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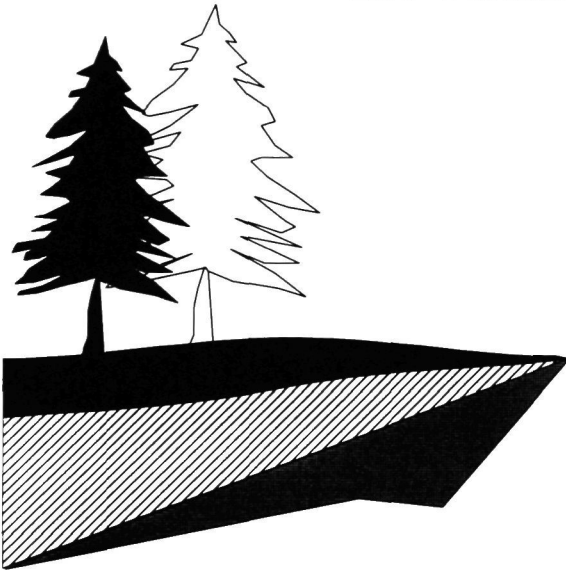
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Precipitation Chemistry at the Greenville, Maine, NADP/NTN Station

1980-1995

Ivan J. Fernandez

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MAINE AGRICULTURAL AND FOREST EXPERIMENT STATION

University of Maine

Precipitation Chemistry at the
Greenville, Maine, NADP/NTN Station

1980-1995

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INTRODUCTION

In 1986 (Fernandez et al.) we reported on the initial years of operation of the Greenville, Maine, National Atmospheric Program/National Trends Network (NADP/NTN) precipitation monitoring site. This site is one of the oldest sites in a national network designed to provide high-quality measurements of precipitation chemistry and volume throughout the United States. Figure 1 shows the location across the nation of approximately 200 sites in the network. The NADP/NTN national monitoring program has now served for more than 15 years providing critical information for both the regulatory and scientific communities. This document reports on 15 years of precipitation characteristics at the Greenville, Maine, site (Figure 1).

The motivation for the establishment of this national program of precipitation monitoring originated with the need to understand the characteristics and changes over time of "acid rain." Although we know much more today about the effects of atmospheric deposition, and some of the precipitation chemistry is improving, significant concern remains over the long-term effects of a changing chemical and physical climate.

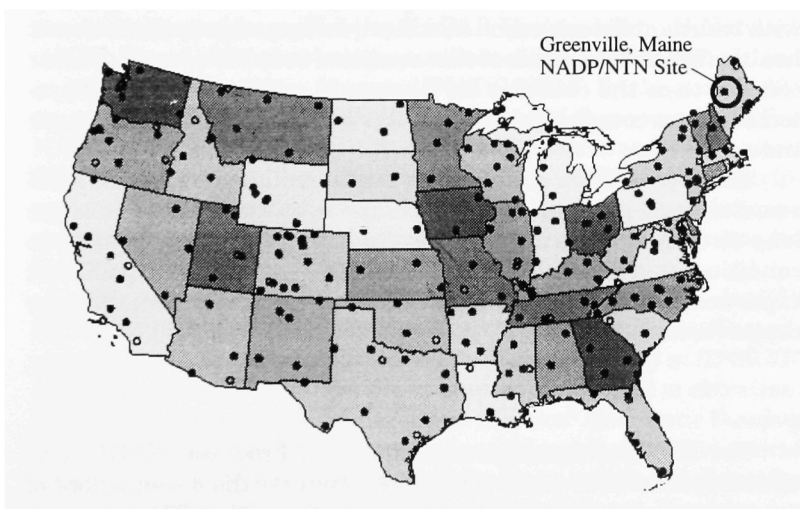


Figure 1. Location of sites in the National Atmospheric Deposition Program/National Trends Network.

Researchers in Maine continue to play a key role in evaluating the effects of inputs of chronically acidic precipitation to ecosystems. One of the long-standing concerns has been for the acidification of soils and the loss of base cations (Falkengren-Grerup et al. 1987; Fernandez 1989; Johnson and Fernandez 1992). Although we know much more about how this process occurs, we also have learned that some of the changes that take place are subtle, complex, and occur over long periods of time. One particular concern is the possible consequences for forest health of an imbalance between calcium (Ca) and aluminum (Al) in the soil (Bondietti et al. 1990; Cronan and Grigal 1995; Lawrence et al. 1995; Shortle and Smith 1988). Studies of experimental acidification have shown how some of these processes work in soils (Fernandez and Rustad 1990; Rustad et al. 1993), or at whole watershed scales (Norton et al. 1994; Kahl et al. 1993). Changes in the terrestrial ecosystem are commonly reflected in the chemical characteristics of associated surface waters (Kahl et al. 1991). Although sulfur (S) has been best known as a cause of acidic deposition, in the past decade it has become clear that nitrogen (N) is just as important and potentially more of an environmental concern. Aber et al. (1989) and others have described the mechanisms and consequences for developing "Nitrogen Saturation" in forested ecosystems. This condition results from long-term, chronic atmospheric deposition of N leading to increased losses of nitrate (NO_3) and possibly ammonium (NH_4) with resultant deterioration in water quality and potentially forest health. The development of this condition could be of even greater concern than the concerns for S, since N cycling through ecosystems is more complex than S, and likely to operate on much longer time scales.

The type of high-quality data made available by NADP/NTN remains more important than ever, and even more valuable as the long-term time series unfolds. We present here an overview of those conditions and trends for those interested in atmospheric pollutant exposure or nutrient cycling in Maine's environment whether for research, management, or policy purposes.

METHODOLOGY

The National Atmospheric Deposition Program (NADP) was established in 1978 to provide a focal point for the development of research to address the problem of acidic deposition. The organizational effort was led by the State Agricultural Experiment Stations (SAES) and the U.S. Department of Agriculture (USDA). The goal

was the development of a program of research and monitoring designed to increase our understanding of atmospheric deposition and its effects on agriculture, forests, rangelands, and freshwater streams and lakes. The NADP was initially organized as a regional project of the North Central Region of the SAES (North Central Regional Project NC-141). At that time, the NADP Technical Committee was formed to provide scientific guidance to the program. In 1982 the project was endorsed by all four SAES regions and became Interregional Project IR-7, and in 1992 it was reclassified as a National Research Support Project, NRSP-3.

The first important initiative of the NADP was the establishment of a long-term atmospheric deposition monitoring network. The first deposition monitoring sites were established in July 1978 through the efforts of the SAES and the USDA Cooperative State Research, Education, and Extension Service (CSREES; formerly known as the Cooperative State Research Service [CSRS]). The Illinois State Water survey was selected to provide chemical analyses for network samples and a coordination office was established at Colorado State University. Subsequently, the network experienced rapid growth from 22 monitoring stations at the end of 1978 to 110 stations by the end of 1982. With the initiation of the federal National Acid Precipitation Assessment Program (NAPAP) in 1982, and under the leadership of the U.S. Geological Survey (USGS), additional sites were added to the NADP network to meet the 150-site design goal of the NAPAP National Trends Network (NTN). These NTN sites became a subset of the NADP network, and in 1983 the network was renamed "NADP/NTN". By the end of 1983 there were 143 stations and by the end of 1986 there were 204. The NADP/NTN network has stabilized at approximately 200 sites. This overview, a bibliography of the network publications, descriptions of all sites, and a listing of all the available network data are available on the World Wide Web at <http://uvb.nrel.colostate.edu/NADP/>.

This report details results from the Greenville, Maine, NADP/NTN site supported by the Maine Agricultural and Forest Experiment Station. The site is located in Piscataquis County at 69°39'52" longitude and 45°29'23" latitude at approximately 322 m elevation. The site consists of a single Aerochem Metrics® Automatic Sensing Wet/Dry Precipitation Collector that provides samples for chemical analysis and a Belfort® Recording Rain Gage and Event Recorder for accurate determinations of precipitation volume. Samples are collected every Tuesday morning 52 weeks a year. The collector is a wet-only collector, and thus is not open to the atmosphere

between precipitation events, thereby avoiding contamination by dry deposition contributions to the samples, and evaporative concentration of the solution. As soon as a precipitation event begins, a sensor opens the instrument cover to begin collections. The sensor is heated so that it dries quickly when a precipitation event is over, at which time the cover closes the collector. A small amount of precipitation is not captured at the beginning of each event by the Aerochem Metrics® collector, which is one of the reasons that the Belfort® rain gage is used to provide accurate and complete volume measurements of each event. Precipitation includes rain, snow, sleet, hail, and heavy dew or fog events.

Samples are carefully handled from the moment of collection until they are analyzed. On-site sample processing occurs at the Moosehead Sanitary District laboratory facilities in Greenville, Maine. Samples from the entire network are shipped to the Central Analytical Laboratory (Illinois State Water Survey, Champaign, Illinois) for analysis under rigorous quality control/quality assurance procedures.

Extensive documentation on the site, laboratory, data, and data quality procedures used in this program is available from the network office and referenced in various manuals as well as the web site noted above. The network design is described in Cowling et al. (1977) and Robertson and Wilson (1985). Field operations are described in Bigelow (1982, 1984), Bigelow and Dossett (1984), and Highsmith (1980); laboratory procedures are in Peden et al. (1979, 1986); quality assurance is in Aubertin et al. (1990).

RESULTS AND DISCUSSION

Characteristics of Greenville, Maine, Precipitation

Table 1 shows the complete seasonal and annual precipitation concentration data for 1995 at the Greenville, Maine, NADP/NTN station. This site is often thought to be the site best representing the most northeasterly NADP/NTN station in a forested region not significantly impacted by marine or agricultural influences. Thus, the Greenville Station data are frequently used in regional and national comparisons. An example of this type of use is in Lawrence and Fernandez (1991) where they relied on Greenville Station data to provide a perspective on regional deposition of SO_4 and NO_3 for their discussion of biogeochemical cycling at the Howland Integrated Forest Study site in east-central Maine.

The data in Table 1 show many similar characteristics of precipitation chemistry as those reported in 1986 (Fernandez et al.

Table 1. Seasonal and annual precipitation chemistry at the Greenville, Maine, NADP/NTN site. Means are derived from the volume-weighted weekly precipitation chemistry for 1995.

	Ca	Mg	K	Na	NH ₄ μeq L ⁻¹	NO ₃	Cl	SO ₄	pH	Cond. μS L ⁻¹
Fall	1.65	2.80	0.38	12.48	3.27	8.45	13.99	12.58	4.81	9.80
Winter	0.70	0.33	0.10	1.87	3.38	13.53	2.03	9.27	4.69	9.90
Spring	2.40	0.90	0.23	2.91	6.10	14.02	2.54	16.81	4.65	11.70
Summer	2.40	0.66	0.28	1.78	13.92	14.86	1.55	27.22	4.54	15.90
Annual	1.80	1.48	0.28	6.26	6.04	11.65	6.69	15.48	4.70	11.10

1986). Precipitation anion concentrations are dominated by the strong acid anion SO₄, derived primarily from the oxidation of sulfur dioxide (SO₂) in the atmosphere forming the strong acid sulfuric acid (H₂SO₄), as well as from dry deposition and wash-out contributions of ammonium sulfate ((NH₄)₂SO₄). Evidence for the (NH₄)₂SO₄ contributions is the relatively high concentration of NH₄. Second in abundance to SO₄ is NO₃, derived from atmospheric oxidation of nitrous oxide (NO_x) compounds with the subsequent formation of the strong mineral acid nitric acid (HNO₃). Both SO₂ and NO_x are introduced in to the atmosphere by the combustion of fossil fuels. The sources of these gases are largely industrial facilities and motor vehicles in Maine and from major emission sources throughout the eastern United States and beyond.

The major nutrient cations in precipitation include Ca, Mg, and NH₄ and these provide important sources of nutrients for most terrestrial ecosystems. Precipitation can sometimes be the sole source of these mineral nutrients for unique ecosystems such as ombrotrophic peatlands (Mitsch and Gosselink 1986). The close agreement between the chemical equivalencies of Na and Cl indicate that they are derived from NaCl salts, most likely associated with road salt or marine aerosols. Although we generally assume there is little marine influence in this interior forested region, these data suggest that in the fall of 1995 marine influences were evident in precipitation chemistry. The high Na and Cl in the fall are not likely attributable to road salts, which should be more evident in winter. In addition, the Na/Cl ratio in seawater is approximately 0.86, and the ratio for the fall of 1995 was 0.89 while winter, spring, and summer were 0.92, 1.15 and 1.15, respectively. The closer agreement in the Na/Cl ratio and the higher magnesium (Mg) concentrations in the fall both suggest a marine influence on

precipitation chemistry for this period of the year likely attributable to autumn storms bringing these solutes in from the Atlantic Ocean.

Table 2 shows the depositional flux of the same constituents shown in Table 1. While the quality of precipitation is reflected in the concentration data, the potential effects on the recipient ecosystems are often best revealed by deposition data which shows how much of the potentially acidifying N and S compounds are being introduced to the environment. For example, during a high precipitation or rainy period, concentrations may be low, but actual deposition may be unusually high with consequently greater impacts on sensitive terrestrial and aquatic ecosystems.

Table 2 shows similar patterns as the concentration data in Table 1, with differences caused by the influence of actual precipitation volumes and the differences between calculations of chemical equivalents versus mass. Both NO_3 and SO_4 still dominate the anionic charge in these data, with their numerical importance even greater due to the atomic weight contributions of oxygen (O) to both NO_3 and SO_4 . Because Na and Cl are predominantly derived from NaCl salts, where they occur in a near 1:1 proportion, their concentrations in Table 1 in μeq were closely balanced.

However, because the atomic weight of Na \sim 23 and Cl \sim 35, we expect the mass of Cl to be greater in total deposition calculations, which is evident in Table 2. Both NH_4 and NO_3 in precipitation are sources of inorganic N. Although both N and S cause acid precipitation, they are also essential plant and animal nutrients and form the basic building blocks of proteins. For terrestrial ecosystems throughout the world, N is the most commonly limiting nutrient frequently applied to agronomic, horticultural, and forest crops as fertilizer. With the advent of elevated modern atmospheric deposi-

Table 2. Seasonal and annual precipitation deposition and depth at the Greenville, Maine, NADP/NTN site. Deposition is calculated from weekly concentration and volume data.

	Ca	Mg	K	Na	NH_4 kg ha^{-1}	NO_3	Inorg. N	Cl	SO_4	Precip cm
Fall	0.15	0.16	0.07	1.31	0.27	2.39	0.75	2.26	2.76	46
Winter	0.03	0.01	0.01	0.09	0.13	1.82	0.51	0.16	0.96	22
Spring	0.11	0.03	0.02	0.16	0.26	2.03	0.66	0.21	1.88	23
Summer	0.11	0.02	0.03	0.10	0.59	2.17	0.95	0.13	3.08	24
Annual	0.42	0.21	0.13	1.68	1.27	8.40	2.88	2.76	8.65	116

tion of N, concern now exists for not only the potential acidifying effect of precipitation, but the potential for "nitrogen saturation" to result in degraded forest health and freshwater quality (Aber et al. 1989). While there is no evidence that widespread nitrogen saturation has occurred in the eastern United States, there is some evidence for this modern occurrence in the Adirondack Mountains of New York (Driscoll and van Dreason 1993), and widespread concern for potential future implications of long-term, elevated N deposition.

It is difficult to determine the degree of concern to assign to current levels of N and S deposition in Maine. Although both N and S deposition in Maine are lower than most of the northeastern states east of the Ohio River Valley, chronic deposition of N and S in Maine remains higher than most of the region west of the Mississippi River. One approach to evaluating risk that has been used is the concept of "critical loads" of N or S deposition, used in the United States and particularly in Europe (Brodin and Kuylenstierna 1992; de Vries et al. 1994; Bull et al. 1995; Holdren et al. 1993; Pardo and Driscoll 1996). Critical load has been defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to our present knowledge," (UN/ECE 1988).

Defining a critical load includes determination of the resource or effect of concern (e.g. surface water acidification, soil acidification, forest health decline) and the appropriate method of calculation. Total protection of environmental resources commonly requires such drastic reductions in N and S deposition that "target loads" are determined, which provide achievable reductions in deposition to achieve less than complete prevention of effects. It is likely that the deposition of N and S in Maine exceeds the critical loads for some of the most sensitive resources, but exposure for Maine ecosystems is notably lower than all other northeastern U.S. states. Ongoing research in Maine will provide a scientific basis for future decisions on emissions regulations. We do not evaluate critical and target load concepts for Maine at this time.

Precipitation pH

Table 1 shows mean volume-weighted precipitation pH by season and as an annual average. Solution pH is a measure of the activity, essentially the concentration of the H ion in solution, on the pH scale from 0 to 14; a pH of 7 is neutral. Precipitation pH at Greenville averaged 4.70 in 1995, reflecting the acidic characteris-

tics of these solutions. The low pH reflects the contributions of atmospherically derived HNO_3 and H_2SO_4 . "Clean" precipitation lacking the influence of the strong acid-forming N and S would likely have a pH one full unit higher, with variations around that mid-5 range reflecting differing influences of carbon dioxide (CO_2) and organic or mineral soil aerosols. Because pH is a logarithmic scale of H ion activity, current precipitation in Maine is at least 10 times more acidic than "clean" precipitation, with significant variations around that mean. Although this means that precipitation represents an important additional source of acidity to ecosystems, as well as nutrients, it is also important to note that the natural processes of forest soil formation commonly results in forest soil horizons with pH values between 3 and 4 (Fernandez 1992).

Figure 2 shows a scatter plot for both NO_3 and SO_4 versus pH for the monthly data for 1980 through 1995. The straight lines represent linear regression calculations for both NO_3 and SO_4 , respectively. Both strong acid anions are significantly correlated with precipitation pH, with increasing concentrations of either or both anions resulting in decreasing precipitation pH. The coefficient of determination for the prediction of pH from NO_3 resulted in an $R^2 = 0.47$, suggesting that approximately half of the variation in pH could be predicted by variations in the concentration of NO_3 in precipitation. The regression calculated for SO_4 versus pH was slightly stronger, with an $R^2 = 0.59$. Interestingly, the regression for NO_3 versus SO_4 (not shown) resulted in only an $R^2 = 0.11$, suggesting that both strong acid anions do not exhibit strongly parallel temporal variations and thus are likely to be at least partly attributable to different source terms. Tables 1 and 2 illustrate those temporal differences by showing that the highest and lowest concentration and deposition values for both NO_3 and SO_4 do not occur in the same seasons in 1995.

Figure 3 is a horizontal needle plot of the mean annual 1994 pH for 168 NADP/NTN sites meeting minimum reporting criteria for pH that year in the network (NADP 1996). This figure shows the relative position of the average pH for each of the four NADP/NTN stations in Maine, including that of *Greenville*. Three other NADP/NTN stations occur in Maine: (a) *Caribou*, in Aroostook County, is the most northerly site operated by the National Oceanographic and Atmospheric Administration (NOAA), (b) *Acadia*, located along the Maine coast in Acadia National Park and operated by the National Park Service (NPS) is the most easterly site, and (c) *Bridgton*, located in Cumberland County and operated by the Maine Departmental of Environmental Protection is the most

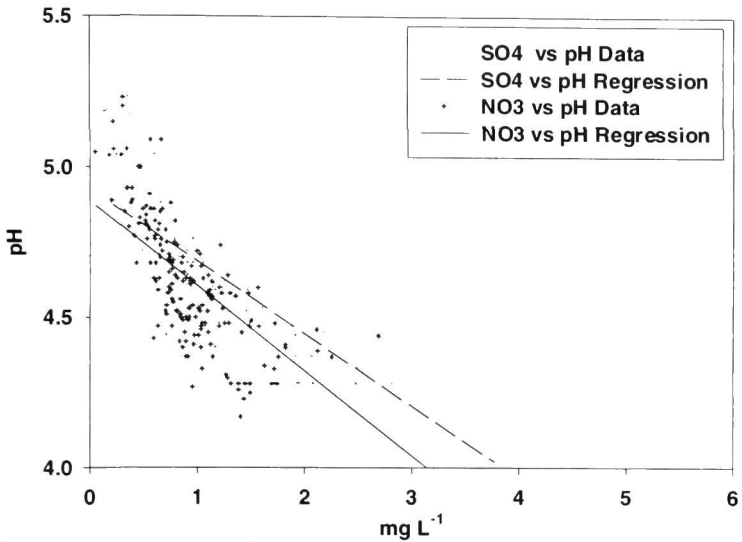


Figure 2. Scatter plot with linear regression lines for the relationship between NO₃ or SO₄ and pH.

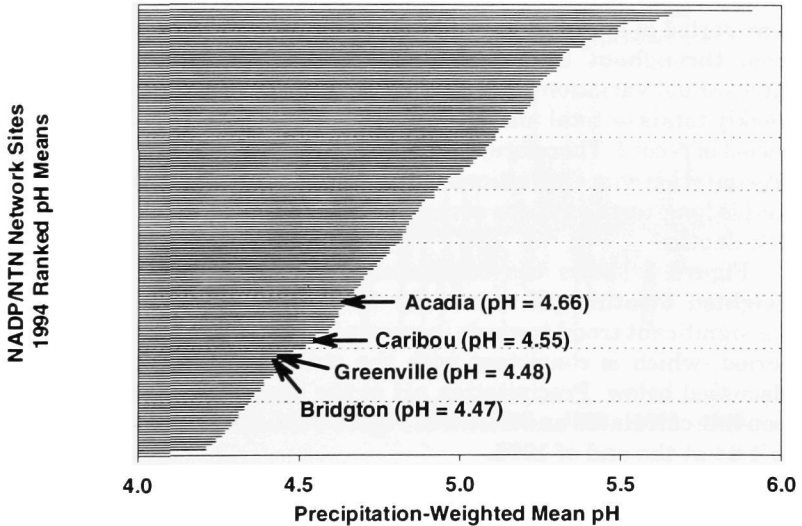


Figure 3. Horizontal needle graph of mean pH for 1994 from all NADP/NTN sites reporting (NADP 1996).

southerly site. Differences among the Maine sites are attributable in part to the alkaline influence of marine aerosols on precipitation pH at Acadia National Park, and agricultural soil and fertilizer aerosols at the Caribou site. Sites with pH levels below the Maine sites are mostly other eastern states, most notably the Northeast and Middle Atlantic region. Likewise, those sites with the highest pH are dominantly west of the Mississippi River, where they are affected either by calcareous aerosol particulate deposition in the drier regions, or are distant from urban sources of fossil fuel combustion. The site with the lowest pH in Figure 3 for 1994 was Caldwell, Ohio, with a pH = 4.10, and the highest was from Davis, California, with a pH = 5.91.

Temporal Patterns of Precipitation Characteristics

One of the most valuable aspects of the data from the Greenville site is the long-term record of precipitation characteristics which was rare prior to the establishment of the NADP network in the late 1970s. Greenville was one of the first stations in the network, and thus we now benefit from 15 years of high-quality data. Figure 4 shows total annual precipitation depths at Greenville from 1980 through 1995. All of the data discussed below will be from this 15-year period of study. Figure 4 also shows individual weekly totals from throughout that period represented by dots. Although interannual variation occurs, no major shifts in the distribution of weekly totals or total annual depths of precipitation occurs in this period of record. Therefore, changes in long-term patterns for other precipitation characteristics over time are not likely attributable to simple long-term patterns of change in weekly or annual precipitation depths.

Figure 5 shows the continuous line plot of mean volume-weighted monthly pH values for the period. There is a slight nonsignificant trend towards increasing pH over the 15-year study period, which is consistent with the patterns in SO_4 deposition discussed below. Precipitation pH at the beginning of the regression line calculated and shown in Figure 5 is 4.59. The pH increases to 4.64 at the end of 1995.

Most important are the findings illustrated in Figures 6 and 7. Both these figures show NO_3 and SO_4 annual mean values for the 15-year period in the upper panel, and cations for the same period in the lower panel. The critical observation from these figures is that there is a clear trend of decreasing concentrations and deposition of SO_4 , but not for NO_3 . This is consistent with a slowing economy (thus less consumption of S-containing fossil fuels), mod-

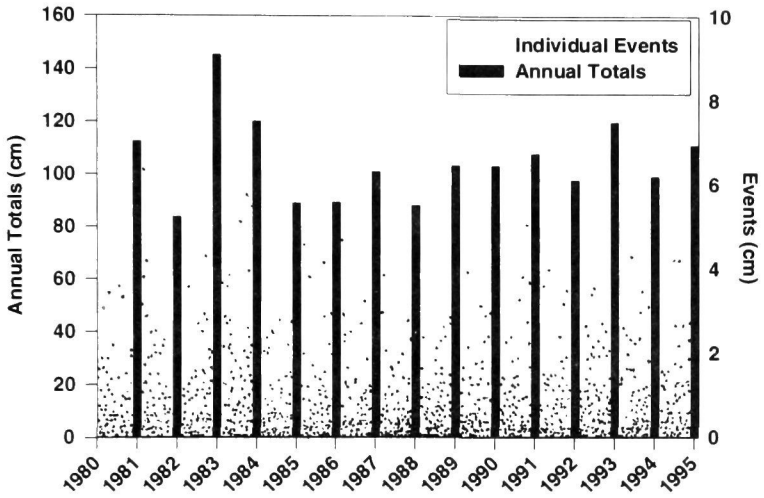


Figure 4. Annual precipitation depths and events at the Greenville, Maine, NADP/NTN station from 1980–1995.

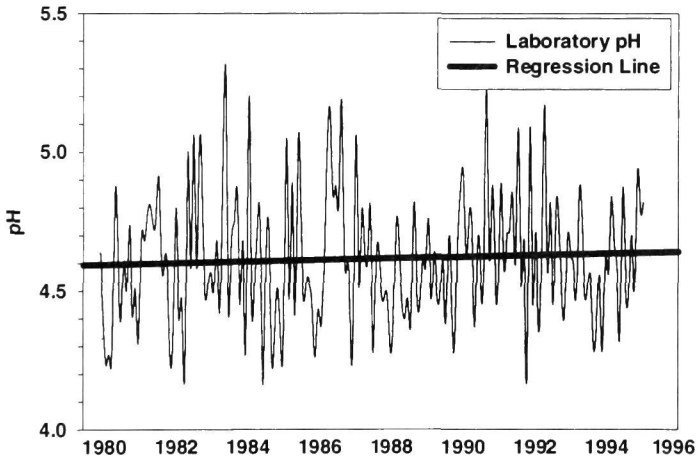


Figure 5. Time series for volume-weighted precipitation pH and the linear regression line for these data.

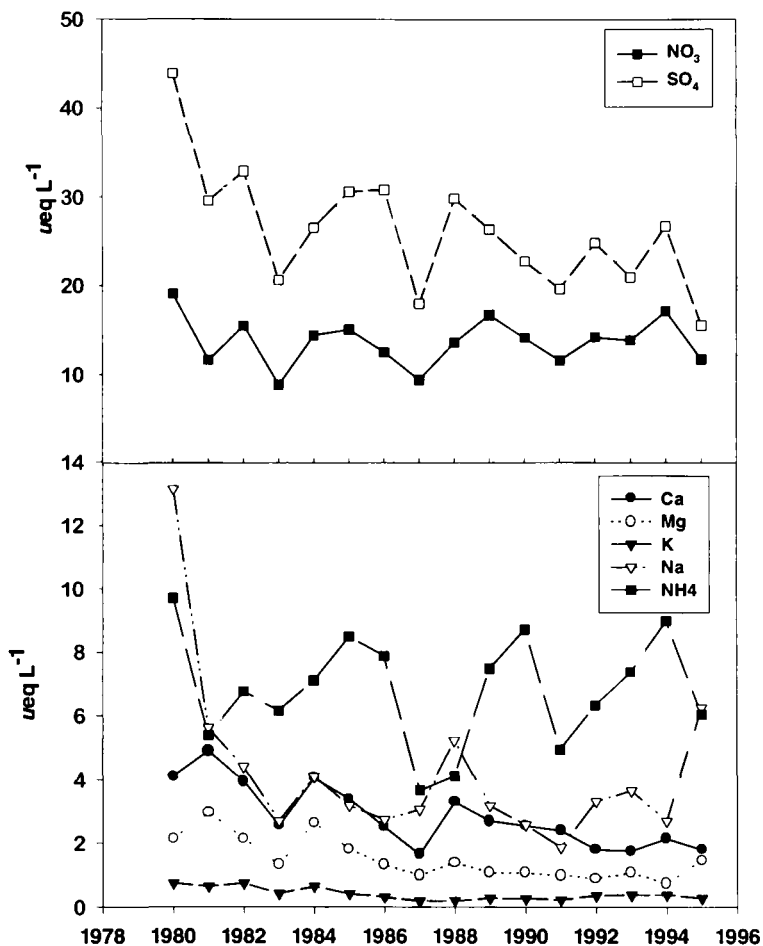


Figure 6. Mean annual concentrations of major cations and anions in precipitation at the Greenville, Maine, NADP/NTN site from 1980–1995.

ernization of industrial technologies, and federal and state regulations which have all contributed to a real decline in the atmospheric deposition of S. While current and projected future levels of S deposition may still contribute to deleterious effects on the more sensitive components of our environment, the existence of consistent, high-quality measurements over this 15-year time period,

such as has been provided by the Greenville site allows us to document significant improvements in environmental exposure. Coincidentally, 1995 appears to be the year when the deposition of SO_4 decreased to a point where it was equal to the deposition of NO_3 (Figure 7). Expressed on a chemical equivalent basis as in Figure 6, or on a mass basis for only elemental N or S, S is still higher than N.

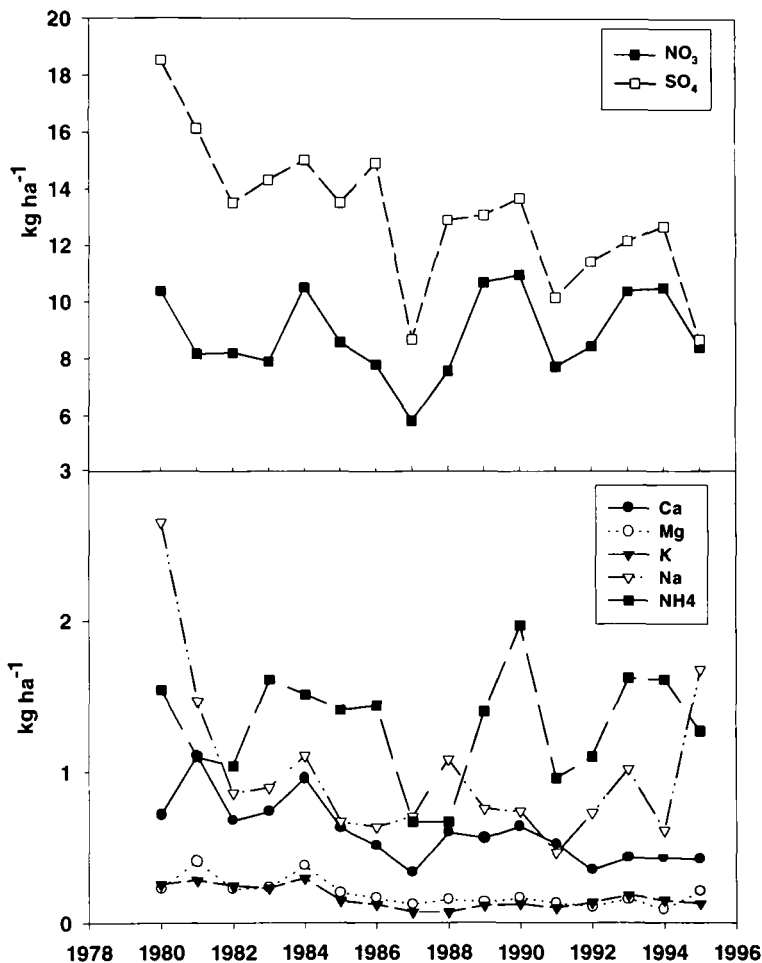


Figure 7. Annual deposition of major cations and anions in precipitation at the Greenville, Maine, NADP/NTN site from 1980-1995.

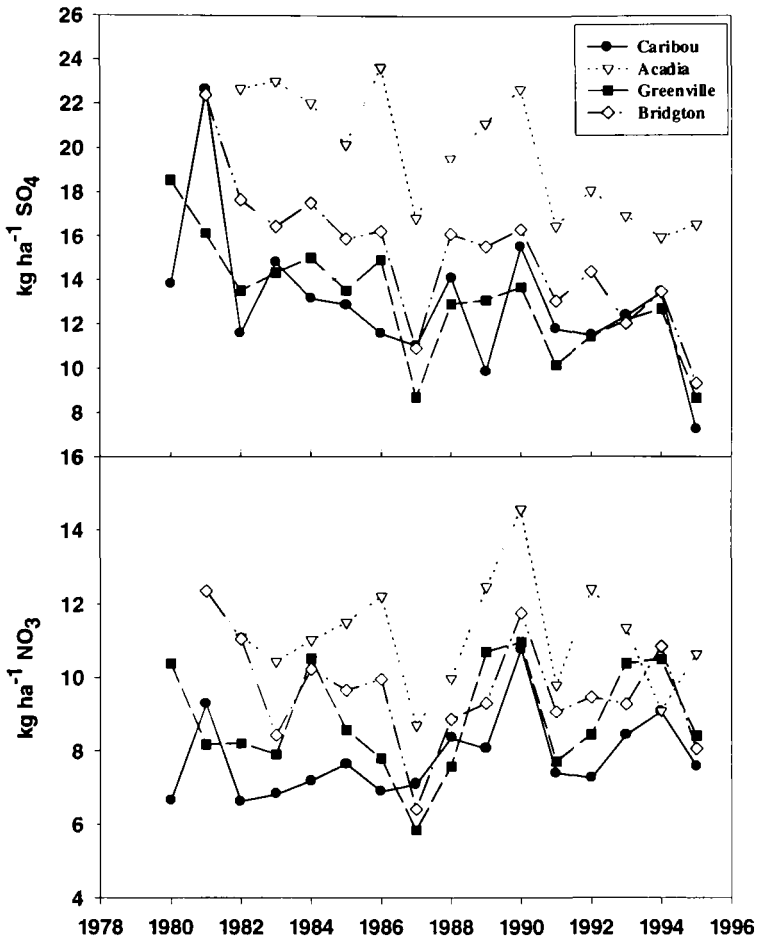


Figure 8. Annual deposition of major anions in precipitation at the four NADP/NTN sites in Maine from 1980–1995.

Equally noteworthy is the absence of any pattern of decline in NO_3 deposition, reinforcing the general belief that N deposition remains relatively unchanged or is still increasing. Because atmospheric N pollution contributes to (a) the formation of tropospheric ozone (O_3), (b) acidic precipitation, and (c) N saturation of terrestrial ecosystems, the long-term patterns and consequences of atmospheric N deposition deserve additional study. Some evidence

exists for a small decline in Ca and Mg over the study period, which may be due to declining agricultural activity (soil dust) in the region or reduced particulate emissions from fossil fuel combustion and possibly local sources of ash. Because the concentrations of these alkaline materials are an order of magnitude smaller than NO_3 and SO_4 , small and subtle changes in air quality over time would have large relative effects on their concentrations.

To be sure that these relatively important observations about the temporal patterns of N and S deposition at Greenville were not due to factors unique to local conditions at that site, we compared the SO_4 and NO_3 annual total deposition in precipitation from Greenville to the other three NADP/NTN sites in Maine (Figure 8). All precipitation monitoring stations showed a long-term decline in SO_4 deposition, with no evidence for change over 15 years of measurements for total NO_3 deposition, or NO_3 concentration over time.

CONCLUSIONS

Precipitation chemistry and deposition over the period 1980–1995 at Greenville, Maine, showed clear evidence of strong acids derived from atmospheric pollution in the form of HNO_3 and H_2SO_4 . No marked trends in the variability of weekly depths or total annual depths of precipitation are evident over this time period to suggest that meteorology is responsible for any changes in chemistry or deposition. The consistency of the precipitation depth record suggests that meteorological processes are not responsible for the patterns of change noted for SO_4 concentrations and deposition. Between 1980 and 1995 precipitation characteristics in Maine show clear evidence for a decline in S concentrations and deposition. No similar change occurs for N, with either consistent or slightly increased deposition of N. While S deposition remains a concern for sensitive ecosystems and processes as a result of long-term chronic exposure, these trends in S deposition are cause for optimism. Perhaps more important is the lack of a trend for improving conditions with respect to N deposition. The potential implications for long-term chronic exposure to current or increased levels of N deposition are even more complex than for S. This calls for increased attention to the consequences of N deposition, in contrast to the 1980s when S received most of the attention prior to the reauthorization of the federal Clean Air Act in 1990.

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