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RAINFALL ELEMENT CONTENT AND ACIDITY
FROM 4/30/76 TO 2/17/78, ATHENS, GEORGIA¹

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B. L. Haines, J. V. Nabholz, S. DuBois²

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Abstract

Precipitation from 99 storm events between 4/30/76 and 2/17/78 had pH values ranging from 3.2 to 4.8 with median pH of 4.1. A subset of samples spanning one year from October 1976 through September 1977 had a volume weighted average pH of 4.19 as determined at time of collection and a volume weighted average of 4.44 after being stored frozen, thawed, and purged with N_2 gas. The correlations between H^+ and anions were for SO_4 , $r = 0.57$, $p < 0.0001$, NO_3^- , $r = 0.35$, $p < 0.004$, and Cl , $r = 0.23$, $p < 0.01$. Thus SO_4 appeared to be the greatest determinant of rainfall acidity. Rainfall with a pH lower than 5.6 resulting from equilibration of pure water with atmospheric CO_2 at $25^\circ C$ can be termed acid rain. According to this definition, the volume weighted average rainfall in north Georgia is acid rain, confirming inferences made by Likens (1976), using data from bordering states, that acid rain occurs in Georgia. Comparison of volume weighted pH values from Athens with values from Coweeta, North Carolina and Gatlinburg, Tennessee, suggest that acid rain is a regional problem in the Southeast.

Introduction

Acidification of rainfall has been documented in Europe (Barret & Brodin, 1955; Brosset, 1973; Oden, 1976) and in the north-eastern United States (Cogbill and Likens, 1974; Likens and Bormann, 1974; Likens, 1976). In a study of experimental watersheds on granite outcrops in central Georgia, (Nabholz, 1978) the pH of input rainfall was frequently below the pH 5.6 value expected from the equilibrium between atmospheric CO_2 with water at $25^\circ C$ (Stumm and Morgan, 1970). Because acid rain had yet to be

1 reported for the Piedmont of Georgia, a systematic study of precipitation
2 chemistry was initiated at the Institute of Ecology on the University of
3 Georgia campus in Athens.

4 Hydrogen ions in acid rain can displace biologically essential ele-
5 ments out of plant leaves (Kratky et al., 1974; Fairfax and Leep, 1975;
6 Wood & Bormann, 1975) and out of soils (Wiklander, 1973-74). They can
7 also decrease rates of elemental uptake by plant roots (Arnon et al.,
8 1942; Jacobson et al., 1960; Rains et al., 1964). Thus acid rain has the
9 potential to disrupt the cycling of biologically essential elements upon
10 which production in farms, forests and fisheries is partly dependent.
11 Because acid rain is thought to be partially the result of atmospheric
12 pollution (Likens, 1976; MacCracken, 1978), assessments of its
13 quantitative input into ecosystems, and its impact are important in
14 guiding development of pollution control strategies.

15 Methods

16 Precipitation was sampled for chemical analysis on an event basis,
17 i.e., every frontal system or thunderstorm, for two years, from April 1976
18 through February 1978. Samples were collected by a water trap-type
19 gauge (Likens et al., 1967) which was about 110 cm above the ground.
20 The collector was placed in the courtyard of the Institute of Ecology,
21 University of Georgia, Athens before or soon after rainfall began.
22 Entire events were sampled, but occasionally an event was sequentially
23 sampled. Samples obviously contaminated were discarded. The collector
24 was rinsed with distilled water after sample collection, and acid washed
25 or replaced as needed. Polyethylene and polypropylene bottles (≥ 60 ml)
26 were used to contain samples. All plastic ware was rinsed five times
27 with 2N HCl and five times with distilled water. Bottles were rinsed

1 with sample, if sample quantity permitted. Two samples were collected:
2 one for chemical analysis and one for pH determination (these bottles
3 were filled to the brim).

4 Samples for chemical determination were frozen at -15°C until analyzed
5 in April 1978. Samples for pH determination were immediately warmed to
6 25°C in a water bath and analyzed. Hydrogen ion activity (pH) was
7 measured with a Beckman Expandomatic S-22^(R) pH meter coupled to a
8 Corning glass combination electrode (#476050). The electrode was insert-
9 ed into the sample bottle and sample was gently swirled by a magnetic
10 stirrer with a teflon-coated impeller. These values are designated as
11 pH-n.

12 Frozen samples were thawed and brought to room
13 temperature. Aliquots were placed in an anaerobic titration vessel of a
14 Radiometer TTA3 titration assembly. The pH was determined with a glass
15 electrode. Then the sample was purged with CO_2 free N_2 gas until a new,
16 steady state pH reading was obtained. These values are designated pH-d.
17 Total H^+ was determined by titrating the sample to pH 9.0 utilizing
18 0.00419N NaOH which had been standardized against 0.0002 N potassium
19 biphthalate. Concentration of $\text{NO}_3^- - \text{N} + \text{NO}_2^- - \text{N}$ was determined colori-
20 metrically following reduction with hydrazine sulfate and CuSO_4 according
21 to Strickland and Parsons (1960). Concentration of $\text{PO}_4^- - \text{P}$ was determined
22 according to Strickland and Parsons (1972), while concentration of
23 $\text{NH}_4^- - \text{N}$ was determined colorimetrically according to Koroleff (1976).
24 Sulfate was quantified turbidometrically according to Tabataba (1974).
25 Chloride was determined using Technicon method #99-70W (1973) with an
26 autoanalyzer.

27 Sodium, potassium, magnesium and calcium were determined with a

1 Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer following stan-
2 dard procedures. Lanthanum was added to samples prior to magnesium and
3 calcium determinations.

4 Resulting data were converted to equivalents/liter. The sum of
5 equivalents of cations, the sum of equivalents of anions, and the anion
6 deficit (sum of cations - sum of anions), were calculated for each sample.
7 Data were subjected to statistical analysis by use of the Statistical
8 Analysis System (SAS) (Barr et al., 1976).

9 The amount of rain in each storm was obtained from records of the
10 US Weather Bureau, Athens Airport, 6 km NE of the Institute of
11 Ecology.

12 Results

13 Three overlapping sets of pH values were obtained. First,
14 early in the study, in January 1976, before the acidic nature of
15 the precipitation was fully appreciated, pH values were determined but
16 no sample was saved for chemical analysis. Second, toward the end of the
17 study, after 7 November 1977, no initial pH was determined but a sample
18 was saved for chemical analysis. The frequencies of observed pH values
19 for the first and second sets are shown in Table 1. The initial pH
20 values (pH_i) ranged from 3.2 to 4.8 with a median value of 4.1 comprising
21 14% of the samples. The volume weighted mean is 4.19 for the annual
22 period from October 1976 to September 1977. Samples frozen and then
23 thawed for analysis had higher pH values (pH_d) which ranged from 3.2 to
24 6.6 with a median value of 4.3 comprising 15% of the cases.

25 The third data set is comprised of samples for which both
26 initial pH (pH_i) and the pH after thawing and N_2 purging (pH_d) deter-
27 mined (Table 2). Storage of samples by freezing increased median pH

1 value from 4.1 (pH_n) to 4.3 (pH_d). This suggests that H⁺ and some
2 unmeasured anion was disappearing from solution.

3 Monthly mean concentrations and annual volume weighted mean con-
4 centrations are shown in Table 3a-b. Mean concentrations of H_n⁺, H_d⁺
5 (calculated from pH_n and pH_d respectively), % free H, Na, K, SO₄, Cl,
6 and anion deficit (ADEF) differed significantly among months while
7 total H⁺, Mg, Ca, NH₄, and NO₃ did not differ significantly. Values
8 of H_n⁺ were greatest in April and May 1976. Highest values for total H⁺
9 occurred in April 1976, and June through October 1977. The range in %
10 free H⁺ (H_d⁺) ranged from 32 to 64% with most values falling between 50
11 and 60%. The greatest concentration of SO₄ occurred in June 1977, and
12 highest NO₃ in December 1976 and July 1977. The highest Cl was in
13 October 1977. For each month, H_d⁺, calculated from the pH at analysis
14 is lower than H_n⁺, calculated from the pH determined at collection.
15 Volume weighted monthly mean contributions of H_n⁺, H_d⁺, total H⁺, SO₄, NO₃,
16 Cl and ADEF were regressed against month. No significant temporal trends
17 were detected in this 22 month data record.

18 In an effort to determine with which anion the H_d⁺ was associated,
19 correlation coefficients were calculated for all variables in all rain
20 samples, and later sorted into pH classes. Correlations between H_d⁺ and
21 selected parameters are shown in Table 4. For all samples, SO₄ was the
22 anion most highly correlated (r = 0.57) with H_d⁺. Correlations with NO₃,
23 Cl, and anion deficit (ADEF) were 0.35, 0.23, and 0.54 respectively.

24 For samples with pH_d values less than 4.0, the correlation between
25 H_d⁺ and SO₄ was 0.65, while for samples with pH_d between 4.0 and 4.5 the
26 correlation with SO₄ was 0.44, and with ADEF, 0.31. H_d⁺, in samples
27 having pH_d values between 4.5 and 5.0, was significantly correlated only

1 with total H. No significant correlations were found between H_d^+ and
2 anions in samples having pHd values greater than 5.0. These correlation
3 suggest that most of the acidity is related to SO_4 . Marine contributions
4 to total SO_4 might mask possible correlations between H^+ and non-marine
5 SO_4 . Correlations recomputed after subtracting out estimated sea sulfate
6 were similar to original correlations. Sea sulfate was estimated from
7 the ratio of sea SO_4 : sea Na times Na in the rain samples.

8 The negative correlation of H_d^+ and rain fall amount ($r = 0.28$, p
9 < 0.003) suggests a wash-out of effect whereby each sequential increment
10 of rain within a storm event washed out less acid. There was no
11 correlation between H_d^+ and the number of days since the previous storm
12 (dry days). This was surprising because in Athens one can observe the
13 air becoming dirty during rain free periods.

14 Elemental concentrations from this study are compared to values from
15 other eastern states in Table 5. Concentrations of Na, K, Mg, Cl and
16 PO_4 at Athens (this study) are relatively similar to the values obtained
17 at Coweeta and at Walker Branch, Tennessee. Among these three sites,
18 NH_4-N is highest in Athens. The SO_4 at Athens is lower than values from
19 Gatlinburg and Walker Branch, however, SO_4 concentration at Athens is
20 lower than those obtained in the 1970's in the northeastern US but
21 greater than values obtained in north Georgia and in eastern North
22 Carolina and southeastern Virginia in the 1950's and 1960's. Con-
23 centrations of NO_3-N at Athens are similar to those from Walker Branch,
24 Tennessee and Gatlinburg, Tennessee, but lower than values from Hubbard
25 Brook, New Hampshire and Ithaca, New York. Athens Cl is similar to values
26 from Coweeta, higher than Gatlinburg, Tennessee and Hubbard Brook, but
27 lower than Ithaca, New York. The volume weighted pH at Athens of 4.19

1 is identical to that for Gatlinburg, Tennessee, higher than values of
2 4.05 from Hubbard Brook and Ithaca, and lower than the value of 4.6 at
3 Coweeta. The similarity of pH values from Athens, Coweeta, and
4 Gatlinburg suggest that acid rain is a regional problem in the south-
5 eastern US. When values from Table 5 are converted to $\mu\text{eq L}^{-1}$ (not
6 shown), the ratios of $\text{SO}_4:\text{NO}_3:\text{Cl}$ are: Athens 47:22:10, Gatlinburg
7 66:21:4, Hubbard Brook 99:31:4 and Ithaca 104:47:13. In each case the
8 dominant anion is SO_4 with NO_3 and Cl in second and third place respec-
9 tively.

10 Although SO_4 remains the dominant anion at Hubbard Brook,
11 increasing acidity during the last decade was closely related to
12 increasing NO_3 input (Likens et al., 1977). In the present short term
13 study no such temporal trends were detected.

14 Using data from Alabama, North Carolina, Florida and Tennessee,
15 Likens (1976) constructed a map showing lines of equal pH. His predicted
16 value for north Georgia was between pH 4.4 and 4.5. The volume weighted
17 pH values 4.19 at collection and 4.44 at analysis obtained in this study
18 validate his prediction.

19 Work in progress at Georgia is designed to quantify the responses
20 of the element processing responses of plant leaves, plant roots and
21 soils to acid rain regimes. These data will be incorporated into
22 system level elemental cycling and production models for a southern
23 Appalachian Forest. Just as these models have been used to evaluate
24 effects different forest product utilization strategies on elemental
25 cycling (Waide and Swank, 1975; Waide and Swank, 1977) they can be used
26 to make preliminary predictions about the impact of acid rain on forested
27 ecosystems from inputs differing in intensity and in duration.

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3 the manuscript.
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Table 1. The pH frequency distributions for samples determined at time of sample collection (pH_n) and at time of complete chemical analysis after N_2 gas purging (pH_d).

pH Range	Frequency (pH_n) At collection 27 Jan 76 to 7 Nov 77	Frequency (pH_d) At analysis 30 Apr. 76 to 1 Feb 78
3.2-3.29	2	1
3.3-3.39	1	
3.4-		
3.5-	1	
3.6-	6	
3.7-	4	1
3.8-	10	2
3.9	11	8
4.0	14	8
4.1-	14	11
4.2-	10	10
4.3	10	15
4.4	7	11
4.5	4	10
4.6	3	8
4.7	1	5
4.8	1	4
4.9		3
5.0		
5.1		2
5.2		1
5.3		2
5.4		
5.5		
5.6		
6.6		1
n = 99		103

Table 2. The pH frequency distributions for samples collected between 30 April 1976 and 7 November 1977 subject to pH determination both at time of collection (pH_n) and after N_2 gas purging (pH_d).

pH Range	Frequency (pH_n) at collection	Frequency (pH_d) at chemical analysis
3.2-3.29	2	1
3.3-3.39	1	
3.4-		
3.5-	1	
3.6-	5	
3.7-	4	1
3.8-	8	2
3.9-	8	5
4.0-	12	6
4.1-	11	9
4.2-	10	8
4.3-	8	12
4.4-	6	7
4.5-	3	8
4.6-	2	7
4.7-	1	4
4.8	1	4
4.9-		3
5.0-		
5.1-		2
5.2-		1
5.3-		2
5.4-		
5.5-		
5.6-		

6.6

n = 83

83

Table 3a. Mean monthly rainfall properties, from 30 April 1976 through 21 February 1978 at Athens, Georgia.

Month	Monthly Mean Concentration								
	Na	K	Mg	Ca	NH ₄ -N	SO ₄	NO ₃ -N	Cl	PO ₄
	μeq l ⁻¹								
Apr. 76	2.9	19.7	4.5	9.0	18.2	23.7	8.7	9.5	7.6
May 76	7.6	4.5	2.8	10.0	21.5	61.0	23.1	10.1	0.0
June 76	10.8	5.7	7.0	19.7	26.4	65.4	25.1	31.1	0.6
July 76	1.6	1.8	0.5	3.1	6.5	22.5	19.7	14.6	0.0
Aug. 76	9.0	5.7	5.8	30.1	9.8	69.0	7.0	10.0	0.0
Sept. 76	3.7	3.6	4.2	23.1	21.5	81.1	16.5	7.9	0.0
Oct. 76	13.7	2.8	4.0	8.6	13.5	34.2	18.2	16.5	0.7
Nov. 76	0.0	0.0	0.0	1.5	3.8	12.5	24.5	1.4	0.0
Dec. 76	8.5	1.6	2.5	4.2	9.8	43.8	39.3	13.6	0.0
Jan. 77	4.3	2.8	1.1	5.7	17.8	52.3	17.4	7.7	0.4
Feb. 77	7.1	2.0	2.6	9.5	11.5	25.6	9.3	6.7	0.0
Mar. 77	17.6	3.2	6.5	18.8	27.3	84.1	17.9	25.6	0.0
Apr. 77	18.4	4.2	7.0	10.5	7.2	34.3	11.4	24.7	0.0
May 77	4.7	3.8	9.5	33.0	2.9	56.8	21.6	8.1	0.0
June 77	11.1	5.8	7.1	26.7	22.0	130.4	37.4	13.8	0.9
July 77	2.6	1.7	1.7	7.1	17.0	46.8	22.3	4.7	0.9
Aug. 77	1.8	1.3	0.8	3.7	13.2	30.9	18.3	3.7	0.0
Sept. 77	9.0	3.2	2.9	6.8	12.2	38.8	18.0	12.0	0.0
Oct. 77	8.3	1.7	3.2	6.1	12.9	14.9	9.0	61.7	0.0
Nov. 77	26.0	3.6	10.8	24.9	25.6	61.4	28.4	44.5	---
Dec. 77	11.5	2.8	4.9	17.7	26.6	40.3	21.6	19.5	---
Jan. 78	8.0	2.2	3.4	9.6	15.7	53.9	22.5	12	---
Feb. 78	18.3	12.0	3.7	23.0	19.0	96.8	24.7	30.7	---
Volume weighted average, μeq l ⁻¹	6.75	2.1	2.5	7.1	13.3	46.6	21.8	9.67	0.07
Volume weighted average, mg l ⁻¹	0.16	0.08	0.03	0.14	0.19	2.25	0.31	0.34	0.002

[†]Oct. 1976 through Sept. 1977.

1 Table 3b. Mean monthly rainfall properties, from 30 April 1976 to 21

2	Month	Number of	H_n^+ at collection		H_d^+ at analysis		Total H^+
3		storms					
4			$\mu\text{eq } \ell^{-1}$	pH^s	$\mu\text{eq } \ell^{-1}$	pH^s	$\mu\text{eq } \ell^{-1}$
5							
6	Apr. 76	1	630.0	3.20	102.0	3.99	160.0
7	May 76	8	218.0	3.70	54.9	4.26	91.0
8	June 76	5	158.0	3.80	52.9	4.28	106.6
9	July 76	3	64.9	4.20	32.7	4.49	60.0
10	Aug. 76	4	85.6	4.07	52.9	4.28	94.5
11	Sept. 76	6	132.7	3.88	80.5	4.09	134.0
12	Oct. 76	8	60.1	4.22	27.5	4.56	56.8
13	Nov. 76	1	20.8	4.69	7.7	5.11	25
14	Dec. 76	4	79.9	4.10	34.9	4.46	61.5
15	Jan. 77	5	96.6	4.02	50.5	4.30	87.2
16	Feb. 77	1	76.0	4.12	15.4	4.81	40.0
17	Mar. 77	6	46.0	4.34	15.6	4.81	51.3
18	Apr. 77	2	42.7	4.37	17.7	4.75	42.0
19	May 77	1	83.1	4.08	42.6	4.37	81.0
20	June 77	6	167.5	3.78	78.7	4.10	134.0
21	July 77	6	111.3	3.95	61.0	4.21	112.6
22	Aug. 77	5	87.2	4.06	59.8	4.22	110.6
23	Sept. 77	8	54.1	4.27	62.1	4.21	137.8
24	Oct. 77	3	86.0	4.07	81.1	4.09	129.6
25	Nov. 77	5	33.8	4.47	40.5	4.39	89.0
26	Dec. 77	2	----	----	39.0	4.41	81.5
27	Jan. 78	6	----	----	44.9	4.35	77.6
28	Feb. 78	1	----	----	31.6	4.50	84.0
29	Volume †		64.5	4.19	36.0	4.44	72.6
30	weighted						
31	average, $\mu\text{eq } \ell^{-1}$						
32	Volume †		0.065	----	0.036	----	0.073
33	weighted						
34	average						
35	$\text{mg } \ell^{-1}$						

36 ‡ Oct. 1976 through Sept. 1977.

37 s Mean pH calculated from mean H^+ concentration.

38 † Cation sums calculated using H^+ concentrations as measured at analysis.

39 ‡ Total for storms which were collected during each month.

40 $^\ddagger^\ddagger$ Anion sums for Nov. 77 through Feb. 78 do not include PO_4 .

1 1976 to 21 February 1978 at Athens, Georgia.

sis	Total H ⁺	% Free H ⁺	Cation sum [†]	Anion sum	Anion deficit	Total rain [†]
pH ^s	μeq ℓ ⁻¹	%	μeq ℓ ⁻¹	μeq ℓ ⁻¹	μeq ℓ ⁻¹	cm
4.99	160.0	63.9	156.0	49.7	106.0	1.3
4.26	91.0	56.2	101.6	94.3	7.2	20.8
4.28	106.6	50.3	122.6	122.3	0.3	2.9
4.49	60.0	51.5	46.5	56.8	-10.3	6.7
4.28	94.5	52.9	113.5	86.0	27.5	11.4
4.09	134.0	58.3	137.1	105.6	31.4	6.3
4.56	56.8	43.6	70.4	69.8	0.6	15.8
5.11	25	31.0	13.1	38.4	-25.3	7.6
4.46	61.5	56.1	61.8	96.0	-35.0	11.1
4.30	87.2	57.8	82.4	77.9	4.5	6.2
4.81	40.0	38.7	48.3	41.7	6.6	3.3
4.81	51.3	32.5	89.3	127.7	-38.3	14.9
4.75	42.0	36.7	65.2	70.6	-5.3	3.7
4.37	81.0	52.6	96.7	86.6	10.0	0.1
4.10	134.0	53.9	151.7	181.7	-30.0	4.1
4.21	112.6	53.5	91.4	74.9	16.5	12.5
4.22	110.6	53.3	80.8	52.99	27.8	14.6
4.21	137.8	51.1	96.5	68.0	27.6	8.3
4.09	129.6	57.9	112.7	112.1	0.6	14.5
4.39	88.0	45.6	131.5	134.3 ^{††}	-2.8	9.5
4.41	81.5	48.7	103.3	81.4 ^{††}	21.9	1.5
4.35	77.6	56.6	84.1	88.4 ^{††}	-4.3	12.5
4.50	84.0	37.6	107.7	152.2 ^{††}	-44.5	-----
						Annual ^{††}
4.44	72.6	50.0	67.8	78.5	-10.7	98.4
-----	0.073	50.0	-----	-----	-----	-----

measured at analysis is in 1978.
th.
e PO₄.

Table 4. Correlation coefficients (r) for H_d^+ ($\mu\text{eq l}^{-1}$) calculated from pH_d and selected rainfall variables. Where total H^+ = titratable acidity, ADEF = sum cations - sum of anions, cm = amount of Rain and, Dry Days = days since last rain.

Statistics	Total H^+	SO_4^{-2}	NO_3^{-1}	CL^{-1}	Anion sum	ADEF	cm	Dry days
All Samples								
r	.91	.57	.35	.23	.54	.32	-.29	-.12
p	.0001	.0001	.0003	.01	.0001	.003	.003	.2
n	101	101	101	101	101	101	96	86
$\text{pH}_d < 4.0$								
r	.72	.65	-.36	.03	.19	.28	-.12	.08
p	.01	.15	.26	.90	.60	.46	.70	.80
n	11	6	11	11	9	9	9	8
$4.0 \leq \text{pH}_d \leq 4.5$								
r	.81	.44	.12	.04	.37	.31	-.10	-.16
p	.001	.0007	.38	.70	.01	.04	.40	.20
n	55	55	55	55	44	44	54	47
$4.5 \leq \text{pH}_d \leq 5.0$								
r	.65	-.09	.12	.17	-.16	.35	-.23	-.18
p	.0001	.60	.51	.36	.40	.09	.2	.30
n	30	30	30	30	24	24	28	26
$\text{pH}_d \geq 5.0$								
r	.42	.36	.58	-.32	.52	-.71	-.02	-.47
p	.47	.50	.30	.50	.37	.17	.90	.40
n	5	5	5	5	5	5	5	5

p = probability

n = sample size

Table 5. Ion concentrations, $\text{mg } \ell^{-1}$, in precipitation at selected locations in the eastern United States.

Location	Concentration									pH
	Na	K	Mg	Ca	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	SO_4	Cl	PO_4P	
Athens, Georgia, (a)	.16	.08	.03	.14	.19	.31	2.25	.34	.002	4.19
Coweeta, North Carolina (b)	.14	.06	.04	.18	.02	.11	--	.31	.006	4.6
Walker Branch, Tennessee (b)	.18	.07	.10	.64	.13 ^h	.25 ^h	3.0 ⁱ	--	.004	--
Gatlinburg, Tennessee, (c)	.05	.07	.03	.20	.15	.29	2.19 3.19	.15	--	4.19
Hubbard Brook, New Hampshire (c)	.07	.07	.05	.24	.29	.44	4.77	.15	--	4.05
Ithaca, New York (d)	.15	.09	.08	.83	.25	.66	4.96	.47	--	4.05
East North Carolina, Southeastern Virginia (e)	.56	.11	.14	.65	--	.14	2.18	.57	--	--
North Georgia (f)	.18	.07	--	.31	--	--	1.15	.13	--	--
NY, New England (g)	.27	.16	.11	.60	.17	.08	4.3	.45	.013	4.38

- a This study: Oct. 1976-Sept. 1977, volume weighted mean in rain.
- b Swank and Douglas (1975), Swank and Henderson (1976) 1970-1973: volume weighted mean in rain as calculated from bulk precipitation minus dry fallout.
- c Cogbill and Likens (1974): June-Aug. 1973, volume weighted means in rain.
- d Cogbill and Likens (1974): Sept. 1972-Aug. 1973, volume weighted mean in rain.
- e Gambell and Fisher (1966): 1962-63, mean, not volume weighted in bulk precipitation.
- f Junge and Werby (1958): July 1955-June 1956, mean, not volume weighted in rain?
- g Pearson and Fisher (1971): 1966-1968, volume weighted mean in bulk precipitation.
- h $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ values for Walker Branch are for bulk precipitation.

1 Table 5 (continued).

2 i Shriner and Henderson (1972): 1973-76, volume weighted mean
3 calculated from annual SO_4 -S input and mean annual rainfall.
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