_{smoke}	3.28	2.61	
							F_{clean}	-2.44	1.87	
							F_{cook}	2.26	2.39	
NO_3^-	91	**Intercept**	**0.53**	**0.21**	0.47	80	Intercept	0.13	0.13	0.75
		F_iC_i	**0.72**	**0.11**			**F_iC_i**	**0.83**	**0.08**	
		F_oC_o	0.18	0.34			**F_oC_o**	**2.26**	**0.38**	
		F_{smoke}	0.18	0.96			F_{smoke}	-0.05	0.12	
		F_{clean}	-0.05	0.10			F_{clean}	-0.02	0.08	
		F_{cook}	-0.03	0.07			F_{cook}	-0.08	0.09	
EC	79	Intercept	0.10	0.09	0.59	72	**Intercept**	**0.72**	**0.24**	0.41
		F_iC_i	**0.69**	0.09			**F_iC_i**	**0.74**	**0.13**	
		F_oC_o	**1.91**	0.95			F_oC_o	0.94	0.78	
		F_{smoke}	0.56	0.96			F_{smoke}	0.12	0.15	
		F_{clean}	0.08	0.08			F_{clean}	-0.01	0.09	
		F_{cook}	0.00	0.06			F_{cook}	-0.03	0.13	

* Bold values indicate factors significant at 0.05 level; italic values represent those factors significant at 0.10 level.
+ Crude R^2 value

Factors affecting personal exposures. Microenvironmental models were constructed to evaluate the importance of indoor and outdoor concentrations to personal exposures (Table 16c). In general, especially in the winter, time-weighted indoor exposures (F_iC_i), were better predictors of personal $PM_{2.5}$ exposures as compared to time-weighted outdoor levels (F_oC_o). For summer $PM_{2.5}$, the intercepts of the personal exposure models were comparable to those for the indoor models, suggesting that the contribution of indoor and personal sources to indoor concentrations and personal exposures were the same. Microenvironmental models explained more than 40% of the variability in personal exposures for all particulate measures and seasons with the exception of wintertime $PM_{2.5-10}$ and summertime $PM_{2.5}$, indicating that these models were generally appropriate methods to estimate personal exposures. The poor model performance for summertime personal $PM_{2.5}$ exposures was unexpected, as our previous Baltimore study showed that microenvironmental models were able to explain a large fraction of the variability in summertime $PM_{2.5}$ exposures (Chang *et al.*, 2002). This poor model performance may be explained by increased measurement error in the summer $PM_{2.5}$ samples, as reflected by the greater variability in blank values, or by increased volatilization of NO_3^- from the $PM_{2.5}$ filters during the summer months, with the degree of volatilization differing by sample type.

Several factors were identified that were important predictors of personal particulate exposures. During the winter, personal exposures to $PM_{2.5}$ were 6.9 ($\pm$2.3) $\mu g/m^3$ lower for people living in coastal areas as compared to inland areas. ETS exposures were also found to be important contributors to personal $PM_{2.5}$ exposures. Staying in an ETS-exposed microenvironment for 1 hour elevated 24-hr personal $PM_{2.5}$ exposures by 2.9 ($\pm$1.4) $\mu g/m^3$, which was comparable to the results from our previous Boston and Baltimore studies (Rojas *et al.*, 2000; Chang *et al.*, 2002).

In addition, in the summer, the personal NO_3^- exposures for participants living in homes within 100 meters of a major road were on average 0.58 ($\pm$0.23) $\mu g/m^3$ higher than participants living farther away from major roads. As was the case with indoor concentrations, few particle-generating activities were found to contribute to personal exposures, which again might be attributed to the fact that participants were relatively inactive and spent little time participating in these activities during the study period.

CONCLUSIONS

Two newly developed small speciation monitors to measure nitrate and EC concentrations were validated in the field. For EC, the mini-sampler performed extremely well, as its measurements agreed well with those of the reference method and showed high precision. Although winter NO_3^- concentrations measured by the mini-sampler were higher than the reference sampler, the high precision of the mini-sampler and its strong association with the reference method made it a suitable measurement method for this and future studies. The ability of ICP-MS techniques to determine elemental concentrations from $PM_{2.5}$ filters was limited given the low sampling volumes used in this study. Only eight elements were detected consistently, with many of these elements of limited utility for source attribution. Further studies should be conducted to determine whether ICP-MS is an appropriate method for elemental analysis of $PM_{2.5}$ filters at higher air sampling volumes.

Participants were relatively inactive during the study period. In both seasons, subjects spent the overwhelming majority of their time indoors at their homes, with subjects spending on average approximately 90% of their time inside their homes. Subjects only spent on average less than 5% of their time in all other microenvironments, with the exception of indoor, non-home microenvironments in which subjects spent an approximate average of 6% of their time in both seasons. Furthermore, participants performed few activities that are known to generate particles, such as cooking or cleaning, with the fraction of time spent performing these activities near zero in both seasons. Air exchange rates and open window usage were significantly higher in the summer as compared to winter months; however, even in the winter a large fraction of homes reported having their windows open for a large part of the monitoring day. These results indicate that homes were generally well ventilated in both seasons, with air exchange rates higher than those observed in eastern U.S. communities.

Significant seasonal differences were found for $PM_{2.5}$, NO_3^- and EC concentrations in each of the three microenvironments, with the exception of outdoor NO_3^-, for which no seasonal difference was observed. Personal $PM_{2.5}$ exposures were higher than corresponding indoor and outdoor concentrations in both seasons. The same pattern was not observed for the NO_3^- and EC. Outdoor NO_3^- concentrations were significantly higher than corresponding indoor and personal levels in both seasons, which reflect the fact that motor vehicles are the major NO_3^- source. EC showed a similar pattern to that for NO_3^-; however, this pattern was less distinct. In addition, personal, indoor, and outdoor concentrations of the eight detectable elements (Al, B, Ba, Cr, Mn, Ni, Pb, Zn) varied seasonally and by element. As compared to other elements, Al (a element related to crustal materials) showed the highest concentrations across the three sample types and both seasons.

Personal exposures were significantly correlated with both indoor and outdoor concentrations for $PM_{2.5}$, NO_3^-, and EC in both seasons. Similarly, correlations between indoor and outdoor concentrations for all three particulate measures were significant. These correlations, however, generally varied by season and by particulate measure. In addition, although the individual-specific correlations tended to be lower than those observed in previous studies, longitudinal analyses demonstrated that the reported relationships between personal exposures and indoor/outdoor concentrations were consistent with those observed in previous studies. For $PM_{2.5}$ and EC, for example, the effective penetration efficiency and the indoor source contribution varied by season, with a greater effective penetration efficiency in the summer and a greater indoor pollutant source contribution in the winter. In addition, indoor concentrations of all three particulate measures were more strongly associated with personal exposures as compared to outdoor concentrations, which may be attributed to the facts that individuals spent most of their time indoors at home. The average contribution of NO_3^- and EC to $PM_{2.5}$ varied by season and by sample type. For all of the personal, indoor, and outdoor samples, both NO_3^- and EC comprised a relatively small proportion of the overall $PM_{2.5}$ mass, demonstrating the need to measure concentrations of other particle components to account for more of the $PM_{2.5}$ mass.

Except for Al, significant positive correlations between personal exposures and indoor and outdoor concentrations were found for each detectable element in both seasons. Associations were strongest for Ba and Ni and were weakest for Al, but differed by season and by element and from those observed for $PM_{2.5}$. Despite this, significant positive correlations between $PM_{2.5}$ and elemental concentrations were found, with associations between $PM_{2.5}$ and elemental levels strongest for indoor and outdoor samples. For personal, indoor, and outdoor samples, Pb and Ba were generally more strongly correlated with $PM_{2.5}$ in the summer, while B had the strongest wintertime correlations with $PM_{2.5}$.

RECOMMENDATIONS

Further research should be conducted to develop methods able to measure elemental concentrations from $PM_{2.5}$ filters at the low sampling air volumes used in this study, which are typical of other exposure assessment studies. In addition, further research should be conducted to identify factors causing the associations between personal exposures and outdoor $PM_{2.5}$

concentrations to be lower than those found in the eastern U.S. In particular, research should focus on whether the loss of nitrate and other semi-volatile particles from the personal, indoor, and outdoor $PM_{2.5}$ filters may affect measured correlations. Additional work should also focus on characterizing the personal, indoor and outdoor associations observed for elemental carbon and nitrate in other areas in the U.S. and for other sensitive populations to determine the generalizability of results from our study. Research investigating the contribution of various sources to $PM_{2.5}$, elemental carbon and nitrate exposures is also needed; however, such research should be conducted using more active study populations and not those that have serious pre-existing disease, as was the case with our COPD study population.

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GLOSSARY OF TERMS

AER	Air exchange rate
CATs	Capillary absorption tubes
C_i	Indoor concentrations
C_o	Outdoor concentrations
COPD	Chronic obstructive pulmonary disease
C_p	Personal exposure levels
EC	Elemental carbon
ETS	Environmental tobacco smoking
F_i	Fraction of time spending indoors in each day
F_o	Fraction of time spending outdoors in each day
HI	Harvard Impactor
LOD	Limit of detection
LPM	Liter per minute
PEM	Personal exposure monitor
PFT	Perfluorocarbon tracer
R^2	Coefficient of determination
r_s	Spearman correlation coefficient
SAM	Stationary ambient monitoring
TAD	Time-activity diary
TOR	Thermal optical reflectance

Appendix A.
ICP-MS Validation Tests

Evaluation of Fluoropore, Acid-Washed Teflo, and Teflo filters for ICP/MS elemental analysis. (Reported November 5, 1999)

As part of an evaluation of ICP/MS as a method to analyze elemental composition of $PM_{2.5}$ samples, a laboratory evaluation of two types of filter media was performed in October of 1999. Fluoropore 37 mm and Teflo 37 mm filters were evaluated for the consistency of elemental composition and blank background masses of all key elements. Teflo 37 mm filters can be acid-washed, so a further evaluation was conducted to see if acid washing the filters could lower the background concentrations.

The elemental background mass of 47 mm Teflo Filters, which are standard FRM filters are presented in Table A1 for reference.

Table A1. Background Elemental Concentrations of 47mm Teflo Filters

Element	Filter 1 (ng)	Filter 2 (ng)	Mean (ng)	Std. Dev. (ng)
Na	487	427	457	89.4
Mg	43.2	29.5	36.35	13.1
Al	31.4	19.9	25.65	28
Si	1480	1710	1595	148
K	277	312	294.5	91.1
Ca	-632	-726	-679	113
Sc	3.28	2.83	3.06	1.82
Ti	2.09	1.66	1.88	0.38
V	8.25	8.74	8.50	0.527
Cr	70.5	66.5	68.5	35.2
Mn	3.24	3.83	3.54	0.35
Fe	59	112	85.5	44.3
Co	0.11	0.11	0.11	0.02
Ni	0.63	0.88	0.76	0.13
Cu	14.8	14.9	14.85	2.92
Zn	8.42	9.59	9.01	6.6
As	6.12	6.79	6.46	0.85
Se	<3	2.29	<3	
Cd	<0.1	<0.1	<0.1	
Cd-1	<0.13	<0.13	<0.13	
Sn	<0.25	<0.25	<0.25	
Ba	1.31	16.3	8.81	7.84
Pb	1.58	1.73	1.66	2.39

The background mass of five blank Fluoropore filters are presented in Table A2 for each of the measured elements. Since the standard deviation of the blank values is used to determine the LODs for the elements, elements for which the standard deviations of the blank values were higher than 20 ng were flagged. For the Fluoropore filters, flagged elements included Na, Si, Ca, Fe, and Zn. With the exception of potassium, all other elements had standard deviations well below 20 ng.

Table A2. Fluoropore Blank 37mm Filters ICP/MS elemental analysis

Element	**116-1 (ng)**	**116-2 (ng)**	**116-3 (ng)**	**116-4 (ng)**	**116-5 (ng)**	**Mean (ng)**	**Std. Dev. (ng)**
Na	173	133	216	309	222	210	65.7
Mg	26.9	28.9	29.3	28.5	35	29.7	3.09
Al	<8.5	30.2	4.59	111	<8.5	32.6	
Si	3800	2680	3510	3060	3610	3330	455
K	72.9	32.9	67.1	64.2	61.2	59.7	15.6
Ca	-847	-854	-804	-785	-811	-820	29.4
Sc	1.83	1.17	1.15	1.03	0.86	1.21	0.369
Ti	1.09	1.72	1.84	1.92	2	1.71	0.364
V	10.6	9.78	10.2	9.31	11	10.2	0.664
Cr	5.96	4.32	5.67	4.35	9.49	5.96	2.11
Mn	0.53	0.3	0.28	0.48	1	0.518	0.291
Fe	27.8	21	23.1	23.2	124	43.8	44.9
Co	0.065	0.07	0.095	0.04	0.04	0.06	0.023
Ni	<0.25	1.02	2.51	0.17	<0.25	0.84	1.19
Cu	2.6	2.53	1.91	1.69	2.23	2.19	0.392
Zn	29.2	20.6	80.5	45	29.5	41	23.8
As	7.21	6.96	7.6	6.55	6.79	7.02	0.403
Se	<3	<3	<3	<3	<3	<3	
Cd	<0.1	<0.1	<0.1	0.15	<0.1	0.11	0.093
Cd-1	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	
Sn	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	
Ba	37.9	30.7	70.6	56.6	41.5	47.5	16
Pb	0.58	0.425	0.44	0.63	0.405	0.496	0.102

The background concentrations for the five blank washed Teflo filters are presented in Table A3 by element. As was the case above, individual elements for which the standard deviation of its blank values exceeded 20 ng were flagged. These elements included Na, Al, Si, K, Ca, Fe, Cu and Zn. For three of these eight elements – Na, Si, Ca – standard deviations were substantially greater than 20 ng, by as much as 20 times higher. All other elements had standard deviations well below 20 ng.

Table A3. Background Elemental Concentrations for Washed Teflo 37 mm Filters as Determined by ICP/MS Analysis

Species	**1-1 (ng)**	**1-2 (ng)**	**1-3 (ng)**	**1-4 (ng)**	**1-5 (ng)**	**Mean (ng)**	**Std. Dev. (ng)**
Na	173	61.5	223	1140	603	440	441
Mg	22.9	6.73	22.4	31.9	19.4	20.7	9.08
Al	38.8	<8.5	<8.5	21.4	<8.5	17.4	33.1
Si	1470	1320	1180	1160	1360	1300	129
K	131	14	150	915	420	326	361
Ca	-761	-884	-714	-670	-796	-765	81.8
Sc	3.13	3.28	3.46	4.13	3.96	3.59	0.434
Ti	1.63	0.86	1.38	0.75	1.08	1.14	0.365
V	11.6	9.22	8.37	10.5	10.6	10.1	1.27
Cr	25.2	19.8	28.6	15.6	20.3	21.9	5.06
Mn	2.72	0.88	0.54	2.3	2.04	1.7	0.93
Fe	74.3	19.4	30.4	31.3	21.3	35.3	22.4
Co	0.28	0.15	0.06	0.125	0.29	0.18	0.102
Ni	0.47	<0.25	0.15	3.62	3.71	1.64	2.08
Cu	15	1.63	5.6	64.7	56.6	28.7	29.7
Zn	5.53	<5.1	44.4	33.3	7.03	19.1	20.9
As	6.22	6.46	6.62	7.34	5.97	6.52	0.519
Se	<2.9	<2.9	<2.9	<2.9	<2.9	<2.9	
Cd	<0.1	<0.1	<0.1	0.14	0.08	0.1	
Cd-1	<0.13	<0.13	<0.13	0.085	<0.13	0.12	
Sn	<0.23	<0.23	<0.23	<0.23	<0.23	0.23	
Ba	0.13	<0.17	0.10	1.14	0.93	0.49	0.552
Pb	0.95	0.37	0.88	1.72	0.55	0.89	0.517

The background mass of 5 blank unwashed Teflo filters are presented in Table A4 by element. Individual elements for which the standard deviation of the blanks exceeded 20 ng were flagged. These elements were identical to those flagged for the washed filters, including Na, Al, Si, K, Ca, Fe, Cu and Zn. However, standard deviations for the elements on the unwashed filters were generally higher.

Table A5 presents the calculated analytical detection limits for the washed Teflo, unwashed Teflo and Fluoropore filters for each of the flagged elements. With the exception of Si and Zn (only in the washed Teflo filter), the LODs for the Fluoropore blank filters were consistently lower than those for the two Teflo filters. These differences were generally substantial, at times the Teflo filters had LODs that were a factor of ten higher than that for the Fluoropore filter. Furthermore, washed Teflo filters had consistently lower blank values as compared to unwashed Teflo filters; however, the discrepancy between their LOD values was less marked.

Table A4. Blank Elemental Concentrations for Unwashed 37 mm Teflo Filters as Determined Using ICP/MS Analysis

Species	Mean (ng)	Std. Dev. (ng)
Na	1020	632
Mg	44.2	17.2
Al	68.4	64.7
Si	2430	302
K	737	564
Ca	-581	153
Sc	1.98	1.01
Ti	2.8	2.06
V	8.14	1.26
Cr	40.4	10.3
Mn	4.81	1.11
Fe	112	61.5
Co	0.19	0.101
Ni	5.72	3.44
Cu	75	42.4
Zn	57.9	28.7
As	6.07	0.625
Se	<2.9	1.27
Cd	0.34	0.10
Cd-1	0.38	0.16
Sn	0.50	0.80
Ba	3.07	0.82
Pb	3.01	1.52

Table A5. Analytical Detection Limits of Washed Teflo, Unwashed Teflo and Fluoropore 37mm Filters[1]

Species	Washed Teflo (ng)	Unwashed Teflo (ng)	Fluoropore (ng)
Na	1323	1896	197.1
Al	99.3	194.1	0
Si	387	906	1365
K	1083	1692	46.8
Ca	245.4	459	88.2
Fe	67.2	184.5	134.7
Cu	89.1	127.2	1.176
Zn	62.7	86.1	71.4

[1] Detection limits are three times the blank standard deviation for each element.

Table A6. Comparison of "Blank" Concentrations as a Percentage of Total Mass of Element in Typical Exposed FRM Samples

Species	Acid Blank	Teflo Washed #1	Teflo Washed #2	Teflo UnWashed	Fluoropore	Gelman Teflo 47 mm
Na	6.0	10.8	21.4	25.1	5.2	10.4
Mg	1.1	2.4	4.3	5.1	3.4	3.1
Al	0.7	1.4	10.5	5.5	2.6	0.1
Si	10.5	13.0	9.5	24.3	33.3	15.0
K	2.1	5.6	10.2	12.6	1.0	3.9
Ca						
Sc	89.9	212.1	247.0	117.0	71.5	242.2
Ti	2.0	1.8	1.7	4.4	2.7	2.8
V	36.4	45.7	51.6	36.8	46.2	37.6
Cr	4.5	14.2	13.1	26.2	3.9	24.7
Mn	1.2	0.7	2.1	1.8	0.2	1.3
Fe	0.3	0.4	3.0	1.4	0.6	0.7
Co	2.8	5.8	11.9	6.1	1.9	3.9
Ni	0.2	0.7	1.9	2.6	0.4	0.4
Cu	3.1	8.0	21.0	20.8	0.6	4.0
Zn	0.4	1.4	1.1	4.1	2.9	0.2
As	4.5	4.8	5.5	4.4	5.1	5.0
Se	0.5	0.3	0.3	0.5	0.3	0.5
Cd	0.7	0.7	0.7	2.4	0.8	0.7
Cd-1	7.4	6.8	1.5	21.7	7.4	7.4
Sn	0.4	0.4	0.3	0.8	0.4	0.7
Ba	0.1	0.2	2.1	1.5	22.8	2.2
Pb	0.0	0.1	0.1	0.2	0.1	0.2

To assign acceptable background concentrations, analysis of two 47mm FRM ambient samples collected from the Steubenville area were compared against the values obtained from two acid washed Telfo filters and an unwashed Teflo and Fluoropore filter (Table A6). For the washed Teflo blank filters elements which showed blank levels at or above 10 percent of typical FRM values were Na, Al, Si, K, Sc, V, Cr, Co, and Cu. For the unwashed Teflo blank filters, elements that had blank levels at or above 10 percent of typical FRM values were Na, Si, K, Sc, V, Cr, and Cu. For the Fluoropore blanks, elements that had blank levels at or above 10 percent of typical FRM values were Si, Sc, V, and Ba.

Other Issues

Fluoropore filters had a strong static charge. There were several issues of concern regarding this charge. Filters would adhere sampling side up to the petri dish, in which the filters and subsequent sampled filters were to be stored. The possibility of transfer of particles from the sampled filter to the petri dish and compromising the collected sample was significant. The washed Teflo filters did not maintain their shape after washing, this warping of the filter was significant enough that it could compromise the integrity of the filter/sampler seal inside the PEM. Also pinholes started to appear on the filters a few days after washing.

Conclusions

Although the blank values of the Fluoropore and washed Teflo filters were lower than those for the unwashed Teflo filters, the static properties of the Fluoropore filters and the loss of integrity of the Teflo filters after washing made them unsuitable replacements for the unwashed Teflo filters. These factors prevented the use of Fluoropore and washed Teflo filters as collection media for $PM_{2.5}$ and subsequent gravimetric and elemental analysis.

Comparison of CONSOL ICP/MS with DRI XRF for elemental analysis of $PM_{2.5}$ samples (Reported on August 8, 2000)

The Desert Research Institute (DRI) has been analyzing particulate PM_{10} samples by X-Ray Fluorescence (XRF) for over 20 years for numerous particulate exposure and air pollution studies. The bulk of the XRF analysis was performed for high volume PM_{10} samples. For personal $PM_{2.5}$ samples, it is likely that XRF is not sensitive enough to perform elemental analysis of these samples. To evaluate the feasibility of using XRF to analyze $PM_{2.5}$ personal filter samples, three sets of collocated samples were analyzed by XRF by DRI and by ICP/MS by CONSOL. Two sample pairs were personal samples collected in the Baltimore Cohort Study, a third pair was of a collocated FRM sample collected in Steubenville, Ohio.

Figure A1. Expected Mass on Filter vs. Particle Concentration

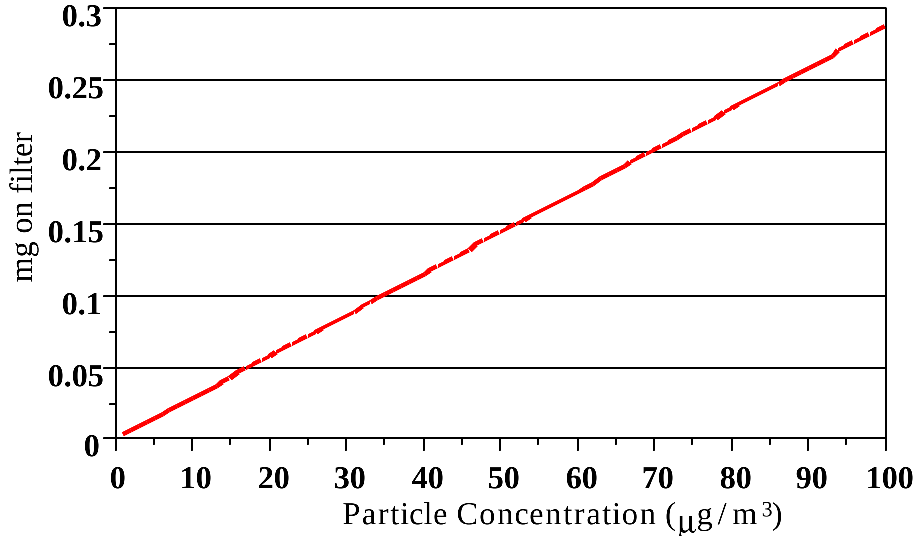


Figure A1 is a plot of expected mass on filter (mg) vs. particle concentration µg/m^3 based on 2 LPM sampling for 24 hours, as used in our study. PM $_{2.5}$ personal exposures typically range between 15 and 75 µg/m^3, which would correspond to between 0.043 and 0.216 mg on the filter.

Figure A2 is a plot prepared by CONSOL showing uncertainty as a percentage of concentration for XRF analysis of FRM samples (ambient high volume) collected by CONSOL and personal samples (at 3.8 LPM) obtained in the Baltimore older adult study (Sarnat et al., 2000). At filter loadings under 100 ng, the uncertainty in the XRF results is high. At over a 1000 ng, the uncertainty in XRF measurements improves dramatically. Since the sample flow rates and thus volumes for our LA exposure study are half that of the Baltimore study, uncertainty in RF measurements are expected to be greater than that shown in Figure A2.

Figure 2A. Uncertainty in XRF Results as a Function of Filter Loadings

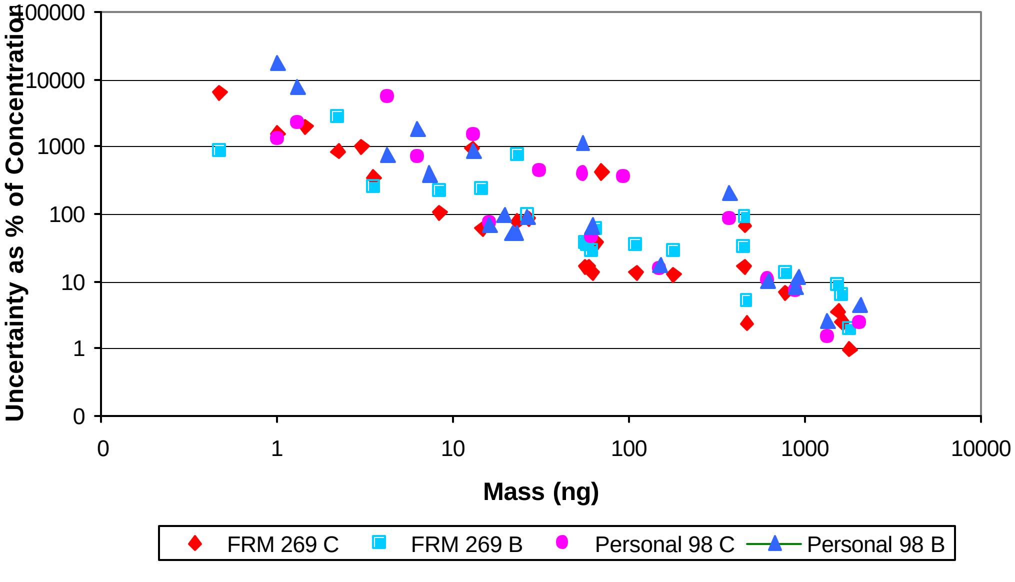


Table A6 shows the raw data from two sets of personal samples collected in the Baltimore Older Adult study (Sarnat et al., 2000). Again, mass for current samples can be expected to be half of what is shown on Table A6 due to lower sample flow rates. For most elements, elemental loadings determined by ICP-MS were greater than those determined by XRF. DRI hypothesized that the lower XRF readings were due to the fact that elemental concentrations are determined in XRF analysis using less than one percent of the entire filter, since a beam is focused only on a small section in the filter center. The total amount of each element is then extrapolated to the entire filter. If the filter does not have a uniform distribution, this extrapolation will not be appropriate and may under or overestimate the actual elemental concentration. Furthermore, XRF was designed for thin films. Heavy particle deposition on the filter may cause the results to be negatively biased due to absorption of incident and emitted x-rays. Heavy particle deposition, however, is unlikely in this analysis based on the flow rates and durations of the collected samples.

Table A6. XRF vs. ICP-MS Results for Two Colocated Personal Samples

Species	COLOCATED FILTERS 92 & BCH 094 PM				COLOCATED FILTERS 98 & BCH 101 PM			
	XRF Mass (ng)	Uncert. (ng)	ICP-MS Mass (ng)	Uncert. (ng)	XRF Mass (ng)	Uncert. (ng)	ICP-MS Mass (ng)	Uncert. (ng)
Ca 40	885	25	2551	16.4	915	25	1435	33
Ca 44	885	25	2988	200	915	25	1997	129
K 39	521	21	1186	54	633	22	1326	84
Al-3 27	554	48	1234	41.2	963	48	2001	51
Cr 50	8.2	29	18.8	1.1	5.8	29.3	23.4	1.9
Mn 55	44.4	8.6	106	1.4	50.7	8.7	72.5	4.9
Se 80	10	11.1	17.0	0.37	20.1	3.7	23.7	0.78
Fe 56	1318	13.4	2149	48.3	1307	13.4	1810	74
Na-1 23	10.4	476	777	57.3	311	433	1667	43
Mg-1 24	87.3	219	408	18.7	75.6	200	515	32
Si-1 28	923	41	9114	3031	2063	44.5	8100	1614
Ti-1 48	65.9	225	120	2.5	108	226	150	2.8
V 51	39.8	94.6	44.8	3.1	30.2	95.2	48.5	2.1
Na 23	10.4	476	846	94.7	311	433	1858	139
Al-2 27	554	48.2	1241	46	963	48	2021	53
Mg 24	87.3	219	428	28.2	75.6	200	560	10
Ti 48	65.9	225	115	2.6	108	226	154	5.1
Cu 63	7	17.6	33.9	1.1	10.2	18	56.0	0.7
Co 59	0	26.7	2.0	0.25	0	26.7	2.6	0.3
Ni 60	20.2	5.5	50.9	1.6	24.2	5.6	59.8	2.8
Zn 66	428	7.9	659	21.2	145	7	345	11
As-1 75	0.8	21.9	9.6	1.3	0.5	20.6	8.8	0.2
Cd 111	0	97.8	2.4	0.11	0	97.7	2.1	0.4
Cd 114	0	97.8	4.5	0.27	0	97.7	4.1	0.2
Sn 118	55.7	138	5.1	0.77	41.3	139	2.8	0.3
Sn 120	55.7	138	33.7	49	41.3	139	3.2	1.2
Ba 135	28.4	566	40.1	2.5	0	568	22.0	1.7
Pb 208	56.1	9.8	55.3	3	42	9.5	52.4	1.4

XRF does not have method to calibrate the instrument on the order of masses expected in personal samples. The XRF is calibrated with a thin film provided by the manufacturer. The masses of the elements are much higher than the masses expected in the personal samples.

In their ICP/MS analysis, CONSOL spiked filters with NIST standard 1648 urban particulate. Based on their percent recovery, elements were placed into two categories: “high confidence” or those for which ICP-MS performed with greater than 80% recovery and “low confidence” or those for which recovery was lower than 80%. For both the high and low confidence elements, mixed results were found when concentrations obtained using ICP-MS at CONSOL were compared to those obtained using XRF at DRI (Table A7). These comparisons were made using 6 collocated pairs (four high volume FRM sample pairs and 2 personal (4 LPM) sample pairs.

Table A7. "High Confidence Elements": Regression of ICP-MS on XRF Results

High Confidence Elements	R^2	Slope	Intercept
Ca 40	0.91	1.9	34.7
Ca	0.76	1	1439
Cr	0.25	0.151	24
Mn	0.81	0.84	41
Se	1.00	0.83	9
Fe	0.95	1.26	273
Ti-1	0.42	0.38	114
V	0.43	0.37	33
Ti	0.59	0.61	99
Co	Poor		
As-1	Poor		
Cd	Poor		
Cd	Poor		
Sn	Poor		
Sn	Poor		
Ba	Poor		
Pb	0.99	1.1	-3.8

Table A8. "Low Confidence Elements": Regression of ICP-MS on XRF Results

Element	**R^2**	**Slope**	**Intercept**
K	0.88	1.01	746
Al-3	0.76	9.1	-5436
Na-1	0.63	2.3	277
Mg-1	0.29	-4.56	2825
Si-1	0.91	12.4	-10792
Na	0.34	1.66	459
Al-2	0.65	2.7	-425
Mg	0	-0.15	780
Cu	0.63	1.88	47
Ni	0.73	0.88	35.4
Zn	0.97	0.94	201

Other Issues. Species generated in the argon plasma are the largest source of isobaric interferences. Ar^+ ions produced at mass 40 completely obliterate the mass spectrum of ^{40}Ca. Similarly, $^{40}Ar^{16}O^+$ ions prohibit the accurate determination of low concentrations of ^{56}Fe. CONSOL has tried to minimize these interferences by adding a series of reaction gases. Data from these tests are still pending.

Table A8. List of Isobaric Interferences for ICP-MS.

Isotope	Isobaric Interferents
^{28}Si	$^{14}N^{14}N$, $^{12}C^{16}O$
^{39}K	^{38}ArH
^{40}Ca	^{40}Ar
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$
^{52}Cr	$^{40}Ar^{12}C$, $^{36}Ar^{16}O$, $^{35}Cl^{16}OH$
^{56}Fe	$^{40}Ar^{16}O$
^{75}As	$^{40}Ar^{35}Cl$
^{80}Se	$^{40}Ar^{40}Ar$

In addition to the interference problem, ICP/MS requires sample digestion or preparation. Every laboratory that performs ICP/MS on particulate filters has a different method of digesting or leaching the filter. This presents the problem that samples analyzed by different laboratories are not comparable. XRF does not require elaborate sample preparation resulting in samples that are comparable across laboratories.

Precision and Accuracy of CONSOL ICP/MS, Lamont Doherty EO ICP/MS and DRI XRF for $PM_{2.5}$ filter elemental analysis.
(Reported on April 26, 2001)

To evaluate the precision and accuracy of the CONSOL ICP/MS elemental analysis of filters, a sample exchange program was conducted with the Lamont Doherty Earth Observatory Trace Metals Laboratory of Columbia University. The Columbia University Laboratory uses a High Resolution ICP-MS, while CONSOL uses a DRC ICP-MS. Although both instruments are ICP-MS, they are configured differently such that the comparison is not only one of two laboratories performing elemental analysis but also of two completely different methods. [The ICP-MS methods used by CONSOL and Columbia "detect" elements using different techniques, allowing them to be used to verify the accuracy of the other method. The high resolution ICP-MS technique used by Columbia resolves polyatomic interferences by using a high-resolution mass spectrometer.]

For this comparision, a series of samples were analyzed by both ICP-MS methods. Both laboratories analyzed NIST Urban Particulate 1648 twice and NIST Water 1643d. CONSOL used the analysis of the 8/29/00 report, the results of which were not known to Jamie Ross of Columbia University. A second round of analysis included the analysis by Columbia researchers of CONSOL extracts of the collocated pairs co-analyzed by DRI (described above). Extracts were used to isolate differences in the analysis procedures, since the ICP-MS laboratories use a different extraction processes. Results from the extract analysis were subsequently used to compare both ICP-MS results with those from XRF. A review of the performance of the DRI XRF, Columbia ICP/MS and the CONSOL ICP/MS is presented in Table III in the main body of the report.

Appendix B.

Technician-Administered Daily Housing Questionnaire

OMB Control No: 2080-005
Approval Expires 7/31/2002

Technician Administered
Daily Follow-Up Questionnaire

1. How many people spent at least four hours in your home (or apartment) today?

   1a. Did you smoke cigarettes or cigars today?

   How many cigarettes?

   How many cigars?

   1b. How many people, including visitors, smoked cigarettes or cigars inside your home today?

   1c. About how many cigarettes were smoked?

   About how many cigars were smoked?

2. Were any meals cooked using the stove in your home today? ☐ Yes ☐ No

   2a. How many times did you use the stove today ?

   2b. Did you use the stove for any of the following activities? At what time? (Mark am or pm box)

   frying, grilling, sauteeing, or broiling
   Time #1: ☐ am ☐ pm
   Time #2: ☐ am ☐ pm
   Time #3 ☐ am ☐ pm

   2c. Did you burn any food today (e.g., toast)? ☐ Yes ☐ No

   2d.Was the exhaust fan used for any cooking activity? ☐ Yes ☐ No

3. Did you use any of the following? About what time? How long? (Mark am or pm box and minutes or hours box)

   candles at ☐ am ☐ pm for about ☐ minutes ☐ hours

   incense at ☐ am ☐ pm for about ☐ minutes ☐ hours

4.Did you use an ultrasonic or “cool mist” humidifier in your home today? ☐ Yes ☐ No

4a. If so, what type of water did you use in the humidifier?

tap water

bottled, distilled, deionized water

other, please specify

4b. About what time did you use a humidifier? (Mark am or pm boxes).

Turned on humidifier at ☐ am ☐ pm and turned off at ☐ am ☐ pm

5. Did you have any windows open today? ☐ Yes ☐ No

5a. How many windows were open today?

5b. About how many inches wide were they open? Window #1 Window #2
Window #3 Window #4

5c. About how many hours were the windows open? Window #1 Window #2
Window #3 Window #4

6. Did you use a gas or kerosene fired space heater or gas stove to heat your home today?

☐ Yes ☐ No

6a. About how many hours did you use either of these? Heater Stove

7. Did you clean today? ☐ Yes ☐ No

7a. Did you do any of the following cleaning activities? About what time? (Mark am or pm box)

vacuuming at ☐ am ☐ pm
dusting at ☐ am ☐ pm
sweeping at ☐ am ☐ pm

8. Did you use an air cleaner today ☐ Yes ☐ No

8a. If so, which of the following air cleaning device(s) did you use?

ion generator

electrostatic precipitator

filter

other, please specify

8b. About what time did you use an air cleaner? (Mark am or pm boxes).

Turned on an air cleaner at ☐ am ☐ pm and turned off at ☐ am ☐ pm

9. Were there any pets inside your home today?: ☐ Yes ☐ No

9a. If so, how many?

Appendix C. Technician-Administered Housing Questionnaire

Technician Survey

Building Characteristics

Type of dwelling?

- detached house
- duplex/triplex
- row house
- low rise apartment (1-3 floors)
- high rise apartment (>3 floors)
- trailer
- other, please specify

Approximate age of building:

Is the dwelling located within 100 yards of a busy roadway?

Is there a dirt drive located within 100 yards of this dwelling?

Are there any other sources of dust (construction, industry, commercial garage, etc.) located within 100 yards of the dwelling?

What type of garage, if any, is there in the dwelling?

- none, detached, or separate carport
- attached
- underneath

Is this garage used for:

- parking one car
- parking two cars
- storage only

Ventilation Characteristics

How many separate central AC or window/wall units are in the home?
- number of central AC units
- number of window/wall units

What are the heating sources in the home?
- radiators (steam or hot water)
- forced air (vents)
- open stove
- electric space heater
- gas space heater
- kerosene space heater
- wood burning stove
- fireplace
- other, please specify

Is there a whole-house or attic fan?

What is the thermostat setting(s)?

Are there storm windows?

How would you best describe the VENTILATION FACTOR in this unit? (0 to 3: 0.5 is fresh, 2.5 is very stuffy)

Cooking/Fuel Characteristics

1. What type of cooking fuel is used?
    - gas
    - electric
    - other, please specify

2. Is there a fan over the cooking stove, range, oven, or elsewhere in the kitchen area?

3. How does this fan work?
    - kitchen exhaust vented outside
    - recirculation of indoor air
    - charcoal filter
    - other, please specify
    - don’t know

4. Is there a pilot light on a:
gas range oven clothes dryer

5. Is there a clothes dryer?

5a. Is the clothes dryer unvented?

6. What type of filter bag is used in the vacuum cleaner?
standard vacuum filter
high efficiency filter (HEPA)
other, please specify

Room Characteristics
Draw a floor plan of the house. Include windows, curtains/drapes, and location of ventilation system suppliers and returns.

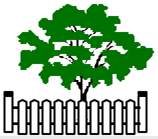
Room Descriptions

	Room	**% of floor covered by rug or carpet**	**Presence of molds, mildew, water damage**	**DUST FACTOR for room (0 to 3: 0.5 is very clean, 2.5 is very dusty)**
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				

	Room	% of floor covered by rug or carpet	Presence of molds, mildew, water damage	DUST FACTOR for room (0 to 3: 0.5 is very clean, 2.5 is very dusty)
14				
15				

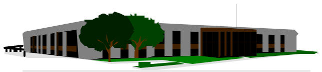
Appendix D. Time-Activity Diary

1. Indoors at Home

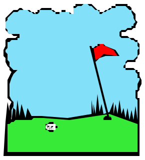


2. In Yard at Home or Nearby

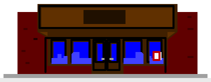
3. In Transit



4. At Work away from Home



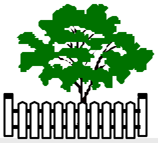
5. Outside away from Home



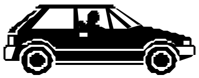
6. Indoors away from Home

Start Time	Activity Description	1	2	3	4	5	6	Near Smoker (Mins.)	Cooking (Mins.) Self	Cooking (Mins.) Other
8:00 AM										
8:15 AM										
8:30 AM										
8:45 AM										
9:00 AM										
9:15 AM										
9:30 AM										
9:45 AM										
10:00 AM										
10:15 AM										
10:30 AM										
10:45 AM										
11:00 AM										
11:15 AM										
11:30 AM										
11:45 AM										
12:00 PM										
12:15 PM										
12:30 PM										
12:45 PM										
1:00 PM										
1:15 PM										
1:30 PM										
1:45 PM										

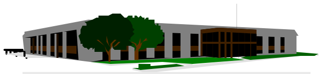
1. Indoors at Home



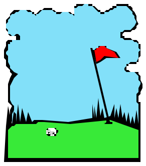
2. In Yard at Home or Nearby



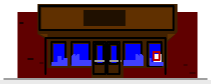
3. In Transit



4. At Work away from Home



5. Outside away from Home



6. Indoors away from Home

								Near Smoker	Cooking (Mins.)	
Start Time	Activity Description	1	2	3	4	5	6	(Mins.)	Self	Other
2:00 PM										
2:15 PM										
2:30 PM										
2:45 PM										
3:00 PM										
3:15 PM										
3:30 PM										
3:45 PM										
4:00 PM										
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5:30 PM										
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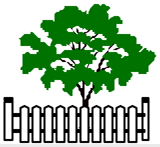
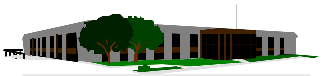
6:00 PM										
6:15 PM										
6:30 PM										
6:45 PM										
7:00 PM										
7:15 PM										
7:30 PM										
7:45 PM										

1. Indoors at Home

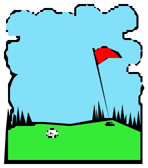


2. In Yard at Home or Nearby

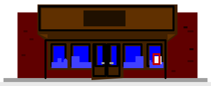
3. In Transit



4. At Work away from Home



5. Outside away from Home



6. Indoors away from Home

Start Time	Activity Description	1	2	3	4	5	6	Nearby Smoker (Mins.)	Cooking (Mins.)	
									Self	Other
8:00 PM										
8:15 PM										
8:30 PM										
8:45 PM										
9:00 PM										
9:15 PM										
9:30 PM										
9:45 PM										
10:00 PM										
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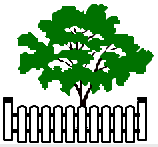
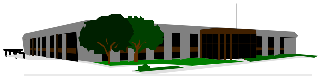
11:45 PM										
12:00 AM										
12:15 AM										
12:30 AM										
12:45 AM										
1:00 AM										
1:15 AM										
1:30 AM										
1:45 AM										

1. Indoors at Home

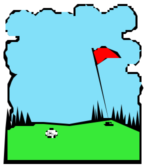


2. In Yard at Home or Nearby

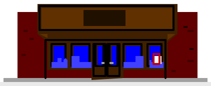
3. In Transit



4. At Work away from Home



5. Outside away from Home



6. Indoors away from Home

								Near Smoker	Cooking (min)	
Start Time	**Activity Description**	**1**	**2**	**3**	**4**	**5**	**6**	**(Mins.)**	Self	Other
2:00 AM										
2:15 AM										
2:30 AM										
2:45 AM										
3:00 AM										
3:15 AM										
3:30 AM										
3:45 AM										
4:00 AM										
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5:00 AM										
5:15 AM										
5:30 AM										
5:45 AM										
6:00 AM										
6:15 AM										
6:30 AM										
6:45 AM										
7:00 AM										
7:15 AM										
7:30 AM										
7:45 AM										

APPENDIX E. Individual-Specific Correlations

Individual-Specific Spearman Correlation Coefficients: $PM_{2.5}$

SEASON	**SUBJECT**	**Indoor vs. Outdoor**			**Personal vs. Indoor**			**Personal vs. Outdoor**		
		n	**r**	**p-value**	**n**	**r**	**p-value**	**n**	**r**	**p-value**
Summer	LPD-16	7	0.61	0.15	5	0.90	0.04	5	0.70	0.19
	LPD-17	7	0.61	0.15	7	0.32	0.48	7	-0.07	0.88
	LPD-18	7	0.89	0.01	6	0.94	0.00	6	0.89	0.02
	LPD-19	6	0.14	0.79	7	0.29	0.53	6	0.54	0.27
	LPD-21	6	0.71	0.11	6	0.14	0.79	7	0.39	0.38
	LPD-22	7	0.82	0.02	6	0.14	0.79	6	0.43	0.40
	LPD-23	7	-0.29	0.53	7	0.32	0.48	7	0.11	0.82
	LPD-24	7	0.43	0.34	6	0.31	0.54	6	0.77	0.07
	LPD-25	7	0.89	0.01	6	-0.03	0.96	6	0.14	0.79
	LPD-26	7	0.61	0.15	7	-0.32	0.48	7	0.29	0.53
	LPD-27	7	0.79	0.04	7	0.43	0.34	7	0.00	1.00
	LPD-28	6	0.54	0.27	7	0.54	0.22	6	0.20	0.70
	LPD-29	7	0.43	0.34	7	0.32	0.48	7	0.32	0.48
	LPD-30	7	0.82	0.02	7	-0.18	0.70	7	-0.43	0.34
Winter	LPD-01A	1	--	--	2	--	--	2	--	--
	LPD-02	7	0.07	0.88	7	0.61	0.15	7	-0.21	0.64
	LPD-03	6	0.49	0.33	3	0.50	0.67	4	0.80	0.20
	LPD-04	7	0.57	0.18	6	0.60	0.21	6	0.49	0.33
	LPD-05	5	0.20	0.75	5	-0.10	0.87	7	0.43	0.34
	LPD-06	3	--	--	3	--	--	2	--	--
	LPD-07	6	0.89	0.02	6	-0.26	0.62	7	0.36	0.43
	LPD-08	6	0.37	0.47	6	0.31	0.54	6	0.94	0.00
	LPD-09	6	0.94	0.00	6	-0.26	0.62	5	0.10	0.87
	LPD-10	5	0.70	0.19	4	-0.60	0.40	6	0.49	0.33
	LPD-11	4	-0.40	0.60	6	0.43	0.40	4	-0.40	0.60
	LPD-12	6	0.49	0.33	5	0.60	0.28	5	0.00	1.00
	LPD-13	7	0.61	0.15	7	0.93	0.00	7	0.50	0.25
	LPD-14	7	0.93	0.00	7	0.89	0.01	7	0.82	0.02
	LPD-15	7	0.57	0.18	7	0.61	0.15	7	0.79	0.04

Individual-Specific Spearman Correlation Coefficients: NO_3^-

SEASON	SUBJECT	Indoor vs. Outdoor			Personal vs. Indoor			Personal vs. Outdoor		
		n	**r**	**p-value**	**N**	**r**	**p-value**	**n**	**r**	**p-value**
Summer	LPD-16	6	0.94	0.00	7	0.71	0.07	6	0.83	0.04
	LPD-17	7	0.75	0.05	7	0.43	0.34	7	0.43	0.34
	LPD-18	7	0.96	0.00	7	0.96	0.00	7	0.89	0.01
	LPD-19	7	0.79	0.04	7	0.32	0.48	7	0.39	0.38
	LPD-21	6	-0.20	0.70	6	0.49	0.33	5	-0.10	0.87
	LPD-22	7	0.32	0.48	7	0.50	0.25	7	0.96	0.00
	LPD-23	7	0.04	0.94	7	-0.29	0.53	7	-0.75	0.05
	LPD-24	7	0.36	0.43	7	0.82	0.02	7	0.29	0.53
	LPD-25	7	0.50	0.25	7	0.57	0.18	7	0.86	0.01
	LPD-26	6	0.14	0.79	6	0.66	0.16	7	-0.18	0.70
	LPD-27	6	0.54	0.27	6	0.83	0.04	7	0.11	0.82
	LPD-28	7	0.75	0.05	7	0.96	0.00	7	0.79	0.04
	LPD-29	6	0.37	0.47	7	0.93	0.00	6	0.66	0.16
	LPD-30	7	0.61	0.15	7	0.68	0.09	7	0.71	0.07
Winter	LPD-01A	4	0.00	1.00	3	--	--	4	0.40	0.60
	LPD-02	7	0.39	0.38	7	0.86	0.01	7	0.18	0.70
	LPD-03	7	0.57	0.18	7	0.46	0.29	7	0.89	0.01
	LPD-04	7	0.39	0.38	7	0.50	0.25	7	0.11	0.82
	LPD-05	5	0.90	0.04	5	1.00	<.0001	7	0.64	0.12
	LPD-06	5	0.90	0.04	6	0.94	0.00	6	0.94	0.00
	LPD-07	5	0.90	0.04	6	0.94	0.00	6	0.77	0.07
	LPD-08	6	0.37	0.47	6	0.71	0.11	7	0.86	0.01
	LPD-09	6	0.60	0.21	7	0.64	0.12	6	0.60	0.21
	LPD-10	5	0.90	0.04	4	0.80	0.20	6	0.94	0.00
	LPD-11	4	1.00	<.0001	6	0.94	0.00	4	0.80	0.20
	LPD-12	6	0.94	0.00	5	0.90	0.04	5	0.90	0.04
	LPD-13	7	0.86	0.01	7	0.96	0.00	7	0.82	0.02
	LPD-14	7	0.93	0.00	7	0.93	0.00	7	1.00	<.0001
	LPD-15	3	--	--	7	0.82	0.02	3	--	--

Individual-Specific Spearman Correlation Coefficients: EC

SEASON	SUBJECT	Indoor vs. Outdoor			Personal vs. Indoor			Personal vs. Outdoor		
		n	r	p-value	n	r	p-value	n	r	p-value
Summer	LPD-16	7	0.71	0.07	2	--	--	2	--	--
	LPD-17	6	0.94	0.00	7	0.64	0.12	6	0.71	0.11
	LPD-18	7	0.79	0.04	7	0.71	0.07	7	0.64	0.12
	LPD-19	7	0.61	0.15	7	0.46	0.29	7	0.36	0.43
	LPD-21	7	0.11	0.82	6	0.14	0.79	6	0.43	0.40
	LPD-22	6	0.60	0.21	4	-0.40	0.60	4	0.40	0.60
	LPD-23	6	0.66	0.16	7	0.32	0.48	6	0.77	0.07
	LPD-24	7	-0.11	0.82	6	0.37	0.47	6	0.77	0.07
	LPD-25	6	0.94	0.00	5	0.90	0.04	4	0.80	0.20
	LPD-26	5	0.50	0.39	5	0.80	0.10	7	0.54	0.22
	LPD-27	7	0.96	0.00	6	0.83	0.04	6	0.77	0.07
	LPD-28	7	0.43	0.34	7	0.82	0.02	7	0.46	0.29
	LPD-29	7	0.18	0.70	7	0.11	0.82	7	0.11	0.82
	LPD-30	7	0.89	0.01	7	0.79	0.04	7	0.75	0.05
Winter	LPD-01A	5	-0.60	0.28	4	0.20	0.80	4	-0.80	0.20
	LPD-02	7	0.75	0.05	7	0.75	0.05	7	1.00	<.0001
	LPD-03	7	0.07	0.88	7	0.00	1.00	7	0.04	0.94
	LPD-04	7	0.71	0.07	7	0.86	0.01	7	0.71	0.07
	LPD-05	6	0.77	0.07	6	0.83	0.04	7	0.79	0.04
	LPD-06	4	0.00	1.00	5	0.80	0.10	6	-0.66	0.16
	LPD-07	5	0.60	0.28	5	-0.70	0.19	7	0.61	0.15
	LPD-08	6	0.54	0.27	6	0.43	0.40	7	0.50	0.25
	LPD-09	6	0.94	0.00	6	0.94	0.00	5	0.90	0.04
	LPD-10	4	0.80	0.20	4	1.00	<.0001	5	1.00	<.0001
	LPD-11	3	--	--	6	0.66	0.16	3	--	<.0001
	LPD-12	4	1.00	<.0001	2	--	--	4	0.80	0.20
	LPD-13	5	0.50	0.39	5	-0.10	0.87	5	0.90	0.04
	LPD-14	7	0.75	0.05	5	0.60	0.28	5	0.20	0.75
	LPD-15	6	0.26	0.62	5	0.70	0.19	5	-0.30	0.62