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THE TRANSFORMATION OF OUTDOOR AMMONIUM NITRATE AEROSOLS IN THE INDOOR ENVIRONMENT

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ABSTRACT

Recent studies associate particulate air pollution with adverse health effects; however, the exposure to indoor particles of outdoor origin is not well characterized, particularly for individual chemical species. In response to this, a field study in an unoccupied, single-story residence in Clovis, California has been conducted. Real-time particle monitors were used both outdoors and indoors to quantify PM_{2.5} nitrate, sulfate, and carbon. The results show that reduced indoor sulfate and carbon levels are primarily due to deposition and penetration losses. However, measured indoor ammonium nitrate levels were often observed to be at significantly lower levels than expected based solely on penetration and deposition losses. The additional reduction appears to be due to the transformation of ammonium nitrate into ammonia and nitric acid indoors, which are subsequently lost by deposition and sorption to indoor surfaces. The size of the effect is dependent upon factors such as temperature, relative humidity, and ventilation rate.

INDEX TERMS

Aerosols, penetration, chemical transformation, ammonium nitrate, nitric acid, ammonia

INTRODUCTION

An understanding of the underlying reasons for the causes of the adverse health effects resulting from ambient particulate matter (PM) is of major scientific importance. These adverse health correlations are based upon data from outdoor regional monitoring sites (Dockery, et al., 1993, Pope, et al., 1995). However, individuals spend, on average, about 90% of their time indoors - 70% of that in homes (Jenkins, et al., 1992). This implies that indoor exposure to PM_{2.5} of outdoor origin may be an important element in determining the causes of these health effects.

To investigate the dynamics of indoor particles of outdoor origin, we performed a controlled series of intensive field experiments on an unoccupied, single-story residence in Clovis, California, a suburb of Fresno, in California's San Joaquin Valley. The conditions in the residence were manipulated to cover a wide range of conditions during several weeks of intensive measurements periods. The measurements focused on providing data on indoor and outdoor concentrations of PM_{2.5} particles as a function of chemical concentration under a variety of house ventilation, heating and cooling conditions. Indoor sources were minimized to enhance understanding the mechanism of the transport of outdoor particles indoors.

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METHODS

The experimental facility is a three-bedroom, single-story home (134 m²) constructed in 1972. The house has standard height ceilings (2.4 m), a forced air heating and cooling system, and ceiling fans. The house is located in a residential suburb, surrounded by homes of similar size and mature trees. The flat topography of the area combined with the mature vegetative growth near the home resulted in low levels of wind loading around the building.

The chemical concentrations of indoor and outdoor aerosols were measured simultaneously with 10-minute time resolution using the integrated collection and vaporization cell (ICVC) system of Stolzenburg and Hering (2000). Particles were collected by humidification and impaction and analyzed by in-situ flash vaporization of the evolved vapor compounds. Nitrate concentrations were measured from the evolved vapors using a chemiluminescent monitor equipped with a molybdenum catalyst to convert higher oxides of nitrogen to nitric oxide. The sulfate quantitation was performed by analysis of the evolved sulfur dioxide by UV-fluorescence and total carbon was converted to carbon dioxide and analyzed by nondispersive infrared absorption. A four-cell ICVC system was used to perform simultaneous indoor and outdoor measurements; one pair for nitrate and one pair for a combined carbon and sulfate measurement. The system was located in the living room of the house, however the outdoor sampling cells were housed in an enclosure ventilated with outdoor air to maintain the system at outdoor temperature.

The important atmospheric gas phase species of ammonia, nitrous acid, nitric acid and sulfur dioxide were measured using an automated on-line ion chromatograph (IC) system. The IC system collects water-soluble gases using wet denuders, followed by concentration and ion chromatographic analysis based upon the technique of Buhr *et al.* (1995). The system utilized a dual-channel IC to enable simultaneous automated measurement of both anion and cation species. Denuders were located both inside and outside the house, and provided data with 30-minute time resolution.

Ventilation rates were measured using a continuous release SF₆ tracer gas measurement system using a photoacoustic analyzer (Breul & Kajer, Model 1302). Temperature and relative humidity were measured both inside and outside the house using dual temperature and relative humidity probes (Vaisala HMD70Y) mounted in aspirated shielded enclosures.

Experiments were conducted during three intensive measurement periods; October 9-23, 2000, December 11-19, 2000 and January 16-23, 2001. During these intensives, entry into the house was limited to a one-hour period at midday to perform instrument checks and flow calibrations. Instrument control and data acquisition for all instruments were performed from outside the house, allowing for minimal disturbance of the indoor environment. Using the house as a laboratory, a range of conditions was explored during the intensives by manipulating the ventilation rate and indoor-outdoor temperature gradient through natural or mechanical means. The house experienced infiltration rates in the range of 0.2 to 0.5 air changes per hour (ACH) when allowed to operate under naturally occurring conditions. When the doors and windows were opened, the ventilation rate could increase up to 1 ACH. In order to further expand the experimental parameter space to a regime where the residence time for air in the house approached the time required for other processes, such as deposition, to occur, we utilized mechanical ventilation techniques to achieve rates in the range of 2 to 6 ACH. The forced-air heating/cooling system was used to provide changes in the indoor/outdoor temperature differential in addition to conditions of either no, continual, or intermittent fan operation.

RESULTS AND DISCUSSION

Figure 1 shows time series of concentrations for measured total carbon, sulfate and nitrate from the ICVC system during the December intensive measurement period. Figure 1 also shows the ventilation rate measured during the same period. Note that the rate measured during 12/16 PM, 12/17 AM, 12/28 PM and 12/19 AM reflect the high values achieved using mechanically driven ventilation. What is immediately apparent is that there is a great deal of variability in both the indoor and outdoor concentration measurements for these three species. The difference between the indoor and outdoor concentrations is also highly variable. In general, however, the difference between the indoor and outdoor concentration decreases appreciably during periods of high air change rates. This result is intuitive as the characteristic time for particle gain by penetration is significantly greater than that for loss by deposition at these high ventilation rates. Of the three particulate species shown in Fig. 1, sulfate is generally considered to be the most stable upon transport from outdoors to indoors. A forward marching fit of the sulfate data using the time-dependent physical mass balance model results in values of 0.95 for the penetration factor and 0.19 hr^{-1} for the deposition loss rate, both of which are reasonable (Thatcher, et al, 2002).

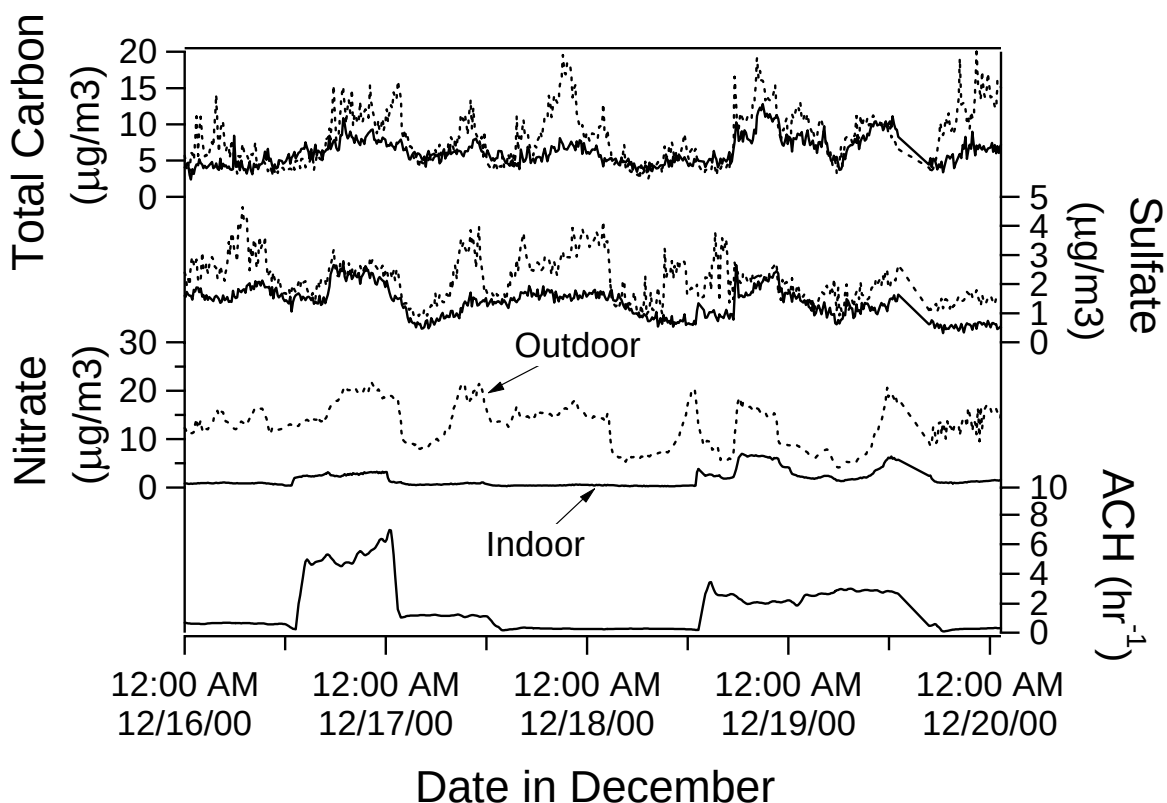
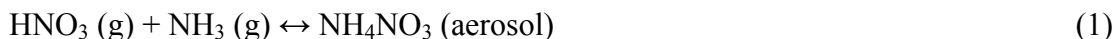


Figure 1. Data from the ICVC system showing the variation in indoor (solid line) and outdoor (dashed line) carbon, sulfate, and nitrate for a four day period during the December intensive. The lowest plot on the diagram shows the ventilation rate as a function of time.

The differences between outdoor and indoor nitrate particle concentrations are significantly larger than those observed for the other particle species. The indoor concentrations are most often quite low, rising to appreciable levels only during periods of high air change rates. Ammonium nitrate is volatile, and the gas-to-particle partitioning is highly dependent on factors such as temperature, relative humidity and the gas phase concentrations of ammonia and nitric acid as outdoor air is transported indoors. Previous experimental investigations

have demonstrated that ammonium nitrate aerosol undergoes phase transitions during transport into houses (Hering and Avol, 1996). During the winter period, the nitrate aerosol moved from a cooler outdoor to a warmer indoor environment, shifting the equilibrium of the nitrate formation reaction,



to the left towards the gas phase. The gases diffuse toward and absorb to surfaces inside the house, further driving the equilibrium toward the gas phase. A final, and important factor affecting equilibrium is how quickly either gas is lost to surface uptake.

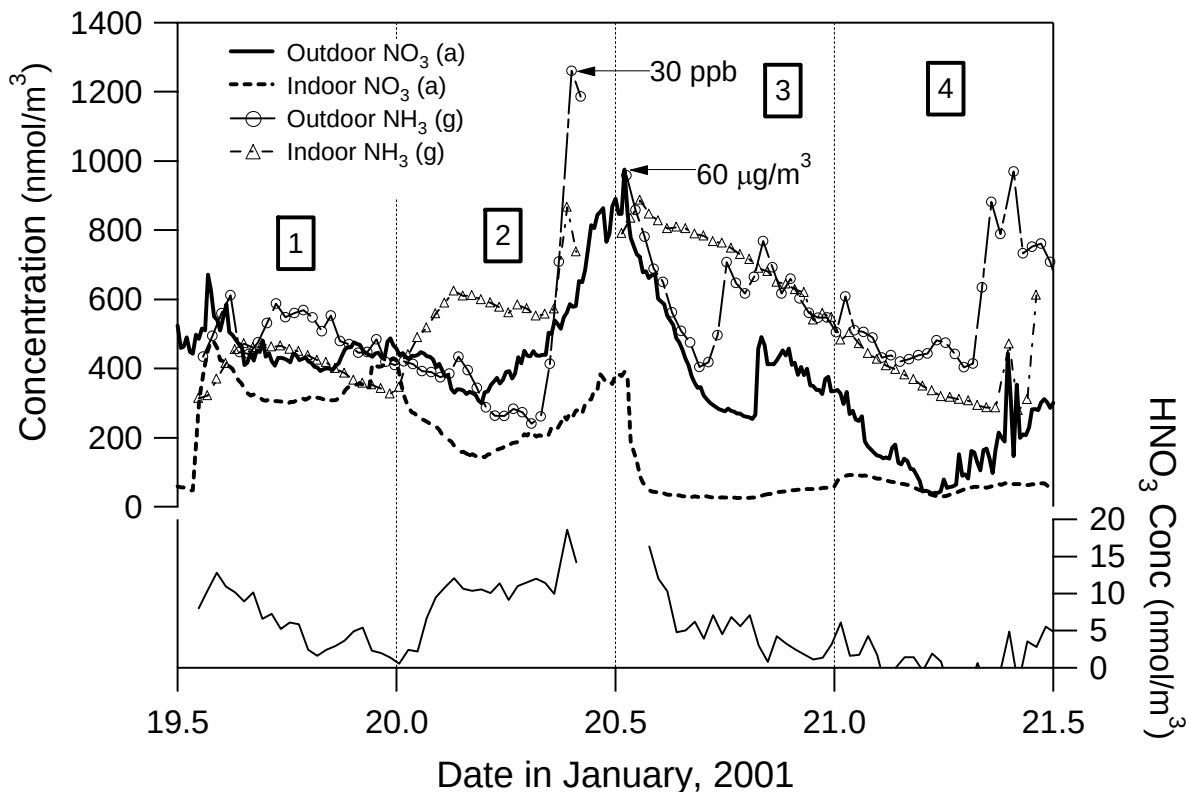


Figure 2. High time resolution measurements of the concentration of ammonium nitrate particulate (NH_4NO_3) and gaseous ammonia (NH_3) measured outside and inside the residence. The lower portion of the graph shows the concentration of the gaseous nitric acid (HNO_3) inside the residence. The numbered periods are described in the text.

The importance of the ammonium nitrate equilibrium can be seen in Fig. 2, which shows results of the ICVC system for nitrate and the automated IC system for ammonia and nitric acid for four different 12 hour periods during the January intensive. The indoor environment for each 12 hour period was manipulated as follows: (1) ventilation rate of approximately 4 h^{-1} with the heat off, (2) $\text{ACH} \sim 5 \text{ h}^{-1}$ with the heat on at 20°C , (3) $\text{ACH} \sim 0.3 \text{ h}^{-1}$ with the heat off, and (4) $\text{ACH} \sim 1 \text{ h}^{-1}$ with the heat off. Note how well the outdoor ammonia (NH_3) and nitrate (NH_4NO_3) measurements are correlated, particularly on Jan 20^{th} . During the period from noon on January 19^{th} to noon on Jan 20^{th} , the indoor ammonia and indoor nitrate are anticorrelated – as the nitrate concentration decreases, the ammonia increases. Indeed, throughout the entire measurement campaign, the indoor ammonia levels were often higher than those found outdoors due to this dissociation. During periods (1) and (2), the

characteristic time for nitrate penetration from outdoors was large enough to balance the amount lost to dissociation, resulting in relatively large indoor nitrate levels. This period was one of the few times when significant levels of indoor nitrate were observed. The addition of heat to the house between conditions (1) and (2) is enough to cause a perceptible shift towards the gas phase. When the air change rate was drastically lowered between conditions (2) and (3), much of the nitrate dissociated, resulting in large indoor ammonia levels.

Throughout the entire experiment, the nitric acid (HNO_3) concentration indoors was low to undetectable. Based on Eq. (1), equal amounts of ammonia and nitric acid should be formed, however the data show a large difference between the concentrations of these two gases. After dissociation, the nitric acid gas is sorbing to the walls at faster rates than for the ammonia gas, which appears to accumulate. We attribute this to acid-base chemistry causing the nitric acid to be more tightly bound to the walls. The loss of nitric acid serves to continue to drive the equilibrium toward the gas phase.

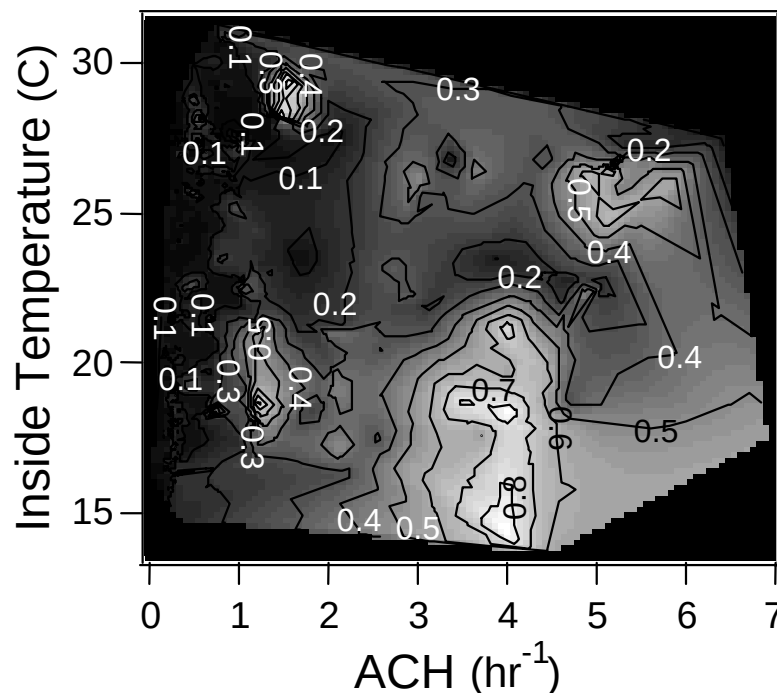


Figure 3. Contours of the ammonium nitrate indoor/outdoor ratio as a function of indoor temperature and ventilation rate.

The fate of ammonium nitrate aerosol once transported into the house is a complex function of the ventilation rate, the constituents in the gas phase, and the temperature. The conditions that result in high nitrate can be seen more clearly in Fig. 3, a contour plot of the indoor/outdoor ratio of ammonium nitrate as a function of both indoor temperature and ventilation rate. Two conditions result in increased indoor nitrate concentrations. In the upper left of the figure, the house was open during the fall intensive. In this case, the indoor and outdoor environments were similar and the ventilation rate was relatively large. Thus, the rate of nitrate loss due to dissociation was smaller than the supply of nitrate due to penetration from outdoors resulting in increased indoor concentrations. The lower center of the graph shows the elevated winter conditions. Air change rates were very large and the temperature was low due to forced ventilation. The large air change rate serves to constantly replenish the ammonium nitrate lost to dissociation and deposition.

CONCLUSIONS

A series of simultaneous indoor and outdoor measurements were performed at a residence, providing real-time, chemically speciated data for the significant aerosol species of nitrate, sulfate, and carbon as well as the gas species ammonia and nitric acid. The highly time resolved data show considerable variability in both the outdoor and indoor concentrations of PM_{2.5} constituents. This results in a wide range of ratios of indoor to outdoor concentrations that might not be evidenced in lower time resolved measurements. More importantly, the dissociation of the nitrate aerosol illustrates that an exposure assessment based on total particle mass measured outdoors may obscure the actual causal relationships, especially for indoor exposures to particles of outdoor origin. Nitrate is a significant outdoor pollutant in the Western United States. The extent to which it may or may not be a significant source of indoor exposure has important policy implications for control of sources that lead to nitrate formation. These results emphasize the need for chemical characterization of particulate, and further studies of the physical and chemical transformation processes that influence the indoor concentration of particles of outdoor origin.

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