

THE EFFECT OF PENETRATION FACTOR, DEPOSITION, AND ENVIRONMENTAL FACTORS ON THE INDOOR CONCENTRATION OF PM_{2.5} SULFATE, NITRATE, AND CARBON

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ABSTRACT

Indoor exposure to particles of outdoor origin constitutes an important exposure pathway. We conducted an intensive set of indoor particle measurements in an unoccupied house under differing operating conditions. Real-time measurements were conducted both indoors and outdoors, including PM_{2.5} nitrate, sulfate, and carbon. Because the time-scale of the fluctuations in outdoor particle concentrations and meteorological conditions are often similar to the time constant for building air exchange, a steady state concentration may never be reached. The time-series experimental data were used to determine the effect of changes in air exchange rate and indoor/outdoor temperature and relative humidity differences on indoor particle concentrations. A multivariate regression was performed to investigate the difference between measured indoor concentrations and results from a simple time-dependent physical model. Environmental conditions had a significant effect on indoor concentrations of all three PM_{2.5} species, but did not explain all of the model variation.

INDEX TERMS

Particle, deposition, penetration factor, ammonium nitrate, ammonium sulfate, carbon

INTRODUCTION

Particulate air pollution is associated with increased morbidity and mortality even at the generally low levels of pollution in United States cities (Samet, et al., 2000). The exact compounds and/or particle size ranges responsible for these health effects have not yet been determined. Exposures to particles of outdoor origin which occur while indoors may constitute a significant fraction of the overall exposure to hazardous particles since typically people spend up to 90% of their time indoors (Jenkins, et al., 1992, Robinson and Nelson, 1995). Indoor concentrations of particles of outdoor origin can be on the same order as outdoor concentrations (Ott et al., 2000; Riley et al., 2001).

Separating the effects of deposition and penetration in a full-scale house is difficult. In this study, we measured the indoor and outdoor concentrations of PM_{2.5} nitrate, sulfate, and carbon over a period of several days. A simple time dependent physical model is then used to determine the penetration factor, defined as the fraction of particle in the infiltrating air which pass through the building shell, and deposition loss rate for each compound. The difference between the modeled and measured values is used in a multiple variable regression to examine the effect of changes in temperature, relative humidity, and air exchange rate on model fit.

METHODS

The experiments were performed in a 134 m² home in Clovis, California. The home was constructed in 1972, with a stucco exterior and sliding aluminum frame windows. The house

is single story, with standard height ceilings (2.4 m), a forced air heating and cooling system, and ceiling fans (which were operated during the experiments to promote mixing). An additional oscillating fan was operated in the living room to disperse tracer gas and promote mixing near the particle measurement equipment. The building is located in a residential suburb, surrounded by mature trees and homes of a similar height and size. The flat terrain and high level of sheltering resulted in relatively low wind speeds near the building.

PM2.5 nitrate, carbon and sulfate were measured with 10-minute time resolution using the integrated collection and vaporization cell (ICVC) method of Stolzenburg and Hering (2001). This method collects PM2.5 particulate matter by humidification and impaction onto a 1 mm diameter spot on a metal substrate. The sample is then analyzed by flash-vaporization and quantitation of the evolved vapor compounds. Nitrate concentrations are measured using low-temperature vaporization in a nitrogen carrier gas with quantitation of the evolved vapors using a chemiluminescent monitor equipped with a molybdenum converter to reduce higher oxides of nitrogen to nitric oxide. 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. Indoor and outdoor measurements were performed simultaneously using a four-cell system. One pair of cells was used for nitrate measurements. A second pair was used for the combined measurement of carbon and sulfate. The nitrate and sulfate-carbon cells used to measure outdoor concentrations were housed indoors inside a box that was ventilated with outdoor air to maintain near-outdoor temperature at the point of sampling. Outside air was transported into the system through a large inlet tube, with the sample drawn through an isokinetic inlet in the center of the tube. Air infiltration rates for the house were continuously measured using a constant injection of sulfur hexafluoride tracer gas and measurement with an photo-acoustic detector system.

For our analysis, we used a simple physical mass balance equation, reduced to include only the effects of deposition and penetration losses:

$$\frac{\partial C_I}{\partial t} = C_o P \lambda_v - C_I (\lambda_v + \beta) \quad (1)$$

Where: C_I = indoor particle concentration at time t ($\# \text{ cm}^{-3}$),
 t = time (h^{-1}),
 C_o = outdoor particle concentration at time t ($\# \text{ cm}^{-3}$),
 P = penetration factor,
 λ_v = air exchange rate (h^{-1}), and
 β = deposition loss rate (h^{-1}).

This equation is solved fairly easily for a constant outdoor concentration and stable infiltration rate. Unfortunately, the system may not reach steady-state conditions, so we solve the equation using a basic ‘forward-marching’ scheme with time step, Δt , as shown below:

$$C_i(t_2) = C_i(t_1) + P C_o(t_1) \lambda_v(t_1) \Delta t - C_i(t_1) (\lambda_v(t_1) + \beta) \Delta t \quad (2)$$

In these experiments, the time step used was 10 minutes, corresponding to the measurement interval. The deposition loss rate and penetration factor were adjusted to minimize the squared relative errors summed over time, where the squared relative error is defined as the square of the difference between the measured and modeled indoor concentration divided by the measured concentration. This weighting scheme gives equal weighting to relative errors

in predictions at both high and low concentrations. The Excel spreadsheet function SOLVE was used to determine the deposition loss rate, β , and penetration factor, P, which minimized the sum of the squared relative errors for each chemical compound.

The outdoor concentrations and infiltration rates entered into the modeled are a time-series of measurements. Variations in these two parameters are expected to have the largest effect on indoor concentration. The model determines the constant deposition loss rate and penetration factor which best fit the data. However, the deposition loss rate and penetration factor may vary with time due to changes in the indoor environment, such as temperature or relative humidity. In addition, the particle size distribution for a PM 2.5 class may change over time, leading to further changes in the deposition and penetration rates. Further analysis is required to assess the importance of these effects on indoor concentrations. The model also assumes that there are no other significant loss or gain mechanisms affecting indoor particles. Volatilization, hygroscopic growth or loss, phase change, or other processes could affect the indoor concentration of PM 2.5 sulfate, nitrate, or total carbon.

To investigate the influence of some of these confounding effects, a multivariate linear regression was performed on the correlations between the model/measurement difference at each point in time and indoor/outdoor relative humidity and temperature differences, air exchange rate, and outdoor concentration.

RESULTS

Figure 1 compares time series of the modeled and measured indoor concentration for each compound. During four 12 hour periods (1/19 PM, 1/20 AM, 1/21 PM, and 1/23 AM), the house was pressurized with outdoor air via a large fan mounted in a windows. During these periods, the penetration factor was set to 1, indicating an assumption of no significant particle losses within the fan. During six 12 hour periods (1/17 AM, 1/18AM, 1/18PM, 1/21 AM, 1/22 AM, and 1/22 PM), the kitchen fan was turned on to depressurize the building and increase the air exchange rate. The HVAC system was also manipulated to change indoor/outdoor temperature difference, in addition to either no, continual, or intermittent HVAC fan operation. The best fit parameters obtained by the physical model and used in Figure 1 are shown in Table 1.

As Figure 1 and the R squared values in Table 1 show, the simple 2 parameter model is not adequate to describe all of the variability in the indoor concentration. Of the three chemical constituents studied, sulfate particles are arguably the most chemically stable.

Table 1: Model fits for data from January 16-23, 2001.

	PM 2.5 Sulfate	PM 2.5 Carbon	PM 2.5 Nitrate
Penetration Factor	0.95	1.03	0.67
Deposition Loss Rate (/h)	0.19	1.34	2.57
R squared	0.63	0.51	0.70

The stability of the PM2.5 sulfate is reflected by the fact that the penetration factor and deposition loss rate for sulfate are consistent with those expected for submicron particles. The carbon measured by the ICVC system includes both organic and inorganic carbon. For this total carbon fraction, there may be additional loss mechanisms, such as degradation or volatilization indoors. These additional loss terms are not distinguished in the model from the

deposition loss rate term and thus will lead to the apparently high deposition losses. For nitrate, volatilization of ammonium nitrate into gaseous ammonia and nitric acid, causes a significant loss of particle nitrate in the indoor environment. Volatilization appears to account for a significant portion of the difference in penetration and deposition loss rates between nitrate and sulfate particles.

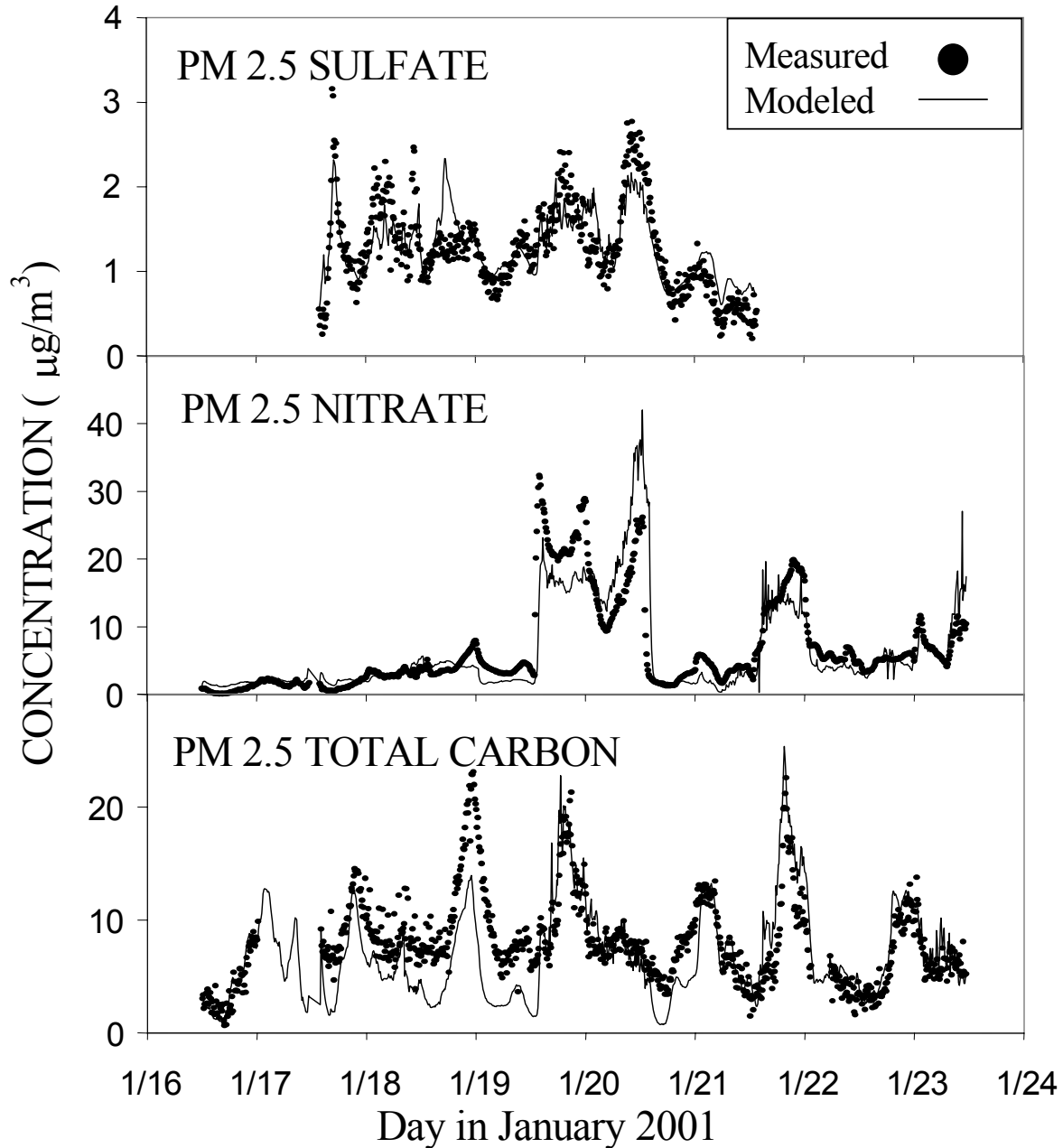


Figure 1: Comparison between the measured and modeled indoor concentrations using equation 2 and the parameters shown in Table 1. Tick marks on the x axis indicate midnight. A multivariable linear regression was performed to investigate possible causes for the discrepancy between measured and modeled concentrations. The difference between the measured and modeled indoor concentration was compared to four variables: (1) outdoor minus indoor temperature, (2) outdoor minus indoor relative humidity, (3) infiltration rate, and (4) outdoor concentration of the compound. While we do not necessarily expect the form

of the relationship between these variables and indoor concentration to be linear, this analysis can be used to explore whether a variable causes a significant effect and thus warrants further study. Table 2 shows the results of the regression. An example of the relationship is shown in Figure 2 where a definite trend is observed, despite considerable scatter in the data.

Table 2: Coefficients and standard errors from the four variable linear regression analysis for the three compounds measured, along with the R squared value for the regression. Coefficients with $P \leq 0.05$ are shown in bold.

	PM 2.5 Sulfate	PM 2.5 Carbon	PM 2.5 Nitrate
T(out) – T (in)	0.015 ± 0.005	-0.026 ± 0.026	0.007 ± 0.033
%RH(out) – %RH(in)	0.085 ± 0.008	0.474 ± 0.046	-0.661 ± 0.058
Infiltration Rate (/h)	0.073 ± 0.011	-1.009 ± 0.050	-0.444 ± 0.070
C (out) (ug/m3)	-0.110 ± 0.027	-0.021 ± 0.011	-0.059 ± 0.012
R squared	0.24	0.44	0.28

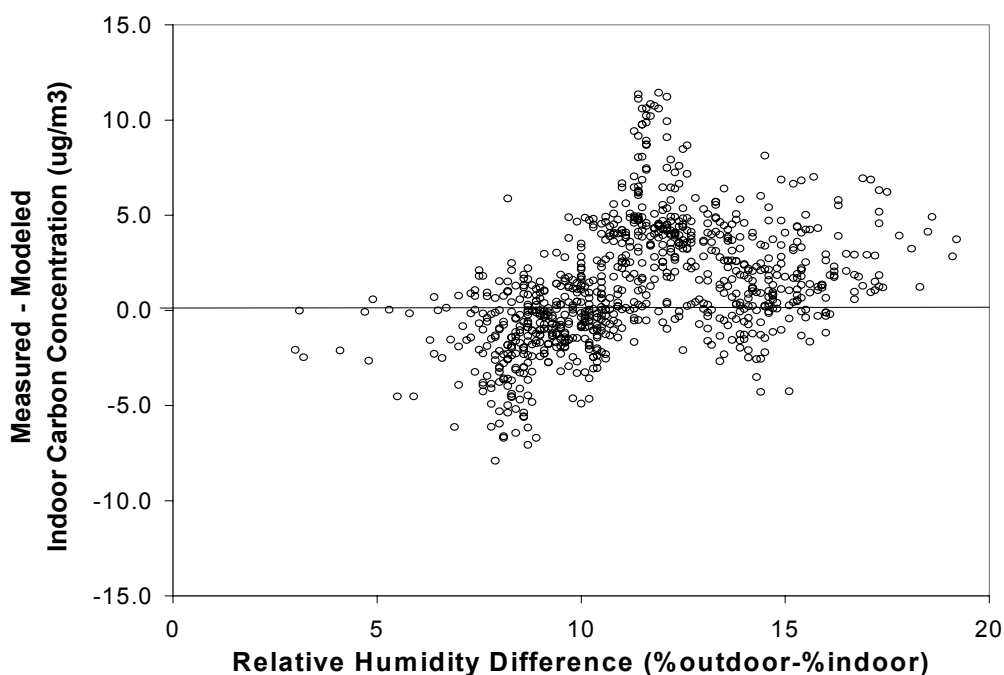


Figure 2: Indoor PM2.5 carbon model fit (measured - modeled concentration) versus relative humidity difference (%RH outdoor - % RH indoor).

The R squared values for the regressions suggest that a substantial fraction of the model/measured difference can be attributed to the factors tested, with the greatest influence found for total carbon. The indoor/outdoor temperature difference showed little or no correlation with the model fit for any of the chemical compounds studied. Both relative humidity difference and infiltration rate showed a significant correlation for all three particle types, although the sign of the correlation varied between compounds. There was a significant correlation with outdoor concentration for sulfate particles, a small but significant correlation for nitrate particles, and a statistically insignificant correlation for carbon particles.

CONCLUSIONS

A time-dependent physical model was used to model indoor concentrations of three components of outdoor PM 2.5: carbon, nitrate, and sulfate. The model was shown to provide reasonable fits to the data over time periods of several days. However, for some time periods the measured indoor concentrations varied significantly from the model values. A multivariable linear regression was used to investigate possible causes for the model/measurement discrepancy. The four variables tested accounted for less than half of the model-measurement discrepancy observed. This indicates that there are likely to be other significant factors which have not been investigated in this study and/or that some effects are non-linear. Possible factors which may cause shifts in the deposition and penetration rates include changes in indoor flow conditions and shifts in the PM 2.5 size distribution for a chemical compound. Changes in wind speed and/or direction could also lead to shifts in the penetration rate if the crack size distribution was not uniformly distributed around the building shell. PM 2.5 carbon may undergo evaporation and/or chemical reaction and shifts in the composition of PM 2.5 carbon could change the rates of these processes. PM 2.5 nitrate, in the form of ammonium nitrate, is highly volatile in the indoor environment and the gaseous composition of the aerosol (ammonia and nitric acid) may affect the rate of volatilization. Considerable work will be required to determine which factors are most important in describing indoor concentrations of specific chemical compounds in outdoor PM 2.5.

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