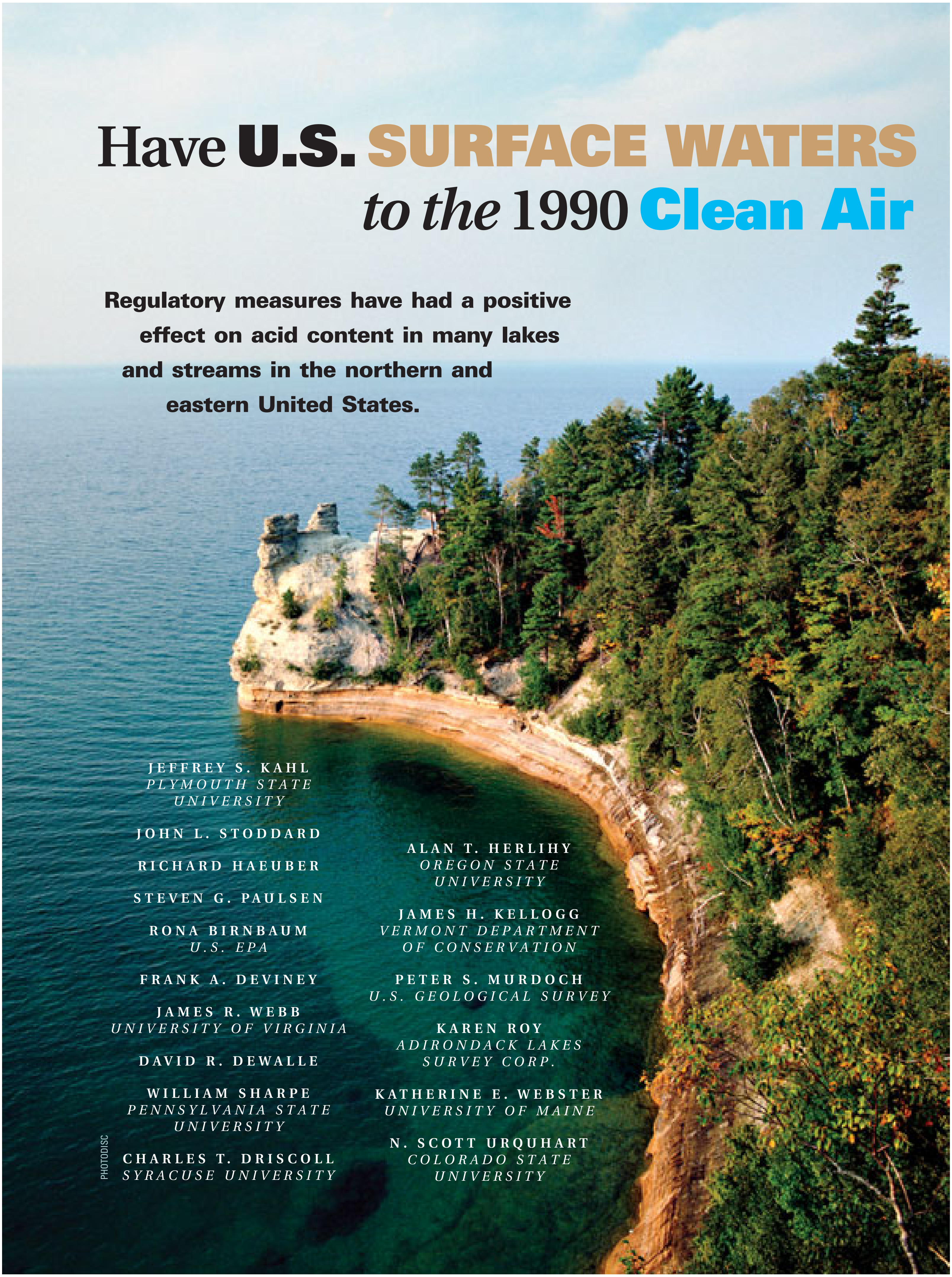

Have U.S. SURFACE WATERS to the 1990 Clean Air

Regulatory measures have had a positive effect on acid content in many lakes and streams in the northern and eastern United States.

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PHOTODISC

Responded Act Amendments?

In the late 1950s, reports first established that acidic lakes existed in North America and Europe (*1*, *2*). However, the effects of acidity on fish were not widely recognized until the mid-1970s (*3*, *4*). As researchers collected more data over the years, they established more robust links between atmospheric deposition and acidic surface waters (*5–8*).

In the past 30 years, the U.S. Congress has modified the Clean Air Act (CAA) several times. In 1990, legislators passed Title IV of the CAA Amendments (CAAA), which was intended to reduce acidic deposition by regulating sulfur and nitrogen emissions, largely from coal-burning power plants. These reductions built on a 20-year trend of decreasing sulfur deposition. The decline accelerated when Phase I controls of the CAAA were implemented in 1995. Nitrogen emissions have decreased only slightly since 1996 (*9*, *10*).

Have the regulations been effective? The results are encouraging. During the 1990s, most regions of concern exhibited declines in the primary acidifying anion, SO_4^{2-}. Several regions showed decreases in lake- and stream-water acidity. By 2000, there were one-third fewer acidic lakes in the Adirondack Mountains than in 1990 (*6*). These are signs of recovery. True recovery should probably be considered to be a return to the conditions of more than 100 years ago, in terms of both chemistry and biology. When only naturally acidic lakes and streams remain in these regions, then we may reasonably conclude that true recovery has occurred, particularly if we can document parallel recovery in the flora and fauna.

In this paper, we summarize nearly 20 years of data from regional U.S. EPA programs specifically designed to meet the congressional assessment requirements of the CAA, including long-term, site-specific records and long-term, repeat surveys of statistical populations.

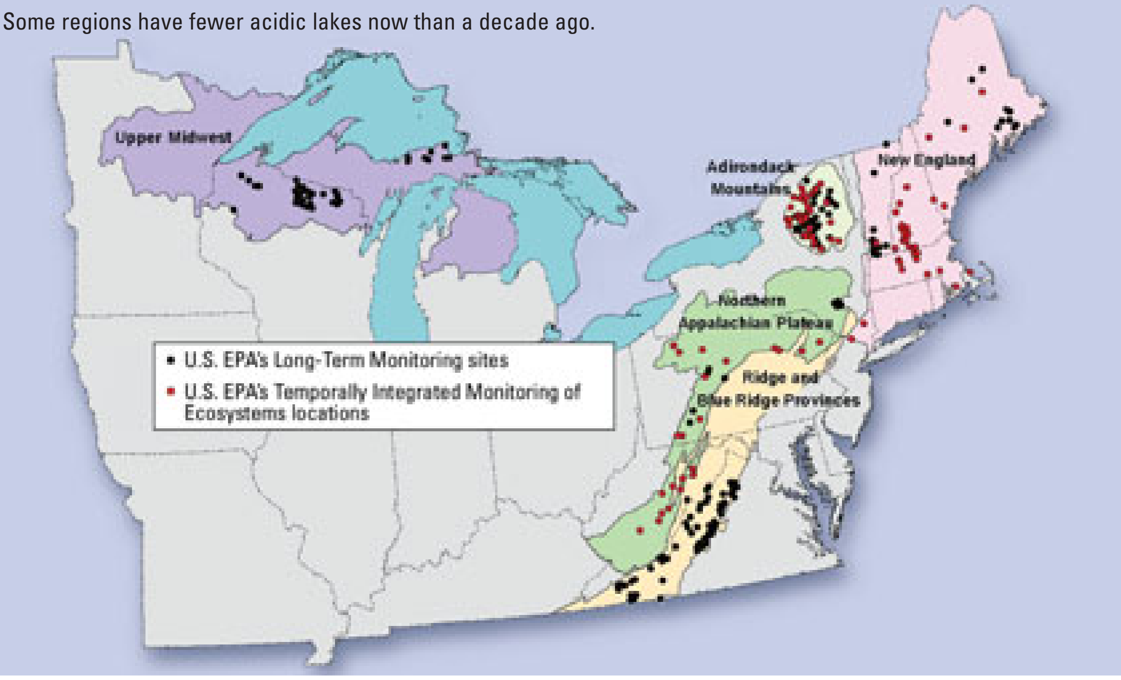
Location, location, location

Intended goals of the CAAA were to decrease the acidity of waters that have low Gran acid neutralizing capacity (ANC), thereby improving their biological condition (*11*). The chronic acid–base chemistry of surface waters has indeed changed, according to data from regions of the northern and eastern United States considered the most likely to respond to decreases in deposition. Because coal-fired emission sources predominate in the eastern United States, implementation of Title IV had the most effect there.

FIGURE 1

Acid-sensitive regions of the northern and eastern United States

Some regions have fewer acidic lakes now than a decade ago.



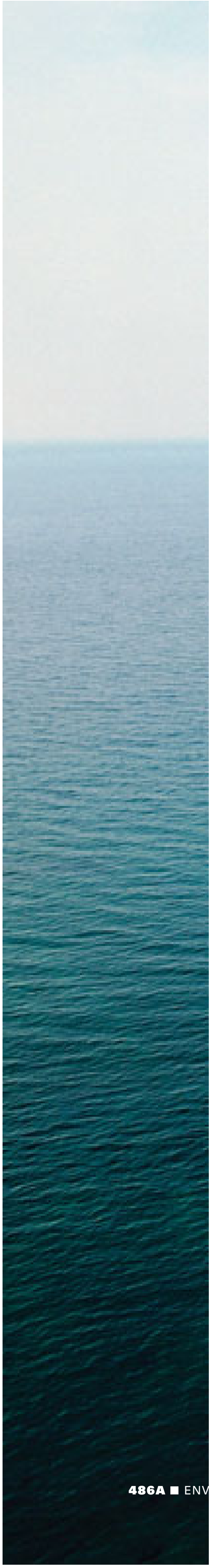


Figure 1 shows the regions that have historically been most affected by acidic deposition: New England, the Adirondack Mountains of New York, the Northern Appalachian Plateau (New York, Pennsylvania, and West Virginia), the Ridge and Blue Ridge Provinces of Virginia, and the Upper Midwest (Wisconsin and Michigan). The measures of expected recovery in these sensitive waters include decreased acidity and lower concentrations of sulfate and toxic dissolved aluminum (*6*).

Surface-water data were gathered from EPA's Long-Term Monitoring (LTM) and Temporally Integrated Monitoring of Ecosystems (TIME) projects, which were both established as part of the Environmental Monitoring and Assessment Program (EMAP; *12*). EPA's Western Ecology Division in Corvallis, Ore., has coordinated the sampling schedules and analytical methods for these projects since their inception in 1983, to ensure reasonable data comparability across the regions of the program. This discussion focuses on data gathered from 1990 through 2000, which is the time period since the last major science review by the National Acid Precipitation Assessment Program in 1990 (*13*) and the implementation of the CAAA.

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Relating emissions and deposition

There is a direct correlation between sulfur emissions and sulfur deposition (*10*). Therefore, reduced emissions from power plants and industry translate directly into lower rates of sulfur deposition. However, correlations between nitrogen emissions and deposition are complicated by the importance of multiple emissions that are not subject to Title IV, such as mobile sources, and those not a result of fossil-fuel combustion, such as nitrogen fertilizers and animal waste. More importantly, nitrogen emissions and deposition changed little from 1990 through 2000, so changes in nitrogen deposition are not expected to have any effect on surface-water acidification and recovery.

Between 1980 and 2000, sulfur emissions from power-generation sources regulated under Phase I of Title IV declined by 35%. Over the same time period, sulfate concentrations in deposition declined by >45% at National Atmospheric Deposition Program (NADP) sites (*10*, *13–15*). In parallel with the decrease in emissions, the decline in wet deposition of sulfate accelerated after 1995 at 74% of NADP sites in the eastern United States (*10*). Sulfate concentrations in wet deposition declined in all the acid-sensitive regions at a median rate between –0.8 and –1.5 microequivalents per liter per year (μeq/L/yr) from 1990 to 2000 (*6*).

Nitrogen deposition declined in the northeastern corridor by only a small amount (*6*). Between 1990 and 2000, nitrogen oxide emissions from power-generation sources affected by Title IV of the 1990 CAAA declined by 18% (*13*). However, electric power generation contributes only ~22% of NO_x emissions from all sources; therefore, the reductions under Title IV have not resulted in substantial reductions in NO_x emissions or deposition.

At many NADP stations, hydrogen ion concentrations decreased significantly between 1900 and 2000; this indicates an increase in the pH of wet deposition (*10*). In the TIME/LTM regions, decreases in wet deposition of hydrogen ion occurred in every region and were significant in every region except the Ridge and Blue Ridge Provinces. Increases in base cation deposition were not significant in the four eastern regions but were significant in the Upper Midwest; this continued a trend established during the past 20 years (*6*).

Status of surface-water chemistry

Changes in deposition have altered surface-water chemistry and in particular have improved those aspects of chemistry most closely linked to biological recovery. For biota, the most important indicators of chemical recovery are increasing pH and Gran ANC and decreasing aluminum concentrations. ANC and pH show moderate but significant increases in most regions, and no region exhibited further acidification (e.g., no trends toward lower Gran ANC or pH). Decreases in aluminum concentrations are modest in TIME and LTM, although other data from the region suggest a stronger decrease in concentrations (*15*, *16*). The quantitative decline in base cations in surface waters is a major uncertainty for recovery, in terms of both future acid–base chemistry and the biological need for Ca^{2+}.

To determine whether the surface-water response is rapid or delayed, we compared rates of sulfate decline in surface waters and deposition, as shown in Figure 2, and concluded that the response of sulfate has been relatively rapid. The chemical changes that result from declines in sulfate, such as an increase in Gran ANC, are much less direct and appear to be mitigated by several other factors that will be discussed in the next section.

Probability surveys are one of the most accurate methods to assess the extent of surface-water acidification (*17*). These statistical survey techniques have been used for two decades in acid-sensitive regions to estimate the number and proportion of acidic lakes and streams. In this type of assessment, "acidic" is

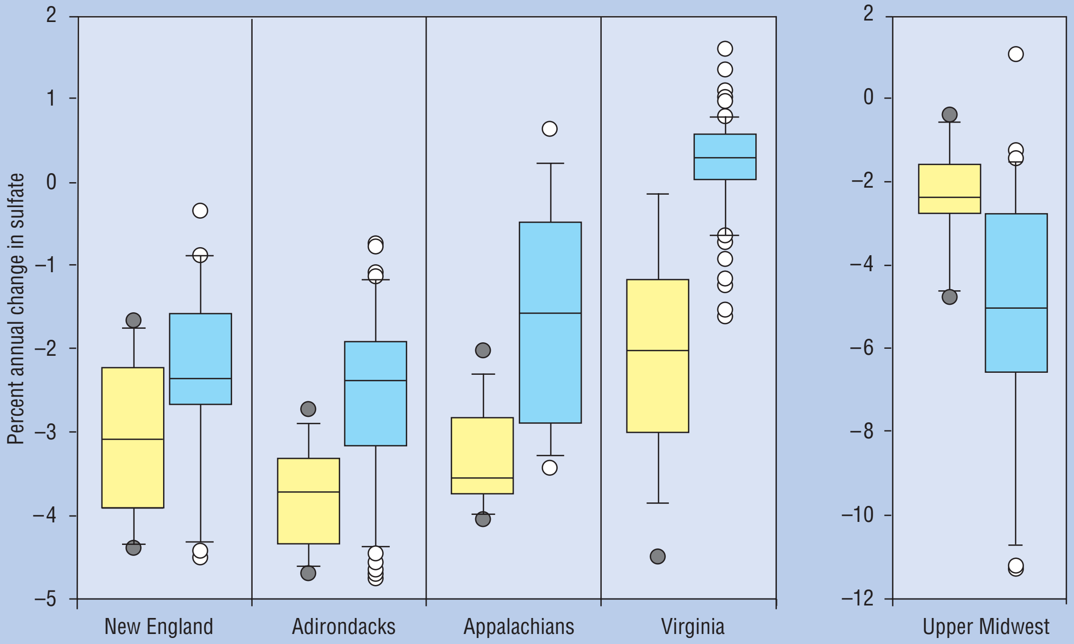


FIGURE 2

Comparing sulfate trends in surface water and deposition

Atmospheric deposition of sulfate declined more steeply than surface-water sulfate in every region except the Upper Midwest. Annual changes in sulfate concentrations between 1990 and 2000 are shown, with yellow boxes for wet deposition and blue boxes for surface waters. Boxes range from 25th to 75th percentiles for each region; a horizontal line indicates the median. Error bars indicate 5th and 95th percentiles. Dots indicate extreme values in each region.

commonly defined by base-flow Gran ANC <0 µeq/L, although biological impacts are not necessarily limited to Gran ANC values of ≤ 0 µeq/L. The National Surface Water Survey (NSWS), conducted between 1984 and 1988, estimated the chemical conditions of 28,300 lakes with areas >4 ha and 56,000 perennial stream reaches in the major acid-sensitive regions of the United States (*18*).

On the basis of the NSWS results, the regions covered in the current assessment are estimated to contain 95% of the lakes and 84% of the streams in the country that have been anthropogenically acidified (*6*). The Adirondacks had the largest proportion of acidic lakes (14%), New England had 5%, and the Upper Midwest had 3%. Because each region has many lakes, these small proportions represent several hundred lakes per region. The Ridge and Blue Ridge Provinces and the Northern Appalachian Plateau had 5% and 6% acidic stream segments, respectively.

Our analysis of surface-water response to changing deposition focuses on the key variables in acidification and recovery: sulfate, nitrate, divalent base cations, aluminum, pH, Gran ANC, and dissolved organic carbon (DOC), which is an indicator of natural organic acidity. Figure 3 (on the next page) shows the major ion chemistry of Darts Lake in the Adirondacks, representing the general patterns observed for lakes and streams in the glaciated terrain of New England, New York, and the Upper Midwest. It demonstrates substantial declines in sulfate and base cations and small increases in pH, Gran ANC, and DOC.

Between 1990 and 2000, surface water sulfate declined in the glaciated northern and eastern regions by median rates between –2 and –4 µeq/L/yr, with the smallest changes in New England and the largest declines in the Upper Midwest (Figure 2). The Ridge and Blue Ridge Provinces region is the exception; there, soil chemistry characteristics minimized the response to changes in deposition (*19*). All of the regional sulfate declines are highly significant and are consistent with previously reported trends, including those in other regions of North America and Europe (*6*, *8*, *20*).

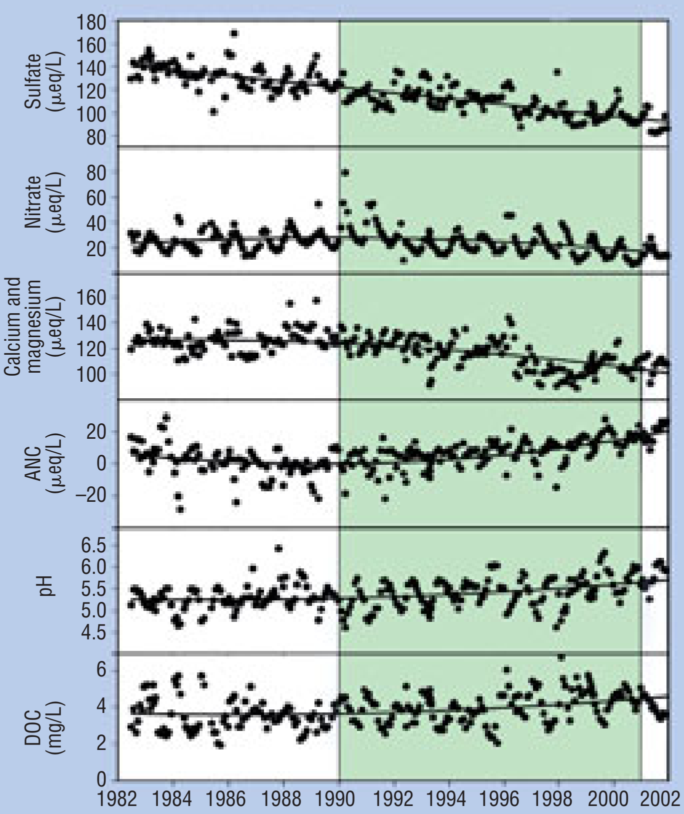
The declines in surface-water sulfate concentrations in the northern and eastern regions seem to be rapid and direct responses to declining emissions and sulfate deposition in the 1990s (Figure 2). Title IV of the CAAA and prior emission reductions were successful in reducing sulfur in both deposition and surface waters. The small increase in sulfate concentrations in the Ridge and Blue Ridge Provinces reflects the sulfate adsorption properties of soils in this nonglaciated region (*21*).

In New England, the Adirondacks, and the Northern Appalachian Plateau, the decline in deposition of sulfate (expressed as % $\mathrm{SO_4^{2-}}$) exceeds the anion's decline in surface waters (Figure 2); this indicates a delayed response in surface waters. Soil desorption of accumulated sulfur and/or net mineralization of accumulated organic sulfur may explain the delayed response (*18*). However, some surface waters had declines in sulfate that paralleled the decline in deposition; this suggests that the most responsive watersheds are acting essentially as pass-through systems. In the Upper Midwest, the rate of decline of % $\mathrm{SO_4^{2-}}$ in lakes

FIGURE 3

Chemistry of Darts Lake in the Adirondack Mountains

Various ions, pH, acid neutralizing capacity (ANC), and dissolved organic carbon (DOC) significantly affect the acidity of lakes. Data for this time series were collected monthly. Trend lines indicate significant trends, and the shaded box indicates the time period for analyses reported in this article.



is greater than the decline in deposition. This region is dominated by seepage lakes with long residence times. The decline in sulfate may reflect the residual effects of a drought in the late 1980s (*22*, *23*).

Changes in nitrate concentrations in surface waters were much smaller than those for sulfate. Lakes in the Adirondacks and streams in the Northern Appalachian Plateau exhibited small but significant downward trends in nitrate in the 1990s (Figure 4) that are reversals of trends in the 1980s (Figure 2 illustrates the typical pattern for these regions). Both regions are central to the debate over whether nitrogen saturation is a threat to the health of forests and surface waters (*24*, *25*). Although declining nitrate concentrations in these regions are a positive development, the changes are not thought to reflect recent trends in deposition (*25*).

Gran ANC is the main target indicator of recovery from acidification, and the Adirondacks, Northern Appalachian Plateau, and Upper Midwest showed moderate to significant increases (Figure 4). Median increases of 1 to 2 µeq/L/yr represent important progress toward recovery from acidification, especially when coupled with small declines of hydrogen ion (–0.1 to –0.2 µeq/L/yr) in each region.

These changes have not been monotonic. Using data though 1995, Stoddard et al. concluded that Gran ANC was not increasing in the Adirondacks (*20*). Our analysis of data from 1990 through 2000 in this region suggests that the pattern of increasing ANC has occurred only recently, as shown by Darts Lake (Figure 3). For New England, we find no increase in ANC from 1990 though 2000, yet Stoddard et al. found significantly increasing ANC in data through 1995 (*20*).

We analyzed Gran ANC trends by ANC class and determined that the waters with the lowest Gran ANC recovered faster in the 1990s. Specifically, we found that for lakes with an ANC < 0 µeq/L in 1990 ($n = 26$), the increase in ANC from 1990 to 2000 averaged 13 µeq/L; for lakes with 0 µeq/L < ANC < 25 µeq/L ($n = 51$), the increase was 8.4 µeq/L ; and for lakes with ANC > 25 µeq/L ($n = 43$), the change was not significant.

The increase in Gran ANC for both classes of lakes with ANC < 25 µeq/L was significant at $p < 0.01$. The response for the most acidic waters suggests that their watershed soils are capable of producing relatively rapid recovery in surface-water chemistry. The lack of response in the class with higher Gran ANC suggests that an ANC of 25 µeq/L may be an upper limit for recovery of currently acidic lakes and streams.

The results from TIME and NSWS probability surveys were combined with rates of change in LTM data to estimate the number of chronically acidic waters (Gran ANC ≤ 0 µeq/L in 1990) that are no longer acidic. In the Adirondacks and Northern Appalachians, approximately one-third of sites deemed acidic in the early 1990s are no longer chronic problems (*6*). In the Upper Midwest, the proportion of acidic lakes declined nearly 70% since the most recent probability survey of lakes in the region in 1984. Neither New England nor the Ridge and Blue Ridge Provinces exhibited significant changes in Gran ANC, so we concluded that the number of acidic systems in these regions has not declined significantly. However, the current rate of Gran ANC change in all regions is small, and recovering lakes and streams remain sensitive to future changes in deposition. Clearly, the interpretation of recovery is subject to the time period analyzed, and reacidification is still possible.

Because our statistical population inferences are based on sampling in the summer and fall base-flow index periods, these results estimate chronic—not episodic—acidification. It is well documented that many nonacidic surface waters undergo short-term, or episodic, acidification during periods of high discharge (*26*). The relationship between mean summer Gran ANC and the spring minimum suggests that lakes and streams with summer values >30 µeq/L did not experience spring acidification (*6*). Therefore, one definable target for recovery is Gran ANC values >30 µeq/L during base-flow conditions; this minimizes occurrence of episodic acidification.

Mobilizing base cations from soils is one of the most universal watershed responses to acidic deposition (*27*). As the supply of acid anions from acidic deposition decreases, the rate of cation mobilization to surface waters is also expected to decrease, which is a change that has been widely observed in the

Northern Hemisphere for more than a decade (*7*, *8*, *15*, *20*, *28*). In surface waters of the glaciated regions in the northern and eastern United States, divalent base cations, such as Ca^{2+} and Mg^{2+}, declined at a rate between –1.5 and –2.5 μeq/L/yr (Figure 4). This decline in base cations has offset some of the observed decline in sulfate concentrations and limited improvements in Gran ANC.

The rate of change in Gran ANC represents the difference between the combined rates of change for acid anions and base cations, as follows:

$$\Delta\,\mathrm{ANC} = \Delta[\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+}] - \Delta[\mathrm{SO}_4^{2-} + \mathrm{NO}_3^{-} + \mathrm{Cl}^{-}]$$

On average, surface-water sulfate decreased by ~–2.5 μeq/L/yr and nitrate decreased at ~–0.5 μeq/L/yr in the region in the 1990s. The sum of these rates of change sets an upper limit to Gran ANC response of +3 μeq/L/yr. The actual increase in Gran ANC was ~+1 μeq/L/yr. The difference between the actual Gran ANC increase and the maximum increase from rates of acid anion change can be almost entirely explained by regional declines in base cations of ~–1.8 μeq/L/yr (Figure 4).

Expected rate of recovery

Lakes with the lowest Gran ANC are recovering faster than lakes with higher ANC, a pattern also observed in other regions of the world (*29*). The recovery of the most acidic waters is a measure of success of the CAAA. This pattern represents the reverse of the acidification process, in which lakes with the lowest initial pHs acidified the most. For example, using paleolimnological assessments, Smol et al. demonstrated that Adirondack lakes with a pre-industrial pH of 5.0–5.5 acidified to the mid-4's, lakes with pH of 5.5–6.3 did not acidify, and lakes with pH > 6.3 became more basic (*30*). They inferred that above Gran ANC of 40 μeq/L, lakes did not acidify. On the basis of the rate of ANC change in the ANC classes, our analyses suggest that reductions in acidic deposition will cause the chemistry of acidified waters to evolve toward a pH range of 5.0–6.0 (ANC 0–30 μeq/L). Studies of pre-industrial lake pH agree that the historical pH values of presently acidified lakes were typically <6.0 before the onset of acidic deposition (*27*). Therefore, we infer that pH of ~6.0 and Gran ANC of ~30 μeq/L will represent full recovery for most acidic waters.

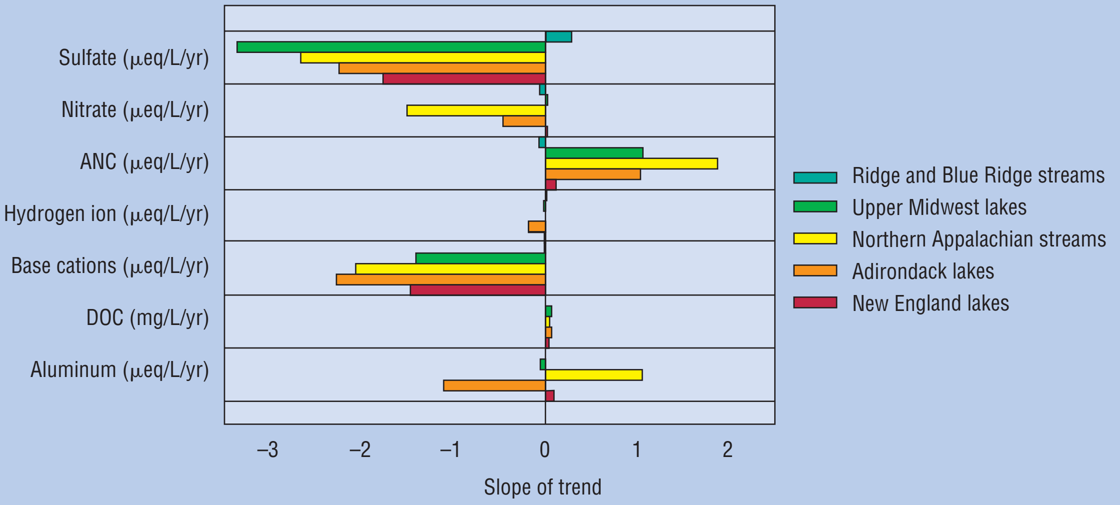
We suggest that the higher rate of response in the most acidic waters indicates that the response is happening faster and more broadly than expected. Moreover, the response of the waters with the lowest pH levels suggests that the mechanisms of recovery have not been irreparably damaged; soils in sensitive watersheds are still capable of progress toward surface water recovery in a time frame of years to decades. We believe that the trend of declining sulfate, nitrate, and base cations represents a return toward the water chemistry of pre-industrial times. Acidic deposition artificially increased the ionic strength of surface waters as part of the neutralization process, and this process is now reversing.

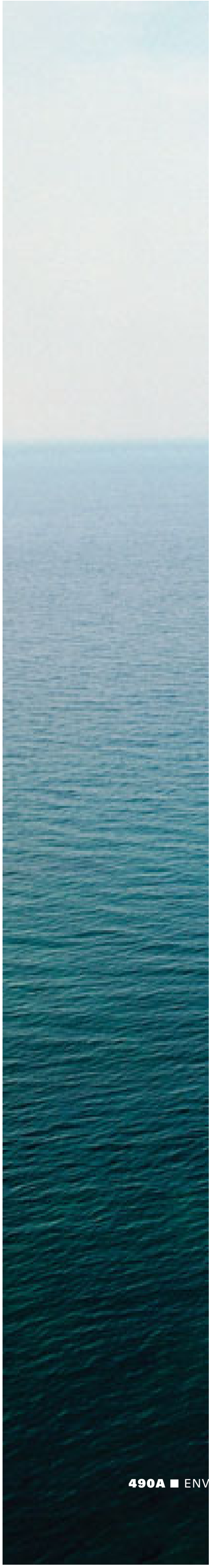
If ANC continues to increase at the rate of the past decade, the "median acidic lake" in the Adirondacks will meet the target (25–30 μeq/L) in less than two decades. However, we do not know whether this rate of increase in ANC will continue without further reductions in deposition. Moreover, the recent decreases in nitrate complicate acidic assessments of recovery: Decreases in nitrate do not appear to be linked to decreases in atmospheric deposition. If watershed retention of nitrogen decreases in the future, increases in nitrate could delay recovery of surface waters. To what extent does current recovery already fully reflect reductions in deposition? Are additional reductions required to maintain the present trends? The only way to answer these questions is to maintain the com-

FIGURE 4

Regional trends in lakes and streams for 1990–2000

Sulfate levels dropped significantly more than nitrate levels did in the 1990s; this decrease has resulted in increases in pH and acid neutralizing capacity (ANC), although much of the decrease in sulfate was offset by declines in base cation concentrations.





mitment to long-term monitoring of regional surface-water chemistry. Assessments based on deposition monitoring alone cannot address the ultimate question of whether ecosystems are recovering in response to changes in emissions and deposition.

We relied entirely on chemical monitoring data to assess recovery, with a focus on biologically relevant chemistry (e.g., pH, Gran ANC, and aluminum, which may be the most direct biologically relevant indicator of recovery), because long-term data collection has not historically addressed the question of biological response. For example, no equivalent monitoring networks to the TIME and LTM programs exist for fisheries or any other important group of aquatic organisms.

For now, we infer that improvements in chemistry will eventually lead to biological recovery. This hypothesis will be tested on data collected in the summer of 2004 by a research team from Plymouth State University, the University of Maine, and Dartmouth College, using analyses of zooplankton populations from lakes that were originally sampled by EPA in 1986. The importance of this assessment is reflected by the coalition of agencies that funded the work: the U.S. Department of Agriculture's Forest Service, the U.S. Geological Survey, and EPA. Differences between populations sampled 18 years apart, combined with the changes in water chemistry, will start to unravel the response of biota to changes in regional water chemistry caused by the CAA.

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