

# Indoor, Outdoor, and Regional Summer and Winter Concentrations of PM<sub>10</sub>, PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>3</sub>, and Nitrous Acid in Homes with and without Kerosene Space Heaters

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Twenty-four-hour samples of PM<sub>10</sub> (mass of particles with aerodynamic diameter ≤ 10 μm), PM<sub>2.5</sub> (mass of particles with aerodynamic diameter ≤ 2.5 μm), particle strong acidity (H<sup>+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ammonia (NH<sub>3</sub>), 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<sub>2.5</sub> and SO<sub>4</sub><sup>2-</sup> 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<sub>2.5</sub> and SO<sub>4</sub><sup>2-</sup> 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<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, and possibly H<sup>+</sup>, as compared to homes without kerosene heaters. During their use, we estimated that kerosene heaters added, on average, approximately 40 μg/m<sup>3</sup> of PM<sub>2.5</sub> and 15 μg/m<sup>3</sup> of SO<sub>4</sub><sup>2-</sup> to background residential levels of 18 and 2 μg/m<sup>3</sup>, 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<sub>10</sub>), particles less than 2.5 μm in diameter (PM<sub>2.5</sub>), 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<sub>10</sub>; PM<sub>2.5</sub>; particle sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), and strong acidity (H<sup>+</sup>); and gaseous SO<sub>2</sub>, nitrous acid (HONO), and NH<sub>3</sub>. 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

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We thank the respondents in Connecticut and southwest Virginia who permitted us to conduct air sampling in their homes. We also thank the following hospitals, from which our population was selected: in Connecticut—Yale–New Haven, Danbury, Veterans, Middlesex, Manchester, Rockville, and Backus; in Virginia—University of Virginia, Virginia Baptist, Roanoke Community, Martha Jefferson, and Danville.

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presence of a gas cooking stove. Kerosene heaters were used in 74 residences during the winter period, whereas 61 reported use of a gas cooking stove. The epidemiologic study design excluded all homes where tobacco combustion occurred, so tobacco smoke was not a source in any of the homes actively sampled.

Central site ambient sampling was conducted in Vinton, Virginia. This site, located approximately 6 km east of Roanoke, Virginia, was selected to represent regional air quality. Twenty-four-hour particle samples were collected during the period from 15 May through 15 September for 1995 and 1996 for comparison with daily summer respiratory symptoms in the infants and their mothers (3) and for comparison with twice-daily peak flow measurements recorded by the mothers over a 2-week period during the summer (4). In this paper 50 days of data from the Vinton site are used, corresponding to days for which indoor or outdoor particle sampling was conducted at residences in the region. Distances from the Vinton site to residences monitored varied from 1 to >175 km, with an average distance of 96 km.

**Measurements.** Samples for  $PM_{10}$  and  $PM_{2.5}$  were collected using inertial impactor samplers. These impactors collect particles with aerodynamic diameters  $\leq 10$  and  $\leq 2.5$   $\mu m$  at flows of 4 and 10 liters per minute, respectively. The filters used for particle sampling were equilibrated for 48 hr at a temperature of  $23 \pm 3^\circ C$  and relative humidity of  $40 \pm 5\%$  before determining pre- and postsampling weights. Particle sulfate, nitrate, strong acidity, and ammonium, and gaseous species nitrous acid, nitric acid, ammonia, and sulfur dioxide were measured using the Harvard glass honeycomb denuder/filter pack sampler (HDS; Ogawa & Co., USA, Pompano Beach, FL). The HDS sampler (5,6) consists of an impactor to remove coarse particles ( $>2.1$   $\mu m$  in diameter) from the air samples, two glass honeycomb denuders, and a three-stage filter pack to collect fine particles. The denuder system draws air at a sampling rate of 10 l/min. Air travels first through the inlet section of the sampler, where an acceleration jet directs the air stream onto a sintered stainless steel impactor plate coated with mineral oil, which removes particles  $>2.1$   $\mu m$ . The air then passes through a transition section that provides a uniform flow through the honeycomb denuders. The first honeycomb denuder is coated with sodium carbonate/glycerol to collect gaseous nitric acid, nitrous acid, and sulfur dioxide. The second honeycomb denuder is coated with citric acid/glycerol to collect ammonia.

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 the 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, nitrous 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  $\mu g/m^3$ , 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  $\mu g/m^3$ , respectively. Coarse particles ( $2.5 < d_p < 10$   $\mu m$ ) 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  $NH_3$  are 6.0  $\eta mol/m^3$ , 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 semivolatiles 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 nitrous 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 all 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 summertime 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.  $\text{SO}_4^{2-}$  and  $\text{H}^+$  were lower indoors, whereas  $\text{NH}_3$  and  $\text{HONO}$  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.  $\text{PM}_{10}$  concentrations measured at the regional site were not significantly different from those measured either inside or outside of homes, nor were  $\text{PM}_{10}$  concentrations measured outside homes different from those measured inside homes. A weak statistically insignificant correlation was seen between outdoor and indoor  $\text{PM}_{10}$  concentrations with even weaker correlations for home versus regional site measurements. Although no statistically significant differences were observed for  $\text{PM}_{2.5}$  concentrations for any of the three comparisons, significant moderate correlations were observed between  $\text{PM}_{2.5}$  measured at the regional site and outside homes and between  $\text{PM}_{2.5}$  concentrations measured inside and outside of homes. Figures 1 and 2 show the regression equation and scatter plot for the correlated  $\text{PM}_{2.5}$  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  $\text{PM}_{2.5}$  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  $\text{SO}_4^{2-}$  and  $\text{H}^+$  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  $\text{SO}_4^{2-}$  and  $\text{H}^+$  were found for regional site versus outside homes and for inside versus

**Table 1.** Summary of summer pollutant concentrations

Pollutant	Site	<i>n</i>	Mean $\pm$ SD	Minimum	Maximum
$\text{PM}_{10}$ ( $\mu\text{g}/\text{m}^3$ )	Regional site	47	26.0 $\pm$ 11.5	10.8	51.9
	Outside all homes	43	28.0 $\pm$ 17.7	5.8	112.6
	Inside AC homes	49	28.9 $\pm$ 18.7	4.8	97.6
	Inside non-AC homes	8	33.3 $\pm$ 14.2	17.7	59.7
$\text{PM}_{2.5}$ ( $\mu\text{g}/\text{m}^3$ )	Regional site	50	20.23 $\pm$ 9.9	5.8	42.4
	Outside all homes	43	21.8 $\pm$ 14.8	3.8	84.2
	Inside AC homes	49	18.7 $\pm$ 13.2	2.5	65.7
	Inside non-AC homes	9	21.1 $\pm$ 7.5	9.6	35.3
Coarse <sup>a</sup> ( $\mu\text{g}/\text{m}^3$ )	Regional site	47	6.3 $\pm$ 2.7	1.5	14.3
	Outside all homes	42	7.7 $\pm$ 6.2	2.4	34.1
	Inside AC homes	48	10.4 $\pm$ 8.5	0	35.1
	Inside non-AC homes	8	11.4 $\pm$ 9.7	0.2	32.6
$\text{SO}_4^{2-}$ (nmol/ $\text{m}^3$ )	Regional site	45	88.4 $\pm$ 51.6	14.1	209.0
	Outside all homes	42	83.7 $\pm$ 53.7	7.9	230.6
	Inside all AC homes	47	47.8 $\pm$ 36.3	2.1	137.7
	Inside non-AC homes	9	63.0 $\pm$ 37.3	20.9	125.6
$\text{H}^+$ (nmol/ $\text{m}^3$ )	Regional site	47	41.0 $\pm$ 28.5	0	136.2
	Outside all homes	45	33.0 $\pm$ 36.9	0	208.6
	Inside AC homes	49	12.4 $\pm$ 15.3	0	84.5
	Inside non-AC homes	9	16.7 $\pm$ 9.4	2.9	34.6
$\text{NH}_4^+$ (nmol/ $\text{m}^3$ )	Regional site	43	124.6 $\pm$ 59.0	30.6	293.0
	Outside all homes	45	129.4 $\pm$ 87.8	0	338.9
	Inside AC homes	49	78.3 $\pm$ 77.2	0	450.6
	Inside non-AC homes	9	96.7 $\pm$ 68.9	6.7	214.4
$\text{NO}_3^-$ (nmol/ $\text{m}^3$ )	Regional site	42	10.2 $\pm$ 5.0	2.6	20.7
	Outside all homes	42	8.0 $\pm$ 5.4	0	22.9
	Inside AC homes	49	5.5 $\pm$ 8.9	0	56.1
	Inside non-AC homes	9	6.8 $\pm$ 4.6	0.5	12.2
$\text{NH}_3$ (ppb)	Regional site	29	1.7 $\pm$ 0.5	0.9	2.7
	Outside all homes	45	2.8 $\pm$ 2.5	0	13.2
	Inside AC homes	49	32.1 $\pm$ 19.4	1.5	93.0
	Inside non-AC homes	9	27.5 $\pm$ 18.4	2.0	49.5
Nitrous acid (ppb)	Regional site	29	0.3 $\pm$ 0.4	0	2.1
	Outside all homes	45	0.3 $\pm$ 0.4	0	2.1
	Inside AC homes	49	1.6 $\pm$ 2.1	0	11.3
	Inside non-AC homes	9	3.5 $\pm$ 2.6	0.4	7.5
	Inside homes without gas stoves	39	0.8 $\pm$ 0.8	0	2.9
	Inside homes with gas stoves	19	4.0 $\pm$ 2.8	0	11.3
$\text{SO}_2$ (ppb)	Regional site	50	1.2 $\pm$ 0.6	0.1	2.9
	Outside all homes	45	1.3 $\pm$ 1.7	0.02	9.4
	Inside AC homes	49	0.3 $\pm$ 0.5	0	3.1
	Inside non-AC homes	7	0.9 $\pm$ 1.0	0.1	3.0

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

<sup>a</sup>This is not a paired comparison, thus there is not always a  $\text{PM}_{10}$  for every  $\text{PM}_{2.5}$  and vice versa.

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

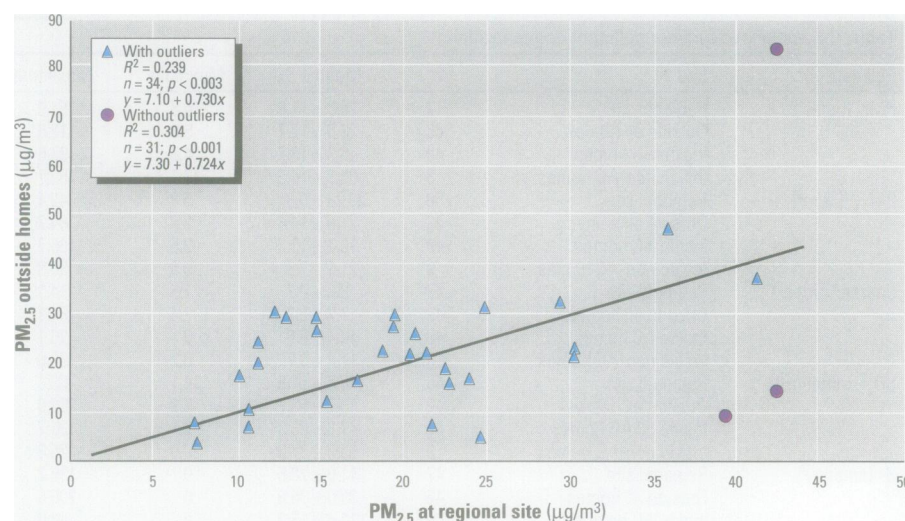
Pollutant	Comparison	<i>n</i>	Concentration differences <sup>a</sup> (mean $\pm$ SD)	Correlation coefficient
$\text{PM}_{10}$ ( $\mu\text{g}/\text{m}^3$ )	Regional site vs outside homes	31	2.29 $\pm$ 3.34	0.21
	Regional site vs inside homes	44	4.84 $\pm$ 3.22	0.11
	Inside homes vs outside homes	40	3.28 $\pm$ 2.66	0.29
$\text{PM}_{2.5}$ ( $\mu\text{g}/\text{m}^3$ )	Regional site vs outside homes	34	1.40 $\pm$ 2.31	0.49***
	Regional site vs inside homes	47	0.89 $\pm$ 2.20	0.08
	Inside homes vs outside homes	41	2.88 $\pm$ 2.08	0.53***
Coarse ( $\mu\text{g}/\text{m}^3$ )	Regional site vs outside homes	30	2.63 $\pm$ 2.86	-0.20
	Regional site vs inside homes	43	4.56 $\pm$ 1.40***	0.24
	Inside homes vs outside homes	39	6.27 $\pm$ 2.89*	-0.22
$\text{SO}_4^{2-}$ (nmol/ $\text{m}^3$ )	Regional site vs outside homes	32	01.8 $\pm$ 1.05	0.40**
	Regional site vs inside homes	42	37.9 $\pm$ 8.5***	0.24
	Inside homes vs outside homes	42	31.3 $\pm$ 7.3***	0.51***
$\text{H}^+$ (nmol/ $\text{m}^3$ )	Regional site vs outside homes	33	11.0 $\pm$ 5.3	0.46***
	Regional site vs inside homes	44	30.0 $\pm$ 4.7***	-0.02
	Inside homes vs outside homes	45	18.1 $\pm$ 5.3***	0.32**

Abbreviations: SD, standard deviation;  $\text{PM}_{10}$ , particle mass  $\leq 10 \mu\text{m}$  in diameter;  $\text{PM}_{2.5}$ , particle mass  $\leq 2.5 \mu\text{m}$  in diameter; coarse, particle mass between 10 and  $2.5 \mu\text{m}$  in diameter ( $\text{PM}_{10}-\text{PM}_{2.5}$ ).

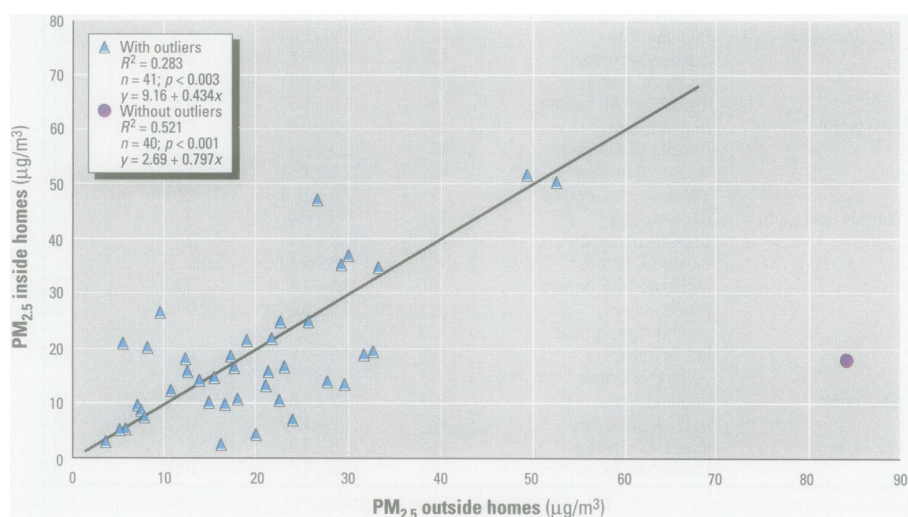
<sup>a</sup>Paired *t*-test.

\*0.05  $< p \leq 0.10$ ; \*\*0.01  $\leq p \leq 0.05$ ; \*\*\* $p < 0.01$ .





**Figure 1.** Comparison of 24-hr particle mass  $\leq 2.5\ \mu\text{m}$  in diameter ( $\text{PM}_{2.5}$ ) measurements made at the regional sampling site in Vinton, Virginia, and outside of homes during summer months.



**Figure 2.** Comparison of 24-hr particle mass  $\leq 2.5\ \mu\text{m}$  in diameter ( $\text{PM}_{2.5}$ ) measurements made outside and inside homes in Virginia during summer months, with and without outliers.

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.  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ , and  $\text{NH}_4^+$  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  $\text{PM}_{2.5}$  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/ $\text{PM}_{2.5}$  association for homes without air conditioning. At the regional site  $\text{PM}_{2.5}$  accounted for approximately 74% of the  $\text{PM}_{10}$  ( $\text{PM}_{2.5}/\text{PM}_{10}$  mean ratio of  $0.74 \pm 0.10$ ) and  $\text{SO}_4^{2-}$  accounted for approximately 41% of the  $\text{PM}_{2.5}$  ( $\text{SO}_4^{2-}/\text{PM}_{2.5}$  mean ratio of  $0.41 \pm 0.10$ ). Outside of homes  $\text{PM}_{2.5}$  accounted for 85% of the mass ( $\text{PM}_{2.5}/\text{PM}_{10}$  mean ratio of  $0.85 \pm 0.62$ ); sulfate accounted for 43% of the  $\text{PM}_{2.5}$  ( $\text{SO}_4^{2-}/\text{PM}_{2.5}$  mean ratio of  $0.43 \pm 0.27$ ). Inside homes using air conditioners,  $\text{PM}_{2.5}$  composed 64% of the mass ( $\text{PM}_{2.5}/\text{PM}_{10}$  mean ratio of  $0.64 \pm 0.18$ ) and sulfate composed 29% of the  $\text{PM}_{2.5}$  ( $\text{SO}_4^{2-}/\text{PM}_{2.5}$  mean ratio of  $0.29 \pm 0.15$ ). Inside homes

without air conditioning,  $\text{PM}_{2.5}$  made up 67% of the mass ( $\text{PM}_{2.5}/\text{PM}_{10}$  mean ratio of  $0.67 \pm 0.17$ ) and sulfate made up 33% of the  $\text{PM}_{2.5}$  ( $\text{SO}_4^{2-}/\text{PM}_{2.5}$  mean ratio of  $0.33 \pm 0.12$ ).  $\text{H}^+$  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  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  and the levels of  $\text{NH}_4^+$  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  $\text{PM}_{2.5}$  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,  $\text{H}^+$  plus  $\text{NH}_4^+$  to equivalents of anions,  $\text{SO}_4^{2-}$ ) for  $\text{SO}_4^{2-}$  aerosol is close to unity, indicating that the sulfate could be accounted for by  $\text{H}^+$  and  $\text{NH}_4^+$  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 ( $4.04 \pm 2.82$  ppb). In one home the HONO level reached 11.3 ppb. Ammonia levels were higher outside of homes ( $2.78 \pm 2.45$  ppb) than at the regional site ( $1.66 \pm 0.51$  ppb) and an order of magnitude higher indoors ( $32.1 \pm 19.4$  ppb for air-conditioned homes;  $27.5 \pm 18.4$  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  $\text{NH}_3$ .

**Winter concentrations.** Wintertime concentrations of  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , coarse mass ( $\text{PM}_{10}-\text{PM}_{2.5}$ ),  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ , 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  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , and coarse mass by site and by indoor source use is shown in Figure 3. There was no significant difference in  $\text{PM}_{10}$  levels between indoors and outdoors for homes without kerosene heaters.  $\text{PM}_{10}$  levels were, however, higher in homes with kerosene heaters.  $\text{PM}_{2.5}$  levels were lowest outside homes and higher inside homes.

**Table 3.** Pearson correlation coefficients between selected summer pollutants at regional site, outside, and inside homes

	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>
Regional site (n = 50)						
PM <sub>2.5</sub>	0.98*	—	—	—	—	—
C	0.63*	0.46*	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	0.86*	0.83*	0.59*	—	—	—
H <sup>+</sup>	0.89*	0.86*	0.56*	0.88*	—	—
NH <sub>4</sub> <sup>+</sup>	0.77*	0.79*	0.40*	0.76*	0.61*	—
NH <sub>3</sub>	0.13	0.03	0.38*	0.06	0.05	0.10
Outside homes (n = 45)						
PM <sub>2.5</sub>	0.46*	—	—	—	—	—
C	0.35*	-0.67*	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	0.78*	0.51*	0.03	—	—	—
H <sup>+</sup>	0.44*	0.52*	-0.19	0.86*	—	—
NH <sub>4</sub> <sup>+</sup>	0.64*	0.54*	-0.04	0.92*	0.66*	—
NH <sub>3</sub>	-0.09	0.23	-0.25	0.19	-0.07	0.11
Inside AC homes (n = 49)						
PM <sub>2.5</sub>	0.92*	—	—	—	—	—
C	0.79*	0.47*	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	0.40*	0.54*	0.07	—	—	—
H <sup>+</sup>	0.22	0.35*	-0.06	0.71	—	—
NH <sub>4</sub> <sup>+</sup>	0.40*	0.60*	-0.04	0.96*	0.70*	—
NH <sub>3</sub>	0.41*	0.24	0.53*	-0.08	-0.29*	-0.18
Inside non-AC homes (n = 9)						
PM <sub>2.5</sub>	0.77*	—	—	—	—	—
C	0.86*	0.33	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	0.60	0.76*	0.02	—	—	—
H <sup>+</sup>	-0.05	0.09	-0.22	0.70*	—	—
NH <sub>4</sub> <sup>+</sup>	0.57	0.72*	0.01	0.99*	0.68*	—
NH <sub>3</sub>	0.37	0.09	-0.40	0.29	-0.65	-0.24

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>10</sub>-PM<sub>2.5</sub>); AC, air conditioned.

\*p < 0.05.

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 8.1 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 indicates 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

**Table 4.** Summary of winter pollutant concentrations

Pollutant	Site	n	Mean ± SD	Min	Max
PM <sub>10</sub> (μg/m <sup>3</sup> )	Outside all homes	53	23.93 ± 22.21	4.73	112.04
	Inside kerosene-heater homes	42	44.36 ± 30.37	6.45	141.41
	Inside nonkerosene-heater homes	84	25.71 ± 21.12	2.82	181.75
PM <sub>2.5</sub> (μg/m <sup>3</sup> )	Outside all homes	48	12.56 ± 7.27	3.21	43.47
	Inside kerosene-heater homes	71	29.97 ± 23.58	2.13	114.58
	Inside nonkerosene-heater homes	145	17.43 ± 23.63	1.72	207.54
Coarse <sup>a</sup> (μg/m <sup>3</sup> )	Outside all homes	46	12.12 ± 22.70	0	105.18
	Inside kerosene-heater homes	41	11.20 ± 8.23	1.86	37.45
	Inside nonkerosene-heater homes	82	12.39 ± 8.85	1.13	48.46
SO <sub>4</sub> <sup>2-</sup> (nmol/m <sup>3</sup> )	Outside all homes	52	30.6 ± 14.9	0	66.2
	Inside kerosene-heater homes	74	82.7 ± 76.2	6.1	379.6
	Inside nonkerosene-heater homes	149	21.6 ± 3.37	0	146.5
H <sup>+</sup> (nmol/m <sup>3</sup> )	Outside all homes	52	6.5 ± 9.8	0	50.3
	Inside kerosene-heater homes	74	5.7 ± 6.9	0	35.8
	Inside nonkerosene-heater homes	149	3.11 ± 5.00	0	21.9
NH <sub>4</sub> <sup>+</sup> (nmol/m <sup>3</sup> )	Outside all homes	52	64.4 ± 38.9	2.2	187.8
	Inside kerosene-heater homes	74	126.1 ± 155.0	0.6	796.7
	Inside nonkerosene-heater homes	147	9.4 ± 21.7	0	125.0
NO <sub>3</sub> <sup>-</sup> (nmol/m <sup>3</sup> )	Outside all homes	52	20.5 ± 22.0	1.8	101.1
	Inside kerosene-heater homes	74	6.5 ± 9.4	0.3	67.2
	Inside nonkerosene-heater homes	149	6.3 ± 9.1	0.3	79.2
NH <sub>3</sub> (ppb)	Outside all homes	52	1.55 ± 4.63	0	33.38
	Inside kerosene-heater homes	74	44.35 ± 45.35	4.06	231.86
	Inside nonkerosene-heater homes	148	37.96 ± 36.02	0.13	234.24
Nitrous acid (ppb)	Outside all homes	53	0.81 ± 1.32	0	9.25
	Inside kerosene-heater homes	74	6.80 ± 6.06	0.15	35.89
	Inside nonkerosene-heater homes	148	3.49 ± 3.61	0.14	20.13
	Inside homes, no kerosene heaters				
	No gas stove	96	2.43 ± 3.05	0.14	20.08
SO <sub>2</sub> (ppb)	Gas stove	52	5.45 ± 3.75	0.37	20.14
	Outside all homes	53	4.00 ± 2.15	0.70	9.59
	Inside kerosene-heater homes	74	16.11 ± 21.34	0.06	107.36
	Inside nonkerosene homes	148	0.83 ± 1.68	0	8.81

Abbreviations: SD, standard deviation; Min, minimum; Max, maximum; PM<sub>10</sub>, particle mass ≤ 10 μm in diameter; PM<sub>2.5</sub>, particle mass ≤ 2.5 μm in diameter; coarse, particle mass between 10 and 2.5 μm in diameter (PM<sub>10</sub>-PM<sub>2.5</sub>).

<sup>a</sup>This is not a paired comparison, thus there is not always a PM<sub>10</sub> for every PM<sub>2.5</sub> and vice versa.

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>4</sub><sup>2-</sup> 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 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  $273 \pm 171$  nmol/m<sup>3</sup>. Strong acidity concentrations measured using the doped filter denuder systems in 15 homes with

kerosene heaters averaged  $29 \pm 7.5$  nmol/m<sup>3</sup>. 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

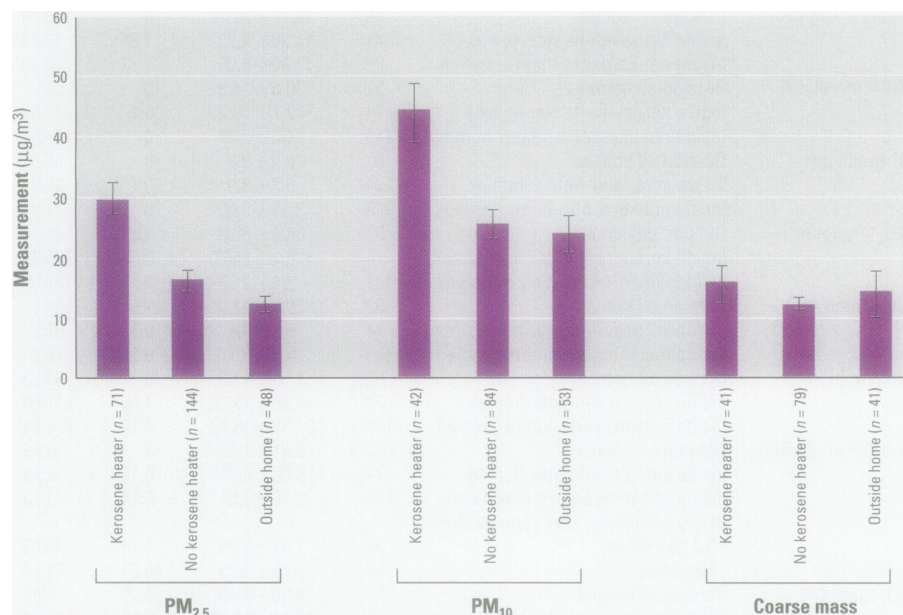
kerosene heaters may be an underestimate of the true concentrations.

## 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 PM<sub>2.5</sub> and SO<sub>4</sub><sup>2-</sup> concentrations by location of measurement. Measured values of outdoor summer PM<sub>10</sub>, PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, and H<sup>+</sup> 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 PM<sub>10</sub>, PM<sub>2.5</sub>, 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 PM<sub>10</sub>, PM<sub>2.5</sub>, 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 PM<sub>2.5</sub>/PM<sub>10</sub> and SO<sub>4</sub><sup>2-</sup>/PM<sub>2.5</sub> ratios were similar between the regional site and outside homes, and PM<sub>2.5</sub> and SO<sub>4</sub><sup>2-</sup> 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  $\leq 10$   $\mu\text{m}$  in diameter (PM<sub>10</sub>),  $\leq 2.5$   $\mu\text{m}$  in diameter (PM<sub>2.5</sub>), and particle mass between 10 and 2.5  $\mu\text{m}$  in diameter (PM<sub>10</sub>-PM<sub>2.5</sub>) (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.

**Table 5.** Pearson correlation coefficients between selected winter pollutants outside and inside homes

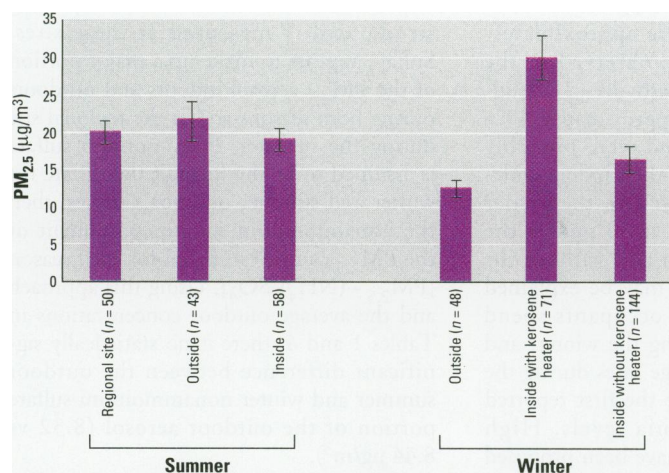
	PM <sub>10</sub>	PM <sub>2.5</sub>	Coarse	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub>	H <sup>+</sup>	NH <sub>3</sub>	SO <sub>2</sub>
<b>Outside homes (n = 53)</b>								
PM <sub>2.5</sub>	0.26	—	—	—	—	—	—	—
Coarse	0.95*	-0.05	—	—	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	0.28	0.59*	0.11	—	—	—	—	—
NH <sub>4</sub> <sup>+</sup>	0.31*	0.54*	0.14	0.66*	—	—	—	—
H <sup>+</sup>	0.17	0.19	0.10	0.45*	0.03	—	—	—
NH <sub>3</sub>	0.02	0.12	-0.07	0.09	0.04	0.03	—	—
SO <sub>2</sub>	0.12	0.18	0.05	0.28*	0.29	0.12	0.17	—
<b>Inside homes no kerosene heater (n = 148)</b>								
PM <sub>2.5</sub>	0.91*	—	—	—	—	—	—	—
Coarse	0.58*	0.019	—	—	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	0.10	0.30*	0.02	—	—	—	—	—
NH <sub>4</sub> <sup>+</sup>	0.06	0.05	-0.01	0.36*	—	—	—	—
H <sup>+</sup>	0.44*	0.24*	0.10	0.02	0.19*	—	—	—
NH <sub>3</sub>	0.19	0.42*	0.14	0.06	0.00	0.00	—	—
SO <sub>2</sub>	0.01	0.02	-0.10	0.06	0.21*	0.02	-0.04	—
<b>Inside homes with kerosene heater (n = 74)</b>								
PM <sub>2.5</sub>	0.85*	—	—	—	—	—	—	—
Coarse	0.64*	0.13	—	—	—	—	—	—
SO <sub>4</sub> <sup>2-</sup>	0.26	0.43*	-0.05	—	—	—	—	—
NH <sub>4</sub> <sup>+</sup>	0.02	0.26*	-0.10	0.94*	—	—	—	—
H <sup>+</sup>	0.12	0.24*	-0.18	0.30*	0.22	—	—	—
NH <sub>3</sub>	-0.11	0.05	-0.10	-0.17	-0.13	-0.07	—	—
SO <sub>2</sub>	0.24	0.41*	-0.10	0.77*	0.67*	0.46*	-0.17	—
Hours <sup>a</sup>	0.28	0.38*	-0.07	0.44*	0.35*	0.18	-0.09	0.45*

Abbreviations: PM<sub>10</sub>, particle mass  $\leq 10$   $\mu\text{m}$  in diameter; PM<sub>2.5</sub>, particle mass  $\leq 2.5$   $\mu\text{m}$  in diameter; coarse, particle mass between 10 and 2.5  $\mu\text{m}$  in diameter (PM<sub>10</sub>-PM<sub>2.5</sub>).

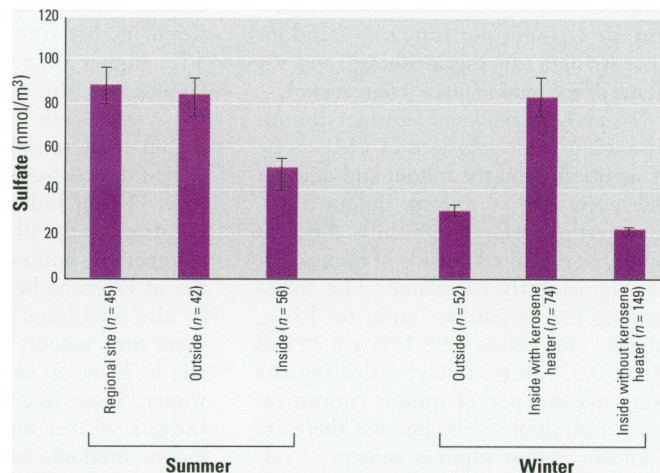
<sup>a</sup>Reported number of hours that the kerosene heater was used.

\* $p \leq 0.05$ .





**Figure 4.** Comparison of 24-hr particle mass  $\leq 2.5$   $\mu\text{m}$  in diameter ( $\text{PM}_{2.5}$ ) measurements made inside and outside homes and at the regional Vinton, Virginia, site for homes with and without kerosene heaters during winter and summer sampling periods for homes in Connecticut and Virginia.



**Figure 5.** Comparison of 24-hr sulfate measurements made inside and outside homes and at the regional Vinton, Virginia, site for homes with and without kerosene heaters during winter and summer sampling periods for homes in Connecticut and Virginia.

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 (PTEAM) 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,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  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  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{H}^+$  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  $\text{H}^+$  measured at the regional site and outside of homes and between outside and inside of homes.

Winter concentrations of  $\text{PM}_{2.5}$  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  $\text{PM}_{2.5}$  to indoor levels (roughly  $9 \mu\text{g}/\text{m}^3$  on average). Indoor winter sources of  $\text{PM}_{2.5}$  in homes without kerosene heaters contribute about as much as outdoors. Correlations between  $\text{PM}_{2.5}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{H}^+$  measured outside and inside of homes without kerosene heaters were much poorer than those measured during the summer. Outdoor winter  $\text{PM}_{2.5}$  concentrations and indoor/outdoor  $\text{PM}_{2.5}$  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, non-kerosene-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  $\mu\text{m}$ ) 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:

$$C_i = PAC_o/(A + K) + (S/V)/(A + K) \quad (1)$$

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  $1.03 \pm 0.74$  and  $0.74 \pm 0.53$ , 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  $<1 \mu m$ , 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 nitrous 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  $NO_x$  sources are three times the levels of those homes in the summer. While the air exchange rates are lower in the winter, the outdoor  $NO_x$  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 [ $PM_{2.5} - (NH_4)_2SO_4$ ]. 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  $\mu g/m^3$ ).

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  $\mu g/m^3$  or more to residential concentrations of  $PM_{2.5}$  and 7–15  $\mu g/m^3$  of  $SO_4^{2-}$ . In the field study reported here, kerosene heaters added approximately 12.5  $\mu g/m^3$  of  $PM_{2.5}$  and 6  $\mu g/m^3$  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  $\mu g/m^3$  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  $\mu g/m^3$  of  $PM_{2.5}$  and 15  $\mu g/m^3$  of  $SO_4^{2-}$  to background residential levels of 18 and 2  $\mu g/m^3$ , 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  $\text{PM}_{2.5}$  and  $\text{SO}_4^{2-}$ , 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  $\text{PM}_{2.5}$  and  $\text{SO}_4^{2-}$  and possibly  $\text{H}^+$  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  $\text{PM}_{2.5}$  and  $\text{SO}_4^{2-}$  and possibly  $\text{H}^+$  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  $\text{PM}_{2.5}$  and  $\text{SO}_4^{2-}$  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  $\text{PM}_{2.5}$ ,  $\text{SO}_4^{2-}$ , and possibly  $\text{H}^+$ . 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.

## REFERENCES AND NOTES

1. U.S. Environmental Protection Agency. Air Quality Criteria for Particulate Matter. EPA Rpt no. EPA/600/AP-95/001c.3v. Research Triangle Park, NC:Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, 1995.
2. Leaderer BP, Belanger K, Triche EW, Hellenbrand K, Holford T, Zheng H, Bracken MB, Beckett WS. Unpublished data.
3. Leaderer BP, Belanger K, Naeher L, Triche EW, Hellenbrand K, Holford T, Zheng H, Bracken MB, Beckett WS. Unpublished data.
4. Naeher L, Belanger K, Triche EW, Hellenbrand K, Holford T, Zheng H, Bracken MB, Beckett WS, Leaderer BP. Daily variations in peak flow in women associated with exposure to  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , sulfate and ozone. *Am J Resp Crit Care Med* (in press).
5. Koutrakis P, Sloutas C, Ferguson ST, Wolfson JM. Development and evaluation of a gas honeycomb denuder/filter pack system to collect atmospheric gases and particles, acidic aerosols and gases. *Environ Sci Technol* 27:2497–2501 (1988).
6. Sloutas C, Wang PY, Ferguson ST, Koutrakis P, Mulik JD. Laboratory and field evaluation of an improved glass honeycomb denuder/filter pack sampler. *Atmos Environ* 30:885–895 (1996).
7. Suh HH, Nishioka Y, Allen GA, Koutrakis P, Burton RM. The Metropolitan Acid Aerosol Characterization Study: results from the summer 1994 Washington, D.C. field study. *Environ Health Perspect* 105:826–834 (1997).
8. Burton RM, Suh HH, Koutrakis P. Spatial variations in particulate concentrations within metropolitan Philadelphia. *Environ Sci Technol* 32:400–407 (1996).
9. Clayton CA, Perritt RL, Pellizzari ED, Thomas KW, Whitmore RW, Ozkaynak H, Spengler JD, Wallace LA. Particle total exposure assessment methodology (PTEAM) study: distributions of aerosol and elemental concentrations in personal, indoor, and outdoor air samples in a southern California community. *J Expo Anal Environ Epidemiol* 3:227–250 (1993).
10. Suh HH, Spengler JD, Koutrakis P. Personal exposures to acid aerosols and ammonia. *Environ Sci Technol* 26:2507–2517 (1992).
11. Bajadori T. Human particulate exposure assessment: Relationship between outdoor, indoor, and personal measurements [PhD dissertation]. Harvard School of Public Health, Boston, MA, 1998.
12. Sheldon LS, Hartwell TD, Cox BG, Sickles JE, Pellizzari ED, Smith ML, Perritt RL, Jones SM. An Investigation of Infiltration and Indoor Air Quality. Albany, NY:New York State Energy Research and Development Authority, 1990.
13. Leaderer BP, Koutrakis P, Briggs SLK, Rizzuto J. The mass concentration and elemental composition of indoor aerosols in Suffolk and Onondaga Counties, New York. *Indoor Air* 4:23–34 (1994).
14. Koutrakis P, Briggs SLK, Leaderer BP. Source apportionment of indoor aerosols in Suffolk and Onondaga Counties, New York. *Environ Sci Technol* 26:521–527 (1992).
15. Brauer M, Koutrakis P, Keeler GJ, Spengler JD. Indoor and outdoor concentrations of inorganic acidic aerosols and gases. *J Air Waste Manage Assoc* 41:171–181 (1991).
16. Leaderer BP. Air pollution emissions from kerosene space heaters. *Science* 218:1113–1115 (1982).
17. Leaderer BP, Boone PM, Hammond SK. Total particle, sulfate and acidic aerosol emissions from kerosene space heaters. *Environ Sci Technol* 24:908–912 (1990).

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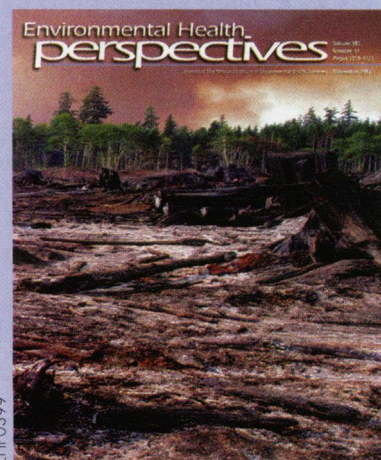
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