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## **INDOOR, OUTDOOR AND REGIONAL PROFILES OF PM<sub>2.5</sub> SULFATE, NITRATE AND CARBON**

SV Hering<sup>1</sup>, MM Lunden<sup>2</sup>, TW Kirchstetter<sup>2</sup>, TL Thatcher<sup>2</sup>, KL Revzan<sup>2</sup>, RG Sextro<sup>2</sup>, NJ Brown<sup>2</sup>, J Watson<sup>3</sup> and J Chow<sup>3</sup>

<sup>1</sup>Aerosol Dynamics Inc., 2329 Fourth Street, Berkeley, CA USA 94710

<sup>2</sup>Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA USA 94720

<sup>3</sup>Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512

### **ABSTRACT**

Fine particle concentrations were measured simultaneously at three locations: a regional monitoring site in Fresno, California, a backyard of an unoccupied residence in Clovis, California located 6 km northeast of the regional site; and indoors at the same residence. Measurements included 10-min determination of PM<sub>2.5</sub> nitrate, sulfate and carbon using an automated collection and vaporization system, and black carbon measured by light attenuation through a filter deposit. Specific outdoor PM<sub>2.5</sub> constituents were compared to assess the appropriateness of using regional data to model indoor concentrations from outdoor sources. The outdoor data show that, in general, the regional results provide a good representation of the concentrations seen at the building exterior. The indoor concentrations showed considerable attenuation as well as a broadening and time-lag for the concentration peaks. The concentration reduction was the largest for PM<sub>2.5</sub> nitrate, which appears to undergo phase changes in addition to indoor deposition and penetration losses.

### **INDEX TERMS**

PM<sub>2.5</sub>, nitrate, sulfate, black carbon

### **INTRODUCTION**

Several epidemiologic studies have found a positive association between airborne particles and increased morbidity and mortality, even at the generally low levels of pollution (Dockery, et al., 1993, Pope, et al. 1995). Important to understanding these associations is assessment of human exposure to these particles. Since people spend most of their time indoors (Jenkins, et al., 1992, Robinson and Nelson, 1995), it is necessary to evaluate indoor exposures to outdoor particles with diameters below 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>).

To better quantify indoor concentrations of outdoor PM<sub>2.5</sub>, a detailed study is being conducted in an unoccupied home in the city of Clovis, California. Simultaneous, time-resolved, indoor and outdoor measurements of particle size distributions and chemical composition have been made to elucidate mechanisms of particle penetration, deposition (Thatcher et al., 2002) and phase transformations (Lunden et al., 2002). These analyses specifically address the dynamic nature of indoor/outdoor concentration relationships, and how the time-dependence of outdoor concentrations influence indoor concentrations. They explicitly examine the dependence on chemical composition, indoor – outdoor temperature relationships, and air exchange rates.

A related question is how well the concentrations measured inside the Clovis study home could be predicted on the basis of measurements at the central monitoring site, located 6 km distant. Important to this question is how well particle concentration data from the central monitoring site represent concentrations immediately outside the residence. This paper examines the variability between the house and monitoring station, and its importance to predicting indoor concentrations.

## METHODS

Measurements were made at a home (134 m<sup>2</sup>) in Clovis, CA, as described by Thatcher et al (2002), and at the California Air Resources Board monitoring station in Fresno, as described by Watson et al (2001). The air monitoring station is located 6 km to the southwest of the study house.

At the study house, indoor and outdoor black carbon were measured with 20-min time resolution by attenuation of light through a particle deposit on a quartz fiber filter. Indoor and outdoor nitrate, sulfate, and carbon were measured with 10-minute time resolution using the integrated collection and vaporization method of Stolzenburg and Hering (2001) whereby particles are collected by humidification and impaction, and analyzed by flash-vaporization and quantification of the evolved vapor compounds. Nitrate concentrations are measured using low-temperature vaporization in a nitrogen carrier gas with assay of the evolved vapors using a chemiluminescent monitor equipped with a molybdenum converter. Sulfate and carbon analyses are performed using high-temperature heating, with analysis of the evolved sulfur dioxide by uv-fluorescence and carbon dioxide by nondispersive infrared absorption. Simultaneous indoor and outdoor measurements were obtained using a multicell system that shared a common set of gas analyzers. The sampling lines and cells for outdoor sampling were mounted within an enclosure through which outdoor air was drawn to maintain near-outdoor temperature at the point of sampling.

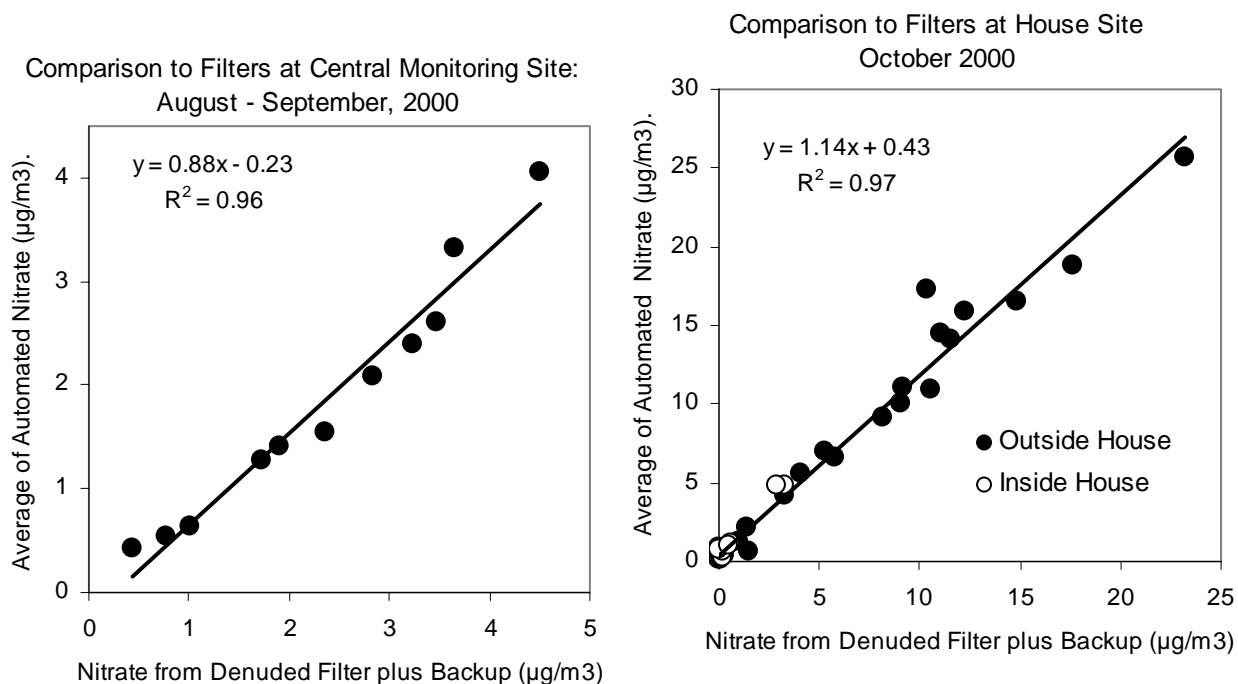
At the central monitoring site, replicate nitrate measurements were provided by two RP8400N monitors and sulfate measurements were obtained with a pre-release RP prototype (Rupprecht and Patashnick, Albany, NY). These are commercial instruments employing the same flash vaporization method used at the Clovis study house. Black carbon was measured with an Aethalometer (Andersen Instruments), which uses a similar measurement principle as the LBL black carbon instrument used at the study house. Integrated filter samples for chemical analyses were collected on selected days. Nitrates were measured on denuded, impregnated filters, sulfates on Teflon filters, and carbon on quartz filters.

The sample inlets at the residential site were located at a height midway between the house eaves and the roof peak. This location was chosen to obtain samples which best represent the particle concentration at the building exterior. However, the chosen location is substantial lower and more sheltered than typical regional monitoring locations. At the central monitoring site, the sample inlets were mounted on the flat roof of a 2 story building and extended 2 m above the rooftop.

## RESULTS

*Quality Assurance:* Time-integrated concentrations from the continuous measurements were compared to those obtained from the 12- and 24-hour filter samples at the Clovis study house and the Fresno central monitoring site. For nitrate, these comparisons yield  $R^2 > 0.96$ , with

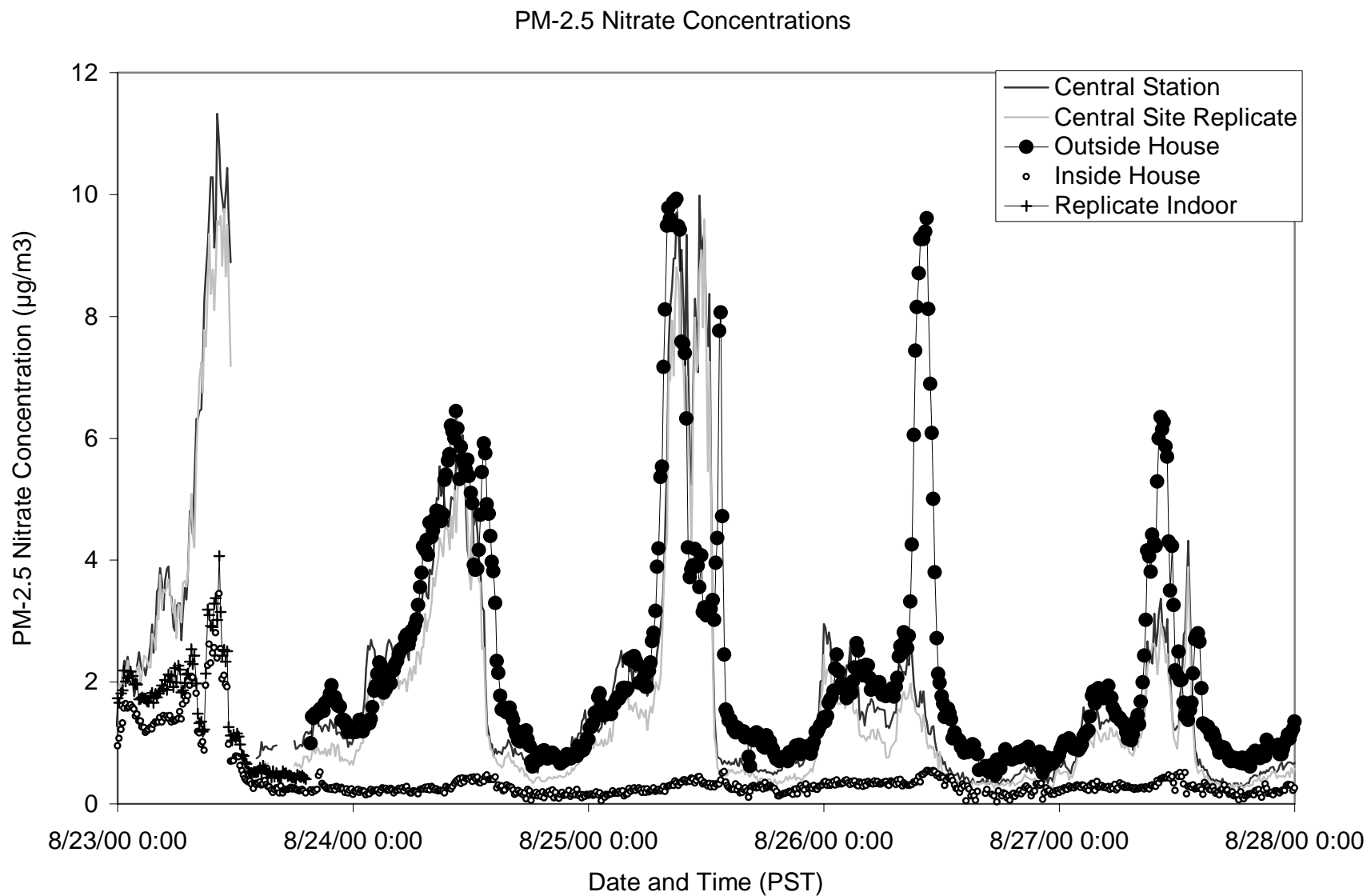
regression slopes of 0.88 and 1.14, respectively (Figure 1). The comparability of the indoor and outdoor cells was evaluated by sampling indoor air with both cells under high ventilation conditions. This was done over a 24-hr period on August 23<sup>rd</sup>, as shown in the first day of the time series plot of Figure 2. The two nitrate cells are correlated with an  $R^2=0.97$ . The indoor cell reported 15% lower values, on average, during this period.



**Figure 1.** Comparison of automated nitrate measurements to parallel filter measurements (a) at the Central Monitoring Site in Fresno, and (b) at the study house in Clovis, 6 km to the northeast.

*Daily Patterns in Nitrate Concentrations:* An example of the daily variations in regional, outdoor and indoor nitrate concentrations is presented for the last four days of the time series in Figure 2 (August 24–27). Ambient concentrations exhibit a late morning to midday maximum, with 10-min peak concentrations reaching a factor of 3 or more higher than the daily average. On most days the concentrations at the study house were comparable to those at the central monitoring site, similar to that shown for August 24<sup>th</sup>. Occasionally the outdoor data showed excursions from the central site data, such as seen on August 26<sup>th</sup>. Notably, the nitrate concentrations inside the house are markedly lower than outside. These data were collected during our set-up period, when there was considerable activity in the house. Average temperature inside the house was warmer than outside by 7C.

Data collected during a two-week intensive study period in October 2000 are summarized in Table 1 below. Listed are the  $R^2$  values (square of the correlation coefficients) and ratio of mean concentrations between measurements at the central monitoring site to those made immediately outside the study house, and between measurements inside the house and immediately outside. Correlations were computed for the 10-min data, and averages of these data to 6-hours. Indoor/outdoor correlations and ratios of mean values are also shown for the 12-hr filter based measurement. For the 10-min and 6-hr averaged nitrate data, the correlation between the central monitoring site and the outdoor measurement taken at the house exterior is much higher than for the comparison between inside the house and immediately outside. Both the automated nitrate system and the integrated filter data indicate mean indoor concentrations are less than 10% of the mean nitrate measured immediately outside during the same period.



**Figure 2.** Example of  $\text{PM}_{2.5}$  nitrate concentrations measured at central monitoring site and inside and outside of the Study House (see text).

*Sulfate and Black Carbon Profiles:* As with nitrate, the time variation and the concentration in PM<sub>2.5</sub> sulfate immediately outside the residence was comparable to that observed at the regional site. This is consistent with the regional nature expected for secondary constituents that are formed as a result of atmospheric oxidation processes. During the two-week intensive when the house was unoccupied, the mean of the indoor sulfate concentrations was approximately one-half of that outside. The correlation between indoor and outdoor measurements is higher than for nitrate, but lower than between outdoors and the central monitoring site. This is attributed to the time lag for infiltration into the building, whose the time constant varies with infiltration rate, and to the variability in depositional losses.

For black carbon, which is a directly emitted pollutant, we find similar patterns in ambient concentrations measured outside the house and at the central monitoring site. The black carbon concentrations were systematically higher at the central monitoring site (ratio of means = 1.7). Elevated black carbon at the central monitoring station is likely attributable to the closer proximity of traffic sources. Outside the house, local concentration peaks of black carbon were sometimes observed, likely originating from highly localized sources observed in the neighboring homes, such as wood burning and lawn mowing. These sharp black carbon peaks did not translate into indoor concentration peaks, presumably due to the short duration and small spatial extent of the carbon plumes, which may not have encompassed the entire building shell. As with the sulfate, correlation in concentrations between the central monitoring site and outside is greater than between indoors and immediately outside.

**Table 1.** Correlation and Ratio of Mean Values between Regional, Outdoor, and Indoor Concentrations for different averaging times and chemical constituents.

<b>Nitrate:</b>	10-min Data	6-hr Average	12-hr Filter Data
R <sup>2</sup> for Replicates at Central Site	0.92	0.97	
R <sup>2</sup> for Outdoor vs Central Site	0.73	0.85	
R <sup>2</sup> for Indoor vs Outdoors	0.28	0.28	0.33
Regional Mean / Outdoor Mean	0.8		
Indoor Mean / Outdoor Mean	0.08		0.06

<b>Sulfate:</b>	10-min Data	6-hr Average	12-hr Filter Data
R <sup>2</sup> for Outdoor vs Central Site	0.81	0.93	
R <sup>2</sup> for Indoor vs Outdoors	0.61	0.44	0.33
Regional Mean / Outdoor Mean	1.2		
Indoor Mean / Outdoor Mean	0.53		0.51

<b>Black Carbon:</b>	20-min Data	6-hr Average	12-hr Filter Data
R <sup>2</sup> for Outdoor vs Central Site	0.53	0.73	
R <sup>2</sup> for Indoor vs Outdoors	0.26	0.55	0.72
Regional Mean / Outdoor Mean	1.7		
Indoor Mean / Outdoor Mean	0.51		0.62

## CONCLUSIONS

By comparison to differences between indoor and outdoor concentrations, the concentrations of sulfate and nitrate immediately outside the house are well-represented by those measured at the central monitoring site. This is true even though the residential samples are taken in a , reduced height, sheltered location near the building in order to approximate concentrations at the building exterior. The similarities between the two sampling locations hold for both the average concentrations and the daily profile of concentration maxima. For black carbon, which is a primary pollutant with a large area source, the daily patterns are similar to the central site, but the absolute concentrations are lower. This indicates that a modeling effort that uses central monitoring data to represent concentrations immediately outside of homes should take into account the density and proximity of local area sources, such as traffic, in estimating these concentrations.

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