

# Acid Rain Revisited

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Elevated emissions of sulfur dioxide, nitrogen oxides and ammonia have resulted in acidic deposition and subsequent effects on terrestrial and aquatic resources in the northeastern U.S. and elsewhere in North America, Europe and Asia. These effects include changes in soil chemistry, stress to forest vegetation, acidification of surface waters and disturbance to aquatic biota. In this overview, a summary will be given : 1) of spatial and temporal patterns in emissions of sulfur dioxide and nitrogen oxides and atmospheric sulfur and nitrogen deposition; 2) effects of acidic deposition on soil, forest vegetation and surface waters; and 3) the response of terrestrial and aquatic ecosystems to possible future controls in emissions of air pollutants.

Emissions of sulfur dioxide in the U.S. increased markedly after the Industrial Revolution, peaking in early 1973 at 28.8 million metric tons (USEPA 2000). These emissions were largely (~60%) associated with electric utilities. In contrast, emissions of nitrogen oxides increased more gradually through the early decades of this century, increased more prominently after World War II, and peaked at 21.8 million metric tons in 1990. Nitrogen oxide emissions have remained relatively uniform since about 1980. Following the 1970 Amendments to the Clean Air Act, there have been marked reductions in emissions of sulfur dioxide. Emissions have decreased 32% from 1973 to values of 19.6 million metric tons in 1998 largely due to controls on electric utilities. These controls have resulted in decreases in concentrations of sulfate and hydrogen ion in atmospheric deposition in the eastern U.S. since the early 1970s (Likens et al. 1996). There is a strong relationship between sulfur dioxide emissions in the emission source area for the northeastern U.S. and atmospheric sulfur deposition for sites in the Northeast (Driscoll et al. 2001). Moreover with Title IV of the 1990 Amendments of the Clean Air Act there have been additional reductions in sulfur dioxide emissions and atmospheric deposition of sulfate and hydrogen ion since 1995 and these reductions are anticipated to continue until 2010.

Elevated emissions of sulfur dioxide, nitrogen oxides and ammonia have resulted in high atmospheric deposition of sulfur and nitrogen in the northeastern U.S.. This disturbance has had deleterious effects on forest ecosystems, including soil, vegetation and surface waters. The response of soil to acidic deposition includes: 1) accumulation of elevated pools of sulfur and nitrogen, 2) depletion of nutrient cations (i.e., calcium, magnesium) from soil exchange sites, and 3) the mobilization of aluminum from soil, resulting in high concentrations of inorganic forms of aluminum in waters draining soil (Driscoll et al. 2001). Clearly acidic deposition has accelerated the acidification of base-poor forest soils.

There is considerable concern about the potential effects of elevated atmospheric deposition on trees. However, it is difficult to make a direct linkage between acidic deposition and forest health because trees are exposed to many diverse stresses. Nevertheless, recent studies have suggested that exposure of high elevation red spruce forests to elevated concentrations of hydrogen ion in atmospheric deposition reduces cold tolerance sufficient to cause freezing injury (DeHayes et al. 1999). Linkages for other tree species are less well established but acidic deposition clearly accelerates the leaching of nutrient cations from foliage and soil, causes the interference of root function by increased availability of aluminum and competitive inhibition of calcium, magnesium and phosphorus assimilation (Cronan and Grigal 1995). Much current research is directed at establishing a linkage between acidic deposition and decline of sugar maple (Horsley et al. 2000).

Elevated atmospheric inputs of sulfate, nitrate and ammonium have had clear effects on surface waters in acid-sensitive regions of the Northeast. Based on the U.S. Environmental Protection Agency Environmental Monitoring and Assessment Program (EMAP) program, of 1,812 lakes in the Adirondack region of New York (>1 ha) 10% are chronically acidic (acid neutralizing capacity < 0  $\mu\text{eq/L}$ ) and 31% potentially experience episodic acidification (acid neutralizing capacity < 50  $\mu\text{eq/L}$ ).

## SESSION II. Research and Analysis: What the Reports Say

L; Driscoll et al. 2001). In 6,834 lakes (>1ha) in New England 5% are chronically acidic while 10% are susceptible to episodic acidification. A total of 1,875 lakes in the Adirondacks and New England are sensitive to acidic deposition (acid neutralizing capacity < 50  $\mu\text{eq/L}$ ). For a large fraction of these lakes (83%) the composition of anions is dominated by sulfate plus nitrate (> 50% of the total anion composition) and therefore have been acidified by acidic deposition. The anion composition of the remainder of these lakes (17%) is dominated by organic anions. While atmospheric deposition contributes to the acidity of these lakes, they are likely naturally acidic due to high inputs of organic acids.

Episodic acidification occurs when a surface water experiences a short-term decrease in acid neutralizing capacity that is generally associated with hydrologic events (i.e., precipitation events, snowmelt). Several mechanisms contribute to episodic acidification, including dilution of basic cation concentrations and increases in concentrations of sulfate, nitrate and organic anions (Wigington et al. 1996). In surface waters with low acid neutralizing capacity values (<50  $\mu\text{eq/L}$ ) in the Northeast, short-term increases in concentrations of nitrate are the dominant mechanism of episodic acidification (Schaefer et al. 1990). These increases in nitrate coincide not only with decreases in acid neutralizing capacity but also marked increases in inorganic monomeric aluminum.

Decreases in pH and increases in concentrations of inorganic monomeric aluminum have diminished species diversity and the abundance of plankton, invertebrates and fish in acid-impacted surface waters of the Northeast. In the Adirondacks, a significant positive relationship exists between pH and acid neutralizing capacity of lakes and the number of fish species present in those lakes (Gallagher and Baker 1990). A survey of 1,469 Adirondack lakes conducted in 1984 through 1987 show that 24% of the lakes in this region (i.e., 346) do not support fish. These lakes had consistently lower pH and acid neutralizing capacity and higher concentrations of aluminum than lakes that contained one or more species of fish. Even acid tolerant fish species such as brook

trout have been eliminated from some waters in the Northeast.

Acid episodes are particularly harmful to aquatic life because abrupt changes in water chemistry allow fish few areas of refuge. High concentrations of inorganic monomeric aluminum are directly toxic to fish and are the primary cause of mortality during acidic episodes. High acidity and concentrations of inorganic monomeric aluminum disrupt the salt and water balance of fish, causing red blood cells to rupture and blood viscosity to increase. Studies show that viscous blood strains the fish's heart, resulting in a lethal heart attack (McAvoy and Bulger 1995).

Recovery from acidic deposition involves decreases in emissions resulting from regulatory controls, which in turn leads to reductions in acidic deposition and allows for chemical recovery. Terrestrial and aquatic biota have clearly been impacted by acidic deposition. Critical chemical conditions for effects on terrestrial biota include a molar ratio of exchangeable calcium to exchangeable aluminum in soil of < 1.0 and soil percent base saturation of < 20% (Cronan and Grigal 1995). Critical chemical conditions for effects on aquatic biota include surface water pH values < 6.0-6.5, values of acid neutralizing capacity < 50  $\mu\text{eq/L}$ , and concentrations of inorganic monomeric aluminum > 1-2  $\mu\text{mol/L}$  (Driscoll et al. 2001). When emission controls and subsequent decreases in acidic deposition are sufficient to ameliorate adverse chemical conditions such that these thresholds are not exceeded, biological recovery will be enhanced. Biological recovery is likely to occur in stages; since organisms vary in sensitivity to acidic deposition they will not recover at the same rate. Current understanding of species response to improvements in chemical conditions is incomplete, but research suggests that stream macro-invertebrates may recover relatively rapidly (i.e., within 3 years), while lake zooplankton may take more than a decade to fully re-establish (Gunn and Mills 1998). Fish populations in streams and lakes should recover in 5-10 years following recovery of macro-invertebrates and zooplankton which serve as food sources. It is possible that, with improved chemical conditions and the return of other components of the aquatic food web, the stocking of streams and lakes could help accelerate

the recovery of fish. The recovery of terrestrial ecosystems is even more difficult to predict than aquatic recovery. Given the life span of trees and delays in the response of soil to decreases in acidic deposition it is reasonable to suggest that decades will be required for affected trees on sensitive sites to recover once chemical conditions in the soil are restored.

The time required for chemical recovery varies widely among ecosystems in the Northeast. This variability is a function of: 1) historical rate of atmospheric sulfur and nitrogen deposition; 2) the rate and magnitude of decreases in acidic deposition; 3) the extent to which exchangeable basic cations have been depleted from soil, 4) the extent to which sulfur and nitrogen have accumulated in soil and the rate at which they are released following decreases in atmospheric deposition; 5) the weathering rate of soil minerals and the associated supply of basic cations to the ecosystem; and 6) the rate of atmospheric deposition of basic cations.

Since widespread monitoring of acid-sensitive surface waters was initiated in New York and New England in the early 1980s, changes have been evident in their chemical composition. There have been uniform decreases in surface water concentrations of sulfate in the Adirondacks, Catskills and New England in response to decreases in sulfur dioxide emissions and atmospheric deposition of sulfate (Stoddard et al. 1999). There have been no systematic trends in concentrations of nitrate. In New England these changes have coincided with modest increases in the acid neutralizing capacity of surface waters. In contrast there has been no significant recovery in the acid neutralizing capacity of Adirondack and Catskill surface waters. The reason for these regional differences in rates of recovery appears to be due to the extent of depletion of exchangeable nutrient cations in soil (i.e., calcium, magnesium). Higher inputs of acidic deposition in New York may have facilitated greater leaching losses of exchangeable nutrient cations than in New England thereby delaying the recovery of surface waters in response to decreases in acidic deposition.

Scientists and engineers have developed models that depict the physical, chemical and biological processes within forest watersheds. Acidic

deposition models can be used as research and management tools to investigate factors responsible for the historical acidification of soil and water, as well as ecosystem response to anticipated future changes in acidic deposition. The model PnET-BGC was used to assess past and potential future changes in soil and stream chemistry in response to changes in acidic deposition at watershed 6 at the Hubbard Brook Experimental Forest, New Hampshire (Gbondo-Tugbawa et al. 2001; Gbondo-Tugbawa and Driscoll 2002; Table 1). Hindcasts suggest that prior to 1850 and the advent of acidic deposition, the soil base saturation at Hubbard Brook was 22%, stream sulfate concentration was 10  $\mu\text{eq/L}$ , acid neutralizing capacity was 40  $\mu\text{eq/L}$ , pH was 6.3, and concentration of monomeric aluminum was 1.5  $\mu\text{mol/L}$ . By 1970, near the peak of acidic deposition, the soil percent base saturation decreased to 12%, stream sulfate concentrations increased to 60  $\mu\text{eq/L}$ , acid neutralizing capacity decreased to 5  $\mu\text{eq/L}$ , pH decreased to 4.8 and monomeric aluminum concentrations increased to 12  $\mu\text{mol/L}$ . Subsequently model predictions of future changes in soil and stream chemistry were made to assess ecosystem response to emission controls associated with the 1990 Amendments of the Clean Air Act and additional reductions in emissions of sulfur dioxide emissions for electric utilities (Table 1). This analysis suggests emission controls have started recovery of acid-impacted forest ecosystems in the Northeast from acidic deposition. However, despite aggressive controls on emissions from electric utilities the rate of chemical recovery of acid-impacted soils and surface waters, like those at the Hubbard Brook Experimental Forest, will be slow.

Acidic deposition is a pervasive problem that has had greater effects on soils, trees and surface waters than had been previously projected. Although the 1970 and 1990 Amendments of the Clean Air Act have had positive effects, emissions remain high compared to background conditions. Given the accumulation of sulfur and nitrogen and the loss of available nutrient cations in soil, many forested areas of the Northeast have become more sensitive to inputs of acidic deposition. These effects will delay the rates of chemical recovery following decreases in atmospheric deposition.

## SESSION II. Research and Analysis: What the Reports Say

Nevertheless model calculations suggest that deeper emissions cuts and faster cuts will accelerate recovery from acidic deposition.

### QUESTIONS

MS. BRADT: Patricia Bradt, Muhlenberg College. How do you anticipate a recovery of the calcium and the magnesium baselines in soil? Do you think that is going to happen? Is it going to leach in from the bedrock?

MR. DRISCOLL: It is a very slow process. These soils have been developing over 14,000, 15,000 years. They are very low in bases to start with because of the nature of the mineralogy.

To redevelop those base cations will take a very long period of time. That is a large part of the reason why we expect recovery to be so slow.

If you want, you can lime. Liming experi-

ments have been done, but that is an artificial way. If you allow nature to take its course, you have to reduce the inputs of acids and allow it to redevelop, which will be a long time frame.

MS. BAUM: Ellen Baum with the Clean Air Task Force. Is there any point where recovery won't happen, if there isn't a certainly level of cut? Could it be so delayed or the input so high that, even with some level of reductions, we are not going to get recovery?

MR. DRISCOLL: I guess it depends on what you mean by recovery. In the Adirondacks, our model calculations suggest that some of those sites that are very sensitive and showing higher loadings than we see in parts of New England, are still losing base resources. Those calculations would suggest that we are still losing this very important stock of material.

In general, I think that, except for maybe the

*Table 1. Results for projections with PnET-BGC showing past and projected future values of critical chemical of stream water and soil at watershed 6 at the Hubbard Brook Experimental Forest, New Hampshire. Background conditions were determined based on historical reconstructions of atmospheric emissions and deposition. Future prediction were made for the year 2050 under the scenarios of the 1990 Amendments of the Clean Air Act (CAAA) and the 1990 CAAA plus an additional 40% reduction in utility emissions of sulfur dioxide and the 1990 CAAA plus an additional 80% reduction in utility emissions of sulfur dioxide.*

Chemical indicator	Background conditions			Emission scenarios		
	1850	threshold	1970	2050 with the 1990 CAAA	2050 with 40% addition utility SO <sub>2</sub> reduction	2050 with 80% addition utility SO <sub>2</sub> reduction
Wet sulfate deposition (gS/m <sup>2</sup> -yr)	0.23	N/A	1.7	0.9	0.7	0.5
Stream sulfate (μmol/L)	10	N/A	62	34	29	24
Stream acid neutralizing capacity (μeq/L)	43	>50	-5	-1	1	3
Stream pH	6.3	>6.0	4.8	5.3	5.5	5.7
Stream aluminum (μmol/L)	1.5	<2.0	12	6.4	5.6	4.3
Soil % base saturation	22	>20	13	12	13	14

most sensitive sites, we have by and large turned the corner and we are starting to move into a direction of recovery driven by these lower sulfate concentrations.

The big question is how long is that going to take. At the current levels for sensitive sites, we are talking many, many decades before we would see significant recoveries in chemical indicators that we would expect to lead to improvement in biological resources.

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## SESSION II. Research and Analysis: What the Reports Say