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The Nature and Origins of Acid Summer Haze Air Pollution in Metropolitan Toronto, Ontario

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During July and August of 1986, 1987, and 1988, a field study was conducted of ambient acidic aerosol levels in Toronto, Ontario. Fine particle mass ($d_a < 2.5$ μm) samples were collected twice daily at a central-city site for the determination of particulate-phase strong acidity (H^+) and sulfate ($SO_4^=$). Two additional H^+-monitoring sites were concurrently operated during the summers of 1986 and 1987 to examine the spatial variability of H^+ within the metropolitan area. During the summer of 1986, a quasicontinuous total sulfate/sulfuric acid analyzer was also deployed to allow a determination of the chemical form of H^+. Results indicate that acid aerosol episodes ($H^+ \geq 100$ nmole/m^3) did occur in this city during the summer months, and that H^+ peaks were well correlated with sulfate peaks. Virtually all of the H^+ was found to be present as ammonium bisulfate (NH_4HSO_4). While H^+ concentrations were highly correlated among the three monitoring sites ($r \simeq 0.9$), the highest $H^+/SO_4^=$ ratios prevailed during $SO_4^=$ episode periods and at the least urbanized site. This latter trend was apparently due to greater neutralization of H^+ by local ammonia at the more urbanized sites. Comparisons of day vs night $H^+/SO_4^=$ ratios, an examination of air mass back-trajectories, and contemporaneous H^+ measurements at surrounding sites collectively indicated that transported regional haze air pollution from the United States is a major contributor to the H^+ events recorded within Toronto.

INTRODUCTION

During July and August of 1986, 1987, and 1988, a field survey was conducted of ambient acidic aerosol air pollution levels in the Toronto, Ontario, metropolitan area. Of primary interest was a determination of the ambient levels of strongly acidic particulate-phase hydrogen ion (H^+) during the three summers. In addition, an assessment was made during the summer of 1986 of the chemical form in which this acidic aerosol was present. This determination was made by simultaneously deploying a size-selective particle sampler to determine total particulate hydrogen ion in conjunction with a quasicontinuous total sulfate/sulfuric acid aerosol analyzer. Daily H^+ samples were also collected during the summers of 1987 and 1988 in order to provide information on the representativeness of the 1986 H^+ data, and as inputs for subsequent health effects analyses for all three summers (Thurston *et al.*, 1994).

The primary impetus for conducting this acid aerosol-monitoring program was to follow up on the findings of Bates and Sizto (1983, 1987), who reported associations between elevated sulfate levels and hospital admissions for respiratory

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causes in southern Ontario. In their first study (1983), a significant correlation was found between acute hospital admissions for respiratory disease and daily O_3 and SO_2 concentrations and ambient temperature, and with 1- and 2-day lags of the environmental data. In the subsequent Bates and Sizto study (1987), using a limited body of every sixth day 24-hr average sulfate ($SO_4^=$) data, the 1-day-lagged $SO_4^=$ was found to be the pollution index most highly correlated with summertime asthma and total respiratory admissions. Lippmann (1985) has suggested that sulfate's active agent (i.e., the sulfate component with potentially the highest level of health significance) is the hydrogen ion concentration (H^+). However, past studies indicate that the mix of the chemical forms of sulfate can be highly variable in the atmosphere (e.g., Morandi *et al.*, 1983; Huntzicker *et al.*, 1984; Thurston *et al.*, 1986). The $SO_4^=$ ion is thus thought to be only an indirect indicator of the presence of the H^+ irritant species, since it represents the sum of the concentrations of various sulfate forms with widely differing degrees of acidity.

In eastern North America, aerosols are often dominated in terms of mass by sulfates, especially in the summer months. These sulfates are most commonly found as sulfuric acid (H_2SO_4), ammonium bisulfate (NH_4HSO_4), or ammonium sulfate ($(NH_4)_2SO_4$). At 50% relative humidity, H_2SO_4 is the most strongly acidic sulfate form (pH $\sim$ 1.0), while ammonium bisulfate is roughly half as acidic (pH = 1–2) and ammonium sulfate is very weakly acidic (pH $>$ 5.0) (Committee on Sulfur Oxides, 1978). Thus, ambient sulfates may range from very acidic to only weakly acidic, depending on the proportion of the sulfate present in each of these three species. Although atmospheric sulfate chemistry is complex, potentially including both gaseous and liquid-phase reactions, it can be qualitatively characterized as involving the initial formation of sulfate as H_2SO_4, followed by its neutralization first to NH_4HSO_4 and then to $(NH_4)_2SO_4$. The particulate acidity of ambient aerosols, then, is largely a function of the rate at which H_2SO_4 is being added (by either primary emissions or atmospheric formation via oxidation of SO_2) and the rate at which neutralizing reactions (usually with dissolved ammonia gas, which is extremely soluble in acidified droplets) can convert that H_2SO_4 to a more neutral sulfate species (U.S. EPA, 1982, 1989). Therefore, our working hypothesis is that, in the Bates and Sizto health effects analyses, $SO_4^=$ was serving as an indirect index of the strongly acidic forms of sulfate.

In this paper, we examine ambient pollution data collected in Toronto during July and August 1986, 1987, and 1988 in detail in order to determine the nature of the H^+ association with sulfate pollution in this city, which comprises almost half of the population of southern Ontario previously studied by Bates and Sizto (1983, 1987). Also, through the examination of these aerosol data in conjunction with both back-trajectories of the most polluted air masses and acidic aerosol measurements made elsewhere concurrently, an assessment is made of the likely origin of the acid aerosols measured in this southern Ontario city.

DATA COLLECTION

Acid aerosols were sampled in the city of Toronto, Ontario, during July and August in 1986, 1987, and 1988. During the 1986 campaign, a continuous sulfate/

sulfuric acid monitor was also operated from July 3 through August 10, 1986 at a monitoring site operated by the New York University Medical Center (NYUMC) on the University of Toronto (UT) Scarborough campus. The campus is located within the Toronto metropolitan area, approximately 20 km east–northeast of downtown Toronto. In addition, fine acidic aerosols were also collected on filters at three sites within the metropolitan area: (1) at the UT Scarborough campus site; (2) at the Ontario Ministry of the Environment and Energy (MOEE) lab at Resources Road, Etobicoke, in northwestern Toronto; and (3) at the MOEE Breadalbane Street air monitoring site (see Fig. 1). Site 1 (at UT Scarborough) was the least urbanized (being located in a park surrounded by residential neighborhoods), Site 2 (at Resources Road, just off the MacDonald Cartier Freeway) was moderately urbanized, and Site 3 (at Breadalbane Street, in center city Toronto) was the most urbanized locale.

The continuous sulfate/sulfuric acid aerosol monitor deployed at the UT Scarborough site during the summer of 1986 represents the product of a series of researchers' efforts to develop a reliable instrument suitable for continuous long-term field observations (Coburn *et al.*, 1978; Tanner *et al.*, 1980; Allen *et al.*, 1984). In brief, the instrument utilizes a flame photometric detector (FPD) to continuously measure the sulfur in the sampled air entering it, preceded in the sampling train by a lead oxide (PbO)-coated gaseous sulfur denuder, which is itself preceded by a thermal ramp capable of raising the air sample's temperature prior to the denuder and FPD (see Fig. 2). The result of this sampling configuration is to allow a discrimination of the fine particulate sulfate ($d_a \leq 2.0$ μm) into several components via a cyclical operation of the thermal ramp at several preset tem-

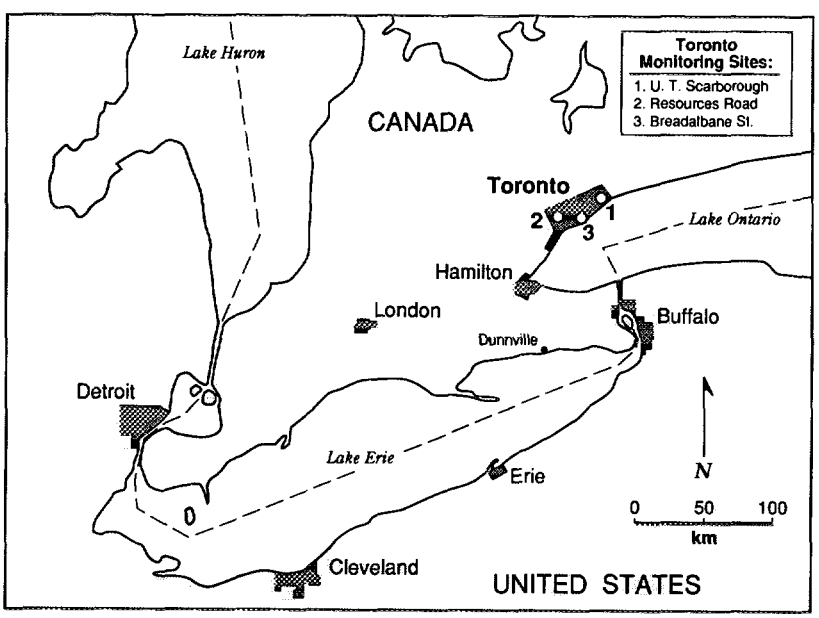

FIG. 1. Map of Toronto and surrounding southern Ontario vicinity.

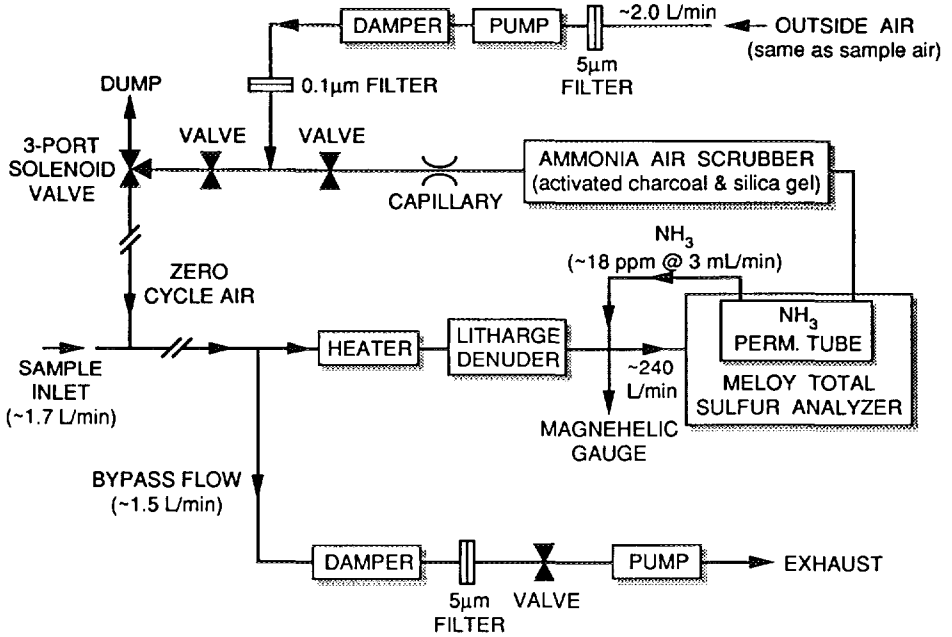

FIG. 2. Flow diagram for the continuous sulfuric acid/sulfate monitor (source: Allen *et al.*, 1984).

peratures. The unit is first operated for 3 min at ambient temperature, so that the denuder removes only gaseous sulfur (i.e., sulfur dioxide, SO_2) prior to the FPD, yielding the total particulate sulfur level. For the next 3 min, the thermal ramp is then used to heat the upstream-sampled air to 120°C. This is a temperature sufficient to volatilize any sulfuric acid (H_2SO_4) present in the air, thereby causing the H_2SO_4 to also be removed by the denuder, resulting in a concomitant drop in the continuously recorded total particulate sulfur. H_2SO_4 volatilizes below its reported boiling point (338°C) because it is present in a submicrometer aerosol droplet, which results in both curvature (Hinds, 1982) and dilution (Kitagawa, 1984) effects. Further heating the thermal ramp to 300°C for the next 3 min causes any ambient ammonium sulfate ($(NH_4)_2SO_4$) or ammonium bisulfate (NH_4HSO_4) to also be volatilized and removed by the denuder. Finally, purified (zero) air is fed through the system to provide a reference point for determining the absolute quantity of each class of sulfates. By differencing the respective 3-min values over the 12-min cycle (which is repeated five times per hour), this instrument provides near real-time measurements of total particulate sulfates, ammonium salts, and H_2SO_4.

Unfortunately, the sulfate acid aerosol monitor cannot discriminate between NH_4HSO_4 and $(NH_4)_2SO_4$ on the basis of temperature of volatilization alone. Because of this, the monitor was also accompanied by a dichotomous size-selective particle sampler in order to provide a simultaneous measurement of the total strong acid hydrogen ion (H^+) concentration in the air, as collected on inert Teflon filters in the sampler's fine aerosol airstream ($d_a < 2.5$ μm). The dichot-

omous sampler employed at each site was the same as those used in the IP network (U.S. EPA, 1980), except that a PM10 ($d_a < 10$ μm) size-selective inlet was employed (as opposed to $d_a < 15$ μm) and that citric acid-coated glass annular denuders were placed in the sampler inlet tube in order to protect the sampled H^+ from neutralization by ambient ammonia after collection on the filter (Stevens *et al.*, 1978). Integrating the H_2SO_4 concentration from the continuous acid aerosol analyzer over the H^+ sample period (e.g., 9 AM–5 PM) yields H^+ associated with the H_2SO_4. This H^+ can then be subtracted from the total (filter) H^+ during the period, and the ammonium bisulfate concentration can thus be inferred, assuming all other strong particulate H^+ contributors to be negligible in this locale. In this manner, the parallel use of a size-selective aerosol sampler and the total sulfate/sulfuric acid aerosol monitor allowed individual determinations of the H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$ concentrations on a routine basis during the 1986 portion of the study.

In addition to the continuous sulfate/sulfuric acid monitor and acid aerosol filter data collected at the Scarborough campus site, pollution data were also collected at the other two Toronto sites noted previously. Twice daily fine aerosol filter samples (i.e., 9 AM–5 PM and 5 PM–9 AM, Eastern Standard Time) were similarly collected concurrent with the UT Scarborough samples during 1986 and 1987. However, due to budget constraints, acid aerosol samples were only collected at the downtown Breadalbane Street site during the summer of 1988. In addition, concentration data for other pollutants, including ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and total suspended particulate matter (TSP), were also routinely collected by the MOEE at the Breadalbane site.

The fine aerosol filter collection and analyses steps employed in this research are summarized in Fig. 3. As described in detail elsewhere (Waldman *et al.*, 1990; Thurston *et al.*, 1992), each sample's total aerosol strong acidity (in nmole/m^3) was determined via the pH method after Teflon filter extraction (Koutrakis *et al.*, 1988), while particulate sulfate was determined via ion chromatography.

Numerous quality assurance procedures were employed throughout the collection and analysis steps. As summarized in Fig. 3, samples were protected from neutralization by ambient ammonia gas both before and after sampling by employing citric acid-coated denuders upstream of sampling and by storing the samples in an ammonia free environment. Appropriate filter blanks and predosed hydrogen ion-positive control field samples were also included in our regular sampling regime, in order to assure the adequacy of these quality control steps. Based on an analysis of these blank field control filters, the H^+ analytical detection limit was determined to be 5 nmole/m^3 (or 0.2 μg/m^3, as H_2SO_4). Also, the H_2SO_4 neutralization of the predosed field control filters (i.e., their paired SO_4–H_2SO_4 differences in nanoequivalents per m^3) were not statistically different from zero ($P = 0.16$, one-way test), indicating that these samples were successfully protected from neutralization during handling and analysis. Furthermore, the samples analyzed were of the fine mass fraction ($d_a < 2.5$ μm), which minimizes possible on-filter neutralization by alkaline coarse particles, and were also collected on inert Teflon filters to avoid filter artifacts. Sample flow rates were checked by the field operators at the beginning and end of each sampling period,

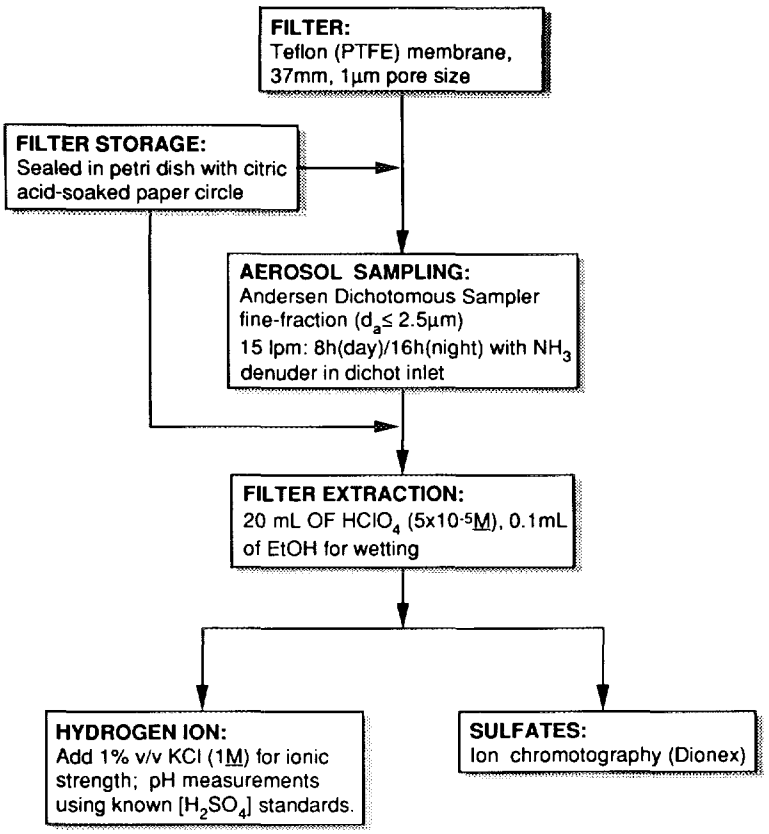

FIG. 3. Sample handling and analytical protocols.

and complete flow calibrations were conducted on each sampler (using a bubble meter) at the beginning and end of each field campaign. Paired simultaneous samples were not collected at any of the sites, so the imprecision of these H^+ data could not be directly determined, but recent precision studies (e.g., Jaques *et al.*, 1993) have indicated that such H^+ measurements have an imprecision on the order of 10–20%.

With regard to meteorological data, temperature and wind speed/direction were also recorded at the MOEE's Kennedy and Lawrence Avenue pollution monitoring site, located between the downtown and Scarborough sites. Furthermore, daily surface 48-hr isobaric air mass back-trajectories were provided by the MOEE for each of the three summers, while the Canadian government's Atmospheric Environment Service (AES) provided select satellite photographs to aid in our interpretation of the meteorological data. Mixing layer mean wind back-trajectories were also computed for each sampling day of the 1986 study using the NOAA ARL-ATAD trajectory model (Heffter, 1980) in order to confirm the MOEE isobaric model results. The trajectory model calculates the upwind air mass path from observed winds in the mixed layer of the atmosphere (roughly surface to 1500 m). In contrast, the MOEE isobaric model assumes that the air

mass travels nearly parallel to (i.e., 15° to the left of) the isobars on the surface maps and at a speed proportional to the horizontal pressure gradients (i.e., 90% of geostrophic velocity) (Yap and Kurtz, 1986). The ARL-ATAD trajectories obtained for the 1986 sampling days matched well with the MOEE isobaric trajectories for that summer, so only the isobaric trajectories are employed in this analysis. The advantages and disadvantages of various air mass trajector models have been previously discussed by Pack *et al.* (1978) and by Takacs and Starheim (1984).

RESULTS

Table 1 presents the mean acid aerosol pollutant concentrations at each site for each summer. These data indicate that sulfate levels were similar among the sites, while H^+ varied more dramatically from site to site. In general, the least urbanized Site 1 in suburban Scarborough averaged highest in particulate acidity, Site 2 in the more urbanized, though residential, Etobicoke was intermediate, and the most urbanized Site 3 in downtown Toronto had the lowest H^+. The $H^+/SO_4^=$ ratios presented in Table 1 reveal that this trend was driven by the fact that Site 1 had the highest fraction of acidic sulfates, Site 2 had the second highest, and Site 3 had the lowest. Also, all sites had slightly higher $H^+/SO_4^=$ ratios during the day than at night. Thus, on average, sulfate aerosols in metropolitan Toronto were found to be present in a somewhat more neutralized state during the night and at more urbanized locales.

Figure 4 displays detailed sulfate/acid aerosol information for the UT Scarborough site on July 25, 1986, the highest H^+ episode day during which the continuous acid aerosol analyzer was in operation. Note that, on this episode day, an additional filter sample (5 PM–9 PM) was collected to provide more detailed total H^+ information. H_2SO_4 occurred only during a brief portion of this major episode,

TABLE 1

DAYTIME (9 AM–5 PM) AND NIGHTTIME (5 PM–9 AM) MEAN ACID AEROSOL AND SULFATE CONCENTRATIONS IN NANOMOLES/CUBIC METER (±SE) RECORDED AT THREE SITES IN TORONTO, ONTARIO DURING JULY AND AUGUST 1986, 1987, AND 1988

	1986		1987		1988	
	Day (n = 40)	Night (n = 40)	Day (n = 41)	Night (n = 41)	Day (n = 42)	Night (n = 42)
Site 1						
H^+	30.7 (8.4)	16.8 (4.0)	36.2 (8.5)	32.5 (9.6)	[b]	[b]
$SO_4^=$	65.6 (12.1)	61.1 (10.5)	70.0 (14.4)	67.1 (14.5)		
$H^+/SO_4^=$ [a]	0.48	0.27	0.52	0.48		
Site 2						
H^+	22.1 (4.4)	16.5 (4.7)	16.5 (4.0)	27.6 (10.2)	[b]	[b]
$SO_4^=$	72.1 (10.6)	70.7 (13.8)	41.1 (7.8)	74.3 (18.8)		
$H^+/SO_4^=$ [a]	0.31	0.23	0.40	0.37		
Site 3						
H^+	21.4 (4.4)	14.7 (2.4)	12.7 (2.6)	20.2 (6.0)	54.6 (10.0)	35.2 (4.8)
$SO_4^=$	74.2 (12.7)	64.7 (11.2)	39.0 (7.9)	65.6 (14.6)	125.9 (17.3)	115.9 (16.1)
$H^+/SO_4^=$ [a]	0.28	0.23	0.32	0.31	0.43	0.30

[a] Ratio of means.
[b] Site not operated during 1988.

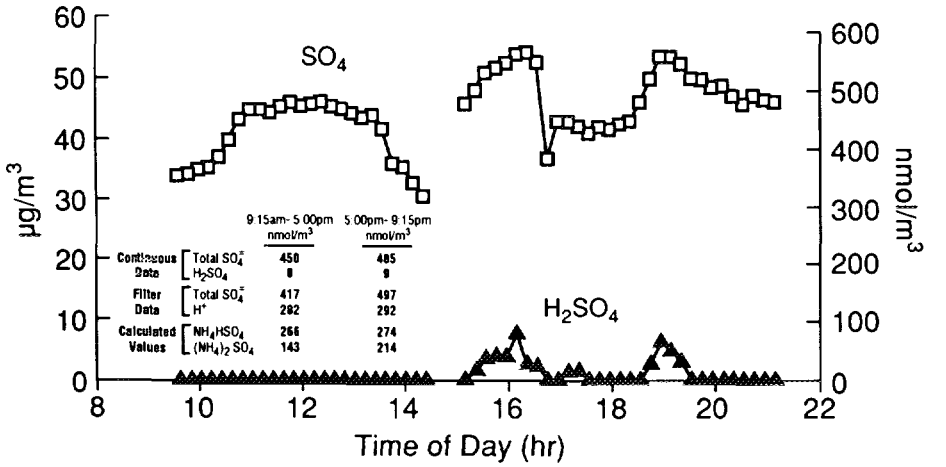

FIG. 4. Continuous (12-min average) $SO_4^=$ and H_2SO_4 record for July 25, 1986 with comparisons to filter data.

and the H_2SO_4 concentration data averaged over the coincident filter sampling period indicate that only about an average 6% of the H^+ was actually in the form of H_2SO_4 (i.e., 8 nmole/m^3 of H_2SO_4 or 16 nmole/m^3 H^+ actually as H_2SO_4, of the 282 nmole/m^3 total H^+ measured on the filter). A majority of the acidity (and indeed of the $SO_4^=$) is therefore calculated as having been present in the form of NH_4HSO_4. This is indicative of a moderately aged acid aerosol air mass, wherein the H_2SO_4 originally formed or emitted has been partially neutralized to NH_4HSO_4. The remaining $SO_4^=$ (as $(NH_4)_2SO_4$) makes up only about 35–45% of the total $SO_4^=$ mass during this acid aerosol event. All of the acid aerosol events during the summer of 1986 were found to have similarly low H_2SO_4 values (relative to total acidity), indicating the predominance of H^+ as NH_4HSO_4 during acid aerosol events in this city.

The relationships among the three sampling sites' H^+ and $SO_4^=$ concentrations from the summers of 1986 and 1987 (when all three sites were operated) were investigated in detail. As shown in the scatterplots in Fig. 5, the $SO_4^=$ plots (Figs. 5a and 5b) clearly indicate that the sulfate concentrations at Sites 1 and 2 agreed well with those recorded at Site 3. The $SO_4^=$ regression slopes presented are not significantly different from 1.0. For the H^+ intersite comparisons (Figs. 5c and 5d), however, the slopes are significantly greater than 1.0, indicating that Site 3 had lower H^+ concentrations than Sites 1 or 2. Also, paired t tests of differences between these sites indicate that the three sites' H^+ concentrations were different from one another ($P < 0.05$), with their ranking being H^+ (Site 1) > H^+ (Site 2) > H^+ (Site 3). Thus, the sulfate data alone would indicate that aerosol exposures are similar throughout the Toronto metropolitan area. However, although the H^+ concentrations are highly spatially correlated among these sites ($r \sim 0.9$), the intersite comparisons suggest that the greater the urbanization around a site, the less acidic the sulfate aerosol in that particular locale.

The H^+:$SO_4^=$ relationship at each of these sites was also investigated further.

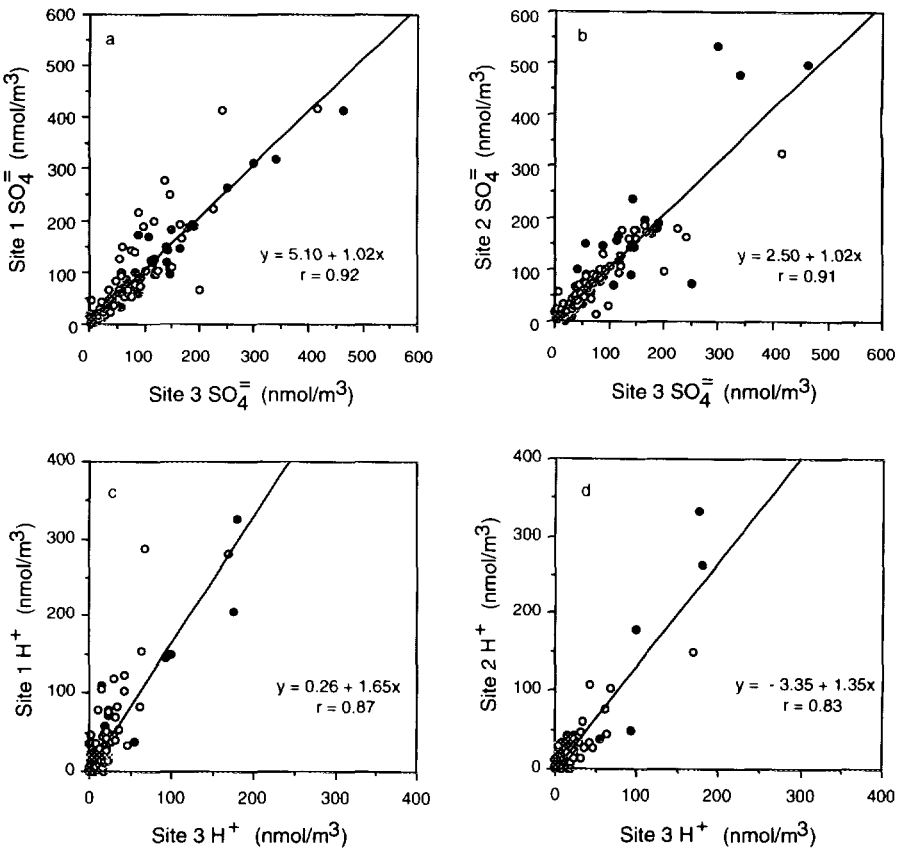

FIG. 5. Intercomparison of hydrogen ion and sulfate concentrations day (9 AM–5 PM) and night (5 PM–9 AM) among three sites within Toronto, Ontario during July and August 1986 and 1987 (n = 160). ○, Day; ●, night.

As shown in Fig. 6, the linear regression slopes indicate that H^+ and $SO_4^=$ were highly correlated at each site, and that the overall $H^+/SO_4^=$ ratio was largest for Site 1, intermediate for Site 2, and smallest for Site 3, as expected from the above analyses of $SO_4^=$ and H^+ site-to-site comparisons. However, the quadratic regressions also included in Fig. 6 indicate that a significantly improved fit ($P \ll 0.05$) is achieved in each case if the model allows the $H^+/SO_4^=$ ratio to increase with increasing $SO_4^=$ concentration. Thus, the fraction of acidic sulfates increases as the sulfate concentration rises, as might be expected if there is a finite amount of neutralizing local ammonia available around each site.

An interesting feature of the day and night acid aerosol data presented in Figs. 5 and 6 is that the highest H^+ and $SO_4^=$ concentrations in this urban area may occur during either day or night. Since acid aerosols would be expected to have been formed from their precursors most rapidly during the daylight hours, when oxidant reactions would occur most rapidly, this suggests that the acid measured in Toronto was not of local origin. Also, the nighttime neutralization rate of H^+

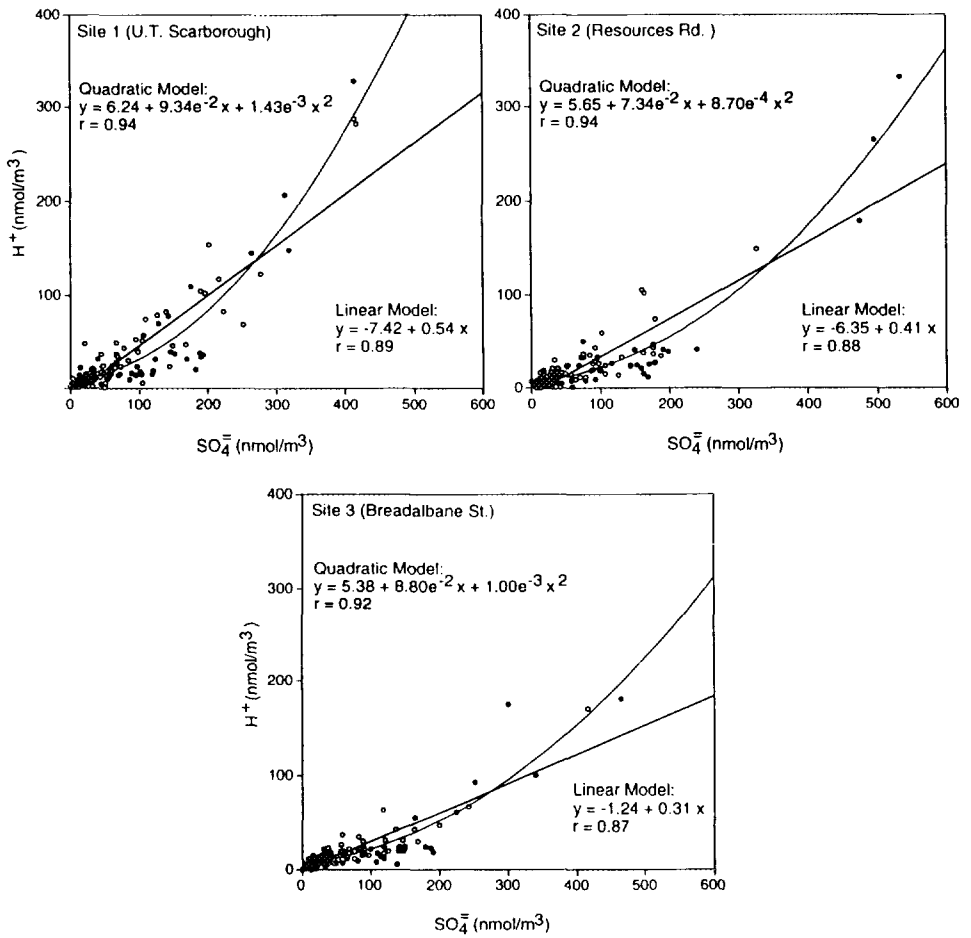

FIG. 6. Scatter plots of H^+ (nmole/m^3) vs $SO_4^=$ (nmole/m^3) for Toronto sites 1, 2, and 3 during July and August 1986 and 1987, day (9 AM–5 PM) and night (5 PM–9 AM) (n = 160). ○, Day; ●, night.

must not have been much higher than the daytime rate, as previously suggested by the $H^+/SO_4^=$ ratios in Table 1. Apparently, high acid aerosol concentrations occurred throughout the Toronto metropolitan area whenever an air mass laden with that pollutant was advected into the city, irrespective of the time of day.

In order to further investigate the potential role of air pollution transport on the H^+ measured in Toronto, Fig. 7 presents the 48-hr isobaric air mass back-trajectories ending in Toronto at 00Z (7 PM EST) on each of the highest 1986–1988 summertime acid aerosol days (i.e., having a 24-hr (9 AM–9 AM) average $H^+ > 100$ nmole/m^3). Also, Fig. 8 displays the locations of the highest SO_2 emissions in this region of North America. Clearly, air masses which first passed over high SO_2 emission areas in the United States, and then across the Great Lakes to southern Ontario, are associated with the highest sulfate and acid aerosol days occurring in

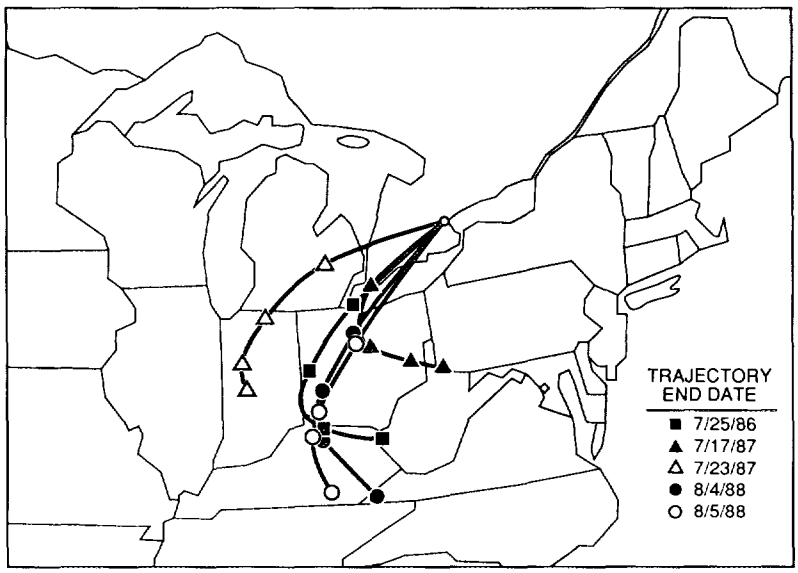

FIG. 7. Forty-eight-hour air mass back-trajectories for study days during which the 24-hr average H^+ concentrations exceeded 100 nmole/m^3 (5 μg/m^3 equivalent H_2SO_4) in downtown metropolitan Toronto, Ontario.

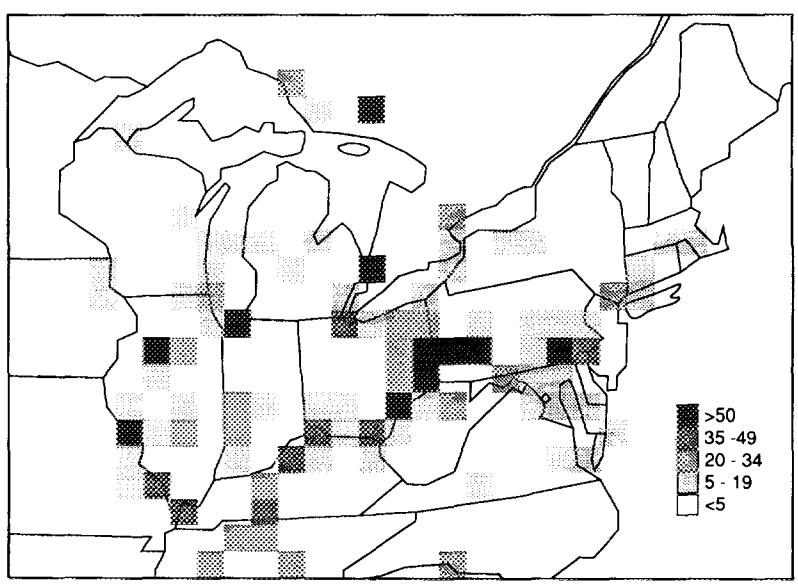

FIG. 8. Gridded annual point source emissions (10,000 ton year^{-1}) of sulfur dioxide for United States and Canada (modified from Clark, 1980).

Toronto during these field-sampling campaigns. In addition, the "tick" marks on each trajectory, which are 12 hr travel time apart from one another, show that these air masses generally stagnated over the high SO_2 emission region prior to more rapid advection into southern Ontario. Overall, these air mass back-trajectories further indicate that the maximum H^+ concentrations recorded in Toronto are caused by transported sulfate pollution, apparently of U.S. origins.

DISCUSSION

Ammonia (NH_3) is the predominant basic gas in the atmosphere and, as such, its concentration in the atmosphere is a major determinant of aerosol acidity neutralization (Committee on Medical and Biological Effects of Environmental Pollutants, 1979). Over 99% of the Earth's atmospheric ammonia is produced by biogenic sources, the main source being the decomposition of organic waste. However, in urban areas, anthropogenic sources may locally increase gaseous ammonia levels. Anthropogenic sources of NH_3 include anaerobic decay (in landfills, ponds, etc.), combustion processes (such a municipal incineration and automotive emissions), and industrial sources (such as fertilizer factories and petroleum refineries). Atmospheric losses of anhydrous ammonia fertilizers and ammonia from poultry houses and cattle feedlots are also sources of ammonia. Aside from reaction with atmospheric acids, major sinks of ammonia include plant absorption and absorption by bodies of water. In general, ambient measurements of ammonia gases suggest that the highest ammonia gas concentrations are recorded in major urban areas, the lowest over large water bodies, and intermediate levels in rural areas (Committee on Medical and Biological Effects of Environmental Pollutants, 1979). For these reasons, it has been commonly thought that sulfates are most likely to be almost exclusively in their most neutralized state in major urban areas (i.e., as $(NH_4)_2SO_4$) (e.g., Tanner *et al.*, 1981).

In light of these and previous discussions of acid aerosol chemistry, the Toronto acid aerosol episodes can be better understood. As shown previously, the air masses with the highest H^+ concentration had previously passed over an area rich in SO_2 emissions (e.g., the Ohio River Valley region), followed by passage over the Great Lakes (which lack ammonia sources and, indeed, may act as gaseous ammonia sinks). Thus, it would appear that such air masses entering southern Ontario from the United States can be very acidic because they carry with them high levels of H_2SO_4 and its formation precursors, probably combined with low levels of neutralizing ammonia gas over the Great Lakes. As the air mass passes over land and enters the Toronto urban area, these acidic aerosols are apparently modified by neutralization, with the greatest neutralization occurring in the most urbanized locales. Therefore, the acid aerosol concentrations found at the various sites in metropolitan Toronto are consistent with the chemistry and meteorology present during sulfate transport episodes in that city.

The evidence that the acid aerosols recorded in Toronto site are largely due to regional scale sulfate transport events is further supported by analyses of contemporaneous data collected at other sites in southern Ontario. First, the H^+ measurements at our multiple Toronto sites during the summer of 1986 confirm that, when elevated acidity and sulfates were recorded at one site, elevated

levels were also recorded at the other two sites (Waldman *et al.*, 1990). The multisite scatterplots presented in Fig. 5 confirm that a high correlation among the H^+ concentrations at these three sites continued in 1987, although the $H^+/SO_4^=$ ratio did appear to be modified by the extent of local urbanization. Moreover, independent acid aerosol measurements were made by researchers from Harvard University during the summer of 1986 in Dunnville, Ontario (along the northeast shore of Lake Erie, 100 km southwest of Toronto). These data, collected as part of the Canadian Federal government's Children's Acute Respiratory Effects Study (CARES), confirmed the regional nature of these episodes and are also consistent with our hypothesis regarding the chemistry involved. Sulfates were also elevated on peak H^+ days in Dunnville, but those sulfates were, as would be expected, less neutralized than the aerosol measured at the downwind (and more urban) Toronto monitoring sites. On July 25, 1986, for example, continuous sulfate/sulfuric acid monitoring at Dunnville indicated that the peak 1-hr average sulfate level exceeded 100 $\mu g/m^3$, and that approximately half (48 $\mu g/m^3$) of the peak sulfate levels were in the form of H_2SO_4 (Spengler *et al.*, 1989), compared to the less than 10 $\mu g/m^3$ H_2SO_4 peaks recorded at UT Scarborough on that date. On that same afternoon, the $H^+/SO_4^=$ ratio (on a nanomole-to-nanomole basis) for the Dunnville and the Toronto Sites 1, 2, and 3 were 0.66, 0.61, 0.46, and 0.39, respectively, illustrating the influence of urbanization on the sulfate acidity during such episodes. Also, analyses by Harvard researchers of particulate trace element concentrations and wind back-trajectories for these 1986 sampling days indicated that the acids were transported across Lake Erie from the United States (Keeler *et al.*, 1990). It appears that, during the July 25, 1986 sulfate episode in southern Ontario, the acid aerosol levels were highest at the point at which the air mass first came off Lake Erie, and that somewhat lower (although still elevated) levels were experienced at more inland sites, depending on their local urbanization.

During July and August of 1988, daily aerosol samples were also collected in Buffalo, New York as part of a separate acid aerosol study in that city conducted for the National Institute of Environmental Health Sciences (Thurston *et al.*, 1992). Since Buffalo is located approximately 60 miles (100 km) southeast of Toronto (on the eastern shore of Lake Erie), it should experience acid aerosol concentrations similar to those found in Toronto if the acid aerosol pollution is indeed regional and primarily of transported origins. Figure 9 displays the 24-hr average H^+ and sulfate concentrations recorded during July and August in Buffalo, New York (midnight–midnight average) and in Toronto, Ontario (9 AM–9 AM average), respectively. Despite slight differences in the aerosol sample averaging periods and collection methods employed, the two sites' H^+ and $SO_4^=$ concentrations track each other well (intersite $r = 0.86$ and 0.78, respectively), as would be expected if these sites are both influenced primarily by sulfate pollution transported from the midwestern United States. While the sulfate levels are similar between Toronto (mean $SO_4^= = 120 \pm 16$ nmole/m^3) and Buffalo (mean $SO_4^= = 142 \pm 15$ nmole/m^3), the H^+ level (while highly correlated between sites) is lower in Toronto (mean $H^+ = 41 \pm 6$ nmole/m^3 vs 71 ± 10 nmole/m^3 in Buffalo). This apparent $H^+/SO_4^=$ ratio difference between cities may, however, be merely due to the fact that the Buffalo monitoring site is located in a suburb of that city, while

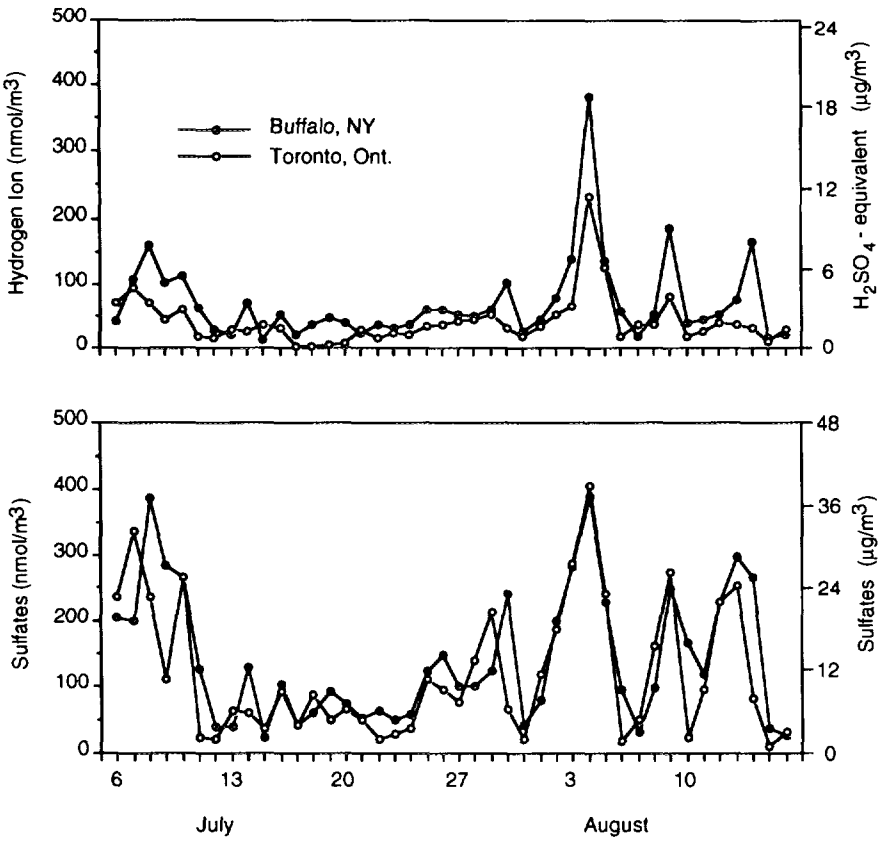

FIG. 9. Comparison of 24-hr average hydrogen ion and sulfates in downtown Toronto, Ontario vs suburban Buffalo, New York during the summer of 1988.

the 1988 Toronto data in Fig. 9 are from its center city site (Breadalbane Street). Overall, these various H^+ sampling results from the summers of 1986, 1987, and 1988 are all consistent with the hypothesis that these acid aerosol episodes were regional in scale, and that such acidic aerosol episodes in Toronto are primarily associated with transported sulfates of midwestern U.S. origins.

CONCLUSIONS

Results from this multiyear air pollution study conducted in Toronto, Ontario during July and August 1986, 1987, and 1988 document that acid aerosol episodes do routinely occur in this city during the summer months, that these acid concentrations are indeed well correlated with sulfate levels in this city, and that the most acidic aerosols occur on the highest sulfate days, as hypothesized by Bates and Sizto (1987). However, it was determined via a continuous acid aerosol analyzer that virtually all of the acid measured during such peak days was actually present as NH_4HSO_4 rather than H_2SO_4. It was also found that higher $H^+/SO_4^=$ ratios prevailed on the highest $SO_4^=$ episode periods (i.e., H^+ rose as the square

of $SO_4^=$), and that more urbanized monitoring sites had lower $H^+/SO_4^=$ ratios, apparently as a result of neutralization of H^+ by local NH_3. However, H^+ neutralization was roughly similar during the day and night in this city, as the $H^+/SO_4^=$ ratio was only marginally lower, on average, at night. Thus, H^+ maxima occurred during either day or night, suggesting that the acid was not formed locally. Furthermore, air mass back-trajectories and comparisons of contemporaneous H^+ measurements at these and other surrounding locations (e.g., Buffalo, NY) indicated that regional air pollution transported across the Great Lakes from the United States contribute strongly to the acid aerosol events recorded within the city of Toronto.

The presence of extremely elevated 24-hr average acid aerosol concentrations within downtown Toronto (e.g., $H^+ > 200$ nmole/m^3 on August 4, 1988) is contrary to past suppositions regarding this pollutant, which would have predicted that urban ammonia sources would "overwhelm" any acid pollution advected into the center of a major city such as Toronto. However, this result can be accounted for in terms of the chemistry of acid aerosols and the geographical location of Toronto, Ontario. It is hypothesized that, as pollution passed from the southwest over the Great Lakes on sunny summer days prior to reaching lakeshore cities such as Toronto, Ontario and Buffalo, New York, the acid aerosols formed from ambient SO_2 were not as readily neutralized as they would be during entirely overland transport. Also, acid aerosols were not as readily neutralized by center city NH_3 as previously suggested. These factors apparently enhanced the summertime acid aerosol concentrations recorded throughout metropolitan Toronto, Ontario, during the summers of 1986, 1987, and 1988.

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