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Acid Rain and Atmospheric Chemistry at Allegheny Mountain

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■ Rain chemistry was measured in August 1983 on Allegheny Mountain and Laurel Hill in southwestern Pennsylvania. The average composition approximated an $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture with a volume-weighted average pH of 3.5 and an $\text{SO}_4^{2-}/\text{NO}_3^-$ mole ratio of 1.8. There was very little undissociated (weak) acidity and very little S(IV). The acidic rains were associated with air masses traversing SO_2 source regions west of the sites; stagnation and intervening precipitation were important influences. The geographic scale for a halving of rain SO_4^{2-} concentration downwind of SO_2 sources was ~ 440 km. Scavenging ratios were inferred for SO_2 , aerosol SO_4^{2-} , and HNO_3 . On average about half of the rain SO_4^{2-} resulted from scavenging of SO_2 , the rest from scavenging of aerosol SO_4^{2-} . The rain H^+ was attributed about 25% to HNO_3 , 55% to scavenging of SO_2 , and 20% to scavenging of aerosol acid SO_4^{2-} . Cumulative deposition totals in rain were compared with deposition in fog and with dry deposition in the same experiment. A crude acid-deposition budget was calculated as follows: 47%, H_2SO_4 in rain; 23%, SO_2 dry deposition without dew; 16%, HNO_3 in rain; 11%, HNO_3 dry deposition without dew; 2%, HNO_3 and H_2SO_4 in fog and dew; 0.5%, aerosol dry deposition without dew.

Introduction

In August 1983, we carried out a field experiment involving various aspects of the acid-deposition phenomenon at two rural sites on Allegheny Mountain and Laurel Hill

in southwestern Pennsylvania (Figure 1). This paper deals with the wet (rain) deposition during the experiment. Other aspects of the experiment have been discussed elsewhere: the chemistry of dew and its role in acid deposition (1), the dry deposition of HNO_3 and SO_2 to surrogate surfaces (2), and the role of elemental carbon in light absorption and of the latter in visibility degradation (3).

The Allegheny and Laurel sites, situated only ~ 150 km downward of the highest density of SO_2 emissions in the U.S. (see ref 4 or Figure 4 of ref 5), lie in the area of the highest rainfall H^+ concentrations and highest annual totals of H^+ wet deposition in the U.S. or, indeed, in North America (6-9). The area moreover has a history of ecological damage ascribed to acid rain; trout kills have been recorded in poorly buffered headwater streams on Laurel Hill since 1960 (8), followed by failures of restocking programs and the disappearance of trout and other fish from some streams—all attributed to acid rain and consequent stream acidification during storm runoff periods (8, 10, 11).

This paper describes the rain chemistry in the 1983 experiment and explores chemical relationships with the atmospheric trace gases and aerosol. Air mass trajectories to the sites are briefly considered.

Experimental Section

The experiment was conducted August 5-28, 1983, on abandoned radio towers atop Allegheny Mountain (at 39.959° N, 78.8525° W, elevation 838 m) and Laurel Hill (at 40.099° N, 79.226° W, elevation 850 m, 35 km northwest of Allegheny Mountain) (Figure 1). Both sites are

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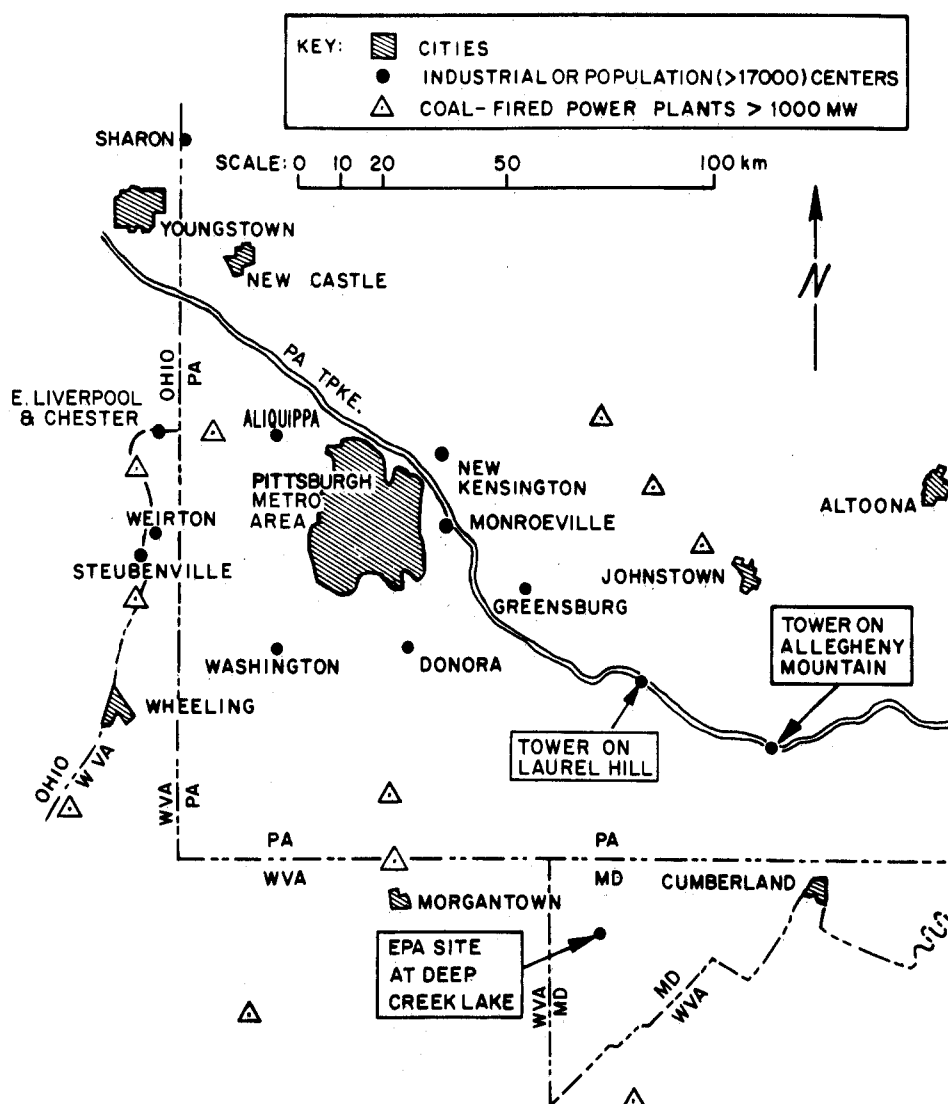


Figure 1. Map of the southwestern Pennsylvania vicinity of the 1983 Allegheny Mountain/Laurel Hill experiment showing the locations of the towers, urban areas and industrial centers, coal-burning power plants, and the site of a concurrent EPA experiment at Deep Creek Lake.

heavily forested. There is no local traffic, though on rare occasions at the Allegheny Mountain site there were brief excursions of condensation nuclei count, NO, and (downward excursions) O₃ with wind from the direction of the east portal of the Allegheny Mountain Tunnel, some 420 m away and 143 m lower in elevation.

At the Allegheny Mountain site, atmospheric aerosol and gas measurements and light-scattering and condensation nuclei count measurements were made atop the tower at 14–17 m above the ground. Wind speed and direction were monitored 20.6 m above the ground (8 m above the tree-tops). Atmospheric temperature, pressure, and humidity were continuously recorded. Rain was collected on an event basis into tared polyethylene bottles, with a wet-only collector (Wong Laboratories Mark V) set up in a 500-m² mowed clearing 60 m north of the tower. Instead of the standard collector bucket, we used a 30.5 cm diameter polyethylene funnel fitted into the tared collection bottle. The mouth of the funnel was 1.8 m above the ground. The rainfall amount (in mm or in kg/m²) was determined from the sample weight and from the funnel diameter (1 mm = 74 mL) and was verified by concurrent collection in a rain gauge. Dew and settled fogwater were collected as described elsewhere (1). The sampling setup was similar at Laurel Hill, with atmospheric aerosol, gas, and light-scattering measurements 18–21 m above the ground, rain collections in an open area 43 m southeast of the tower,

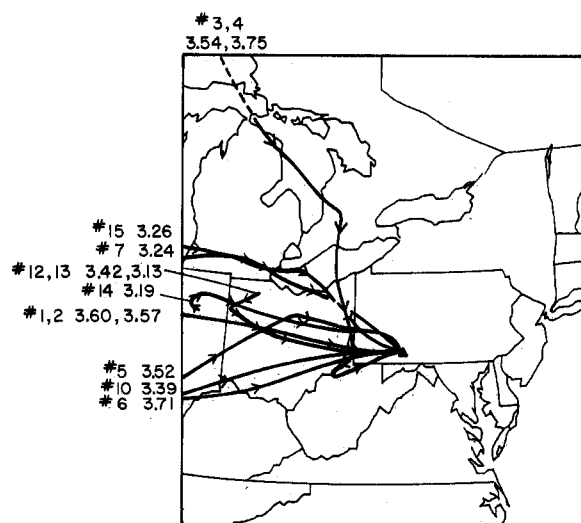


Figure 2. Mixed-layer trajectories associated with (arriving at the 6-h time closest to) each Allegheny rain. Arrowheads every 12 h. Rain number and pH are as shown. The Laurel rains had similar trajectories.

and wind speed and direction monitored 24.5 m above the ground.

Mixed-layer trajectories for air arriving at the sites at 0200, 0800, 1400, and 2000 EDT daily were generated from

National Weather Service (NWS) data by methods described by Heffter (12) and Samson (13) as illustrated in Figure 2. Storms were classified by inspection of surface weather maps from the National Climatic Center. Rains were classified as warm front, cold front, warm sector, and summer convective (WF, CF, WS, and SC, respectively). The classifications were verified, and the exact time of frontal passage was determined, by the recorded temperature, pressure, humidity/dew point, and wind speed and direction.

As soon as each rain was seen to have stopped, the rain sample was removed, capped, and refrigerated at the site. Within a few hours the sample was transported in an ice-filled container to the field laboratory in the town of Somerset, midway between the two sites, where it was weighed and kept refrigerated (never frozen). Aliquots were usually analyzed on the day of collection. The analytical procedures were similar to those previously described (1) for dew samples. Quantities measured included pH, conductivity, total titratable acid, and (by ion chromatography) SO_4^{2-} , NO_3^- , NO_2^- , PO_4^{3-} , F^- , Cl^- , and Br^- . (Part of one rain sample was centrifuged before analysis; no effect on subsequent analytical results was observed.)

The unused portions of the rain samples were transported to Dearborn, Michigan, still refrigerated. Some 7 months later they were reanalyzed; to selected samples H_2O_2 was added before this reanalysis (final $[\text{H}_2\text{O}_2] = 1.5\%$) to make certain that all S(IV) had been oxidized to sulfate. S(IV) was estimated by the difference between this "delayed" analysis and the initial or "prompt" analysis. At this time, NH_4^+ , Na, and K were determined by ion chromatography. Some 13–15 months after collection, the samples were analyzed for trace metals, all as previously described (1).

Stability of the rain samples against decay and wall losses was considered. In the 7 months between analyses, NO_3^- in the samples showed an insignificant change ($5 \pm 8\%$). The same was true of SO_4^{2-} ($4 \pm 5\%$). Substantial NH_4^+ decay has been reported (14) in 8 months of refrigerated storage at pH above 4.0 and NH_4^+ concentrations below $11 \mu\text{equiv/L}$, though these conditions are met by none of our rain samples. Wall losses were significant for Al, Mn, and Fe but not for most other elements (e.g., Pb loss = $2 \pm 1\%$), as described before (1). Experiments with sulfite solutions in distilled deionized water indicated that, in the pH range of the rain samples in this study, S(IV) is stable against oxidation to SO_4^{2-} during ion chromatographic analysis, during refrigerated storage prior to prompt analysis, and even during a few hours standing at room temperature.

Of the atmospheric constituents, NO_2 [together with peroxyacetyl nitrate (PAN)] and NO were monitored by chemiluminescence, and PAN was monitored by gas chromatography with an electron-capture detector (15), SO_2 by a peroxide impinger method (16) and by pulsed UV fluorescence, and O_3 by UV absorption. Light scattering was measured by integrating nephelometers. $\text{HNO}_3(\text{g})$ and aerosol NO_3^- were measured by the denuder-difference method (17–19) by using MgO-coated denuder tubes and nylon membrane filters (nominal pore diameter $1 \mu\text{m}$), with ion chromatographic nitrate determination on alkaline filter extracts. The inlet of the denuder-difference apparatus was a cyclone with a $1.5\text{-}\mu\text{m}$ cutoff (20) to exclude large-particle nitrate that might otherwise deposit in the denuder and be mistaken for HNO_3 . N_2O_5 , significant amounts of which can be expected at night (21), could register to some degree as HNO_3 in the denuder-difference apparatus at high humidities (22); this possibility was not

Table I. Time-Weighted Average Atmospheric Concentrations and Other Rain-Relevant Variables, Allegheny Mountain, August 5–28, 1983 (nequiv = $2 \times \text{nmol}$ for SO_2 , SO_4^{2-} , and Aerosol S) (Values from Laurel Hill Are Similar)

| | nequiv/ m^3 | ppb | $\mu\text{g}/\text{m}^3$ | % fine ^a |
|---|----------------------|------------------|--------------------------|---------------------|
| aerosol mass | | | 64 | 76 |
| H^+ | 194 | | 0.2 | 90 |
| NH_4^+ | 169 | | 3 | 82 |
| NO_3^- | 8 | | 0.5 ^b | |
| SO_4^{2-} | 384 | | 18 | 90 |
| total S | 413 ^c | | 7 ^c | 87 |
| NH_3 | <i>d</i> | <i>d</i> | <i>d</i> | |
| NO | 12 | 0.3 | | |
| $\text{NO}_2 + \text{PAN}$ | 217 | 5.6 | | |
| PAN | 47 ^e | 1.2 ^e | | |
| HNO_3 | 71 | 1.8 | 4.5 | |
| SO_2 | 805 | 10 | 26 | |
| O_3 | 2139 | 55 | 103 | |
| condensation nuclei count, cm^{-3} | | | 5800 | |
| b_{scat} , m^{-1} | | | 1.9×10^{-4} | |
| temperature, $^{\circ}\text{C}$ | | | 20 | |
| dewpoint, $^{\circ}\text{C}$ | | | 14 | |
| humidity, % | | | 76 | |
| barometer, mmHg | | | 698 | |
| wind speed at surface, m/s | | | 3.43 | |

^a Fine = $2.5\text{-}\mu\text{m}$ diameter and smaller; dichotomous sampler or impactor. ^b Particles $\leq 1.5\text{-}\mu\text{m}$ diameter only (cyclone inlet nominal cutoff). ^c Aerosol total S includes the SO_4^{2-} . ^d NH_3 was 5, ≤ 14 , and ≤ 15 nequiv/ m^3 on the first three Allegheny runs and 1.3, 5, ≤ 18 , and ≤ 7 nequiv/ m^3 on the first four Laurel runs. No further valid NH_3 data were obtained. Average must have been \ll aerosol NH_4^+ (see text). ^e PAN GC/ECD data were obtained for only the last half (12.5 days out of 24) of the experiment. ^f From vane on tower at Allegheny.

evaluated in this study. $\text{NH}_3(\text{g})$ was determined by oxalic acid coated denuder tubes (23), a method that in principle should not be subject to the usual artifact problems (24) in $\text{NH}_4^+/\text{NH}_3$ measurement. Valid $\text{NH}_3(\text{g})$ data were obtained in a few instances but not in any of the rain periods because of problems of water condensation in the denuder tubes and NH_4^+ instability during storage.

Aerosol samples were collected on quartz-fiber HiVol filters, on 142 mm diameter Teflon membrane filters (nominal mean pore diameter $0.2 \mu\text{m}$), in dichotomous samplers on 37-mm Teflon membrane filters (pore diameter $1 \mu\text{m}$), on eight-stage Andersen impactors with cellulose filters (Whatman 41) for impaction substrates and with quartz-fiber backup filters, and on the nylon membrane filters of the denuder-difference apparatus. Aerosol H^+ , NH_4^+ , SO_4^{2-} , and trace elements were determined on extracts of various filters and impactor stages by pH measurements, ion chromatography, inductively coupled argon plasma atomic emission (ICP/AES), and atomic absorption. The possibility that $\text{NH}_3(\text{g})$ was collected on acidic aerosol deposits to produce artificially high aerosol NH_4^+ values (24) is considered inconsequential, given the low $\text{NH}_3(\text{g})$ concentration in comparison with the total represented by $\text{NH}_3(\text{g})$ and aerosol NH_4^+ combined (Table I). X-ray fluorescence and neutron activation (by NEA, Inc.) on the dichotomous sampler filters measured aerosol S and other elements in the fine ($< 2.5\text{-}\mu\text{m}$ diameter) and coarse (2.5 to 10 or $15 \mu\text{m}$) particle size ranges. Total aerosol S was also determined by combustion (1).

The filter, denuder, and impinger samples were collected in 0.5–24-h periods synchronized with each other but not generally with the onset or cessation of rain. The impactor samples were collected over even longer times spanning several wet and dry periods. Accordingly, it should be understood that, in the treatment that follows, the at-

Table II. Rain Data: Allegheny Mountain and Laurel Hill, August 1983

| sample | EDT start | pptn type ^a | duration, min | kg/m ² | Λ, μmho/cm | pH | μequiv/L ^b | | | | | | | | |
|---------------------|-------------------------|---------------------------|------------------|-------------------|---------------|------|-----------------------|----------------|------------------------------|---------------------|------------------------------|------------------------------|-------------------------------|---------|-----------------|
| | | | | | | | total acid | H ⁺ | NH ₄ ⁺ | metals ^c | NO ₂ ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | | Cl ⁻ |
| | | | | | | | | | | | | | prompt | delayed | |
| Allegheny Mountain | | | | | | | | | | | | | | | |
| 1 | 1332, 8/5 | SC (T) | 50 | 12.94 | 111 | 3.60 | 289 | 250 | 55 | 41 | ~1 | 58 | 253 | 260 | 11.6 |
| 2 | 1552, 8/5 | SC (T) | 104 | 3.12 | 113 | 3.57 | 318 | 269 | 35 | 21 | ~1 | 70 | 218 | 207 | 7.5 |
| 3 | 1245, 8/11 ^d | WF (T) | 60 | 14.17 | 116 | 3.54 | 353 | 286 | 58 | 43 | ~0.9 | 63 | 276 | 276 | 6.9 |
| 4 | 1540, 8/11 | WS | 30 | 0.42 | 67 | 3.75 | | 178 | 15 | 12 | | 63 | 125 | 137 | 3.8 |
| 5 | 0300, 8/12 | CF | <i>e</i> | 0.16 | | 3.52 | | 302 | 59 | 7.8 | | 150 | 207 | 229 | 10.7 |
| 6 | 0021, 8/18 | SC | 73 | 7.37 | 78 | 3.71 | 227 | 195 | 37 | 15 | ~0.6 | 41 | 141 | 164 | 3.1 |
| 7 | 2352, 8/18 | SC | 10 | 0.02 | | 3.24 | | 575 | | | | | | | |
| 10 | 1418, 8/22 | CF | 21 | 0.18 | 176 | 3.39 | | 407 | | | | 139 | 700 | | 15.0 |
| 12 | 1537, 8/27 | SC | 34 | 11.16 | 125 | 3.42 | 351 | 380 | 58 | 28 | | 79 | 274 | 284 | 6.3 |
| 13 | 1612, 8/27 ^f | SC | 16 | 0.76 | 271 | 3.13 | 763 | 741 | 116 | | | 212 | 608 | 650 | 22.6 |
| 14 | 2013, 8/27 | SC (T) | 30 | 0.25 | 232 | 3.19 | | 646 | 100 | 91 | | 252 | 518 | 537 | 25.1 |
| 15 | 1636, 8/28 | CF | 39 | 0.42 | 211 | 3.26 | 697 | 550 | 98 | 60 | | 161 | 515 | 541 | 17.2 |
| volume- weighted av | | | | | 115 | 3.54 | 324 | 290 | 53 | 39 | ~0.9 | 68 | 256 | 262 | 7.9 |
| Laurel Hill | | | | | | | | | | | | | | | |
| 1 | 2125, 8/11 | WS ^g | 58 ^g | 1.20 | 141 | 3.57 | 360 | 269 | 119 | 156 | ~1.3 | 135 | 381 | 392 | 17.9 |
| 2 | 2000, 8/17 | SC | 215 | 6.44 | 109 | 3.59 | 317 | 257 | 61 | 47 | ~0.6 | 63 | 249 | 252 | 6.6 |
| 3 | 0618, 8/22 | WF (T) | 7 | 4.04 | 112 | 3.46 | 325 | 343 | 64 | 56 | ~1.1 | 72 | 269 | 273 | 5.6 |
| 4 | 1410, 8/22 | CF | 6 | 0.19 | | 3.47 | | 339 | | | | 194 | 575 | | 20.7 |
| 5 | 1518, 8/27 | <i>h</i> | 22 | 1.07 | 220 | 3.26 | 615 | 550 | 98 | 143 | | 202 | 506 | 513 | 18.8 |
| volume- weighted av | | | | | 122 | 3.51 | 349 | 311 | 70 | 70 | ~0.8 | 86 | 294 | 299 | 8.5 |

^aPrecipitation types: WF, warm front; CF, cold front; WS, warm sector; SC, summer convective. T signifies thunderstorm. ^bFor H⁺, NH₄⁺, NO₂⁻, NO₃⁻, and Cl⁻, 1 μequiv = 1 μmol . For SO₄²⁻, 1 μequiv = 0.5 μmol . For metals Mⁿ⁺, 1 μequiv = 1/n μmol . ^cMetals include Li⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺ by ICP/AES (mostly Ca²⁺). ^dCollected in two separately analyzed portions. First 97% had pH 3.54; the remaining 3% had pH 3.69. ^eThree brief showers between 0300 and 0515. ^fRain 13 was actually a continuation of rain 12. ^gIncludes a light 13-min WF thunderstorm beginning at 1225 on 8/11. ^hLaurel rain 5 does not correspond to any of the stated classifications.

Table III. Comparison of Rain Properties at Allegheny and Laurel, August 1983, with Allegheny Dew and Settled Fogwater (Volume-Weighted Averages)

| | rain | | dew | fog |
|--|-----------------------|-------------------|---------------|----------------------|
| | Allegheny (n = 12) | Laurel (n = 5) | (n = 15) | (n = 1) ^a |
| pH | 3.5 (3.1-3.75) | 3.5 (3.3-3.6) | 4.0 (3.5-5.3) | 3.47 |
| titratable acid, $\mu\text{equiv/L}$ | 324 (227-763) | 349 (317-615) | 108 (16-382) | 350 |
| H ⁺ , $\mu\text{equiv/L}$ | 290 (178-741) | 311 (257-550) | 91 (5.5-347) | 340 |
| NH ₄ ⁺ , $\mu\text{equiv/L}$ | 53 (15-116) | 70 (61-119) | 8 (0-55) | 144 |
| Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , $\mu\text{equiv/L}$ | 39 (8-99) | 70 (48-159) | 41 (14-99) | 155 |
| NO ₂ ⁻ , $\mu\text{equiv/L}$ | 0.6-1.0 | 0.6-1.3 | 0.7 (0.1-2.0) | |
| NO ₃ ⁻ , $\mu\text{equiv/L}$ | 68 (41-252) | 86 (63-202) | 32 (3-138) | 230 |
| SO ₄ ²⁻ prompt, $\mu\text{equiv/L}$ | 256 (125-700) | 294 (249-575) | 73 (10-254) | 387 |
| SO ₄ ²⁻ delayed, $\mu\text{equiv/L}$ | 262 (138-700) | 299 (251-575) | 81 (14-251) | 373 |
| Cl ⁻ , $\mu\text{equiv/L}$ | 8 (3-25) | 8.5 (6-21) | 5 (0.3-16) | 26 |
| ion balance Σ^+/Σ^- | 1.15 | 1.16 | 1.27 | 0.99 |
| Λ , $\mu\text{mho cm}^{-1}$ | 115 (67-271) | 122 (109-220) | 42 (10-137) | 159 |
| % of Λ accounted for | 106 | 111 | 94 | 107 |

^aDoes not include all fog events.

mospheric concentrations of aerosol components, HNO₃, and impinger SO₂ that we will associate with the rain samples are the average concentrations over the several-hour air-sampling period during which the given rain occurred and not the concentrations just during the rain itself.

Results and Discussion

Table I summarizes average concentrations of atmospheric trace gas and aerosol species and average values of certain other atmospheric properties relevant to the discussion to follow. There was no attempt to measure H₂O₂ in the air or in the rain. Judging from other studies (25), peroxide concentrations in the rain might have been 5 (range 0-60) $\mu\text{mol/L}$.

Rain Chemistry. The characteristics of the 17 rain events at the two sites are summarized in Table II and compared in Table III to the 15 dew samples collected on

Teflon collectors at Allegheny Mountain and to the one settled fogwater sample (1). (The dew was sampled in a manner that excluded prior dry deposition. The representativeness of the fogwater sample is unknown—other fogs occurred, but no samples were collected.) The averages are volume-weighted. The prompt and delayed sulfate data are respectively the field-laboratory results and the reanalyses 7 months later.

The following summary statements can be made from Table II and III:

- (1) The rain was acidic, with a volume-average pH of 3.5.
- (2) H⁺ accounted for about 90% of the total rain acidity.
- (3) The rain H⁺ could be accounted for in terms of H₂SO₄ and HNO₃.
- (4) The SO₄²⁻/NO₃⁻ equivalents ratio in the rain was about 3.7 (mole ratio about 1.8) on the average.
- (5) Rains with the highest SO₄²⁻ concentrations tended also to have the highest NO₃⁻ concentrations (correlation

coefficient $r = 0.81$, $n = 16$).

(6) Rain acidity had no obvious relation to storm type (WF, CF, WS, and SC).

(7) Concentrations in rain were inversely related to rainfall amount. Thus, rains with $[\text{NO}_3^-] < 100 \mu\text{equiv/L}$ were an order of magnitude heavier, on the average ($7.5 \pm 4.9 \text{ kg/m}^2$), than those with $[\text{NO}_3^-] > 100 \mu\text{equiv/L}$ ($0.5 \pm 0.4 \text{ kg/m}^2$). Similarly, rains with $[\text{SO}_4^{2-}] < 500 \mu\text{equiv/L}$ were an order of magnitude heavier, on the average ($6 \pm 5 \text{ kg/m}^2$), than those with $[\text{SO}_4^{2-}] > 500 \mu\text{equiv/L}$ ($0.5 \pm 0.4 \text{ kg/m}^2$).

(8) There is evidence for only a relatively minor amount of S(IV) in the collected rain samples (compare prompt vs. delayed SO_4^{2-} analysis, explained below).

Generally, good cation-anion balances were obtained, and conductivities were close to those predicted from the equivalent conductances of the separate ions together with the measured ion concentrations, as intimated in Table III. Evidently, therefore, no important ions were overlooked. The concentration of HCO_3^- , though not measured, would have to have been insignificant ($< 0.03 \mu\text{equiv/L}$) at even the highest pH values encountered. Concentrations of organic acids (formic, acetic, etc.) must also have been small (at least at the time of prompt analysis), given the $\text{H}^+/(\text{NO}_3^- + \text{SO}_4^{2-})$ ratios and H^+ /(total acidity) ratios. Our failure to detect S(IV) consistently in the rain (delayed SO_4^{2-} minus prompt $\text{SO}_4^{2-} \sim 5$ or $6 \mu\text{equiv/L}$ on the average, Table II) is supported by Dana's (26) observations of insignificant S(IV) ($< 5 \mu\text{equiv/L}$, $\text{S(IV)}/\text{SO}_4^{2-} < 0.01$) in summer rains in the northeast. At the average rain pH and ambient SO_2 and temperature in the 1983 Allegheny experiment, Dana's calculations predict that the rain S(IV) should be $< 1 \mu\text{equiv/L}$.

The composition of the rain is compared with that of the dew and the fog in Table III; see ref 1 for detailed discussion. The $\text{SO}_4^{2-}/\text{NO}_3^-$ concentration ratio in the rain was higher than that in the dew; this is not surprising since significant amounts of sulfate are introduced into rain by nucleation scavenging (27) while aerosol sulfate deposition to dew is minimal (1).

The $\text{SO}_4^{2-}/\text{NO}_3^-$ ratios in the rain were in the range characteristic of summer rains in the northeast (28–36), which typically show 2.3–4 equivalents of SO_4^{2-} per equivalent of NO_3^- . Normalized to SO_4^{2-} , the weighted-average concentrations of H^+ , NH_4^+ , and NO_3^- were essentially identical with (within a few percent) the values for the same period in rain at the MAP3S site at The Pennsylvania State University (PSU) some 140 km to the northeast (37).

Our Allegheny/Laurel rains were more acidic than is usual for summer rains in the northeast (28–33). This is expected since the sites lie in the area of maximum rain acidity (6–9). In addition, August 1983 was an exceptional period locally, judging from rain H^+ , NO_3^- , and SO_4^{2-} data over several years at the PSU MAP3S site (37) and at another PSU site on Laurel Hill only 12 km to the south of ours (6, 38) (their August 1983 data are similar to ours), and also judging from comparison (Table IV) with rain SO_4^{2-} and ambient SO_4^{2-} and SO_2 (16) at the Allegheny site at about the same time in 1977. At the MAP3S site, for example, August 1983 had the second highest average rain H^+ of any month in at least 7 years (37).

One factor favoring high acidity in the 1983 rains is that the trajectories describing the mixed-layer air movement were all from the west (Figure 2), that is, from the direction of the strong SO_2 sources; however, the same was basically true of the 1977 experiment, when rain SO_4^{2-} was never-

Table IV. Allegheny Mountain Rain SO_4^{2-} , July/August 1977 vs. August 1983

| | 1977, ^a 7/24 to 8/10, 17.5 days, $n = 8$ | 1983, 8/5 to 8/28, 24 days, $n = 12$ |
|--|--|---|
| water av deposition, $\text{L m}^{-2} \text{ week}^{-1}$ | 13 | 15 |
| SO_4^{2-} av deposition, $\mu\text{equiv m}^{-2} \text{ week}^{-1}$ | 1480 | 3890 |
| SO_4^{2-} , $\mu\text{equiv/L}^b$ | 115 (71–238) | 262 (138–700) ^c |
| ambient aerosol SO_4^{2-} , nequiv/m^3 | 292 | 384 ^d |
| ambient SO_2 , nequiv/m^3 | 572 | 805 ^d |

^a Ref 16. ^b Volume-average concentration, $\Sigma(\mu\text{equiv/m}^3)/\Sigma(\text{L/m}^3)$. ^c Delayed analysis. ^d Time-average concentration, $\Sigma(t \cdot \text{nequiv/m}^3)/\Sigma(t)$.

theless lower (16). A more detailed meteorological analysis is instructive. Although relative frequencies of the various storm types in the 1983 experiment were not abnormal, the average scalar wind speed at the tower (Table I) was less than half of the average in the 1977 experiment (16). The 72-h mixed-layer back-trajectory wind speeds for air masses delivering rain at the site were generally 3 times lower in the 1983 experiment than in the 1977 experiment. Thus, dispersion/stagnation surely played a role.

Also important is upwind rain and its times and places of occurrence relative to stagnation and passage through source regions. When there was more upwind stagnation, less upwind rain, and especially no rain en route to the site following stagnation, the rain SO_4^{2-} concentrations at the sites tended to be higher. These conditions prevailed in the 1983 study more than in the 1977 study. The high acidity of the rain in the 1983 experiment therefore can probably be rationalized in terms of the occurrence 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).

Finally, our practices of collection on an event basis (rather than, say, weekly) and of prompt refrigeration and early analysis may have made a difference, as not all rain sampling networks employ such practices and rain samples do undergo composition changes (including H^+ losses) with time (39–41).

The pronounced atmospheric acidity that might accompany such acidic rains as in 1983 is evident in the high aerosol $\text{H}^+/\text{SO}_4^{2-}$ ratio, high HNO_3 /aerosol NO_3^- ratio, and low NH_3 that can be seen in Table I and that has been documented at Allegheny before (16).

Transport Distance Scale. The fact that the mixed-layer air was from the west whenever there was rain at the sites (e.g., Figure 2) offers an unusual opportunity to ask about the distance scale of the decline of SO_4^{2-} concentration in rain as one moves downwind (eastward). We consider the August 1983 volume-average SO_4^{2-} concentrations in rain at 17 sites scattered throughout Pennsylvania. These consist of the 13-station statewide PSU network (week-long wet-only accumulations) (6), the MAP3S site at PSU (event sampling) (37), the Utility Acid Precipitation Study Program (UAPSP) site at Tunkhannock (event sampling) (42), and our two sites. Westerly directions were the rule for air masses associated with rains at each of these sites during August 1983—though a given rain generally affected but one site.

From west to east across the state we find a substantial decline in volume-average rain SO_4^{2-} concentration, describable as an exponential with a half-distance of ~ 440

Table V. Deposition Totals and Deposition Fluxes Associated with Rain at Allegheny and Laurel, August 1983 (Allegheny Dew and Settled Fogwater Shown for Comparison)

| | rain | | dew | fog |
|---|-----------------------|-------------------|----------|-------------------|
| | Allegheny (n = 12) | Laurel (n = 5) | (n = 15) | (n = 1) |
| August 5–28 Accumulations | | | | |
| water, g/m ² | 51 000 | 12 940 | 2722 | ~590 ^a |
| titratable acid, μequiv/m ² | 16 500 | 4 513 | 295 | ~210 ^a |
| H ⁺ , μequiv/m ² | 14 800 | 4 017 | 247 | ~200 ^a |
| NH ₄ ⁺ , μequiv/m ² | 2 570 | 898 | 22 | ~185 ^a |
| NO ₃ ⁻ , μequiv/m ² | 3 440 | 1 113 | 88 | ~140 ^a |
| SO ₄ ²⁻ prompt, μequiv/m ² | 13 100 | 3 799 | 197 | ~230 ^a |
| SO ₄ ²⁻ delayed, μequiv/m ² | 13 400 | 3 860 | 220 | ~230 ^a |
| Fluxes (Accumulations/Collection Times) | | | | |
| water, mg m ⁻² s ⁻¹ | 1 700 | 700 | 5 | 3.3 |
| titratable acid, nequiv m ⁻² s ⁻¹ | 550 | 244 | 0.53 | 1.2 |
| H ⁺ , nequiv m ⁻² s ⁻¹ | 490 | 217 | 0.44 | 1.1 |
| NH ₄ ⁺ , nequiv m ⁻² s ⁻¹ | 85 | 49 | 0.04 | 0.5 |
| NO ₃ ⁻ , nequiv m ⁻² s ⁻¹ | 115 | 60 | 0.16 | 0.8 |
| SO ₄ ²⁻ prompt, nequiv m ⁻² s ⁻¹ | 440 | 206 | 0.35 | 1.28 |
| SO ₄ ²⁻ delayed, nequiv m ⁻² s ⁻¹ | 450 | 209 | 0.39 | 1.24 |

^a Order of magnitude estimate, based on the estimate that 5 times as much was deposited during the experiment as in the one 10-h sample that was analyzed. The representativeness of the sample composition is not known.

km. (If the effect of the relatively modest SO₂ emissions in the central and eastern part of the state could be subtracted, the attenuation scale presumably would be shorter.) Similar statements appear possible for other rain species—H⁺, NH₄⁺, and NO₃⁻.

Acid Deposition Fluxes in Rain. Table V lists cumulative amounts of various species deposited per unit area in rain, dew, and fog during the experiment. These were obtained from the concentrations in each sample, multiplying by the respective amounts of water per unit area and summing the products. Table V also shows the fluxes obtained by dividing the accumulation by the sum of collection times. It is apparent that the greater frequency of rain at Allegheny Mountain produced about a 4-fold greater accumulation of all ionic species there than at Laurel Hill. This difference in frequency reflects the randomness of summer convective precipitation (Table II; approximately 70% of the precipitation at Allegheny Mountain was convective in nature), as the annual rainfall averages at the two sites are similar (43). In terms of fluxes to ground, however, the results at the two sites are similar for all the species.

Comparison of the 21-day accumulations on Allegheny Mountain in Table V shows that rain was responsible for the deposition of 60 times more acidity (together with related species) than was deposited to the dew collector during dew periods or during fog. Precipitation on Allegheny Mountain or Laurel Hill is about 107–135 cm/year (6, 8, 9, 43), or close to the rate recorded in Table V. If the deposition to dew during the study is also representative of the year, then it follows that the annual total acid deposited in rain is roughly 60 times as great as that deposited to dew or in settling (not intercepted) fog.

Scavenging Ratios for SO₄²⁻ and NO₃⁻ by Rain. Scavenging ratios to be discussed below are defined as follows:

$$W(\text{SO}_4^{2-}) \equiv \frac{[\text{SO}_4^{2-}]_{\text{rain}} \text{ derived from aerosol SO}_4^{2-}}{[\text{SO}_4^{2-}]_{\text{air}}}$$

$$W(\text{SO}_2) \equiv \frac{[\text{SO}_4^{2-}]_{\text{rain}} \text{ derived from SO}_2(\text{g})}{[\text{SO}_2]_{\text{air}}}$$

$$W(\text{S}) \equiv \frac{[\text{SO}_4^{2-}]_{\text{rain}}}{[\text{SO}_4^{2-} + \text{SO}_2]_{\text{air}}}$$

$$W(\text{NH}_4^+) \equiv \frac{[\text{NH}_4^+]_{\text{rain}} \text{ derived from aerosol NH}_4^+}{[\text{NH}_4^+]_{\text{air}}}$$

$$W(\text{HNO}_3) \equiv \frac{[\text{NO}_3^-]_{\text{rain}} \text{ derived from HNO}_3(\text{g})}{[\text{HNO}_3]_{\text{air}}}$$

$$W(\text{aerosol NO}_3^-) \equiv \frac{[\text{NO}_3^-]_{\text{rain}} \text{ derived from aerosol NO}_3^-}{[\text{aerosol NO}_3^-]_{\text{air}}}$$

$$W(\text{N}) \equiv \frac{[\text{NO}_3^-]_{\text{rain}}}{[\text{HNO}_3 + \text{aerosol NO}_3^-]_{\text{air}}}$$

The concentrations in rainwater will be expressed in equivalents per cubic meter of liquid water (i.e., milli-equivalents per liter). Concentrations in air will be expressed in equivalents per cubic meter of air. In these dimensions, 100% scavenging efficiency from initially clear air would correspond to $W = 10^6$ if the liquid water content of the air were 1 g/m³.

In this study, concentrations are determined at ground (tower) level. To impute physical significance to the results in terms of scavenging processes, one must assume that the ground-level pollutant data are representative of the air where the scavenging is taking place. This assumption, said to be justified at locations remote enough from sources for vertical mixing to have occurred (27), perhaps is better at mountaintop locations than at lower elevations and is strengthened in this case by the convective nature of the storms. On the other hand, one should consider the proximity of sources (Figure 1) and the rapid (time scale of an hour) fluctuations in ground-level concentrations of SO₂, NO_x, etc. Limited aircraft observations in this general area on other occasions (44–46) support (though weakly) the assumption of vertical uniformity.

In what follows, atmospheric concentrations are those averaged over a several-hour sampling period containing, but longer than, the time interval over which rain fell. Inspection of the continuous traces for SO₂ (UV fluorescence), NO and NO_x, O₃, condensation nuclei count, and light scattering [a good index, at these locations, of aerosol SO₄²⁻ concentration (16)] gave no consistent indication that the ground-level concentrations during rain were materially lower than the concentrations in the hour or two beforehand or afterward. The changes when they did appear were generally not large.

If the rain NO₃⁻ is considered to arise from the scavenging of HNO₃, and aerosol NO₃⁻ and the rain SO₄²⁻ from the scavenging of SO₂ and aerosol SO₄²⁻, then the NO₃⁻ is overrepresented in the rain, in the sense that

$$\frac{[\text{NO}_3^-]_{\text{rain}}/[\text{HNO}_3 + \text{aerosol NO}_3^-]_{\text{air}}}{[\text{SO}_4^{2-}]_{\text{rain}}/[\text{SO}_2 + \text{aerosol SO}_4^{2-}]_{\text{air}}} \sim 4$$

on the basis of the overall averages (Tables I and II). This suggests that the N species are more efficiently scavenged than the S species (SO₂ and aerosol SO₄²⁻) or else that HNO₃ and aerosol NO₃⁻ are not the only N species being scavenged. Indeed, even if SO₂ were assumed to be scav-

Table VI. Rain Scavenging Ratios: NO₃⁻

| | ambient nequiv/m ³ | | |
|--------------------|-------------------------------|---|---------------------|
| rain ^a | HNO ₃ ^b | total NO ₃ ^{- b,c} | W(N) ^{d-f} |
| Allegheny Mountain | | | |
| 1 | 47.0 | 55.9 | 10(5) ^e |
| 2 | 47.0 | 55.9 | 13(5) |
| 3 | 19.5 | 21.3 | 30(5) |
| 4 | 19.5 | 21.3 | 30(5) |
| 5 | 27.9 | 43.4 | 35(5) |
| 6 | 73.7 | 87.5 | 5(5) |
| 10 | 152.6 | 154.0 | 9(5) |
| 12 | 70.0 | 74.5 | 11(5) |
| 13 | 70.0 | 74.5 | 28(5) |
| 14 | 70.0 | 74.5 | 34(5) |
| 15 | 75.9 | 81.7 | 20(5) |
| Laurel Hill | | | |
| 1 | 36.7 ^g | 49.0 ^g | 28(5) |
| 2 | <i>h</i> | 78.5 | 8(5) |
| 3 | 77.8 | 83.8 | 9(5) |
| 4 | 103.4 | 116.6 | 17(5) |
| arithmetic av | | | 19(5) ± 11(5) |

^aFor the rain constituents, see Table II. ^b1 equiv = 1 mol. ^cTotal NO₃⁻ = HNO₃ + aerosol NO₃⁻. ^dW = (equiv/m³ of liquid water)/(equiv/m³ of air). Divide by 890 to convert to (equiv/g of water)/(equiv/g of air). ^e10(5) means 10 × 10⁵, etc. ^fW(N) = scavenging ratio for total nitrate (HNO₃ + aerosol NO₃⁻). ^gAverage of two atmospheric runs during which the rain fell. ^hNo data.

enged not at all, the data suggest that the N species are scavenged more efficiently than the SO₄²⁻. A large increase in the [HNO₃ + aerosol NO₃⁻]_{air}/[SO₂ + aerosol SO₄²⁻]_{air} ratio with increasing height, if it happens (from whatever cause), might also be an explanation.

HNO₃ represented on the average 90% of the total atmospheric inorganic nitrate (HNO₃ plus aerosol NO₃⁻) at both sites and is expected to be efficiently scavenged. W(N), which is straightforward to calculate, therefore should be slightly less than W(HNO₃). Scavenging of NO₂ is discounted on account of its low solubility [Henry's Law coefficient *H* = 0.007 M atm⁻¹ at 10 °C (47)] and the observation that nitrite, a major product of NO₂ dissolution at ambient conditions (47), is at very low concentration in the rain (NO₂ << NO₃⁻, Table I). Scavenging of PAN is discounted (see, however, ref 44) on grounds of its low solubility in acid solution [*H* = 5 M atm⁻¹ at 10 °C (48)] and its only modest ambient concentration (Table I). Scavenging of NO₃ and N₂O₅ were not considered although they could be significant at night.

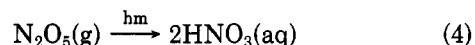
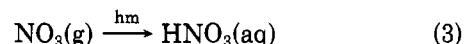
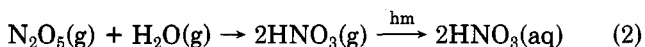
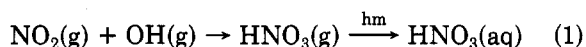
Table VI lists the W(N) values. If HNO₃ is the dominant contributor, then Table VI suggests that W(HNO₃) ≥ W(N) ~ 2 × 10⁶. [Division by 890 (the ratio between the density of liquid water and that of air at the altitude and average temperature at Allegheny) gives mass scavenging ratios, (equiv/g of liquid H₂O)/(equiv/g of air).] The large scatter in W(N) values is typical of all species examined in this study. Analytical uncertainties in some of the low trace element concentrations in the rain, and the time incongruities between rain and atmospheric sampling in the case of species whose atmospheric concentrations may fluctuate rapidly with time, undoubtedly cause some of the scatter so that for some species the *W* values have meaning only in an average sense. But generally speaking, the order of magnitude scatter in *W* values must be mostly real. A corollary of the scatter is that correlations between concentrations in the rain and in the atmosphere are generally insignificant, e.g., *r* = 0.33 between HNO₃(g) and rain NO₃⁻. This holds even for the

trace metals, where chemical transformation is not an issue (e.g., *r* = 0.1 for Pb).

A special problem in the W(HNO₃) and W(N) determinations for the nighttime rains is the dry-deposition depletion of HNO₃(g) in the boundary layer during the overnight (from about 2030 to 0700) collection of HNO₃(g). Overnight depletion of HNO₃(g) does not seem to have been pronounced, however, in that the average nighttime HNO₃(g) concentration was not much less than the daytime average. The effect on W(HNO₃) and W(N) could be an error in either direction depending on when during the overnight HNO₃(g) measurement the rain occurred.

The W(HNO₃) result can be compared with the Henry's Law coefficient for HNO₃ (2.1 × 10⁵ M atm⁻¹ at 25 °C, ref 49). The latter, in the dimensions in which W(HNO₃) is expressed above, becomes 5.6 × 10⁶. From this standpoint, then, it is not necessary to assume that atmospheric species other than HNO₃(g) were involved as precursors to the NO₃⁻ in the rain.

Further regarding the various atmospheric precursors to rain NO₃⁻, Chang (50) has calculated for frontal storms the ground-level rainwater NO₃⁻ from in-storm generation of HNO₃



where hm (hydrometeor) signifies a cloud droplet, raindrop, or snowflake. (Reactions leading to NO₃ and N₂O₅, involving O₃ and so forth, are included in the calculation but are not written here.) Direct scavenging of NO₂(g) is ignored because of its low solubility. Oxidation of NO₃(g) by aldehydes is calculated to be negligible. The products of the NO₃(g) aqueous reaction are not known, but reaction 3 is assumed. Besides the rainwater HNO₃ generated by the in-cloud processes (reactions 1–4), rainwater NO₃⁻ is produced by the scavenging of the HNO₃(g) and aerosol NO₃⁻ that existed prior to cloud formation. Below-cloud processes are included but are relatively unimportant. Daytime in-cloud OH is calculated according to light penetration vs. depth in the cloud layer; nighttime OH is neglected.

Given the ambient O₃ and NO₂ levels encountered in this study (Table I), Chang's treatment predicts 10–35 μequiv/L as the rainwater NO₃⁻ concentrations arising from in-storm HNO₃ generation (reactions 1–4) in summer frontal storms. The figure should be lower for convective storms. Comparison with the observed 41–252 μequiv/L (Table II) suggests that at most 25% of the rainwater NO₃⁻ stemmed from in-storm HNO₃ generation. Scavenging of preexisting HNO₃(g) was probably the major process. This probably includes some below-cloud washout (51). Most of the rainwater NO₃⁻ generally would not be accounted for by in-storm NO₂ processes (reaction 1).

Not all literature results support the conclusions last stated. Generally, the scavenging ratios are quite consistent; that is, one has W(N) ~ 10⁶ (52) or 2 × 10⁶ (27) under conditions where HNO₃ was probably (53), as here, more abundant than aerosol NO₃⁻; W(HNO₃) = 7.7 × 10⁵ and W(aerosol NO₃⁻) = 2.9 × 10⁵ in the warm half of the year (54). But in the same series of studies, most of the rainwater NO₃⁻ is said to have originated from in-cloud NO₂ oxidation (27) and/or below-cloud HNO₃ washout (55). In studies by Hegg et al., a search for NO₃⁻ generation

Table VII. Rain Scavenging Ratios: SO_4^{2-} , SO_2 , and $\text{SO}_4^{2-} + \text{SO}_2$

| | | | | | | | | | | | SO ₂ contribution to rain SO ₄ ²⁻ , % | |
|---------------------------------|---|-------------------------------|-------------------|--|------------------------------|--|------------------|-------------------------------------|------------------|---------------------|---|------------|
| rain | rain Pb, μequiv/ L ^{a,b} | ambient nequiv/m ³ | | | | W(SO ₄ ²⁻) ^{c-e} | | W(SO ₂) ^{c-e} | | W(S) ^{c-f} | via SO ₂ | |
| | | aerosol | | | SO ₂ ^b | via NH ₄ ⁺ | via Pb | via NH ₄ ⁺ | via Pb | | via NH ₄ ⁺ | via Pb |
| | | NH ₄ ⁺ | Pb ^b | SO ₄ ²⁻ ^b | | | | | | | | |
| Allegheny Mountain | | | | | | | | | | | | |
| 1 | 0.15 | 164 | 0.48 | 440 | 653 | 34(4) ^e | 32(4) | 17(4) | 18(4) | 24(4) | 43 | 46 |
| 2 | 0.09 | 164 | 0.48 | 440 | 653 | 21(4) | 19(4) | 19(4) | 21(4) | 20(4) | 57 | 62 |
| 3 | 0.05 | 132 | 0.21 | 213 | 681 | 44(4) | 24(4) | 27(4) | 33(4) | 31(4) | 66 | 81 |
| 4 | 0.07 | 132 | 0.21 | 213 | 681 | 11(4) | 35(4) | 17(4) | 9(4) | 15(4) | 82 | 46 |
| 5 | 0.17 | 110 | 0.29 | 176 | 704 | 53(4) | 58(4) | 19(4) | 18(4) | 26(4) | 59 | 55 |
| 6 | 0.05 | 285 | 0.49 | 811 | 1181 | 13(4) | 11(4) | 5(4) | 7(4) | 8(4) | 36 | 47 |
| 10 | <i>g</i> | 165 | 0.68 | 388 | 980 | | | | | 51(4) | | |
| 12 | 0.09 | 437 | 0.50 | 755 | 849 | 12(4) | 18(4) | 23(4) | 17(4) | 18(4) | 67 | 50 |
| 13 | <i>g</i> | 437 | 0.50 | 755 | 849 | 27(4) | | 53(4) | | 41(4) | 69 | |
| 14 | <i>g</i> | 437 | 0.50 | 755 | 849 | 23(4) | | 43(4) | | 33(4) | 68 | |
| 15 | <i>g</i> | 517 | 0.34 | 733 | 754 | 19(4) | | 53(4) | | 36(4) | 74 | |
| Laurel Hill | | | | | | | | | | | | |
| 1 | 0.22 | 105 ^h | 0.33 ^h | 190 ^h | 814 ^h | 118(4) | 69(4) | 24(4) | 37(4) | 39(4) | 45 | 65 |
| 2 | 0.13 | 315 | 0.62 | 830 | 660 | 19(4) | 22(4) | 14(4) | 11(4) | 17(4) | 36 | 29 |
| 3 | 0.08 | 99 | 0.36 | 158 | 864 | 65(4) | 22(4) | 20(4) | 28(4) | 27(4) | 63 | 87 |
| 4 | <i>g</i> | 189 | 0.64 | 377 | 1404 | | | | | 32(4) | | |
| arith- metic av ⁱ | | | | | | 35(4) ± 30(4) | 31(4) ± 19(4) | 26(4) ± 15(4) | 20(4) ± 10(4) | 28(4) ± 11(4) | 59 ± 15 | 57 ± 17 |

^aFor the other rain constituents, see Table II. ^bFor Pb, SO_4^{2-} , and SO_2 , 1 equiv = 0.5 mol. ^cDelayed SO_4^{2-} used in calculation when available and when $>$ prompt SO_4^{2-} . ^d $W = (\text{equiv}/\text{m}^3 \text{ of liquid water})/(\text{equiv}/\text{m}^3 \text{ of air})$. Divide by 890 to convert to $(\text{equiv}/\text{g of water})/(\text{equiv}/\text{g of air})$. ^e34(4) means 34×10^4 , etc. ^f $W(\text{S}) = \text{scavenging ratio for total sulfur } (\text{SO}_2 + \text{aerosol } \text{SO}_4^{2-})$. ^gNo data. ^hAverage of two atmospheric runs during which the rain fell. ⁱBoth sites combined.

in cumuliiform clouds proved inconclusive in one case (56), while, in another case (57), cloudwater data could be used to deduce that in-cloud generation of NO_3^- by unspecified reactions accounted for conservatively $44 \pm 10\%$ of the cloudwater NO_3^- .

In order to calculate $W(\text{SO}_4^{2-})$ or $W(\text{SO}_2)$, it is necessary to estimate how much of the SO_4^{2-} in the rain came from the scavenging of aerosol SO_4^{2-} and how much came from the scavenging of SO_2 . We employ two ways to do this: use of NH_4^+ as a surrogate for SO_4^{2-} and use of Pb as a surrogate for SO_4^{2-} .

The NH_4^+ surrogate approach requires that $W(\text{NH}_4^+)$ equals $W(\text{SO}_4^{2-})$ and that the ambient NH_3 contribution to the rain NH_4^+ is zero. The rain, at the pH values observed, should be an efficient $\text{NH}_3(\text{g})$ scavenger (58), causing $W(\text{SO}_4^{2-})$ to be overestimated and $W(\text{SO}_2)$ to be underestimated. [The reverse holds if any NH_4^+ in the rain samples disappeared during storage or if $\text{NH}_3(\text{g})$ collected on the acidic aerosol deposit.] But there was probably not enough $\text{NH}_3(\text{g})$ ($<18 \text{ nequiv}/\text{m}^3$ or $<0.1 \times \text{aerosol } \text{NH}_4^+$, Table I) even in the cloud-free air to account for most of the NH_4^+ in the rain. [Such low $\text{NH}_3(\text{g})$ levels may not be atypical of the eastern U.S. (59, 60).]

The presumption of equality of $W(\text{NH}_4^+)$ and $W(\text{SO}_4^{2-})$ is supported by the similarity of the aerosol NH_4^+ and SO_4^{2-} size distributions (Figure 3), especially since this similarity itself tends to bear out the expectation that the aerosol NH_4^+ is internally mixed with at least some of the SO_4^{2-} and hence that the two should be removed together. (NH_4^+ and SO_4^{2-} also have the similarity that solubility is not an issue.) The question is whether the aerosol $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio at ground level is representative of the (unknown) aerosol $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio aloft where the scavenging of aerosol SO_4^{2-} takes place. Ratios increasing, decreasing, or varying little with altitude have all been observed (61–63) or inferred (46, 64) in other settings; usually it decreases. An aerosol $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio decreasing with increasing altitude will cause $W(\text{SO}_4^{2-})$ to be

underestimated and $W(\text{SO}_2)$ to be overestimated. The high correlation ($r = 0.89$, $n = 13$) between the NH_4^+ and SO_4^{2-} concentrations in the rain suggests that the two ions come predominantly from the internally mixed aerosol.

The Pb surrogate approach presupposes that $W(\text{Pb})$ equals $W(\text{SO}_4^{2-})$. The support for the assumption is the similarity of size distributions (Figure 3). The percent fine ($<2.5 \mu\text{m}$) on the dichotomous samplers was 89 for aerosol S (nearly all is SO_4^{2-}) and 85 for Pb. The Pb in the rain, like the SO_4^{2-} , undoubtedly was fully soluble (65). However, as with NH_4^+ , there is the question of $\text{Pb}/\text{SO}_4^{2-}$ ratio at ground level and aloft. If the aerosol $\text{Pb}/\text{SO}_4^{2-}$ ratio decreases with increasing altitude, the Pb surrogate approach will underestimate $W(\text{SO}_4^{2-})$ and overestimate $W(\text{SO}_2)$.

$W(\text{SO}_4^{2-})$ and $W(\text{SO}_2)$ calculated by the NH_4^+ and Pb surrogate approaches are tabulated in Table VII, along with total S scavenging ratios $W(\text{S})$. Representative or approximate average values (1983, both sites) are $W(\text{SO}_4^{2-}) \sim 3 \times 10^5$, $W(\text{SO}_2) \sim 2 \times 10^5$, and $W(\text{S}) \sim 3 \times 10^5$, where the dimensions are $(\text{equiv}/\text{m}^3 \text{ of liquid water})/(\text{equiv}/\text{m}^3 \text{ of air})$. For the 1977 Allegheny experiment (16), average $W(\text{S})$ was $(19 \pm 6) \times 10^4$, $n = 8$. The very large scatter in scavenging ratios in Table VII undoubtedly reflects not only the poor overlap between rain and atmospheric sampling times but also the fact that the scavengeability of SO_2 is subject to a variety of factors.

The process of estimating $W(\text{SO}_4^{2-})$ and $W(\text{SO}_2)$ by the surrogate approaches also yielded estimates, shown in Table VII, of the relative contributions of SO_2 and aerosol SO_4^{2-} (atmospheric $\text{SO}_2/\text{aerosol } \text{SO}_4^{2-}$ mole ratio ~ 2 , Table I) to the rain SO_4^{2-} . On the average, just over half of the rain SO_4^{2-} resulted from the scavenging of SO_2 .

We were unable to discern any differences in $W(\text{SO}_4^{2-})$, $W(\text{SO}_2)$, or $W(\text{N})$ according to site, storm type (WF, CF, WS, and SC), rain pH, or day vs. night.

Misra et al. (52) have reported $W(\text{S}) \approx 3 \times 10^5$ and $W(\text{N}) \approx 10^6$, with a range of better than an order of

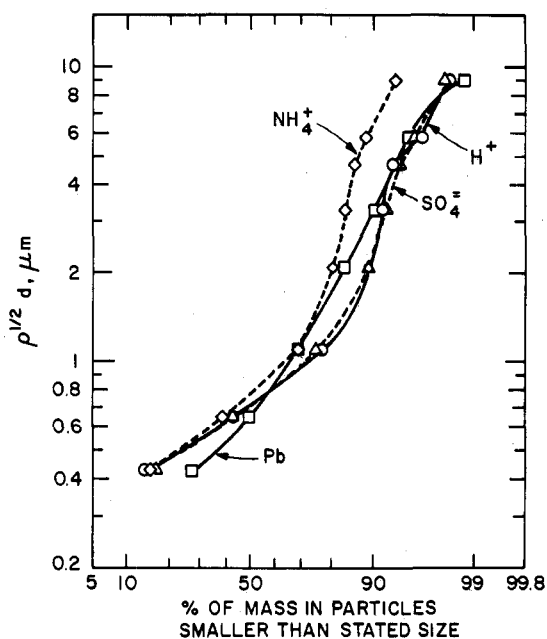


Figure 3. Size distributions of aerosol H^+ , NH_4^+ , and SO_4^{2-} at Allegheny in 1983, August 12–17, 19–22, 23–27, and 28 (480 m^3 of air sampled).

magnitude in both, under conditions where the ambient SO_2 /aerosol SO_4^{2-} and HNO_3 /aerosol NO_3^- ratios were similar to ours. The treatment did not differentiate among precipitation types (rain, snow, etc.). Subsequently, Chan and Chung (54) were able to obtain $W(\text{SO}_4^{2-})$, $W(\text{SO}_2)$, etc.; for rain during May through October, $W(\text{SO}_4^{2-}) = 3.4 \times 10^5$, $W(\text{SO}_2) = 1.8 \times 10^5$, $W(\text{HNO}_3) = 7.7 \times 10^5$, and $W(\text{aerosol NO}_3^-) = 2.9 \times 10^5$. Scavenging of SO_2 was said to be responsible for 28% of the SO_4^{2-} in precipitation on an annual basis at the site nearest to ours ($\sim 400 \text{ km}$ away); since scavenging of SO_2 by snow was reported to be effectively zero, we infer that in rain a good deal more than 28% of their SO_4^{2-} came from the scavenging of SO_2 . Half of the rain SO_4^{2-} in Barrie's study (27) is said to have come from the scavenging of SO_2 . His very wide variations in atmospheric SO_2 /aerosol SO_4^{2-} ratio (5) are not accompanied by a systematic variation in $W(\text{S})$ as would have been expected if $W(\text{SO}_4^{2-}) \gg W(\text{SO}_2)$.

These results are consistent with ours, with $W(\text{SO}_4^{2-})$ perhaps twice as big as $W(\text{SO}_2)$ and with $\text{SO}_2(\text{g})$ and aerosol SO_4^{2-} contributing comparably to the SO_4^{2-} in the rain. We are surprised that $W(\text{SO}_4^{2-})$ is so much smaller than $W(\text{HNO}_3)$, given that nucleation scavenging of SO_4^{2-} should be a highly efficient process. In the case of $W(\text{SO}_4^{2-})$ vs. $W(\text{SO}_2)$, reported scavenging efficiencies (66, 67) would lead one to expect $W(\text{SO}_4^{2-})$ values 3–10 times higher than $W(\text{SO}_2)$ [although there are data to support more nearly comparable values (67)]. Nucleation scavenging of SO_4^{2-} should have been especially favored over SO_2 scavenging in the highly acidic rains at Allegheny and Laurel.

If at our two sites the NH_4^+ and Pb surrogate approaches were to underestimate $W(\text{SO}_4^{2-})$ and overestimate $W(\text{SO}_2)$ for any of the reasons enumerated earlier, thus causing the apparent lack of separation between $W(\text{SO}_4^{2-})$ and $W(\text{SO}_2)$, then agreement as observed between the two approaches would be extraordinary, given that the sources of error differ qualitatively or quantitatively between the two approaches. We conclude that the lack of separation between $W(\text{SO}_4^{2-})$ and $W(\text{SO}_2)$ may be real. There are several possibilities for enhanced $W(\text{SO}_2)$: recent data (68) indicate that below-cloud washout of SO_2 can be an efficient process; cloudwater with dissolved H_2O_2 is able to

scavenge $\text{SO}_2(\text{g})$ on a time scale short compared to cloud lifetimes, especially in summer (69, 70), though the amount of dissolved H_2O_2 needed to account for much of the rain SO_4^{2-} in Table II would have to be large ($\sim 10^{-4} \text{ M}$). Below-cloud HNO_3 washout may have contributed to the wide separation between $W(\text{HNO}_3)$ and $W(\text{SO}_4^{2-})$ (51); in-cloud production of HNO_3 , for example, by reactions 1 and 4 above, might also have been a factor.

Many literature reports (27, 44, 54, 57, 63, 71–75) indicate that the $\text{SO}_2(\text{g})$ contribution to cloudwater and rainwater SO_4^{2-} is relatively important. Indeed, the NH_4^+ surrogate approach has been applied in one study (63) and can be applied to another (44) to deduce that in-cloud scavenging of SO_2 can account for most (5/8, 2/3, or more) of the SO_4^{2-} in rain; it is also argued (63) that below-cloud washout of SO_2 may additionally be significant. Most modeling estimates (71–74) indicate that, under conditions typical of summer storms in the northeastern U.S., in-cloud scavenging of SO_2 should account for 35–70% of the rain SO_4^{2-} . If these reports are true, then the relative magnitudes of $W(\text{SO}_4^{2-})$ and $W(\text{SO}_2)$ stated for Allegheny/Laurel must be at least roughly correct. Ambient $\text{SO}_2(\text{g})$ concentrations in the relevant areas are generally only a few times greater than the aerosol SO_4^{2-} concentrations (76); accordingly, if SO_2 and SO_4^{2-} are to be comparable contributors to rain SO_4^{2-} , and especially if SO_2 scavenging is to be the major source of SO_4^{2-} in rain (75), then $W(\text{SO}_4^{2-})$ cannot be more than a few times greater than $W(\text{SO}_2)$. A number of reports (45, 46, 66, 77, 78) discount the $\text{SO}_2(\text{g})$ contribution, though not always under the convective storm conditions that predominated in this experiment.

Trace Element Scavenging Ratios. We can estimate trace element scavenging ratios averaged over the whole study period by using experiment-average values for concentrations in the atmosphere and in the rain. Time-average atmospheric concentrations and volume-average concentrations in the rain are used. The quotient between the two averages is what we are calling the average scavenging ratio. For the atmospheric concentrations we used the time averages over the whole experiment; the result is similar if we average over only those atmospheric sampling runs during which rain occurred or if we calculate for a given element the scavenging ratio in each rain event and take the mean. Certain elements have to be excluded from this treatment because of wall losses during storage of the rain samples or because, as in the case of Cl, of the likelihood that some is present in the gas phase, e.g., $\text{HCl}(\text{g})$.

By analysis of dichotomous sampler filters (1) not only were the atmospheric concentrations determined, but also it was ascertained what mass fraction of each aerosol species existed in particles smaller than $2.5 \mu\text{m}$ diameter; for calculations of NH_4^+ , the distribution of its mass on either side of $2.5 \mu\text{m}$ was determined from the cascade impactor size distributions. Thus, scavenging ratios could be examined as a function of particle size in a rough sense, that is, mass fraction in fine (smaller than $2.5 \mu\text{m}$) particles.

Figure 4 shows the results, with uncertainties as illustrated by the error bars on Na. The scavenging ratios for the nine species are in the range 2×10^5 to 3×10^6 .

These scavenging ratios are of the same order of magnitude as trace element scavenging ratios measured by other authors (79, 80). All studies are similar in showing considerable scatter and a substantial increase with increasing particle size.

Apportionment of Rain H^+ to Atmospheric Precursors. We can apportion the rain H^+ as to atmospheric

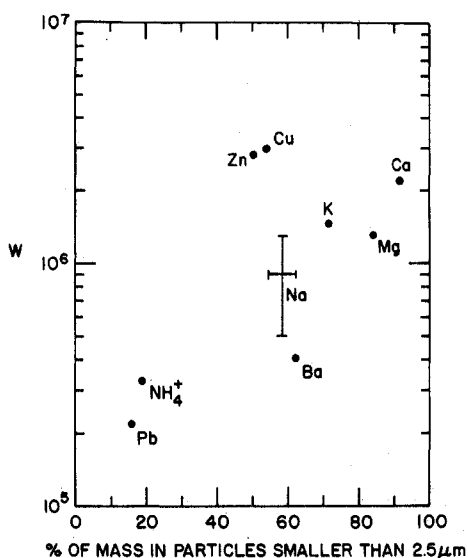


Figure 4. Average scavenging ratios for NH_4^+ and eight trace metals as a function of particle size (fraction of mass in particles $2.5 \mu\text{m}$ or larger), Allegheny Mountain and Laurel Hill, August 1983. For explanation, see text. Uncertainties are illustrated by the error bars on Na. The NH_4^+ scavenging ratio is the upper limit (assumes zero contribution of atmospheric NH_3 to rain NH_4^+).

species of origin $\text{HNO}_3(\text{g})$, $\text{SO}_2(\text{g})$, and aerosol acid SO_4^{2-} . We assume as before that ambient $\text{NH}_3(\text{g})$ contributes nothing to the rain NH_4^+ , i.e., that all of the rain NH_4^+ is from aerosol NH_4^+ . The aerosol NH_4^+ is considered to be wholly associated with the aerosol SO_4^{2-} since there is virtually no aerosol NO_3^- (Table I). The rain NO_3^- is attributed to HNO_3 [from the scavenging of $\text{HNO}_3(\text{g})$, $\text{NO}_3(\text{g})$, $\text{N}_2\text{O}_5(\text{g})$, etc.], so an amount of H^+ stoichiometric with the rain NO_3^- is assigned to the scavenging of HNO_3 . From the SO_2 and SO_4^{2-} scavenging results (Table VII), an amount of H^+ stoichiometric with 58% of the rain SO_4^{2-} is ascribed to the scavenging of SO_2 (two H^+ per SO_2 -derived SO_4^{2-}). The other 42% of the rain SO_4^{2-} is multiplied by the aerosol $\text{H}^+/\text{SO}_4^{2-}$ ratio to yield the amount of H^+ attributable to the scavenging of aerosol SO_4^{2-} . The apportionment of responsibility for the rain H^+ becomes 25% $\text{HNO}_3(\text{g})$, 55% $\text{SO}_2(\text{g})$ scavenging, and 20% aerosol SO_4^{2-} scavenging as a rough average.

Another approach (45) is to consider the acid enrichment of the rain over the available aerosol. Here we compare H^+ to the sum of the major anions (SO_4^{2-} and NO_3^-) in the rain and do the same in the aerosol. For the rains reported in Table II, we have $\text{H}^+/\sum(\text{anions}) = 0.78 \pm 0.16$ (range 0.43–0.98), while for the atmospheric aerosol measured during corresponding periods we have $\text{H}^+/\sum(\text{anions}) = 0.33 \pm 0.10$ at Allegheny and 0.49 ± 0.11 at Laurel. Clearly for both sites there is a substantial enrichment of rain acidity over aerosol acidity. We take this to mean that the scavenging of acidic gases must be contributing to the rain acidity. It is a straightforward exercise to calculate the relative contribution of acidic gases needed to raise the $\text{H}^+/\sum(\text{anion})$ ratio in the aerosol to that in the rain; we find in this way that the scavenging of acidic gases can account for ~85% of the rain acidity at Allegheny and ~75% of the rain acidity at Laurel. [To whatever extent that $\text{NH}_3(\text{g})$ may contribute to the rain NH_4^+ , these are underestimates.] This agrees with the estimate above that HNO_3 and SO_2 together lead to 80% of the rain acidity on the average. The same procedure applied to the data from the autumn 1979 Ohio River area experiment (44) yields a figure of about 92%.

It should be recognized that these apportionments are subject to some of the same objections that pertained to

Table VIII. Sources of NO_3^- and SO_4^{2-} Deposition at Allegheny Mountain, August 5–28, 1983^a

| | NO_3^- , $\mu\text{equiv}/\text{m}^2$ | SO_4^{2-} , $\mu\text{equiv}/\text{m}^2$ |
|-------------------|---|--|
| rain (12 events) | 3440 | 13400 |
| fog (1 event) | 140 | 230 |
| dew (15 events) | 88 | 220 |
| dry (without dew) | 2400 ^b | 5000 ^c |

^aFor NO_3^- , 1 $\mu\text{equiv} = 1 \mu\text{mol}$; for SO_4^{2-} , 2 $\mu\text{equiv} = 1 \mu\text{mol}$.
^bOn the basis of deposition to nylon surrogate surfaces; does not include substances not depositing to nylon (e.g., NO_2).
^cOn the basis of the measurement of dry deposition to nylon surrogate surfaces, we estimate that SO_2 contributed about 5000 $\mu\text{equiv}/\text{m}^2$ of dry deposition to the SO_4^{2-} total. Aerosol SO_4^{2-} adds another 300 $\mu\text{equiv}/\text{m}^2$ or less.

the calculation of $W(\text{SO}_4^{2-})$ and $W(\text{SO}_2)$. But the non-aerosol contribution to the rain H^+ must have been at least 25% (as HNO_3); and if SO_2 and aerosol SO_4^{2-} were comparable to each other as contributors to rain SO_4^{2-} as appears to have been the case, then it still must be true that most of the rain acidity (H^+) arose *not* from the aerosol but instead from gases dissolved in cloudwater and rainwater.

Estimation of Wet and Dry Acid Deposition Budgets at Allegheny Mountain. To gauge the relative importance of wet and dry deposition, the wet deposition measurements need to be accompanied by dry deposition estimates. Nighttime dry deposition to dew was measured in the present experiment (1), but we lack good estimates of dry deposition at night when dew was absent and, more important, we lack a good estimate of dry deposition during the day when deposition velocities are expected to be largest. To deal with this deficiency, two alternative approaches are adopted as follows.

First, nylon and Teflon 142 mm diameter membrane filters were set out as surrogate collection surfaces above the canopy at Allegheny during daylight on 5 days during the 1983 experiment to gauge the relative importance of aerosol NO_3^- and SO_4^{2-} deposition (on Teflon) and the deposition of HNO_3 and SO_2 (nylon–Teflon difference) (2). The applicability of surrogate surfaces to real ones, however, is questionable on several grounds. For HNO_3 the sticking efficiency to nylon is probably (81) 100%; for SO_2 the sticking efficiency is less than 100% but greater than zero (82); and sticking efficiencies are by no means the only issue. The second approach was to use the measured ambient concentrations in combination with deposition velocities reported in the literature (82–85).

The two approaches give effectively the same results. For example, the average HNO_3 deposition velocity $v_d(\text{HNO}_3)$ measured by micrometeorological methods above a forest in east Tennessee or on summer days over an Illinois pasture (83, 84) is about the same as the $2.5 \pm 1.5 \text{ cm/s}$ measured by the surrogate collectors (together with atmospheric concentrations) in this experiment. The SO_2 deposition velocity $v_d(\text{SO}_2)$ to the surrogate collectors is about 0.5 cm/s, which is in the range reported to vegetation (85) (average ~0.7 cm/s). The deposition velocity of aerosol SO_4^{2-} to the surrogate collectors is about 0.05 cm/s, which is in the range given in the literature (85).

The results employing daytime dry deposition velocities from the surrogate collectors are given in Table VIII; these deposition velocities are used, together with measured atmospheric concentrations, to estimate dry deposition during all day and night periods without rain, fog, or dew. While rain accounted for some 60% of the NO_3^- deposition, dry deposition of HNO_3 in the absence of dew appears also

to be important. This is similar to the estimate made by Huebert (83, 84) in the Illinois experiment that HNO_3 dry deposition accounted for 48% of the NO_3^- wet/dry deposition. For SO_4^{2-} deposition, rain is again the dominant medium; however, the dry deposition of SO_2 must also be considered. The contributions of dry-deposited aerosol nitrate and sulfate, not listed in Table VIII, were small (about 5% of the dry total) at the site.

If we suppose that dry-deposited SO_2 is tantamount to H_2SO_4 in acidifying potential on grounds that SO_2 readily oxidizes to H_2SO_4 , then the total strong acid deposited in the experiment can be apportioned roughly as follows:

47% (37–56%) = H^+ associated with SO_4^{2-} in rain
(SO_2 scavenging, 34%; aerosol SO_4^{2-} scavenging, 13%)
23% (17–30%) = SO_2 dry deposition without dew
16% (12–19%) = HNO_3 in rain
11% (6–19%) = HNO_3 dry deposition without dew
~2% = HNO_3 and H_2SO_4 in fog and dew
~0.5% = aerosol dry deposition without dew

At the rates implied by Tables V and VIII, total wet and dry H^+ deposition would be about 300 mol of H^+ ha^{-1} month $^{-1}$, in August.

We assessed the uncertainties in the foregoing estimates by adopting two extreme sets of assumptions: (a) the maximum daytime and nighttime $v_d(\text{SO}_2)$ over land in eastern North America in April 1981 as given in ref 86, averaged together, and similarly for HNO_3 ; (b) the minimum daytime $v_d(\text{SO}_2)$ over land from ref 86, averaged with the nighttime $v_d(\text{SO}_2)$ to dew at Allegheny (0.04 cm/s, ref 1), and similarly for HNO_3 . It is by this procedure that the ranges shown above in parentheses were generated.

Summary

An investigation of rain chemistry was carried out during August 1983 on Allegheny Mountain and Laurel Hill in southwestern Pennsylvania. Results from 17 rains were analyzed in terms of atmospheric chemistry and air-mass movements.

The average rain composition approximated that of an $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture with a volume-weighted average pH of 3.5 and an $\text{SO}_4^{2-}/\text{NO}_3^-$ mole ratio of 1.8. (Dew was qualitatively similar but more dilute.) Weak acids accounted for only about 10% of the total rain acidity. There was evidence of little S(IV) in the rains [in contrast with dew where up to 40% of the S was present as S(IV) at the end of the night]. Over the course of the Allegheny Mountain experiment, some 60 times more acidity (and related species) was deposited in rain than to dew or in settled fogwater.

Scavenging ratios were inferred for SO_2 , aerosol SO_4^{2-} , and HNO_3 . From these results it was concluded that on the average about half of the rain SO_4^{2-} resulted from the scavenging of SO_2 and the rest from the scavenging of aerosol SO_4^{2-} . In terms of rain H^+ , on the average about 25% was attributed to HNO_3 , 55% to the scavenging of SO_2 , and only about 20% to the scavenging of aerosol SO_4^{2-} . These estimates are subject to some open assumptions as spelled out under Results and Discussion. Together they suggest that most (~80%) of the rain acidity arose not from the aerosol but instead from gases dissolved in cloudwater and rainwater.

Cumulative deposition totals in rain were compared against deposition in fog and against dry deposition (to surrogate surfaces and to dew-covered surfaces) in the same experiment, and a crude acid-deposition budget was

calculated (with considerable uncertainty associated with dry deposition without dew):

47% = H^+ associated with SO_4^{2-} in rain
(SO_2 scavenging, 34%; aerosol SO_4^{2-} scavenging, 13%)
23% = SO_2 dry deposition without dew
16% = HNO_3 in rain
11% = HNO_3 dry deposition without dew
2% = HNO_3 and H_2SO_4 in fog and dew
0.5% = aerosol dry deposition without dew

By comparison of these results with concurrent data from precipitation sampling sites in the rest of Pennsylvania and by capitalizing on the fact that westerly trajectories were the rule for rain events at all sites, we infer that the average rain SO_4^{2-} concentration diminishes downwind of SO_2 sources with a half-distance of the order of 440 km.

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Registry No. H^+ , 12408-02-5; NH_4^+ , 14798-03-9; Na^+ , 7440-23-5; K^+ , 7440-09-7; Mg^{2+} , 7439-95-4; Ca^{2+} , 7440-70-2; SO_2 , 7446-09-5.

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Indoor Air Pollution due to Emissions from Wood-Burning Stoves

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■ Four wood-burning stoves, three airtight and one non-airtight, were operated in a single-floor 236-m³ residence and tested for indoor pollutant emissions. Results showed the airtight stoves emitted minor amounts of carbon monoxide and respirable suspended particles during door-opening operations, while the nonairtight stove continuously injected pollutants indoors under certain operating conditions. During airtight stove operation, carbon monoxide levels reached a maximum of 4 ppm, while average total suspended particulate levels ranged from 24 to 71 µg/m³. During "normal" nonairtight stove operation, carbon monoxide levels reached a maximum of 8 ppm, while total suspended particulate levels ranged from 30 to 650 µg/m³. Outdoor carbon monoxide levels were 1.1 ppm or less, and outdoor particulate levels ranged from 7 to 31 µg/m³. Five polycyclic aromatic hydrocarbons, including benzo[a]pyrene, were measured in the collected particulate samples, and the results are reported. Source strengths for carbon monoxide, total suspended particles, and five polycyclic aromatic hydrocarbons are reported.

Introduction

Two areas of concern to both the scientific community and the general public are energy conservation and indoor air pollution. Strategies designed to reduce energy costs are not always compatible with acceptable indoor air quality. For example, the increased use of alternative fuels aimed at reducing residential heating cost—such as the shift to wood-burning stoves—can have a detrimental effect on indoor air quality if the alternative-fuel appliance emits pollutants indoors.

Wood-burning stoves have been found under some conditions to contribute to indoor concentrations of carbon monoxide, nitric oxide, nitrogen dioxide, and suspended particles containing polynuclear aromatic hydrocarbons (PAH) including benzo[a]pyrene (1-6). Indoor pollutants emitted from wood-burning stoves can enter into the indoor environment during fire-starting and -tending operations, or they can be emitted continuously if a leak or crack exists in the stove or its vent system. In this study we investigated the impact on indoor air quality from the

use of four different wood-burning stoves in an occupied house under simulated use conditions. Measurements of carbon monoxide (CO), nitric oxide (NO), nitrogen dioxide (NO₂), formaldehyde (HCHO), total suspended particles (TSP), submicron suspended particles (<0.6 µm), and five PAH compounds are discussed in this paper. The PAH compounds investigated were benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[ghi]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP).

Experimental Methods

Test House. The house used in this study was in a residential, wooded area of Truckee, CA (elevation 1800 m) where wood stoves are common home-heating appliances. The house was a single-floor, ranch-type structure with a volume of 236 m³. The house was occupied by the project staff during the tests. Figure 1 shows the floor plan and the location of the stove and air sampling sites. All windows, closet doors, and outside doors were closed during the tests, while all bedroom doors were left open.

Wood-Burning Stoves. Four models of wood-burning stoves were tested to determine their contribution to indoor air pollution. Basic information on each stove is listed in Table I. Three models were considered airtight, while one was not. The flue vent system was 20 cm (8 in.) in diameter and was equipped with a damper. Stoves A, C, and D were designed for 20-cm flues. Stove B was designed for a 15-cm flue, and an adaptive collar was used. Stove A was operated both with its doors opened, as a fireplace, and with its doors closed; stoves B-D were operated with their doors closed. All stoves had upstream dampers in the door, while stove D had both an upstream damper in the door and a downstream damper near the flue connection. The flue itself was of single-walled steel construction within the house interior and multiwalled steel construction through and above the roof.

Instrumentation and Analytical Methods. Gaseous pollutant concentrations, except for HCHO, were measured with the Lawrence Berkeley Laboratory Mobile Atmospheric Research Laboratory (MARL) (7, 8). These pol-