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ATMOSPHERIC ACIDITY MEASUREMENTS ON ALLEGHENY MOUNTAIN AND THE ORIGINS OF AMBIENT ACIDITY IN THE NORTHEASTERN UNITED STATES

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Abstract—Atmospheric acidity as $HNO_3(g)$, $SO_2(g)$, and aerosol H^+ was measured on Allegheny Mountain and Laurel Hill in southwest Pennsylvania in August 1983. The aerosol H^+ appeared to represent the net after H_2SO_4 reaction with $NH_3(g)$. The resulting H^+/SO_4^{2-} ratio depended on SO_4^{2-} concentration, approaching that of H_2SO_4 at the highest SO_4^{2-} concentrations. The atmosphere was acidic; the average concentrations of HNO_3 (78 nmole m^{-3}) and aerosol H^+ (205 nmole m^{-3}), NH_4^+ (172 nmole m^{-3}) and SO_4^{2-} (201 nmole m^{-3}), and the dearth of NH_3 (< 15 nmole m^{-3}), show that the proton acidity (HNO_3, H_2SO_4) of the air exceeded the acid-neutralizing capacity of the air by a factor of > 2, with one 10-h period averaging 263 and 844 nmole m^{-3} for HNO_3 and aerosol H^+, respectively. SO_2 added another 900 nmole m^{-3} (average) of potential H^+ acidity. HNO_3 and aerosol H^+ episodes were concurrent, on 7–8 day cycles, unrelated to SO_2 which existed more in short-lived bursts of apparently more local origin. NO_x was sporadic like SO_2. Laurel and Allegheny, separated by 35.5 km, were essentially identical in aerosol SO_4^{2-}, and in aerosol H^+, less so in HNO_3 and especially less so in SO_2; apparently, chemistry involving HNO_3 and aerosol H^+ or SO_4^{2-} was slow compared to inter-site transport times (1–2 h). From growth of b_{scat} and decline of SO_2 during one instance of inter-site transport, daytime rate coefficients for SO_2 oxidation and SO_2 dry deposition were inferred to have been, respectively, ~ 0.05 and ⩽ 0.1 h^{-1}.

HNO_3 declined at night. Aerosol H^+ and SO_4^{2-} showed no significant diurnal variation, and O_3 showed very little; these observations, together with high PAN/NO_x ratios, indicate that regional transport rather than local chemistry is governing. The O_3 concentration (average 56 ppb or 2178 nmole m^{-3}) connotes an oxidizing atmosphere conducive to acid formation.

Highest atmospheric acidity was associated with (1) slow westerly winds traversing westward SO_2 source areas, (2) local stagnation, or (3) regional transport around to the back side of a high pressure system. Low acidity was associated with fast-moving air masses and with winds from the northerly directions; upwind precipitation also played a moderating role in air parcel acidity. Much of the SO_2 and NO_x, and ultimately of the HNO_3 and aerosol H^+, appeared to originate from coal-fired power plants. An automotive contribution to the NO_x and HNO_3 could not be discerned.

Size distributions of aerosol H^+ and SO_4^{2-} were alike, with MMED ~ 0.7 μm, in the optimum range for efficient light scattering and inefficient wet/dry removal. Thus, light scattering and visual range degradation were attributable to the acidic SO_4^{2-} aerosol, linking the issues of acid deposition and visual air quality in the Northeast. With inefficient removal of aerosol H^+, and inefficient night-time removal of HNO_3, strong acids may be capable of long-distance transport in the lower troposphere.

We obtained an accounting of aerosol mass in terms of composition, including aerosol H_2O which was shown to account for much of the light scattering.

Key word index: Acid rain, acid deposition, atmospheric acidity, atmospheric aerosols, nitric acid, regional transport, sulfate.

INTRODUCTION

Ten years ago on Allegheny Mountain in Pennsylvania, we conducted an experiment which revealed a strong and persistent acidity in aerosol in that part of the country (Pierson *et al.*, 1980). The aerosol was found to consist essentially of H_2SO_4 in various degrees of neutralization by $NH_3(g)$, together with its water of hydration, the degree of neutralization being greatest at the lowest SO_4^{2-} concentrations. $NH_3(g)$ levels were very low (average < 1.1 ppb). The most acidic aerosol and the highest SO_4^{2-} levels were associated with air masses arriving from westward, especially when there had been stagnation over SO_2 source

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regions along the Ohio River (Samson, 1980). Visibility degradation at Allegheny was also very much governed by the light scattering of this fine (~ 0.8 μm mass median diameter) acidic sulfate aerosol. Coincidentally, acidic aerosol SO_4^{2-} episodes and associated haze were being detected at sites in North Carolina, New Jersey and New York (Lioy *et al.*, 1980; Stevens *et al.*, 1978; Tanner *et al.*, 1981)—and, indeed, in a network (SURE) encompassing the whole Northeast (Mueller *et al.*, 1980)—thus demonstrating that the phenomena observed on Allegheny Mountain in 1977 were regional in nature. It is now established (Charlson *et al.*, 1978; Cunningham and Johnson, 1976; Dzubay *et al.*, 1979; Ferek *et al.*, 1983; Ferman *et al.*, 1981; Lioy and Lippmann, 1986; Lioy *et al.*, 1980; Morandi *et al.*, 1983; Pierson, 1981; Stevens *et al.*, 1978, 1980, 1984; Tanner *et al.*, 1977, 1981, 1984; Weiss *et al.*, 1982) that the aerosol in the eastern U.S. is commonly acidic and that the acidity identifies with H_2SO_4 and NH_4HSO_4.

SO_2(g), largely uncorrelated with aerosol SO_4^{2-}, was about twice as abundant as the SO_4^{2-}, on a mole average basis, in the experiment ten years ago. However, knowledge of the total amount of acid in the air was lacking in that there were no measurements of HNO_3(g). Moreover, interpretation of the aerosol H^+ and SO_4^{2-} data was limited by absence of O_3 data.

In 1983 we conducted a larger experiment on top of Allegheny Mountain and concurrently 35.5 km away on Laurel Hill. This time HNO_3(g) and O_3 were included. Acidity deposited in rain, dew, and to dry surrogate surfaces in this study are discussed elsewhere (Japar *et al.*, 1985; Pierson *et al.*, 1986, 1987), including estimates of the acid deposited during the study and of the relative contributions to it of wet and dry deposition of SO_2, HNO_3 and aerosol H^+ (Pierson *et al.*, 1987).

The present paper deals with these three atmospheric gas and aerosol acidic species—SO_2, HNO_3, aerosol H^+—as the proximate cause of the acidity deposited in the 1983 experiment. SO_2 is included because it is a strong Lewis acid and is responsible for much of the H^+ and SO_4^{2-} in rain (e.g. Pierson *et al.*, 1987) and because SO_2 dry deposition is tantamount to deposition of H_2SO_4 by virtue of the ease of SO_2 conversion to H_2SO_4. Atmospheric HCl, HONO and carboxylic acids were not evaluated, but analyses of rain, dew and fog in this study (Pierson *et al.*, 1986, 1987) indicate that their atmospheric concentrations must have been relatively meager, or at least that their contributions to deposited acidity in dew, rain and fog were meager. Weak acids, including dicarboxylic acids, are said (Ferek *et al.*, 1983) to have constituted $26 \pm 12\%$ of the total acidity in a situation in the Northeast less acidic than the present one, suggesting that their contribution here was likely $< 25\%$. PAN was measured here but played no discernible role in acid deposition (rain, dew, fog; Pierson *et al.*, 1986, 1987) and is therefore excluded from our atmospheric acidity totals. NO and NO_2 were measured also, and played no discernible role in dew acidity (Pierson *et al.*, 1986); accordingly, and because they are not acid anhydrides, they too are excluded from the acid totals. NO_2 could have contributed to local in-stormgenerated HNO_3 through reaction with OH (Chang, 1986). NO_3 and especially N_2O_5, neither of which were evaluated by measurement, and both of which are excluded from the acid totals, could have contributed to the HNO_3 in dew (Chang *et al.*, 1987) and to in-storm-generated HNO_3 (Chang, 1986). We estimate, however, that most of the HNO_3 in the local rain came from scavenging of pre-existing HNO_3 rather than from in-stormgeneration of HNO_3 (Pierson *et al.*, 1987). Thus the exclusion of NO_2, NO_3 and N_2O_5 is probably a minor issue (at most $\sim 20\%$ of the potential acidity; see later). Under the humid night-time conditions prevailing at Allegheny or Laurel, it could be that some of the N_2O_5 was counted as HNO_3 as discussed below.

EXPERIMENTAL

The measurements in the present study were conducted in August 1983 (5–28 August) at two abandoned mountaintop radio towers in a rural area in southwestern Pennsylvania (Fig. 1), some 150 km east of the highest density of SO_2 emissions in the U.S. (Barrie *et al.*, 1984; Clark, 1980). One tower, on Allegheny Mountain (39.959°N, 78.8525°W, elevation 838 m), was the site used in the 1977 study (Pierson *et al.*, 1980). The other, on Laurel Hill (40.099°N, 79.226°W, elevation 850 m), lies 35.5 km WNW (bearing 296° True) from the Allegheny tower. There are no significant industrial sources near or in the tableland between the two mountaintops. Both sites are heavily forested. There is no local traffic, though occasionally at Allegheny brief excursions of condensation nuclei count (CNC), NO and (downward excursions) O_3 were noted with wind from the direction of the east portal of the Allegheny Mountain Tunnel (Pennsylvania Turnpike), some 420 m slant distance away (bearing 120°T) and 143 m lower in elevation.

At Allegheny the atmospheric aerosol and gas measurements were made on the tower 14–17 m above the ground. The plane of the treetops was 12.3 m above the ground. Light scattering (by heated-inlet integrating nephelometer, cell temperature ~ 16°C above ambient), light absorption (by an integrating-plate method; see Japar *et al.*, 1986), CNC, and ultraviolet radiation intensity were measured at the same elevation. Visual ranges to natural targets 3.2–35.5 km away were recorded from time to time and hourly visual range observations were obtained from the NWS (National Weather Service) stations at Johnstown and Altoona/Martinsburg, Pennsylvania (see Fig. 1). Wind speed and direction at the towers were monitored 20.6 m above the ground. Atmospheric temperature, pressure, relative humidity (r.h.) and dewpoint were continuously recorded.

At Laurel the atmospheric aerosol and gas measurements, as well as the measurements of light scattering and u.v. radiation intensity, were made on the (slightly taller) tower 18–21 m above the ground. Wind speed and direction were monitored 24.5 m above the ground. Atmospheric temperature, pressure and r.h. were continuously recorded. Mixing height was monitored with an acoustic sounder. Pibals were released on most days, equipped with radiosonde and tracked by theodolite, to obtain vertical profiles of wind speed, wind direction and temperature and pressure. The plane of the treetops at Laurel was 16.5 m above the ground.

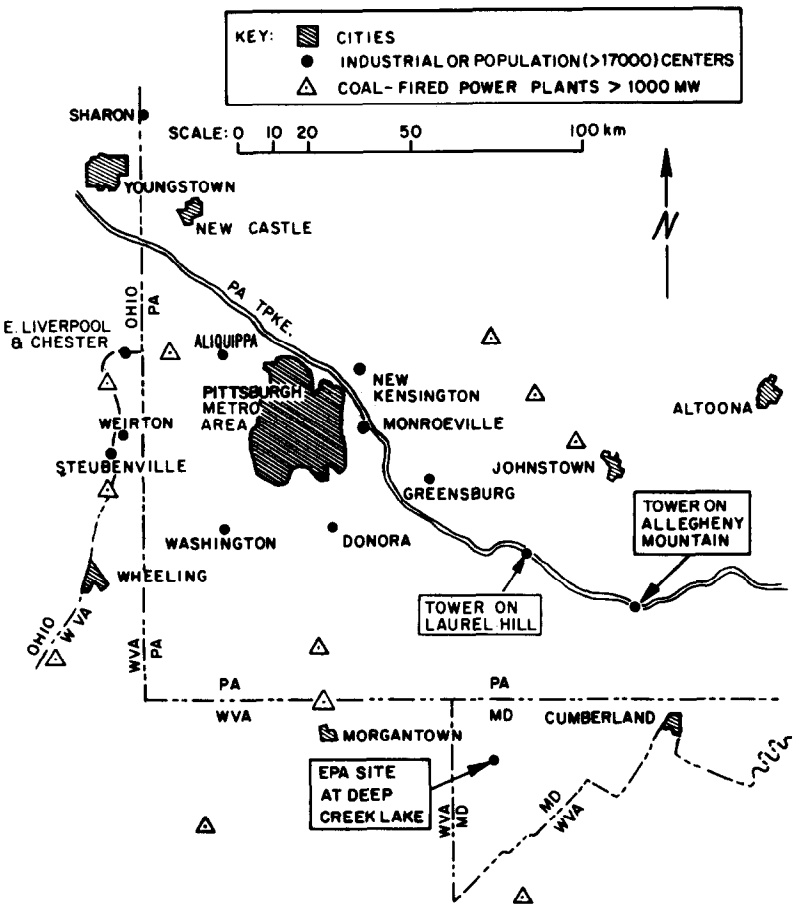

Fig. 1. Map of the sourthwestern Pennsylvania vicinity of the Allegheny Mountain/Laurel Hill experiment.

Mixed-layer 72-h back trajectories for air arriving at the sites at 0200, 0800, 1400 and 2000 EDT daily were generated from NWS data by methods described by Heffter (1980) and by Samson (1980). Exact times of frontal passage were determined from the recorded temperature, pressure, humidity/dewpoint and wind speed and direction. Surface trajectories and 850-mb trajectories were also obtained from the NWS for 0800 and 2000 EDT arrival each day.

The atmospheric gases measured at Allegheny included NO_2 (together with PAN) and NO continuously, by a chemiluminescence NO_x monitor; PAN semi-continuously by a gas chromatograph with an electron-capture detector (Holdren and Spicer, 1984); O_3 continuously by u.v. absorption; SO_2 by a H_2O_2 impinger collection method followed by ion chromatographic analysis as SO_4^{2-} (Pierson *et al.*, 1980); and SO_2 continuously by pulsed u.v. fluorescence. $HNO_3(g)$ and aerosol NO_3^- were measured by the denuder-difference method (Appel *et al.*, 1981; Shaw *et al.*, 1982; Spicer *et al.*, 1982) using MgO-coated denuder tubes and nylon membrane filters (nominal pore diameter 1 μm), with ion chromatographic NO_3^- determination on dilute-base extracts of the filters. The inlet of the denuder-difference apparatus was a Teflon cyclone with a 1.5-μm cutoff ("Cyclone II" of Smith *et al.*, 1979) to exclude large-particle NO_3^- that might otherwise deposit in the denuder and be mistaken for HNO_3. Significant amounts of $N_2O_5(g)$ can be expected at night (Chang *et al.*, 1987); the possibility that N_2O_5 could register to some degree as HNO_3 in the denuder-difference apparatus at high humidities (Spicer, 1986), as often occur at night at Allegheny, was not evaluated. $NH_3(g)$ was determined by oxalic-acid-coated denuder tubes (Ferm, 1979; Hara *et al.*, 1982). Valid $NH_3(g)$ data were obtained in only a few runs because of problems of water condensation in the denuder tubes.

The Laurel gas measurements included NO_x (meaning NO + NO_2 + PAN), but not NO and NO_2 separately, by chemiluminescence; SO_2 as above; $HNO_3(g)$ as above; and $NH_3(g)$ as above and with the same problems.

Aerosol samples at Allegheny and Laurel were collected as follows:

(1) with HiVol samplers equipped with cyclone preseparators to exclude particles larger than 2.5 μm, using 8″ × 10″ quartz-fiber filters prefired in air overnight at 600°C;
(2) on 142-mm diameter Teflon membrane filters, nominal pore diameter 0.2 μm, using an inlet to exclude particles larger than ~ 10 μm;
(3) in dichotomous samplers on pairs of preweighed (at 20°C and 50% r.h.) 37-mm Teflon membrane filters, nominal pore diameters 1.0 μm, one filter for fine (< 2.5 μm) particles and the other for coarse (> 2.5 μm), each sampler being equipped with an inlet to exclude particles > 15 μm (first 16 runs) or > 10 μm (subsequent runs);
(4) in 8-stage Andersen cascade impactors at Allegheny only, with cellulose filters (Whatman 41) for impactor plates and with quartz-fiber backup filters;
(5) on the nylon membrane filters of the denuder-difference apparatus.

The HiVol filters, 142-mm filters, and impaction substrates were sealed in airtight bags or other containment immediately after collection to keep out NH_3. All samples were stored in the dark at room temperature. Even so, it is recognized that reactions with ambient $NH_3(g)$ *during* sampling will cause aerosol H^+ to be underestimated and aerosol NH_4^+ commensurately overestimated; this effect was suppressed in other work (Stevens *et al.*, 1978) by means of a NH_3 denuder upstream of the filter.

The aerosol filter samples were analyzed as follows.

(1) The HiVol filters were analyzed for H^+, NH_4^+, and SO_4^{2-} within a few weeks after sampling, by pH measurement and ion chromatography on aqueous extracts. They were also analyzed for total S by combustion using a LECO analyzer, for elemental and organic carbon (EC and OC) by a thermal/optical technique (Huntzicker *et al.*, 1982), and for trace elements by inductively coupled argon plasma atomic emission spectroscopy (ICP/AES). For the trace elements, samples were prepared by strong acid digestion in Parr bombs.
(2) The 142-mm Teflon membrane filters were analyzed for H^+, NH_4^+ and SO_4^{2-} as above.
(3) The dichotomous sampler filters were analyzed for fine and coarse mass gravimetrically (at 20°C and 50% r.h.), and for S and 47 other elements by x-ray fluorescence and neutron activation analysis (by NEA, Inc.).
(4) The cascade impactor size distributions of H^+, NH_4^+ and SO_4^{2-} were determined by pH measurement and ion chromatography on aqueous extracts. The size distributions of 23 trace elements were determined on acid-digested samples by ICP/AES and by atomic absorption.
(5) The nylon filters were analyzed for NO_3^- and SO_4^{2-} by extraction and ion chromatography as stated above.

There were 44 air sampling runs at Allegheny ranging in duration from 23 to 1610 min and 39 runs at Laurel ranging from 200 to 1409 min. The sampling schedule was the same for filters, denuders and impingers at a given site and, with a few exceptions, between sites. The samplers generally were started each morning when the acoustic sounder and other meteorological data indicated the development of a mixed layer and were stopped in the early evening when the layer was seen to be collapsing. At night the sampling times were generally dictated by the onset and end of dew formation. On a few occasions, sampling was timed to coincide with rain.

The sampling schedule for the cascade impactors was dictated by the analytical detection limits and by the attempt to obtain size distributions during rain only; five impactor samples ranging in duration between 146 and 9497 min spanned the experiment.

RESULTS

The most important results of the present study are as follows.

(1) The air was decidedly acidic, with an overwhelming predominance of $HNO_3(g)$ and aerosol H^+ over any base including $NH_3(g)$ or aerosol trace minerals. Aerosol H^+ contributed not quite 3 times as much acidity as did $HNO_3(g)$, with averages 205 and 78 nmole m^{-3}, respectively, and one overnight period averaging 844 and 263 nmole m^{-3}, respectively. The potential for acidification by SO_2 was even greater since its average concentration was ~450 nmole m^{-3} or, in potential H^+, ~900 neq m^{-3} (3600 neq m^{-3} maximum).
(2) The aerosol was mostly aqueous H_2SO_4 partly neutralized to NH_4^+ salts, with mean particle diameter ~0.8 μm and with SO_4^{2-} constituting ~1/3 of the aerosol mass on the average (~1/2 at maximum). The SO_4^{2-} concentration ranged between 36 and 1156 neq m^{-3} (2–55 μg m^{-3}). The aerosol SO_4^{2-} was essentially stoichiometric with the sum of NH_4^+ and H^+. The aerosol H^+/SO_4^{2-} ratio was a function of SO_4^{2-} concentration, and ranged from 0.4 mole/mole at the lowest SO_4^{2-} concentrations to 1.46 at the highest, with a mean of 1.0.
(3) Episodes of high SO_4^{2-} occurred every 7 or 8 days and lasted several days.
(4) Consistent with the high aerosol H^+ levels, $NH_3(g)$ was extremely low (< 15 nmole m^{-3} or < 0.4 ppb).
(5) Also consistent with the high aerosol H^+ levels, ~90% of the inorganic nitrate (HNO_3 + aerosol NO_3^-) existed as $HNO_3(g)$.
(6) The $HNO_3(g)$ concentrations followed 7- or 8-day cycles similar to, and concurrent with, the SO_4^{2-} cycles.
(7) The night-time average $HNO_3(g)$ concentration was lower than the daytime average. The O_3 diurnal variation was small.
(8) High concentrations of $HNO_3(g)$, SO_2 and aerosol H^+ and SO_4^{2-} all tended to be associated with stagnation and air masses from westward, though the HNO_3 and SO_2 were not particularly well correlated with each other or with the aerosol H^+ and SO_4^{2-}.
(9) Low concentrations of $HNO_3(g)$, SO_2, O_3 and aerosol H^+ and SO_4^{2-} were associated with fast-moving air masses and air masses from northerly directions. Upwind precipitation also made for lower concentrations.
(10) The correlations of the aerosol species H^+, NH_4^+, SO_4^{2-} at Allegheny with their counterparts at Laurel were extremely high (r ~0.96), demonstrating that the distance scale for the chemistry involving these species was ≫ 35 km. The inter-site couplings in the case of HNO_3 and SO_2 were weaker (r ~0.8).
(11) Light scattering and visibility degradation were attributable to the acidic SO_4^{2-} aerosol.

The results will be discussed in more detail below. Many of them confirm results from the 1977 experiment.

Weather during the experiment

Average values of some of the meteorological variables are listed in Table 1. The mixed-layer winds (averaged from the surface to the top of the mixing layer; Heffter, 1980; Samson, 1980) were mostly westerly but there were many exceptions, including a 4-day period beginning on 12 August when winds were steadily out of the NNE. This period was character-

Table 1. Averages of some meteorological variables during the August 1983 Allegheny Mountain/Laurel Hill experiment

	Allegheny	Laurel
Wind speed ($m\,s^{-1}$), mixed layer	4.5	4.4
Wind speed ($m\,s^{-1}$), at tower	3.9	3.1
Wind direction origin at tower (°True)	270	267
Temperature (°C)	20	21
Relative humidity (%)	78	72
Dewpoint (°C)	14.5	–
Barometer (mm Hg)	699	700
Daily maximum mixing ht (m)	–	1500[a]
Daytime u.v. intensity ($W\,m^{-2}$)	16.9	16.9
Visual range (km)	21[b]	–
b_{scat} (m^{-1})	(1.9×10^{-4})[c]	(1.9×10^{-4})[c]
b_{abs} (m^{-1})	1.9×10^{-5}	–
Condensation nuclei count (cm^{-3})	5776	–
Daily average rainfall (mm)	2.2	0.6

[a] Median value of the daily maxima, obtained from acoustic sounder and radiosonde data and estimates of heights of cloud tops.
[b] Daytime only and without fog.
[c] With heated nephelometer inlet. Cell temperature is ~ 15°C above ambient.

ized by low temperature, about-average humidity, no rain, maximum visual range (> 35 km), minimum b_{scat} (Fig. 2, runs 12–19) and minimum or near-minimum values of most species including HNO_3, SO_2 and aerosol mass (coarse and fine), H^+, NH_4^+ and SO_4^{2-} (Fig. 2).

With one or two exceptions, a surface inversion developed every night. The night-time inversion began to break at about 0745, and by noon a well-mixed layer had developed, of height 550 to > 2500 m, which collapsed quickly (within 1-h or so) around 1915. As is typical of this locality and elevation, the average overnight r.h. was high (85% at Allegheny, 78% at Laurel), and there was always heavy dew on a clear night (Pierson *et al.*, 1986). The sites were in cloud on at least seven occasions at Allegheny and four at Laurel.

The mixing-height measurements were difficult, and the radiosonde and acoustic sounder data did not always agree. On all but one day (19 August), the maximum mixing height exceeded the range setting of the acoustic sounder chart (500 m in the first 10 days, 1000 m afterwards); when the range was exceeded, mixing heights were obtained by visual estimate of the height of the cloud tops (believed to be gaugeable to within ± 300 m) and/or from the radiosonde data.

Average concentrations

Time-average concentrations of the atmospheric species pertinent to the present discussion are listed in Table 2. The numbers document some of the results already stated. The ambient acidity is evident in the HNO_3(g) and in the larger amounts of aerosol H^+, the lack of NH_3(g) or potentially alkaline aerosol constituents (Mg, Ca, etc.), and the further acidification potential represented by SO_2. The near stoichiometry of the aerosol H^+ and NH_4^+ with the SO_4^{2-}, which in turn represents much of the aerosol mass, and the lack of other ions in significant amounts, suggests an aqueous $(NH_4)_xH_{(2-x)}SO_4$ aerosol with $0<x<2$ and $\bar{x}$ approximately 1.0. The dearth of NH_3(g) is consistent with the pronounced aerosol acidity, as is also the lack of aerosol NO_3^-—most of the inorganic NO_3^- is present as HNO_3(g)—or of aerosol Cl. Comparison of the (NH_3 + aerosol NH_4^+) with (HNO_3 + aerosol NO_3^- + aerosol SO_4^{2-}) suggests that generally there was initially only enough NH_3(g) to neutralize about 35% of the HNO_3 and H_2SO_4 produced or emitted.

The average compositions at the two sites are similar. Concentrations tended to be marginally higher at Laurel than at Allegheny and the Laurel aerosol was less neutralized than the Allegheny aerosol ($H^+/NH_4^+/SO_4^{2-} = 1.05/0.83/1$ at Laurel vs 1.01/0.88/1 at Allegheny). Since Allegheny was usually downwind of Laurel, these differences are qualitatively plausible.

Figure 3 shows that high H^+/SO_4^{2-} ratios in the aerosol were favored at high SO_4^{2-} concentrations, and that high NH_4^+/SO_4^{2-} ratios were favored at the lowest SO_4^{2-} concentrations though a fully neutralized $(NH_4)_2SO_4$ aerosol was never observed. Finally, the sum of H^+/SO_4^{2-} and NH_4^+/SO_4^{2-} mole ratios, 1.88 or essentially 2.0, was independent of SO_4^{2-} concentration. The same behavior was seen in the 1977 Allegheny experiment, and suggests that the degree of neutralization of the H_2SO_4 aerosol depends on how much there was to neutralize.

Figure 2 shows that in the most pronounced SO_4^{2-} episode, the one that ran from around 16 August to 20 August, the first half of the episode had a more acidic aerosol than did the second part. That is, the high H^+ (or H^+/SO_4^{2-} ratio) tended to be in the build-up phase of the episode and the high NH_4^+ tended to be in the

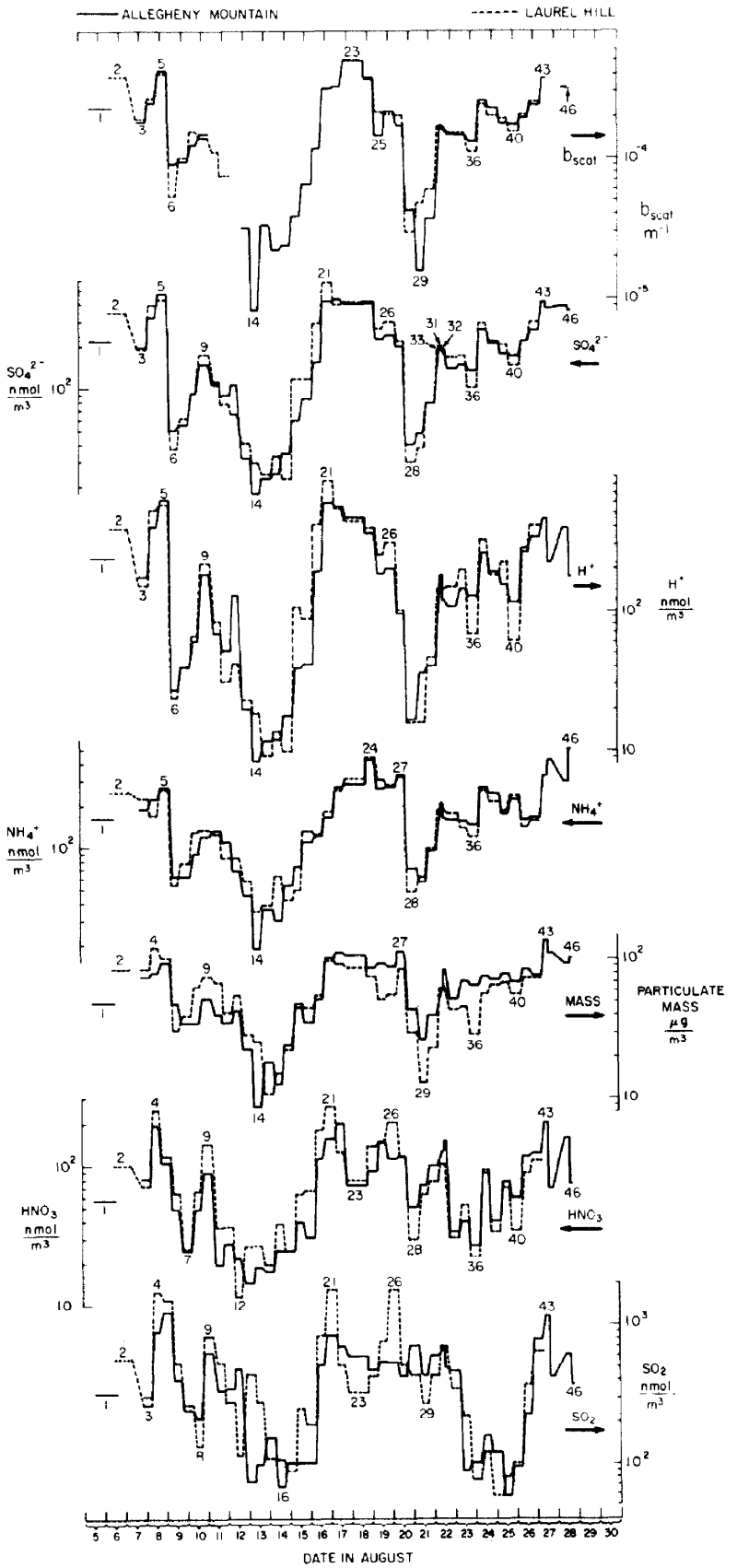

Fig. 2. Plot of run-average aerosol mass, H^+, NH_4^+ and SO_4^{2-}, the gases HNO_3 and SO_2, and b_{scat}, vs time, Allegheny Mountain and Laurel Hill, August 1983. Solid lines: Allegheny Mountain. Broken lines: Laurel Hill. Run number designations indicated are those used throughout the paper.

Table 2. Time-average atmospheric concentrations, Allegheny Mountain and Laurel Hill, August 1983

	Allegheny Mountain 5–28 August			Laurel Hill 6–27 August		
	nanomole m^{-3}	ppb	$\mu g\,m^{-3}$	nanomole m^{-3}	ppb	$\mu g\,m^{-3}$
SO_2	409	11	26	490	13	31
O_3	2178	56	105	–	–	–
NH_3	[a]	[a]	[a]	[a]	[a]	[a]
NO	11	0.3	0.3	[b]	[b]	[b]
NO_2 + PAN	220	5.7		(316)[b]	(8.1)[b]	
PAN	46[c]	1.2[c]	6[c]	–	–	–
HNO_3	71	1.8	4.5	85	2.2	5.3
Aerosol Total Mass			64[d,e]			59[d,f]
H^+	193		0.2	216		0.2
NH_4^+	173		3.1	171		3.1
NO_3^-	8[g]		0.5[g]	10[g]		0.6[g]
SO_4^{2-}	195		18.7	206		19.8
Other S	15[h]		0.5[h]	21[h]		0.7[h]
Cl	3		0.1	2		0.08
C elemental	102[i]		1.2	116[i]		1.4
organic	169[i]		2.0	188[i]		2.3
Na	3.9[j]		0.089[j]	3.4[j]		0.079[j]
Mg	2.8[j]		0.069[j]	2.8[j]		0.068[j]
Al	15.8[j]		0.43[j]	15.9[j]		0.43[j]
Si	57.2[j]		1.61[j]	55.6[j]		1.56[j]
K	3.6[j]		0.142[j]	3.5[j]		0.136[j]
Ca	7.00[j]		0.28[j]	7.06[j]		0.28[j]
Fe	4.9[j]		0.27[j]	5.4[j]		0.30[j]
Se	0.028		0.0022	0.032		0.0025
Br	0.067		0.0054	0.068		0.0055
Pb	0.207		0.043	0.236		0.049
Other elements			0.13[k]			0.14[k]
Not attributed			34[l]			27[l]

[a] NH_3(g) was 5, $\leqslant 14$, $\leqslant 15$ nanomoles m^{-3} on the first three Allegheny runs, and 1.3, 5, $\leqslant 18$, $\leqslant 7$ nanomoles m^{-3} on the first four Laurel runs. No further valid NH_3 data were obtained.

[b] Laurel NO data are questionable. This could affect NO_2 + PAN values. See text.

[c] PAN GC/ECD data were obtained only for the last half (12.5 days out of 24 days) of the experiment.

[d] Mass in weighing room at 20°C and 50% r.h.

[e] 76% = fine (MMED $\leqslant 2.5\ \mu m$).

[f] 78% = fine (MMED $\leqslant 2.5\ \mu m$).

[g] Includes particles $\leqslant 1.5\ \mu m$ only.

[h] Difference between total S (by combustion) and SO_4^{2-}. The chemical nature of the non-SO_4^{2-} aerosol S is not known. It is larger relative to SO_4^{2-} at the lowest SO_4^{2-} concentrations.

[i] Nanogram-atoms C m^{-3}.

[j] Mostly coarse ($\geqslant 2.5\ \mu m$).

[k] P, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Dy, Tm, Lu, Hf, Ta, W, Au, Hg, Th.

[l] Probably chiefly water at 50% weighing-room humidity. See text.

trailing part. Such behavior is not obvious at other times in this study or in the 1977 study. The episode began with local stagnation and continued with advection from the west, ending with fast-moving air from the NW.

The $SO_4^{2-}/(SO_2 + SO_4^{2-})$ ratio was higher at Allegheny than at Laurel, both in the night runs (average ratio 0.29 at Allegheny vs 0.26 at Laurel) and in the day runs (Allegheny 0.33 vs Laurel 0.29). These results would be consistent with $SO_2 \rightarrow SO_4^{2-}$ conversion and/or SO_2 dry deposition in transit from Laurel to Allegheny. The existence of approximately 30% of the $SO_2 + SO_4^{2-}$ as SO_4^{2-} suggests that considerable conversion has already taken place, and hence suggests a considerable aging time for the SO_4^{2-} aerosol. To the extent that the SO_2 has been augmented by highly localized (in time, and hence also in space) SO_2 puffs, as illustrated by the spikes in Fig. 4, the conversion corrected for these local SO_2 puffs would be higher still. The substantial O_3 at Allegheny signifies an oxidizing condition conducive to the formation of HNO_3 and H_2SO_4 from atmospheric NO_x and SO_2 precursors. The high NO_2/NO ratios and significant PAN and HNO_3 concentrations are indicative of the same and support the perception of a polluted air mass that has undergone some photochemical aging.

Carbon, though a small part of the aerosol mass, was a leading chemical component on an atom basis; hence its inclusion in Table 2. Some of the organic carbon probably consists of gas-phase compounds

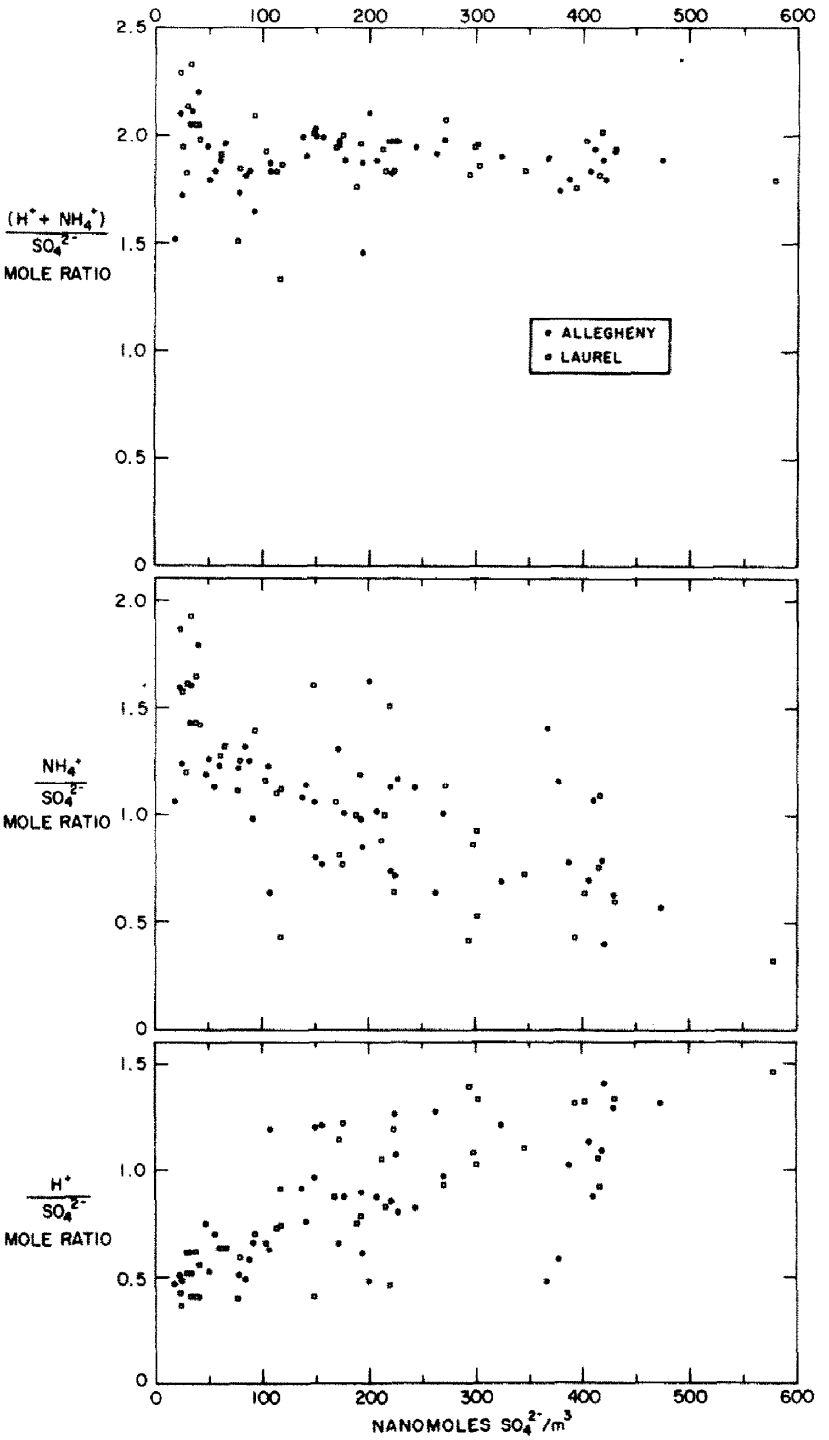

Fig. 3. Plot of aerosol H^+/SO_4^{2-} and NH_4^+/SO_4^{2-} mole ratios, and their sum $(H^+ + NH_4^+)/SO_4^{2-}$, as a function of aerosol SO_4^{2-} concentration, Allegheny Mountain and Laurel Hill, August 1983. Filled circles = Allegheny Mountain data. Open squares = Laurel Hill data.

adsorbed onto the quartz fibers of the HiVol filters (Cadle *et al.*, 1983) during aerosol sampling.

The aerosol mass not recorded in Table 2 probably was chiefly water. At the 50% r.h. of the weighing room, an aqueous H_2SO_4 solution in vapor-pressure equilibrium with the air is 43.1% H_2SO_4 by mass (Stokes and Robinson, 1949). The vapor pressure lowering by $(NH_4)_2SO_4$ or NH_4HSO_4 per mole is only slightly less than that by H_2SO_4. The water estimated by this means would account for 71% of the

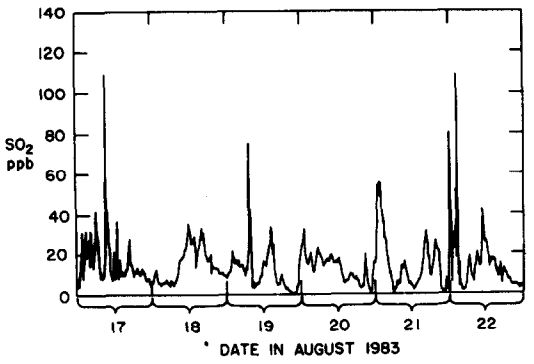

Fig. 4. A section of the record of SO_2 concentrations measured continuously by pulsed u.v. fluorescence at Allegheny Mountain, August 1983.

unrecorded mass at Allegheny and 96% at Laurel. Another 10% of the unrecorded mass is implied by the trace elements—i.e. for Si one can assume SiO_2, for Ca perhaps CaO or $CaCO_3$, etc.

Qualitative evidence for the contribution of water to the aerosol mass comes from the nephelometry measurements. When the nephelometer incoming air was cooled by $\sim 5°C$ by turning off the inlet heater, b_{scat} increased by a factor of 1.2 in clear air at 67% r.h. and by a factor of 1.6 in cloud at 92% r.h. Even without the inlet heater, the air in the nephelometer exit (and hence in the cell) was still 4 or 5°C above ambient temperature. Therefore there apparently was enough water in the aerosol *in situ* to contribute substantially to the light scattering. The effect is at least qualitatively consistent with summertime measurements in the Shenandoah Valley where much of the light scattering was traceable to SO_4^{2-}-associated water (Ferman *et al.*, 1981; Weiss *et al.*, 1982).

Concentration spikes, of half-width sometimes only a few min, were exhibited by SO_2 (Fig. 4) and by NO, NO_2 and CNC, traversing one or the other (seldom both) of the two sites. Given the surface wind speeds in Table 1, the spatial dimension corresponding to a 5-min spike is only ~ 1 km. There were four SO_2 spikes at Allegheny, and ten at Laurel, with peak 2-min averages between 80 and 459 ppb. Most of them were < 20 min half-width, the shortest being 5 min. They were predominantly associated with surface winds from the west ($276 \pm 63°T$) and were accompanied by NO_x spikes of amplitude between 9 and 163 ppb, predominantly NO_2 at the lower NO_x concentrations but reaching $NO/NO_2 = 1$ at the highest NO_x level. These SO_2/NO_x spikes sometimes were accompanied by an O_3 deficit spike but not much change in CNC. None of these large SO_2 spikes occurred between 0930 and 1650 (EDT); one interpretation would be that the spikes result from poorly dispersed power plant plumes injected and transported above the surface mixing layer.

NO and NO_2 spikes often occurred together, usually with $NO/NO_2 \leqslant 0.15$ and with half-width $\leqslant 10$ min, a few as short as 2 min FWHM. There were 14 NO_x spikes at Allegheny, and 23 at Laurel, with peak 2-min averages between 40 and 163 ppb. Many were not accompanied by SO_2 spikes. Only 3 of the 37 occurred between 0910 and 1840 (EDT). The NO spikes are estimated to have accounted for over half of the NO at Allegheny during the study. The largest NO_x spikes were of three types. One type, seen primarily at Allegheny, was associated with surface winds from the ESE octant and was accompanied by a CNC spike and by an equally sharp deficit spike of O_3, but never an SO_2 spike. Such spikes accounted for $\sim 70\%$ of the run-average NO_x in one run (run 38, night of 24 August, 694 min long) at Allegheny. The second type, seen at either site, was the same as the first but was associated with surface winds from the opposite direction ($303 \pm 17°T$). For both types, the O_3 was suppressed, occasionally to as low as 2 ppb. The third type, and the most prevalent at Laurel, was associated with surface winds from the west ($278 \pm 40°T$) and were accompanied by enormous SO_2 spikes—usually ~ 2.5 times as large (in ppb) as the NO_x. This type was not represented among the larger NO_x spikes at Allegheny. (None of the largest 14 NO_x peaks at Allegheny had an SO_2 peak associated with them.)

The one obvious nearby NO_x source to the ESE at each site is the Turnpike traffic, which fits the description of the first type of NO_x spikes; indeed, on most mornings at Allegheny there was an order-of-magnitude (~ 1 ppb) increase in hourly-average NO accompanied by an increase (also ~ 1 ppb) in NO_2. This in turn suggests Turnpike traffic as responsible for the similar NO_x spikes from the opposite direction (WNW). The third type of NO_x spikes and the accompanying SO_2 spikes are ascribed to plumes from the several large power plants in the vicinity (Fig. 1).

None of the largest SO_2 or NO_x spikes was accompanied by any discernible change in b_{scat}. This implies that the aerosol responsible for the light scattering is not directly emitted from the sources of the SO_2 or NO_x spikes.

The mid-day u.v. intensities and relative concentrations of O_3, NO and NO_2 at Allegheny are in reasonable accord with the photostationarity condition. At Laurel, there are questions about the NO data. In addition, O_3 was not measured there, so that the NO data cannot be validated against the photostationarity criterion. Accordingly, we have opted to ignore the Laurel NO data. (Since $NO_2 + PAN$ is a difference measurement between NO_x and NO, a small percentage error in $NO_2 + PAN$ at Laurel is implied.)

Diurnal variability

Night/day ratios, and night and day averages, are listed in Table 3. For wind speed, b_{scat}, condensation nuclei count (CNC), O_3, NO, $NO_2 + PAN$, PAN and $\Sigma(NO + NO_2 + PAN)$, all-day averages and all-night averages of all data from the continuous monitoring were used. For each of the other variables it was

Table 3. Diurnal variations, night/day[a], Allegheny Mountain and Laurel Hill, August 1983. Night and day time-weighted averages are given in parentheses, in the dimensions indicated

	Allegheny	Laurel
Surface wind speed ($m\,s^{-1}$)	1.1 (4.1/3.7)	1.0 (3.1/3.0)
$b_{scat}(10^{-4}\,m^{-1})$	1.0[b] (1.9/1.9)	1.1[b] (1.9/1.8)
CNC (cm^{-3})	0.7 (4700/6700)	--
SO_2 ($nmol\,m^{-3}$)	1.05 (823/783)	1.2 (1057/895)
O_3 ($nmol\,m^{-3}$)	0.95 (2067/2168)	--
NO ($nmol\,m^{-3}$)	0.3 (6/18)	[c]
NO_2 + PAN ($nmol\,m^{-3}$)	1.3 (286/219)	(1.0 (355/339))[c]
PAN ($nmol\,m^{-3}$)	0.8 (41/49)	--
$\Sigma(NO + NO_2 + PAN)$ ($nmol\,m^{-3}$)	1.2 (292/237)	1.0 (414/404)
HNO_3 ($nmol\,m^{-3}$)	0.7 (64/86)	0.9 (80/89)
Aerosol mass, coarse ($\mu g\,m^{-3}$)	1.3 (17/13)	1.1 (12.5/11)
fine ($\mu g\,m^{-3}$)	0.8 (42/54)	0.9 (40/46)
H^+ ($nmol\,m^{-3}$)	0.9 (168/178)	1.0 (189/190)
NH_4^+ ($nmol\,m^{-3}$)	0.9 (158/178)	1.1 (160/150)
NO_3^- ($nmol\,m^{-3}$)	1.6 (9/6)	1.3 (11/9)
SO_4^{2-} ($nmol\,m^{-3}$)	0.9 (342/377)	1.0 (368/360)
Other S ($nmol\,m^{-3}$)	0.7 (28/41)	0.8 (39/51)
C elemental ($\mu g\,m^{-3}$)	1.1 (1.24/1.14)	1.0 (1.31/1.37)
organic ($\mu g\,m^{-3}$)	0.8 (1.91/2.27)	1.0 (2.27/2.31)

[a] For wind speed, b_{scat}, CNC, O_3, NO, NO_2 + PAN, PAN, and $\Sigma(NO + NO_2 + PAN)$, all night-time ($\equiv$ 2000 to 0700 EDT) and daytime ($\equiv$ 0700 to 2000 EDT) data from the continuous monitoring were used. For everything else, time-weighted averages of night-time runs and of daytime runs (two Allegheny runs and two Laurel runs were excluded as covering longer periods) were used.

[b] Heated nephelometer inlet. Cell temperature is $\sim$ 15°C above ambient.

[c] Laurel NO data are questionable. This could affect NO_2 + PAN values. See text.

necessary to use the time-weighted average from the night-time runs and the time-weighted average from the daytime runs; two long runs at Allegheny and two at Laurel were excluded as falling into neither category, and hence the overall averages in Table 2 do not always fall between the night and day averages in Table 3. When a ratio differs significantly from unity, then obviously the diurnal peak/valley ratio exceeded the ratio given in Table 3. Representative diurnal variations constructed from continuous data for certain of the species are illustrated in Fig. 5. Composite valley/peak ratios include 0.4 for PAN and 0.8 for O_3 (night/day, Fig. 5), 0.4 for CNC (night/day), 0.8 for wind speed (day/night).

The large diurnal variation in NO (Fig. 5) is basically as expected: Oxidation of NO by the considerable excess of O_3 proceeds all the time while NO_2 photolysis is arrested at night. In addition, however, there was an order-of-magnitude NO excursion on most mornings, reaching a maximum at about 1000 EDT (Fig. 5). Much or most of the NO_x peak ($NO + NO_2$ + PAN, Fig. 5) occurring at that time consisted of NO. Concurrently there was an O_3 minimum (Fig. 5), deeper in terms of ppb than the increase in NO_x or NO. The surface mixing layer is building up at that time, perhaps allowing NO emitted and stored overnight at lower elevation to reach the site, its rapid conversion to NO_2 upon mixing with the O_3 being offset somewhat by NO_2 photolysis.

Total NO_x had a pronounced diurnal maximum at around 2100 EDT consisting wholly of an increase in NO_2 with little or no change in NO or PAN (Fig. 5). The upslope coincided more or less with the collapse of the daytime mixing layer, and is interpreted as signifying the confinement of NO_x emissions to the increasingly thinner layer. The downside of the peak would then set in as the nocturnal surface inversion forms below the mountaintop and air that is cut off from ground-level emissions begins to be sampled. The wide daytime valley in the NO_x concentration (between the 1000 and 2100 peaks) is then a reflection of dilution attending the evolution of the mixing layer.

PAN declined during the night—presumably because its photochemical production ceases while its thermal dissociation continues—with a decay half-life of 7 to 8 h (Fig. 5). The PAN diurnal maxima and minima were at about 1800 and 0830 EDT, respectively.

HNO_3 was lower at night presumably because its photochemical production stopped. The relatively small diurnal change compared, for example, to the situation in the Los Angeles basin (Pierson *et al.*, 1988) indicates that most of the HNO_3 is transported to the site rather than locally formed. Meanwhile, at night aerosol NO_3^- increased, possibly because of the gas/particle equilibrium effects of humidity and temperature. The low HNO_3 deposition velocity found in the present experiment under stratified night-time condi-

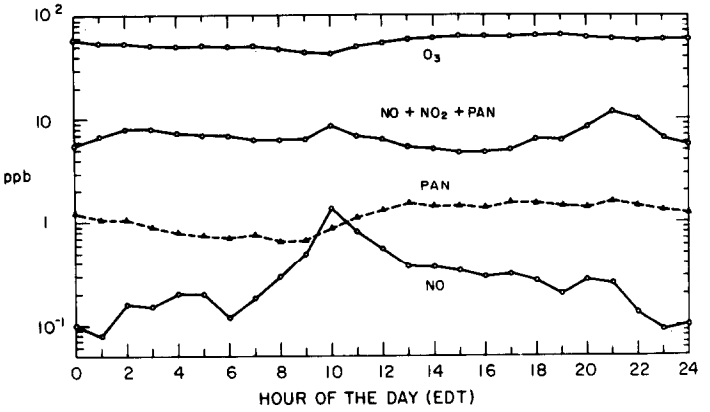

Fig. 5. Diurnal variations of O_3, PAN, NO and "NO_x" ($\equiv NO + NO_2 + PAN$) representing the composite of hourly averages of continuous data for the entire study, Allegheny Mountain, August 1983.

tions (0.24 cm s^{-1}; Pierson *et al.*, 1986), in contrast to order-of-magnitude higher daytime values, suggests that long-distance transport of HNO_3 at night is possible.

The CNC diurnal pattern (not illustrated), with a flat minimum from 0000 to 0900 followed by build-up to a peak around 1230, appears consistent with photochemical production. The u.v. peak was at 1400 EDT.

The $SO_4^{2-}/(SO_2 + SO_4^{2-})$ ratio was 10% lower at night than in the daytime, at both sites, mostly because the daytime ratio was raised by an afternoon subsidence in the SO_2 concentration. This subsidence, commencing around noon, is almost a mirror image of the afternoon O_3 enhancement. But there was little, if any, corresponding increase in b_{scat} (hence, in real-time SO_4^{2-}). Because of dilution effects attending changes in mixing depth, and because of the possibility of enhanced SO_2 dry deposition from the unstable afternoon atmosphere, these observations argue neither for nor against a significant local daytime component in the $SO_2 \rightarrow SO_4^{2-}$ conversion.

We did not see any daytime increase in H^+/SO_4^{2-} ratio or in H^+/NH_4^+ ratio at either site (Table 3). Such increases would have been indicative of daytime local $SO_2 \rightarrow SO_4^{2-}$ conversion, and have been unequivocally seen in other work at other sites (Stevens *et al.*, 1980, 1984; Weiss *et al.*, 1982). Our interpretation is that the Allegheny and Laurel sites are above the surface inversion which forms in the evening so that (1) the acid aerosol is cut off from further ground-level NH_3 emissions and (2) removal processes are suppressed. The lack of diurnal variation in H^+/SO_4^{2-} or H^+/NH_4^+ then means that local daytime $SO_2 \rightarrow SO_4^{2-}$ conversion is relatively unimportant. In other words, the H^+, NH_4^+, SO_4^{2-}, and their ratios, as seen at the sites are the composition of what is transported rather than what is locally generated. (If $SO_2 \rightarrow SO_4^{2-}$ rate coefficients are of the order of 10^{-2} h^{-1} as generally thought, then this is plausible.)

The O_3 diurnal variation (Fig. 5) was only ~20% except for the minimum coinciding with the midmorning NO peak. This lack of diurnal variation would be expected at high-altitude rural sites where night-time ground removal of O_3 is inhibited by the night-time atmospheric stability (the sites are above the surface inversion) and NO has become depleted.

Finally, it appears that the coarse aerosol mass was higher at night than in the daytime, whereas the fine was higher in the daytime than at night. This is consistent with a slight particle-size shift with the higher r.h. that existed at night (Keeler *et al.*, 1988).

Intra-site correlations

Table 4 lists intra-site correlation coefficients of run-average data obtained at Allegheny and at Laurel. Only those variables thought to be of importance to the present discussion are included. Si, Se, Pb, and elemental C(EC)—coarse plus fine in each instance—are included as candidate markers for soil dust, coal burning, automotive emissions and fuel combustion in general (including diesel trucks, woodburning, etc.), respectively; V, a potential marker for fuel-oil burning, was omitted because it showed no significant correlation with anything else. Mn was included because its peak concentrations tended to coincide with SO_2 peak concentrations.

The highest correlations are of b_{scat}, aerosol H^+, and aerosol SO_4^{2-} with one another. Figure 6 shows that the relationship between b_{scat} and SO_4^{2-} is linear. The variance in one accounts for some 92% ($r^2 = 0.92$) of the variance in the other, with a slope of 8.8 ± 0.3 m^2 per gram of SO_4^{2-}. Clearly b_{scat} can be used as a real-time index of aerosol SO_4^{2-}. This is as expected, given the domination of the aerosol mass by SO_4^{2-} together with its associated cations and water.

According to regressions of day-only runs and night-only runs, the b_{scat}/SO_4^{2-} ratio tended to be ~12% higher in the night runs than in the day runs. This is qualitatively reasonable since the nephelometer cell was ~6°C cooler at night than in the daytime and since water associated with the SO_4^{2-} was playing a role in scattering.

Table 4. Intra-site correlation coefficients (r) from run-average data, Allegheny Mountain and Laurel Hill, August 1983. Data are arranged in pairs; top = r at Allegheny, bottom = r at Laurel. Values in parentheses are not significant at the 99% confidence level[a,b]

b_{scat}	CNC	SO_2(g)	O_3(g)	NO(g)	NO_2(g)[c]	PAN(g)[d]	HNO_3(g)	M[e]	H^+	NH_4^+	NO_3^-	SO_4^{2-}	EC[f]	Si	Mn	Se	Pb	
1	−0.57	0.57	0.50[h]	(−0.04)[i]	0.48[j]	0.83[k]	0.58[l]	0.84[m]	0.90	0.80	0.67	0.96	0.73	(0.28)	0.59	0.76	0.60	b_{scat}
1	–	0.47[k]	–	–	(0.21)[i]	–	0.53[n]	0.77[o]	0.89	0.77	(0.47)[p]	0.95	0.78	(0.08)	0.46	0.59	0.59	
	1	(0.02)[i]	(−0.09)[i]	0.82[k]	0.72[k]	(−0.09)[i]	(−0.06)[i]	(−0.23)[i]	(−0.27)[i]	(−0.21)[i]	(−0.15)[i]	−0.45[j]	(−0.20)	(0.13)	(−0.03)	(−0.13)	(−0.29)	CNC
	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
		1	0.59[i]	(−0.02)[i]	(0.20)[i]	(0.08)[i]	0.69[q]	0.54	0.70	(0.35)[i]	0.64[j]	0.63	0.58	0.56	0.65	0.86	(0.29)	SO_2(g)
		1	–	–	0.54[r]	–	0.85	0.55	0.70	(0.28)[i]	0.48[j]	0.64[s]	0.58	0.47	0.60	0.78	(0.25)	
			1	(−0.18)[i]	(−0.31)[i]	0.70[j]	0.77	0.68	0.59	0.59[j]	0.52[j]	0.62	0.46	0.65	0.50	0.42	(0.31)	O_3(g)
			–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
				1	0.39[t]	(0.13)[i]	(0.00)[i]	(−0.06)[i]	(−0.07)[i]	(0.03)[i]	0.50[k]	(−0.04)[i]	(0.06)	(−0.16)	(−0.14)	(−0.13)	(−0.13)	NO(g)
				u	–	–	–	–	–	–	–	–	–	–	–	–	–	
					1	(−0.15)[i]	(−0.06)[i]	(0.15)[i]	(0.07)[i]	(0.29)[i]	0.61[k]	(0.16)[i]	(0.36)	(0.02)	(0.17)	(0.25)	0.38	NO_2(g)
					1	–	0.63[j]	0.46[j]	(0.38)[i]	(0.31)[i]	0.61[j]	0.41	0.41	(0.18)	0.41	0.68	0.46	
						1	(0.44)[i]	0.71[k]	0.69[k]	0.78[k]	0.65[k]	0.78[k]	(0.36)	(0.40)	0.45	(0.19)	(0.29)	PAN(g)
						–	–	–	–	–	–	–	–	–	–	–	–	
							1	0.76	0.71[v]	0.51	0.72[j]	0.71[w]	0.50	0.61	0.47	0.56	(0.34)	HNO_3(g)
							1	0.65	0.82	0.49	0.63[j]	0.81	0.78	0.51	0.43	0.71	(0.37)	
								1	0.76	0.84	0.50	0.89	0.66	0.46	0.56	0.70	0.56	M
								1	0.78	0.65	(0.37)[i]	0.83	0.80	0.55	0.62	0.65	0.57	
									1	0.58	0.51[x]	0.93	0.78	(0.32)	0.52	0.76	0.46	H^+
									1	0.57	(0.38)[i]	0.97	0.88	(0.40)	0.48	0.73	(0.40)	
										1	0.47	0.83	0.52	(0.24)	0.47	0.57	0.60	NH_4^+
										1	0.73	0.75	0.58	(0.36)	0.46	0.61	0.63	
											1	0.53	0.52	(0.04)	(0.22)	0.52	0.53	NO_3^-
											1	0.53	(0.38)	(0.14)	(0.33)	0.50	0.50	
												1	0.74	(0.32)	0.56	0.76	0.59	SO_4^{2-}
												1	0.88	0.43	0.52	0.77	0.52	
													1	0.42	0.50	0.67	0.44	EC
													1	0.50	0.46	0.60	0.48	

[a] $|r_{crit}|$ for most of the Allegheny data (44 data pairs) is 0.384 at $p = 0.01$, 0.297 at $p = 0.05$; $|r_{crit}|$ for most of the Laurel data (39 data pairs) is 0.407 at $p = 0.01$, 0.316 at $p = 0.05$.
[b] In column and row headings, (g) signifies gas; all others refer to the particulate phase, coarse plus fine.
[c] NO_2 measurement includes PAN also.
[d] PAN data were obtained for only 25 runs.
[e] M ≡ gross particulate mass, coarse plus fine, as weighed at 20°C and 50% humidity.
[f] EC ≡ elemental C.
[g] Day-only value; 0.03 (insignificant) at night.
[h] 0.68 day, 0.49 night.
[i] Insignificant, day or night.
[j] Day-only value; insignificant at night.
[k] Night-only value; insignificant in the day.
[l] 0.74 day, 0.67 night.
[m] 0.87 day, 0.91 night.
[n] 0.67 day, 0.54 night.
[o] 0.76 day, 0.83 night.
[p] 0.56 day, 0.54 night.
[q] 0.76 day, 0.76 night.
[r] 0.78 day, 0.46 night.
[s] 0.58 day, 0.74 night.
[t] 0.65 day, 0.84 night.
[u] Laurel NO data questionable, not used. See text.
[v] 0.81 day, 0.78 night.
[w] 0.75 day, 0.76 night.
[x] 0.71 day, insignificant at night.

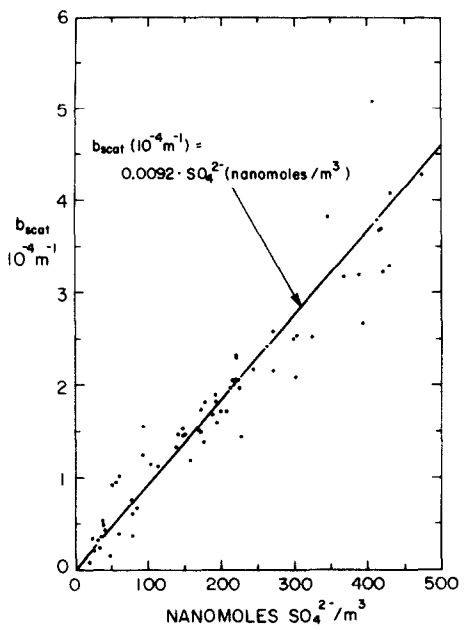

Fig. 6. Plot of run-average b_{scat} vs aerosol SO_4^{2-}, Allegheny Mountain and Laurel Hill combined, August 1983. The nephelometer inlet air is heated. The drawn line is a fit by eye, taking into account the uncertainties in each region. For comparison, linear least-squares regression yields $y = (0.00849 \pm 0.00032) \cdot x + 0.124 \pm 0.075$, $r = 0.96$.

The slope dH^+/dSO_4^{2-} (mole ratio) of the H^+ vs SO_4^{2-} regression line was 1.14 ± 0.07 at Allegheny and 1.34 ± 0.06 at Laurel, without a consistently significant night/day difference and with a very high correlation ($r = 0.93$ at Allegheny, 0.97 at Laurel). The actual relationship between aerosol H^+ and SO_4^{2-} is probably stronger than is implied by their correlation, first on the grounds that the $\sim \pm 10\%$ H^+ measurement uncertainty (± 0.02 pH units) surely degraded the correlation. Second, linear regression of H^+ vs SO_4^{2-} is not rigorously valid in that the slope of H^+ vs SO_4^{2-} is not a straight line; the H^+/SO_4^{2-} ratio is not constant but rather is a function of SO_4^{2-} concentration (Fig. 3). The same holds for NH_4^+ vs SO_4^{2-}, where again NH_4^+ is not linear in SO_4^{2-} (Fig. 3).

The partial neutralization of the light-scattering aqueous H_2SO_4 by whatever $NH_3(g)$ is available would be consistent with the lower, but still high, correlation of aerosol NH_4^+ with b_{scat} or SO_4^{2-} ($\bar{r} = 0.79$) and the significant but still lower correlation between aerosol NH_4^+ and H^+ ($\bar{r} = 0.57$). There is a correlation (though small) between aerosol NO_3^- and NH_4^+, qualitatively consistent with the fact that H_2SO_4 has to be mostly neutralized before significant amounts of NO_3^- can exist in the condensed phase:

$$NH_3(g) + HNO_3(g) \rightarrow NH_4^+ + NO_3^-$$

$$NO_3^- + HSO_4^- \rightarrow HNO_3(g)\uparrow + SO_4^{2-}. \quad (1)$$

The SO_2 correlation to the acidic aerosol H^+ and SO_4^{2-} and to b_{scat} was marginal ($\bar{r} = 0.64$), as was the case in 1977 (Pierson *et al.*, 1980) when SO_2 was uncorrelated to aerosol SO_4^{2-} ($r = 0.30$). We have mentioned already that the SO_2 spikes were not accompanied by any discernible change in b_{scat}. Given that b_{scat} is an index of SO_4^{2-}, it becomes clear that the SO_2 and SO_4^{2-} are decoupled, both overall and in detail; i.e. most of the aerosol SO_4^{2-} is not in the SO_2 plumes and does not accompany the SO_2 in general. The sources responsible for the SO_2 spikes are evidently near enough for only minimal $SO_2 \rightarrow SO_4^{2-}$ conversion to have occurred. The major b_{scat} features are far broader (0.5–5 h) than the SO_2 spikes (0.1–0.3 h), implying a more diffuse or less localized behavior for the SO_4^{2-} aerosol.

$HNO_3(g)$ was correlated moderately ($\bar{r} = 0.74$) to b_{scat} and to the acidic aerosol H^+ and SO_4^{2-}, as well as to SO_2 ($r \simeq 0.8$). As we have seen, SO_2 is at best marginally related to b_{scat} or to aerosol H^+ or SO_4^{2-}. $HNO_3(g)$ therefore appears to be associated in part with each of the two sulfur regimes, i.e. the more local SO_2 one and the less local SO_4^{2-} one. Indeed Se, our candidate marker for coal burning, is moderately well correlated to SO_2, to b_{scat} and aerosol H^+ and SO_4^{2-}, and to $HNO_3(g)$. Multiple regression of Se onto SO_4^{2-} and SO_2 gave $r = 0.91$ at Allegheny, 0.85 at Laurel.

$HNO_3(g)$ is correlated moderately well to O_3. We take this as reflecting the photochemically oxidizing conditions under which HNO_3 is expected to form.

The intercorrelations of O_3 and PAN in Table 4 are consistent with photochemical activity. During the day, PAN was correlated with O_3 ($r = 0.70$). The correlation became insignificant at night ($r = 0.33$; with only nine data pairs at night, $r_{crit} = 0.67$ at $p = 0.05$). Examination of the continuous traces shows similarities between O_3 and PAN, less at night than in the daytime. The composite diurnal patterns of O_3 and PAN shown in Fig. 5 are strongly correlated ($r = 0.88$). These observations are consistent with a more-or-less local component in the O_3 and PAN photochemistry.

Meanwhile, in the presence of the large excess of O_3 (Table 2), an Allegheny NO vs NO_2 correlation exists but is clear only if one deals separately with the daytime (when NO_2 photodissociation can occur) and night-time (when it cannot). For the day-only and night-only run averages we have $r = 0.65$ and 0.84, respectively, for NO vs NO_2 at Allegheny. The continuous traces show that the NO and NO_2 are closely related.

Night-time PAN, while not correlated with O_3, was significantly correlated with b_{scat} and with aerosol mass, H^+, NH_4^+ and SO_4^{2-}. This is important in that PAN implies an aged polluted photochemical air mass. (However, in the daytime there were no significant correlations of run-average PAN with any variable except O_3.)

There were several occasions when PAN composed most of the $NO + NO_2 + PAN$ sum. On those occasions the PAN trace was similar to those of O_3 and b_{scat}. Detailed inspection of the continuous data re-

vealed numerous instances, all between noon and midnight and lasting for 1 to 13 h, when PAN, O_3 and b_{scat} all had similar patterns. Winds tended to be either omnidirectional or, more often, out of the southerly semicircle between 125° and 305°. The several-hour widths of the peaks were in contrast to the short-lived spikes of the NO_x or SO_2. These observations, together with the modest but significant correlations of run-average b_{scat} with O_3 and PAN (Table 4), attest to photochemical formation of at least some of the aerosol SO_4^{2-} on these occasions.

NO and NO_2 (and NO_x, not listed in Table 4) were for the most part not significantly correlated with HNO_3 or SO_2. They did show significant night-time run-average correlations with CNC. The lack of correlation between NO_x and SO_2 was unexpected since 70% of the NO_x from upwind areas is supposed to come from nonautomotive (hence, mostly SO_2-producing) sources. Turnpike traffic may have played a role here. A difference in time scales for removal—NO_x much more rapid than SO_2—possibly is involved also.

Over most of the experiment, the CNC continuous trace was very similar to NO_2—and not to NO or SO_2. But by far the highest CNC registered in the study occurred on an exceptionally clear day (21 August) with the lowest humidity and dew point of the study, with low PAN and O_3, and with no discernible relation to O_3, NO, NO_2, SO_2 or b_{scat}. None of these features (nor the CNC correlations in Table 4) suggest any relation of CNC to the acidity issue.

It is seen in Table 4 that simple regressions onto the source-marker elements, other than Se (coal-burning), are of little help in placing the origins of the acid components in the air. Pb, the automotive marker, exhibited only indifferent correlations to the other species, and in particular an insignificant one to HNO_3(g) and the other NO_x and NO_x-derived species (Table 5). On the other hand, the ratio between study-average $\Sigma(NO + NO_2 + PAN + HNO_3)$ and study-average Pb, 1388 moles (g-atom^{-1}), is only perhaps twice the all-vehicle automotive NO_x/Pb ratio; thus the automotive portion of the $\Sigma(NO + NO_2 + PAN + HNO_3)$ may have been significant.

The high correlations of EC with some of the acidity components in Table 4 probably do not imply a common source for the two, since EC correlations with SO_2 or Se are not very strong. It is likely that the EC is just a concomitant of the generally polluted aged air mass in which these acidic species evolve.

In the 1977 Allegheny experiment we found aerosol NO_3^- to be correlated to Mg and Ca ($r = 0.69$ each), essentially alone of all species measured, and we ascribed the correlation to scavenging of HNO_3 by alkaline particles containing, e.g. $CaCO_3$, either in the air or on the accumulating filter deposit. In the present study no correlation was found ($r \leqslant 0.2$); but only the aerosol NO_3^- finer than 1.5 μm was measured in the present study, whereas the Mg and Ca were found to be predominantly in large particles (MMED = 4 or 5 μm). While HNO_3 reactions may have occurred as formerly proposed, this could not have affected the present (fine-particle) aerosol NO_3^- measurement very much. Thus the correlation of aerosol NO_3^- with Mg and Ca in 1977, and the contrary result in the present study, could both be correct, accounted for by particle-size measurement differences. It is known (Wolff, 1984) that summertime aerosol NO_3^- in the eastern U.S. is predominantly in the coarse size fraction owing, evidently, to reaction of atmospheric HNO_3(g) with airborne soil dust.

Inter-site correlations

Table 6 shows strong inter-site correlations of the variables related to aerosol acidity—that is, b_{scat} and aerosol H^+, NH_4^+ and SO_4^{2-} ($\bar{r} = 0.96$). The 'real' H^+ inter-site correlation is probably better than that shown, because of the H^+ measurement uncertainty. Aerosol fine mass is largely related to SO_4^{2-} and therefore its inter-site correlation is fairly high—again adversely affected by measurement errors.

These high correlations imply dimensions $\gg 35$ km for the acid aerosol 'blob'. The situation is quite evident in the continuous b_{scat} traces, which are very similar at the two sites. Typically a given feature appearing at Laurel develops concurrently at Allegheny or arrives essentially unaltered at Allegheny an hour or so later.

The HNO_3(g) inter-site correlations at night and in the day are $r = 0.88$ and 0.82, respectively. The inter-site correlations for total inorganic NO_3^- (HNO_3(g) + aerosol NO_3^-) are $r = 0.87$ and 0.83 night and day, respectively.

The moderate SO_2(g) inter-site correlation ($r = 0.75$ night, 0.80 day) is consistent with its more local scale as exemplified by the fact that high SO_2 concentrations observed at one site usually miss the other. Inspection of the SO_2 continuous traces reveals that there is actually a fair amount of similarity between the two sites but with usually a time shift of 1 to 4 h, which of course destroys the correlation to the extent that features narrower than several hours are involved. The time shifts are generally consistent with the wind speeds and directions, i.e. transport. Basically there are three types of SO_2 features, namely, (1) the spikes, which usually do not match up well between the sites, (2) peaks and valleys a few hours wide, which match more often, and (3) broad features of the time scale of a day which, on the few occasions when they are seen, are clearly reproduced at both sites.

Finally, the NO_x inter-site correlation is quite poor, for four reasons revealed in the continuous NO_x traces. (1) The NO_x spikes at one site seldom have a counterpart at the other and, when they do, the time shift exceeds the spike width so the correlation is degraded rather than enhanced. (2) Even when the spikes are simultaneous the amplitudes are nearly always vastly different; sometimes the weaker one was the upwind one, in which cases impact parameter must have been important as opposed to chemistry during

Table 5. Correlation coefficients (r) between run-average Pb and oxidized N species, Allegheny Mountain and Laurel Hill, August 1983. Data are arranged in pairs; top = r at Allegheny, bottom = r at Laurel. Values in parentheses are not significant at the 99% confidence level[a]

	Pb Fine	Pb Total
NO	(−0.13) [b]	(−0.13) [b]
$NO_2 + PAN$[c]	(0.22)	(0.38)
	0.45	0.46
$NO + NO_2 + PAN$[c]	(0.20)	(0.35)
	(0.40)	0.42
HNO_3[d]	(0.37)	(0.34)
	(0.36)	(0.37)
$NO + NO_2 + PAN + HNO_3$	(0.33)	0.46
	0.44	0.46

[a] $|r_{crit}|$ for $p = 0.01$ is 0.384 at Allegheny, 0.407 at Laurel.
[b] Laurel NO data questionable, not used. See text.
[c] Chemiluminescence NO_2 and NO_x measurements include PAN.
[d] HNO_3 from denuder-difference measurements.

Table 6. Inter-site correlation coefficients (r)[a] between Allegheny Mountain and Laurel Hill data, August 1983

b_{scat}	0.969[b]
SO_2	0.754
NO_x	(0.464)[c]
HNO_3	0.810
Aerosol mass, coarse	0.685
fine	0.798
total	0.784
H^+	0.945
NH_4^+	0.975
NO_3^-	0.669
SO_4^{2-}	0.959
C elemental	0.829
organic	0.807
Soil elements[d]	0.899
V	0.967
Mn	0.941
Se	0.876
Br	0.737
Pb	0.753

[a] Usually there are 37 data pairs, for which $|r_{crit}| = 0.325$ at 95% probability of being real, 0.418 at 99% probability of being real.
[b] Heated nephelometer inlet. Cell temperature is ~15°C above ambient.
[c] NO_x measurement includes NO, NO_2 and PAN. Laurel NO data are questionable; see text.
[d] Average r for Al, Si, K, Ca, Fe.

transport. (3) The large broad features are not so common in the case of NO_x and consequently the importance of the spikes is emphasized. (4) Even the major broad features at one site are often absent at the other. These features all suggest that the closer point sources are more emphasized in the case of NO_x than in the case of SO_2, perhaps connoting less efficient transport of NO_x than of SO_2.

Among the candidate marker elements, the inter-site correlation for EC was 0.83 (0.91 in the daytime), and ~0.9 for most of the others. The high correlation for V demonstrates that the failure to find significant intra-site correlations involving V did not stem from problems with the V data quality. The inter-site correlation for Se lies between those for SO_2 and SO_4^{2-}. The significantly lower inter-site correlation for Pb (and for Br, though Br is less straightforward since it can be volatilized) implies that Pb may not be a reliable regional tracer of automotive emissions in this study because of analytical errors or local emissions.

In general the inter-site correlations are as strong at night as in the daytime (e.g. b_{scat} inter-site $r = 0.99$ on night-time runs). This suggests that meteorological coupling between the two sites was as good at night as in the daytime—that is, that the collapse of the daytime mixing layer and the formation of the night-time inversion did not isolate the sites from each other.

SO_2 oxidation and deposition between the sites

There was a b_{scat} peak (2.74×10^{-4} m^{-1}) at Laurel at 1016 on 22 August (Fig. 7), with surface wind from 225°T at 13.6 m s^{-1}. At 1104 this peak (now 3.30 $\times 10^{-4}$ m^{-1}) reached Allegheny, at which time the surface wind was from 294°T at 8.3 m s^{-1} at Allegheny (and 222°T at 6.8 m s^{-1} at Laurel). The increase in peak height measured from the continuum (Fig. 7) was actually $(0.59 \pm 0.18) \times 10^{-4}$ m^{-1}. The 35.5 km covered in 48 min corresponds to a transport speed of 12 m s^{-1}. The peak had a half-width of 116 min at Laurel and 120 min at Allegheny, which at the transport speed just given corresponds to a spatial half-width of 90 km. If we assume $b_{scat}/SO_4^{2-} = 849$ m^2 mole^{-1} (the regression coefficient in the caption in Fig. 6 corresponds to 849 ± 32 m^2 mole^{-1}), then the 0.59×10^{-4} m^{-1} increase in b_{scat} in transit from Laurel to Allegheny corresponds to a SO_4^{2-} increment of 69 ± 21 nanomoles m^{-3}. The SO_2 accompanying the b_{scat} peak was 45.1 ± 2 ppb (1751 nanomoles m^{-3}) at Laurel and 42.5 ± 2 ppb at Allegheny, i.e. no detectable change ($\Delta SO_2 = 101 \pm 110$ nanomoles m^{-3}). The fact that the change in the sum of SO_2 and (inferred) SO_4^{2-} was only a few per cent means that dispersion was not governing. These data imply a daytime rate coefficient of 0.049 ± 0.015 h^{-1} for SO_2 oxidation (higher, if SO_2 deposition is non-zero) and ≤ 0.1 h^{-1} for SO_2 dry deposition. (In the same b_{scat} peak, the sum of $NO + NO_2 + PAN$ declined from 19.2 ppb at Laurel to 13.3 ppb at Allegheny, for a rate coefficient of ~0.5 h^{-1} for disappearance of ($NO + NO_2 + PAN$) via deposition and chemical reaction).

Particle size distributions

The particle size distributions (Figs 8, 9) of H^+, NH_4^+ and SO_4^{2-} are all alike, with mass median aerodynamic diameters 0.72, 0.79 and 0.73 μm, respectively. Figure 8 shows a roughly log-normal dis-

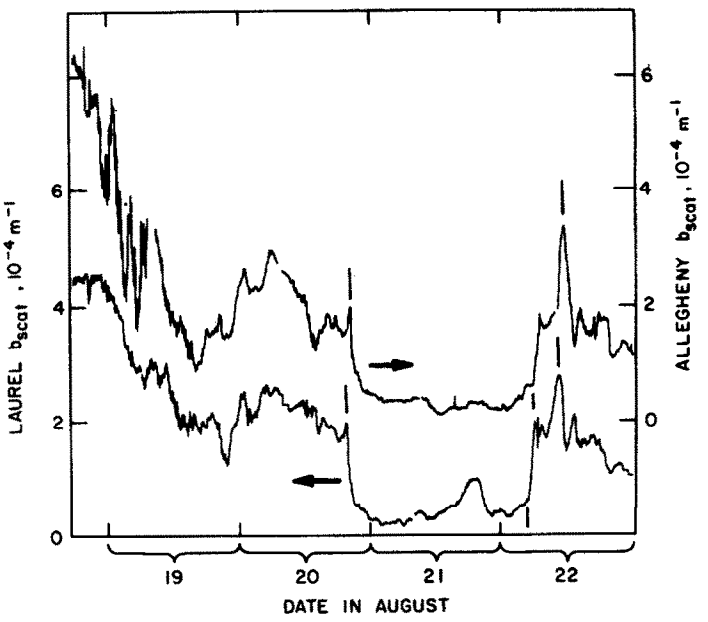

Fig. 7. Aerosol b_{scat} at Allegheny Mountain and Laurel Hill (heated-inlet nephelometers), 19–22 August 1983. To separate the curves, the Allegheny ordinate is offset upwards.

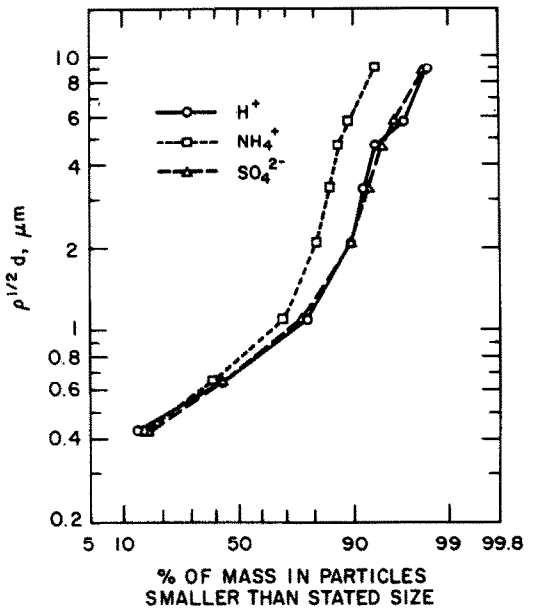

Fig. 8. Log probability plot of particle H^+, NH_4^+ and SO_4^{2-} size distributions at the tower on Allegheny Mountain, 12–17, 19–22, 23–27 and 28 August 1983 (480 m^3 sampled in 17,055 minutes). No rain.

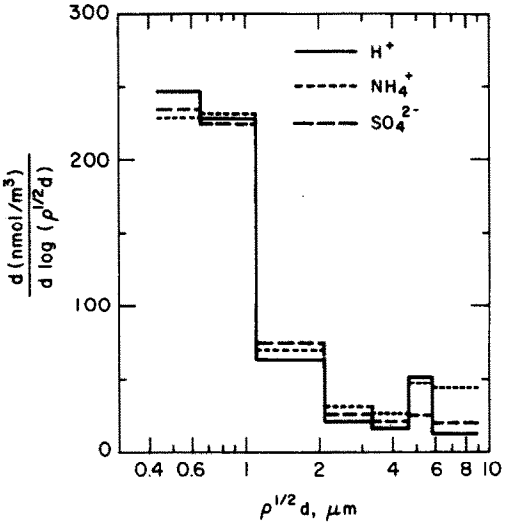

Fig. 9. Differential size distributions of particle H^+, NH_4^+ and SO_4^{2-}, same sample as in Fig. 8.

tribution in the accumulation size mode, with MMED ~ 0.67 μm and $\sigma_g \sim 1.6$ for all three species. The five impactor collections spanning the study gave similar distributions, with MMED 0.62–0.9 μm for H^+, 0.64–0.84 for NH_4^+ and 0.59–0.86 for SO_4^{2-}. Most of the H^+ and SO_4^{2-} was on the two stages corresponding to the size range 0.43–1.1 μm.

In the limited impactor data obtained in rain-only periods, the SO_4^{2-} maximum shifted upwards in size from the 0.43–1.1 μm collection stages to the 0.65–2.1 μm collection stages and the MMED increased from ~ 0.7 μm to ~ 0.9 μm.

The impactor H^+/SO_4^{2-} ratio was highest between 0.43 and 1.1 μm, which is where H^+ and SO_4^{2-} were highest also.

Figure 8 shows 90, 82 and 90% of the H^+, NH_4^+ and SO_4^{2-}, respectively, in particles < 2.5 μm, the nominal dividing line between coarse and fine fractions in the dichotomous sampler. XRF total aerosol S analysis of

dichotomous sampler filters for the same period (it is evident in Table 2 that total aerosol S is a close approximation to SO_4^{2-}) gave a time-weighted average of 93% fine. The time-weighted average total aerosol S over the whole study including both sites was 90% fine (range 31%–100%). The daytime average was 95.5% and the night-time average was 87%, the difference resulting largely from a relatively few high-humidity runs with extraordinarily low per cent fine (Keeler *et al.*, 1988).

The sum-of-stages H^+, NH_4^+, and SO_4^{2-} for all impactor data combined were 153.6, 177.5, and 162.8 nanomoles m^{-3}, respectively, for an overall H^+/SO_4^{2-} ratio of 0.94, consistent with the filter data, and an ion balance $(H^+ + NH_4^+)/SO_4^{2-} = 1.02$. The H^+ and SO_4^{2-} concentrations are ~82% of the Allegheny best-estimate values (Table 2), suggesting sample recoveries of that magnitude from the impactors.

The observed MMED values for H^+ and SO_4^{2-} are near that for maximum light scattering per unit mass, consistent with the strong relationship observed between these species and b_{scat}. The MMED values are also within the respirable range, and this may be of some significance since respiratory responses to H_2SO_4 aerosols are reported at 1-h concentrations as low as 100 $\mu g\, m^{-3}$, only twice the maximum run-average SO_4^{2-} level encountered in the present study (see Lioy and Lippmann, 1986). With regard to acid deposition, for these particle sizes both wet removal and dry removal are relatively slow.

It was not possible to extract useful information on Se from the impactor samples. The dichotomous sampler filters showed that ~87% of the Se (vs 90% of the aerosol S) was in the fine ($< 2.5\ \mu m$) particle mode.

The size distributions shown here are consistent with the Shenandoah Valley measurements (Weiss *et al.*, 1982) showing some 58% of the NH_4^+ and SO_4^{2-} in particles $< 1\ \mu m$. They are also consistent with H^+, NH_4^+ and SO_4^{2-} size distributions in the 1977 Allegheny study (Pierson *et al.*, 1980).

Relationships between concentrations and wind direction

It will be helpful in this discussion to consider Figs 2, 10 and 11 together, using the run-number designations to identify the interrelationships of concentrations, times, air-mass movements and local wind directions. Figure 10 shows mixed-layer trajectories associated with the highest and lowest concentrations of species of major interest, i.e. HNO_3(g), SO_2(g) and aerosol H^+ and SO_4^{2-}. Here we show total inorganic nitrate ($\equiv HNO_3$(g) plus fine aerosol NO_3^-) instead of HNO_3(g) alone since the former avoids the issue of NH_4NO_3 association/dissociation; the difference between HNO_3(g) and total inorganic NO_3^- is small (~10%). One must recognize that the mixed-layer trajectories are calculated by averaging the winds from the surface to the top of the mixing layer (Heffter, 1980; Samson, 1980) and should be viewed conceptually rather than in a literal sense. Figure 10 shows concentrations plotted against measured surface wind direction at the towers. The wind direction for each run is the vector resultant of the continuously varying wind vectors during the run. There often was considerable difference between surface wind direction—either estimated by the NWS or measured at the towers—and mixed-layer-trajectory wind direction. For example, from the evening of 12 August to the evening of 15 August (runs 13–19), with 72-h mixed-layer trajectories persistently from $035 \pm 005°T$ (Fig. 10), the winds measured at the towers came from $120 \pm 45°T$. (Of course there were also many periods when the directions were the same, and there is no reason that the surface and mixed-layer wind directions should be identical.)

In the set of four species dealt with here—HNO_3, SO_2 and aerosol H^+ and SO_4^{2-}—the highest (or lowest) concentrations of one species tended to be associated with the same trajectories as the highest (or lowest) concentrations of the other three (Fig. 10). In fact the set for low H^+ is identical to the set for low SO_4^{2-}. It is useful, however, to separate the trajectories into four categories: (I) high H^+, SO_4^{2-}, HNO_3, SO_2; (II) low H^+ and SO_4^{2-}, low to high HNO_3 and SO_2 (two subcategories); (III) moderate to high H^+ and SO_4^{2-}, low to moderate HNO_3, low SO_2; (IV) low H^+, SO_4^{2-}, HNO_3, SO_2.

(I) *High* H^+, SO_4^{2-}, HNO_3, SO_2. These were associated with trajectories and local winds from the west (Figs 10, 11). The local west winds with high SO_4^{2-} also tended to have speeds slightly above average, so that in terms of advection flux (moles $m^{-2}\, s^{-1}$) the westerly preference was even stronger. This is consonant with the fact that the two sites lie ~150 km east of the highest density of SO_2 emissions in the U.S. (Barrie *et al.*, 1984; Clark, 1980). Mixed-layer transport times from this source region to the sites would have been on the order of 12 h.

High H^+, SO_4^{2-}, HNO_3 and SO_2 were also the aftermath of severe local stagnation. The day of 16 August (run 20), in the middle of the ascent toward high H^+, SO_4^{2-}, HNO_3 and SO_2 (and also PAN, NO_x, O_3, EC), coincided with essentially zero wind at the Allegheny tower (0.3 $m\, s^{-1}$ vector, 0.8 scalar) and an ill-defined tower wind direction (indeed, opposite of that at Laurel). Mixed-layer trajectories ending at Allegheny or Laurel during this local stagnation period had started 72 h earlier in the vicinity of the sites, gone west to the Ohio River, and doubled back. By far the highest run-average NO in the study occurred at Allegheny on this run (1.96 ppb, NO/NO_2 mole ratio 0.24), much of it contained in a 13-min 31-ppb spike with NO/NO_2 ~1.0 occurring at 0912 along with high CNC, O_3 suppression and wind from 090°T, signifying a sudden influx of Turnpike traffic pollutants (probably accumulated during the preceding night when most of the traffic was diesel trucks, as the run-average Pb was low and the NO_x/Pb ratio, 3050 moles (g-atom)$^{-1}$, was ~4 times too high for a

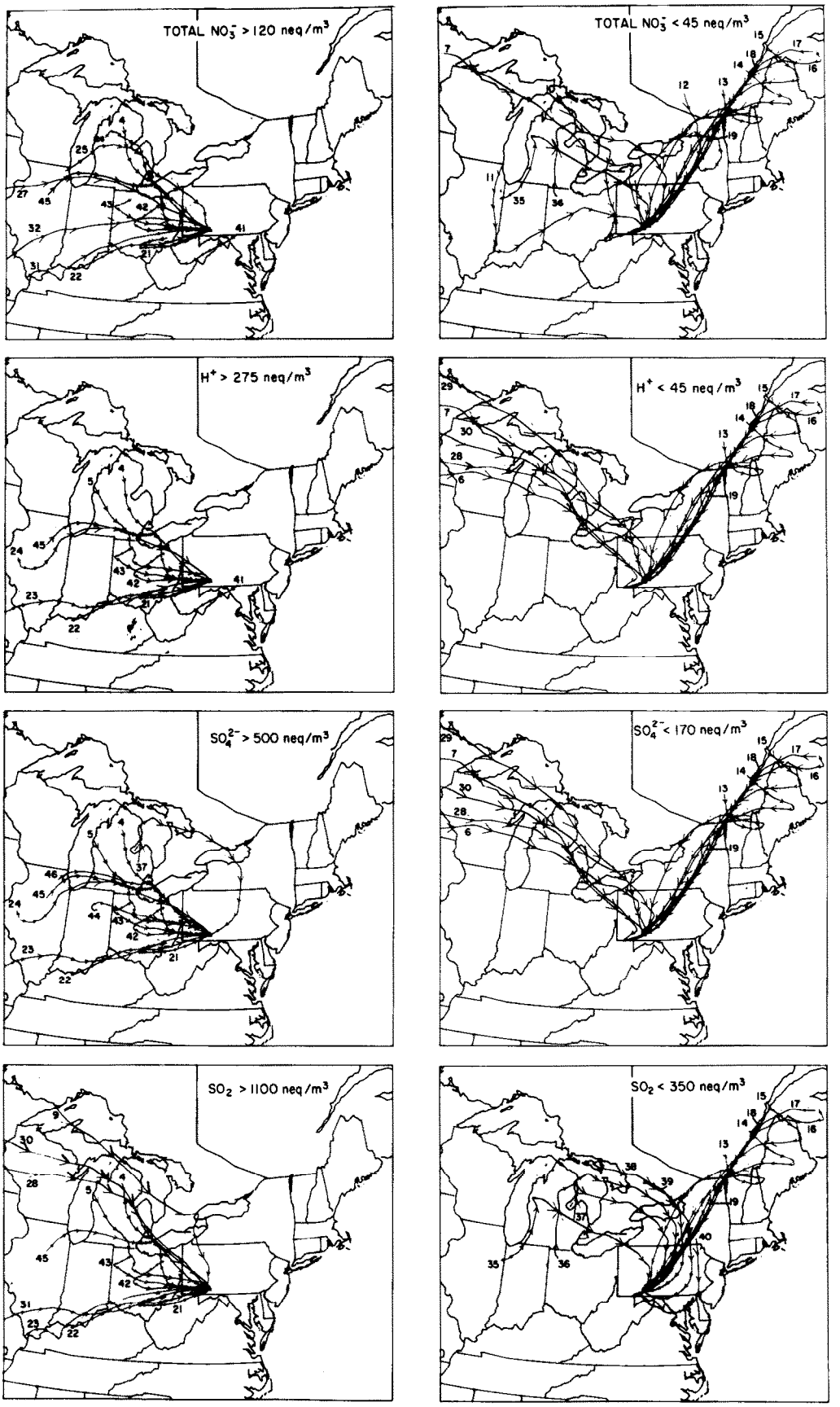

Fig. 10. Mixed-layer trajectories associated with (arriving at 0200 or 1400 EDT during) sampling runs with highest and lowest run-average concentrations of the indicated species at Allegheny Mountain, August 1983. The Laurel Hill data were similar. The high and low cutoffs were chosen to include about a quarter of the trajectories in each frame. Arrowheads every 6 h signify wind speed. The run number applicable to each trajectory, with designations as in Fig. 2, is shown. Total $NO_3^- = HNO_3(g) + \text{fine-particle } NO_3^-$.

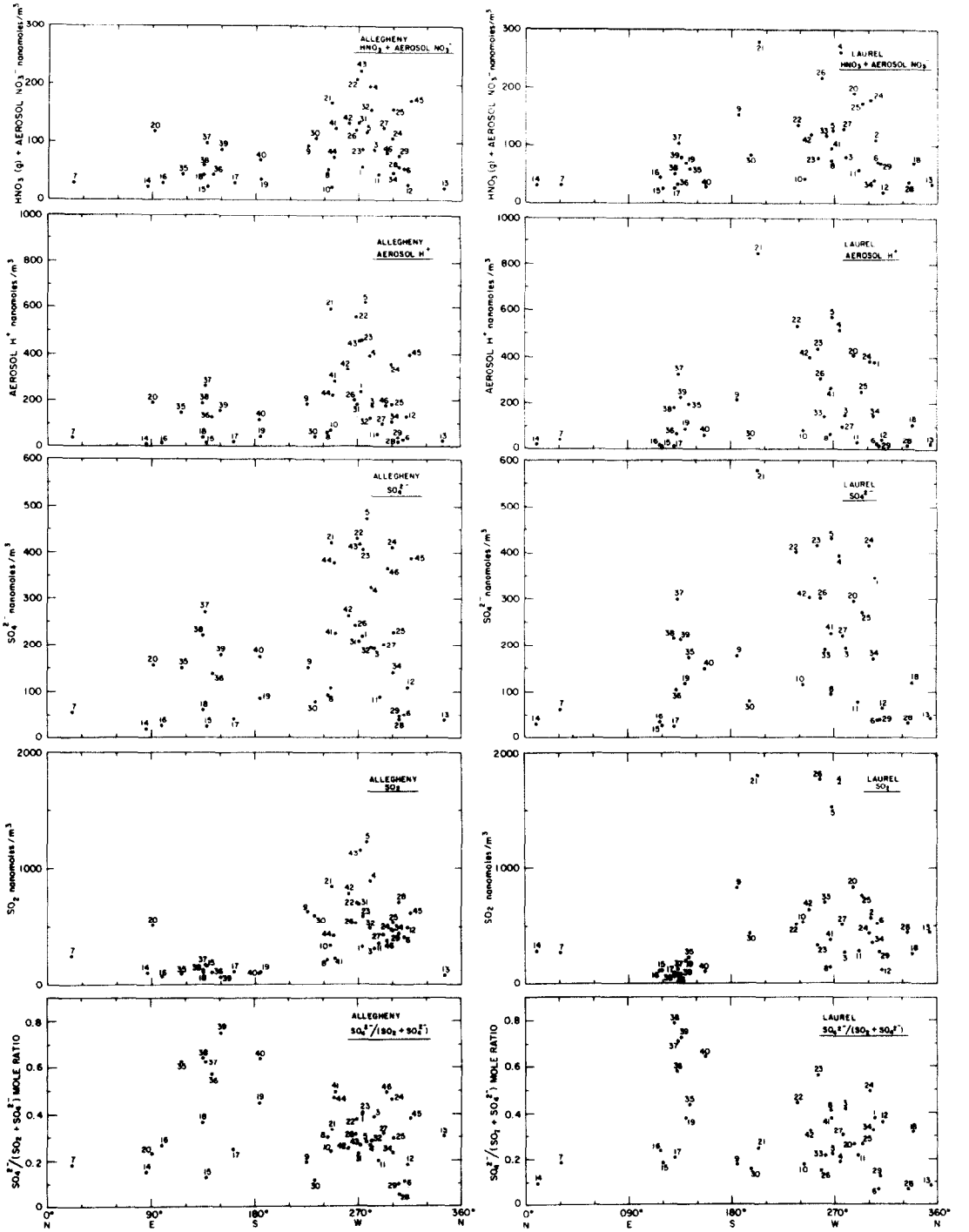

Fig. 11. Run-average concentrations vs local surface wind direction (direction the wind is *from*) at the Allegheny Mountain and Laurel Hill towers, August 1983. Wind direction for each run is the vector resultant of all wind speeds and directions during the run. Run number designations are as in Fig. 2. Runs 13 through 19 were associated with trajectories from NNE ("Whiteface trajectories"). The trajectories for runs 35–40 were associated with a high pressure system. Run 20 at Allegheny corresponds to an extremely low wind speed (0.3 $m\,s^{-1}$) at the tower.

traffic signature). During this day there was a considerable b_{scat} increase.

The effect of this stagnation manifested itself on the night of 16 August (run 21)—especially at Laurel (see Figs 2 and 11), where maximum run averages for the study were registered for HNO_3 (and total NO_3^-), SO_2 and aerosol H^+, SO_4^{2-} and EC. Near-maximum values of all of these quantities were registered at Allegheny. The H^+/SO_4^{2-} ratio was at its maximum at both sites (mole ratio 1.46 at Laurel). Aerosol mass

and Se were high at both sites. Run-average b_{scat} was high, PAN near maximum and O_3 the highest of the study. NO_x was maximum at Laurel but low at Allegheny. The $SO_4^{2-}/(SO_2 + SO_4^{2-})$ ratio was ordinary or low. Surface wind (vector) was from 203.5°T at 1.1 ms^{-1} at Laurel, 247°T at 2.15 ms^{-1} at Allegheny, as measured at the towers. NWS surface trajectories ending at Laurel on this night ($\sim$ 205°T at 0.6 ms^{-1}) were roughly consistent with the tower measurements, and similarly at Allegheny. The arriving mixed-layer air, meanwhile, had been near the sites 72 h earlier, moved west to the Ohio River area, and doubled back (see Fig. 10). These observations suggest localized behavior in response to local stagnation, i.e. that local wind direction and speed were important. This was the beginning of the main acid episode of the study.

In succeeding days as the stagnation ended and persistent westerly winds again set in (runs 22–24, Fig. 10), the HNO_3 and SO_2 declined quickly but SO_4^{2-} took several days to clear out.

The prospect that aerosol H^+ and SO_4^{2-} might exhibit localized behavior along with the SO_2 was not anticipated. The closest strong SO_2 sources in a southerly direction are $\sim$ 100 km from Laurel (Fig. 1) which, at the surface wind speed recorded, translates to a transport time of $\sim$ 25 h. The high levels of EC and other pollutants presumably are a consequence of a general build-up under the stagnant conditions.

(II) *Low* H^+ *and* SO_4^{2-}, *low to high* HNO_3 *and* SO_2. These were associated with fast-moving trajectories out of the west (e.g. runs 11, 31; see Figs 10, 11). Even though they passed right through the source region, these trajectories did not deliver high H^+ or SO_4^{2-} and the $SO_2 \rightarrow SO_4^{2-}$ conversion was low. Wind speed evidently differentiates this category from the preceding one; inspection of westerly trajectories associated with *high* H^+, SO_4^{2-}, HNO_3 and SO_2 reveals a good deal of meandering and stagnation in some of them in areas to the west.

Low H^+ and SO_4^{2-}, low to medium HNO_3 and low to high SO_2 were associated also with fast-moving trajectories out of the northwest (runs 6, 7, 28–30, Figs 2, 10, 11), similar to the trajectories in the 1977 study that brought low H^+ and SO_4^{2-} but no particular pattern of SO_2 (Pierson *et al.*, 1980; Samson, 1980). The variability of SO_2 probably has to do with the power plants nearby to the northwest (Fig. 1) and the chance of impact from their plumes. Run 29 (daytime 21 August) was especially low in all species—not only the four under discussion here, but all species including trace elements; the associated trajectory was a fast-moving trajectory from the northwest which apparently missed all of the large cities and industrial centers lying in that direction; it had especially high SO_2/Se ratio and especially low SO_4^{2-}/Se ratio, indicating that most of the SO_2 was picked up only shortly before arrival.

(III) *Moderate to high* H^+ *and* SO_4^{2-}, *low to moderate* HNO_3, *and low* SO_2. These were associated with air arriving from the southeast after having travelled in a long clockwise loop out of the midwest and around through the north and northeast (runs 35–40). This pattern set in on the morning of 23 August and continued through the night of 25 August. The sites during this interval were on the back side of a high pressure center located to the north and proceeding in a southeasterly direction. The arriving air had been in transit from the Midwest (say, Ohio and Indiana) for $\geqslant$ 72 h and $>$ 1000 km.

This low-SO_2 air upon arrival contained low O_3, ordinary levels of HNO_3, and greatly elevated H^+ and SO_4^{2-} by comparison with other occasions when local winds were from the southeast (see Fig. 11). PAN and NO_x levels were ordinary. This air had the highest $SO_2 \rightarrow SO_4^{2-}$ conversions ever encountered in this study; some 65% of the $SO_2 + SO_4^{2-}$ during the 3 days existed as SO_4^{2-} (Fig. 11). All of this is consistent with above-average aging time and concomitant SO_2 oxidation/removal.

Maximum SO_4^{2-}/Se ratios ($\geqslant$ 20,000 $g\,g^{-1}$) were observed during this same period (actually, runs 35–39). Se supposedly traces both SO_2 and SO_4^{2-}; enhancement of the SO_4^{2-}/Se ratio (vs the study average, which was 8400 at Allegheny, 7800 at Laurel, 5300 in 1977 at Allegheny) cannot be achieved by SO_2 deposition but can be achieved by SO_2 oxidation or by Se deposition. Se deposition velocities at Allegheny, at least at night, were $<$ 0.1 $cm\,s^{-1}$ (Pierson *et al.*, 1986), consistent with their small particle size (87% of the mass $<$ 2.5 μm). Thus Se deposition can probably be discounted to a first approximation and the enhanced SO_4^{2-}/Se ratios probably have to be explained by $SO_2 \rightarrow SO_4^{2-}$ conversion during transport from the source area around the high pressure center to the sites, at rates of the order of 1% h^{-1}. (In order that $\sim$ 65% of the $SO_2 + SO_4^{2-}$ exist as SO_4^{2-} during these runs as stated in the preceding paragraph, in the absence of SO_2 deposition during a 3-day journey from the SO_2 source region, the conversion rate would have to be $\sim$ 0.015 h^{-1}.)

The long transport times involved in these trajectories, together with the high daytime HNO_3(g) deposition velocity, probably explain the fact that the HNO_3(g) concentrations were not particularly high in this category.

(IV) *Low* H^+, SO_4^{2-}, HNO_3, SO_2. These were associated with the Whiteface trajectories—that is, trajectories out of the NNE (runs 13–19) over the 3-day period from the night of 12–13 August and into the evening of 15 August. For much of this time the trajectories to Allegheny/Laurel passed directly over the ASRC (SUNY-Albany) site on Whiteface Mountain (NY). Extremely low SO_4^{2-} levels were measured during this period also at Whiteface and at Underhill, Vermont (Husain *et al.*, 1984; Poirot and Wishinski, 1986).

In summary, we have identified three meteorological regimes for high acidity: (1) stagnation over upwind source regions lying to the west, followed by slow advection from the source region, with high HNO_3,

SO_2 and aerosol H^+ and SO_4^{2-}; (2) local stagnation, with high concentrations of the same species; and (3) regional transport around to the back side of a high pressure system, with elevated aerosol H^+ and SO_4^{2-}, modest HNO_3 and depletion in SO_2. Low acidity occurs with air masses from northerly sectors.

V concentrations at Laurel were highest when the tower winds were from the sector $131° \leqslant \theta \leqslant 157°$T (runs 37–40). V concentrations at Allegheny were highest in the same runs, where now the sector limits are $135° \leqslant \theta \leqslant 184°$, similar to the 1977 Allegheny situation in which an order-of-magnitude increase in V was encountered with tower winds from 160°T. The series of looping trajectories associated with the back side of the high pressure system (runs 35–40) began with low V concentrations (runs 35, 36) and then, as the loops reached progressively farther into the East, the V concentrations delivered at Allegheny rapidly increased (runs 37–40). Though advection from the Northeast might appear to explain the high V, the SO_4^{2-}/V mass ratios even at the highest V concentrations (runs 38–40) were an order of magnitude higher than East Coast nonurban ratios given by Altshuller (1976); and advection of extraordinarily high V from 160° in the 1977 Allegheny study was not preceded by traverses of the Northeast. A local V source to the SSE (say, in Cumberland, MD), on the other hand, is inconsistent with the lack of high V in runs 35 and 36. We have to leave the very interesting (for example, see Rahn and Lowenthal, 1985) V behavior once again unresolved.

Further regarding the NO_x/Pb ratios, the Pb run-average concentrations at Allegheny have their maximum at tower winds from 270° like the other species in Fig. 11, whereas NO_x has two maxima and they are at 130° and 300°. NO_x thus seems to be more subject than is Pb to the influence of local traffic, probably in part because most of the traffic Pb is emitted from spark-ignition vehicles which predominate during the daytime when the atmospheric dispersion/dilution of local emissions is greater. Night-time traffic emissions are dominated by heavy-duty diesels, with high NO_x (Gorse, 1984) and low Pb (Pierson and Brachaczek, 1983).

Relationships between concentrations and wind speed history

We have mentioned in the preceding section the enhancing effect of local stagnation on concentrations, as well as the enhancing effect of slow-moving meandering trajectories and upwind stagnation compared to fast-moving trajectories from the same direction. This upwind stagnation/transport time effect can be quantified as was done by Samson (1980). Samson found that the SO_4^{2-} concentration at a number of Northeast sites (including 1977 Allegheny) was correlated with the inverse of the mixed-layer wind speed $\geqslant 24$ h upwind of the sampling point, and interpreted this to mean that maximum SO_4^{2-} concentrations accompanied upwind wind speeds low enough to permit SO_2 accumulation over source areas and oxidation to SO_4^{2-} during transport. It is interesting that at High Point, NJ, the time needed for the correlation to reach critical values was ~48 h, vs ~36 h at Allegheny, in excellent agreement with the ~12-h downwind displacement of High Point from Allegheny.

The 1983 Allegheny/Laurel data demonstrated the existence of correlations not only for SO_4^{2-} but for aerosol H^+ as well and, to a lesser degree, for HNO_3(g) and aerosol NH_4^+ (Fig. 12). This time they reached critical values at upstream offsets of ~24 h. SO_2 (not illustrated) also showed correlations but they barely reached the critical line.

Atmospheric concentrations at Allegheny were higher in 1983 than in 1977 (e.g. H^+ average at Allegheny 193 nanomoles m^{-3} in 1983 vs 155 in 1977). Wind speed could have been a factor; the average scalar wind at the tower was over twice as high in 1977 as in the present study, and the mixed-layer average wind speed calculated from the mixed-layer trajectories was about 3 times as high in 1977 as in the present study. The implied dilution effect of wind speed history is confounded a bit by the fact that northerly trajectories were more prevalent in the present study; these trajectories have high wind speeds and low SO_4^{2-}, however, so that removing them would only further amplify the SO_4^{2-} and wind speed differences between 1983 and 1977.

Relationship between concentrations and upwind precipitation

The occurrence of precipitation upwind of the sites, and the place of occurrence relative to the pollutant sources, may explain some of the difference between the 1977 and 1983 concentrations of SO_2 and aerosol H^+ and SO_4^{2-}. The major SO_2 source regions west of Allegheny/Laurel are typically < 1 day's transport distance away from the sites. The occurrence of rain several days upwind of the sites should have less effect on the concentrations at the sites than the occurrence

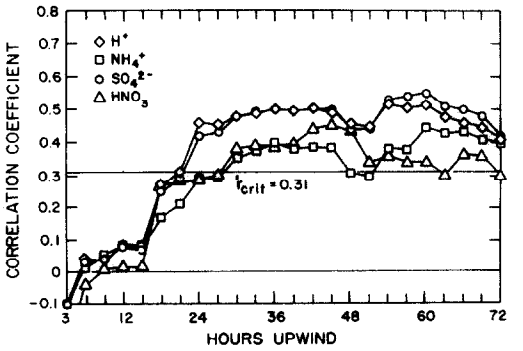

Fig. 12. Correlation coefficients, as a function of hours upstream, between the inverse of mixed-layer wind speed upstream and resultant concentrations at Allegheny Mountain, August 1983. The r_{crit} line is for $p = 0.05$.

of rain between the sources and the sites. Upwind precipitation was more frequent in the 1977 experiment than in the present one, and this was especially true of rain between the source region and the sampling sites. These matters have been discussed (Pierson *et al.*, 1987) in connection with the concentrations of acidic species in rain, which were much higher in 1983 than in 1977. The discussion applies equally to atmospheric concentrations: The differences can probably be rationalized in terms of upwind rain and upwind stagnation, their order of occurrence relative to each other and to passage through SO_2 source regions, and average wind speed (dispersion/stagnation).

Regarding the 1983 data alone, rain occurred within 72 h upwind along about half of the trajectories, but it tended to occur along the ones advecting lower SO_4^{2-}. In fact, the highest 15% of the aerosol H^+ and SO_4^{2-} concentrations were all associated with air masses which had encountered *no* rain within 72 h. Cases of low SO_4^{2-} without prior rain were also recorded but the trajectories in these instances were from the northerly directions. The HNO_3 dependence on 72-h upwind precipitation was relatively weak, consistent with its shorter transport scale.

Visual range

Figure 13 shows that ambient SO_4^{2-} at Allegheny was a determinant or predictor of visual range L_v, just as it had been for b_{scat}. This holds for local L_v as well as for L_v at Altoona, as illustrated, and for Johnstown (for locations, refer to Fig. 1). An exception is seen at the lowest SO_4^{2-} concentrations, where SO_4^{2-} overpredicts L_v because, presumably, other substances such as EC (e.g. Japar *et al.*, 1986) are now able to play a significant role in L_v degradation. This coupling between high SO_4^{2-} and low L_v links the issues of acidity and visual air quality in the Northeast, in that high SO_4^{2-} implies both poor visibility and high acidity.

The vertical scales of SO_4^{2-} and L_v^{-1} in Fig. 13 were matched in such a way as to get maximum overlap between SO_4^{2-} and L_v. This normalization turns out to be

$$L_v(\text{km}) \cdot SO_4^{2-}\ (\text{nanomole m}^{-3}) = 1680$$

or, in terms of SO_4^{2-} mass, 0.16 g m^{-2}. The correlation coefficient was 0.77 between SO_4^{2-} and L_v^{-1} at Allegheny, 0.82 between SO_4^{2-} at Allegheny and L_v^{-1} at Altoona. There was no discernible relationship between $L_v \cdot SO_4^{2-}$ and r.h.

If we multiply the clear-air instantaneous b_{scat} by 1.2 (to correct for the nephelometer heating) and add 0.2 $\times 10^{-4}$ m^{-1} (Rayleigh scattering from the gas phase) to obtain B_{scat}, then the product $L_v \cdot B_{scat}$ at Allegheny is 2.5 ± 1.0. The corresponding contrast threshold, 8.5%, is poorer than the 2–5% considered realistic for a trained observer and ideal targets (neither of which we had), but the discrepancy corresponds to an underestimate of only ~ 25% in visual range. Allegheny and NWS Altoona L_v values were similar on the average. The correlation between B_{scat} and L_v^{-1} at Allegheny was high ($r = 0.92$).

The dominance of SO_4^{2-} in L_v is consistent not only with the dominance of SO_4^{2-} in b_{scat} but also with the observation that scattering constituted ~ 87% of the aerosol-caused light extinction on the average during this study (Japar *et al.*, 1986). This 87% figure in turn is the same as has been reported in other studies of the Northeast aerosol (Ferman *et al.*, 1981; Wolff *et al.*, 1982).

As expected since the aerosol mass is composed largely of SO_4^{2-}, aerosol mass was highly correlated to L_v^{-1} ($r = 0.73$). Stevens *et al.* (1984) have found even better correlations of L_v^{-1} with SO_4^{2-} ($r = 0.89$) and with aerosol mass ($r = 0.95$) than were found here.

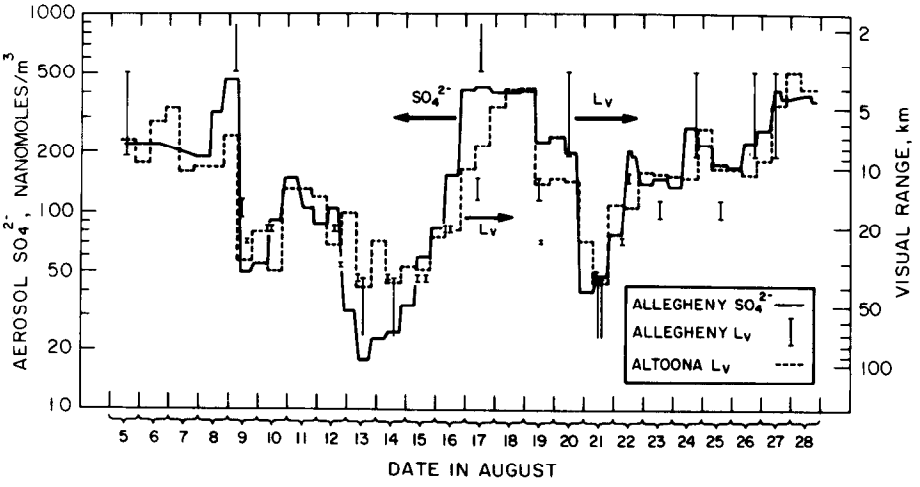

Fig. 13. Comparisons of ambient SO_4^{2-} and visual range (L_v), August 1983. Solid line: SO_4^{2-} concentrations on the tower on Allegheny Mountain. Bars: L_v^{-1} at the Allegheny tower. Broken line: 12-h averages of hourly visual ranges at the Altoona/Martinsburg NWS station. L_v sightings in cloud or fog are excluded.

Regression of aerosol mass concentration against heated-nephelometer b_{scat} gave mass scattering coefficients of $3.3 \pm 0.6\ m^2\ g^{-1}$ ($\bar{r} = 0.75$) for fine, and $3.2 \pm 0.5\ m^2\ g^{-1}$ ($\bar{r} = 0.8$, Table 4) for coarse plus fine. Weiss *et al.* (1982) report $4.3\ m^2\ g^{-1}$ for fine ($\leqslant 1\ \mu m$) dilution-dried particles in the Shenandoah Valley summertime SO_4^{2-} haze.

Oddly, the SO_4^{2-} episode that began about 16 August (Fig. 13) did not begin at the same time at Altoona, only 60 km away, or at Johnstown, only 40 km away. Pronounced L_v degradation lagged the Allegheny Mountain air-quality degradation by fully 24 h at Altoona (Fig. 13) and by nearly as much at Johnstown. The lag time is at least consistent with the surface wind speeds and directions recorded at Allegheny during that time.

DISCUSSION

The results of the study present a fairly coherent picture of summertime atmospheric acidity in the northeastern U.S. near the main precursor source region. The main species involved are HNO_3(g), SO_2(g) and aerosol H^+ associated with partially neutralized (by NH_3) H_2SO_4. The amount of NH_3(g) is almost too small to matter. In terms of their respective H^+ equivalents or potential H^+ equivalents (2 per SO_2 molecule, 1 per HNO_3, etc.), the average atmospheric acidity contributions of the three components are

HNO_3(g)	78 neq m^{-3}	(7%)
SO_2(g)	900 neq m^{-3}	(75%)
aerosol H^+	205 neq m^{-3}	(17%)
	1181 neq m^{-3}	Total

at the two sites taken together. The apportionment is actually quite dependent on a number of factors such as the depletion of SO_2 associated with longer travel times/distances, as we have seen.

Another 10 or 20% could be contributed by acids that were ignored such as HCl, carboxylic acids, HONO and N_2O_5 (the HNO_3 anhydride). NO_2 and PAN are excluded on grounds stated in the Introduction, i.e. they did not contribute directly to acid deposition at the site. Their *potential* role as acid precursors, however, is significant (about 20%, Table 2).

Most of the interest in acid deposition in the Northeast has centered upon receptor regions distant from sources and upon the long-range transport between source and receptor regions, almost as if the source regions themselves were not also receptors. Actually the deposition flux near the source obviously can be quite high and stream studies on Laurel Hill (DeWalle *et al.*, 1985; Sharpe *et al.*, 1984, 1987) have revealed considerable environmental damage evidently caused by acid deposition. The Allegheny and Laurel sites are in the area of highest rainfall H^+ concentrations and highest annual totals of H^+ deposition in all of North America (Barrie and Hales, 1984; Hicks *et al.*, 1984; Lynch *et al.*, 1984, 1985; Olsen and Slavich, 1986; Sharpe *et al.*, 1984).

The results described here resemble those in the acid sulfate 'white episodes' in Sweden (Brosset, 1978, 1980), but generalization to regions other than western Europe and the northeast U.S. is inappropriate. In remote areas, atmospheric acidity can be dominated by carboxylic acids (Keene and Galloway, 1984; Keene *et al.*, 1983) which, together with HNO_3, also figure prominently in the Los Angeles basin (Grosjean, 1988; Kawamura and Kaplan, 1987; Kawamura *et al.*, 1985; Pierson and Brachaczek, 1988a, 1988b; Pierson *et al.*, 1988).

Many of the results reported here had already been seen in the 1977 Allegheny Mountain experiment, such as the acidity and chemical composition of the aerosol, the trend of H^+/SO_4^{2-} ratio with SO_4^{2-} concentration, the strong relationships among b_{scat} and aerosol H^+ and SO_4^{2-}, the relationship between SO_4^{2-} and L_v, the aerosol H^+ and SO_4^{2-} size distributions, the time duration of the acid SO_4^{2-} episodes, the lack of relationship between SO_2 and aerosol SO_4^{2-}, the regionality of the aerosol acidity and SO_4^{2-} phenomena observed, the sporadic behavior of SO_2 concentrations, and the wind directions and air-mass trajectories associated with high and low SO_4^{2-} concentrations (Pierson *et al.*, 1980; Samson, 1980). The agreement between the present study and 1977 adds further evidence that the phenomena reported are not an anomaly as originally sometimes supposed, but instead may be typical of summertime in this part of the country.

Data on O_3, lacking in the 1977 study, were considered important because of the perception (e.g. Lioy and Lippmann, 1986; Lioy *et al.*, 1979, 1980, 1982; Wolff, 1979; Wolff *et al.*, 1979a, 1979b, 1981, 1982) that O_3 is central to the summertime haze episodes in the Northeast. Undoubtedly this perception is correct; but the amount of O_3 throughout the present study (and, evidently, in general in this region during the summer) is in such overwhelming excess of the NO_x and SO_2 at all times (e.g. Table 2) that the O_3 concentration must surely be irrelevant to the $SO_2 \rightarrow SO_4^{2-}$ conversion or to HNO_3 formation except possibly as a surrogate for concentrations of trace oxidants such as H_2O_2 or OH. High summertime O_3 and SO_4^{2-} levels are said (Lioy *et al.*, 1979, 1980; Whelpdale, 1978; Wolff, 1979; Wolff and Lioy, 1980; Wolff *et al.*, 1979b, 1982) to be associated with flow around the back side of a high pressure system moving southeastward; and indeed the sites were on the back side of such a system during the period 23–25 August, which did deliver moderately high SO_4^{2-} concentrations to the sites and gave the highest SO_4^{2-}/SO_2 ratios seen in the study; but the O_3 levels in this period were only about 55 ppb (2140 nanomoles m^{-3}), or about at the study average. High H^+ and SO_4^{2-} on the night of 18 August (run 24) were accompanied by relatively low O_3 (42 ppb). The

correlation between instantaneous b_{scat} and O_3 was unexceptional ($r = 0.42$), as was the correlation of run-average O_3 with H^+, SO_4^{2-}, or b_{scat} (Table 3). Other recent evidence is said (Lioy and Lippmann, 1986) to suggest that increases in acid and O_3 concentrations are not always correlated.

We have considered the idea (Hidy *et al.*, 1978; Whelpdale, 1978; Wolff, 1979) that high regional summertime SO_4^{2-} in the Northeast is linked with synoptic-scale circulation of warm humid air of maritime tropical (mT) origin moving up on southerly and westerly winds into the Midwest and on into the Northeast. Changes in SO_4^{2-} with temperature and dewpoint that support this picture have been noted (Hidy *et al.*, 1978). However, using dewpoint and ambient temperature as the diagnostics, we find little encouragement for this idea in the present study. The highest dewpoints are indeed all associated with westerly trajectories. The correlations of run-average dewpoint with b_{scat} and SO_4^{2-} are fairly strong ($r = 0.75$ and 0.72, respectively). But the issue is confounded by the circumstance that the trajectories with the highest dewpoints all traverse the SO_2 source region as well. And the overlap between highest dewpoint and highest SO_4^{2-} is by no means complete, chiefly because the high-dewpoint trajectories with high wind speeds are accompanied by SO_4^{2-} levels that are sometimes only average; trajectory wind speed is important to SO_4^{2-} levels but evidently not to dewpoint. The trajectories associated with the four highest run-average dewpoints (and moderately high SO_4^{2-}) all passed over Lake Michigan and Lake Erie on the way to Allegheny. Highest ambient temperatures were associated with westerly trajectories but not with maximum SO_4^{2-}.

Since the aerosol H^+ reported in the present study (and by others) is an important part of the total of the atmospheric acidity, it is necessary to ask how this H^+, as reported, relates to the H^+ actually existing in the aerosol particle or droplet. This droplet consists essentially of $(NH_4)_xH_{(2-x)}SO_4$(aq) with $0 \leqslant x \leqslant 2$. In the laboratory measurement the supposed aqueous solution constituting the aerosol droplet undergoes a dilution of $\geqslant 10^3$-fold. The HSO_4^- ion ($K_d = 0.012$) is completely dissociated in this situation. Now let us first imagine an H_2SO_4(aq) aerosol ($x = 0$) in vapor-pressure equilibrium with ambient air at 25°C and at r.h. 75% (the time-average r.h. that was measured at Allegheny and Laurel combined). From Stokes and Robinson (1949) we find that the H_2SO_4 concentration at equilibrium would be about 3.94 M. From the K_d, at this concentration we would have $[H^+] = 3.95$ M (pH = −0.6), $[HSO_4^-] = 3.93$ M, $[SO_4^{2-}] = 0.012$ M. If the species in the aerosol is NH_4HSO_4(aq), then we find the HSO_4^- about half dissociated: $[H^+] = [SO_4^{2-}] \simeq 1.7$ M, $[HSO_4^-] \sim 2.3$ M. Thus the H^+ and SO_4^{2-} neq m^{-3} results reported in this study are 'infinite-dilution' values; the concentrations actually existing in the aerosol will be less for H^+ (though not an order of magnitude less), and less for SO_4^{2-}, much of the reported H^+ and SO_4^{2-} actually being present as HSO_4^-.

The fact that there seems to have been initially present only enough ambient NH_3(g) to neutralize about 35% of the aerosol H_2SO_4 raises an interesting question: what would happen to the atmospheric acidity if SO_2 emissions were further curtailed? There is currently some debate about whether a given decrease in SO_2 emissions will cause a proportionate decrease in acid deposition, it being thought in some quarters that large decreases in SO_2 emissions would be necessary before any benefit in acid deposition could begin to be realized because in the atmospheric processes involved the SO_2 is present in excess. We are not dealing with that question, but rather the question of neutralization of the H_2SO_4 however produced. Thus, if SO_2 emissions were curtailed in such a way as to decrease the amount of SO_4^{2-} produced, and there were no other changes, then there would be disproportionately *large* decrease in atmospheric acidity. For example, if the ambient NH_3(g) presently can titrate 35% of the aerosol H_2SO_4 formed, a halving of the latter would drop the residual aerosol acidity by a factor of 4.

CONCLUSIONS

This paper explores some air chemistry and meteorology from the standpoint of atmospheric acidity in a summertime study at two mountaintop sites (Allegheny Mountain and Laurel Hill) in southwestern Pennsylvania. (Deposition during the study is discussed in other papers.) The sites are ~150 km downwind of the highest density of SO_2 emissions in the U.S. and within the region of the greatest wet/dry acid deposition flux in all of the Northeast, in an area where environmental damage ascribed to acid deposition has been reported.

With SO_2 taken to represent potentially two H^+ per SO_2 molecule, the average atmospheric acidity from SO_2(g), aerosol H^+ and HNO_3(g) was ~1200 neq m^{-3} all together, generally in the order SO_2 > aerosol H^+ > HNO_3, with enormous temporal variabilities, occasionally with HNO_3 > aerosol H^+, rarely with aerosol H^+ > SO_2, and never with HNO_3 > SO_2. Amounts of NH_3(g) and other acid-neutralizing substances (e.g. alkaline soil elements) were practically negligible by comparison.

The behavior of aerosol H^+ in strong association with aerosol SO_4^{2-} implies an aqueous H_2SO_4 aerosol in varying stages of neutralization by atmospheric NH_3(g). The degree of neutralization depended primarily on the SO_4^{2-} concentration, with higher H^+/SO_4^{2-} ratios at higher SO_4^{2-} concentrations. Allegheny, usually 1–2 h downwind of Laurel, tended to have ~7% higher NH_4^+/SO_4^{2-} ratios and ~6% lower H^+/SO_4^{2-} ratios, indicative of very slow ongoing neutralization. Average H^+/SO_4^{2-} mole ratio was 1.0. A fully neutralized $(NH_4)_2SO_4$ aerosol was never encountered. In general the amount of HNO_3,

NH_3 and aerosol H^+ and NH_4^+ present was consistent with the proposition that the amount of summertime anthropogenic acid (H_2SO_4, HNO_3) pollution in this part of the Northeast currently exceeds the acid-neutralizing capacity of the air by a factor of 2 or 3.

The stoichiometry between H^+, NH_4^+ and SO_4^{2-} in the aerosol, and the mass balance between these species and gravimetric mass with allowance for water of hydration, indicate that the aerosol was generally an aqueous $(NH_4)_xH_{2-x}SO_4$ aerosol with only minor amounts of other constituents except carbon. There was very little aerosol NO_3^-, consistent with the acidic nature of the aerosol; some 90% of the inorganic NO_3^- on the average existed as HNO_3(g).

The aerosol SO_4^{2-} episodes occurred in cycles of 7 or 8 days on the average and lasted several days each time, usually without a great deal of hour-to-hour fluctuation (as judged by b_{scat}, which was found to be a real-time surrogate for aerosol SO_4^{2-} and H^+), and with a spatial scale of $\gg 35$ km, in line with the already-recognized regional nature ($> 10^5$ km^2) of such episodes. Aerosol H^+ exhibited the same pattern as SO_4^{2-}, signifying that H^+, like SO_4^{2-}, was produced by regional $SO_2 \rightarrow H_2SO_4$ atmospheric conversion and advection to the sites, rather than emitted or formed locally. SO_2 behaved quite differently, existing largely in short-lived bursts (believed to represent fumigation by plumes from the numerous coal-fired power plants upwind), and in general decoupled from the regional H^+ and SO_4^{2-}. The SO_2 sources proved not to be significant sources of directly-emitted light-scattering aerosol or SO_4^{2-}. Correlations with Se indicate that the main origin of the SO_2, and ultimately of the regional H^+ and SO_4^{2-}, was coal combustion.

One instance was encountered of inter-site transport with growing b_{scat} and marginally declining SO_2; with b_{scat} as a surrogate for SO_4^{2-} it was calculated that daytime SO_2 oxidation and dry deposition rate coefficients were ~ 0.05 and $\leqslant 0.1$ h^{-1}, respectively.

The HNO_3 (and total nitrate) pattern was like the SO_4^{2-} pattern but with more day-to-day and inter-site variability, signifying a regional pollutant with a local component and faster formation/removal rates. HNO_3/SO_2/Se intercorrelations indicate that the local HNO_3 source is the power plants. HNO_3 and SO_2 responded much more rapidly to general wind changes than did aerosol H^+ or SO_4^{2-}, again indicating the regionality of the latter two. Thus the atmospheric acidity consisted of regional aerosol H^+ (associated with SO_4^{2-}), regional and local HNO_3(g), and substantially local SO_2(g).

Poor correlations between HNO_3 (or NO_x) and Pb made it impossible to demonstrate an automotive contribution to the HNO_3. One would expect it to have been significant but not major in this area.

In addition, there was a significant role of local photochemistry in HNO_3 formation; HNO_3 concentrations were lower at night, despite a much lower night-time deposition velocity and a lack of diurnal variation in O_3. This inference is supported by correlations among HNO_3, O_3 and PAN. (PAN, a photochemical product formed in polluted air masses, decayed at night in the present study with $t_{1/2} \sim 7$ to 8 h.) Photochemical production of SO_4^{2-} was also suggested by modest correlations of b_{scat} with PAN and O_3; but the local component of the photochemical $SO_2 \rightarrow SO_4^{2-}$ conversion could not have been large compared to the SO_4^{2-} formed at a distance and advected to the site, since there was no significant night/day alternation of $SO_2/(SO_2 + SO_4^{2-})$ ratio, H^+/SO_4^{2-} ratio, or H^+/NH_4^+ ratio.

A large excess of O_3 relative to SO_2 and NO_x was present at all times. Clearly there existed an oxidizing atmosphere, conducive to acid formation. By the same token, O_3 itself must not have been a limiting oxidant in acid formation.

The size distributions of aerosol H^+ and SO_4^{2-} (and NH_4^+) were substantially the same, further illustrating their close association, with MMED ~ 0.7 μm. The particles are in the optimum size range for efficient light scattering (much of it evidently attributable to aerosol H_2O) and inefficient wet or dry removal. Thus a close relationship between aerosol acidity and visibility degradation was expected and found. And the suggestion by Tanner *et al.* (1984), that strong acids may be available for long-distance transport in the lower troposphere, must certainly be correct at least with regard to aerosol H^+. Low HNO_3 deposition velocities found in this study under stratified night-time conditions (0.24 cm s^{-1}; Pierson *et al.*, 1986) indicate that HNO_3 too can be transported at night.

The highest SO_4^{2-} and aerosol H^+ were associated with winds from the west. Not all westerly trajectories through the SO_2 source region lying to the west gave high SO_4^{2-}, however, but rather more often the slow-moving ones. Wind speed upwind was important; in general, high concentrations of H^+, SO_4^{2-}, HNO_3 and SO_2 were associated with stagnation and meandering slow-moving trajectories from the west, while low values were associated with some fast-moving trajectories from that direction and with air masses from northerly directions. Maximum H^+ and SO_4^{2-} concentrations tended to be associated with low wind speeds > 24 h upstream, suggesting SO_2 accumulation during stagnation over a source region followed by enough transport time (> 24 h) to permit substantial $SO_2 \rightarrow H_2SO_4$ conversion en route. HNO_3 and aerosol NH_4^+ showed qualitatively similar behavior but their association with upstream inverse wind speed was weaker. Wind speed may also have been a factor in the lower concentrations observed in 1977 when average speed was over twice as high.

Fairly high H^+ and SO_4^{2-}, but only moderate HNO_3 and O_3, and low SO_2, were encountered when air reached the sites from SE on the back side of a high pressure system centered to the N and moving SE. This situation also gave especially high SO_4^{2-}/SO_2 ratios, perhaps more through $SO_2 \rightarrow SO_4^{2-}$ conversion than through SO_2 deposition during the long trip

from the source region. Evidently HNO_3 transport was not particularly efficient. High SO_4^{2-}/SO_2 ratios and substantial PAN levels indicated an aged photochemical air mass.

Very high concentrations of all pollutants including H^+, SO_4^{2-}, HNO_3, SO_2, O_3 and PAN developed during a severe local stagnation interval, indicating that local sources under sufficiently stagnant conditions can give rise to pronounced atmospheric acidity. Thus we identify three meteorological regimes for high atmospheric acidity: (1) slow westerly winds, with stagnation and meandering over SO_2 source areas lying to the west, (2) local stagnation, and (3) regional transport around to the back side of a high pressure system. Upwind rain is also a factor, especially when it occurs between the source areas and the sampling sites. In most of the cases with maximum atmospheric acidity there had been no rain for at least 72 h upwind.

Agreement between the results of this study and the earlier one in 1977 at the same site, as well as other studies in the Northeast, indicate that the situation herein described is not anomalous and indeed could be quite typical for summertime rural conditions in that region.

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