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GEOLOGICAL SURVEY CIRCULAR 910

U.S. DEPARTMENT OF THE INTERIOR
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Evidence for Acid-Precipitation-Induced Trends in Stream Chemistry at Hydrologic Bench-Mark Stations

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ABSTRACT

Ten- to 15-year water-quality records from a network of headwater sampling stations show small declines in stream sulfate concentrations at stations in the northeastern quarter of the Nation and small increases in sulfate at most southeastern and western sites. The regional pattern of stream sulfate trends is similar to that reported for trends in SO_2 emissions to the atmosphere during the same period. Trends in the ratio of alkalinity to total major cation concentrations at the stations follow an inverse pattern of small increases in the Northeast and small, but widespread decreases elsewhere. The undeveloped nature of the sampled basins and the magnitude and direction of observed changes in relation to SO_2 emissions support the hypothesis that the observed patterns in water quality trends reflect regional changes in the rates of acid deposition.

INTRODUCTION

During the past decade evidence has accumulated suggesting that the phenomenon of acid precipitation may involve the transport of air pollutants over long distances and the deposition of acidic materials in basins with widely differing geochemical capacities for neutralizing acids (National Research Council, 1981; 1983). These two characteristics of the acid deposition problem give rise to the need for a more detailed geographic understanding of the phenomenon than presently exists for the Nation as a whole. A recent analysis of available data from eastern North America by the National Research Council (1983) links historical trends in atmospheric emissions of SO_2 and NO_x to trends in precipitation chemistry at a single site, the Hubbard Brook Experimental Forest in New Hampshire. A major conclusion of that study is that the lack of long-term records of precipitation chemistry at sites in other regions of the country greatly hinders efforts to associate specific source areas of acid-producing materials with the sensitive areas receiving those materials.

In this report we describe a geographic pattern in recorded changes in water chemistry at a nationwide network of stream sampling stations. The nature of these stations, and the geographic pattern of atmospheric SO_2 emissions occurring during the period of sampling, suggest that the stream chemistry changes result from regional changes in the rates of acid deposition. There are difficulties inherent in the use of stream chemistry data to indicate changing rates of acid deposition. Because of the numerous natural and human sources of materials entering streams in general, it is difficult to separate atmospheric factors from other possible causes of chemical change in the absence of simultaneous records of precipitation chemistry. This problem is greatly alleviated in the present study, however, by virtue of the predominantly undeveloped nature of the drainage basins in which the sampling stations are located.

The principal advantage to the use of stream chemistry records over precipitation data in discerning trends in acid deposition is the larger number and wider geographic distribution of sampling sites for which long-term (> 10 year) records are available. A further advantage of stream data is that streams tend to carry acidic material deposited in both wet and dry forms so that effects on stream chemistry tend to reflect the total deposition rate. To date, direct quantification of dry deposition rates at precipitation monitoring sites

TABLE 1.—*Drainage area, mean discharge, and annual precipitation at Bench-Mark stations*

STATION NUMBER	STATION NAME AND LOCATION	DRAINAGE AREA (km^2)	MEAN DISCHARGE (m^3 sec^{-1})	ESTIMATED ANNUAL PRECIPITATION[1] (cm yr^{-1})
10542.00	WILD RIVER AT GILEAD, ME	180.0	4.53	112
13621.98	ESOPUS CREEK AT SHANDAKEN, NY	154.1	3.79	107
14665.00	MCDONALDS B IN LEBANON STATE FOREST, NJ	6.0	0.03	112
15456.00	YOUNG WOMANS CREEK NEAR RENOVO, PA.	119.7	2.01	97
20388.50	HOLIDAY CREEK NEAR ANDERSONVILLE, VA.	22.1	0.20	109
21353.00	SCAPE ORE SWAMP NEAR BISHOPVILLE, SC	248.6	2.78	114
21973.00	UPPER THREE RUNS NEAR NEW ELLENTON, SC	225.3	3.09	112
22126.00	FALLING CREEK NEAR JULIETTE, GA.	187.0	1.50	112
23271.00	SOPCHOPPY RIVER NR SOPCHOPPY, FLA.	264.2	4.42	142
24502.50	SIPSEY FORK NEAR GRAYSON, AL	233.4	4.39	132
24791.55	CYPRESS CREEK NR JANICE, MS.	135.2	2.69	152
32372.80	UPPER TWIN CREEK AT MCGAW, OH	31.6	0.34	109
32767.00	SOUTH HOGAN CREEK NEAR DILLSBORO, IND.	98.7	1.08	102
34600.00	CATALOOCHEE CREEK NEAR CATALOOCHEE, NC	127.4	3.14	124
36040.00	BUFFALO RIVER NEAR FLAT WOODS, TENN.	1157.7	21.35	132
40010.00	WASHINGTON CREEK AT WINDIGO, MICH.	34.2	0.45	71
40637.00	POPPLE RIVER NEAR FENCE, WI	360.0	3.40	74
50649.00	BEAVER CREEK NR FINLEY, ND	414.4	0.42	48
51244.80	KAWISHIWI RIVER NEAR ELY, MN	655.3	6.00	71
53760.00	NORTH FORK WHITEWATER RIVER NEAR ELBA, MN	261.6	1.16	76
62882.00	BEAUVAIS CREEK NEAR ST. XAVIER, MT.	259.0	0.62	36
63325.15	BEAR DEN CREEK NR MANDAREE, ND	191.7	0.20	38
64090.00	CASTLE CR ABOVE DEERFIELD RES NEAR HILL CITY, SD	215.0	0.28	51
66238.00	ENCAMPMENT RIV AB HOG PARK CR NR ENCAMPMENT, WYO	188.3	3.03	76
67759.00	DISMAL RIVER NR THEDFORD, NEBR	2486.4	5.38	51
68979.50	ELK CREEK NEAR DECATUR CITY, IOWA	136.0	0.68	81
70607.10	NORTH SYLAMORE CREEK NEAR FIFTY SIX, ARK.	150.5	1.19	114
70830.00	HALFMOON CREEK NEAR MALTA, CO.	61.1	0.74	76
73112.00	BLUE BEAVER CREEK NR CACHE, OK	63.7	0.25	74
73357.00	KIAMICHI RIVER NR BIG CEDAR, OK	103.9	2.07	142
73730.00	BIG CREEK AT POLLOCK, LA	132.1	1.47	142
81039.00	SOUTH FORK ROCKY CREEK NEAR BRIGGS, TEX.	86.2	0.37	76
83779.00	RIO MORA NEAR TERRERO, NM	137.8	0.76	61
93529.00	VALLECITO CREEK NEAR BAYFIELD, CO.	186.7	3.85	102
94306.00	MOGOLLON CREEK NEAR CLIFF, NM	178.7	0.76	33
95083.00	WET BOTTOM CREEK NR CHILDS, ARIZ.	94.3	0.34	64
101722.00	RED BUTTE CREEK AT FT. DOUGLAS NR. SLC, UTAH	18.8	0.08	64
102449.50	STEPTOE C NR ELY, NV	28.7	0.17	30
102493.00	S TWIN R NR ROUND MOUNTAIN, NV	51.8	0.14	20
112645.00	MERCED R AT HAPPY ISLES BRIDGE NR YOSEMITE,CALIF	468.8	14.75	140
114755.60	ELDER CREEK NEAR BRANSCOMB, CALIF	16.8	0.65	203
120393.00	NORTH FORK QUINAULT R NEAR AMANDA PARK, WASH.	191.9	23.87	508
124160.00	HAYDEN CK BELOW N FK, NR HAYDEN LAKE, IDAHO	57.0	0.68	102
124473.90	ANDREWS CREEK NEAR MAZAMA, WASH.	57.2	0.91	89
130183.00	CACHE CREEK NEAR JACKSON, WYO	27.5	0.34	76
131695.00	BIG JACKS CREEK NEAR BRUNEAU, ID	655.3	0.25	25
133315.00	MINAM RIVER AT MINAM,OREG.	621.6	12.23	102

[1] Estimates of annual precipitation are from Cobb and Biesecker, 1971.

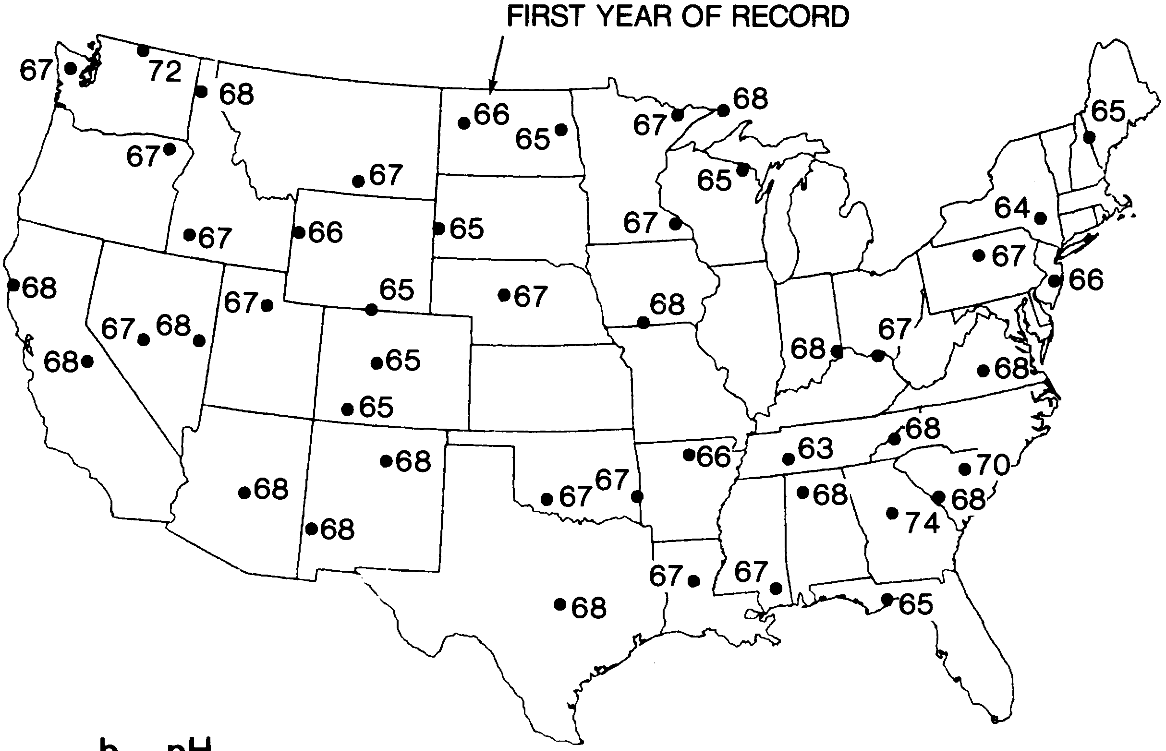
has proved very problematic (Hicks, and others, 1981). Moreover, stream chemistry data provide direct evidence of the geochemical sensitivity of an area to acid deposition and are thus, in a sense, a step closer to the problem.

Since 1964 the U.S. Geological Survey has operated the Hydrologic Bench-Mark Network of 47 streamflow and water quality monitoring stations in small, predominantly undeveloped stream basins (table 1; Cobb and Biesecker, 1971). The network includes stations in 37 states and was originally established to help define baseline hydrologic conditions in a variety of natural environments. Because of little or no changes in land use in these basins and the application of consistent sampling and analytical methods (Skougstad and others, 1979) for a 10–15-year period at each site, water-quality records from the network are particularly appropriate for investigating atmospheric influences on water quality during the past decade.

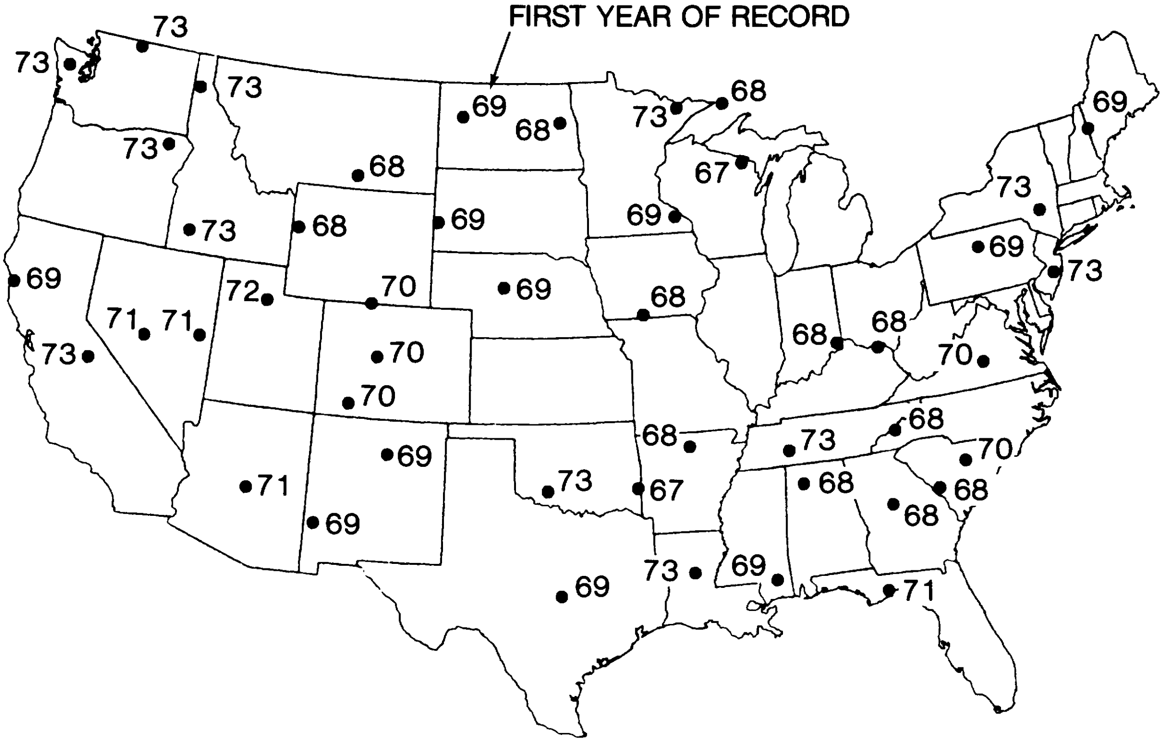
METHODS

In this report we present the results of applying the Seasonal Kendall test for trend (Hirsch and others, 1982) to monthly records of stream sulfate, pH, alkalinity, and the ratio of alkalinity to total major cation concentration at Bench-Mark stations.

Records of sulfate, alkalinity, and major cation concentrations begin generally in the mid- to late 1960's (fig. 1a), while pH records begin generally



a SULFATE, ALKALINITY, CATIONS



b pH

FIGURE 1.—First year of record for (a) sulfate concentration, alkalinity, and total major cation concentrations, and (b) pH at Bench-Mark stations.

TABLE 2.—*Summary statistics for sulfate concentrations at Bench-Mark stations, for the period of record through 1981*

STATION NUMBER	STATION NAME AND LOCATION	NUMBER OF SAMPLES	MEAN (meq L-1)	TREND SLOPE (μeq L-1 yr-1)	SIGNIFICANCE LEVEL (p)	ESTIMATED PRECIPITATION CONCENTRATION[1] (μeq L-1)
10542.00	WILD RIVER AT GILEAD, ME	87	0.10	-1.7	0.000	50
13621.98	ESOPUS CREEK AT SHANDAKEN, NY	155	0.16	-2.4	0.000	65
14665.00	MCDONALDS B IN LEBANON STATE FOREST, NJ	79	0.13	-2.9	0.034	60
15456.00	YOUNG WOMANS CREEK NEAR RENOVO, PA.	143	0.16	-0.9	0.088	75
20388.50	HOLIDAY CREEK NEAR ANDERSONVILLE, VA.	84	0.06	-1.0	0.040	55
21353.00	SCAPE ORE SWAMP NEAR BISHOPVILLE, SC	124	0.06	2.9	0.001	50
21973.00	UPPER THREE RUNS NEAR NEW ELLENTON, SC	77	0.02	1.0	0.007	50
22126.00	FALLING CREEK NEAR JULIETTE, GA.	62	0.08	0.6	0.696	50
23271.00	SOPCHOPPY RIVER NR SOPCHOPPY, FLA.	172	0.09	7.8	0.000	46
24502.50	SIPSEY FORK NEAR GRAYSON, AL	73	0.08	1.1	0.016	45
24791.55	CYPRESS CREEK NR JANICE, MS.	68	0.04	2.3	0.002	35
32372.80	UPPER TWIN CREEK AT MCGAW, OH	167	0.54	11.6	0.000	80
32767.00	SOUTH HOGAN CREEK NEAR DILLSBORO, IND.	128	1.20	-4.3	0.239	75
34600.00	CATALOOCHEE CREEK NEAR CATALOOCHEE, NC	76	0.02	1.0	0.031	60
36040.00	BUFFALO RIVER NEAR FLAT WOODS, TENN.	89	0.08	-0.7	0.048	55
40010.00	WASHINGTON CREEK AT WINDIGO, MICH.	71	0.12	-1.3	0.308	40
40637.00	POPPLE RIVER NEAR FENCE, WI	146	0.16	-2.1	0.034	50
50649.00	BEAVER CREEK NR FINLEY, ND	79	6.02	29.2	0.513	30
51244.80	KAWISHIWI RIVER NEAR ELY, MN	53	0.10	-1.0	0.118	35
53760.00	NORTH FORK WHITEWATER RIVER NEAR ELBA, MN	134	0.32	2.0	0.157	50
62882.00	BEAUVAIS CREEK NEAR ST. XAVIER, MT.	125	11.72	100.2	0.032	40
63325.15	BEAR DEN CREEK NR MANDAREE, ND	141	12.99	167.9	0.001	30
64090.00	CASTLE CR ABOVE DEERFIELD RES NEAR HILL CITY, SD	167	0.16	2.6	0.001	35
66238.00	ENCAMPMENT RIV AB HOG PARK CR NR ENCAMPMENT, WYO	124	0.08	4.0	0.000	40
67759.00	DISMAL RIVER NR THEDFORD, NEBR	81	0.15	2.4	0.001	40
68979.50	ELK CREEK NEAR DECATUR CITY, IOWA	107	1.07	-8.7	0.541	50
70607.10	NORTH SYLAMORE CREEK NEAR FIFTY SIX, ARK.	157	0.12	2.1	0.001	50
70830.00	HALFMOON CREEK NEAR MALTA, CO.	161	0.11	0.7	0.351	40
73112.00	BLUE BEAVER CREEK NR CACHE, OK	43	0.31	-3.6	0.367	30
73357.00	KIAMICHI RIVER NR BIG CEDAR, OK	149	0.07	0.6	0.391	30
73730.00	BIG CREEK AT POLLOCK, LA	119	0.04	3.2	0.000	30
81039.00	SOUTH FORK ROCKY CREEK NEAR BRIGGS, TEX.	41	0.38	11.8	0.044	30
83779.00	RIO MORA NEAR TERRERO, NM	81	0.18	2.0	0.064	45
93529.00	VALLECITO CREEK NEAR BAYFIELD, CO.	123	0.18	2.1	0.051	45
94306.00	MOGOLLON CREEK NEAR CLIFF, NM	73	0.33	-0.9	0.743	40
95083.00	WET BOTTOM CREEK NR CHILDS, ARIZ.	105	0.18	-0.7	0.661	50
101722.00	RED BUTTE CREEK AT FT. DOUGLAS NR. SLC, UTAH	144	1.84	22.0	0.000	30
102449.50	STEPTOE C NR ELY, NV	120	0.18	1.3	0.086	25
102493.00	S TWIN R NR ROUND MOUNTAIN, NV	108	0.12	-0.5	0.316	20
112645.00	MERCED R AT HAPPY ISLES BRIDGE NR YOSEMITE,CALIF	108	0.03	0.3	0.954	20
114755.60	ELDER CREEK NEAR BRANSCOMB, CALIF	130	0.07	0.0	0.947	10
120393.00	NORTH FORK QUINAULT R NEAR AMANDA PARK, WASH.	110	0.19	1.8	0.024	20
124160.00	HAYDEN CK BELOW N FK, NR HAYDEN LAKE, IDAHO	80	0.06	1.9	0.009	25
124473.90	ANDREWS CREEK NEAR MAZAMA, WASH.	87	0.05	0.2	0.778	20
130183.00	CACHE CREEK NEAR JACKSON, WYO	164	0.13	-2.7	0.005	30
131695.00	BIG JACKS CREEK NEAR BRUNEAU, ID	62	0.14	1.4	0.225	20
133315.00	MINAM RIVER AT MINAM,OREG.	104	0.03	2.8	0.000	20

[1] Estimates of precipitation sulfate concentration are from 1981 N.A.D.P. data (Gibson and Baker, written communication, 1982).

in the late 1960's to the early 1970's (fig. 1b). The pH of samples collected prior to dates given in figure 1b were measured in the laboratory and are not comparable to in-stream measurements. Records of stream nitrate concentrations are available only since the mid- to late 1970's and are considered too short for comparison with the other records.

The Seasonal Kendall test is nonparametric and is intended for analysis of time trends in seasonally varying water-quality data from fixed, regularly sampled monitoring sites such as those which the Bench-Mark Network comprises (Hirsch and others, 1982; see also Smith and others, 1982). In addition to a test for trend, the statistical procedure includes an estimate of the median rate of change of quality over the sampling period (trend slope) and a method for adjusting the data to correct for effects of changing stream flow on trend in the water-quality record. Trend is defined here simply as monotonic change with time, occurring either as an abrupt or gradual change in water quality.

ATMOSPHERIC CONTRIBUTIONS TO STREAM SULFATE

An important assumption of the present analysis is that stream sulfate concentrations at most Bench-Mark stations are low enough to be significantly influenced by changes in the rate of atmospheric deposition of sulfur. Annual average sulfate concentrations of precipitation in the United States, based on 1981 data from the National Atmospheric Deposition Program (table 2), range from approximately 20μeq L^{-1} in the West to 70μeq L^{-1} or more over the Ohio Valley (J. H. Gibson and C. V. Baker, National Atmospheric Deposition Program, Fort Collins, Colorado, 1982, written communication). These data can be used to estimate the contribution of wet deposition to stream sulfate, provided that the tendency for evapotranspiration to increase the concentration of dissolved constituents in precipitation is taken into account. Correction factors for the effects of evapotranspiration are calculated as the ratio of annual precipitation to annual runoff (table 1; Cobb and Biesecker, 1971) and range from 10 or greater for much of the West to about 2 in New England and as low as 1.5 in the far Northwest.

After adjusting for the effects of evapotranspiration, precipitation is estimated to contribute at least 90 percent of the mean sulfate concentration at half of the Bench-Mark stations and at least 22 percent of the mean sulfate concentration at all but six stations. The Bench-Mark stations at which precipitation is estimated to contribute less than 22 percent of stream sulfate are: South Hogan Creek near Dillsboro, Indiana (19 percent); North Fork Quinault River near Amanda Park, Washington (11.5 percent); Beaver Creek near Finley, North Dakota (9.2 percent); Red Butte Creek at Ft. Douglas near Salt Lake City, Utah (6.5 percent); Bear Den Creek near Mandaree, North Dakota (2 percent); and Beauvais Creek near St. Xavier, Montana (1.5 percent).

The above estimates of the precipitation contribution to stream sulfate at Bench-Mark stations are conservative estimates of the total atmospheric contribution because dry deposition is not included. Dry deposition has proved difficult to quantify (Hicks and others, 1981) but, depending on climatic and other factors, has been estimated to contribute anywhere from a few percent to 60 or 70 percent of the total sulfate deposition (Niemann, 1983).

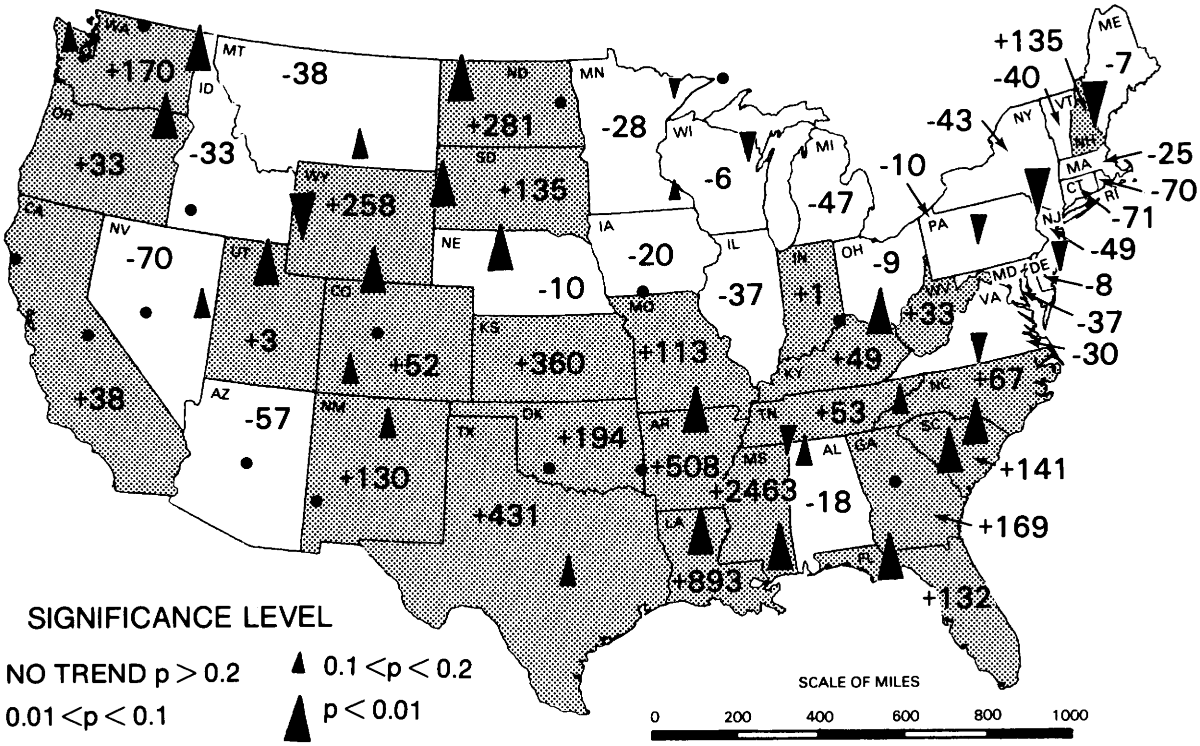


FIGURE 2.—Comparison of trends in stream sulfate concentrations at Bench-Mark stations for the period of record through 1981 with trends in SO_2 emissions to the atmosphere by State, 1965–1980. Triangles indicate direction and significance level of trends in stream sulfate. Numbers give percentage change in SO_2 emissions from 1965 to 1980 for each State. States showing increasing levels of SO_2 emissions are shaded; States showing decreasing levels of SO_2 emissions are unshaded. Source of emission data: G. Gschwandtner and K. Gschwandtner, written communication (1983).

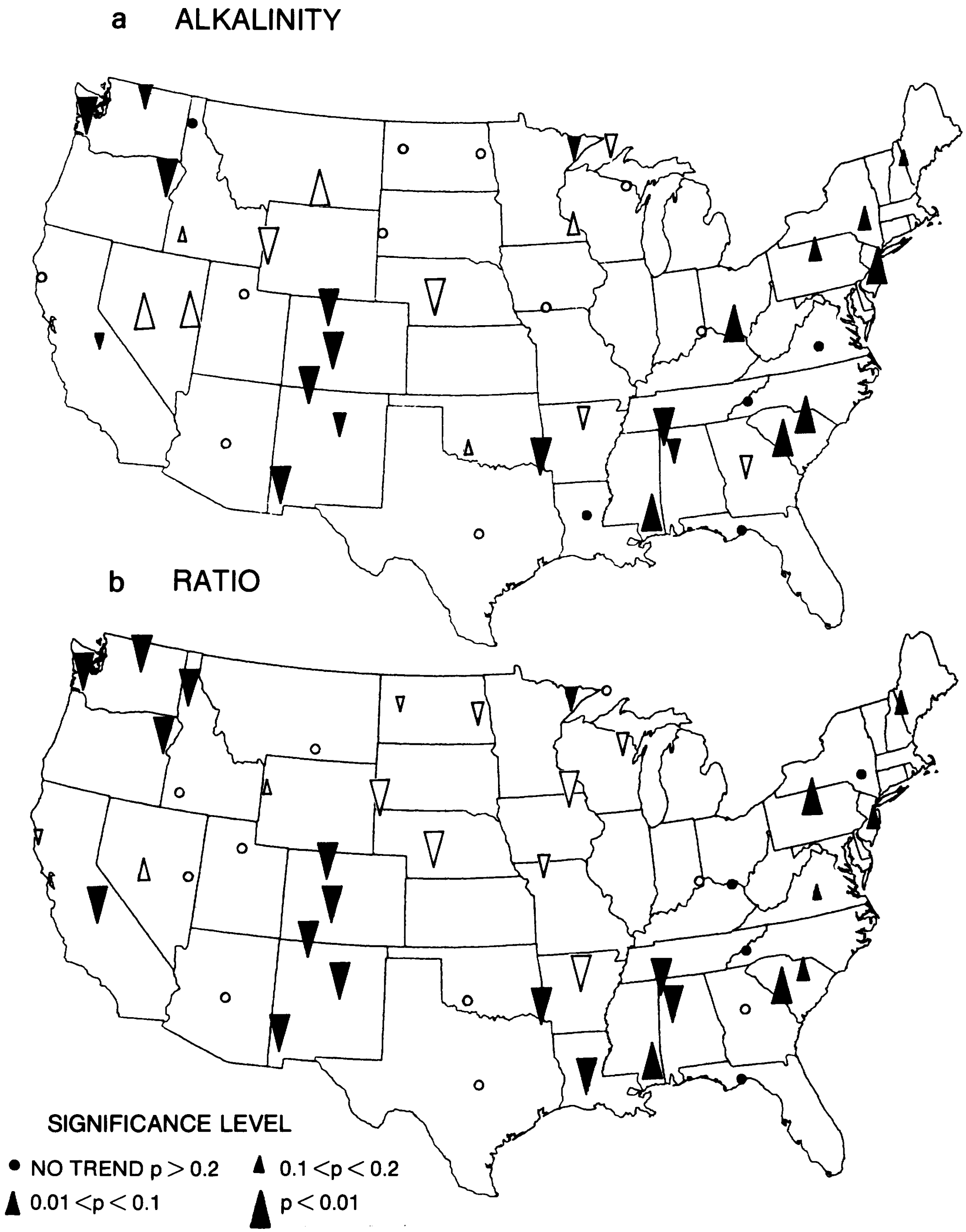


FIGURE 3.—Trends in (a) alkalinity, and (b) the ratio of alkalinity to total major cation concentration at Bench-Mark stations for the period of record through 1981. Symbols indicate direction and significance level of trends. Dark symbols indicate stations with mean alkalinity less than 1 meq L^{-1}.

TABLE 3.—*Summary statistics for alkalinity at Bench-Mark stations, for the period of record through 1981*

STATION NUMBER	STATION NAME AND LOCATION	NUMBER OF SAMPLES	MEAN (meq L^{-1})	TREND SLOPE (μeq L^{-1} yr^{-1})	SIGNIFICANCE LEVEL (p)
10542.00	WILD RIVER AT GILEAD, ME	77	0.12	1.6	0.153
13621.98	ESOPUS CREEK AT SHANDAKEN, NY	148	0.23	1.5	0.079
14665.00	MCDONALDS B IN LEBANON STATE FOREST, NJ	48	0.01	0.7	0.006
15456.00	YOUNG WOMANS CREEK NEAR RENOVO, PA.	134	0.17	3.3	0.010
20388.50	HOLIDAY CREEK NEAR ANDERSONVILLE, VA.	80	0.26	0.9	0.390
21353.00	SCAPE ORE SWAMP NEAR BISHOPVILLE, SC	101	0.07	3.1	0.001
21973.00	UPPER THREE RUNS NEAR NEW ELLENTON, SC	72	0.06	1.9	0.009
22126.00	FALLING CREEK NEAR JULIETTE, GA.	61	1.03	-15.5	0.030
23271.00	SOPCHOPPY RIVER NR SOPCHOPPY, FLA.	124	0.60	2.0	0.458
24502.50	SIPSEY FORK NEAR GRAYSON, AL	66	0.74	-11.8	0.042
24791.55	CYPRESS CREEK NR JANICE, MS.	65	0.07	2.8	0.008
32372.80	UPPER TWIN CREEK AT MCGAW, OH	155	0.27	3.9	0.002
32767.00	SOUTH HOGAN CREEK NEAR DILLSBORO, IND.	118	3.53	-4.9	0.735
34600.00	CATALOOCHEE CREEK NEAR CATALOOCHEE, NC	77	0.11	0.7	0.278
36040.00	BUFFALO RIVER NEAR FLAT WOODS, TENN.	76	0.74	-7.1	0.000
40010.00	WASHINGTON CREEK AT WINDIGO, MICH.	70	1.25	-7.5	0.013
40637.00	POPPLE RIVER NEAR FENCE, WI	147	1.61	-5.2	0.203
50649.00	BEAVER CREEK NR FINLEY, ND	74	4.74	-37.5	0.294
51244.80	KAWISHIWI RIVER NEAR ELY, MN	49	0.22	-2.8	0.040
53760.00	NORTH FORK WHITEWATER RIVER NEAR ELBA, MN	131	5.08	24.2	0.021
62882.00	BEAUVAIS CREEK NEAR ST. XAVIER, MT.	125	3.67	51.1	0.006
63325.15	BEAR DEN CREEK NR MANDAREE, ND	132	13.69	51.6	0.256
64090.00	CASTLE CR ABOVE DEERFIELD RES NEAR HILL CITY, SD	151	5.07	1.5	0.825
66238.00	ENCAMPMENT RIV AB HOG PARK CR NR ENCAMPMENT, WYO	120	0.53	-6.0	0.000
67759.00	DISMAL RIVER NR THEDFORD, NEBR	80	1.71	-9.6	0.000
68979.50	ELK CREEK NEAR DECATUR CITY, IOWA	99	4.42	-19.2	0.219
70607.10	NORTH SYLAMORE CREEK NEAR FIFTY SIX, ARK.	150	2.79	-9.6	0.019
70830.00	HALFMOON CREEK NEAR MALTA, CO.	159	0.73	-9.3	0.000
73112.00	BLUE BEAVER CREEK NR CACHE, OK	40	1.22	22.2	0.183
73357.00	KIAMICHI RIVER NR BIG CEDAR, OK	132	0.13	-3.0	0.007
73730.00	BIG CREEK AT POLLOCK, LA	123	0.23	-1.2	0.211
81039.00	SOUTH FORK ROCKY CREEK NEAR BRIGGS, TEX.	42	4.53	28.6	0.684
83779.00	RIO MORA NEAR TERRERO, NM	77	0.86	-6.7	0.025
93529.00	VALLECITO CREEK NEAR BAYFIELD, CO.	128	0.54	-9.3	0.000
94306.00	MOGOLLON CREEK NEAR CLIFF, NM	71	0.76	-14.5	0.005
95083.00	WET BOTTOM CREEK NR CHILDS, ARIZ.	97	2.36	15.2	0.320
101722.00	RED BUTTE CREEK AT FT. DOUGLAS NR. SLC, UTAH	131	4.75	-1.7	0.875
102449.50	STEPTOE C NR ELY, NV	117	3.40	21.6	0.000
102493.00	S TWIN R NR ROUND MOUNTAIN, NV	109	1.12	10.3	0.000
112645.00	MERCED R AT HAPPY ISLES BRIDGE NR YOSEMITE,CALIF	107	0.13	-1.0	0.192
114755.60	ELDER CREEK NEAR BRANSCOMB, CALIF	125	1.07	1.9	0.421
120393.00	NORTH FORK QUINAULT R NEAR AMANDA PARK, WASH.	110	0.54	-4.5	0.002
124160.00	HAYDEN CK BELOW N FK, NR HAYDEN LAKE, IDAHO	76	0.66	-3.5	0.270
124473.90	ANDREWS CREEK NEAR MAZAMA, WASH.	85	0.48	-8.7	0.011
130183.00	CACHE CREEK NEAR JACKSON, WYO	152	3.55	-11.8	0.000
131695.00	BIG JACKS CREEK NEAR BRUNEAU, ID	62	1.15	9.0	0.149
133315.00	MINAM RIVER AT MINAM,OREG.	99	0.48	-5.3	0.003

RESULTS AND DISCUSSION

TRENDS IN STREAM SULFATE

The significance levels[1] and directions of apparent trends in sulfate concentration for the period of record at Bench-Mark stations are shown in figure 2. Sulfate concentrations have tended to increase during the 10–15-year period over a broad area of the continental United States extending from the Southeast to the mountain States and the Northwest. By contrast, stations in the northeastern quarter of the Nation have tended to show either no trend or declines in sulfate concentrations. This geographic pattern occurs more or less independently of the significance criteria used in mapping the trend test results (see table 2 for test results at all stations). Although the statistical significance of trends at many of the stations is high ($p < .01$), the magnitude of change has been small in most cases (table 2). The median slope of 2μeq L^{-1} yr^{-1} among stations showing trend in sulfate concentration corresponds to a median relative change in stream sulfate of 1.7 percent per year or about 25 percent over the period of record.

TRENDS IN SO_2 EMISSIONS

There is evidence (G. Gschwandtner and K. Gschwandtner, 1983, Pacific Environmental Services, Durham, North Carolina, written communi-

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[1] Significance level (p) is the probability of incorrectly rejecting the null hypothesis that there is no trend in the data. The significance level provides a measure of the confidence to be placed in the validity of an observed trend. For example, if p is greater than 0.1 but less than 0.2 ($0.1 < p < 0.2$), there is an 80 to 90 percent likelihood that the observed trend is real and does not occur through chance alone.

TABLE 4.—*Summary statistics for the ratio of alkalinity to total major cation concentrations at Bench-Mark stations, for the period of record through 1981*

STATION NUMBER	STATION NAME AND LOCATION	NUMBER OF SAMPLES	MEAN	TREND SLOPE (yr^{-1})	SIGNIFICANCE LEVEL (p)
10542.00	WILD RIVER AT GILEAD, ME	76	0.51	0.010	0.087
13621.93	ESOPUS CREEK AT SHANDAKEN, NY	146	0.47	0.001	0.543
14665.00	MCDONALDS B IN LEBANON STATE FOREST, NJ	45	0.04	0.003	0.024
15456.00	YOUNG WOMANS CREEK NEAR RENOVO, PA.	134	0.46	0.009	0.002
20388.50	HOLIDAY CREEK NEAR ANDERSONVILLE, VA.	80	0.71	0.007	0.172
21353.00	SCAPE ORE SWAMP NEAR BISHOPVILLE, SC	99	0.27	0.009	0.022
21973.00	UPPER THREE RUNS NEAR NEW ELLENTON, SC	70	0.49	0.019	0.002
22126.00	FALLING CREEK NEAR JULIETTE, GA.	60	0.80	-0.008	0.315
23271.00	SOPCHOPPY RIVER NR SOPCHOPPY, FLA.	89	0.53	0.002	0.555
24502.50	SIPSEY FORK NEAR GRAYSON, AL	63	0.81	-0.006	0.009
24791.55	CYPRESS CREEK NR JANICE, MS.	59	0.38	0.015	0.006
32372.80	UPPER TWIN CREEK AT MCGAW, OH	154	0.29	0.001	0.603
32767.00	SOUTH HOGAN CREEK NEAR DILLSBORO, IND.	118	0.65	0.000	0.855
34600.00	CATALOOCHEE CREEK NEAR CATALOOCHEE, NC	75	0.74	0.003	0.434
36040.00	BUFFALO RIVER NEAR FLAT WOODS, TENN.	72	0.82	-0.006	0.002
40010.00	WASHINGTON CREEK AT WINDIGO, MICH.	69	0.79	-0.001	0.524
40637.00	POPPLE RIVER NEAR FENCE, WI	146	0.82	-0.002	0.091
50649.00	BEAVER CREEK NR FINLEY, ND	74	0.41	-0.005	0.074
51244.80	KAWISHIWI RIVER NEAR ELY, MN	52	0.58	-0.008	0.027
53760.00	NORTH FORK WHITEWATER RIVER NEAR ELBA, MN	131	0.88	-0.003	0.001
62882.00	BEAUVAIS CREEK NEAR ST. XAVIER, MT.	125	0.23	0.000	0.942
63325.15	BEAR DEN CREEK NR MANDAREE, ND	131	0.49	-0.002	0.158
64090.00	CASTLE CR ABOVE DEERFIELD RES NEAR HILL CITY, SD	150	0.93	-0.004	0.000
66238.00	ENCAMPMENT RIV AB HOG PARK CR NR ENCAMPMENT, WYO	119	0.83	-0.009	0.002
67759.00	DISMAL RIVER NR THEDFORD, NEBR	76	0.87	-0.005	0.000
68979.50	ELK CREEK NEAR DECATUR CITY, IOWA	97	0.73	-0.004	0.021
70607.10	NORTH SYLAMORE CREEK NEAR FIFTY SIX, ARK.	148	0.93	-0.002	0.010
70830.00	HALFMOON CREEK NEAR MALTA, CO.	153	0.82	-0.006	0.000
73112.00	BLUE BEAVER CREEK NR CACHE, OK	38	0.66	0.004	0.422
73357.00	KIAMICHI RIVER NR BIG CEDAR, OK	127	0.49	-0.020	0.000
73730.00	BIG CREEK AT POLLOCK, LA	118	0.56	-0.010	0.000
81039.00	SOUTH FORK ROCKY CREEK NEAR BRIGGS, TEX.	39	0.85	-0.001	0.475
83779.00	RIO MORA NEAR TERRERO, NM	77	0.79	-0.008	0.000
93529.00	VALLECITO CREEK NEAR BAYFIELD, CO.	113	0.70	-0.020	0.000
94306.00	MOGOLLON CREEK NEAR CLIFF, NM	71	0.62	-0.006	0.004
95083.00	WET BOTTOM CREEK NR CHILDS, ARIZ.	97	0.76	-0.001	0.770
101722.00	RED BUTTE CREEK AT FT. DOUGLAS NR. SLC, UTAH	131	0.67	-0.002	0.251
102449.50	STEPTOE C NR ELY, NV	108	0.92	0.001	0.801
102493.00	S TWIN R NR ROUND MOUNTAIN, NV	104	0.87	0.002	0.045
112645.00	MERCED R AT HAPPY ISLES BRIDGE NR YOSEMITE,CALIF	90	0.62	-0.013	0.008
114755.60	ELDER CREEK NEAR BRANSCOMB, CALIF	124	0.86	-0.003	0.188
120393.00	NORTH FORK QUINAULT R NEAR AMANDA PARK, WASH.	103	0.71	-0.009	0.000
124160.00	HAYDEN CK BELOW N FK, NR HAYDEN LAKE, IDAHO	75	0.89	-0.008	0.010
124473.90	ANDREWS CREEK NEAR MAZAMA, WASH.	82	0.91	-0.025	0.000
130183.00	CACHE CREEK NEAR JACKSON, WYO	152	0.95	0.001	0.138
131695.00	BIG JACKS CREEK NEAR BRUNEAU, ID	61	0.81	0.005	0.239
133315.00	MINAM RIVER AT MINAM,OREG.	100	0.89	-0.016	0.000

cation) that trends in SO_2 emissions to the atmosphere from 1965 to 1980 followed a similar geographical pattern to that described above for trends in sulfate at Bench-Mark stations (fig. 2; see also table 6). Substantial declines in emissions occurred from 1965 to 1980 in the Northeast and northern Midwest while increases occurred in the Southeast and in most States west of the Mississippi. Based on previous literature, it is difficult to construct a comparable nationwide picture of trends in stream and precipitation sulfate concentrations due to the limited number and uneven distribution of sampling sites with adequate record lengths (Bubenick and others, 1983). For the Northeast, however, there are other recent reports of declining stream and precipitation sulfate concentrations from scattered locations (National Research Council, 1983; Peters and others, 1982; Ritter and Brown, 1981; Likens and others, 1980).

TRENDS IN STREAM ALKALINITY

Trends in alkalinity at Bench-Mark stations (fig. 3a) display a geographic pattern that is the approximate inverse of that of sulfate trends: over a broad area from the Southeast to the Northwest, down trends in alkalinity greatly outnumber up trends, while in the Northeast, alkalinity trends are consistently up. The inverse relation with sulfate trends is somewhat stronger among stations with low average alkalinity (dark symbols in fig. 3a) although a number of important exceptions to the pattern exist (for example, stations in South

Carolina and Minnesota). On average, alkalinity trend slopes are of the same order of magnitude as sulfate trend slopes (see tables 2 and 3), but may differ considerably in magnitude from sulfate trends in a station-by-station comparison.

An inverse relationship between sulfate and alkalinity is expected if the sulfate represents the introduction of sulfuric acid to the stream system and if that acid acts to reduce stream alkalinity rather than to dissolve minerals in the stream basin (Burns and others, 1981; Kramer and Tessier, 1982). To the extent the acid reacts with rock and soil, however, it is not available to reduce stream alkalinity. Also, because alkalinity itself occurs as a result of mineral dissolution, it follows that an inverse relationship between trends in sulfate and alkalinity will be strongest in low alkalinity waters. In fact, in basins characterized by carbonate weathering (and very high alkalinity) the introduction of strong acid may result in an increase in alkalinity (Kilham, 1982).

Several investigators (Burns and others, 1981; Kramer and Tessier, 1982) have suggested using the ratio of alkalinity to major cation concentrations as an index of acidification of surface waters in order to overcome the confounding alternative effects of acidification in different basins (that is, a loss of alkalinity versus an increase in mineral dissolution). The ratio can only decrease (slowly in the presence of carbonate minerals in the drainage basin, more rapidly in their absence) as a result of an increased acid input to the system.

In accordance with the above theory, trends in the ratio of alkalinity to total major cation concentration (sum of sodium, potassium, calcium, and magnesium) at Bench-Mark stations (fig. 3b; see also table 4) follow a more consistent inverse relation to sulfate trends than do alkalinity trends: declining values have occurred over a broad region extending from the Mississippi Valley westward, while rising values have occurred at most eastern stations as far south as South Carolina.

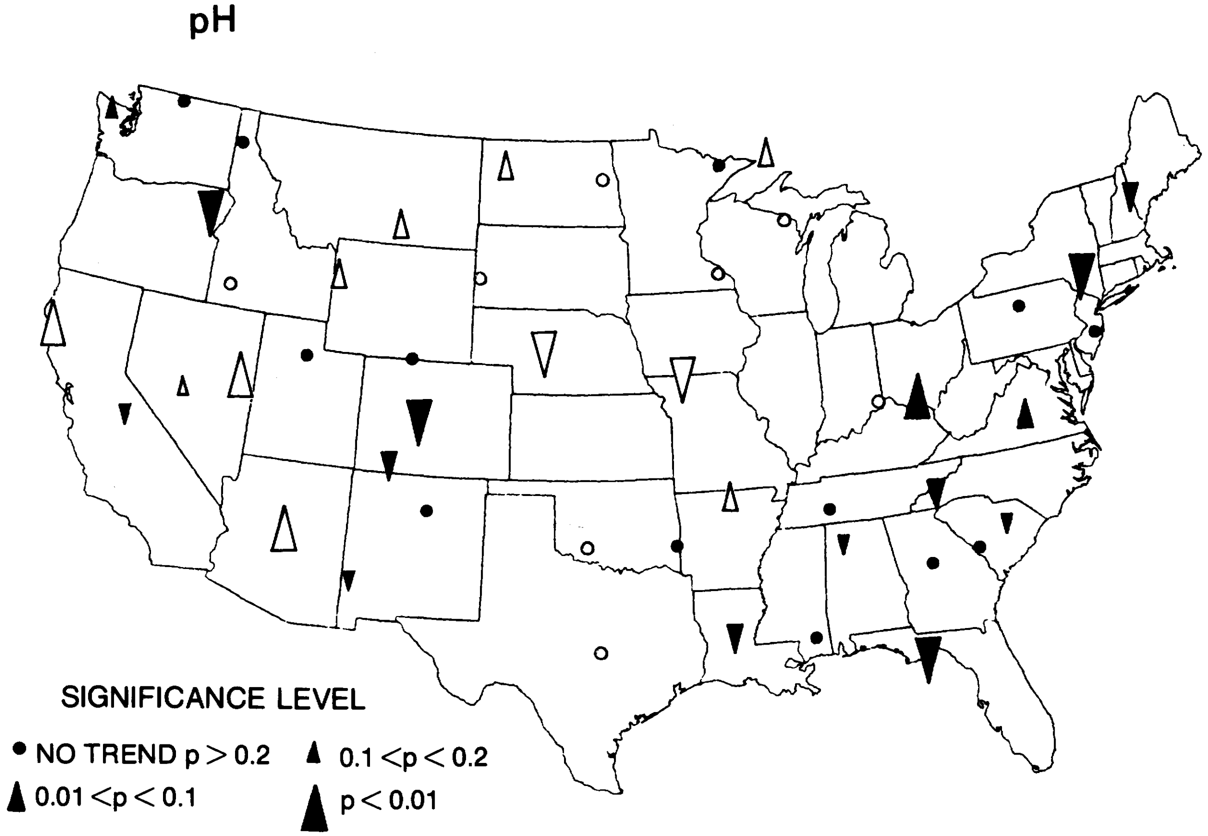

Figure 4.—Trends in pH at Bench-Mark stations for the period of record through 1981. Symbols indicate direction and significance level of trends. Dark symbols indicate stations with mean alkalinity less than 1 meq L^{-1}.

TABLE 5.—*Summary statistics for pH at Bench-Mark stations, for the period of record through 1981*

STATION NUMBER	STATION NAME AND LOCATION	NUMBER OF SAMPLES	MEAN (std. units)	TREND SLOPE (std. units yr^{-1})	SIGNIFICANCE LEVEL (p)
10542.00	WILD RIVER AT GILEAD, ME	60	6.5	-0.03	0.011
13621.98	ESOPUS CREEK AT SHANDAKEN, NY	86	6.8	-0.08	0.001
14665.00	MCDONALDS B IN LEBANON STATE FOREST, NJ	43	4.2	-0.02	0.320
15456.00	YOUNG WOMANS CREEK NEAR RENOVO, PA.	119	6.8	-0.01	0.217
20388.50	HOLIDAY CREEK NEAR ANDERSONVILLE, VA.	57	6.8	0.03	0.034
21353.00	SCAPE ORE SWAMP NEAR BISHOPVILLE, SC	129	5.6	-0.01	0.116
21973.00	UPPER THREE RUNS NEAR NEW ELLENTON, SC	81	6.0	-0.01	0.480
22126.00	FALLING CREEK NEAR JULIETTE, GA.	104	7.0	0.01	0.500
23271.00	SOPCHOPPY RIVER NR SOPCHOPPY, FLA.	112	5.2	-0.04	0.003
24502.50	SIPSEY FORK NEAR GRAYSON, AL	65	7.2	-0.02	0.187
24791.55	CYPRESS CREEK NR JANICE, MS.	42	6.1	0.04	0.274
32372.80	UPPER TWIN CREEK AT MCGAW, OH	109	6.8	0.04	0.002
32767.00	SOUTH HOGAN CREEK NEAR DILLSBORO, IND.	84	7.9	0.01	0.360
34600.00	CATALOOCHEE CREEK NEAR CATALOOCHEE, NC	78	7.0	-0.04	0.059
36040.00	BUFFALO RIVER NEAR FLAT WOODS, TENN.	50	7.2	-0.01	0.778
40010.00	WASHINGTON CREEK AT WINDIGO, MICH.	47	7.4	0.03	0.060
40637.00	POPPLE RIVER NEAR FENCE, WI	120	7.4	0.01	0.398
50649.00	BEAVER CREEK NR FINLEY, ND	63	8.1	0.00	1.000
51244.80	KAWISHIWI RIVER NEAR ELY, MN	28	7.2	-0.00	1.000
53760.00	NORTH FORK WHITEWATER RIVER NEAR ELBA, MN	106	8.1	-0.00	0.598
62882.00	BEAUVAIS CREEK NEAR ST. XAVIER, MT.	74	8.0	0.04	0.028
63325.15	BEAR DEN CREEK NR MANDAREE, ND	115	8.4	0.01	0.053
64090.00	CASTLE CR ABOVE DEERFIELD RES NEAR HILL CITY, SD	134	8.3	-0.00	0.573
66238.00	ENCAMPMENT RIV AB HOG PARK CR NR ENCAMPMENT, WYO	95	7.4	0.01	0.696
67759.00	DISMAL RIVER NR THEDFORD, NEBR	78	7.7	-0.04	0.000
68979.50	ELK CREEK NEAR DECATUR CITY, IOWA	105	8.0	-0.03	0.003
70607.10	NORTH SYLAMORE CREEK NEAR FIFTY SIX, ARK.	123	8.0	0.02	0.015
70830.00	HALFMOON CREEK NEAR MALTA, CO.	109	7.4	-0.06	0.000
73112.00	BLUE BEAVER CREEK NR CACHE, OK	20	7.2	-0.01	0.837
73357.00	KIAMICHI RIVER NR BIG CEDAR, OK	93	7.1	0.01	0.307
73730.00	BIG CREEK AT POLLOCK, LA	78	6.4	-0.07	0.033
81039.00	SOUTH FORK ROCKY CREEK NEAR BRIGGS, TEX.	37	7.7	0.02	0.623
83779.00	RIO MORA NEAR TERRERO, NM	77	7.9	-0.00	0.597
93529.00	VALLECITO CREEK NEAR BAYFIELD, CO.	101	7.7	-0.05	0.041
94306.00	MOGOLLON CREEK NEAR CLIFF, NM	67	7.8	-0.03	0.149
95083.00	WET BOTTOM CREEK NR CHILDS, ARIZ.	74	7.8	0.11	0.000
101722.00	RED BUTTE CREEK AT FT. DOUGLAS NR. SLC, UTAH	101	8.2	0.01	0.234
102449.50	STEPTOE C NR ELY, NV	77	8.4	0.03	0.000
102493.00	S TWIN R NR ROUND MOUNTAIN, NV	87	8.0	0.01	0.178
112645.00	MERCED R AT HAPPY ISLES BRIDGE NR YOSEMITE,CALIF	75	6.7	-0.05	0.102
114755.60	ELDER CREEK NEAR BRANSCOMB, CALIF	106	7.7	0.03	0.008
120393.00	NORTH FORK QUINAULT R NEAR AMANDA PARK, WASH.	72	7.2	0.03	0.153
124160.00	HAYDEN CK BELOW N FK, NR HAYDEN LAKE, IDAHO	52	7.2	0.01	0.502
124473.90	ANDREWS CREEK NEAR MAZAMA, WASH.	80	7.6	-0.02	0.314
130183.00	CACHE CREEK NEAR JACKSON, WYO	137	8.3	0.01	0.027
131695.00	BIG JACKS CREEK NEAR BRUNEAU, ID	30	8.1	0.03	0.681
133315.00	MINAM RIVER AT MINAM,OREG.	60	7.3	-0.06	0.008

TRENDS IN STREAM pH

Trends in pH at Bench-Mark stations (fig. 4; see also table 5) do not follow a clear regional pattern and are only partly consistent with trends in sulfate and alkalinity. Approximately equal numbers of increasing and decreasing trends in pH have occurred nationally with down trends occurring much more frequently than up trends at low alkalinity stations (shaded symbols). An important divergence from the geographical pattern evident in figures 2 and 3 is that stations in New York and Maine show down trends in pH despite the fact that sulfate and alkalinity trends in those states suggest a slight lessening of acidification.

Several possible explanations for the apparent inconsistencies between trends in pH and the other major ions are worth noting. First, pH records at Bench-Mark stations are somewhat shorter than records for the other major ions (compare figs. 1a and 1b) and in some basins do not not cover periods when significant changes occurred in the other constituents. Second, alkalinities at most Bench-Mark stations (fig. 3a) are high enough to provide considerable resistance to changes in pH; the sulfate changes reported here are mostly small (see above) and would not be expected to cause significant changes in pH at the prevailing alkalinities of many stations. Third, the lack of comparable nitrate records makes it difficult to evaluate the role of atmospheric nitrogen in acid deposition at these stations. Precipitation data from Hubbard Brook, New Hampshire (Likens and others, 1980) show an increase in nitrate from 1964 until the early 1970's, followed by a leveling off or slight decline since that time. Pre-

TABLE 6.—*SO_2 emissions by state for period of record 1965–1980. Data are recent revisions of SO_2 emissions presented in Rivers and Riegal, 1982 (G. Gschwandtner and K. Gschwandtner, Pacific Environmental Services, Durham, NC, written communicatin, 1983).*

STATE	YEAR (1000 tons)				
	1965	1970	1975	1978	1980
Alabama	897	869	1055	718	738
Arizona	1829	2211	1393	869	779
Arkansas	13	22	57	113	79
California	293	485	314	343	404
Colorado	95	69	95	128	144
Connecticut	300	281	94	108	87
Delaware	104	73	51	57	96
D.C.	50	124	33	17	7
Florida	358	500	655	651	832
Georgia	295	381	637	676	792
Idaho	24	12	18	20	16
Illinois	2567	2520	2135	1625	1625
Indiana	2115	1985	2026	1807	2135
Iowa	408	368	303	386	328
Kansas	75	113	276	283	345
Kentucky	894	1325	1356	1375	1328
Louisiana	29	41	102	194	288
Maine	54	72	62	59	50
Maryland	532	440	281	303	337
Massachusetts	452	552	267	392	338
Michigan	1678	1595	1465	1078	884
Minnesota	307	383	284	239	221
Mississippi	8	51	139	250	205
Missouri	595	796	1229	1224	1265
Monatana	270	264	199	232	168
Nebraska	72	74	48	75	65
Nevada	204	304	263	54	62
New Hampshire	40	94	80	67	94
New Jersey	607	532	275	271	307
New Mexico	218	412	379	403	501
New York	1584	1378	1039	983	900
North Carolina	331	539	532	555	551
North Dakota	36	48	62	98	137
Ohio	3173	3182	3180	2882	2878
Oklahoma	35	19	24	54	103
Oregon	40	49	40	42	53
Pennsylvannia	2514	2319	2020	1926	2259
Rhode Island	43	59	24	21	13
South Carolina	128	197	199	293	309
South Dakota	20	62	40	56	47
Tennessee	768	1024	1453	1176	1173
Texas	144	113	342	580	765
Utah	308	237	222	343	316
Vermont	10	12	6	9	6
Virginia	409	463	345	335	288
Washington	64	78	105	171	173
West Virginia	882	955	1440	1219	1173
Wisconsin	680	879	665	969	640
Wyoming	64	56	102	161	229

cipitation pH at the same site has varied considerably since 1964 but has shown no clear trend over the period.

SUMMARY

Water-quality records collected over a 10–15-year period from the Hydrologic Bench-Mark Network, a nationwide network of sampling stations in predominantly undeveloped stream basins, show small declines in stream sulfate at stations in the northeastern quarter of the Nation and small increases in sulfate at a number of southeastern and western sites. Stream sulfate concentrations at most Bench-Mark stations are low enough to be significantly influenced by changes in the rate of atmospheric deposition of sulfur. The geographic pattern of trends in atmospheric SO_2 emissions from 1965 to 1980 approximately coincides with the pattern of sulfate trends at Bench-Mark stations, and tends to support the hypothesis that the stream sulfate trends reflect regional trends in sulfur deposition rates.

Trends in stream alkalinity at Bench-Mark stations follow a regional pattern that is the approximate inverse of that of the sulfate trends: small increases have occurred at most stations in the Northeast and small decreases have occurred at many stations in the South and West. The inverse relationship is strongest at stations with relatively low mean alkalinity (< 1 meq L^{-1}).

The ratio of stream alkalinity to the total major cation concentration can be used as an index of the geochemical effects of acidification in a stream basin because of the tendency of that ratio to decrease in response to increased acid inputs even in cases where the acid acts to dissolve minerals in the basin rather than reduce stream alkalinity. Accordingly, trends in the ratio of alkalinity to total major cation concentration at Bench-Mark stations follow a more consistent inverse relation to sulfate trends than do alkalinity trends: declining values have occurred over a broad region extending from the Mississippi Valley westward, while rising values have occurred at most eastern stations as far south as South Carolina.

Trends in pH at Bench-Mark stations do not follow a clear regional pattern and are only partly consistent with trends in sulfate and alkalinity. Several factors make a strong relationship between pH trends and sulfate trends unlikely, however. These include shorter record lengths for pH data, possible conflicting effects of the nitrogen component of acid deposition, and sufficient alkalinity in many basins to resist significant changes in pH.

Despite inconsistencies at individual stations, on a broad regional basis the data presented in this report show a consistent relationship between trends in SO_2 emissions and trends in stream sulfate, alkalinity, and the ratio of alkalinity to the total major cation concentration.

In the northeastern quarter of the country, SO_2 emissions have decreased over the past 15 years and the trends in the cited chemical characteristics of Bench-Mark streams are consistent with a hypothesis of decreased acid deposition in that region. Throughout much of the remainder of the country, SO_2 emissions have increased and trends in stream sulfate, alkalinity, and alkalinity/total cation ratios are consistent with a hypothesis of increased acid deposition.

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