

# Exposures to Acidic Aerosols

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Ambient monitoring of acid aerosols in four U.S. cities and in a rural region of southern Ontario clearly show distinct periods of strong acidity. Measurements made in Kingston, TN, and Steubenville, OH, resulted in 24-hr H<sup>+</sup> ion concentrations exceeding 100 nmole/m<sup>3</sup> more than 10 times during summer months. Periods of elevated acidic aerosols occur less frequently in winter months. The H<sup>+</sup> determined during episodic conditions in southern Ontario indicates that respiratory tract deposition can exceed the effects level reported in clinical studies. Observed 12-hr H<sup>+</sup> concentrations exceeded 550 nmole/m<sup>3</sup> (approximately 27 μg/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>). The maximum estimated 1-hr concentration exceeded 1500 nmole/m<sup>3</sup> for H<sup>+</sup> ions. At these concentrations, an active child might receive more than 2000 nmole of H<sup>+</sup> ion in 12 hr and in excess of 900 nmole during the hour when H<sub>2</sub>SO<sub>4</sub> exceeded 50 μg/m<sup>3</sup>.

## Introduction

It is now established that atmospheric pollutants can be quite acidic. The precursors of these acidic species, sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>2</sub>), originate mostly from fossil fuel combustion sources. Unfortunately, there are only a limited number of locations where aerosol acidity measurements have been conducted. Figure 1 summarizes these studies, most of which were of a short duration and were performed in the summer months. Sampling durations, intervals, and frequency varied as did the instrumentation and methods. Figure 1 provides an indication of the range in equivalent sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) concentrations expressed in micrograms per cubic meter equivalents of H<sub>2</sub>SO<sub>4</sub> obtained from these studies. More details will be reported in the EPA document "An Acid Aerosols Issue Paper: Health Effects and Aerometrics" (1).

In contrast to short duration studies, the Harvard School of Public Health has been engaged in an intensive effort to characterize ambient acidic aerosol concentrations as part of its prospective epidemiologic study on chronic respiratory effects of air pollution. Acid aerosol measurements were conducted as part of the ongoing Harvard Six-Cities Study (2,3) and Health and Welfare's Canada Acute Respiratory Effects Studies, CARES 1986 (4,5).

Acid aerosol measurements conducted as part of the

Harvard Six-Cities Study involved daily measurements of aerosol strong acidity and have been conducted for a minimum of nine consecutive months in four U.S. cities: Portage, WI; St. Louis, MO; Steubenville, OH; and Kingston, TN. The methods for measuring strong acidity of atmospheric aerosols and its temporal variation in Kingston, TN, and St. Louis, MO, are reported in Koutrakis et al. (3). Figure 2 summarizes the distributions of strong acidic aerosol reported as H<sup>+</sup> and equivalent H<sub>2</sub>SO<sub>4</sub> concentrations for these four cities.

Kingston/Harriman and St. Louis were monitored December 1985 through early September 1986. Steubenville and Portage were monitored from November 1986 to early September 1987. Despite possible year-to-year differences in atmospheric acidity due to variations in source emissions, formation, and neutralization processes, the acid content of fine aerosols appears different in these cities. In St. Louis and Portage aerosols are less acidic than in Kingston and Steubenville. This observation is intriguing because Kingston and St. Louis experience similar concentrations of fine particles (d<sub>a</sub> < 2.5 μm) and aerosol sulfate. It is difficult to fully understand the apparent differences in the measured aerosol activity, as ambient ammonia (NH<sub>3</sub>) measurements were not included in the sampling scheme. Such information will lead to a better understanding of the spatial variations in acid aerosol content.

Examining the plots of daily H<sup>+</sup> ion concentrations reveals a seasonal pattern with lower concentrations in the winter months (Fig. 3). In all four cities, concentrations in the winter months are substantially lower

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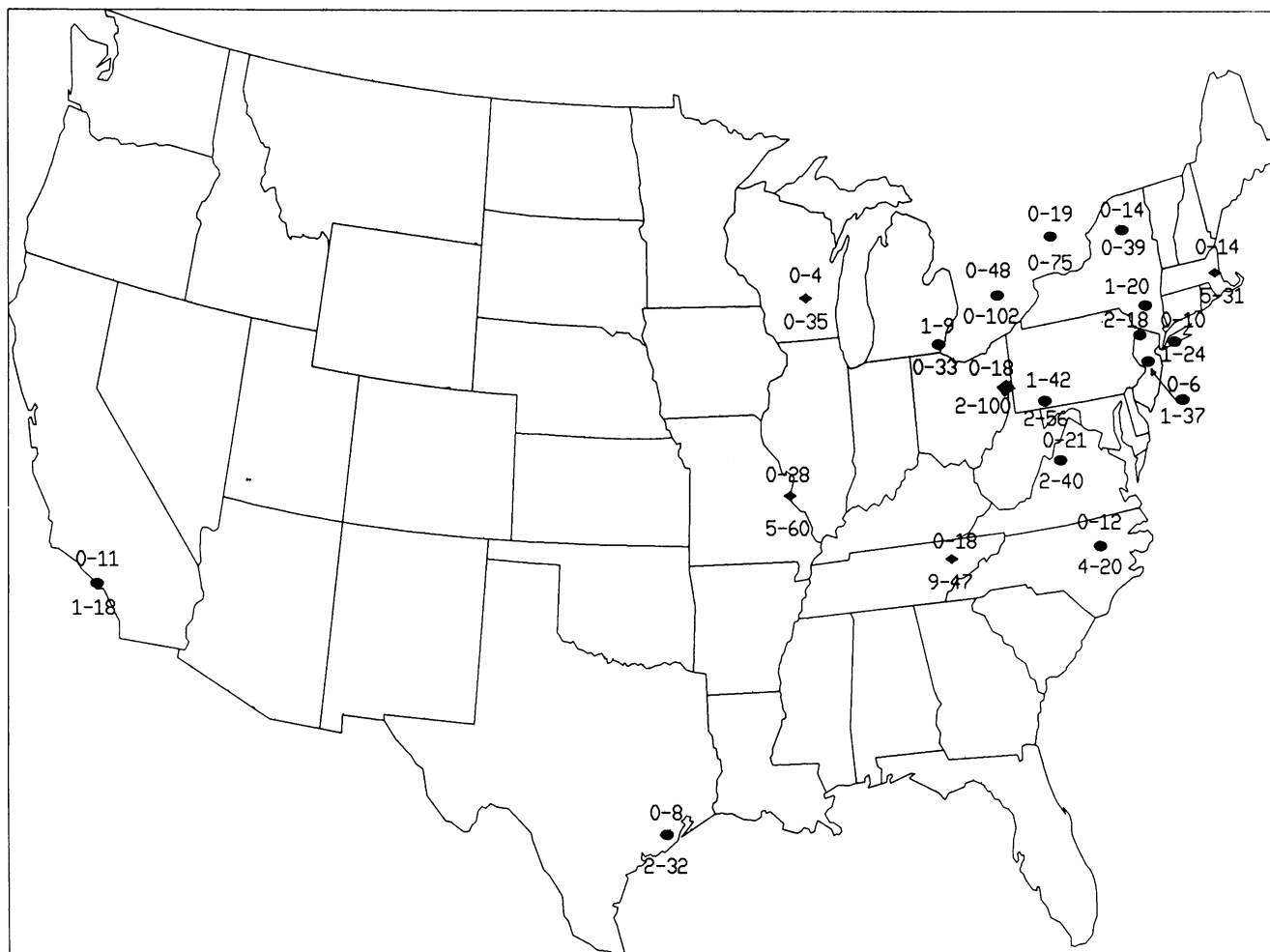


FIGURE 1. Summary of studies in the U.S. and Canada reporting ambient concentrations of acidic aerosols (expressed as  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$ ) and particulate sulfate ( $\mu\text{g}/\text{m}^3$ ). Range of sulfuric acid concentrations above location indicator ( $\blacklozenge$ ,  $\bullet$ ); particulate sulfur concentrations below. Averaging times varied from 1 hr to 24 hr.

than in late spring and the summer months. However, daily  $\text{H}^+$  concentrations two to four times the winter season average were observed in Kingston and Steubenville.

The frequency of elevated 24-hr  $\text{H}^+$  observations was also quite different at the four sites. Steubenville had 8 summer days where  $\text{H}^+$  ion concentrations exceeded  $100 \text{ nmole}/\text{m}^3$ , Kingston had 13 days, St. Louis had only 1, and Portage had none. These results imply that distinction in acidic aerosol concentrations among cities and across seasons have important implications to exposures.

## Exposures

Exposures to acidic aerosols for the Harvard's Six-Cities Study and the Canadian Acute Respiratory Effects Study (CARES) can be estimated by using microenvironmental exposure model concepts (6,7). Ott proposed that an individual's exposure could be

calculated from the time-weighted sum of concentrations experienced in different microenvironments. Letz et al. developed a modeling scheme that used the mean and variance of concentrations in different locations and the mean time and variance that populations spend in those locations to assess the mean and variance in exposure. This approach has been expanded to a full Monte Carlo simulation of exposures. Duan recognized the complicating feature of covariance between the time people were in certain locations and the concentrations in these locations (8). One approach to account for the interaction of human activities and contaminant generation is to subdivide the microenvironments into smaller subsets.

Acidic aerosols occurring indoors are assumed to originate from outdoors. Indoors, unvented fuel combustion may produce some nitrous and nitric acid vapors or even sulfuric acid aerosols; however, there are insufficient measurements to quantify either acid production or neutralization indoors. Indoor gaseous ammonia ( $\text{NH}_3$ ) concentration is expected to be higher

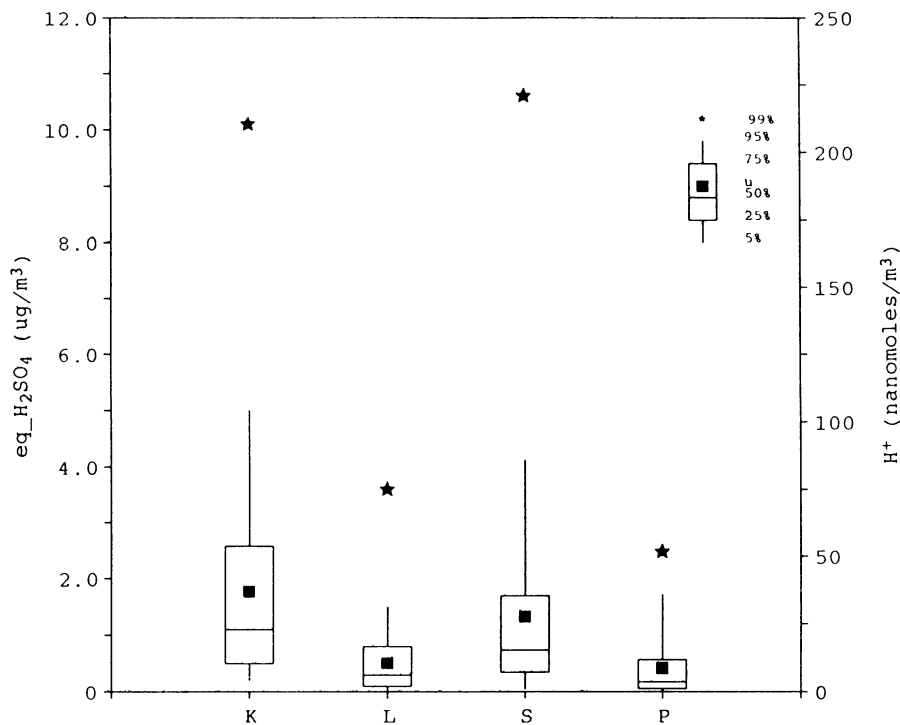


Figure 2. Distributions of daily acid aerosol concentrations expressed as  $H^+$  ion ( $\text{nmole}/\text{m}^3$ ) and equivalent  $\text{H}_2\text{SO}_4$  ( $\mu\text{g}/\text{m}^3$ ) in four U.S. cities. K: Kingston, TN (1986); L: St. Louis, MO (1986); S: Steubenville, OH (1987); P: Portage, WI (1987).

compared to outdoors since it is produced by people, pets, and household products. When air exchange rates are lower (winter months), neutralization of ambient acidic species indoors is more likely because of increased residence times. In the absence of direct measurement during the summer months, indoor concentrations can be proportioned to outdoor concentrations using the penetration ratio of conserved outdoor tracers. There are several reports of indoor to outdoor ratios of fine aerosol trace elements (9–12). Using the results of Spengler et al. (13) and Dockery and Spengler (14) for fine particulate sulfates, a typical wintertime ratio of 0.4 and summertime ratio of 0.8 allow estimation of the amount of outdoor originated acidic aerosol in the indoor environment. These values are consistent with those of Yocum, who found that sulfates have I/O ratios in the range of 0.5 to 1.0 (15). Indoor sulfate concentrations may be affected by match use and gas cooking. Air conditioning may reduce the I/O ratios.

The outdoor microenvironment can be considered as two distinct environments: day and night. The distinction is important because 24-hr strong acidity measurements will underestimate elevated concentrations that are commonly observed during the daytime hours under convective mixing. At night, the acidic aerosol near the ground tends to be neutralized by ammonia from ground level sources. The day/night average ratio of  $H^+$  ion concentrations was 1.6 over the 42 summer days of acidic aerosol monitoring in southern Ontario (5).

The second reason for distinguishing between daytime and nighttime has to do with time/activity patterns. Children are more likely to be outdoors during the day, particularly in the summer. The time that an individual spends in particular locations or doing certain activities will contribute to the overall time-weighted exposure. Information on the time-activity patterns of children is limited. Time activity studies have been conducted mostly on adults (16–19).

To understand the time-use patterns of children with the specific intention to study air pollution exposures, a survey was conducted involving approximately 300 elementary-school-age youngsters. A survey was conducted in Portage, WI, and Steubenville, OH, during the winter and summer of 1987. A combined recall interview and prospective self-administered diary was used. While in the home, trained interviewers elicited recall of the child's activities for the previous day up until the time of the interview. The child and/or mother were instructed to complete the diary through the following day. The diary was designed to account for every hour in 15-min time resolution over a 3-day period. The locations of interest were home (by room), outdoors, transportation (by mode), school, and other indoor locations. Table 1 summarizes the percentages of time that children spent in various locations.

A microenvironmental exposure model for acidic aerosols involves just two primary locations: indoors and outdoors. Therefore, time-activity patterns for children in Portage, WI, and Steubenville, OH, have

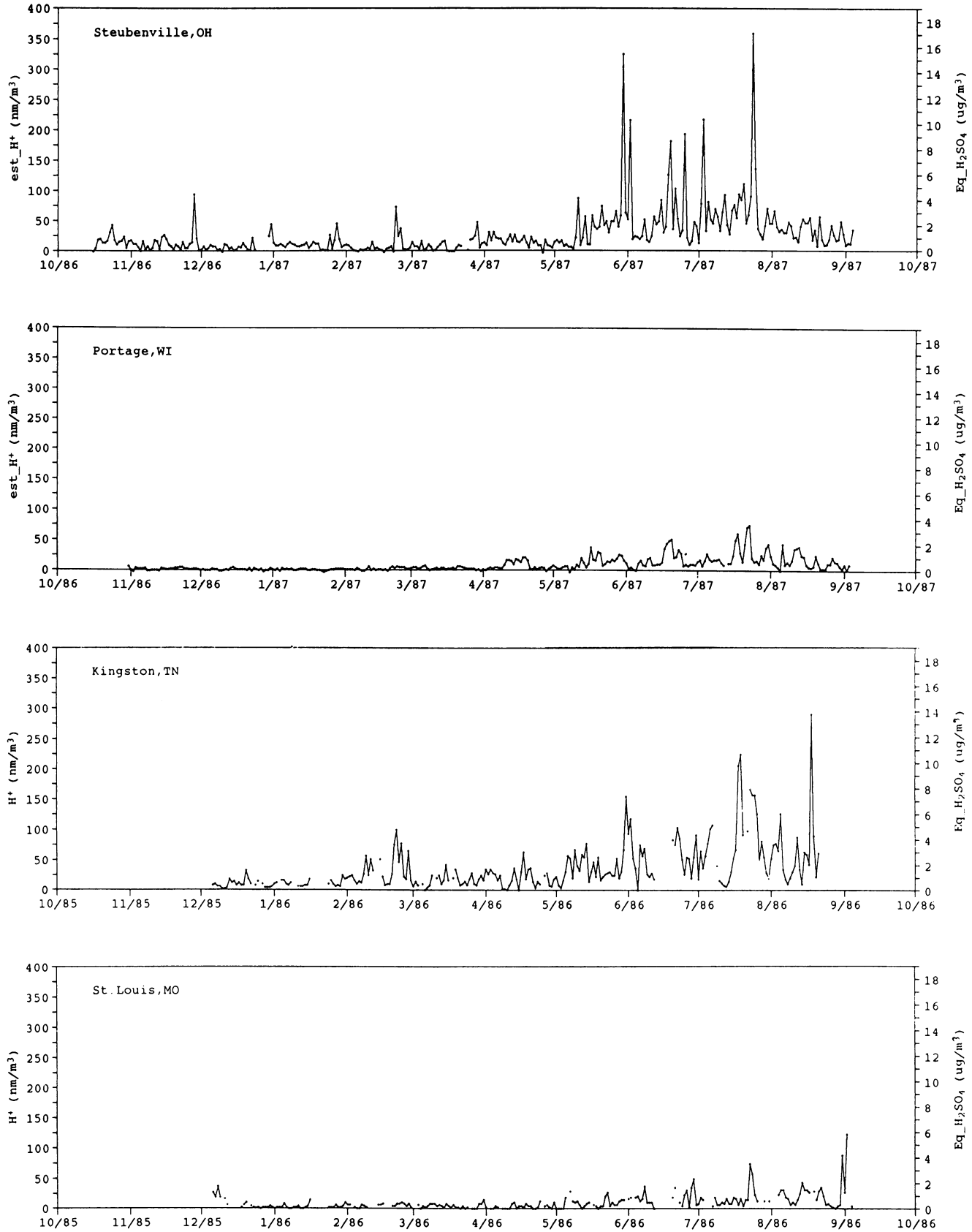


FIGURE 3. Daily acid aerosol concentrations expressed as  $H^+$  ion (nmole/m<sup>3</sup>) and equivalent  $H_2SO_4$  concentration ( $\mu\text{g}/\text{m}^3$ ) in four U.S. cities.

Table 1. Percent of time a child spends in various locations.<sup>a</sup>

Location	Portage		Steubenville	
	Winter <sup>b</sup>	Summer <sup>c</sup>	Winter	Summer
Home	65.9	61.5	64.9	64.0
School	20.2	10.9	20.2	11.1
Transit	3.2	3.5	2.7	2.0
Outdoors	5.4	14.6	3.8	16.0
Other indoors	5.3	9.5	8.4	6.9

<sup>a</sup>Children, aged 8 to 12.

<sup>b</sup>Winter, January–March.

<sup>c</sup>Summer, May–August.

been simplified to just indoor and outdoor time. The weekend versus weekday distinctions have been dropped. The diary does provide a breakdown of activities and locations by time of day. Ambient acidity is usually greater during daytime hours, particularly in spring and summer. Also, it is expected that the time a child spends outdoors will covary with H<sup>+</sup> concentrations. Therefore, the microenvironmental model for H<sup>+</sup> ion exposure is composed of winter, summer daytime, and summer nighttime components. Exposure (*E*), the effective exposure in equivalent micrograms per cubic meter, can be expressed in terms of the outdoor concentration, the penetration indoors, and the fractional times spent in the two microenvironments.

$$E = C_{ow} t_{ow} + f_w C_{ow} t_{iw} + C_{osd} t_{osd} + f_s C_{osd} t_{isd} + C_{osn} t_{osn} + f_s C_{osn} t_{isn} \quad [1]$$

The mean annual seasonal, daily, or hourly exposure to H<sup>+</sup> could be estimated from Equation 1. Knowing the mean and standard deviations of each term will permit the estimation of a distribution of exposures expected in a population of children (20). The terms are defined as follows: *C*<sub>o</sub>, outdoor H<sup>+</sup> ion concentration in nmole/m<sup>3</sup> for (w) winter, (sd) summer day, (sn) summer night; *f*, fractional penetration of acidic aerosol indoors for (w) winter and (s) summer conditions, dimensionless; *t*, fractional proportion of time a child spends (o) outdoors, (i) indoors in the (w) winter, in (sd) summer days, and in (sn) summer nights, dimensionless. The mean and standard deviations for each of these terms are derived from data obtained in our studies. Table 2 gives the values used in the model to estimate acidic aerosol exposures for children living in Portage, WI, and Steubenville, OH.

Table 3 displays the distributions of H<sup>+</sup> exposures for children living in Portage, WI, and Steubenville, OH. Distributions for annual, as well as for summer daytime, exposures are presented. As expected, the acidic aerosol exposures in these populations are different in the mean and extremes of the distributions. The distinction is quite clear when comparing the expected exposures during summer daytime periods. It is worth noting these differences because the distributions of expected annual exposures overlap in the upper

Table 2. Input parameters for a microenvironmental model to estimate seasonal and annual exposures to sulfuric acid.

Parameter	Portage		Steubenville	
	Mean	SD	Mean	SD
<i>C</i> <sub>ow</sub>	2.7	± 3.9	11.7	± 13.2
<i>C</i> <sub>osd</sub>	21.2	± 10.0	63.03	± 37.74
<i>C</i> <sub>osn</sub>	12.7	± 10.0	37.82	± 37.74
<i>f</i> <sub>w</sub>	0.4	± 0.1	0.4	± 0.1
<i>f</i> <sub>s</sub>	0.8	± 0.1	0.8	± 0.1
<i>t</i> <sub>iw</sub>	0.94	± 0.038	0.96	± 0.047
<i>t</i> <sub>ow</sub>	0.06	± 0.038	0.04	± 0.054
<i>t</i> <sub>isd</sub>	0.72	± 0.199	0.73	± 0.23
<i>t</i> <sub>osd</sub>	0.27	± 0.195	0.28	± 0.228
<i>t</i> <sub>isn</sub>	0.97	± 0.064	0.95	± 0.093
<i>t</i> <sub>osn</sub>	0.03	± 0.042	0.05	± 0.093

10% of Portage children and in the lower 25% of Steubenville children. During summer days, when most of the acidic aerosol exposure is expected to occur, these populations are more distinct.

## Short-Term Exposures

Long-term acidic aerosol exposures may not be the exposure measure most relevant to respiratory effects and pulmonary changes. Studies of airway reactivity, mucociliary clearance, and pulmonary function in humans and animals have investigated the influence of acidified and neutralized aerosols (1).

Drawing upon the more recent studies, some insight on the relevant exposure parameters can be derived (1). In human subject studies where controlled exposures were done in chambers or with mouthpieces, the exposure durations were typically short. During some exposures, subjects engaged in moderate exercise to increase their ventilation rates. Particle size, humidity conditions, and acidic species varied among studies.

General observations indicate that changes in pulmonary function and airway resistance occurred at lower concentrations in asthmatics than in non-asthmatics. Also, some studies showed a delayed effect where symptoms were not immediately associated with exposures but were apparent a week later (21). Observations of delayed effects have also been noted by Utell and Spektor (22,23).

Asthmatics were the subject of several clinical studies. Utell et al., evoked an increase in airway resistance and a change in forced expired ventilation (FEV<sub>1</sub>) in adult asthmatics that was consistent with increasing dose of acidic aerosol (24,25) acidity. That is, H<sub>2</sub>SO<sub>4</sub> evoked more response than did ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>). While changes were noted even at 100 μg/m<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub>, consistent and significant responses were established for exposure regimes of 450 μg/m<sup>3</sup> and higher. These findings are consistent with the notion derived from animal studies, suggesting that the irritant potency is related to titratable H<sup>+</sup> concentration (26,27).

Koenig et al. exposed adolescent asthmatics via a

Table 3. Calculated mean and distribution of H<sup>+</sup> exposures.<sup>a</sup>

Exposure	Mean	SD	5%	10%	25%	50%	75%	90%	95%	99%
Portage										
Winter	1.2	1.9	0.0	0.0	0.1	0.5	1.5	3.3	4.7	9.4
Summer daytime	17.9	10.2	5.2	6.7	10.7	15.9	23.1	31.0	37.1	51.1
Summer nighttime	10.1	8.0	1.4	2.1	4.2	8.1	13.9	20.6	26.3	36.7
Annual average	7.6	3.5	3.0	3.6	5.0	7.1	9.6	12.1	14.1	18.6
Steubenville										
Winter	5.1	6.2	0.1	0.3	1.0	2.9	6.6	12.7	17.4	28.2
Summer daytime	54.6	38.1	11.0	15.5	27.3	45.7	72.8	105.1	128.3	184.9
Summer nighttime	31.2	32.1	1.6	3.2	8.6	21.7	42.6	72.1	92.7	153.6
Annual average	23.9	13.0	8.1	10.1	14.7	21.0	30.6	41.2	49.5	63.6

<sup>a</sup>Mean and distribution in nmole/m<sup>3</sup>.

mouthpiece to 100 µg/m<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> particles with a diameter of 0.6 µg (28). The tests were conducted over 40 min; 30 min the subject was at rest, and 10 min the subject exercised (V<sub>e</sub> = 40 L/min). As a first approximation to inhaled dose, we assumed that the subject had inspired 0.65 m<sup>3</sup> of air during this test. Under the described conditions, this would have yielded H<sup>+</sup> ion dose slightly in excess of 1300 nmole. Koenig reported significant reductions in several pulmonary functions following the H<sub>2</sub>SO<sub>4</sub> exposure. The decreases in pulmonary function exceeded the decreases observed for NaCl aerosol exposure tests.

To compare Koenig's results to those of Utell, we assumed that his subjects had a resting minute ventilation rate of 8 L/min during the 16-min resting exposure. Interestingly, Utell's subjects would have received approximately 1200 nmole of H<sup>+</sup> ion dose while breathing 450 µg/m<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> aerosols. Notwithstanding differences in subjects age, particle size, and humidity conditions, these two independent studies might be reinterpreted as indicating similar results when the exposure measure is expressed as total delivered H<sup>+</sup> ion. This discussion is relevant to understanding the exposures experienced by children in ambient settings.

During the summer of 1986, Health and Welfare Canada conducted a study of air pollution effects on pulmonary function changes and respiratory symptoms in 112 young girls attending an outdoor camp (4,29). Camp Kiawa is located on the north shore of Lake Erie, 60 km west of Buffalo, NY. Ambient 12-hr H<sup>+</sup> ion concentrations as well as particulate mass, ozone, and other air contaminants were measured over 42 days (5). Figure 4 plots the 12-hr averaged aerosol strong acidity expressed in terms of H<sup>+</sup> concentrations in nmole/m<sup>3</sup> and its equivalent H<sub>2</sub>SO<sub>4</sub> in µg/m<sup>3</sup>. The 12-hr periods distinguished daytime (8:00 A.M.–8:00 P.M.) versus nighttime (8:00 A.M.–8:00 P.M.) conditions.

Late in July an extreme air pollution event occurred. Ozone and fine particulate sulfate concentrations increased sharply in the late morning of July 24. After decreasing slightly over night, the levels increased during the morning of July 25. Ozone averaged about 120 ppb for 12 hr during the daytime of July 25. The continuous particulate sulfate monitor (30) indicated

a maximum hourly sulfate concentration of greater than 100 µg/m<sup>3</sup> with sulfuric acid concentrations approaching 50 µg/m<sup>3</sup> between noon and 1:00 P.M. on July 25 (Fig. 5). The continuous particulate sulfate instrument cannot distinguish between the ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] and (NH<sub>4</sub>)HSO<sub>4</sub>. However, when measurable levels of sulfuric acid are present, it implies that the particulate sulfur is in an acidic form, being only partly neutralized by gaseous ammonia.

The 12-hr average concentrations of H<sup>+</sup> ion over the 36 hr comprising this event were 200, 560, and 250 nmole/m<sup>3</sup>. During the most extreme hour of this event H<sub>2</sub>SO<sub>4</sub> made up approximately 50% of the total particulate sulfate measured. An upper bound on the H<sup>+</sup> ion concentration for this hour can be estimated by assuming that total sulfate aerosols consisted of a mixture of 50% H<sub>2</sub>SO<sub>4</sub> and 50% (NH<sub>4</sub>)HSO<sub>4</sub>. On this assumption, which is supported by making a similar calculation over the 12-hr period, the 1-hr concentration would be 1555 nmole/m<sup>3</sup>.

In order to calculate the H<sup>+</sup> exposure to children during this episode, we would have to know the following: concentration of H<sup>+</sup>; minute ventilation rate of the child or total inhalation volume of the time period of interest; fraction of inhaled aerosol deposited in the respiratory tract. A child's minute volume depends on

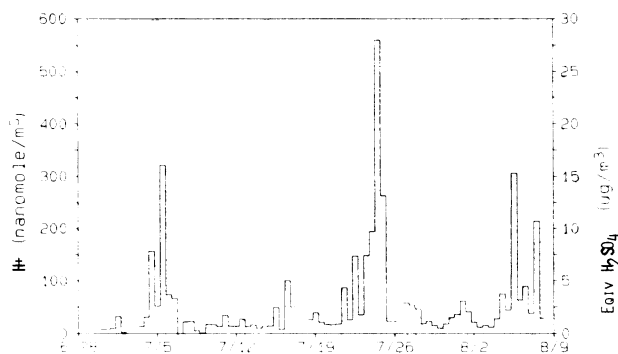


FIGURE 4. Twelve-hour acid aerosol concentrations expressed as H<sup>+</sup> ion (nmole/m<sup>3</sup>) and equivalent H<sub>2</sub>SO<sub>4</sub> concentration (µg/m<sup>3</sup>) over the 42-day sampling period near Dunnville, Ontario, during the summer of 1986.

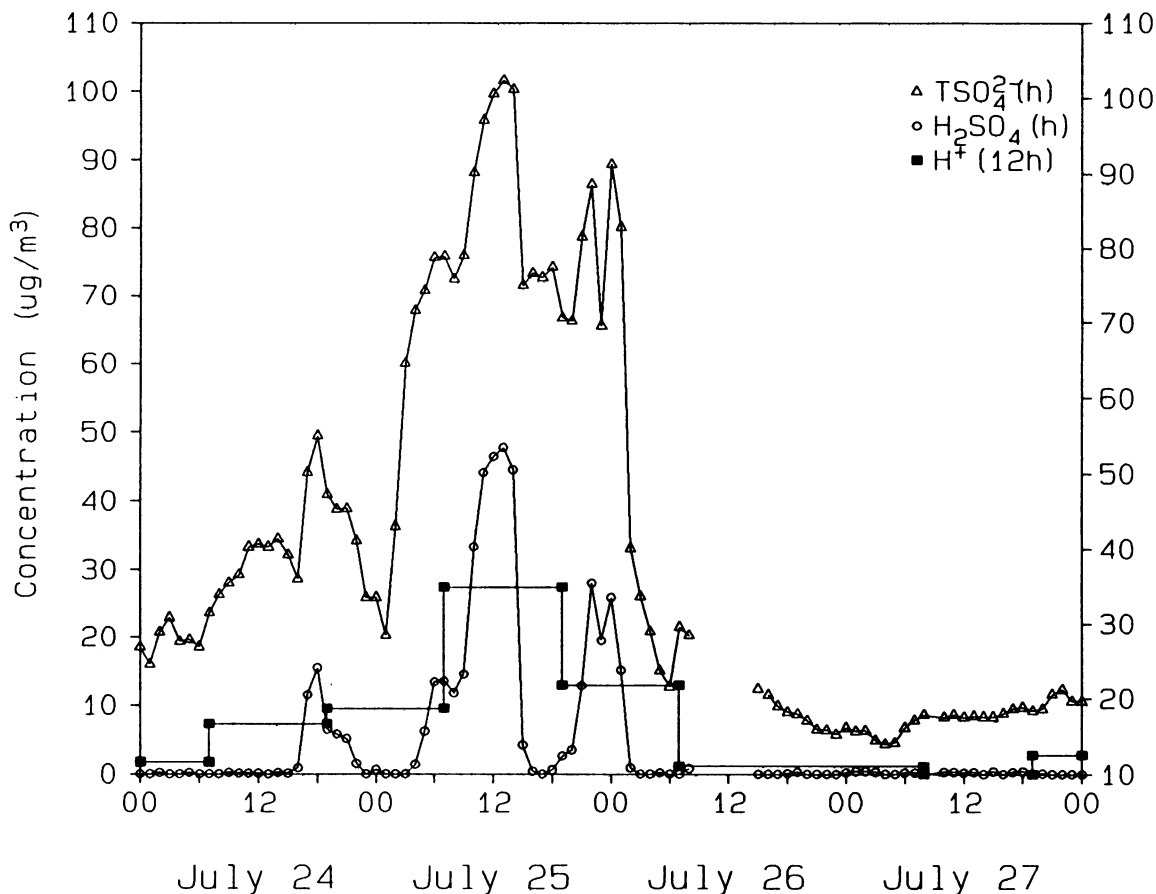


FIGURE 5. Hourly concentration of total particulate sulfate ( $\mu\text{g}/\text{m}^3$ ) and strong acidity expressed as equivalent  $\text{H}_2\text{SO}_4$  ( $\mu\text{g}/\text{m}^3$ ) over a 72-hr period late July 1986 near Dunnville, Ontario. Twelve-hour strong acid particle concentrations  $\text{H}^+$  are expressed as equivalent  $\text{H}_2\text{SO}_4$  ( $\mu\text{g}/\text{m}^3$ ).

factors such as sex, age, height, weight, basal metabolism, and physical activity level. During this camp study, some of the children volunteered to wear portable heart rate monitors and to have their heart rates and ventilation rates tested under standardized exercise routines. The details of these tests will be reported elsewhere. Here, we will use only the group averaged results from the heart beat monitoring. Applying an empirical relationship derived by Colucci (31), minute ventilation ( $V_e$ ) for children (average age was 12) is expressed as a function of heart rate (BPM):

$$V_e = 1.635 \exp(0.0185 \text{ BPM}) \quad [2]$$

A heart rate of 65 BPM corresponds to 5.5 L/min, which is consistent with other studies (32,33). The group's average heart rate varied over the course of an active day (9:00 A.M.–7:00 P.M.). The overall group average was 107 BPM with a standard deviation of 18. The hour with the highest group average BPM was 7:00 P.M. with 113 BPM. The hour with the lowest value was 11:00 A.M. with 101 BPM.

Particle deposition in the lungs depended on particle size, solubility, shape, breathing patterns, and lung morphology (34). Koutrakis et al. have shown that the

$\text{H}^+$  at the camp site was associated with particles having geometric mean aerodynamic diameters between 0.23 and 0.64  $\mu\text{m}$  (35). Based on particle deposition curves for the respiratory tract, an overall 40% retention might be expected with 80% of retained particles depositing in the respiratory bronchioles and alveoli (36). However, there is little direct evidence on particle deposition in young children. Smaller airways, combined oral and nasal breathing, increased ventilation during exercise, and inhalation of water-soluble acidic aerosols may greatly influence overall retention and compartment-specific retention. Because diffusional deposition increases as bronchioles decrease in diameter and because hygroscopic aerosols should have enhanced deposition, the actual lung retention of acidic particles may be closer to 60% (37).

The delivered dose of  $\text{H}^+$  can be calculated from the following equation:

$$D = \sum r V_e t [\text{H}^+] \quad [3]$$

Where  $D$  is the dose of  $\text{H}^+$  ion delivered to respiratory tract (nmole);  $r$ , aerosol retention in lung compartment (unitless);  $V_e$ , minute ventilation rate (L/

Table 4. Calculated 12-hr averaged H<sup>+</sup> ion dose to the respiratory tract.<sup>a</sup>

Mean	SD	5%	10%	25%	50%	75%	90%	95%	99%
2153	610	1242	1391	1720	2108	2532	2984	3243	3735

min)/1000;  $t$ , exposure time (min);  $[H^+]$ , hydrogen ion concentration (nmole/m<sup>3</sup>).

By way of illustration, we can calculate the H<sup>+</sup> deposition for the highest hourly concentration of H<sub>2</sub>SO<sub>4</sub> and total particulate sulfate occurring at 1:00 P.M. on July 25 at Camp Kiawa. As previously calculated, the upper bound for H<sup>+</sup> ion concentration is estimated at 1555 nmole/m<sup>3</sup>. Further, assume that a child was exercising at a moderate level and ventilating at 15 L/min. With 60% retention, the child would receive approximately 840 nmole of H<sup>+</sup>. A child ventilating at 20 L/min would receive approximately 1100 nmole.

To further illustrate the range of dose delivered to campers during the 12 daytime hours when the concentrations were highest, Equation 3 can be recast in a form similar to the exposure equation. In this case, we assume that the retention function,  $r$ , is 0.6 with a 0.1 SD. Concentration is given as the 12-hr integrated value of 550 nmole/m<sup>3</sup>. Time,  $t$ , is 720 min. Ventilation is calculated by a child's heart rate. Based on measurements during the day, the BPM averaged 107 with an SD of 18. From Equation 2 this would translate to a minute ventilation of approximately 11.5 L/min. Calculating the SD is not straightforward because of the exponential form. An SD increase in BPM results in 5 L/min increase in the ventilation rate, while a two SD decrease results in 5 L/min decrease in the minute ventilation. Because the calculated average minute ventilation appears too high for these young girls, age 7 to 13, we adjusted the daytime ventilation rate to 9 L/min with a 2 L/min SD. Table 4 presents the distribution of expected H<sup>+</sup> ion deposition in a population of children that results from a 12-hr ambient exposure of 550 nmole/m<sup>3</sup>. The calculated averaged H<sup>+</sup> ion dose is 2150 nmole. Approximately 75% would have been delivered during the 5 hr of highest concentration. Given the expected variation in ventilation and particle deposition, 90% of the children would experience an H<sup>+</sup> dose ranging between 1240 and 3240 nmole.

## Discussion

This paper presents evidence that the ambient aerosols can be very acidic. On the average, acidic aerosol concentrations during winter months are quite low. Days with measurable acidity are more prevalent during spring and summer months. Concentrations are substantially higher in the north central locations of Kingston, TN, and Steubenville, OH, than in midwestern locations of St. Louis, MO, and Portage, WI. While the particulate sulfate concentrations in Kingston and St. Louis are similar, the H<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> molar ratios indicate that Kingston aerosols tend to be acidic more often.

Based on the acid aerosol measurements conducted in southern Ontario, aerosols tend to be approximately 60% more acidic during the daytime. Temporal and seasonal differences in acidity and time/activity patterns influence the exposures experienced by populations living in these cities. While a portion of the populations may overlap, there is a distinct difference in annual exposures to acidic aerosols between Portage, WI, and Steubenville, OH.

Intrigued by inconsistencies in the results of human exposure studies and the apparent discrepancy between the ambient concentrations and reported effect levels in clinical studies, we reexamined exposure in terms of delivered dose of aerosol H<sup>+</sup> ions. It turns out that subjects in the Utell et al. study (25) and the Koenig et al. study (28) were experiencing approximately the same airway dose of 1200 nmole H<sup>+</sup> ions at the level evoking a response even though they reported their exposures as 450 μg/m<sup>3</sup> and 100 μg/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> concentrations, respectively.

Finally, it is demonstrated that children engaged in summertime outdoor activities can experience H<sup>+</sup> doses comparable to effects levels reported in human clinical studies. During one prolonged acidic aerosol event occurring in southern Ontario, it was likely that children received an average 1-hr respiratory tract dose of 840 nmole and a 12-hr dose of 2150 nmole H<sup>+</sup> ions. While the actual averaging time for the exposure metric is not established, it does appear that on the basis of dose, actual ambient acid aerosol concentrations can be within the range of exposures evoking responses in human clinical studies.

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