Indoor, Outdoor, and Regional Summer and Winter Concentrations of PM$_{10}$, PM$_{2.5}$, SO$_4^{2-}$, H$^+$, NH$_4^+$, NO$_3^-$, NH$_3$, and Nitrous Acid in Homes with and without Kerosene Space Heaters

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Twenty-four-hour samples of PM$_{10}$ (mass of particles with aerodynamic diameter ≤10 μm), PM$_{2.5}$ (mass of particles with aerodynamic diameter ≤ 2.5 μm), particle strong acidity (H$^+$), sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonia (NH$_3$), nitrous acid (HONO), and sulfur dioxide were collected inside and outside of 281 homes during winter and summer periods. Measurements were also conducted during summer periods at a regional site. A total of 58 homes of nonsmokers were sampled during the summer periods and 223 homes were sampled during the winter periods. Seventy-four of the homes sampled during the winter reported the use of a kerosene heater. All homes sampled in the summer were located in southwest Virginia. All but 20 homes sampled in the winter were also located in southwest Virginia; the remainder of the homes were located in Connecticut. For homes without tobacco combustion, the regional air monitoring site (Vinton, VA) appeared to provide a reasonable estimate of concentrations of PM$_{2.5}$ and SO$_4^{2-}$ during summer months outside and inside homes within the region, even when a substantial number of the homes used air conditioning. Average indoor/outdoor ratios for PM$_{2.5}$ and SO$_4^{2-}$ during the summer period were 1.03 ± 0.71 and 0.74 ± 0.53, respectively. The indoor/outdoor mean ratio for sulfate suggests that on average approximately 75% of the fine aerosol indoors during the summer is associated with outdoor sources. Kerosene heater use during the winter months, in the absence of tobacco combustion, results in substantial increases in indoor concentrations of PM$_{2.5}$, SO$_4^{2-}$, and possibly H$^+$, as compared to homes without kerosene heaters. During their use, we estimated that kerosene heaters added, on average, approximately 40 μg/m$^3$ of PM$_{2.5}$ and 15 μg/m$^3$ of SO$_4^{2-}$ to background residential levels of 18 and 2 μg/m$^3$, respectively. Results from using sulfuric acid-doped Teflon (E.I. Du Pont de Nemours & Co., Wilmington, DE) filters in homes with kerosene heaters suggest that acid particle concentrations may be substantially higher than those measured because of acid neutralization by ammonia. During the summer and winter periods indoor concentrations of ammonia are an order of magnitude higher indoors than outdoors and appear to result in lower indoor acid particle concentrations. Nitrous acid levels are higher indoors than outdoors during both winter and summer and are substantially higher in homes with unvented combustion sources. Key words: gas stoves, indoor/outdoor concentrations, kerosene heaters, particle air pollution. Environ Health Perspect 107:223–231 (1999). [Online 8 February 1999] http://ehpnet1.niehs.nih.gov/docs/1999/107p223-231leaderer/abstract.html

There is an increasing body of epidemiologic evidence which suggests that exposures to short-term ambient levels of suspended particles are associated with adverse health effects. The effects range from changes in respiratory function and symptoms and exacerbation of respiratory disease to excesses in daily mortality (1). Several studies have suggested that particles less than 10 μm in diameter (PM$_{10}$), particles less than 2.5 μm in diameter (PM$_{2.5}$), and the sulfate or strong acid aerosol component of the ambient aerosol are implicated in the observed particle/effect associations (1).

Exposures to particulate matter occur in a variety of microenvironments (outdoors, residences, public buildings, etc.). Because outdoor concentrations can vary considerably in time and space and indoor aerosol concentrations are associated with both indoor and outdoor sources, particle mass concentrations must be measured for different microenvironments. Size and chemical composition of the aerosols are also important. Altogether, this exposure assessment information serves the needs of epidemiologic studies, risk assessment evaluations, and the development of mitigation strategies.

As part of a prospective epidemiologic investigation of the nature of an association between particulate exposures and daily reported (over a 1-year period) respiratory symptoms in 918 infants and their mothers, we conducted an extensive exposure assessment study (2). The study protocol employed a nested design that utilized questionnaires and passive and active pollutant monitors. Active monitoring consisted of measuring particle and gaseous species both indoors and outdoors at residences as a function of season and indoor sources. Outdoor central site daily monitoring was also conducted during the summer months. In this paper we report on the following measurements: PM$_{10}$; PM$_{2.5}$; particle sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), and strong acidity (H$^+$); and gaseous SO$_2$, nitrous acid (HONO), and NH$_3$. Measurements were made indoors and outdoors at residences in Connecticut and southwest Virginia and at a central outdoor regional site in southwest Virginia. Indoor/outdoor/central site comparisons by indoor source and season for particle size and chemical composition are presented and discussed.

Methods

Sites and residence selection. Twenty-four-hour particle sampling was conducted at 20 residences in Connecticut between August 1994 and June 1995 and at 261 homes in southwest and central Virginia between July 1995 and January 1998. Sampling was conducted as part of a prospective epidemiologic study of the respiratory effects on infants and their mothers from indoor exposures to vapor and particle phase acids associated with kerosene heater use (2). Sampling was conducted in 58 residences during the summer seasons and in 223 residences during the winter seasons. Air-conditioning use during the summer period was reported in 49 of the residences, with 21 reporting the...
Fine particles are collected from the air stream leaving the denuders on a Teflon (E.I. Du Pont de Nemours & Co., Wilmington, DE) filter in front of the filter pack. Sodium carbonate-coated and citric acid-coated glass fiber filters were used downstream of the Teflon filter to collect acidic gases and ammonia volatilized from the collected fine particles. The concentration of aerosol acidity was determined from pH analysis of the Teflon filter extract. The denuder and filters were extracted and analyzed by ion chromatography to determine both gaseous (sulfur dioxide, nitric acid, nitric acid, and ammonia) and particle (sulfate, nitrate, nitrite, and ammonium) components.

The sampling preparation, chemical analysis, and quality assurance procedures used in this study are described in detail elsewhere (5–8). Limits of detection (LOD) for PM$_{2.5}$ and PM$_{10}$ samples, which were estimated to equal three times the root mean square error of the blank filter measurements, were 3.6 and 3.3 pg/m$^3$, respectively. These values are similar to those found in a Philadelphia-based study that used the same sampling methods as Suh et al. (7), where the LOD for PM$_{2.5}$ and PM$_{10}$ were 3.4 and 2.8 µg/m$^3$, respectively. Coarse particles (2.5<d$_{p}$<10 µm) mass concentrations were calculated as the difference between measured PM$_{10}$ and PM$_{2.5}$ concentrations. Because PM$_{2.5}$ concentrations cannot by definition exceed PM$_{10}$, negative coarse values were set to 0. LOD for chemical determinations from the HDS system were equal to those previously estimated for 24-hr HDS samples, which for SO$_4^{2-}$, H$^+$, and NH$_4^+$ are 6.0 nmol/m$^3$, 4.0 nmol/m$^3$, and 0.3 ppb (7).

There was concern that the complex nature and amount of particle and gas phase contaminant emissions from kerosene heaters might introduce interferences in the HDS system, resulting in lower collection efficiencies for gases. It is possible, for example, that semivolatile including organic acid emissions from the kerosene heaters could deposit on the denuder surfaces, thus blocking the intended gases (i.e., nitrous acid) from reaching the sodium carbonate coating. Also, the citric acid coated denuder could become similarly overloaded or masked, such that ammonia could have passed through the denuder and into the filter pack. In the first case the denuders would have underestimated nitric acid levels, and in the second case the ammonia that passes through the denuders could neutralize acid aerosol collected on the first filter (Teflon) of the filter pack. In an effort to address these potential interferences our protocol used four honeycomb denuders for indoor sampling (two sodium carbonate coated and two citric acid coated) to minimize the potential for saturation by higher indoor levels of ammonia and other gaseous contaminants. Two honeycomb denuders (one sodium carbonate coated and one citric acid coated) were used for outdoor sampling at the Vinton site and four denuders were used outside homes. In addition, parallel HDS systems were used with sulfuric acid treated (doped) Teflon filters during winter sampling in 15 homes where kerosene heaters were used and in 20 homes where kerosene heaters were not used. By comparing acid loss on the acid-doped filters collected in the homes with and without the use of kerosene heaters, a qualitative evaluation of the potential for kerosene heater generated acid aerosol could be made.

Samplers in residences were located in the main living area of the home, typically the family room or living room. Outdoor samplers were located within 8 m of the residence and away from any potential sources. Indoor and outdoor samples at residences were collected at a distance of approximately 1 m above the ground or floor. Particle and denuder samplers at the central Vinton site were 1.5 m off the ground. Sampling times for the denuder and particle mass measurements inside and outside residences as well as at the central site were 24-hr samples and were collected over the same time periods. Denuder systems and particle mass samplers were colocated at all sites. Available resources prevented the simultaneous measurement of all particle variables inside and outside at all residences monitored. All parameters were, however, measured daily at the central outdoor site during the summer months.

Results

Summer concentrations. Mean summer-time concentrations of PM$_{10}$, PM$_{2.5}$, coarse mass (PM$_{10}$–PM$_{2.5}$), SO$_4^{2-}$, H$^+$, NH$_4^+$, NO$_3^-$, NH$_3$, HONO, and SO$_2$ by location (inside and outside of residences or at the central outdoor site) and by use of air conditioning in the homes are summarized in Table 1. Of the 58 homes monitored, 49 reported the use of air conditioning. Samples with 24-hr durations were collected for all contaminants at all locations during the course of the summer sampling period. Average concentrations for PM$_{10}$, PM$_{2.5}$, NH$_4^+$, and NO$_3^-$ were similar among sites and indoor source categories. Average concentrations for NH$_4^+$ and NO$_3^-$ demonstrated a trend toward lower concentrations indoors rather than outdoors, but the differences were not significant. Indoor
concentrations of coarse mass were higher than outdoors. SO$_{2}^{2-}$ and H$^+$ were lower indoors, whereas NH$_3$ and HONO concentrations were markedly higher indoors. Concentrations of sulfur dioxide were low at all sites, with outdoor concentrations higher than indoor concentrations. Nitric acid levels were typically at or below the LOD (0.2 ppb).

Table 2 shows the results of the statistical analyses of the differences between concentrations measured at different sites for selected particle contaminants shown in Table 1. The analysis is for paired measurements among sites (paired t-test). Because paired samples were obtained for only five homes reporting no air conditioners, these homes were combined with homes reporting the presence of an air conditioner. The correlation coefficients for paired site measurements for those contaminants are also shown in Table 2. Overall, the correlations are low, indicating considerable scatter. PM$_{10}$ concentrations measured at the regional site were not significantly different from those measured either inside or outside of homes, nor were PM$_{10}$ concentrations measured outside homes different from those measured inside homes. A weak statistically insignificant correlation was seen between outdoor and indoor PM$_{10}$ concentrations with even weaker correlations for home versus regional site measurements. Although no statistically significant differences were observed for PM$_{2.5}$ concentrations for any of the three comparisons, significant moderate correlations were observed between PM$_{2.5}$ measured at the regional site and outside homes and between PM$_{2.5}$ concentrations measured inside and outside of homes. Figures 1 and 2 show the regression equation and scatter plot for the correlated PM$_{2.5}$ comparisons (regional site vs outside homes and inside vs outside homes, with and without outliers). The explained variation in comparisons improved with the elimination of outliers, particularly for the comparison for the comparison of PM$_{2.5}$ inside and outside homes. No significant correlations among sites were observed for coarse mass, although significant concentration differences were observed for the comparisons of regional site with inside homes and for outside homes with inside homes.

Significant differences (p<0.05) were found in the concentration values for SO$_{2}^{2-}$ and H$^+$ for the regional site versus inside homes and outside versus inside homes, but not for the sulfate comparison between the regional site and outside homes. Significant correlations by site for SO$_{2}^{2-}$ and H$^+$ were found for regional site versus outside homes and for inside versus outside homes.

### Table 1. Summary of summer pollutant concentrations

| Pollutant | Site | n | Mean ± SD | Minimum | Maximum |
|-----------|------|---|-----------|---------|---------|
| PM$_{10}$ (µg/m$^3$) | Regional site | 47 | 26.0 ± 11.5 | 10.8 | 51.9 |
| Outside homes | 43 | 28.0 ± 17.7 | 5.8 | 112.6 |
| Inside AC homes | 48 | 28.9 ± 18.7 | 4.8 | 97.9 |
| Inside non-AC homes | 39 | 33.3 ± 14.2 | 17.7 | 59.7 |
| PM$_{2.5}$ (µg/m$^3$) | Regional site | 50 | 20.23 ± 9.9 | 5.8 | 42.4 |
| Outside homes | 43 | 21.8 ± 14.8 | 3.8 | 84.2 |
| Inside AC homes | 48 | 18.7 ± 13.2 | 2.5 | 85.7 |
| Inside non-AC homes | 28 | 21.1 ± 7.5 | 3.6 | 35.3 |
| Coarse (µg/m$^3$) | Regional site | 47 | 6.3 ± 2.7 | 1.5 | 14.3 |
| Outside homes | 42 | 7.7 ± 6.2 | 2.4 | 34.1 |
| Inside AC homes | 48 | 10.4 ± 8.5 | 0 | 35.1 |
| Inside non-AC homes | 38 | 11.4 ± 9.7 | 0.2 | 32.6 |
| SO$_{2}^{2-}$ (nmol/m$^3$) | Regional site | 45 | 88.4 ± 51.6 | 14.1 | 200.9 |
| Outside homes | 42 | 83.7 ± 53.7 | 7.9 | 220.6 |
| Inside AC homes | 47 | 47.8 ± 36.3 | 2.1 | 137.7 |
| Inside non-AC homes | 9 | 63.0 ± 37.3 | 20.9 | 125.6 |
| H$^+$ (nmol/m$^3$) | Regional site | 47 | 41.0 ± 28.5 | 0 | 136.2 |
| Outside homes | 45 | 30.0 ± 26.9 | 0 | 208.6 |
| Inside AC homes | 49 | 12.4 ± 15.3 | 0 | 84.5 |
| Inside non-AC homes | 9 | 16.7 ± 9.4 | 2.9 | 34.6 |
| NH$_3$ (nmol/m$^3$) | Regional site | 47 | 124.6 ± 59.0 | 30.6 | 293.0 |
| Outside homes | 45 | 129.4 ± 87.8 | 0 | 338.9 |
| Inside AC homes | 49 | 78.3 ± 77.2 | 0 | 450.6 |
| Inside non-AC homes | 9 | 96.7 ± 68.9 | 6.7 | 214.4 |
| NO$_{2}^{2-}$ (nmol/m$^3$) | Regional site | 42 | 10.2 ± 5.0 | 2.6 | 20.7 |
| Outside homes | 42 | 9.0 ± 5.4 | 0 | 22.9 |
| Inside AC homes | 49 | 5.5 ± 8.9 | 0 | 56.1 |
| Inside non-AC homes | 9 | 6.8 ± 4.8 | 0.5 | 12.2 |
| NH$_3$ (ppb) | Regional site | 29 | 1.7 ± 0.5 | 0.9 | 2.7 |
| Outside homes | 45 | 2.8 ± 2.5 | 0 | 13.2 |
| Inside AC homes | 49 | 32.1 ± 19.4 | 1.5 | 93.0 |
| Inside non-AC homes | 9 | 27.5 ± 18.4 | 0 | 49.9 |
| Nitrous acid (ppb) | Regional site | 25 | 0.3 ± 0.4 | 0 | 2.1 |
| Outside homes | 45 | 0.3 ± 0.4 | 0 | 2.1 |
| Inside AC homes | 49 | 1.6 ± 2.1 | 0 | 11.3 |
| Inside non-AC homes | 9 | 3.5 ± 2.6 | 0.4 | 7.5 |
| Inside homes | 39 | 0.8 ± 0.8 | 0 | 2.9 |
| with gas stoves | 19 | 4.0 ± 2.8 | 0 | 11.3 |
| SO$_{2}$ (ppb) | Regional site | 50 | 1.2 ± 0.6 | 0.1 | 2.9 |
| Outside homes | 45 | 1.3 ± 1.7 | 0.02 | 9.4 |
| Inside AC homes | 49 | 0.3 ± 0.5 | 0 | 3.1 |
| Inside non-AC homes | 7 | 0.9 ± 1.0 | 0 | 3.0 |

Abbreviations: SD, standard deviation; PM$_{10}$, particle mass ≤10 µm in diameter; PM$_{2.5}$, particle mass ≤2.5 µm in diameter; coarse, particle mass between 10 and 2.5 µm in diameter (PM$_{10}$ - PM$_{2.5}$); AC, air conditioned.

*This is not a paired comparison, thus there is not always a PM$_{10}$ for every PM$_{2.5}$ and vice versa.

### Table 2. Comparison of selected pollutant concentrations by site measurement

| Pollutant | Comparison | n | Concentration differences* (mean ± SD) | Correlation coefficient |
|-----------|------------|---|--------------------------------------|------------------------|
| PM$_{10}$ (µg/m$^3$) | Regional site vs outside homes | 31 | 2.29 ± 3.34 | 0.21 |
| Regional site vs inside homes | 44 | 4.94 ± 3.22 | 0.11 |
| Inside homes vs outside homes | 40 | 3.28 ± 2.66 | 0.29 |
| PM$_{2.5}$ (µg/m$^3$) | Regional site vs outside homes | 34 | 1.40 ± 2.31 | 0.49*** |
| Regional site vs inside homes | 47 | 0.89 ± 2.20 | 0.08 |
| Inside homes vs outside homes | 41 | 2.88 ± 2.08 | 0.53*** |
| Coarse (µg/m$^3$) | Regional site vs outside homes | 30 | 2.63 ± 2.06 | -0.20 |
| Regional site vs inside homes | 43 | 4.56 ± 1.40*** | 0.24 |
| Inside homes vs outside homes | 39 | 6.27 ± 2.89** | -0.22 |
| SO$_{2}^{2-}$ (nmol/m$^3$) | Regional site vs outside homes | 32 | 0.18 ± 1.05 | 0.40** |
| Regional site vs inside homes | 42 | 3.79 ± 8.55*** | 0.24 |
| Inside homes vs outside homes | 41 | 31.3 ± 7.33*** | 0.51*** |
| Inside homes vs inside homes | 33 | 11.0 ± 5.33** | 0.46*** |
| Nitrous acid (ppb) | Regional site vs outside homes | 30 | 30.0 ± 4.77*** | -0.02 |
| Regional site vs inside homes | 44 | 18.1 ± 5.33*** | 0.32** |

Abbreviations: SD, standard deviation; PM$_{10}$, particle mass ≤10 µm in diameter; PM$_{2.5}$, particle mass ≤2.5 µm in diameter; coarse, particle mass between 10 and 2.5 µm in diameter (PM$_{10}$ - PM$_{2.5}$).

*Paired t-test.
*0.05<p<0.10; **0.01<p<0.05; ***p<0.01.
outside homes. The correlation between sulfate measured at the regional site and outside of homes was 0.58; the correlation between sulfate measured outside and inside of homes was 0.51.

Correlations between the various measured particle parameters by the site of measurement for the summer data are shown in Table 3. PM$_{10}$, PM$_{2.5}$, SO$_4^{2-}$, H$^+$, and NH$_4^+$ concentrations were significantly and strongly correlated with each other at the regional site and significantly, but somewhat less strongly, correlated outside and inside residences. Coarse mass was correlated with all aerosol parameters at the regional site, but was not correlated with these parameters outside or inside homes. A positive and significant ($p<0.05$) correlation was found between coarse mass and PM$_{2.5}$ for inside air-conditioned homes, but not for homes without air conditioning. The small sample size ($n=9$), however, makes it difficult to interpret the meaning of the observed poor coarse mass/PM$_{2.5}$ association for homes without air conditioning. At the regional site PM$_{2.5}$ accounted for approximately 74% of the PM$_{10}$ (PM$_{2.5}$/PM$_{10}$ mean ratio of 0.74 ± 0.10) and SO$_4^{2-}$ accounted for approximately 41% of the PM$_{2.5}$ (SO$_4^{2-}$/PM$_{2.5}$ mean ratio of 0.41 ± 0.10). Outside of homes PM$_{2.5}$ accounted for 85% of the mass (PM$_{2.5}$/PM$_{10}$ mean ratio of 0.85 ± 0.62); sulfate accounted for 43% of the PM$_{2.5}$ (SO$_4^{2-}$/PM$_{2.5}$ mean ratio of 0.43 ± 0.27). Inside homes using air conditioners, PM$_{2.5}$ composed 64% of the mass (PM$_{2.5}$/PM$_{10}$ mean ratio of 0.64 ± 0.18) and sulfate composed 29% of the PM$_{2.5}$ (SO$_4^{2-}$/PM$_{2.5}$ mean ratio of 0.29 ± 0.15). Inside homes without air conditioning, PM$_{2.5}$ made up 67% of the mass (PM$_{2.5}$/PM$_{10}$ mean ratio of 0.67 ± 0.17) and sulfate made up 33% of the PM$_{2.5}$ (SO$_4^{2-}$/PM$_{2.5}$ mean ratio of 0.33 ± 0.12). H$^+$ was strongly correlated with sulfate at all sites, suggesting the presence of acid sulfate even indoors, where ammonia levels were found well in excess of outdoor levels (Table 1). The strong correlation between NH$_4^+$ and SO$_4^{2-}$ and the levels of NH$_4^+$ at all sites suggests that the major form of the sulfate indoors and outdoors is ammonium sulfate or bisulfate. Higher ammonia concentrations both outside and inside homes, as compared to the regional site, probably were responsible for lower values of strong particle acid at these sites. Sulfate appears to make up a major portion of the PM$_{2.5}$ aerosol at all sites. Sulfur dioxide was not correlated to any of the pollutants outdoors, suggesting a regionally formed sulfate. The mean ion balance (ratio of equivalents of the cations, H$^+$ plus NH$_4^+$ to equivalents of anions, SO$_4^{2-}$) for SO$_4^{2-}$ aerosol is close to unity, indicating that the sulfate could be accounted for by H$^+$ and NH$_4^+$ at all locations (negligible values for particle nitrate indicate no appreciable particle ammonium nitrate).

For nitrous acid, regional site concentrations were no different from those measured outside of homes and indoor concentrations were higher than outdoors (Table 1). Indoor levels in homes without gas stoves were on average more than twice the concentrations outdoors. The highest average levels of HONO were found in homes with gas stoves (4.04 ± 2.82 ppb). In one home the HONO level reached 11.3 ppb. Ammonia levels were higher outside of homes (2.78 ± 2.45 ppb) than at the regional site (1.66 ± 0.51 ppb) and an order of magnitude higher indoors (32.1 ± 19.4 ppb for air-conditioned homes; 27.5 ± 18.4 ppb for non-air-conditioned homes) than outdoors (Table 1). Lower strong acidity levels measured inside of homes are consistent with the higher indoor levels of NH$_3$.

Winter concentrations. Wintertime concentrations of PM$_{10}$, PM$_{2.5}$, coarse mass (PM$_{10}$-PM$_{2.5}$), SO$_4^{2-}$, H$^+$, NH$_4^+$, NO$_3^-$, NH$_3$, SO$_3^-$, and HONO by location (inside and outside of residences) and by use of a kerosene heater in the home are summarized in Table 4. A comparison of PM$_{10}$, PM$_{2.5}$, and coarse mass by site and by indoor source use is shown in Figure 3. There was no significant difference in PM$_{10}$ levels between indoors and outdoors for homes without kerosene heaters. PM$_{10}$ levels were, however, higher in homes with kerosene heaters. PM$_{2.5}$ levels were lowest outside homes and higher inside homes.

![Figure 1. Comparison of 24-hr particle mass ≤2.5 μm in diameter (PM$_{2.5}$) measurements made at the regional sampling site in Vinton, Virginia, and outside of homes during summer months.](image1)

![Figure 2. Comparison of 24-hr particle mass ≤2.5 μm in diameter (PM$_{2.5}$) measurements made outside and inside homes in Virginia during summer months, with and without outliers.](image2)
Table 3. Pearson correlation coefficients between selected summer pollutants at regional site, outside, and inside homes

| Pollutant | Site                | Pearson Correlation Coefficient |
|-----------|---------------------|---------------------------------|
| PM<sub>10</sub> | PM<sub>2.5</sub> | C | SO<sub>4</sub><sup>-2</sup> | H<sup>+</sup> | NH<sub>4</sub><sup>+</sup> | NH<sub>3</sub> |
| Regional site (n = 50) | 0.98* | — | — | — | — | — |
| Outside homes (n = 45) | 0.92* | 0.79* | 0.54* | 0.07 | — | — |
| Inside AC homes (n = 49) | 0.93* | 0.40* | 0.54* | 0.07 | — | — |
| Inside non-AC homes (n = 9) | 0.77* | 0.33* | 0.54* | 0.07 | — | — |

Abbreviations: PM<sub>10</sub>, particle mass ≤10 μm in diameter; PM<sub>2.5</sub>, particle mass ≤2.5 μm in diameter; C, particle mass between 10 and 2.5 μm in diameter (PM<sub>2.5</sub>-PM<sub>10</sub>); AC, air conditioned.

The highest PM<sub>2.5</sub> levels were observed in homes using kerosene heaters. An average kerosene heater-use of 6.9 hr was recorded for the 24-hr air quality sampling period in heater use homes. Indoor PM<sub>2.5</sub> concentrations in homes without kerosene heaters (17.43 ± 23.63 μg/m<sup>3</sup>) were about 40% higher than outdoor levels (12.56 ± 7.27 μg/m<sup>3</sup>) and homes with kerosene heaters had indoor PM<sub>2.5</sub> concentrations almost 2.5 times the outdoor levels (29.97 ± 23.58 μg/m<sup>3</sup>). The difference between indoor PM<sub>2.5</sub> concentrations for homes with and without use of kerosene heaters is approximately 12.5 μg/m<sup>3</sup>; for sulfate the difference is approximately 5.9 μg/m<sup>3</sup> (61 nmol/m<sup>3</sup>), corresponding to approximately 81 μg/m<sup>3</sup> of ammonium sulfate. Thus, it appears that approximately 4 μg/m<sup>3</sup> of fine mass added by kerosene heaters indoor is nonsulfate material, presumably mostly organics. No differences by location and source category for the coarse mass indicate that the PM<sub>10</sub> concentration differences are mostly due to changes in concentration of PM<sub>2.5</sub>.

Sulfate concentrations outdoors (30.6 ± 14.9 nmol/m<sup>3</sup>) were higher than in homes without a kerosene heater (21.6 ± 3.37 nmol/m<sup>3</sup>) and lower than levels in homes with a kerosene heater (82.8 ± 76.6 nmol/m<sup>3</sup>) (Table 4). Strong acidity was low at all sites and did not vary by location. NH<sub>4</sub><sup>+</sup> concentrations followed the pattern of sulfate, with the highest concentrations observed in homes where kerosene heaters were used; the lowest concentrations were in homes without kerosene heaters. Ammonia levels followed a pattern similar to that observed during the summer, with indoor concentrations an order of magnitude or more higher than those outdoors. No significant differences in indoor ammonia concentrations were observed between homes with or without a kerosene heater. Measured indoor concentrations of ammonia for homes with kerosene heaters may be underestimated because of potential masking/collection inefficiencies of citric-acid-coated denuders. Indoor sulfur dioxide concentrations were higher in homes with kerosene heaters. Outdoor SO<sub>2</sub> levels were higher than in homes without kerosene heaters. Nitrous acid levels were considerably lower outdoors (0.81 ± 1.32 ppb) than indoors (3.50 ± 3.61 ppb). For homes without kerosene heaters, indoor concentrations were higher in homes with gas stoves (5.46 ± 3.75 ppb) than in those without (2.43 ± 0.14 ppb). Homes with kerosene heaters and no gas stove had an average HONO concentration of 6.74 ± 6.4 ppb (n = 65)—levels comparable to homes with gas stoves only (data not shown). As with the ammonia measurements, possible inefficiencies of the carbonate-coated denuders may have resulted in the underestimation of HONO levels in homes with kerosene heaters.

Correlation coefficients for selected pollutants by location and use of a kerosene heater are shown in Table 5. Unlike the summer data, most correlations are not significant (p>0.05) for both outside and inside homes. Correlations among indoor sulfur dioxide, sulfate, PM<sub>2.5</sub>, strong acid concentrations, and hours of kerosene heater use indicate the importance of the contribution of kerosene heater emissions. In homes with kerosene heater use, the strong correlation between NH<sub>4</sub><sup>+</sup> and SO<sub>2</sub> and the high indoor levels of NH<sub>4</sub><sup>+</sup> suggests that the major form of the sulfate associated with kerosene heater emissions is 

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emissions is ammonium sulfate or bisulfate. Strong acidity concentrations measured in 20 homes without kerosene heaters and using the sulfuric acid-treated (doped) Teflon filters in the denuder samplers averaged 273 ± 171 nmol/m³. Strong acidity concentrations measured using the doped filter denuder systems in 15 homes with kerosene heaters averaged 29 ± 7.5 nmol/m³. The decrease in strong acidity on the doped filters in the homes with the use of kerosene heaters suggests that neutralization of particle strong acidity may be occurring by ammonia not adequately collected by the citric-acid-coated denuders. This suggests that the acid aerosol levels measured in homes with kerosene heaters may be an underestimate of the true concentrations.

**Discussion**

Numerous studies have been conducted to characterize the physical and chemical nature, spatial and temporal concentration distribution, and sources of ambient aerosol in the northeastern quarter of the United States, particularly during the summer season when fine particle and sulfate concentrations are high and regional in nature. Among the most recent studies was the EPA-sponsored Metropolitan Acid Aerosol Characterization Study (7). Relatively few studies, however, have sought to characterize the physical and chemical relationship of outdoor to indoor particles and the nature of the relationship of summer regional ambient particle concentrations to those measured inside and outside of homes in a region.

This study investigated the relationship between indoor and outdoor particle concentrations in summer and winter for a sample of homes drawn primarily from southwest Virginia. Figures 4 and 5 contrast measured summer and winter PM₁₀, PM₂.₅, and SO₄²⁻ concentrations by location of measurement. Measured values of outdoor summer PM₁₀/PM₂.₅ and SO₄²⁻ concentrations are similar to those measured in a more densely populated portion of the same region (Washington, DC) during an intensive aerosol characterization conducted during 1994 (7). These measured values are also similar to PM₁₀/PM₂.₅ and coarse particle levels measured in 1992 and 1993 summer studies conducted within the Philadelphia metropolitan area (8).

In our summer study, homes were located as far as 175 km from the regional sampling site; yet no significant differences in mean concentrations of PM₁₀/PM₂.₅ or sulfate were observed between concentrations outside the homes and the regional site. However, for all of these parameters, although most had statistically significant correlations, these correlations were all relatively low (a lot of scatter); for coarse mass, correlations were actually slightly negative (r = -0.20). The PM₁₀/PM₂.₅ and SO₄²⁻/PM₂.₅ ratios were similar between the regional site and outside homes, and PM₂.₅ and SO₄²⁻ concentrations at the central site and outside homes were correlated. These findings suggest a strong regional nature to the summer aerosol and that during the summer in our study area an ambient regional sampling site is a reasonable predictor of fine particle concentrations measured outside homes. This finding is consistent with the identified regional nature of aerosol in both the Washington, DC (7), and Philadelphia (8) studies, although these studies used results

![Figure 3. Comparison of 24-hr indoor and outdoor particle mass ≤10 μm in diameter (PM₁₀), ≤2.5 μm in diameter (PM₂.₅), and particle mass between 10 and 2.5 μm in diameter (PM₁₀-PM₂.₅) (coarse) mass measurements made at homes with and without kerosene heaters during winter sampling periods in homes in Connecticut and Virginia, with and without outliers.](image-url)
from sampling stations whose location was intended to represent geographical areas not immediately outside homes. It is also consistent with the findings of the particle total exposure (PTTEAM) study (9), the Nashville, Tennessee, study (10) and the Uniontown, Pennsylvania, study (11). The PTEAM study was conducted in Riverside, California, in the fall of 1990 and the Nashville study was conducted in the summer of 1995. Concentrations in the PTEAM study were generally 2–3 times those observed in our study. In the PTEAM study, PM_{10} and PM_{2.5} levels measured at a central monitoring site, although significantly different than those measured outside of homes, were good predictors of levels outside of 178 homes in the region. In the PTEAM study, however, homes monitored were within 5 m of the central site.

The Uniontown study (11) investigated the relation among indoor, outdoor, personal, and centrally measured acid aerosol concentrations monitored for 27 days during the summer of 1990 for 24 children. In the Uniontown study, concentrations of SO_{2}^{2−}, NH_{4}^{+}, and H^{+} at the central monitoring site were found to be strong predictors of, and not significantly different from, concentrations of these same species measured outside homes, suggesting a strong regional nature to the sulfate aerosol consistent with the findings of this study. Strong acidity levels indoors in our study, however, were markedly lower than those measured outdoors or at the regional site, indicating that during the summer particle acidity levels indoors are low. Higher indoor levels of ammonia may result in the neutralization of acid aerosol. Correlations were found, however, between H^{+} measured at the regional site and outside of homes and between outside and inside of homes.

Winter concentrations of PM_{2.5} exhibited a pattern different from that of the summer. Concentrations outside of homes during the winter were approximately 57% of the concentrations measured during the summer. Indoor levels during the winter in homes without a kerosene heater were approximately 39% higher than outdoor concentrations and similar to indoor summer levels. Sulfate levels in these homes in the winter were approximately 70% of the outdoor level, suggesting a substantial contribution of outdoor PM_{2.5} to indoor levels (roughly 9 μg/m³ on average). Indoor winter sources of PM_{2.5} in homes without kerosene heaters contribute about as much as outdoors. Correlations between PM_{2.5}, SO_{2}^{2−}, NH_{4}^{+}, and H^{+} measured outside and inside of homes without kerosene heaters were much poorer than those measured during the summer. Outdoor winter PM_{10}, PM_{2.5}, and indoor/outdoor PM_{2.5} ratios for homes without kerosene heaters found in this study are similar to those found in the winter New York State Energy Research Development Authority (12–14) study for nonsmoking, nonkerosene-heater homes in their sample of more than 400 homes drawn from Onondaga and Suffolk counties in New York State.

Coarse mass concentrations measured during the summer months at the regional site were not correlated with coarse mass concentrations measured inside or outside of homes and the concentration differences for both were statistically significant. Concentrations inside homes were higher than concentrations outside and those outside of homes tended to be higher, though not significantly higher, than concentrations measured at the regional site. This suggests that the larger particle size (2.5–10 μm) aerosol is not as regionally well distributed as the fine aerosol. Regional ambient coarse aerosol mass measurements may not adequately represent levels outside or inside of homes. The results which indicate that indoor coarse levels during the summer are on average 33% higher than levels outdoors reflect both the expected relatively low penetration of outdoor coarse particle to indoors as well as the presence of significant indoor sources. Coarse particle concentrations were higher both outdoors and indoors during the winter as compared to the summer. Indoor coarse mass concentrations during the winter were not significantly different from outdoors. Higher outdoor levels during the winter may be related to higher wind speeds and street salting. Additional factors contributing to higher indoor winter concentrations are related to greater amounts of time spent indoors by residents, possibly greater occupant activity, and indoor winter sources (i.e., wood-burning fireplaces or stoves). These higher winter indoor concentrations could also be explained by typically lower air exchange rates in the winter as compared to rates in the summer. Given the same amount of indoor emissions, decreased air exchange results in higher indoor concentrations. The interaction of factors contributing to indoor concentrations of pollutants, under equilibrium conditions for a single compartment with complete mixing and no air cleaning, can be expressed as:

\[ C_i = \frac{PAC_i(A + K) + (S/V)(A + K)}{A + K} \]  \hspace{1cm} (1)

where \( C_i \) = the indoor concentration of particles, \( P \) = penetration efficiency (dimensionless), \( C_o \) = outdoor concentration, \( A \) = air exchange rate (air changes per hour), \( K \) = removal rate of contaminants by indoor
surfaces or chemical transformations (equivalent air changes per hour), \( S \) = indoor source strength (micrograms/hour), and \( V \) = volume of the indoor space (cubic meter).

Differences between summer indoor and outdoor concentrations of PM\(_{2.5}\) were not significant and the indoor and outdoor values were well correlated. Indoor SO\(_4^{2-}\) concentrations were significantly different from those measured outside of homes, but were significantly correlated. The corresponding indoor/outdoor ratios for PM\(_{2.5}\) and SO\(_4^{2-}\) for homes were 1.03 ± 0.74 and 0.74 ± 0.53, respectively, reflecting the strong dependence of indoor concentrations on outdoor levels. Because there are no known indoor summer sources of sulfate and because sulfate particles are generally <1 μm, sulfate can serve as a marker for the contribution of outdoor PM\(_{2.5}\) (9). Thus the sulfate ratio suggests that, on average, approximately 75% of the indoor fine aerosol during the summer is contributed by outside aerosol and 25% may be generated by indoor sources or activities. In this sample of homes 85% reported using an air conditioner and 15% reported no air-conditioner use. Doors and windows in air-conditioned homes are closed, resulting in lower air exchange rates and longer particle residence times, with greater potential for particles to deposit on interior surfaces. Inline filters, typically found in air conditioners, and deposition to the interior of air-conditioning systems also contribute to particle removal. The associations between indoor and outdoor particles would presumably be stronger for homes without air conditioning than for those with air conditioning, as it is likely that homes without air conditioning would be more open with higher air exchange rates. Our small sample size of homes without air conditioning does not allow for a statistical distinction to be made between indoor/outdoor ratios for air-conditioned homes versus homes without air conditioning. A comparison of the indoor/outdoor ratio for SO\(_4^{2-}\) for air-conditioned homes (0.71) versus homes without air conditioning (0.86), however, indicated a trend toward outdoor aerosol contributing a higher portion of the fine mass in homes without air conditioning. Other studies have investigated the indoor/outdoor relationship for particle mass (7,9,11), but these studies have typically included smokers, have been conducted over only summer periods, or have not monitored a comparable set of variables (i.e., SO\(_4^{2-}\)).

Indoor levels of ammonia and nitric acid (Tables 1 and 4) were significantly higher than outdoor levels measured either at the regional site or outside homes. Indoor summer levels of ammonia measured in this study were approximately 40% higher than those observed in the Uniontown (10) and Nashville (11) studies. Winter levels were approximately 40% higher than summer and were probably related to occupants and their indoor activities. Higher indoor levels in the winter (approximately 40 ppb vs 30 ppb in the summer) in homes with and without the use of kerosene heaters may be explained by the likelihood that occupants spend more time indoors during the winter, and also by lower air exchange rates during the winter. These results are the first reported indoor winter ammonia levels. High indoor ammonia levels have been proposed to be responsible for lower indoor acid aerosol levels because of ammonia's ability to neutralize strong acidity (10).

This study represents the most extensive database to date on indoor levels of nitrous acid. Nitrous acid levels during winter and summer were higher indoors than outdoors. Indoor levels were higher in homes with gas stoves, especially during the winter season. Indoor levels in homes with gas stoves and kerosene heaters were several times higher than homes without gas stoves. Winter indoor levels of HONO in homes without NO\(_3^-\) sources are three times the levels of those homes in the summer. While the air exchange rates are lower in the winter, the outdoor NO\(_3^-\) concentrations are higher. With these conditions, in the winter there is more time for the accumulation of nitrous acid formed through heterogeneous reactions indoors. Twenty-four-hour average HONO concentrations as high as 36 ppb were recorded. Nitrous acid concentrations indoors represent an important gas phase acid exposure. The heterogeneous reaction of nitrogen dioxide originating from outdoors with water vapor on indoor surfaces is thought to be the mechanism responsible for indoor HONO levels in homes without nitrogen dioxide sources (15). HONO levels in homes with nitrogen dioxide sources (i.e., gas stoves) may result from direct emissions as well as the heterogeneous reaction of gas stove-generated nitrogen dioxide on internal surfaces. This study found that indoor exposures to HONO were appreciable in both winter and summer, particularly in homes with unvented combustion sources.

The strong correlations observed between NH\(_4^+\) and SO\(_4^{2-}\) and the levels of NH\(_4^+\) observed at all sampling locations and seasons suggests that a major form of sulfate indoors and outdoors during both winter and summer is ammonium sulfate or bisulfate. Ammonia concentrations both outside and inside of homes probably were responsible for the lower values of particle strong acidity measured at these sites. Sulfate appears to make up a major portion of the PM\(_{2.5}\) aerosol indoors and outdoors during both seasons and at the regional site during the summer. If ammonium sulfate is assumed to be the form of the sulfate for winter and summer outdoor samples, then the nonammonium sulfate component of the PM\(_{2.5}\) can be estimated for each season [PM\(_{2.5}\) - (NH\(_4^+)\)]SO\(_4^{2-}\). Using this approach and the average outdoor concentrations in Tables 1 and 4, there is no statistically significant difference between the outdoor summer and winter nonammonium sulfate portion of the outdoor aerosol (8.32 vs 8.44 μg/m\(^3\)).

There was concern that the complex nature and amount of particle and gas phase contaminant emissions from kerosene heaters might introduce interferences in the HDS system, resulting in inefficient collection of gases, and thus affecting measurements of both particle and gas phase acids. The doped filter sampling protocol used in this study suggests that such interferences were encountered, and may have resulted in an underestimation of both H\(^+\) and HONO in homes with kerosene heaters.

Chamber and field studies have identified unvented kerosene heaters as an important source of both gas and particle phase air contaminants indoors (16,17). One chamber study measured emission rates of PM\(_{2.5}\) and SO\(_4^{2-}\) and determined the chemical composition of the sulfate emissions for a variety of kerosene heaters operated under a range of burner conditions (17). That chamber study estimated that under typical use conditions, kerosene heaters could add approximately 20 μg/m\(^3\) or more to residential concentrations of PM\(_{2.5}\) and 7-15 μg/m\(^3\) of SO\(_4^{2-}\). In the field study reported here, kerosene heaters added approximately 12.5 μg/m\(^3\) of PM\(_{2.5}\) and 6 μg/m\(^3\) of SO\(_4^{2-}\) to residences during an average use period of 6.9 hr over the 24-hr sampling period. This compares to 15.8 μg/m\(^3\) observed in the New York State Energy Research and Development Authority study for kerosene heaters in Suffolk County, New York (12). A simple regression model of hours of heater use against fine particle mass and sulfate indicates that PM\(_{2.5}\) concentrations during heater use, on average, added approximately 40 μg/m\(^3\) of PM\(_{2.5}\) and 15 μg/m\(^3\) of SO\(_4^{2-}\) to background residential levels of 18 and 2 μg/m\(^3\), respectively.

The present study did not measure the elevated residential H\(^+\) concentrations associated with kerosene heater use that were predicted by the chamber studies. A comparison
of indoor winter samples using acid-doped Teflon filters and nondoped Teflon filters in kerosene-heater and nonkerosene-heater homes suggested that substantial amounts of collected strong acidity in homes with kerosene heater use may be neutralized on the Teflon filter in the denuder system used to collect particle acid. The mechanism for this possible neutralization is suspected to be denuder breakthrough of ammonia. In the present study, kerosene heater use resulted in elevated indoor concentrations of PM$_{2.5}$ and SO$_4^{2-}$, with the potential for a substantial portion of the sulfate to be in the form of acid particles.

Occupants in homes using kerosene heaters are likely to experience peak exposures (several hours at a time) to PM$_{2.5}$ and SO$_4^{2-}$ and possibly H$^+$ in excess of levels typically experienced outdoors during the summer months. Frequent users of kerosene heaters are likely to experience longer term exposures (weeks or months) to PM$_{2.5}$ and SO$_4^{2-}$ and possibly H$^+$ during the winter months that are in excess of summer exposures and substantially in excess of winter levels in nonkerosene-heater homes. Only tobacco combustion indoors is likely to result in higher indoor fine particle exposures.

**Conclusions**

Our study results indicate that a regional air monitoring site may provide a reasonable estimate of concentrations of PM$_{2.5}$ and SO$_4^{2-}$ during summer months outside and inside of homes (in the absence of tobacco combustion) within a region, even when a substantial number of the homes use air conditioning. Kerosene heater use during the winter months in homes of nonsmokers results in a substantial increase in indoor concentrations of PM$_{2.5}$, SO$_4^{2-}$, and possibly H$^+$. During the summer and winter periods, indoor concentrations of ammonia are an order of magnitude higher indoors than outdoors and appear to result in lower indoor acid particle concentrations. Nitrous acid levels are higher indoors than outdoors during both winter and summer and are substantially higher in homes with unvented combustion sources.

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