

Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies

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Acidic deposition is the transfer of strong acids and acid-forming substances from the atmosphere to the surface of the Earth. The composition of acidic deposition includes ions, gases, and particles derived from the following: gaseous emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3), and particulate emissions of acidifying and neutralizing compounds. Over the past quarter century of study, acidic deposition has emerged as a critical environmental stress that affects forested landscapes and aquatic ecosystems in North America, Europe, and Asia. This complex problem is an example of a new class of environmental issues that are multiregional in scale and are not amenable to simple resolution by policymakers. Acidic deposition can originate from transboundary air pollution and can affect large geographic areas. It is highly variable across space and time, links air pollution to diverse terrestrial and aquatic ecosystems, and alters the interactions of many elements (e.g., sulfur [S], nitrogen [N], hydrogen ion [H^+], calcium [Ca^{2+}], magnesium [Mg^{2+}], and aluminum [Al]). It

THE EFFECTS OF ACIDIC DEPOSITION IN THE NORTHEASTERN UNITED STATES INCLUDE THE ACIDIFICATION OF SOIL AND WATER, WHICH STRESSES TERRESTRIAL AND AQUATIC BIOTA

also contributes directly and indirectly to biological stress and to the degradation of ecosystems. Despite the complexity of the effects of acidic deposition, North American and European management actions directed toward the recovery of damaged natural resources have resulted in recent decreases in both emissions and deposition of acidic S compounds. Accordingly, acidic deposition presents an instructive case study

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for coordinating science and policy efforts aimed at resolving large-scale environmental problems.

Acidic deposition was first identified by R. A. Smith in England in the 19th century (Smith 1872). Acidic deposition emerged as an ecological issue in the late 1960s and early 1970s with reports of acidic precipitation and surface water acidification both within Sweden and around Scandinavia (Oden 1968). The first report of acidic precipitation in North America was made at the Hubbard Brook Experimental Forest (HBEF) in the remote White Mountains of New Hampshire, based on collections begun in the early 1960s (Likens et al. 1972). Controls on SO_2 emissions in the United States were first implemented after passage of the 1970 amendments to the Clean Air Act (CAAA). In 1990, Congress passed Title IV of the Acid Deposition Control Program of the CAAA to further decrease emissions of SO_2 and to initiate controls on NO_x from electric utilities, which contribute to acidic deposition. The Acid Deposition Control Program had two goals: (1) By 2010, a 50% decrement from 1980 levels of SO_2 utility emissions (amounting to 9.1 million metric tons per year, or 10 million short tons); (2) also by 2010, an NO_x emission rate limitation (0.65 lbs NO_x /m BTU in 1990 to 0.39 lbs NO_x /m BTU in 1996), which will achieve a reduction of 1.8 million metric tons per year (2 million short tons) as NO_2 in NO_x utility emissions from the amount that would have occurred without emission rate controls. Both SO_2 and NO_x provisions focus on large utilities. The legislation capped total utility emissions of SO_2 at 8.12 million metric tons per year (8.95 million short tons), whereas nonutility emissions of SO_2 were capped at 5.08 million metric tons per year (5.6 million short tons). Because the legislation did not specify caps for NO_x emissions, emissions may increase over time as the demand for electricity increases.

The beginning of the 21st century offers the opportunity to assess the effects of three decades of clean air legislation on emissions reductions; on air pollution levels, trends, and chemical effects of acidic deposition; and on ecosystem recovery. The opportunity also exists to look ahead to the anticipated reauthorization of the Clean Air Act and to the next national assessment of acidic deposition, scheduled for mid-2001. In this article we examine the ecological effects of

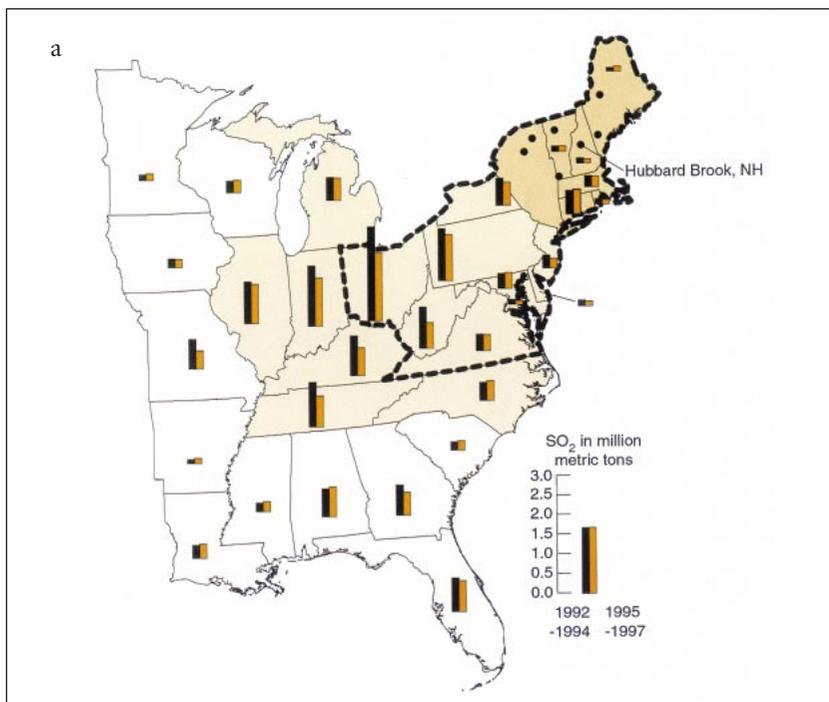
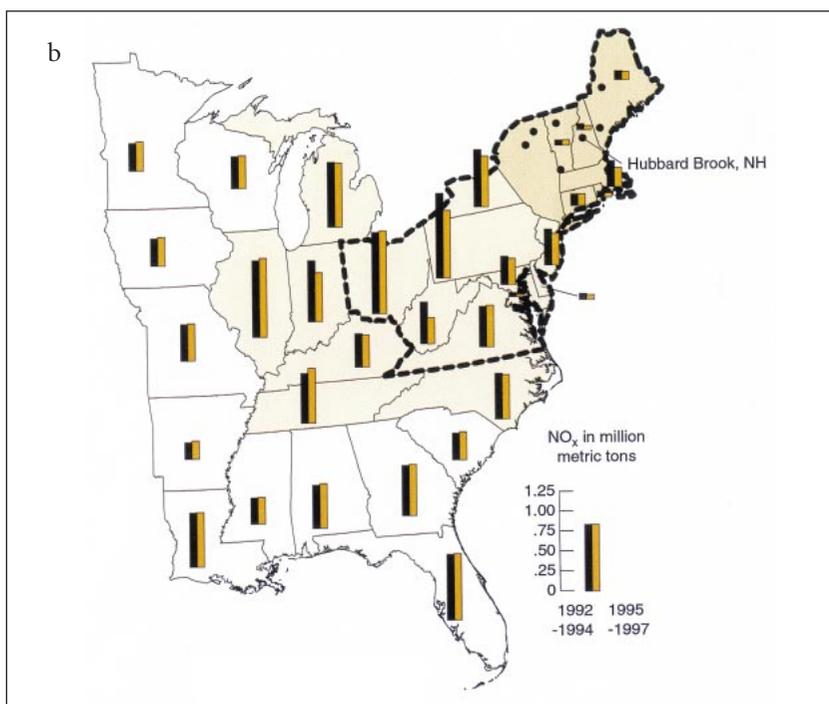


Figure 1. Study region for the analysis of acidic-deposition effects on forest and aquatic ecosystems is indicated by the shaded area. Solid circles designate the location of Hubbard Brook Experimental Forest and other National Atmospheric Deposition Program sites in the study region. Solid bars show state emissions of (a) SO_2 and (b) NO_x for the eastern United States for 1992–1994. Shaded bars are for 1995–1997. The emissions source area for the study region, based on 15-hour back trajectories, is indicated by boldface dashed lines. The emissions source area, based on 21-hour back trajectories, is indicated by lighter shading (as calculated from Butler et al. 2001).



acidic deposition in the study region of New England and New York (Figure 1), and we explore the relationship between emissions reductions and ecosystem recovery, by focusing on three critical questions.

This analysis draws on research conducted in the northeastern United States, with additional information from the mid-Atlantic and southeastern United States and from eastern Canada. We rely heavily on data from HBEF, a research site that provides the longest continuous records of precipitation and stream chemistry (Likens and Bormann 1995). Because the HBEF is located in a region with bedrock that is resistant to chemical weathering and acidic soils, surface waters are representative of areas of the Northeast that are sensitive to acidic deposition. When we compared stream chemistry from the biogeochemical reference watershed (Watershed 6) at HBEF with results from the US Environmental Protection Agency (EPA) synoptic survey of lakes in the Northeast, which had been collected through the Environmental Monitoring and Assessment Program (EMAP), only 4.9% of the lakes had lower concentrations of the sum of base cations (i.e., $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{sodium} [\text{Na}^+] + \text{potassium} [\text{K}^+]$) (Larsen et al. 1994, Stevens 1994). In addition, 67% had lower concentrations of sulfate (SO_4^{2-}), and 5.7% had lower pH values. However, when compared to populations of acid-sensitive EMAP lakes (acid-neutralizing capacity [ANC] less than $50 \mu\text{eq L}^{-1}$), then 28%, 77%, and 32% of the lakes have lower concentrations of the sum of base cations, of SO_4^{2-} , and of pH, respectively, than found in the stream water draining Watershed 6 at HBEF.

Periodic review of knowledge gained from long-term monitoring, process-level research, and modeling is critical for assessing regulatory programs and for solving complex environmental problems. The need to resolve the problem of acidic deposition is made more apparent as the many linkages between acidic deposition and other environmental issues are more clearly documented (Table 1). Much of the report that follows focuses on what has been learned since the 1990 CAAA. That act concerned the effects of acidic deposition on forest vegetation, soils, and surface waters and the influence of past and, potentially, future reductions of

emissions on ecosystem recovery in the northeastern United States.

Question 1: What are the spatial patterns and temporal trends for emissions, precipitation concentrations, and deposition of anthropogenic S, N, and acidity across the northeastern United States?

Emissions

The United States has experienced marked changes in emissions of SO_2 over the past 100 years. Total emissions of SO_2 increased from 9 million metric tons (9.9 million short tons) in 1900 to a peak of 28.8 million metric tons (31.7 million short tons) in 1973, of which 60% was from electric utilities (USEPA 2000). By 1998, total annual SO_2 emissions for the United States had declined to 17.8 million metric tons (19.6 million short tons). From 1970 to 1998, SO_2 emissions from electric utilities decreased by 24%, largely as a result of the 1970 and 1990 amendments to the Clean Air Act. Emissions of NO_x have increased from about 2.4 million metric tons (2.6 million short tons) in 1900 to 21.8 million metric tons (24 million short tons) in 1990. They have remained fairly constant since then.

Emissions of SO_2 in the United States are highest in the Midwest. States clustered around the Ohio River Valley (Illinois, Indiana, Kentucky, Ohio, Pennsylvania, Tennessee, and West Virginia) comprised 7 of the 10 states with the highest SO_2 emissions in the nation in 1998 (Figure 1a). Those seven states accounted for 41% of the national SO_2 emissions during this period. Five of those states (Illinois, Indiana, Ohio, Pennsylvania, and Tennessee) were also among the 10 states with the highest total NO_x emissions for 1998, and these states make up 20% of national emissions (Figure 1b). High emissions in this region result primarily from electric utilities and from heavy manufacturing.

The 1990 CAAA required additional reductions in the emissions of SO_2 from electric utilities, starting in 1995 with Phase I of the Acid Deposition Control Program. This legislation helped to promote the continuing pattern of declining emissions between 1992–1994 and 1995–1997 for most states in the eastern United States (Figure 1a). For the

Table 1. Linkages between emissions of SO_2 and NO_x and important environmental issues.

Problem	Linkage to acidic deposition	Reference
Coastal eutrophication	Atmospheric deposition is important in the supply of N to coastal waters	Jaworski et al. 1997
Mercury accumulation	Surface water acidification enhances mercury accumulation in fish	Driscoll et al. 1994b
Decreased visibility	Sulfate aerosols are an important component of atmospheric particulates; they decrease visibility	Malm et al. 1994
Climate change	Sulfate aerosols increase atmospheric albedo, cooling the Earth and offsetting some of the warming potential of greenhouse gases; tropospheric O_3 and N_2O act as greenhouse gases	Moore et al. 1997
Tropospheric ozone	Emissions of NO_x contribute to the formation of ozone	Seinfeld 1986

United States, SO_2 emissions decreased 14% during the same periods, whereas emissions decreased by 24% in the seven high-emission states in the Midwest. Decreases in emissions of NO_x between those periods, however, were only 2% nationally and 3% for the seven high-emission states in the Midwest (Figure 1b).

Atmospheric deposition of ammonium (NH_4^+) is derived from emissions of NH_3 and can contribute to the acidification of soil and water if these inputs are oxidized by soil microbes to nitrate (NO_3^-). The EPA has a national emissions inventory for NH_3 ; however, little information is available on past emissions. Local and regional studies, however, have identified agricultural activities as the primary source of US emissions of NH_3 (Jordan and Weller 1996). Manure from livestock and poultry is generally considered the largest contributor. Emissions from crop senescence may be as large but are difficult to measure accurately (Lawrence et al. 2000). Application of N fertilizer also contributes NH_3 to the atmosphere, but the amount from this source is less than 10% of emissions from manure handling in the Mississippi River Basin (Goolsby et al. 1999). Small sources of NH_3 emissions include automobiles and industrial processes (Fraser and Cass 1998).

Patterns of precipitation and deposition of S and N

Acidic deposition can occur as wet deposition; as rain, snow, sleet, or hail; as dry deposition; as particles or vapor; or as cloud or fog deposition, which is more common at high elevations and in coastal areas. Wet deposition is monitored at more than 200 US sites by the interagency-supported National Atmospheric Deposition Program/National Trends Network (NADP/NTN), which was initiated in 1978. The Northeast study region has 20 NADP/NTN sites. In addition, precipitation chemistry has been studied at several independent sites (e.g., HBEF), sometimes for an even longer period. Spatial patterns of wet deposition in the eastern half of the United States have been described by combining NADP/NTN deposition data with information on topography and precipitation (Grimm and Lynch 1997).

Dry deposition is monitored by the EPA Clean Air Status and Trends Network (CASTNet) at approximately 70 sites, as well as by the National Oceanic and Atmospheric Administration AIRMoN (Atmospheric Integrated Monitoring Network)-dry program at 13 sites. Most sites in these two networks are located east of the Mississippi River and began operation around 1988. Seven CASTNet and five AIRMoN-dry sites are in the study region. Both CASTNet and AIRMoN-dry use an inferential approach to estimate dry deposition. This approach depends on detailed meteorological measurements and on vegetation characteristics, which can vary markedly over short distances in complex terrains (Clarke et al. 1997). Consequently, the spatial patterns of dry deposition in the United States are poorly characterized.

To support specific investigations (e.g., Weathers et al. 1988; Anderson et al. 1999), cloud and fog depositions in the

northeastern United States have been monitored for limited periods at selected coastal and high-elevation (more than 1100 m) sites. In recent years, the Mountain Acid Deposition Program (MADPro), as part of the EPA CASTNet program, has involved the monitoring of cloud water chemistry at several sites in the eastern United States, including one site in the northeastern United States. Regional patterns and long-term trends are not well characterized, even though cloud and fog depositions often contribute between 25% and more than 50% of the total deposition of S and N to high-elevation sites in the northeastern United States (Anderson et al. 1999).

Prevailing winds from west to east cause pollutants emitted in the Midwest to be deposited in New England and Canada. During atmospheric transport, some of the SO_2 and NO_x will be converted to sulfuric and nitric acids; to ammonium sulfate and ammonium nitrate, which can be transported long distances; and to nitric acid vapor, which has a shorter atmospheric residence time (Lovett 1994).

Long-term data collected at HBEF indicate that annual volume-weighted concentrations of SO_4^{2-} in bulk precipitation (precipitation sampled from an open collector) has declined (Figure 2) along with the national decreases in SO_2 emissions that followed the 1970 CAAA (Likens et al.

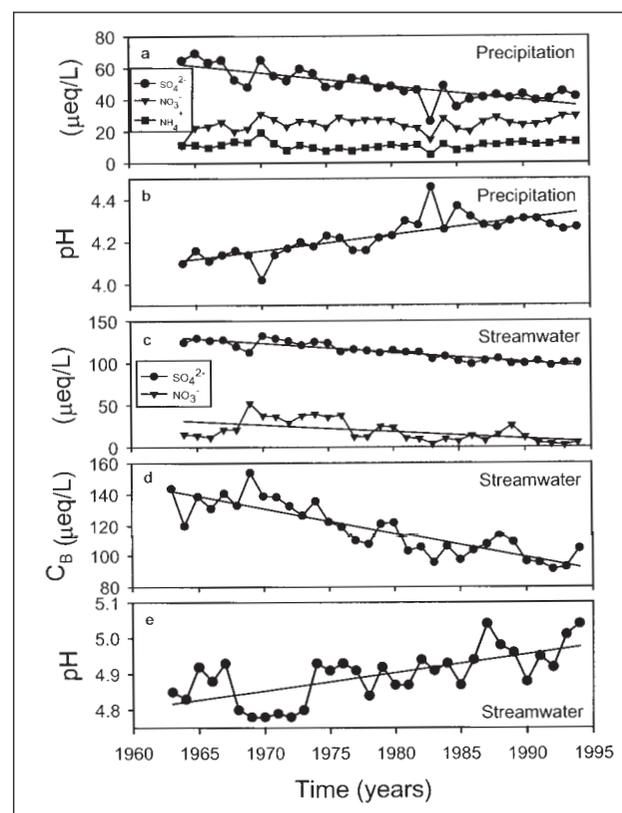


Figure 2. For 1963–1994, trends in volume-weighted, annual mean concentrations of SO_4^{2-} , NO_3^- , and NH_4^+ (a); pH in bulk precipitation (b); SO_4^{2-} and NO_3^- (c); the sum of base cations (C_B) (d); and pH in stream water in Watershed 6 of the Hubbard Brook Experimental Forest (e).

2001). Using back-trajectory analysis of air masses (Draxler and Hess 1998), Butler et al. (2001) identified the approximate emissions source region for atmospheric deposition of S and N compounds into their study region in the northeastern United States (Figure 1). Annual mean concentrations of SO_4^{2-} in bulk precipitation at the HBEF were strongly correlated with annual SO_2 emissions, based on both 15-hour ($r^2 = 0.74$; Figure 3) and 21-hour ($r^2 = 0.74$) back trajectories (Likens et al. 2001). Emissions from Ontario and Quebec appear to have contributed little (less than 10%) to the SO_4^{2-} deposition in the study region during the 1990s (Environment Canada 1998, Butler et al. 2001). In contrast to findings for SO_4^{2-} , researchers found no long-term trends in annual volume-weighted concentrations of NO_3^- in bulk precipitation at HBEF (Figure 2). This lack of a long-term pattern is consistent with the minimal changes in NO_x emissions over the past 30 years.

The beneficial influence of national clean air legislation is also reflected in the strong relationship between the historical reductions in air emissions from the source region and the decreased deposition of S throughout the northeastern United States, including HBEF. As SO_2 emissions declined during the 1980s and 1990s in response to the CAAA, researchers found a decrease in the geographic area exposed to elevated wet deposition of S in excess of $25 \text{ kg SO}_4^{2-} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ (Figure 4). In 1995–1997, after the implementation of Phase I of the Acid Deposition Control Program, emissions

of SO_2 in the source area and concentrations of SO_4^{2-} in (1) bulk deposition at HBEF (Watershed 6) and (2) wet-only deposition at NADP sites in the Northeast were about 20% lower than in the preceding 3 years. However, these decreases were not significantly different from the long-term trend (Likens et al. 2001). Nitrate and NH_4^+ concentrations decreased less than 10% during the same period. Year-to-year variations in precipitation across the region influenced the magnitude and the spatial distribution of changes in S and N wet deposition between the periods of 1992–1994 and 1995–1997. Such variations complicated the relationships between emissions and deposition (Lynch et al. 2000; Likens et al. 2001).

The Midwest is also a significant source of atmospheric NH_3 . About half of the NH_3 emitted to the atmosphere is typically deposited within 50 km of its source (Ferm 1998). However, high concentrations of SO_2 and NO_x can greatly lengthen atmospheric transport of NH_3 through the formation of ammonium sulfate and ammonium nitrate aerosols. Like SO_2 , these submicron particles are transported distances greater than 500 km. Ammonium is an important component of atmospheric N deposition. For example, an average of 31% of dissolved inorganic N in annual bulk deposition at HBEF occurs as NH_4^+ .

Dry deposition contributes a considerable amount of S and N to the Northeast, although accurate measurements are difficult to obtain, as noted above. At 10 sites scattered across the United States, Lovett (1994) estimated, dry deposition of S was 9%–59% of total deposition (wet + dry + cloud), dry deposition of NO_3^- was 25%–70% of total NO_3^- deposition, and dry deposition of NH_4^+ was 2%–33% of total NH_4^+ deposition. This variability is due in part to the proximity of the sites to high emission areas and to the relative contribution of cloud and fog depositions.

Question 2: What are the effects of acidic deposition on terrestrial and aquatic ecosystems in the northeastern United States, and how have these ecosystems responded to changes in emissions and deposition?

Terrestrial–aquatic linkages

Many of the effects of acidic deposition depend on the rate at which acidifying compounds are deposited from the atmosphere, compared with the rate at which acid neutralizing capacity (ANC) is generated within the ecosystem. ANC, a measure of the ability of water or soil to neutralize inputs of strong acid, is largely the result of terrestrial processes such as mineral weathering, cation exchange,

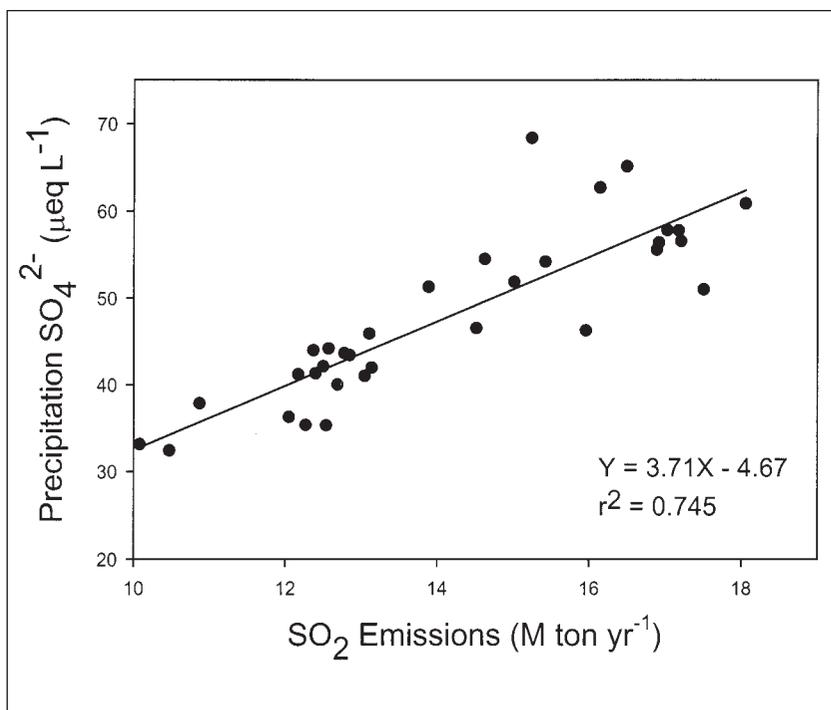


Figure 3. Volume-weighted annual concentrations of SO_4^{2-} in bulk precipitation at Hubbard Brook Experimental Forest as a function of annual emissions of SO_2 for the source area, based on 15-hour back trajectories (see Figure 1; modified after Likens et al. 2001).

and immobilization of SO_4^{2-} and N (Charles 1991). Acid neutralizing processes occur in the solution phase, and their rates are closely linked with the movement of water through terrestrial and aquatic ecosystems. The effects of acidic deposition on ecosystem processes must, therefore, be considered within the context of the hydrologic cycle, which is a primary mechanism through which materials are transported from the atmosphere to terrestrial ecosystems and eventually into surface waters.

The effects of acidic deposition on surface waters vary seasonally and with stream flow. Surface waters are often most acidic in spring after snowmelt and rain events. In some waters ANC values decrease below $0 \mu\text{eq L}^{-1}$ only for short periods (i.e., hours to weeks), when discharge is highest. This process is called episodic acidification. Other lakes and streams, referred to as chronically acidic, maintain ANC values less than $0 \mu\text{eq L}^{-1}$ throughout the year.

Precipitation (which includes snowmelt) can raise the water table from the subsoil into the upper soil horizons, where acid neutralizing processes (e.g., mineral weathering, cation exchange) are generally less effective than in the subsoil. Water draining into surface waters during high-flow episodes is therefore more likely to be acidic (i.e., ANC value less than $0 \mu\text{eq L}^{-1}$) than water that has discharged from the subsoil, which predominates during drier periods.

Both chronic and episodic acidification can occur either through strong inorganic acids derived from atmospheric deposition, by natural processes, or both. Natural acidification processes include the production and transport of organic acids derived from decomposing plant material or of inor-

ganic acids originating from the oxidation of naturally occurring S or N pools (i.e., pyrite, N_2 fixation followed by nitrification) from the soil to the surface waters. Here, we focus on atmospheric deposition of strong inorganic acids, which dominate the recent acidification of soil and surface waters in the northeastern United States.

Effects of acid deposition on soils

The observation of elevated concentrations of inorganic monomeric Al in surface waters provided strong evidence of soil interactions with acidic deposition (Driscoll et al. 1980, Cronan and Schofield 1990). Recent studies have shown that acidic deposition has changed the chemical composition of soils by depleting the content of available plant nutrient cations (i.e., Ca^{2+} , Mg^{2+} , K^+), by increasing the mobility of Al, and by increasing the S and N content.

Depletion of base cations and mobilization of aluminum in soils.

Acidic deposition has increased the concentrations of protons (H^+) and strong acid anions (SO_4^{2-} and NO_3^-) in soils of the northeastern United States, which has led to increased rates of leaching of base cations and to the associated acidification of soils. If the supply of base cations is sufficient, the acidity of the soil water will be effectively neutralized. However, if base saturation (exchangeable base cation concentration expressed as a percentage of total cation exchange capacity) is below 20%, then atmospheric deposition of strong acids results in the mobilization and leaching of Al, and H^+ neutralization will be incomplete (Cronan and Schofield 1990).

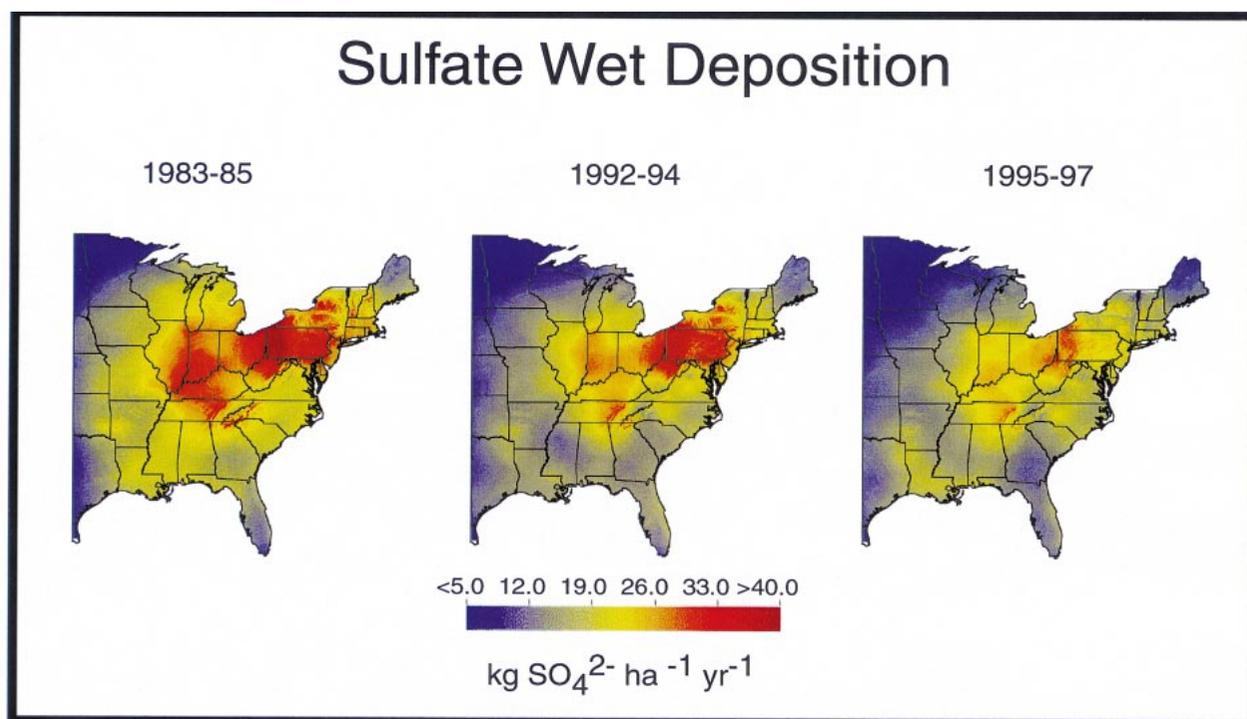


Figure 4. Annual wet deposition of SO_4^{2-} (in $\text{kg SO}_4^{2-} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) in the eastern United States for 1983–1985, 1992–1994, and 1995–1997. Data were obtained for the NADP/NTN and for the model of Grimm and Lynch (1997).

Mineral weathering is the primary source of base cations in most watersheds, although atmospheric deposition may provide important inputs to sites with very low rates of supply from mineral sources. In acid-sensitive areas, rates of base cation supply through chemical weathering are not adequate to keep pace with leaching rates accelerated by acidic deposition. Recent studies based on the analysis of soil (Lawrence et al. 1999), the long-term trends in stream water chemistry (Likens et al. 1996, 1998, Lawrence et al. 1999), and the use of strontium stable isotope ratios (Bailey et al. 1996) indicate that acidic deposition has enhanced the depletion of exchangeable nutrient cations in acid-sensitive areas of the Northeast. At HBEF, Likens et al. (1996) reported a long-term net decline in soil pools of available Ca^{2+} during the last half of the 20th century, as acidic deposition reached its highest levels. Loss of ecosystem Ca^{2+} peaked in

the mid-1970s and abated over the next 15–20 years, as atmospheric deposition of SO_4^{2-} declined.

Without strong acid anions, cation leaching in forest soils of the Northeast is driven largely by naturally occurring organic acids derived from the decomposition of organic matter, which takes place primarily in the forest floor. Once base saturation is reduced in the upper mineral soil, organic acids tend to mobilize Al through formation of organic–Al complexes, most of which are deposited lower in the soil profile through adsorption to mineral surfaces. This process, termed podzolization, results in surface waters with low concentrations of Al. Such concentrations are primarily in a nontoxic, organic form (Driscoll et al. 1988). Acidic deposition has altered podzolization, however, by solubilizing Al with inputs of mobile inorganic anions, which facilitates transport of inorganic Al into surface waters. Acidic deposition to forest soils with base saturation values less than 20% increases Al mobilization and shifts chemical

speciation of Al from organic to inorganic forms that are toxic to terrestrial and aquatic biota (Cronan and Schofield 1990).

Accumulation of sulfur in soils. Watershed input–output budgets developed in the 1980s for northeastern forest ecosystems indicated that the quantity of S exported by surface waters (primarily as SO_4^{2-}) was essentially equivalent to inputs from atmospheric deposition (Rochelle and Church 1987). Those findings suggested that decreases in atmospheric S deposition, from controls on emissions, should result in equivalent decreases in the amount of SO_4^{2-} that enters surface waters. Indeed, there have been long-term decreases in concentrations of SO_4^{2-} in surface waters throughout the Northeast following declines in atmospheric S deposition after the 1970 CAAA (Likens et al. 1990, Stoddard et al. 1999). However, recent studies of watershed mass balances in the Northeast have shown that watershed loss of SO_4^{2-} exceeds atmospheric S deposition (Driscoll et al. 1998). This pattern suggests that decades of atmospheric S deposition have resulted in the accumulation of S in forest soils. With recent declines in atmospheric S deposition and a possible warming-induced enhancement of S mineralization from soil organic matter, previously retained S is gradually being released to surface waters (Driscoll et al. 1998).

Past accumulation of atmospherically deposited S is demonstrated by a strong positive relationship between wet deposition of

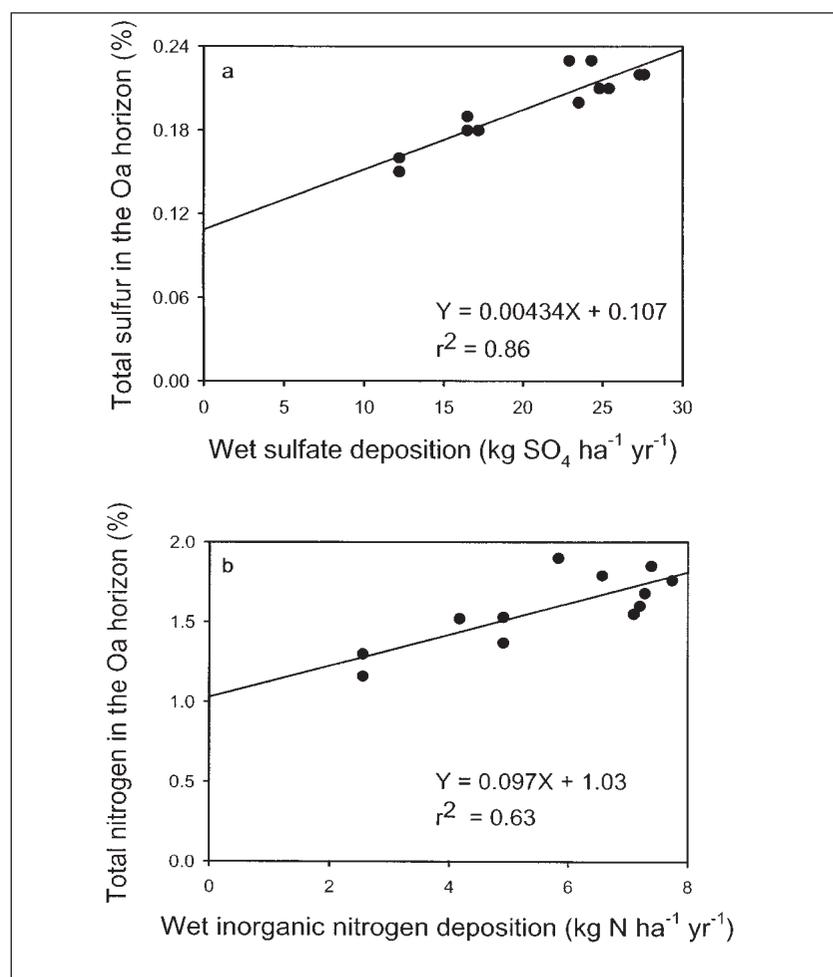


Figure 5. The concentration of total S in the soil Oa horizons as a function of (a) wet SO_4^{2-} deposition and (b) total N in the soil Oa horizons as a function of total inorganic N (NO_3^- and NH_4^+) in wet deposition in 12 red spruce stands located from the western Adirondack Mountains in New York to eastern Maine.

SO_4^{2-} and concentrations of total S in the forest floor of red spruce stands in the Northeast (Figure 5a). It is now expected that the release of SO_4^{2-} that previously accumulated in watersheds from inputs of atmospheric S deposition will delay the recovery of surface waters in response to SO_2 emissions controls (Driscoll et al. 1998). Imbalances in ecosystem S budgets may also be influenced by the weathering of S-bearing minerals or by the underestimation of dry deposition inputs of S. Further effort is needed to quantify such processes more accurately.

Accumulation of nitrogen in soils. Nitrogen is generally considered the growth-limiting nutrient for temperate forest vegetation, and retention by forest ecosystems is generally high. As a result, concentrations of NO_3^- are often very low in surface waters that drain forest landscapes. However, recent research indicates that atmospheric N deposition has accumulated in soils, and some forest ecosystems have exhibited diminished retention of N inputs. Total N concentration in the forest floor of red spruce forests is correlated with wet N deposition at both low (Figure 5b) and high elevations in the Northeast (McNulty et al. 1990). A record of stream chemistry in forest watersheds of the Catskill Mountains (New York) has shown increasing NO_3^- concentrations since 1920, apparently in response to increases in atmospheric N deposition (Charles 1991). Increased stream NO_3^- concentrations have also been observed after experimental additions of N to a small watershed in Maine (Norton et al. 1994). Nitrate behaves much like SO_4^{2-} , thereby facilitating the displacement of cations from the soil and acidifying surface waters.

Increased losses of NO_3^- to surface waters may indicate changes in the strength of plant and soil microbial N sinks in forest watersheds. Because microbial processes are highly sensitive to temperature, fluctuations in microbial immobilization and mineralization in response to climate variability affect NO_3^- losses in drainage waters. Murdoch et al. (1998) found that annual mean NO_3^- concentrations in stream water were not related to annual wet N deposition but rather to mean annual air temperature. Increases in temperature corresponded to increases in stream-water concentrations. Mitchell et al. (1996) found that unusually low winter temperatures that led to soil freezing corresponded to the increased loss of NO_3^- to surface waters. The sensitivity of NO_3^- release to climatic fluctuations tends to increase the magnitude and the frequency of episodic acidification of surface waters.

Despite the linkage between the atmospheric deposition of NH_4^+ and NO_3^- and the loss of NO_3^- from forest ecosystems (Dise and Wright 1995), future effects of atmospheric N deposition on forest N cycling and surface water acidification are likely to be controlled by climate, forest history, and forest type (Aber et al. 1997, Lovett et al. 2000). For example, forests regrowing after agricultural clearing or fire tend to have a higher capacity than undisturbed forests for accumulating N without release to surface waters (Hornbeck

et al. 1997, Aber et al. 1998). The complexity of linkages of NO_3^- loss to climatic variation, to land-use history, and to vegetation type has slowed efforts to predict how ANC in surface waters will respond to anticipated changes in atmospheric N deposition associated with NO_x or NH_3 emission controls. Improved predictions will depend on continued progress in understanding how forest ecosystems retain N and in determining regional-scale information about land-use history. Despite this uncertainty, it is apparent that additional NH_4^+ and NO_3^- inputs to northeastern forests will increase the potential for greater leaching losses of NO_3^- , whereas reductions in NO_x and NH_3 emissions and subsequent N deposition will contribute to long-term decreases in watershed acidification.

Effects of acidic deposition on trees

Researchers noted extensive dieback—reduced growth that leads to mortality—in stands of high-elevation red spruce beginning in the 1960s (Siccama et al. 1982) and in sugar maple stands starting in the 1980s (Houston 1999). Their observations led to investigations of the effects of acidic deposition on trees, both the direct effects of acidic precipitation and cloud water on foliage and the indirect effects from changes in soils that alter nutrient uptake by roots. The mechanisms by which acidic deposition causes stress to trees are only partially understood, but they generally involve interference with Ca^{2+} nutrition and Ca-dependent cellular processes (DeHayes et al. 1999). The depletion of Ca^{2+} in forest soils, described above, raises concerns about the health and productivity of northeastern forests (DeHayes et al. 1999, McLaughlin and Wimmer 1999). Progress on understanding the effects of acidic deposition on trees has been limited by the long response time of trees to environmental stresses, the difficulty in isolating possible effects of acidic deposition from other natural and anthropogenic stresses, and the insufficiency of information on how acidic deposition has changed soils. To date, investigations of possible effects of acidic deposition on trees in the Northeast have focused primarily on red spruce and sugar maple.

Red spruce. There is strong evidence that acidic deposition causes dieback of red spruce by decreasing cold tolerance. Red spruce is common in Maine, where it is an important commercial species. It is also common at high elevations in mountainous regions throughout the Northeast, where it is valued for recreation and aesthetics, as well as for providing a habitat for unique and endangered species. Dieback has been most severe at high elevations in the Adirondack and Green Mountains, where more than 50% of the canopy trees died during the 1970s and 1980s. In the White Mountains, about 25% of the canopy spruce died during that same period (Craig and Friedland 1991). Dieback of red spruce trees has also been observed in mixed hardwood–conifer stands at relatively low elevations in the western Adirondack Mountains, an area that receives high inputs of acidic deposition (Shortle et al. 1997).

Results of controlled exposure studies show that acidic mist or acidic cloud water reduces the cold tolerance of current-year red spruce needles by 3–10° C (DeHayes et al. 1999). This condition can be harmful because current-year needles are only marginally tolerant of the minimum winter temperatures that are typical of upland regions in the Northeast. Hydrogen ion in acidic deposition leaches membrane-associated Ca^{2+} from needles, which increases their susceptibility to freezing. The increased frequency of winter injury in the Adirondack and Green Mountains since 1955 coincides with increased exposure of red spruce canopies to highly acidic cloud water (Johnson et al. 1984). Recent episodes of winter injury (loss of current-year needles) have been observed throughout much of the range of red spruce in the Northeast (DeHayes et al. 1999).

Calcium depletion and Al mobilization may also affect red spruce in the Northeast. Low ratios of Ca^{2+} to Al in soil have been associated with the dysfunction of fine roots, which are responsible for water and nutrient uptake (Shortle and Smith 1988). Aluminum can block the uptake of Ca^{2+} , which can lead to reduced growth and increased susceptibility to stress. From an extensive review of the literature, Cronan and Grigal (1995) concluded that a Ca^{2+} :Al ratio of less than 1.0 in soil water indicated a greater than 50% probability of impaired growth in red spruce. They also cited examples from studies from the Northeast where soil solutions in the field were found to exhibit Ca:Al ionic ratios less than 1.0. Those findings suggest that a Ca:Al ratio of 1.0 in soil waters of forest ecosystems may serve as a useful index for tracking the recovery of terrestrial ecosystems from the deleterious effects of acidic deposition.

To establish a stronger direct link between Ca:Al ionic ratios and red spruce dieback, several issues need to be addressed: the uncertainty of extrapolating from controlled seedling experiments to the complex responses of mature trees in the field; the fact that declining forest stands may be exposed simultaneously to multiple stresses, complicating assessment of the effects of acidic deposition alone; and the difficulty of quantifying how roots of mature trees respond to the rhizosphere solution chemistry and Ca:Al ionic ratios of soil horizons. Other studies of historical changes in wood chemistry of red spruce have found a strong relationship between Ca concentrations in tree rings, trends in atmospheric deposition, and presumed changes in soil Ca^{2+} availability, suggesting that acidic deposition has altered the mineral nutrition of red spruce (Shortle et al. 1997). Although Ca concentrations in sapwood typically decrease steadily from older to younger wood, a steady increase of Ca concentration in tree rings formed from about 1950 to 1970 has been documented in red spruce trees throughout the Northeast. Peak levels of acidic deposition during that period apparently caused elevated concentrations of Ca^{2+} in soil water and increased uptake of Ca^{2+} by roots (Shortle et al. 1997). After that pulse of soil leaching, it is hypothesized, depletion of soil Ca resulted in decreased Ca^{2+} concentrations in soil water, decreased plant uptake of Ca^{2+} ,

and diminished Ca concentrations in subsequent tree rings. This scenario is illustrated by a trend in enrichment frequency of Ca concentrations in wood (the percentage of samples with a higher Ca concentration in 10 years of wood tissue than in the previous 10 years of wood tissue) that was relatively stable from 1910 to 1950, increased from 1950 to 1970, and then decreased to low levels in the period 1970–1990 (Shortle et al. 1997).

Sugar maple. Dieback of sugar maple has been observed at several locations in the Northeast since the 1950s. That disturbance has recently been most evident in Pennsylvania, where crown dieback has led to extensive mortality in some forest stands (that is, with the basal area of dead sugar maple ranging from 20% to 80% of all sugar maple trees; Drohan et al. 1999). High rates of tree mortality tend to be triggered by periodic stresses such as insect infestations and drought. Periodic dieback of sugar maple has been attributed to forest- and land-use practices that have encouraged the spread of this species to sites that either are drought prone or have nutrient-poor soils. On those sites, the trees are less able to withstand stresses without experiencing growth impairment and mortality (Houston 1999).

Acidic deposition may contribute to episodic dieback of sugar maple by causing depletion of nutrient cations from marginal soils. Long et al. (1997) found that liming (addition of CaCO_3) significantly increased sugar maple growth, improved crown vigor, and increased flower and seed crops of overstory sugar maple in stands that were experiencing dieback. Liming also increased exchangeable base cation concentrations in the soil and decreased concentrations of exchangeable Al.

Further evidence of a link between soil base cation status and periodic dieback of sugar maple has been reported by Horsley et al. (1999), who found that dieback at 19 sites in northwestern and north-central Pennsylvania and southwestern New York was correlated with combined stress from defoliation and deficiencies of Mg and Ca. Dieback occurred predominantly on ridgetops and on upper slopes, where soil base availability was much lower than at mid and low slopes of the landscape (Bailey et al. 1999). These studies suggest that depletion of nutrient base cations in soil by acidic deposition may have reduced the area favorable for growing sugar maple trees in the Northeast. Factors such as soil mineralogy and landscape position affect soil base status, as well as acidic deposition, thereby complicating assessments of the extent of sugar maple dieback that can be attributed to acidic deposition.

Effects on surface waters

Inputs of acidic deposition to regions with base-poor soils have resulted in the acidification of soil waters, shallow groundwaters, streams, and lakes in parts of the northeastern United States and elsewhere. In addition, perched seepage lakes, which derive water largely from direct precipitation inputs, are highly sensitive to acidic deposition (Charles

1991). These processes usually result in lower pH and, for drainage lakes, higher concentrations of inorganic monomeric Al. Such changes in chemical conditions are toxic to fish and other aquatic animals.

Surface water chemistry. To evaluate the regional extent of lake acidification, we used data from a survey of lakes in the Northeast for the period 1991–1994 (EMAP; Larsen et al. 1994, Stevens 1994). This probability-based survey allows inferences to be made about the entire population of lakes in the Northeast (10,381 lakes with surface area greater than 1 ha both within New York and around New England). Other surveys conducted at different times, or with different criteria for minimum lake size, have shown somewhat different results (e.g., Kretser et al. 1989, Charles 1991).

The Northeast EMAP survey was conducted during low-flow summer conditions, so the water chemistry very likely represents the highest ANC values for the year. Lakes were subdivided into ANC classes. Lakes with ANC values below $0 \mu\text{eq L}^{-1}$ are considered to be chronically acidic (that is, those lakes are acidic throughout the year). Lakes with ANC values between 0 and $50 \mu\text{eq L}^{-1}$ are considered susceptible to episodic acidification; ANC may decrease below $0 \mu\text{eq L}^{-1}$ during high-flow conditions in these lakes. Finally, lakes with ANC values greater than $50 \mu\text{eq L}^{-1}$ are considered relatively insensitive to inputs of acidic deposition.

Results from the EMAP survey indicate that, in the Adirondack region of New York (1812 lakes), 41% of the lakes are chronically acidic or sensitive to episodic acidification (10% have ANC values of less than $0 \mu\text{eq L}^{-1}$, and 31% have ANC values between 0 and $50 \mu\text{eq L}^{-1}$). In New England and in the eastern Catskill region of New York (6834 lakes), 5% of the lakes have ANC values of less than $0 \mu\text{eq L}^{-1}$, and 10% have ANC values between 0 and $50 \mu\text{eq L}^{-1}$. Most of the acidic and acid-sensitive surface waters in New York State are located in the Adirondack and Catskill regions. This regional variation in ANC is largely controlled by the supply of Ca^{2+} and Mg^{2+} to surface waters ($\text{ANC} = -58 + 0.85 \times [\text{Ca}^{2+} + \text{Mg}^{2+}]$; $r^2 = 0.94$; concentrations expressed in $\mu\text{eq L}^{-1}$).

To quantify the nature of the acid inputs, we examined the distribution of anions (i.e., SO_4^{2-} , NO_3^- , chloride $[\text{Cl}^-]$, bicarbonate $[\text{HCO}_3^-]$, and organic anions) in acid-sensitive lakes of the Northeast (ANC less than $50 \mu\text{eq L}^{-1}$; 1875 lakes). Naturally occurring organic anions were not measured directly, but were estimated using the charge-balance approach (Driscoll et al. 1994a). Results of the analysis can be summarized as follows: Of the acid-sensitive lakes (ANC less than $50 \mu\text{eq L}^{-1}$), 83% were dominated by inorganic anions, with SO_4^{2-} constituting 82% of the total anionic charge. Of the acid-sensitive lakes, 17% were dominated by naturally occurring organic anions and were assumed to be naturally acidic lakes—organic anions accounted for an average of 71% of the total anions in that group of lakes. The acidity of organic-acid-dominated lakes was supplemented by sulfuric acid from atmospheric deposition, so that SO_4^{2-} con-

tributed an average of 19% of the anionic charge in these naturally acidic lakes.

Seasonal and episodic acidification of surface waters. In the Northeast, the most severe acidification of surface water generally occurs during spring snowmelt (Charles 1991). Short-term acid episodes also occur during midwinter snowmelts, and large precipitation events occur in summer or fall (Wigington et al. 1996).

Data from Buck Creek in the Adirondack Mountains, which is part of the Episodic Response Project (ERP), illustrate the seasonal and episodic changes in water chemistry of acid-sensitive surface waters in the Northeast (Figure 6). In the ERP, acidic events and subsequent mortality of brook trout and blacknose dace were monitored in streams in the Adirondack and Catskill Mountains of New York and in the Appalachian Plateau of Pennsylvania (Wigington et al. 1996). All streams had low ANC values and physical habitats that were judged suitable for fish survival and reproduction, and all had indigenous fish populations in at least part of the stream ecosystem (Baker et al. 1996).

Buck Creek exhibited both seasonal and event-driven changes in chemistry. The seasonal pattern in ANC values

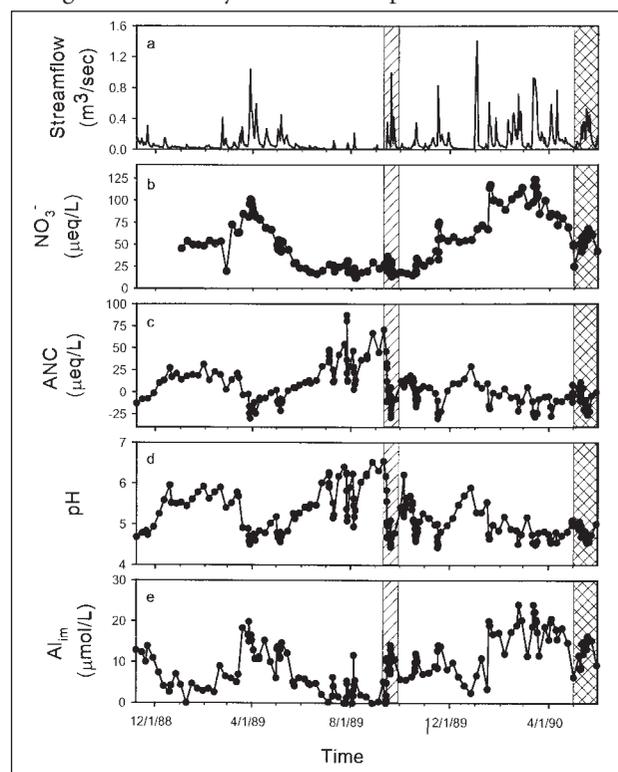


Figure 6. Seasonal changes in (a) flow, (b) nitrate (NO_3^-), (c) acid-neutralizing capacity (ANC), (d) pH, and (e) inorganic monomeric aluminum (Al_{im}) at Buck Creek in the Adirondack region of New York. The crosshatched area represents a significant event of episodic acidification. The double crosshatched area represents the period over which an *in situ* bioassay was conducted (see Figure 9).

corresponded to seasonal changes in NO_3^- ($r^2 = 0.44$). Stream NO_3^- concentrations were lowest in summer because of vegetation uptake of N, and ANC values were at the annual maximum. Stream NO_3^- increased and ANC values decreased during fall, coinciding with increased flow and decreased plant activity. Nitrate concentrations increased and ANC values decreased during winter, with maximum NO_3^- concentrations and minimum ANC values occurring during spring snowmelt. Seasonal increases in NO_3^- were also associated with increases in inorganic monomeric Al concentrations ($r^2 = 0.93$). Superimposed on those seasonal patterns were event-driven changes in stream chemistry, such as occurred at Buck Creek on 15 September 1989 (see Figure 6). During that event, flow increased from 0.008 to $0.36 \text{ m}^3 \text{ s}^{-1}$, which resulted in increases in NO_3^- concentrations (from 20 to $37 \text{ } \mu\text{eq L}^{-1}$), decreases in ANC (46 to $30 \text{ } \mu\text{eq L}^{-1}$) and pH (6.2 to 4.7), and increases in concentrations of inorganic monomeric Al (0.8 to $10 \text{ } \mu\text{mol L}^{-1}$).

Long-term changes in surface water chemistry.

Unfortunately, there are limited data to document the responses to atmospheric deposition since the time of the Industrial Revolution (Charles 1991) and few tools to predict the future effects of atmospheric deposition. Acidification models have been used to estimate past and future acidification effects (Eary et al. 1989). The model PnET (PnET-CN; Aber and Federer 1992; Aber and Driscoll 1997; Aber et al. 1997) is a simple, generalized, and well-validated model that provides estimates of forest net primary productivity, nutrient uptake by vegetation, and water balances. Recently, PnET was coupled with a soil model that simulates abiotic soil processes (e.g., cation exchange, weathering, adsorption, and solution speciation), resulting in a comprehensive forest–soil–water model, PnET-BGC; PnET-BGC is designed to simulate element cycling in forest and interconnected aquatic ecosystems (Kram et al. 1999, Gbondo-Tugbawa et al. forthcoming). The PnET models have been used extensively at HBEF to investigate the effects of disturbance (e.g., cutting, climatic disturbance, and air pollution) on forest and aquatic resources (Aber and Driscoll 1997, Aber et al. 1997, Gbondo-Tugbawa et al. forthcoming).

Using relationships between current emissions and deposition (e.g., Figure 3), plus estimates of past emissions (USEPA 2000), we reconstructed historical patterns of atmospheric deposition of S and N at HBEF. In addition, we considered land disturbances to the watershed, including logging in 1918–1920 and hurricane damage in 1938. We calculated the response of vegetation, soil, and stream water to this deposition scenario with PnET-BGC (Figure 7). A detailed description of the application of PnET-BGC to HBEF is available in Gbondo-Tugbawa et al. (forthcoming). We estimated that total atmospheric deposition (wet + dry) of S at HBEF increased from $7 \text{ kg SO}_4^{2-} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ in 1850 to a most recent peak of $68 \text{ kg SO}_4^{2-} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ in 1973 and the total atmospheric deposition has decreased since that time. We also estimated that past soil base saturation (circa 1850)

was approximately 20%; stream SO_4^{2-} concentration was approximately $10 \text{ } \mu\text{eq L}^{-1}$; stream ANC was about $40 \text{ } \mu\text{eq L}^{-1}$; stream pH was about 6.3; and stream Al concentration was below $2 \text{ } \mu\text{mol L}^{-1}$, more than 50% of which was in an organic form.

Compared with model hindcast approximations, current conditions at HBEF indicate that soil percentage base saturation has decreased to about 10% in response to acidic deposition and to accumulation of nutrient cations by forest biomass. Further, acidic deposition has contributed to a

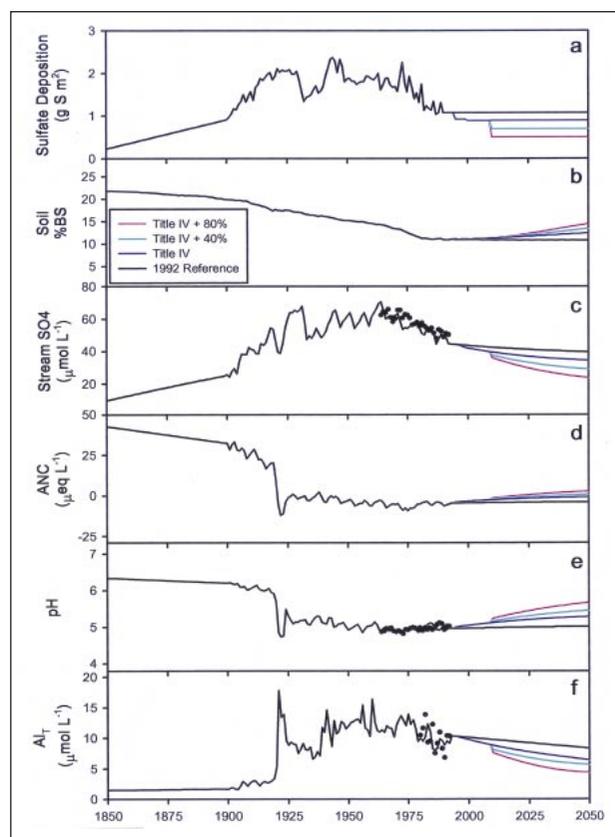


Figure 7. Estimates of past and future atmospheric sulfur deposition (a) and predictions of soil and stream water chemistry, using the model PnET-BGC for Watershed 6 of the Hubbard Brook Experimental Forest, New Hampshire. Model predictions include (b) percentage of soil base saturation, (c) stream sulfate (SO_4^{2-}) concentrations, (d) stream acid-neutralizing capacity (ANC), (e) pH, and (f) stream concentrations of aluminum (Al_T). Future predictions include four scenarios of atmospheric sulfur deposition: constant values from 1992, values anticipated following the 1990 amendments to the Clean Air Act, 22% reduction in atmospheric sulfur deposition in 2010 beyond the 1990 amendments to the Clean Air Act, and 44% reduction in atmospheric sulfur deposition in 2010 beyond the 1990 amendments to the Clean Air Act. These latter two scenarios depict 40%–80% reductions in utility emissions of sulfur dioxide. Actual annual volume-weighted concentrations of stream water are shown for comparison.

nearly fourfold increase in stream SO_4^{2-} ; a decrease in ANC from positive to negative values; a decrease in stream pH to below 5.0; and increases in stream Al, largely occurring as the toxic inorganic form (greater than $10 \mu\text{mol L}^{-1}$). Substantial deterioration in the acid–base status of soil and water at HBEF is indicated during the 1850–1970 period. Model calculations suggest that strong acid inputs associated with mineralization of soil organic matter after forest cutting in during the 1910s resulted in the short-term (i.e., 2–3 years) acidification of stream water.

Since 1964, stream water draining the HBEF reference watershed (Watershed 6) has shown a significant decline in annual volume-weighted concentrations of SO_4^{2-} ($-1.1 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$; Figure 2). This decrease in stream SO_4^{2-} corresponds to both decreases in atmospheric emissions of SO_2 and to bulk precipitation concentrations of SO_4^{2-} (Likens et al. 2001). In addition, there has been a long-term decrease in stream concentrations of NO_3^- that is not correlated with a commensurate change in emissions of NO_x or in bulk deposition of NO_3^- . Those long-term declines in stream concentrations of strong acid anions ($\text{SO}_4^{2-} + \text{NO}_3^-$; $-1.9 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$) have resulted in small but significant increases in pH. The increase in stream pH has been limited because of marked, concurrent decreases in the sum of base cations ($-1.6 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$).

A similar pattern is evident both within the Adirondack and the Catskill regions of New York and across New England. Analysis of data from the EPA's Long-Term Monitoring (LTM) Program, which was initiated in the early 1980s, showed significant declines in surface water SO_4^{2-} and in the sum of strong acid anions ($\text{SO}_4^{2-} + \text{NO}_3^-$) in the Adirondack and Catskill subregion, as well as in the New England subregion (Stoddard et al. 1999). Note that the rate of decline in SO_4^{2-} for Adirondack and Catskill surface waters ($-1.9 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$) was somewhat greater than the values observed for New England ($-1.3 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$). In contrast to the patterns at HBEF, regional sites showed no significant trends in concentrations of NO_3^- . Surface waters in New England showed modest increases in ANC values ($+0.8 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$), but no increase in ANC values was evident in the Adirondack and Catskill subregion. This difference is attributable to the marked decrease in the sum of base cations in the Adirondack and Catskill subregion ($-2.7 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$) compared with the New England subregion ($-0.7 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$). Such patterns suggest that the lack of recovery of Adirondack and Catskill surface waters, when compared to New England surface waters, is due to the historically higher loading of acidic deposition in New York than in most of New England (Figure 4). This higher acid input has evidently resulted in greater depletion of exchangeable base cations in acid-sensitive watersheds in New York (Stoddard et al. 1999).

Effects on aquatic biota. Acidification has marked effects on the trophic structure of surface waters. Decreases in pH and increased Al concentrations contribute to declines in species richness and in the abundance of zooplankton,

macroinvertebrates, and fish (Schindler et al. 1985; Keller and Gunn 1995).

High concentrations of both H^+ (measured as low pH) and inorganic monomeric Al are directly toxic to fish (Baker and Schofield 1982). Although Al is abundant in nature, it is relatively insoluble in the neutral pH range and thus unavailable biologically. Acid-neutralizing capacity largely controls pH and the bioavailability of Al (Driscoll and Schecher 1990). Thus, surface waters with low ANC and pH as well as high concentrations of inorganic monomeric Al are less hospitable to fish. Calcium, however, directly ameliorates the toxic stress caused by H^+ and Al (Brown 1983). Watershed supply of Ca^{2+} also contributes to ANC. Therefore, lakes with higher Ca^{2+} are more hospitable to fish, as indicated by the synoptic survey conducted by the Adirondack Lakes Survey Corporation (ALSC; Gallagher and Baker 1990). Of the 1469 lakes surveyed by the ALSC, at least one fish species was caught in 1123 lakes (76%), whereas no fish were caught in 346 lakes (24%). The 346 fishless lakes in the Adirondack region had significantly ($p < .05$) lower pH, Ca^{2+} concentration, and ANC values, as well as higher concentrations of inorganic monomeric Al, when compared to lakes with fish (Gallagher and Baker 1990).

Small, high-elevation lakes in the Adirondack region are more likely to be fishless than larger lakes at low elevation (Gallagher and Baker 1990), because they have poor access for fish immigration, poor fish spawning substrate, or low pH, or they may be susceptible to periodic winterkills. Nevertheless, small, high-elevation Adirondack lakes with fish also had significantly higher pH compared with fishless

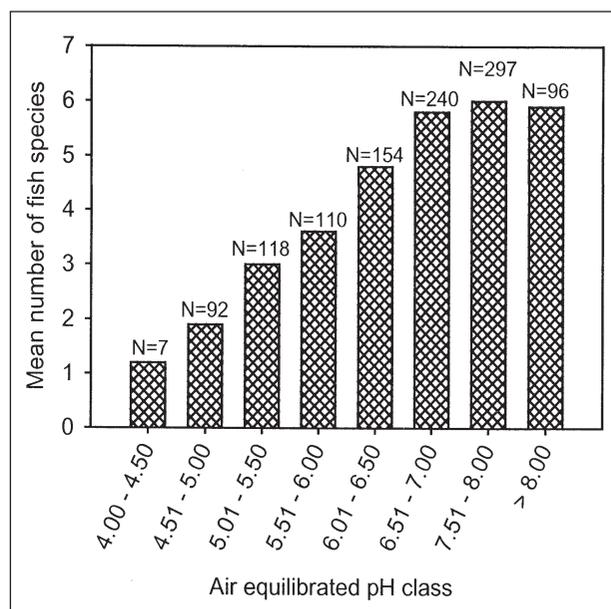


Figure 8. Distribution of the mean number of fish species for ranges of pH from 4.0 to 8.0 in lakes in the Adirondack region of New York. N represents the number of lakes in each pH category (modified from Kretser et al. 1989).

lakes; acidity is likely to play an important role in the absence of fish from such lakes.

Numerous studies have shown that fish species richness (the number of fish species in a water body) is positively correlated with pH and ANC values (Figure 8; Rago and Wiener 1986, Kretser et al. 1989). Decreases in pH result in decreases in species richness by eliminating acid-sensitive species (Schindler et al. 1985). Of the 53 species of fish recorded by the ALSC (Kretser et al. 1989), about half (26 species) are absent from lakes with pH less than 6.0. Those 26 species include important recreational fishes, such as Atlantic salmon, tiger trout, redbreast sunfish, bluegill, tiger musky, walleye, alewife, and kokanee (Kretser et al. 1989), plus ecologically important minnows that serve as forage for sport fishes. Significantly, the most common fish species caught by the ALSC (brown bullhead, yellow perch, golden shiner, brook trout, and white sucker) also show the greatest tolerance of acidic conditions, as evidenced by their occurrence in lakes with relatively low pH and high Al concentrations (Gallagher and Baker 1990).

A clear link exists between acidic water, which results from atmospheric deposition of strong acids, and fish mortality. *In situ* bioassays conducted during acidic events (pulses of low pH, Al-rich water after precipitation events or snowmelt) provide an opportunity to measure the direct, acute effects of stream chemistry on fish mortality. Those experiments show that even acid-tolerant species, such as brook trout, are killed by acidic water in the Adirondack region (Figure 9; Baker et al. 1996, Van Sickle et al. 1996). Episodic acidification is particularly important in streams and rivers (compared with lakes) because these ecosystems experience large abrupt changes in water chemistry and provide limited refuge areas for fish. Baker et al. (1996) concluded that episodic acidification can have long-term negative effects on fish communities in small streams because of mortality, emigration, and reproductive failure.

The ERP study showed that streams with moderate to severe acid episodes had significantly higher fish mortality during bioassays than nonacidic streams (Van Sickle et al. 1996). The concentration of inorganic monomeric Al was the

Table 2. Summary of estimated utility emissions resulting from the 1990 amendments of the Clean Air Act and proposed federal legislation aimed at reducing electric utility emissions that contribute to acidic deposition and ground-level ozone. Emissions are in million metric tons, with values of million short tons indicated in parentheses. Also shown is the percentage of total US emissions that utility emissions would contribute if each proposal were implemented.

Proposal and sponsor	NO _x		SO ₂		Time frame for full implementation	Cap and trade structure
	Estimated utility emissions	Total emissions ^a (%)	Estimated utility emissions	Total emissions ^b (%)		
1990 Clean Air Act	5.16 (5.7)	24.8	8.07 (8.9)	54.6	2010	Yes (for SO ₂)
S. 172 Moynihan (and H.R. 657 Sweeney and H.R. 25 Boehlert)	2.14 (2.36)	12	4.04 (4.45)	37.6	2005	Yes
S. 1369 Jeffords (and H.R. 2645 Kucinich)	1.5 (1.66)	8.8	3.24 (3.58)	32.6	2005	Yes
H.R. 2900 Waxman	1.63 (1.8)	9.4	2.8 (3.11)	29.6	2005	No
S. 1949 Leahy	1.27 (1.4)	7.5	2.63 (2.9)	28.2	2010	No
H.R. 2980 Allen	1.45 (1.6)	8.5	2.9 (3.2)	30.2	2005	No

^aAssumes that total NO_x emissions from other sources are constant and that total emissions decrease by the same amount as the reduction in utility emissions. NO_x emissions figures are based on 1997 levels for total (21.3 metric tons or 23.5 million short tons) and utility emissions (5.62 metric tons or 6.2 million short tons).

^bAssumes that total SO₂ emissions from other sources remain constant and that total emissions decrease by the same amount as utility emissions. SO₂ figures are based on 1997 levels for total (18.5 metric tons or 20.4 million short tons) and utility emissions (11.8 metric tons or 13 million short tons).

chemical variable most strongly related to mortality in the four test species (brook trout, mottled sculpin, slimy sculpin, and blacknose dace). Because of their correlations with Al, variations in pH and Ca^{2+} concentrations were of secondary importance in accounting for mortality patterns. The ERP streams with high fish mortality during acid episodes had lower brook trout density and biomass and lacked the more acid-sensitive species (blacknose dace and sculpins). In streams that exhibited episodic acidification, radio-tagged brook trout emigrated downstream during episodes, whereas radio-tagged fish in nonacidic streams did not. In general, trout abundance was lower in ERP streams with median episode pH less than 5.0 and with a concentration of inorganic monomeric Al greater than $3.7\text{--}7.4\ \mu\text{mol L}^{-1}$. Acid-sensitive species were absent from streams with median episode pH less than 5.2 and with a concentration of inorganic monomeric Al greater than $3.7\ \mu\text{mol L}^{-1}$.

Question 3: How do we expect emissions and deposition to change in the future, and how might ecosystems respond to these changes?

To date, major electric utilities in the United States have met or surpassed the Phase I SO_2 emissions reduction target established by the Acid Deposition Control Program of the 1990 CAAA (see Figure 1; Lynch et al. 2000). Nevertheless, reports suggest that this emissions target will not protect sensitive ecosystems (USEPA 1995, Likens et al. 1996, Stoddard et al. 1999). Concern about these findings has spurred Congress to introduce several bills that call for deeper cuts in utility emissions of SO_2 and NO_x . With acidic deposition resurfacing as a national environmental issue, decision-makers need to determine whether additional emissions reductions are needed and to what extent further reductions will promote recovery from acidic deposition. To help address these issues, we present a conceptual framework for understanding ecosystem recovery from acidic deposition, suggest numerical indicators of chemical recovery, review current bills that call for reducing emissions by utilities, and use the model PnET-BGC to estimate changes in deposition that proposed emissions reductions would bring about and to predict ecosystems responses at the HBEF.

Ecosystem recovery

Acidic deposition disturbs forest and aquatic ecosystems by giving rise to harmful chemical conditions. Atmospheric S deposition to the northeastern United States has increased more than fivefold over the past 150 years (Figure 7; Charles 1991), and most acid-sensitive ecosystems have been exposed to high inputs of strong acids for many decades. Since the 1970 CAAA, there have been significant decreases in atmospheric S deposition; as a result, some aquatic ecosystems in the Northeast have been experiencing some chemical recovery (Stoddard et al. 1999). Several critical chemical thresholds appear to coincide with the onset of deleterious effects to biotic resources. For example, a molar Ca:Al ratio

of soil water that is less than 1 and a soil percentage base saturation that is less than 20% indicate that forest vegetation is at risk with respect to soil acidification from acidic deposition (Cronan and Schofield 1990, Cronan and Grigal 1995). Also, surface water pH that is less than 6.0, ANC less than $50\ \mu\text{eq L}^{-1}$, or concentrations of inorganic monomeric Al greater than $2\ \mu\text{mol L}^{-1}$ indicate that aquatic biota are at risk from surface water acidification because of acidic deposition (MacAvoy and Bulger 1995). Those values can also be used as indicators of chemical recovery (e.g., soil water Ca:Al greater than 1, soil percentage base saturation greater than 20%, surface water pH greater than 6.0, ANC greater than $50\ \mu\text{eq L}^{-1}$, and inorganic monomeric Al less than $2\ \mu\text{mol L}^{-1}$). Knowledge of such indicators is necessary for restoring ecosystem structure and function.

Although experience and understanding of acidification recovery is limited, particularly at the ecosystem level, we envision that the process will involve two phases. Initially, decreases in acidic deposition following emissions controls will facilitate a phase of chemical recovery in forest and aquatic ecosystems. Recovery time for the first phase will vary widely across ecosystems and will be a function of the following:

- the magnitude of decreases in atmospheric deposition

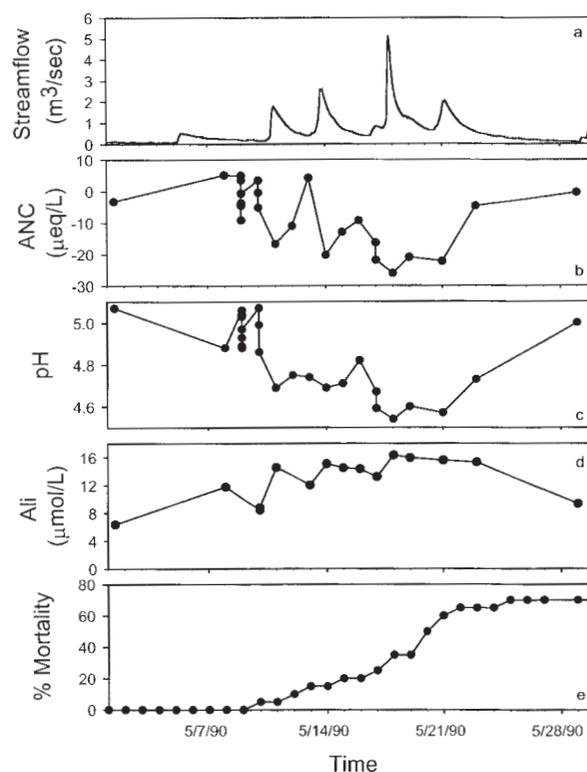


Figure 9. Results of an *in situ* bioassay in Buck Creek, Adirondack Mountains, in spring 1990: (a) discharge, (b) acid-neutralizing capacity, (c) pH, (d) concentration of inorganic monomeric aluminum, and (e) cumulative percentage of mortality of brook trout over time. This figure represents the bioassay performed during the double crosshatched time period in Figure 6.

- the local depletion of exchangeable soil pools of base cations
- the local rate of mineral weathering and atmospheric inputs of base cations
- the extent and rate to which soil pools of S and N are released as SO_4^{2-} or as NO_3^- to drainage waters (Galloway et al. 1983)

In acidic soils with low base saturation, we expect that reductions in concentrations of strong acid anions will result in little initial improvement in the ANC of surface waters (Likens et al. 1996, 1998, Stoddard et al. 1999) and in the soil Ca:Al ionic ratios. Only as the soil base status increases will such sites begin recovery of ANC. Other delays may occur in soils in which atmospheric deposition has caused accumulation of S and N that will be released gradually through desorption or mineralization under conditions of lower atmospheric loading. In most cases, it seems likely that chemical recovery will require decades, even with additional controls on emissions. Chemical recovery can be enhanced at specific sites (e.g., lakes, streams, and watersheds of interest) by base addition (e.g., liming; Driscoll et al. 1996).

The second phase in ecosystem recovery is biological recovery, which can occur only if chemical recovery is sufficient to allow survival and reproduction of plants and animals. The time required for biological recovery is uncertain. We know little about the mechanisms and time frame for recovery of terrestrial ecosystems after decreases in acidic deposition, but it is likely to be at least decades after soil chemistry is restored because of the long life of tree species and the complex interactions of soil, roots, microbes, and soil biota. Research suggests that stream populations of macroinvertebrates may recover relatively rapidly (approximately 3 years) in response to improved chemical conditions, whereas lake populations of zooplankton are likely to recover more slowly (approximately 10 years) (Gunn and Mills 1998). Some fish populations may recover in 5 to 10 years after the recovery of zooplankton populations. Recovery of fish populations could be accelerated by stocking. Although it is unlikely that aquatic ecosystems could be restored to the exact conditions that existed before acidification, improvement in the chemical environment is expected to allow recovery of the ecosystem function that supports improved biotic diversity and productivity.

Proposed emissions reductions

The rate and extent of ecosystem recovery is related to the timing and degree of emissions reductions. We reviewed SO_2 and NO_x emissions reductions associated with the 1990 CAAA and with five prominent bills aimed at controlling utility emissions (Table 2), which were introduced in Congress. We used the results of this review to define inputs to a model of acidic deposition and ecosystem effects at the HBEF.

The five bills analyzed here call for significant cuts in utility emissions of SO_2 and NO_x . We adopt the emissions estimates for each of the bills as reported by the Congressional

Research Service, and we assume equal levels of compliance under each bill (Parker 2000). We rely on EPA estimates for emission levels after implementation of the 1990 CAAA (USEPA 2000). Under these estimates, the five bills would reduce utility SO_2 emissions by another 50%–67% and would decrease utility NO_x emissions another 56%–72% beyond Phase II of the Acid Deposition Control Program of the 1990 CAAA. At present, Senate Bill 172 and House Bills 25 and 657 would modify CAAA standards least, whereas Senate Bill 1949 would reduce emissions most (Table 2).

For four of the bills we reviewed, the implementation deadline is 2005; Senate Bill 1949 sets a deadline of 2010. All bills establish year-round requirements for utility emissions of SO_2 and NO_x . Senate Bill 172 includes additional NO_x cuts from May to September to achieve a higher level of protection during the ozone season. Several bills retain the cap and trade structure, expanding that approach to include NO_x . All bills pertain to the 50 US states and the District of Columbia, except Senate 172, which is limited to the 48 contiguous states and the District of Columbia. The size of the utilities affected varies somewhat among the bills. Most bills apply to units with a generating threshold of 15 MW or greater. Senate Bill 1949 applies to all electric utility generating units, and Senate Bill 172 sets a threshold of 25 MW or greater.

Modeling of emissions scenarios

We used information from the bills (Table 2) as input to the PnET-BGC model so we could predict ecosystem responses at the HBEF to a range of emissions reductions (Figure 7). We determined calculations for three conditions:

- Condition A: S deposition without implementation of the 1990 CAAA
- Condition B: S deposition after implementation of the 1990 CAAA
- Condition C: S deposition after the 1990 CAAA, with additional 40% and 80% cuts in utility SO_2 emissions in 2010.

The latter percentages, 40% and 80%, represent the full range of emissions reductions embodied in the five bills reviewed here; these cuts would amount to 22% and 44% of the total US emissions of SO_2 , respectively. We assume that these decreases in SO_2 emissions will result in commensurate decreases—22% and 44%, respectively—in total S deposition in 2010. Recent observations by Butler et al. (2001) support this one-to-one relationship between SO_2 emissions and SO_4^{2-} deposition. Because the proposed SO_2 emissions reductions should therefore have a marked effect on atmospheric S deposition in the Northeast, we focused our analysis on S controls.

We did not consider decreases in NO_3^- or NH_4^+ deposition. Controls on N emissions should also mitigate the effects of acidic deposition. Should NO_3^- losses in surface waters equal atmospheric N deposition in the Adirondack region within 50 years, the EPA projects, the percentage of lakes with ANC values of less than $0 \mu\text{eq L}^{-1}$ will increase

from 19% to 43% (USEPA 1995). Because utilities contribute less than one-fourth of total NO_x emissions (Table 2), it is unlikely that reductions in utility NO_x emissions alone will be sufficient to improve the N or acid–base status of sensitive forest ecosystems in the Northeast. Indeed, these bills do not consider atmospheric N deposition that originates from NH_3 or vehicle NO_x emissions, which are both important sources of N to the atmosphere.

As anticipated, model calculations show that reductions in atmospheric S deposition will render beneficial changes in soil and surface water chemistry at the HBEF. The model calculations indicate that the Acid Deposition Control Program will result in modest improvements in average stream water chemistry at the HBEF for the period 1994–2005 (condition B). Specifically, SO_4^{2-} will decrease by $12 \mu\text{eq L}^{-1}$, ANC values will increase by about $2 \mu\text{eq L}^{-1}$, and pH will increase slightly (about 0.1 units). Additional controls on SO_2 emissions, such as those suggested in current proposals, should yield greater improvements in soil and water chemistry. The model predicts, for example, that a 40% reduction in utility emissions of SO_2 from levels anticipated under the 1990 CAAA (condition C) would yield a 22% decrease in atmospheric S deposition in 2010, which would decrease stream SO_4^{2-} concentrations by $8.1 \mu\text{eq L}^{-1}$ by 2025. In contrast, a 44% decrease in S deposition (80% decrease in utility SO_2 emissions) would decrease stream SO_4^{2-} concentrations by about $15 \mu\text{eq L}^{-1}$ by 2025.

Despite marked reductions in atmospheric S deposition over the past 34 years (Likens et al. 2001), stream water ANC values at the HBEF remain below $0 \mu\text{eq L}^{-1}$. Because of the loss of available soil pools of nutrient cations from atmospheric S deposition during the past century, the recovery of stream water ANC after decreases in strong acid loading has been delayed. If there were no controls beyond the 1990 CAAA (condition B), the rate of ANC increase predicted by the model for 2010–2025 is $0.06 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$. Decreases of 22% and 44% in atmospheric S deposition in 2010 (condition C) increase the predicted rate of ANC change to 0.09 and $0.15 \mu\text{eq L}^{-1} \cdot \text{yr}^{-1}$, respectively. The 44% reduction in atmospheric S deposition in 2010 would result in positive stream ANC values in 2023. For a 22% decrease in atmospheric S deposition, stream ANC would reach positive values by 2038. Furthermore, the model predictions indicate that a 44% reduction in S deposition beyond requirements of the 1990 CAAA would result in stream pH values over 5.5 and in concentrations of inorganic monomeric Al at $2.7 \mu\text{mol L}^{-1}$ by 2050. At the HBEF, calculations indicate that, although marked improvements might be expected, full chemical and biological recovery might not be achievable by 2050, even with implementation of the most aggressive proposals for reducing utility emissions.

Model calculations suggest that the greater the reduction in atmospheric S deposition at the HBEF, the greater the magnitude and rate of chemical recovery. Less aggressive proposals for controls on S emissions will result in slower chem-

ical and biological recovery and in delays in regaining the services of a fully functional ecosystem. Unfortunately, model calculations do not exist for the entire Northeast region. We do know, however, that about 6% of the total lakes and 32% of the acid-sensitive lakes (ANC less than $50 \mu\text{eq L}^{-1}$) are currently more acidic than Watershed 6 of the HBEF, so it seems probable that recovery of these surface waters would lag behind the values predicted for the HBEF. Note that all model calculations assume that land disturbance (cutting and fire, e.g.) and climatic change will remain constant; changes in these conditions could significantly alter model predictions.

Summary

North America and Europe are in the midst of a large-scale experiment. Sulfuric and nitric acids have acidified soils, lakes, and streams, thereby stressing or killing terrestrial and aquatic biota. It is therefore critical to measure and to understand the recovery of complex ecosystems in response to decreases in acidic deposition. Fortunately, the NADP, CASTNet, and AIRMoN-dry networks are in place to measure anticipated improvements in air quality and in atmospheric deposition. Unfortunately, networks to measure changes in water quality are sparse, and networks to monitor soil, vegetation, and fish responses are even more limited. There is an acute need to assess the response of these resources to decreases in acid loading. It would be particularly valuable to assess the recovery of aquatic biota—which respond directly to acid stress—to changes in surface water chemistry (Gunn and Mills 1998).

We used long-term research from the HBEF and other sites across the northeastern United States to synthesize data on the effects of acidic deposition and to assess ecosystem responses to reductions in emissions. On the basis of existing data, it is clear that in the northeastern United States

- reductions of SO_2 emissions since 1970 have resulted in statistically significant decreases in SO_4^{2-} in wet and bulk deposition and in surface waters
- emissions of NO_x and concentrations of NO_3^- in wet and bulk deposition and in surface waters have shown no increase or decrease since the 1980s
- estimates of NH_3 emissions are uncertain, although atmospheric deposition of NH_4^+ remains important for forest management and stream NO_3^- loss
- acidic deposition has accelerated the leaching of base cations from soils, thus delaying the recovery of ANC in lakes and streams from decreased emissions of SO_2 (at the HBEF the available soil Ca pool appears to have declined 50% over the past 50 years)
- sulfur and N from atmospheric deposition have accumulated in forest soils across the region, and the slow release of these stored elements from soil has delayed the recovery of lakes and streams after emissions have been reduced
- acidic deposition has increased the concentration of toxic forms of Al in soil waters, lakes, and streams

- acidic deposition has leached cellular Ca from red spruce foliage, which has made trees susceptible to freezing injury and led to more than 50% mortality of canopy trees in some areas of the Northeast
- deficiencies of Ca^{2+} and Mg^{2+} have caused extensive mortality of sugar maple in Pennsylvania, and acidic deposition contributed to the depletion of these cations from soil
- forty-one percent of lakes in the Adirondack Mountains and 15% of lakes in New England have exhibited chronic or episodic acidification or both; 83% of the affected lakes are acidic because of atmospheric deposition
- the ANC of surface waters in New England has increased only modestly, and the Adirondack and Catskill regions have experienced no significant improvement, after decreases in atmospheric S deposition in recent decades
- acidification of surface waters has resulted in a decrease in the survival, size, and density of fish and in the loss of fish and other aquatic biota from lakes and streams
- emissions of air pollutants have important linkages to other large-scale environmental problems, including coastal eutrophication, mercury contamination, visibility impairment, climate change, and tropospheric ozone

Moreover, we anticipate that recovery from acidic deposition will be a complex, two-phase process in which chemical recovery precedes biological recovery. The time for biological recovery is better defined for aquatic than for terrestrial ecosystems. For acid-affected aquatic ecosystems, we expect that stream populations of macroinvertebrates and lake populations of zooplankton will recover 3–10 years after favorable chemical conditions are reestablished; recovery of fish populations would follow. For terrestrial ecosystems, trees would probably respond positively to favorable atmospheric and soil conditions only over decades.

Indicators of chemical recovery (soil percentage base saturation, soil Ca:Al ion ratios, and surface water ANC) were used to evaluate ecosystem response to proposed policy changes in SO_2 emissions. Projections made using an acidification model (PnET-BGC) indicate that full implementation of the 1990 CAAA will not afford substantial chemical recovery at the HBEF and at many similar acid-sensitive locations. Although uncertainties remain, our analysis indicates that current regulations will not adequately achieve the desired outcomes of the 1990 CAAA. Those desired outcomes include greater ANC for lakes and streams, greater diversity and health of fish populations, and less degradation of forest soil and stress to trees (USEPA 1995).

Model calculations indicate that the magnitude and rate of recovery from acidic deposition in the northeastern United States is directly proportional to the magnitude of emissions reductions. Model evaluations of policy proposals calling for additional reductions in utility SO_2 and NO_x emissions, year-round emissions controls, and early implementation (2005) indicate greater success in facilitating the recovery of sensitive ecosystems and in accomplishing the

goals of the Clean Air Act than current 1990 CAAA targets could deliver. Note that improvements in the rate of acidic deposition from SO_2 controls on utilities may be offset by NO_x emissions unless transportation emissions of NO_x are curtailed. Specific targets for reducing emissions should be based on clear goals that meet the extent and schedule of recovery of sensitive aquatic and terrestrial ecosystems envisioned under the Clean Air Act.

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