TREND ANALYSIS OF SULFATE, NITRATE AND pH DATA COLLECTED AT NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK STATIONS BETWEEN 1980 AND 1991

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U.S. GEOLOGICAL SURVEY

Open-File Report 93-56

Reston, Virginia

1993

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ABSTRACT

Data from 33 National Atmospheric Deposition Program/National Trends Network stations were analyzed for trends in concentration of sulfate, nitrate and pH in precipitation using data from 1980 through 1991. A regression analysis of the data was performed to determine and remove seasonality and collector volume effects. A Kendall's tau statistical test was then used to identify trends in the regression residuals. Results of analyses indicate downward trends in sulfate concentrations at 26 stations between 1980 and 1991. Slight downward trends in nitrate concentrations as well as upward trends in pH were also observed.

INTRODUCTION

This report summarizes results from a statistical analysis of trends in wet atmospheric deposition data at 33 National Atmospheric Deposition Program/National Trends Network (NADP/NTN) stations from 1980 to 1991. The stations were identified as meeting selection criteria established by the NADP for calculating annual statistics for concentrations and deposition of chemical constituents [NADP/NTN, 1991]. Sulfate, nitrate and pH data were analyzed using a modified Kendall's tau procedure [Schertz and Hirsch, 1985].

TREND ANALYSIS OF SULFATE, NITRATE CONCENTRATIONS AND pH IN PRECIPITATION

Data Sources

Wet atmospheric deposition data were collected as part of the NADP/NTN program using protocols documented in [NADP/NTN, 1991]. This program provides weekly observations of precipitation chemistry at approximately 200 sites across the Nation. Thirty three of the stations having the most complete and longest period of record were selected for analysis. These sites, however, do not necessarily represent a random sample of atmospheric deposition throughout the

Nation. Therefore, caution should be used when drawing inferences about National trends from this sample.

A general outline of the sampling and analysis procedures taken from the 1990 NADP/NTN Annual Data Summary follows. An Aerochem Metrics[1] Wet/Dry Precipitation Collector and a Belfort 5-780 Universal Rain Gage were installed at each station. The Aerochem collector, equipped with two 13-liter polyethylene buckets, collects cumulative weekly samples of precipitation. One bucket is covered only during precipitation events. The other bucket, the "wet-side" bucket, is covered only during non-precipitation events. The Belfort Rain Gage, equipped with an event pen, simultaneously collects an independent precipitation measurement. Once a week the "wet-side" bucket is removed and sent to the Central Analytical Laboratory, Champaign, Illinois for chemical analysis. The collector volume (volume of water in the bucket) is also recorded. Analysis for sulfate (SO_4) and nitrate (NO_3) is conducted using Ion Chromatography with a detection limit of 0.03 mg/L for both. The Electrometric method is used to measure pH. An independent quality-assurance program is used to verify the precision and accuracy of the data. The data collected at a station must meet four completeness criteria before that station will be included in NADP/NTN Annual Data Summary tables.

Data Editing

Fewer than one percent of the collector volumes were reported as missing values. For this analysis, missing collector volumes at a station were replaced by that station's average observed collector volumes for all valid samples between 1980 and 1991. Generally, this should preserve the total volume of annual precipitation. Samples taken during weeks without precipitation (that is, reporting zero collector volume) presumably correspond to dry deposition. These samples were excluded from this wet-deposition analysis.

In addition to collector volumes, some concentrations of NO_3 and SO_4 were reported as missing. Missing concentration values were discarded from the data set prior to analysis.

Concentrations of NO_3 and SO_4 reported as below the analytical detection limits were replaced with estimated values obtained through a modified expectation-maximization (EM) algorithm [Dempster and others, 1977].

Statistical Methods

After editing the data set, each station contained approximately 600 observations for each analyte. These data were analyzed statistically, without modification, for trends. However, inspection of the data indicated both seasonality and dependence on collector volume. Removal of seasonality and dilution effects is desirable because these factors can obscure trends in the data.

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1 The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U. S. Geological Survey.

Using the approach of Schertz and Hirsch [1985], the linear model shown below was fitted to the natural logarithms of sulfate and nitrate data:

$$\ln[C] = \beta_0 + \beta_1 \ln[V] + \beta_2 \sin(2\pi t) + \beta_3 \cos(2\pi t) + \varepsilon \quad (1)$$

where

V	=	collector volume, in liters,
C	=	analyte concentration, in milligrams per liter,
t	=	time, measured in years from 1980,
β_0, β_1, β_2 and β_3	=	model parameters, and
ε	=	residual error

This model removes much of the collector-volume and seasonality effects [Schertz and Hirsch, 1985; Cohn and others, 1992]. The same model was fitted to pH data without logarithmic transformation of pH data.

The Kendall's tau statistical procedure [Hirsch and others, 1991; Hirsch and Gilroy, 1985; Hirsch and others, 1982] was then used to identify trends in the regression's residuals. Sen's slope estimator was used to estimate the direction and magnitude of the observed trends [Helsel and Hirsch, 1992].

Results of Trend Analysis

Table 1 presents the Kendall's tau results from the sulfate, nitrate and pH models. The first four columns identify the station and state. Columns five and six report the trend slope in percent per year and the corresponding p-value for sulfate. Columns seven and eight report the same information for nitrate; with columns nine and ten reporting pH. For pH the trend slope is reported in pH units per year.

Table 2 uses the same format as Table 1 to present Kendall's tau results from the analysis of the analyte concentration data without seasonal or volume adjustment. The two methods yield nearly-identical trend estimates. Thus the adjustments for collector volume and seasonality appear not to have induced the trends observed in Table 1.

The information shown in Table 1 is illustrated in Figures 1-6. Figure 1 depicts the p-values and directions (appearing in Table 1) corresponding to the trends observed in residuals of the sulfate concentration model. The location of the arrows on the map correspond to the station location. Figure 2 portrays the magnitude of trends at each site. Figure 3 and Figure 4 present the corresponding information for the residuals of the nitrate concentration model. Figures 5 and 6 correspond to residuals from the pH model.

CONCLUSIONS

A trend analysis was conducted on the residuals of a linear model fit to atmospheric deposition data from 33 sites across the United States. The results indicate substantial and statistically-significant ($p = 0.05$) downward trends in sulfate at 26 of the 33 stations. Results for nitrate indicate significant downward

trends at 3 stations. Significant upward trends in pH were observed at nine stations, and a significant downward trend was observed at one station. Collectively, the trends suggest a decrease in precipitation acidity between 1980 and 1991.

Table 1.--Kendall's tau and Sen's Estimates of Trends in Model Residuals at Selected Sites, 1980-1991.

[p, attained level of significance; %, percent per year; pH, units per year]

Site	NAPAP Number	State	Station Name	SO_4		NO_3		pH	
				Trend	p-value	Trend	p-value	Trend	p-value
1	054540	CA	Hopland	-6.78%	0.000	-0.70%	0.633	0.000	0.959
2	058840	CA	Davis	-0.20%	0.872	0.16%	0.921	0.030	0.000
3	061560	CO	Sand Spring	-6.21%	0.000	0.81%	0.470	0.021	0.016
4	062120	CO	Manitou	-5.11%	0.000	-0.22%	0.864	-0.004	0.532
5	062220	CO	Pawnee	-7.41%	0.000	-1.49%	0.241	0.038	0.000
6	100360	FL	Bradford Forest	-2.07%	0.041	0.82%	0.458	-0.015	0.023
7	114140	GA	Georgia Station	-3.55%	0.001	-1.47%	0.169	-0.005	0.402
8	141160	IL	Bondville	-1.72%	0.015	-1.52%	0.066	0.003	0.459
9	143580	IL	Southern Illinois Univ.	-3.46%	0.000	-0.57%	0.536	0.007	0.157
10	146340	IL	Dixon Springs	-1.95%	0.011	-0.58%	0.527	0.003	0.501
11	200935	ME	Greenville Station	-3.22%	0.001	-0.48%	0.681	0.002	0.654
12	230920	MI	Douglas Lake	-3.60%	0.000	-0.54%	0.522	0.009	0.100
13	232660	MI	Kellogg Bio. Station	-2.64%	0.000	-1.22%	0.127	0.011	0.045
14	235340	MI	Wellston	-2.15%	0.008	-0.29%	0.704	0.012	0.018
15	241660	MN	Marcell Exp. Forest	-4.42%	0.000	-1.28%	0.136	0.019	0.026
16	242720	MN	Lamberton	-4.67%	0.000	-0.05%	0.964	0.013	0.133
17	281520	NE	Mead	-3.64%	0.001	-0.29%	0.775	0.025	0.004
18	300240	NH	Hubbard Brook	-1.81%	0.043	-0.71%	0.463	0.004	0.308
19	330860	NY	Aurora Res. Farm	-1.65%	0.033	-1.00%	0.222	0.002	0.588
20	332020	NY	Huntington Wildlife	-2.24%	0.005	-1.81%	0.033	0.006	0.118
21	340320	NC	Lewiston	-4.00%	0.000	-0.90%	0.434	0.005	0.355
22	342500	NC	Coweeta	-2.28%	0.013	-0.99%	0.253	-0.002	0.704
23	343460	NC	Piedmont Res. Station	-2.59%	0.007	-0.28%	0.783	0.006	0.304
24	343560	NC	Clinton Crop Res. Station	-1.86%	0.047	-0.17%	0.871	0.008	0.210
25	344160	NC	Finley Farm	-1.91%	0.052	-1.67%	0.117	0.014	0.018
26	361760	OH	Delaware	0.03%	0.962	0.32%	0.683	0.008	0.040
27	364900	OH	Caldwell	-0.56%	0.339	-0.71%	0.367	0.002	0.610
28	367160	OH	Wooster	-0.42%	0.490	0.15%	0.857	0.006	0.110
29	380200	OR	Alsea Guard Ranger Station	-5.51%	0.000	-0.42%	0.751	-0.007	0.097
30	392940	PA	Kane Exper. Forest	-0.88%	0.194	-0.63%	0.390	-0.002	0.622
31	394200	PA	Leading Ridge	0.18%	0.804	0.97%	0.238	-0.002	0.519
32	501860	WV	Parsons	-1.47%	0.036	-1.71%	0.042	0.001	0.833
33	513640	WI	Trout Lake	-5.40%	0.000	-1.77%	0.043	0.013	0.063

Table 2.--Kendall's tau and Sen's Estimates of Trends in Analyte Concentrations at Selected Sites, 1980-1991.

[p, attained level of significance; %, percent per year; pH, units per year]

Site	NAPAP Number	State	Station Name	SO_4		NO_3		pH	
				Trend	p-value	Trend	p-value	Trend	p-value
1	054540	CA	Hopland	-6.37%	0.000	0.00%	0.766	0.000	0.956
2	058840	CA	Davis	0.00%	0.570	0.00%	0.455	0.029	0.000
3	061560	CO	Sand Spring	-5.25%	0.000	1.46%	0.188	0.020	0.011
4	062120	CO	Manitou	-4.39%	0.000	0.00%	0.671	-0.001	0.668
5	062220	CO	Pawnee	-7.37%	0.000	-1.21%	0.209	0.037	0.000
6	100360	FL	Bradford Forest	-1.11%	0.129	0.74%	0.230	-0.014	0.014
7	114140	GA	Georgia Station	-3.18%	0.002	-1.01%	0.218	-0.005	0.277
8	141160	IL	Bondville	-1.68%	0.018	-1.66%	0.034	0.002	0.431
9	143580	IL	Southern Illinois Univ.	-3.52%	0.000	-0.45%	0.499	0.005	0.200
10	146340	IL	Dixon Springs	-2.15%	0.005	-0.69%	0.324	0.001	0.644
11	200935	ME	Greenville Station	-2.75%	0.007	-0.25%	0.660	0.000	0.725
12	230920	MI	Douglas Lake	-3.82%	0.000	-0.63%	0.292	0.008	0.094
13	232660	MI	Kellogg Bio. Station	-2.80%	0.000	-1.29%	0.068	0.008	0.057
14	235340	MI	Wellston	-2.36%	0.009	-0.21%	0.621	0.012	0.010
15	241660	MN	Marcell Exp. Forest	-4.06%	0.000	-1.05%	0.153	0.018	0.025
16	242720	MN	Lamberton	-4.65%	0.000	0.00%	0.837	0.010	0.193
17	281520	NE	Mead	-3.64%	0.000	0.00%	0.722	0.023	0.009
18	300240	NH	Hubbard Brook	-2.06%	0.045	-0.59%	0.527	0.005	0.215
19	330860	NY	Aurora Res. Farm	-1.57%	0.071	-1.11%	0.176	0.001	0.692
20	332020	NY	Huntington Wildlife	-2.53%	0.005	-1.98%	0.016	0.005	0.135
21	340320	NC	Lewiston	-4.27%	0.000	-1.23%	0.240	0.004	0.437
22	342500	NC	Coweeta	-2.63%	0.004	-1.55%	0.084	0.000	0.688
23	343460	NC	Piedmont Res. Station	-2.85%	0.004	-0.21%	0.701	0.005	0.351
24	343560	NC	Clinton Crop Res. Station	-1.90%	0.027	-0.28%	0.546	0.005	0.236
25	344160	NC	Finley Farm	-1.80%	0.047	-1.56%	0.090	0.014	0.014
26	361760	OH	Delaware	-0.04%	0.816	0.00%	0.967	0.007	0.071
27	364900	OH	Caldwell	-0.77%	0.263	-0.65%	0.397	0.003	0.348
28	367160	OH	Wooster	-0.78%	0.255	0.00%	0.941	0.006	0.065
29	380200	OR	Alsea Guard Ranger Station	-5.25%	0.000	0.00%	0.767	-0.007	0.043
30	392940	PA	Kane Exper. Forest	-0.47%	0.309	-0.09%	0.573	0.000	0.914
31	394200	PA	Leading Ridge	-0.28%	0.748	0.55%	0.516	0.000	0.825
32	501860	WV	Parsons	-1.46%	0.087	-1.67%	0.052	0.000	0.807
33	513640	WI	Trout Lake	-5.68%	0.000	-1.92%	0.021	0.011	0.077

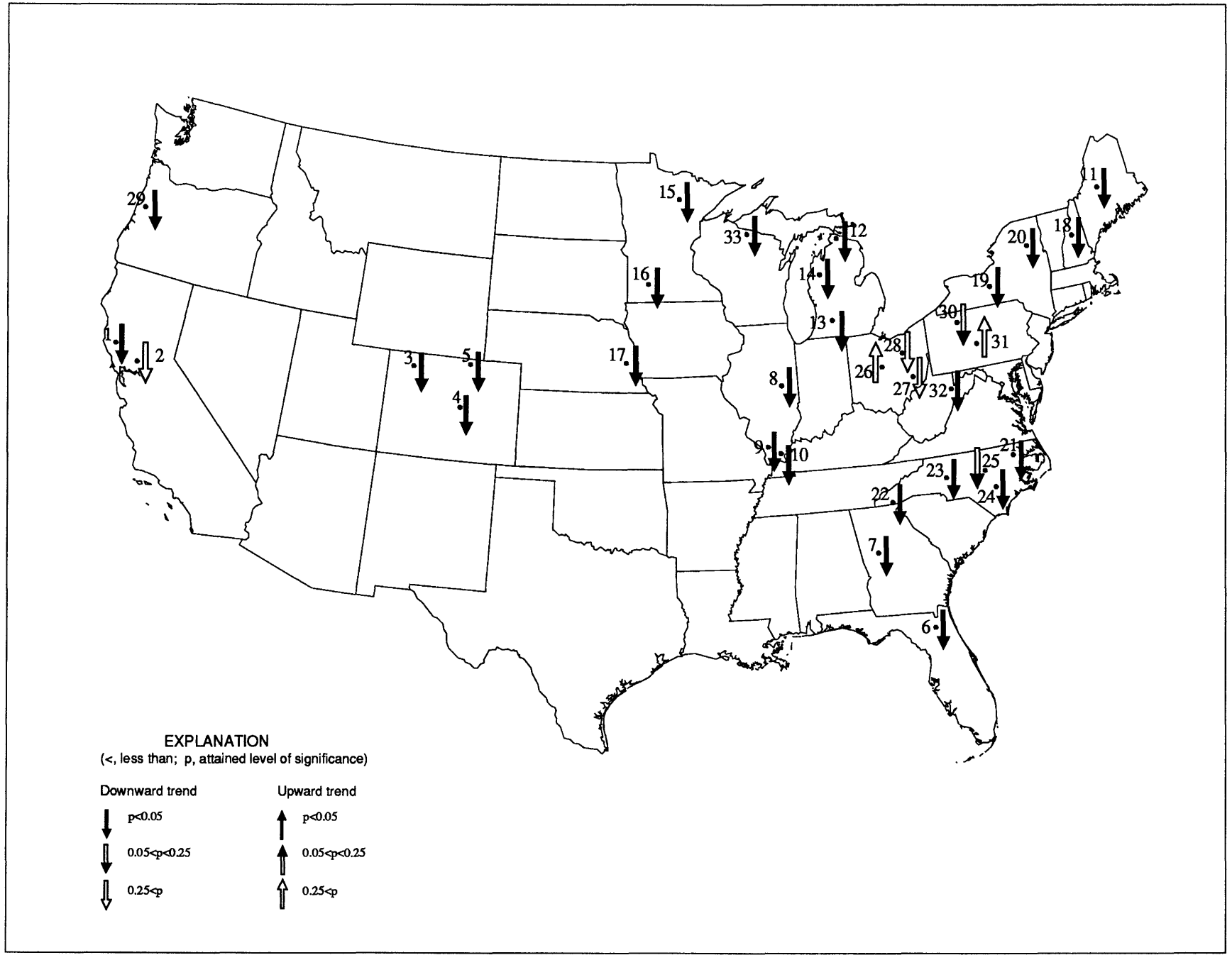

Figure 1: Kendall's tau Estimates of Significance of Trends in Sulfate Concentrations in Precipitation at Selected Sites, 1980-1991

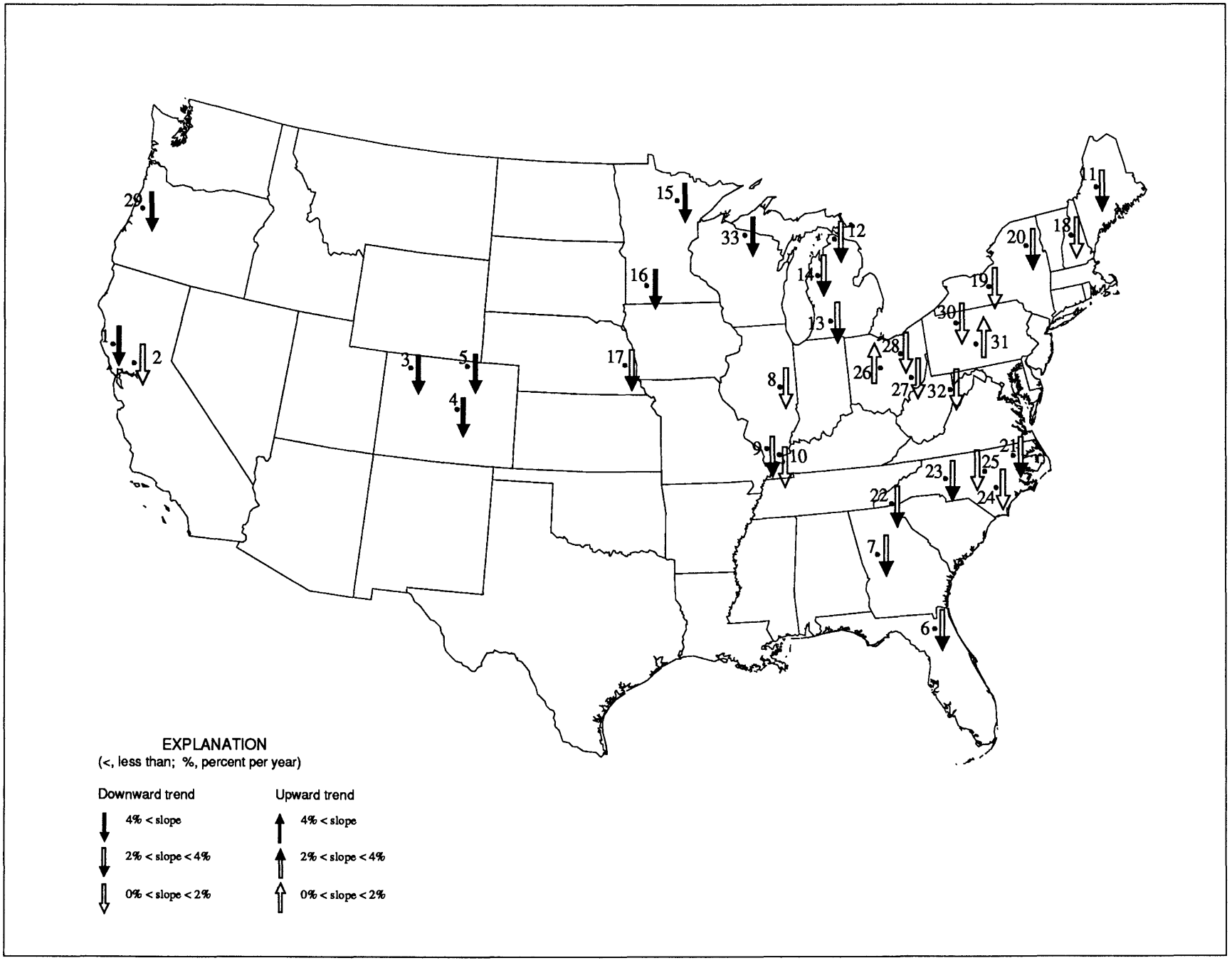

Figure 2: Sen's Estimates of Magnitude of Trends in Sulfate Concentrations in Precipitation at Selected Sites, 1980-1991

Figure 3: Kendall's tau Estimates of Significance of Trends in Nitrate Concentrations in Precipitation at Selected Sites, 1980-1991

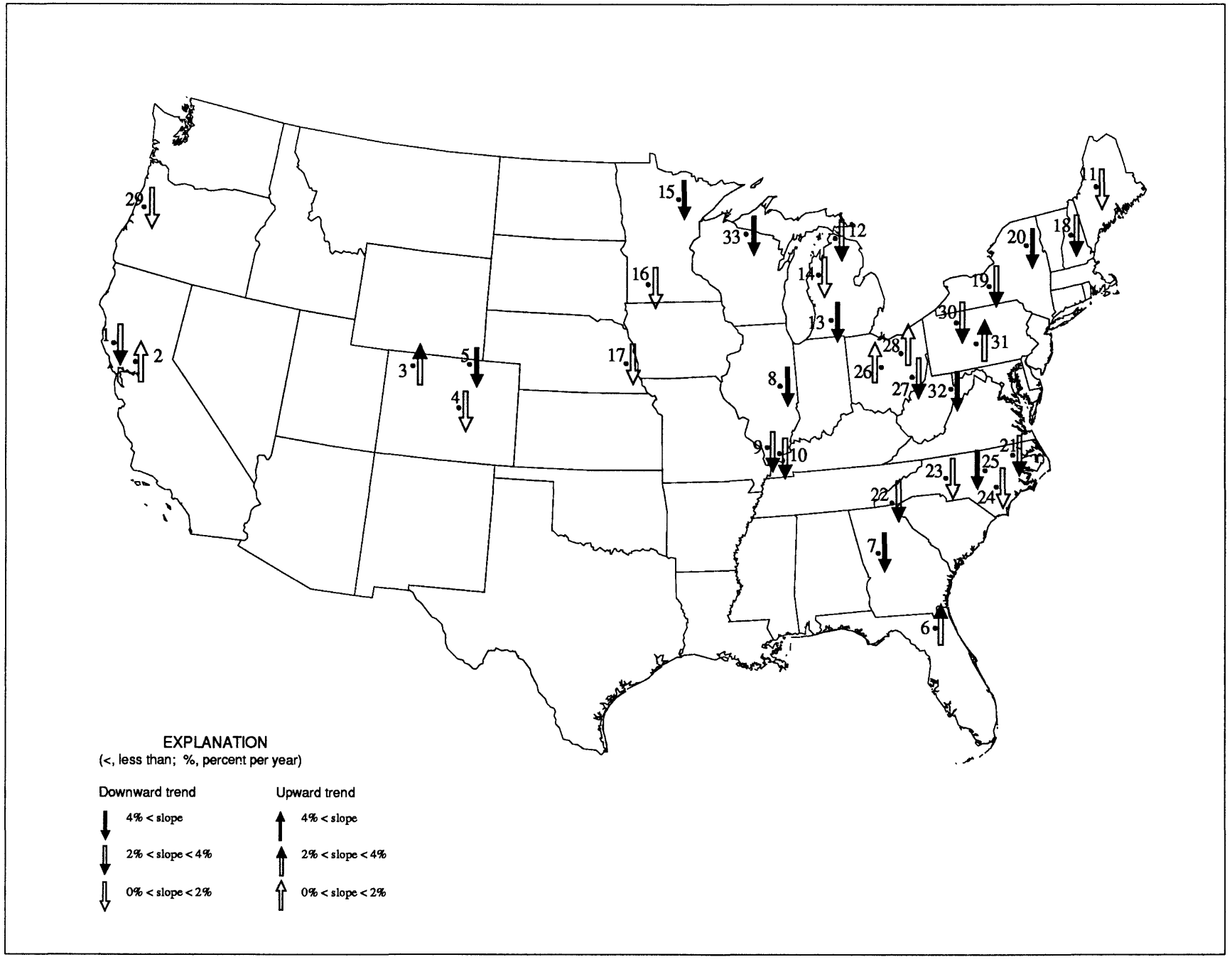

Figure 4: Sen's Estimates of Magnitude of Trends in Nitrate Concentrations in Precipitation at Selected Sites, 1980-1991

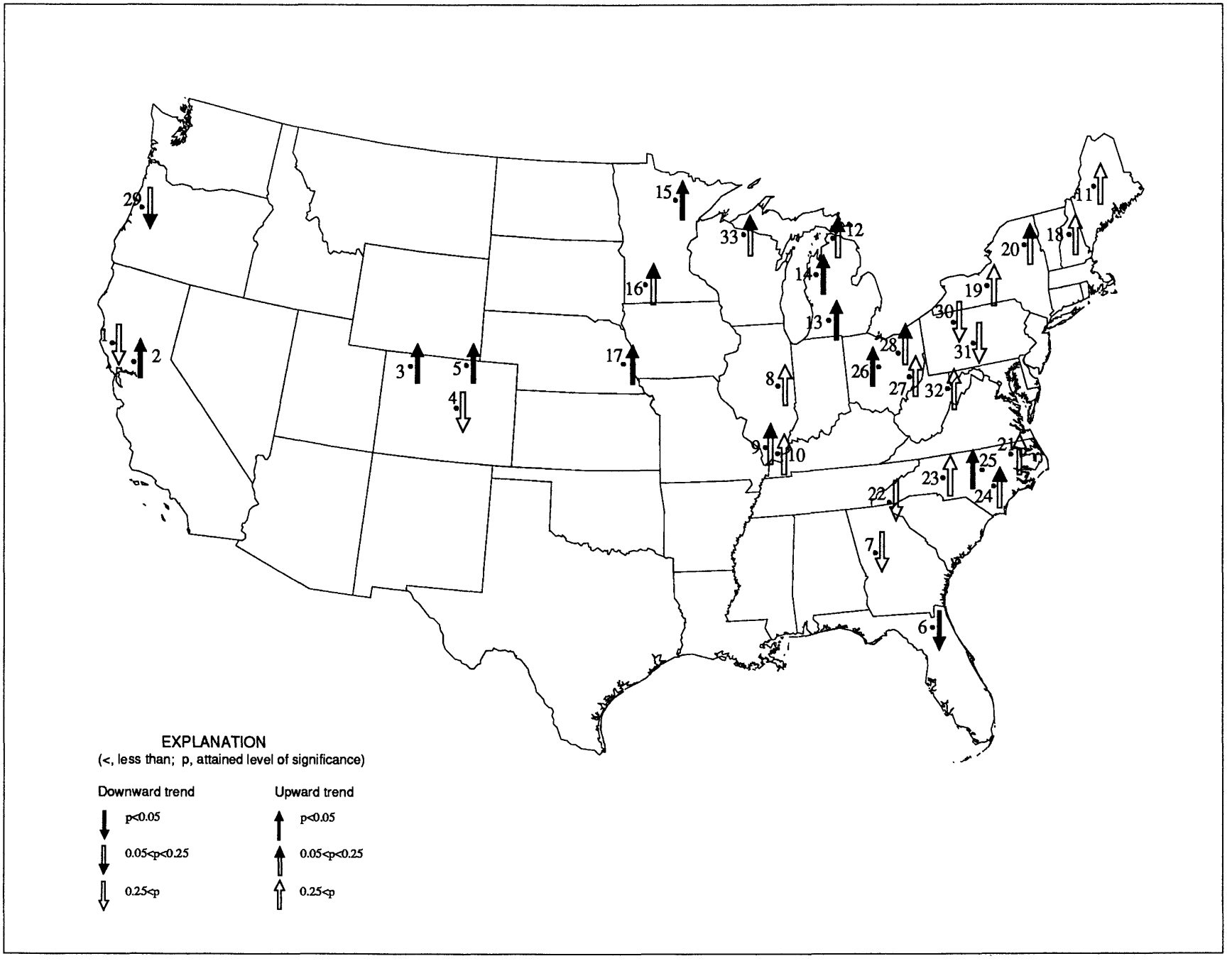

Figure 5: Kendall's tau Estimates of Significance of Trends in pH in Precipitation at Selected Sites, 1980-1991

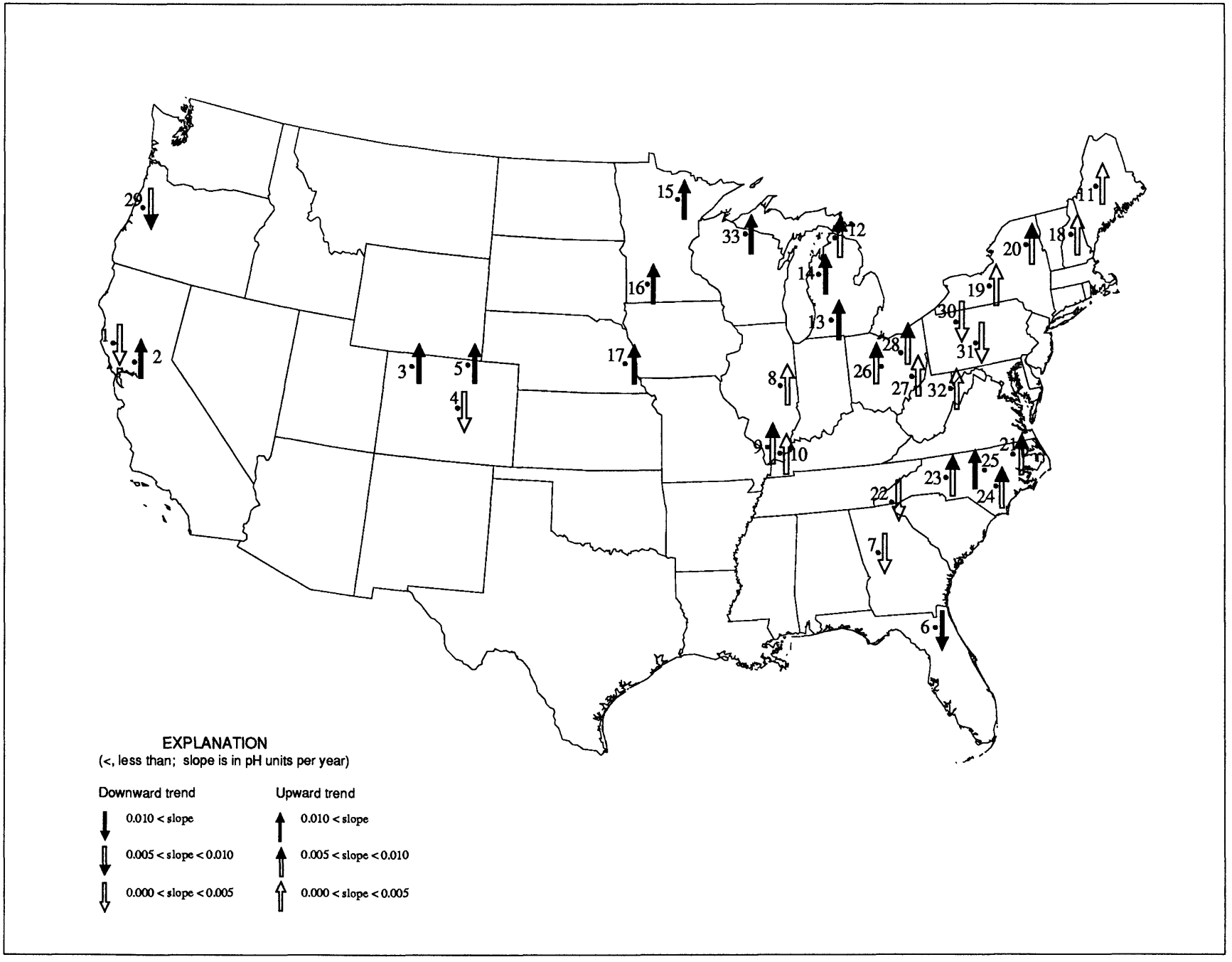

Figure 6: Sen's Estimates of Magnitude of Trends in pH in Precipitation at Selected Sites, 1980-1991

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