

The Metropolitan Acid Aerosol Characterization Study: Results from the Summer 1994 Washington, D.C. Field Study

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An ambient particle monitoring study was conducted in Washington, D.C. during the summer of 1994 as part of the Metropolitan Acid Aerosol Characterization Study (MAACS). Acid aerosol and inhalable (particulate matter with aerodynamic diameters $<10\text{ }\mu\text{m}$; PM_{10}) and fine (particulate matter with aerodynamic diameters $<2.5\text{ }\mu\text{m}$; $\text{PM}_{2.5}$) particle samples were collected for 24-hr periods (9 A.M.–9 A.M. EDT) on alternate days at six monitoring sites located throughout the greater Washington, D.C. area. Monitoring sites were located in both urban and rural areas and were generally situated along a southwest to northeast line due to the prevailing winds. Information on site characteristics, including population density and distance from the city center, was also obtained, as were data on meteorological parameters. Results from this study show strong correlations among the particulate measures, PM_{10} , $\text{PM}_{2.5}$, SO_4^{2-} , and H^+ . These strong correlations resulted from the fact that $\text{PM}_{2.5}$ comprised 77% of PM_{10} , with SO_4^{2-} -related species accounting for 49% of total $\text{PM}_{2.5}$. PM_{10} , $\text{PM}_{2.5}$, SO_4^{2-} , and H^+ concentrations were found to be uniform across the metropolitan Washington area. Spatial variation was found, however, for coarse particles ($\text{PM}_{2.5-10}$) and NH_3 concentrations. In our previous Philadelphia study, population density was an important determinant of spatial variation in coarse particles and NH_3 concentrations; however, in Washington, D.C., population density was not associated with observed spatial patterns in coarse particle concentrations, but was an important determinant of NH_3 concentrations. When data from one site (Reservoir) was excluded from the analysis, population density explained a larger percentage of the variability in NH_3 levels and became an important determinant of the $\text{H}^+/\text{SO}_4^{2-}$ ratio as well. Ambient H^+ models developed from Philadelphia data were found to predict H^+ concentrations in Washington, D.C. reasonably well, representing an improvement over measurements made at a single stationary ambient monitoring site. **Key words:** ambient concentrations, ammonia, particulate matter, population density, spatial variation. *Environ Health Perspect* 105:826–834 (1997)

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The Metropolitan Acid Aerosol Characterization Study (MAACS) is an EPA-sponsored study intended to characterize the spatial and temporal variations in acidic sulfate and particulate mass concentrations within urban areas. This study was designed to occur over a 5-year period in four eastern U.S. cities: Philadelphia, Pennsylvania, in 1992 and 1993 (1,2); Washington, D.C., in 1994; Nashville, Tennessee, in 1995; and Boston, Massachusetts, in 1996. These cities were selected based on numerous factors, with one of the major factors being the importance of sulfate-related particles to overall air pollutant levels. The monitoring plans for the four cities were similar so that results from the cities would be comparable.

In each of the MAACS cities, acidic sulfate and particulate mass concentrations were measured simultaneously at multiple monitoring sites located throughout the metropolitan area. Site selection criteria were established based on findings from earlier spatial variation studies conducted in the metropolitan New York (3) and Toronto (4) areas. In these early studies, sulfate (SO_4^{2-}) concentrations were found to be uniform across the metropolitan areas, while aerosol strong acid-

ity (H^+) concentrations were shown to vary spatially, with concentrations highest in areas distant from the city center. In addition, high SO_4^{2-} and H^+ concentrations in the two metropolitan areas were associated with air parcels that originated in the midwestern United States. This association suggested that pollutant transport from large regional sources was a primary determinant of acidic SO_4^{2-} concentrations in these and other eastern North American cities. Further support for this hypothesis was provided in a study by Liu et al. (5), which found SO_4^{2-} concentrations to be uniform across large distances in western Pennsylvania. As a result of these findings, monitoring sites in the MAACS cities were selected to maximize our ability to examine the effects of regional transport on metropolitan particulate concentrations. Accordingly, monitoring sites were located along the direction of the hypothesized prevalent summertime wind direction. Monitoring sites were also located in areas with different population densities, in order to assess the impacts of local particulate and ammonia (NH_3) sources.

Results from Philadelphia, the first of the MAACS cities, confirmed findings

from the New York and Toronto studies and increased our general understanding of the behavior of particles in urban environments (1,2). In Philadelphia, SO_4^{2-} -related species were found to be the major constituents of particulate matter with aerodynamic diameters (d_p) of $<10\text{ }\mu\text{m}$ (PM_{10}) and $<2.5\text{ }\mu\text{m}$ ($\text{PM}_{2.5}$). High SO_4^{2-} , and thus high PM_{10} and $\text{PM}_{2.5}$, concentrations were again associated with regional transport of pollution from the midwestern United States. As a result, PM_{10} , $\text{PM}_{2.5}$, and SO_4^{2-} concentrations were not surprisingly found to be uniform across the metropolitan area. Coarse particle ($\text{PM}_{2.5-10}$) concentrations, on the other hand, varied spatially within Philadelphia. This spatial variation was found to be related to population density, suggesting that human activities such as traffic and construction are important local sources of coarse particles. Although also associated with regional transport, H^+ concentrations were found to vary spatially across the city. This variation was due to corresponding spatial variation in NH_3 concentrations, which increased with population density. As a result, densely populated sites had more NH_3 available to neutralize particulate acidity, thus lowering H^+ concentrations. Ambient H^+ models that included a H^+-NH_3 neutralization term were able to account for much of the spatial variation in H^+ concentrations within Philadelphia, representing a substantial improvement over measurements made at a single stationary ambient monitoring (SAM) site alone.

In this paper, we continue to examine the summertime spatial patterns of PM_{10} , $\text{PM}_{2.5}$, $\text{PM}_{2.5-10}$, SO_4^{2-} , H^+ , and NH_3 using air pollution, meteorological, and site-specific data collected in Washington, D.C., the second of the MAACS cities. Data from

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Washington are used to 1) characterize the relationship among the various particulate species, 2) examine the influence of local wind direction and site-specific characteristics on particulate species concentrations, and 3) validate spatial H^+ models developed using Philadelphia data. Findings from Washington are compared to those from Philadelphia and from the earlier Toronto and New York studies as well. The implications of these results to epidemiologic studies of particulate matter are also discussed.

Methods

Acidic sulfate (SO_4^{2-} , H^+ , NH_4^+), particulate mass (PM_{10} and $PM_{2.5}$), and NH_3 concentrations were measured at multiple sites located throughout the metropolitan Washington, D.C. area from June to August 1994. Sampling was conducted simultaneously at six SAM sites (Fig. 1). Sites were selected based on their local population density and on their distance and direction from downtown Washington (Table 1). Four of the SAM sites were positioned along a southwest to northeast line to correspond to the hypothesized prevailing summer wind direction. Other sites were located south of the city center (within the city limits) at the Martin Luther King Library (MLK) and in Cub Run, Virginia (CUB), a rural site located approximately 35 km west of the city center. The CUB site was located upwind from Washington and served as the background monitoring site. The elevations of all sites were comparable. None of the sites were impacted by large stationary particulate or sulfate sources; however, both the MLK and Bladensburg, Maryland (BLD) sites were located near highways (≈ 0.25 and 0.75 miles, respectively), which may be a source of both particulate mass and NH_3 (6,7).

Air pollution sampling was performed for 24-hr periods (9 A.M.–9 A.M. EDT) on alternate days at four monitoring sites and every day at two sites [the West End Library (LIB) and the reservoir (RES)]. Samplers were placed on the roof of a trailer or low-story building. [Samplers at the

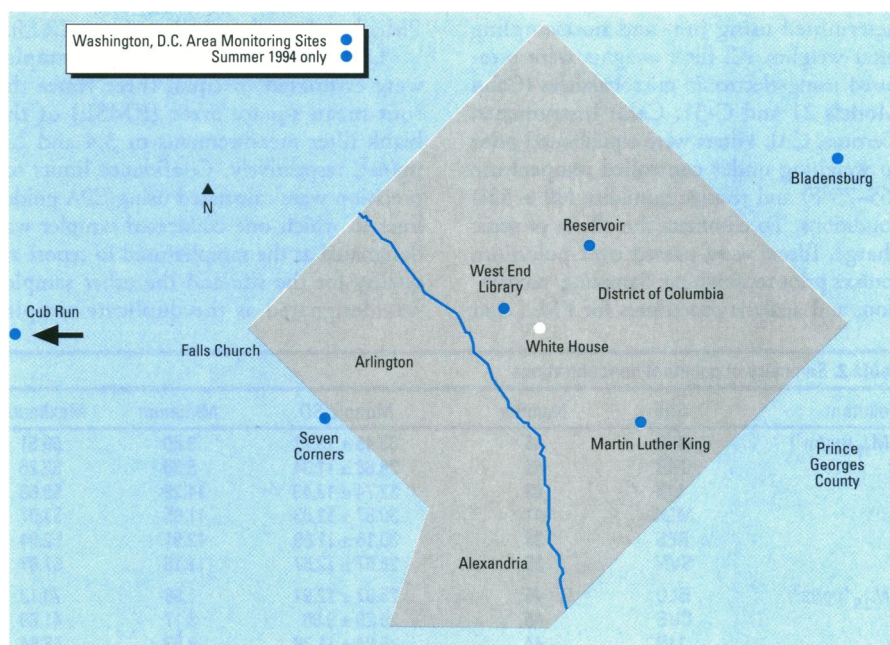


Figure 1. Monitoring site locations. The distance from Seven Corners to Bladensburg is 20.5 km. Cub Run is 35 km west of the White House.

Seven Corners, VA (SVN) and RES sites were placed atop four-story buildings, while samplers at other sites were placed atop one-story buildings or trailers.] Sampler inlets were placed approximately 1.5 m above the roof. Population density for each monitoring site was estimated using a radius of 0.5 miles around the site and was determined using the Geographic Information System (GIS) (8) and 1990 census TIGER files (9,10).

Acidic sulfate and ammonia measurements. Acidic sulfate and NH_3 samples were collected using modified Harvard–EPA annular denuder systems (HEADS) (11). Modified HEAD samplers consisted of an inlet-impactor section to remove coarse particles ($>2.1 \mu m$), a citric acid-coated annular denuder to collect NH_3 , and a Teflon filter to collect fine particles. H^+ concentrations were determined by pH analysis and SO_4^{2-} and NH_3 concentrations were determined by ion chromatography. Quality assurance and control measures included a check of

the ion balance to verify that interference from alkaline particles was minimal which would ensure that H^+ collected on the filter would not be affected by the presence of alkaline particles (12). Limits of detection (LODs) were assumed to equal those previously estimated for 24-hr HEADS samples, which for SO_4^{2-} , H^+ , and NH_3 are 6.0 nmol/m^3 , 4.0 nmol/m^3 , and 0.3 ppb , respectively (13). Sampling, preparation, and analysis procedures have been described previously (11,14).

Particulate mass measurements. $PM_{2.5}$ and PM_{10} samples were collected at flow rates of 10 lpm using Harvard–Marple impactors (HMI; Turner Group, Harrison, ME). The impactors consisted of an inlet-impactor section with a 50% cut-size of either 2.5 or $10 \mu m$ in diameter followed by a Teflon filter mounted in a plastic holder to collect $PM_{2.5}$ or PM_{10} , respectively (15). The impaction plate was oiled to minimize particle bounce and to provide a sharp particle cut point. Particle concentrations were

Table 1. Summary of site characteristics

Site	Distance from city center (km)	Population density (persons/mile ²) ^a	Site descriptors
West End Library	1.6	16,068.6	Located in an urban area bordered by heavily traveled streets
Reservoir	3.6	13,793.2	Located in open clearing of a reservoir in an urban/suburban area
Cub Run, VA	35.4	653.8	Located in a sparsely populated area with minimal traffic
Seven Corners, VA	9.7	8,713.4	Located in a commercial/suburban area
Martin Luther King	5.6	10,921.8	Located in a commercial/residential urban area bordered by a moderately traveled street; heavily traveled highways are 1/4 mile to NW and SW; major road construction occurred near the building for part of sampling period
Bladensburg, MD	10.5	4,274.3	Located in a suburban area; heavily traveled highways are approximately 1/2 mile to NW and S

^aPopulation density data was obtained using a radius of 0.5 miles.

determined using pre- and postsampling filter weights. All filter weights were measured using electronic microbalances (Cahn Models 21 and C-31, Cahn Instruments, Cerritos, CA). Filters were equilibrated prior to weighing under controlled temperature (65–75°F) and relative humidity ($40 \pm 5\%$) conditions. To eliminate the effects of static charge, filters were passed over polonium sources prior to weighing. Sampling, preparation, and analysis procedures for $PM_{2.5}$ and

PM_{10} have been described previously (2,15).

LODs for $PM_{2.5}$ and PM_{10} samples were estimated to equal three times the root mean square error (RMSE) of the blank filter measurements or 3.4 and 2.8 $\mu\text{g}/\text{m}^3$, respectively. Confidence limits for precision were calculated using EPA guidelines in which one collocated sampler was designated as the sampler used to report air quality for the site and the other sampler was designated as the duplicate sampler

(16). The percentage difference for each collocated sample pair was calculated using the formula $(x_1 - x_2)/x_1$. The mean and the standard deviation (SD) of the percentage differences were used to calculate the 95% and 5% confidence limits for precision (mean ± 1.96 SD). Using this method, the 95% and 5% confidence limits for precision were found to equal 18.1% and -12.8% for $PM_{2.5}$, respectively. For PM_{10} , the 95% and 5% confidence limits for precision were determined to equal 10.7% and -6.1%, respectively. (In Philadelphia, the RMSE method was used to calculate precision, defined as the root mean square error of the difference between the collocated measurements divided by the mean concentration. Using this method, the precision of the measurements in Washington, D.C. was found to equal 12.8% for $PM_{2.5}$ and 6.1% for PM_{10} , which was similar to that found in Philadelphia.)

Coarse particle ($2.5 < d_a < 10 \mu\text{m}$) mass concentrations were calculated as the difference between measured PM_{10} and $PM_{2.5}$ concentrations, with negative values set to zero because, by definition, $PM_{2.5}$ concentrations cannot exceed PM_{10} concentrations. (Negative values were few and resulted primarily when PM_{10} concentrations were near or below the limit of detection.) The 95% and 5% limits for precision of coarse particle concentrations was determined to equal 43.0% and -41.6%, respectively, using collocated $PM_{2.5}$ and PM_{10} data collected in Washington, D.C. As was the case with PM_{10} and $PM_{2.5}$, the upper and lower limits for precision were calculated using EPA guidelines (16). This method differs from that used in Philadelphia, where a more conservative method to calculate precision was used.

Meteorological measurements. Hourly wind direction data were measured at the Washington, D.C. National Airport. Data were obtained using official national weather service data from the National Center for Atmospheric Research (NCAR). The most prevalent wind direction was used to represent the weather conditions for each 24-hr period. Prevalent wind directions were determined using vector-resultant values for the 24-hr period and were categorized as north, east, west, or south. (Wind directions could not be stratified further due to sample size considerations.)

Data analysis. Data capture was 90% and 80% of a possible 368 HEADS and particulate mass samples, respectively. All statistical analyses were performed using the Statistical Analysis System (SAS Institute, Cary, NC) (17). H^+ concentrations in micrograms per cubic meter are expressed as equivalent sulfuric acid (H_2SO_4). Air

Table 2. Summary of pollutant concentrations

Pollutant	Site	Number	Mean $\pm$ SD	Minimum	Maximum
PM_{10} ($\mu\text{g}/\text{m}^3$)	BLD	46	33.45 ± 13.21	3.60	60.51
	CUB	45	28.88 ± 11.34	5.36	52.26
	LIB	43	32.74 ± 12.49	14.29	59.63
	MLK	41	30.87 ± 12.03	11.85	57.97
	RES	38	30.16 ± 11.69	12.91	52.94
	SVN	35	28.67 ± 12.57	11.15	57.67
$PM_{2.5}$ ($\mu\text{g}/\text{m}^3$)	BLD	45	25.87 ± 12.97	1.68	70.13
	CUB	45	20.29 ± 9.96	3.17	41.60
	LIB	44	25.94 ± 11.38	8.53	48.64
	MLK	42	22.91 ± 10.58	4.95	47.04
	RES	38	22.63 ± 10.70	7.77	43.31
	SVN	37	23.17 ± 11.44	8.16	50.56
Coarse ($\mu\text{g}/\text{m}^3$)	BLD	45	7.95 ± 4.22	0.00	25.42
	CUB	44	8.21 ± 2.54	2.19	15.70
	LIB	43	6.72 ± 3.78	0.00	14.98
	MLK	41	8.73 ± 5.32	0.00	28.01
	RES	37	6.73 ± 1.99	3.85	13.51
	SVN	34	5.75 ± 2.21	3.10	13.49
SO_4^{2-} ($\mu\text{g}/\text{m}^3$)	BLD	44	9.31 ± 6.46	0.33	26.56
	CUB	41	8.89 ± 5.30	1.10	22.16
	LIB	87	10.14 ± 6.62	0.93	24.55
	MLK	40	8.77 ± 6.68	0.00	22.98
	RES	41	10.05 ± 6.67	0.96	24.65
	SVN	37	9.91 ± 6.46	2.46	24.46
H^+ ($\mu\text{g}/\text{m}^3$) ^a	BLD	44	1.95 ± 2.19	0.00	9.99
	CUB	41	2.48 ± 2.11	0.00	7.94
	LIB	44	1.76 ± 1.77	0.00	7.45
	MLK	40	1.71 ± 1.73	0.00	7.24
	RES	41	2.09 ± 1.98	0.37	9.09
	SVN	37	2.49 ± 2.54	0.10	9.77
NH_3 (ppb)	BLD	46	1.56 ± 0.65	0.30	3.05
	CUB	43	0.46 ± 0.30	0.00	1.06
	LIB	45	2.52 ± 0.86	1.35	4.88
	MLK	39	1.78 ± 0.82	0.04	4.05
	RES	41	1.43 ± 0.98	0.24	4.63
	SVN	37	0.81 ± 0.38	0.07	1.73

Abbreviations: SD, standard deviation; PM_{10} , particulate matter with aerodynamic diameters $<10 \mu\text{m}$; $PM_{2.5}$, particulate matter with aerodynamic diameters $<2.5 \mu\text{m}$; BLD, Bladensburg, MD; CUB, Cub Run, VA; LIB, West End Library; MLK, Martin Luther King Library; RES, reservoir; SVN, Seven Corners, VA.

^aExpressed as equivalent H_2SO_4 .

Table 3. Correlation coefficients for comparisons of particulate measure concentrations

	PM_{10}	$PM_{2.5}$	Coarse PM	SO_4^{2-}	H^+
$PM_{2.5}$	0.94*	—	—	—	—
$PM_{2.5-10}$	0.37*	0.03	—	—	—
SO_4^{2-}	0.79*	0.82*	0.07	—	—
H^+	0.60*	0.62*	0.07	0.80*	—
NH_3	0.02	-0.01	0.13	-0.11	-0.29*

Abbreviations: PM_{10} , particulate matter with aerodynamic diameters $<10 \mu\text{m}$; $PM_{2.5}$, particulate matter with aerodynamic diameters $<2.5 \mu\text{m}$; coarse PM, particulate matter with aerodynamic diameters between $10 \mu\text{m}$ and $2.5 \mu\text{m}$.

* $p < 0.05$.

pollutant concentrations measured at each site were characterized and compared using Pearson correlation coefficients and one-way analysis of variance (ANOVA), Tukey honest significant difference (HSD), and univariate regression procedures. For the LIB and RES sites, at which samples were collected every day, only those data collected on alternate days were included in the analyses. The influences of population density and wind direction on outdoor PM_{10} , $PM_{2.5}$, $PM_{2.5-10}$, SO_4^{2-} , H^+ , and NH_3 concentrations were examined using Spearman and Pearson correlation coefficients and regression techniques. Models to estimate 24-hr H^+ levels were validated using summer 1994 data collected in Washington, D.C. and regression and physicochemical modeling techniques. With a few exceptions, statistical significance was based on p -values of 0.05.

Results

Mean summertime PM_{10} , $PM_{2.5}$, SO_4^{2-} , and H^+ concentrations (averaged over all sites) were found to equal 30.9, 23.5, 9.5, and 2.1 $\mu g/m^3$, respectively. Coarse particle concentrations were generally low, with mean coarse particle concentrations ranging between 5.8 and 8.2 $\mu g/m^3$. $PM_{2.5}$ concentrations were found to comprise on average 77% of PM_{10} , while SO_4^{2-} -related particles were found to comprise an average of 49% of $PM_{2.5}$. Summary statistics for each pollutant stratified by site are presented in Table 2.

Relationship among the particulate parameters. PM_{10} , $PM_{2.5}$, SO_4^{2-} , and H^+ concentrations were strongly correlated with one another (Table 3). Strong correlations among these particulate measures were expected because SO_4^{2-} -related particles (which include H^+) constitute the majority of $PM_{2.5}$ and thus a large fraction of PM_{10} as well. Although significant, the correlation between PM_{10} and coarse particle concentrations was weaker, resulting in a correlation coefficient of 0.28. This weaker correlation can be attributed to the fact that coarse particles contribute relatively little to the overall PM_{10} levels and also that coarse particle measurements are less precise. All other pair-wise comparisons between coarse particle concentrations and other particulate measure concentrations were statistically insignificant, which was expected because sources of coarse particles differ from those for $PM_{2.5}$, SO_4^{2-} , and H^+ .

NH_3 was negatively correlated to H^+ ($r = -0.29$). The negative correlation with H^+ was due to the fact that H^+ is neutralized by NH_3 . When data were stratified by site, PM_{10} , $PM_{2.5}$, SO_4^{2-} , and H^+ concentrations remained strongly correlated. However,

correlation coefficients for pair-wise comparisons with either coarse particles or NH_3 were unstable, particularly for comparisons with coarse particles. This result is consistent with the fact that sources for the two pollutant groups differ. Coarse particles and NH_3 tend to originate from local sources, while SO_4^{2-} -associated particles and a large fraction of $PM_{2.5}$ and PM_{10} tend to originate from large regional sources.

Relationship with local wind direction.

As expected, the most prevalent local wind direction during the summer of 1994 in Washington, D.C. was from the south, as 51.1%, 20.2%, 19.1%, and 9.6% of the 24-hr sample periods had prevalent winds from the south, west, north, and east, respectively. PM_{10} , $PM_{2.5}$, SO_4^{2-} , and H^+ concentrations measured at all sites were found to vary significantly by wind direction, with the variation for $PM_{2.5}$ significant only at the 0.10 level (Fig. 2A–D). PM_{10} and $PM_{2.5}$ concentrations were highest when winds were from the west as compared to the north. Similarly, SO_4^{2-} concentrations were highest during westerly winds as compared to northerly and easterly winds, while H^+ concentrations were significantly higher during westerly and southerly winds as compared to northerly winds. Wind direction was found to have an effect on the ratio of H^+ to SO_4^{2-} concentrations similar to that for H^+ , as the H^+/SO_4^{2-} ratio was highest when winds were from the south and west as compare to the north. These results, which are consistent with earlier work by Lioy et al. (3), suggest that fine particulate pollution in Washington, D.C. results primarily from regional transport from areas to the west and south of the city. (Since $PM_{2.5}$ comprises the majority of PM_{10} , PM_{10} variation by wind direction probably results from corresponding variation in $PM_{2.5}$ levels.) This regional transport is consistent with emissions of sulfur dioxide (SO_2), the SO_4^{2-} precursor, from large coal- and oil-fired utility plants located to the south and west of Washington, D.C. In contrast, sources of NH_3 and coarse particle concentrations, which did not vary with wind direction, were probably local and site-specific (Fig. 2E, F).

Spatial variation. PM_{10} and $PM_{2.5}$ concentrations did not vary significantly by site, as the concentration differences for the sites with the highest and lowest mean concentrations were only 4.8 and 5.6 $\mu g/m^3$, respectively (Table 2). Coarse mass concentrations varied spatially at the 0.10 level, as mean concentrations measured at the CUB site were significantly higher than those measured at the SVN site; however, the mean concentration difference between the CUB and SVN sites was small, equaling

only 2.5 $\mu g/m^3$. Lower coarse particle concentrations at the SVN site may be attributed to the fact that samplers at this site were placed atop of a four-story building away from the ground-level coarse particulate sources. Samplers at the CUB site, on the other hand, were placed on the roof of a trailer with a dirt access road nearby.

PM_{10} and $PM_{2.5}$ concentrations at all of the sites were strongly correlated to one another, suggesting similar sources for PM_{10} and $PM_{2.5}$ at the sites (Table 4). Correlations for PM_{10} and $PM_{2.5}$ concentrations measured at MLK, however, were substantially lower than those for other sites. Lower correlation coefficients for the MLK site may be attributed to local motor vehicle traffic, which may be a source of both fine and coarse particles at this site. This hypothesis is supported by the observed high mean coarse particle concentrations at this site and by the observed insignificant correlation coefficients for comparisons of coarse particle concentrations measured at the MLK site (Table 4). In general, correlation coefficients for pair-wise site comparisons for coarse particle were substantially lower than those for both PM_{10} and $PM_{2.5}$ (Table 4). This result was expected because sources of coarse particles tend to be site-specific.

Concentrations of SO_4^{2-} and H^+ did not vary significantly by site; however, the ratio of H^+ to SO_4^{2-} was found to vary spatially. The mean H^+ to SO_4^{2-} ratios at the CUB and SVN sites were found to be statistically higher than that at the LIB site. Spatial variation was also observed in NH_3 concentrations, as mean NH_3 concentrations fell into three groups, which in order of descending NH_3 concentrations are the LIB site, followed by the MLK, BLD, and RES sites, and finally by the SVN and CUB sites. This spatial pattern was opposite to that found for the mean H^+/SO_4^{2-} ratio and, although not statistically significant, generally for H^+ as well.

SO_4^{2-} and H^+ concentrations at the six sites were moderately to strongly correlated to one another, with correlation coefficients for pair-wise comparisons ranging between 0.5 and 0.9 for both pollutants (Table 4). Note that the correlation coefficients for SO_4^{2-} tended to be slightly lower than those for H^+ , which was unexpected. These lower correlation coefficients may result from the fact that on several days SO_4^{2-} and H^+ concentrations were substantially lower at one of the sites as compared to the remaining sites. (No explanation for this drop was apparent. Furthermore, the days on which concentrations were lower at one site were not continuous.) Since SO_4^{2-} concentrations tended to be substantially higher than

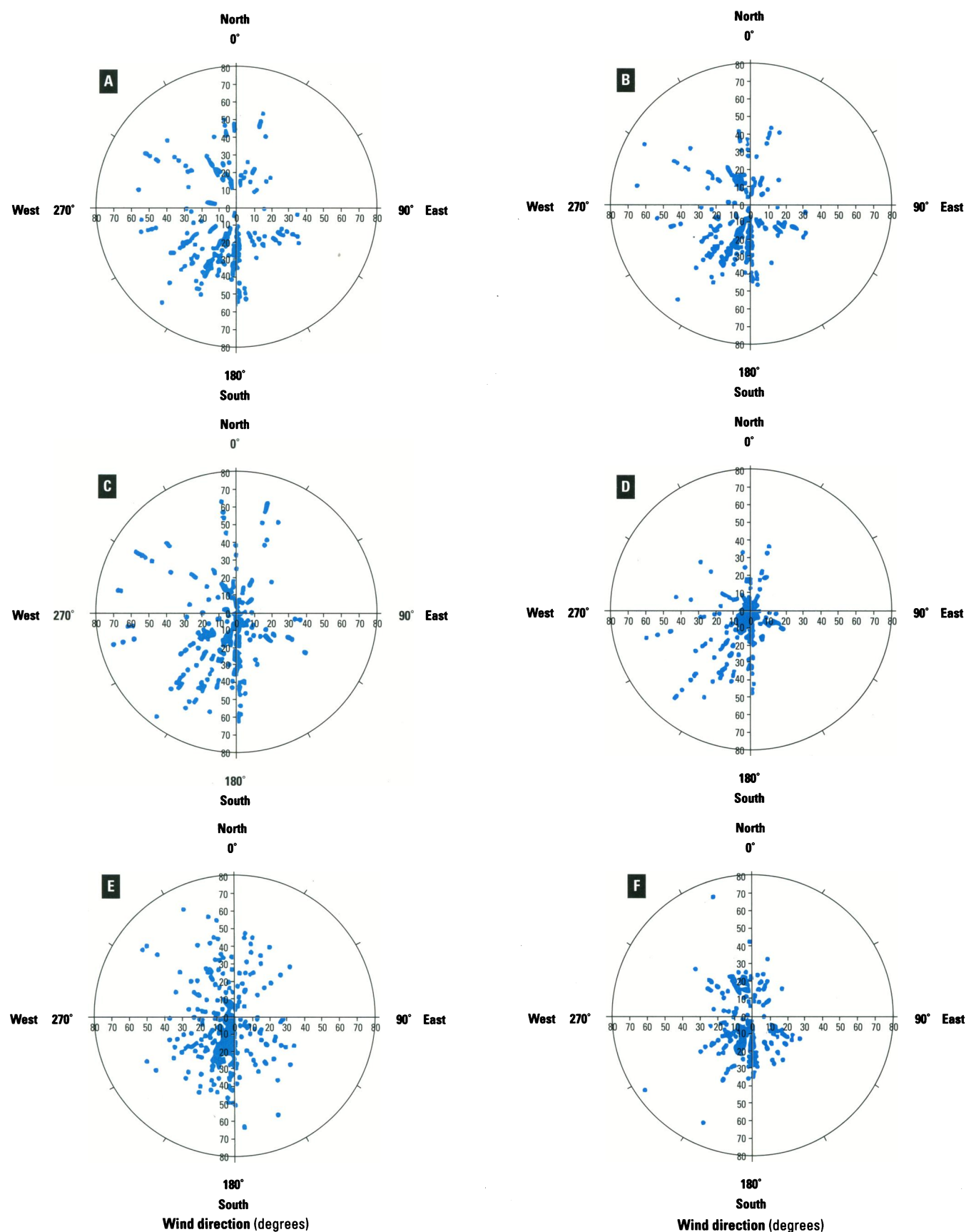


Figure 2. Concentrations by wind direction of (A) PM_{10} ($\mu\text{g}/\text{m}^3$); (B) $\text{PM}_{2.5}$ ($\mu\text{g}/\text{m}^3$); (C) SO_4^{2-} ($\mu\text{g}/\text{m}^3$); (D) H^+ ($\mu\text{g}/\text{m}^3$; equivalent H_2SO_4); (E) NH_3 (ppb); and (F) $\text{PM}_{2.5-10}$ ($\mu\text{g}/\text{m}^3$). Abbreviations: PM_{10} , particulate matter with aerodynamic diameters $<10\ \mu\text{m}$; $\text{PM}_{2.5}$, particulate matter with aerodynamic diameters $<2.5\ \mu\text{m}$. Wind direction is expressed as vector-resultant values. Data for all summer 1994 monitoring days are included.

H⁺ levels, these lower concentrations had a greater effect on correlations among the SO₄²⁻ concentrations as compared to H⁺. Evidence for this hypothesis was provided by an examination of the daily concentration differences at the sites for the two pollutants, which showed that SO₄²⁻ concentrations were more uniform across the sites as compared to H⁺. (The daily site concentration difference provides an indication of the magnitude of the concentration difference at the sites and is expressed relative to the mean daily concentration.) The mean daily concentration difference was 28% for H⁺ and 17% for SO₄²⁻. With the exception of the background CUB site, NH₃ concentrations at the sites were also significantly correlated to one another (Table 4). The mean daily concentration difference between sites for NH₃ was the largest of the three pollutants at 41%.

Population density was found to be an unimportant determinant of all particulate concentrations. Population density explained none of the variability in PM₁₀, PM_{2.5}, coarse particulate, SO₄²⁻, and H⁺ concentrations and the H⁺/SO₄²⁻ ratio, with R² values for regressions of pollutant concentrations on population density near zero. Population density remained an insignificant predictor of particulate concentrations when data were stratified by wind direction.

Population density was, however, a significant, albeit weak, predictor of site NH₃ levels, resulting in a slope of 9.5×10^{-5} ($\pm 9.7 \times 10^{-6}$) ppb · mile²/person, an intercept of 0.59 (± 0.10) ppb, and an R² of 0.28 when site NH₃ concentrations were regressed on population density. The predictive ability of population density for site NH₃ concentrations increased substantially when data for the RES site were excluded from the analysis, resulting in an improved R² of 0.40, a slope of 1.1×10^{-4} ($\pm 9.7 \times 10^{-6}$) ppb · mile²/person, and an intercept of 0.54 (± 0.09) ppb when NH₃ concentrations were regressed on population density. When data were further stratified by wind direction, population density remained an important determinant of site NH₃ concentrations, explaining between 31% (western wind direction) and 54% (eastern wind direction) of the variability in site NH₃ levels. The slopes of the regression lines of NH₃ on population density for each wind direction were similar, ranging between 1.1×10^{-4} and 1.3×10^{-4} ppb · mile²/person. These values are comparable to those observed in Philadelphia (1.5×10^{-4}), suggesting that the influence of population density on site NH₃ levels is relatively consistent from city to city and year to year and results in an increase of approximately 1.5 ppb for every 10,000 persons/mile² (1).

Population density was also found to be a significant predictor of the H⁺/SO₄²⁻ ratio when data from the RES site were excluded from the analysis. Regression of the H⁺/SO₄²⁻ ratio on population density yielded a slope of -4.9×10^{-6} ($\pm 1.3 \times 10^{-6}$) mile²/person and an intercept of 0.24 (± 0.01). However, population density explained only a small percentage of the variation in the H⁺/SO₄²⁻ ratio (R²=0.07). When data were stratified by wind direction, the slopes of the regression lines varied substantially, ranging between -5.7×10^{-6} ($\pm 2.0 \times 10^{-6}$) and -3.2×10^{-6} ($\pm 3.4 \times 10^{-6}$) mile²/person. Again, the predictive ability of population density was poor, with the model insignificant for the eastern wind direction. The values for the slopes were higher and more variable than those in Philadelphia (-9.3×10^{-6} to -8.7×10^{-6} for the different wind directions), indicating that population density alone is a poor predictor of the H⁺/SO₄²⁻ ratio within Washington, D.C.

Model validation. Model validation procedures were performed on spatial H⁺ models that were developed using data collected in Philadelphia, Pennsylvania, during the summer of 1992 (1). The developed models estimate 24-hr H⁺ concentrations at a site *i* ([H⁺]_{*i*}) using the following expression:

$$[H^+]_i = [H^+]_{\text{background}} - k_{\text{NH}_3} [H^+]_{\text{background}} [\text{NH}_3]_i$$

where [H⁺]_{background} represents the H⁺ concentration at a background site, [NH₃]_{*i*} the ammonia concentration at the site *i*, and *k*_{NH₃} the neutralization constant for the H⁺-NH₃ reaction. The value for the neutralization *k*_{NH₃} was found to equal 0.1/ppb using optimization procedures on the Philadelphia data.

Validation procedures showed that this model was a fair predictor of 24-hr H⁺ concentrations within the metropolitan Washington, D.C. area, resulting in a slope near unity (0.94 ± 0.03 , no-intercept model). The model explained 74% of the variation in outdoor H⁺ concentrations (Fig. 3). Model performance was similar for all sites, explaining between 60% (at BLD) to 84% (at SVN) of the variation in the site H⁺ concentrations. At H⁺ concentrations greater than approximately 150 nmol/m³, however, the model underestimated H⁺ concentrations. Model underestimates at these high H⁺ levels may result from the fact that pollutant concentrations were measured over 24-hr periods, which may hide temporal variations in both H⁺ and NH₃ levels. H⁺ concentrations, for example, are highest during the mid-afternoon hours, when NH₃ concentrations are

lowest. Similarly, H⁺ concentrations are lowest at night when NH₃ concentrations are highest. As a result, during high air pollution periods, 24-hr samples may overestimate the amount of NH₃ available to neutralize H⁺ during its peak afternoon levels, causing the model to underestimate site H⁺ concentrations.

Discussion and Summary

As was the case in Philadelphia, summertime PM_{2.5} concentrations in Washington, D.C. comprised approximately 75% of corresponding PM₁₀ concentrations. Similarly, SO₄²⁻-related particles were the major component of PM_{2.5} and of PM₁₀ as well. SO₄²⁻-related particles, however, comprised a slightly smaller fraction of particulate mass levels, accounting for almost 50% of PM_{2.5} as compared to 65% in Philadelphia. The smaller fraction of SO₄²⁻-related particles in

Table 4. Correlation coefficients for pair-wise comparisons between site concentrations

	CUB	SVN	BLD	RES	LIB
SVN					
PM ₁₀	0.97*				
PM _{2.5}	0.97*				
PM _{2.5-10}	0.39*				
SO ₄ ²⁻	0.91*				
H ⁺	0.91*				
NH ₃	0.05				
BLD					
PM ₁₀	0.90*	0.91*			
PM _{2.5}	0.91*	0.94*			
PM _{2.5-10}	0.38*	0.34*			
SO ₄ ²⁻	0.71*	0.63*			
H ⁺	0.76*	0.79*			
NH ₃	0.05	0.80*			
RES					
PM ₁₀	0.95*	0.97*	0.94*		
PM _{2.5}	0.95*	0.98*	0.96*		
PM _{2.5-10}	0.36*	0.47*	0.73*		
SO ₄ ²⁻	0.87*	0.90*	0.73*		
H ⁺	0.88*	0.97*	0.84*		
NH ₃	0.02	0.65*	0.59*		
LIB					
PM ₁₀	0.96*	0.98*	0.92*	0.98*	
PM _{2.5}	0.96*	0.98*	0.93*	0.98*	
PM _{2.5-10}	0.36*	0.48*	0.37*	0.58*	
SO ₄ ²⁻	0.91*	0.93*	0.68*	0.93*	
H ⁺	0.88*	0.97*	0.84*	0.97*	
NH ₃	0.08	0.84*	0.79*	0.76*	
MLK					
PM ₁₀	0.68*	0.64*	0.66*	0.70*	0.69*
PM _{2.5}	0.70*	0.69*	0.71*	0.77*	0.71*
PM _{2.5-10}	0.11	0.26	0.30	0.02	0.22
SO ₄ ²⁻	0.73*	0.84*	0.56*	0.79*	0.79*
H ⁺	0.86*	0.89*	0.77*	0.86*	0.87*
NH ₃	-0.07	0.55*	0.67*	0.42*	0.57*

Abbreviations: PM₁₀, particulate matter with aerodynamic diameters <10 μm; PM_{2.5}, particulate matter with aerodynamic diameters <2.5 μm; SVN, Seven Corners, VA; BLD, Bladensburg, MD; RES, reservoir; LIB, West End Library; MLK, Martin Luther King Library; CUB, Cub Run, VA.

**p*<0.05.

Washington may indicate the importance of other non-SO₄²⁻ particulate sources in the metropolitan Washington area. Support for this hypothesis is provided by PM₁₀ and PM_{2.5} concentrations measured simultaneously in Philadelphia during the summer of 1994. As shown in Figure 4, PM₁₀ and PM_{2.5} concentrations in Washington and Philadelphia were highly correlated over the summer ($r = 0.76$ for both PM₁₀ and PM_{2.5}), which is consistent with the fact that the two cities are impacted by similar

regional SO₄²⁻ sources and meteorological conditions. At the same time, the mean PM_{2.5} concentration in Washington was higher than that in Philadelphia, suggesting that Washington was impacted by additional non-SO₄²⁻-related PM_{2.5} sources. The impact of these additional PM_{2.5} sources was small, however, as the mean PM_{2.5} concentration in Washington was only 3.2 µg/m³ higher than that in Philadelphia.

PM₁₀, PM_{2.5}, and SO₄²⁻ concentrations were strongly correlated with one another,

indicating that variability in PM₁₀ concentrations was driven primarily by corresponding variability in PM_{2.5} and SO₄²⁻ levels. Similarly, results indicate that variability in PM_{2.5} concentrations was driven primarily by variability in SO₄²⁻ levels. As would be expected from this interdependence, the spatial behavior of PM₁₀, PM_{2.5}, and SO₄²⁻ was identical within the Washington, D.C. area, as the concentrations of these species were all uniform across the city. This spatial uniformity suggests that a single stationary ambient monitoring site, which is typically used by epidemiologic studies of particulate matter, will be sufficient to estimate the ambient exposures for these particulate measures.

Similar spatial uniformity was also found for H⁺, which was unexpected, since results from Philadelphia (1), New York (3), and Toronto (4) consistently showed H⁺ concentrations to vary spatially. Reasons for this discrepancy are not apparent and are complicated by the fact that NH₃ concentrations were found to vary spatially, as expected. It is possible that the impact of NH₃ on site H⁺ concentrations was less pronounced in Washington than in other cities due to higher overall H⁺ levels. Because the mean H⁺ concentration at the background CUB site (2.48 µg/m³) in Washington was almost two times higher than that at the background site in Philadelphia (1.31 µg/m³), differences in the amount of H⁺ neutralized at the sites may have been small relative to the overall H⁺ concentration. The observed spatial uniformity suggests that a single SAM site monitor will sufficiently estimate mean outdoor H⁺ concentrations across the metropolitan Washington, D.C. area. It is important to note, however, that even though mean concentrations did not differ, H⁺ concentrations on some days varied substantially across the city (Fig. 5), differing by as much as 500%. As a result, errors associated with single SAM site exposure estimates may be high and may necessitate the use of additional area monitors for H⁺.

In contrast, spatial variation was found for coarse particles because concentrations at the CUB site were significantly higher than those at the SVN site. This spatial variation, however, was less pronounced than that in Philadelphia and, unlike Philadelphia, was not related to population density. These results suggest that coarse particle concentrations measured at a single SAM site will be poor estimators of the coarse particle concentrations and exposures across the metropolitan Washington area. Furthermore, the observed weak site-to-site correlations for coarse particles indicate that single SAM site measurements will also be poor indicators of

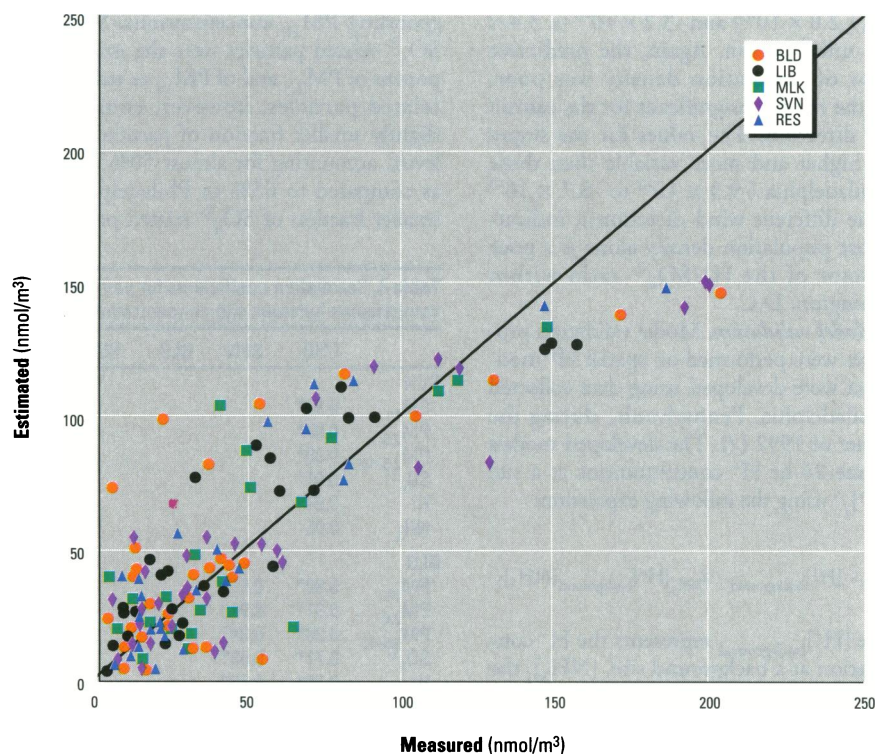


Figure 3. Estimated versus measured ambient H⁺ concentrations by site. Abbreviations: BLD, Bladensburg, MD; LIB, West End Library; MLK, Martin Luther King Library; SVN, Seven Corners, VA; RES, reservoir. The solid line represents the 1:1 line.

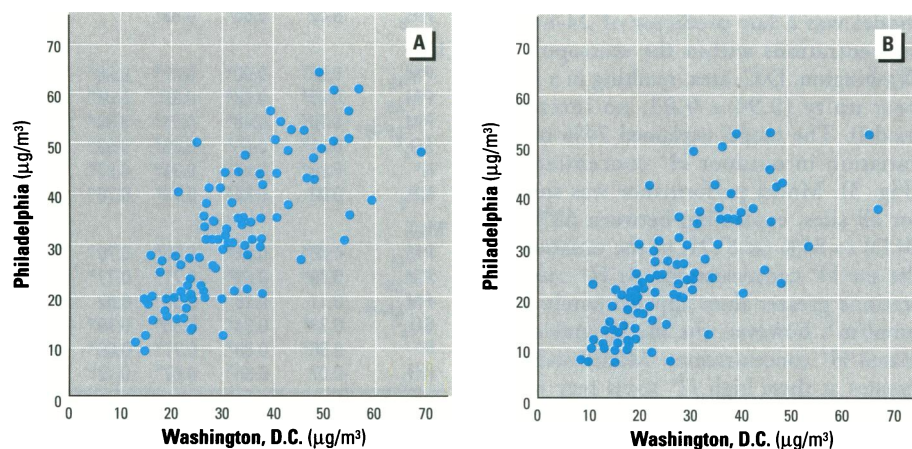


Figure 4. Concentrations of (A) PM₁₀ and (B) PM_{2.5} measured simultaneously in Philadelphia, Pennsylvania, (PBY site) and Washington, D.C., (LIB site) during the summer of 1994. Abbreviations: PM₁₀, particulate matter with aerodynamic diameters <10 µm; PM_{2.5}, particulate matter with aerodynamic diameters <2.5 µm. Data for Philadelphia from Suh et al. (7).

coarse particle exposures because errors associated with these exposure estimates will be large, relative to the observed low mean coarse particle concentrations at the sites. Our ability to estimate coarse particle exposures for epidemiologic studies may be further complicated by the fact that local coarse particle sources in Washington probably encompass a variety of source types. At the MLK site, for example, coarse particles probably originated from nearby motor vehicle traffic, while at the CUB site, coarse particles probably arose from wind blown dust. This heterogeneity in source types is likely to reduce our ability to detect exposure-disease relationships for $PM_{2.5-10}$ since the impact of coarse particles on human health is likely to differ by source type. More detailed analysis of coarse particles and source types is not possible with the Washington data because coarse particle concentrations were low and were not measured directly. As a result, the precision of their measurements was relatively low. This imprecision of coarse particle measurements also makes the interpretation of coarse particle results difficult.

With the exception of NH_3 , population density was an insignificant factor in determining the spatial pattern in summertime pollutant concentrations. This result again conflicts with that from Philadelphia,

which found population density to be an important determinant of summertime $PM_{2.5-10}$, H^+ , and NH_3 concentrations and in H^+/SO_4^{2-} ratios. The relative unimportance of population density in Washington may be due to the rapid changes in population density that occur over short distances within the Washington metropolitan area. In addition, the population density of Washington may exhibit greater temporal variability, especially during the summer when tourism is at its peak. As a result, population density numbers based on census tract data (as used in this analysis) may not appropriately reflect the population densities at the sites. This may be particularly true for the RES site, which was located in a reservoir/park area. Its population density, as obtained using a radius of 0.5 miles, indicated that the site was located in a densely populated area. However, the immediate area surrounding the RES site was relatively devoid of any streets, houses, and other buildings, suggesting that the effective population density for this site was actually much lower. This overestimation would result in misclassification bias, which would obscure any associations between H^+ or NH_3 concentrations and population density. Evidence for this is provided by the fact that when data for the RES site were

excluded from the analysis, population density was found to explain a larger percentage of the variability in NH_3 concentrations and, to a lesser extent, in H^+/SO_4^{2-} ratios as well.

Resolution of many of the issues raised by data from Washington and Philadelphia will be possible when data from Nashville, Tennessee, and Boston, Massachusetts, the third and fourth of the MAACS cities, are analyzed. Together, results from the MAACS cities should provide a clearer and more comprehensive understanding of the behavior of particulate matter in large metropolitan areas, and with this, a better understanding of the health impacts of particulate matter as well.

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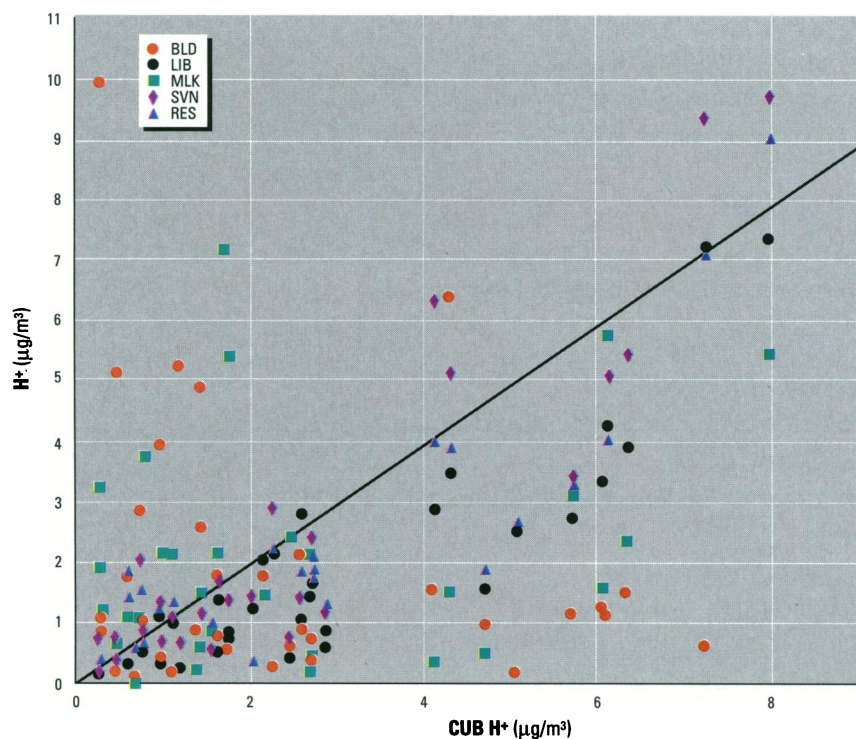


Figure 5. H^+ concentrations measured at the urban sites versus H^+ concentrations measured at the CUB site. Abbreviations: CUB, Cub Run, VA; LIB, West End Library; MLK, Martin Luther King Library; RES, reservoir; SVN, Seven Corners, VA; BLD, Bladensburg, MD. H^+ concentrations are expressed as equivalent H_2SO_4 . The solid line represents the 1:1 line.

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