Acidic deposition delivers acids and acidifying compounds to the Earth's surface, which are then transported through soil, vegetation, and surface waters and, in turn, set off a cascade of adverse ecological effects. Acidic deposition has altered forest soil by accelerating the leaching of available base cations, enhancing the accumulation of sulfur and nitrogen, and increasing the concentration of dissolved inorganic aluminum in soil waters. Soils that are compromised by acidic deposition are less able to neutralize additional amounts of acidic deposition, and provide poorer growing conditions for plants. Acidic deposition has impaired the surface water quality by lowering pH, decreasing acid-neutralizing capacity (ANC), and increasing concentrations of dissolved inorganic aluminum. These changes have reduced the species diversity and abundance of aquatic life. Regulatory controls initiated in Europe and North America over the last three decades have decreased emissions of sulfur dioxide and to a lesser extent nitrogen oxides. Emission reductions have resulted in widespread decreases in concentrations of sulfate in surface waters, with some waters showing an increase in ANC. Given the loss of acid-neutralizing base cations and the accumulation of sulfur and nitrogen in soil, many ecosystems have become more sensitive to additional acidic deposition and recovery will likely be delayed. Long-term research shows that deeper emissions cuts will lead to greater and faster recovery from acidic deposition in impacted regions.

Acidic deposition was first reported in the United Kingdom in the latter half of the nineteenth century (Gorham, 1989). Ecological effects were first documented in Scandinavia in the 1960s with the link between acidic deposition, surface water acidification, and loss of fisheries (Gorham, 1989). Atmospheric deposition of sulfate, nitrate, and ammonium are elevated in eastern North America, Europe, and large portions of Asia (Rodhe et al., 1995). Electric utilities account for the greatest proportion of anthropogenic sulfur dioxide emissions in Europe and North America. For example in the United States in 2002, the major sources of sulfur dioxide emissions were electric utilities (67%), industrial combustion (15%), and industrial processes (9%; EPA 2004). Transportation sources – including cars, trucks, and non-road vehicles (i.e. construction equipment) – accounted for more than 50% of anthropogenic nitrogen oxide emissions in the United States. Other major sources of nitrogen oxides include electric utilities (22%) and industrial combustion (14%). Ammonia emissions are derived largely from livestock waste and fertilized soil (83% of total ammonia; Driscoll et al., 2003). Motor vehicles and industrial processes also contribute to ammonia emissions.
Acidic deposition occurs in three forms: wet deposition, which falls as rain, snow, sleet, and hail; dry deposition, which includes particles, gases, and vapor; and cloud or fog deposition which occurs at high altitudes and coastal areas. In the United States, wet deposition has been monitored at more than 200 sites, by both independent researchers and the interagency National Atmospheric Deposition Program/National Trends Network. Dry deposition is monitored at 70 sites in the United States by the U.S. Environmental Protection Agency Clean Air Status and Trends Network, and at 13 other sites by the National Oceanic and Atmospheric Administration AIRMON-dry Network. Cloud and fog deposition has been monitored for limited periods at selected high-elevation sites, largely by independent researchers. Dry and cloud deposition patterns are extremely variable over space and time, making it difficult to characterize patterns. Therefore, even though cloud and dry deposition comprise a significant proportion of total deposition, this report primarily presents general patterns and trends of wet deposition. Some researchers also measure bulk deposition, in which deposition is collected in an open collector. Bulk deposition is greater than wet deposition because it includes some dry deposition.

An airshed or source area is an area where “significant portions of emissions result in deposition of air pollutants to a region” (www.epa.gov). In North America, emissions of sulfur dioxide are highest in the midwestern United States (hereafter the Midwest), with seven states in the Ohio River Valley accounting for 51% of the total sulfur dioxide emissions in the United States in 2002 (Figure 1a). Five of these states are also amongst the highest emitters of nitrogen oxides (Figure 1b). Moreover, the Midwest is a significant source of atmospheric ammonia. In addition to regional pollution sources, local emissions of sulfur dioxide and nitrogen oxides from electric utilities and motor vehicles have significant impacts on local air quality. Analysis of continental air currents shows that a multistate region, including the Midwest comprise the source area for sulfur dioxide, nitrogen oxide, and ammonium emissions that are transported downwind to acid-sensitive areas of eastern North America (Butler et al., 2001d).

There have been significant efforts to reduce emissions of acidic and acidifying substances in North America and Europe over the past three decades. Although regulatory controls have decreased emissions, levels remain high compared to background conditions. Importantly, emissions and deposition of base cations (i.e. elements such as calcium and magnesium that help counteract acidic deposition) have declined substantially since the early 1960s with the enactment of pollution controls to reduce fine particulate matter (Hedin et al., 1994).
on electric utilities is set at 8.9 million metric tons and the cap on industrial sources is 5.6 million metric tons to be reached by 2010.

Nitrogen oxide emissions in the United States have increased over the past decades, peaking at nearly 22.7 million metric tons in 1990. From 1990 to 2002, nitrogen oxide emissions have decreased by 12%. The 1990 CAAA calls for an additional reduction that will result in the emission of 1.8 million fewer tons of nitrogen oxide than the level that would have occurred without the CAAA. However, no cap on total annual emissions of nitrogen oxides was set. Nevertheless, it is expected that nitrogen emissions will decrease gradually in the future because of a variety of federal and state emission control programs. In contrast to sulfur dioxide, the multistate source area for the eastern North America has shown little change in nitrogen dioxide emissions since the early 1970s although some decrease has been evident in recent years (Figure 2).

Ammonia emissions play an important role in the acidification of soil and surface waters. Deposition of ammonium accounts for approximately 30% of the total nitrogen deposition measured in eastern North America and has not changed appreciably over the past 30 years. Trends in ammonia emissions in the United States are consistent with this pattern and have shown little change over the past 10 years.

European efforts to reduce emissions of air pollutants have been brought together in a series of protocols under the United Nations Economic Council for Europe (UN/ECE) Convention on Long Range Transboundary Air Pollution (LRTAP; Sundqvist et al., 2002; Ferrier et al., 2001). The first binding protocol was the 1985 Protocol on the Reduction of Sulfur Emissions that was intended to reduce sulfur dioxide emissions by at least 30% by 1993 compared to the 1980 levels. This was expanded in 1994 with the Protocol on Further Reductions of Sulfur, with the objective of decreasing sulfur dioxide emissions by 80% by 2010 from 1980 values. In 1988, the Protocol concerning Control of Emissions of Nitrogen Oxides stabilized nitrogen oxide emissions. Finally, the 1999 Protocol to Abate Acidification, Eutrophication, and Ground-level Ozone established national caps for multiple air pollutants, including sulfur dioxide, nitrogen oxides, and ammonia, with attainment expected by 2010 (Kurz et al., 2001). These actions have resulted in marked reductions in emissions of sulfur dioxide (65%) and nitrogen oxides (30%) from 1990 to 2002. Ammonia emissions have remained essentially constant over the same period. Once implemented, sulfur dioxide emissions will decrease by at least 63%, nitrogen oxide emissions by 41%, and ammonia emissions by 17% relative to 1990 values.

An important framework for emission reductions and ecosystem recovery is “critical loads.” Critical loads are based on the idea that emission control strategies should be effect-driven. A critical load is the total deposition of a pollutant to an ecosystem below which significant harmful ecological effects do not occur (Nilsson and Grennfelt, 1988). Following the UN/ECE Convention on LRTAP, maps of critical loads were developed for Europe (Posch et al., 1995). These maps have been revised (Posch and Hettelingh, 2001) and the resulting critical loads were used

Figure 2  Annual emissions of sulfur dioxide and nitrogen oxides for the source area of the Hubbard Brook Experimental Forest. The source area was determined by 24-h back trajectory analysis. Shown are emissions from both United States and Canadian sources. A color version of this image is available at http://www.mrw.interscience.wiley.com/ehs
to regulate emissions through the 1999 Protocol. Critical loads have only been applied to a limited extent in the United States.

In contrast to North America and Europe, emissions in Asia have been increasing and are expected to continue to increase in the coming decades (Galloway, 1995; Klimont et al., 2001).

Trends in acidic deposition mirror emission trends in the source area. For example, over the past 30 years in eastern North America, sulfate deposition has declined, but nitrogen and ammonium deposition have remained relatively stable (Figure 3). Decreases in precipitation sulfate have coincided with increases in pH. The Hubbard Brook Experimental Forest in New Hampshire has one of the longest continuous records of precipitation chemistry (see Box 2). Long-term data from the Hubbard Brook show declining concentrations of sulfate in bulk deposition since the mid-1960s and wet deposition since the late 1970s (see Figure 3). On the basis of these long-term data, there is a strong positive correlation that exists between sulfur dioxide emissions in the source area and sulfate concentrations in precipitation at Hubbard Brook.

**Box 2 The Hubbard Brook Experimental Forest**

The Hubbard Brook Experimental Forest is a long-term ecological research site established by the United States Department of Agriculture Forest Service in the White Mountains of New Hampshire to investigate the structure and function of forest and aquatic ecosystems, and their response to disturbance (Likens and Bormann, 1995; Groffman et al., 2004). Hubbard Brook was the site where acidic deposition was first reported in North America (Likens et al., 1972). Hubbard Brook receives elevated inputs of acidic deposition and the forest ecosystem is very sensitive to these inputs. There have been long-term measurements and studies of acidic deposition and its effects on forests and streams at Hubbard Brook (Likens et al., 1996; Driscoll et al., 2001).

**Figure 3** Annual volume-weighted sulfate, nitrate, and ammonium concentrations and pH in bulk and wet deposition at the Hubbard Brook Experimental Forest, New Hampshire, 1963–2000. A color version of this image is available at http://www.mrw.interscience.wiley.com/ehs.
Effects of Acidic Deposition on Forest Ecosystems

Until recently, understanding the effects of acidic deposition on soils was limited. However, current research has shown that acidic deposition has chemically altered forest soils with serious consequences for acid-sensitive ecosystems. Soils compromised by acidic deposition lose their ability to neutralize continuing inputs of strong acids, provide poorer growing conditions for plants, and extend the time needed for ecosystems to recover from acidic deposition. Acidic deposition has altered and continues to alter base-poor forest soils in three important ways. Acidic deposition alters soils, stresses forest vegetation, acidifies lakes and streams, and harms fish and other aquatic life. These effects can alter important ecosystem services such as forest productivity and water quality (see Chapter 193, Markets for Watershed Services, Volume 5). Decades of acidic deposition have also made many ecosystems more sensitive to continuing pollution. Moreover, the same pollutants that cause acidic deposition contribute to a wide array of other important environmental issues at local, regional, and global scales (see Table 1).
deposition depletes available calcium and other nutrient cations (e.g. magnesium, potassium) from soil, facilitates the mobilization of dissolved inorganic aluminum into soil water, and increases the accumulation of sulfur and nitrogen in soil.

The cycling of calcium and other nutrient cations in forest ecosystems involves the inputs and losses of these materials (Figure 7; see Chapter 69, Solute Transport in Soil at the Core and Field Scale, Volume 2). For most forest ecosystems, the supply of calcium and other nutrient cations largely occurs by weathering (i.e. the breakdown of rocks and minerals in soil). Calcium and other nutrient cations may also enter forests by atmospheric deposition, although this pathway is generally much smaller than weathering. Losses largely occur by vegetation uptake and drainage waters. An important pool of ecosystem calcium and nutrient cations is the soil-available pool, or the soil cation exchange complex. Plants are generally able to utilize this source of nutrients. Forest ecosystems that are naturally sensitive to acidic deposition are generally characterized by low rates of weathering and generally low quantities of available base cations (i.e. calcium, magnesium, sodium, potassium). Under conditions of elevated inputs of acidic deposition and subsequent transport of sulfate and nitrate in drainage waters, nutrient cations will be displaced from available pools and leached from soil (Ruess and Johnson, 1986). This condition is not problematic for areas with high weathering rates and high
Table 1  The links between sulfur dioxide and nitrogen oxide emissions, acidic deposition, and a range of environmental issues

<table>
<thead>
<tr>
<th>Problem</th>
<th>Linkage to acid deposition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coastal eutrophication</td>
<td>Atmospheric deposition adds nitrogen to coastal waters.</td>
<td>Paerl et al., 2002</td>
</tr>
<tr>
<td>Mercury</td>
<td>Deposition of sulfate enhances methylation of mercury. Surface water acidification increases mercury accumulation in fish.</td>
<td>Branfireun et al., 1999; Driscoll et al., 1994</td>
</tr>
<tr>
<td>Visibility</td>
<td>Sulfate aerosols diminish visibility and views.</td>
<td>Malm et al., 1994</td>
</tr>
<tr>
<td>Climate change</td>
<td>Sulfate, nitrate, and ammonium aerosols may offset global warming in the short-term, but nitrous oxide is a potent greenhouse gas.</td>
<td>Moore et al., 1997 (see Chapter 195, Acceleration of the Global Hydrologic Cycle, Volume 5) NAPAP (1998)</td>
</tr>
<tr>
<td>Tropospheric ozone</td>
<td>Emissions of nitrogen oxides contribute to the formation of ozone.</td>
<td></td>
</tr>
<tr>
<td>Airborne particulate matter</td>
<td>Emissions of sulfur dioxide, nitrogen oxides, and ammonia contribute to airborne particulate matter and associated health effects.</td>
<td><a href="http://www.epa.gov/air/urbanair/pm/index.html">http://www.epa.gov/air/urbanair/pm/index.html</a></td>
</tr>
<tr>
<td>Corrosion and damage to structures and monuments</td>
<td>Acidic substances enhance corrosion</td>
<td>Sherwood and Lipfert, 1990</td>
</tr>
</tbody>
</table>

Figure 7  Conceptual diagram illustrating calcium cycle in forest watersheds. Inputs of calcium include weathering and atmospheric deposition; of these weathering is usually the greatest. Losses of calcium include tree accumulation and stream runoff. Under conditions of elevated acidic deposition stream losses increase, potentially depleting available calcium from the ecosystem, particularly from the soil exchange complex. A color version of this image is available at http://www.mrw.interscience.wiley.com/ehs

pools of available nutrient cations. However, over the past century, acidic deposition has accelerated the loss of large amounts of available calcium and magnesium from the soil in acid-sensitive areas (Likens et al., 1996; Kirchner and Lydersen, 1995; Huntington et al., 2000). Depletion occurs when base cations are displaced from the soil by acidic deposition at a rate faster than they can be replenished by the slow breakdown of rocks or the deposition of base cations from the atmosphere. This depletion of base cations fundamentally alters soil processes, compromises the nutrition of some trees, and hinders the capacity for sensitive soils to recover from inputs of acidic deposition.

Dissolved inorganic aluminum is often released from soil to soil water, vegetation, lakes, and streams in forested regions with high acidic deposition, low stores of available calcium, high soil acidity, and limited watershed retention of atmospheric inputs of sulfate and/or nitrate (Cronan and Schofield, 1990). High concentrations of dissolved inorganic aluminum can be toxic to plants, fish, and other organisms. Concentrations of dissolved inorganic aluminum in streams and lakes in acid-sensitive regions
receiving high inputs of acidic atmosphere are often above levels considered toxic to fish and much greater than concentrations observed in forested watersheds with low inputs of acidic deposition (Driscoll et al., 1988).

Acidic deposition results in the accumulation of sulfur and nitrogen in forest soils. As sulfate is released from the soil in response to decreases in emissions and atmospheric deposition of sulfur, it is transported to adjacent streams and lakes (Likens et al., 2000). The recovery of surface waters in response to emission controls has therefore been delayed and will not be complete until the sulfate left by a long legacy of acidic deposition is released from the soil.

Similarly, nitrogen has accumulated in soil beyond the amount needed by the forest and appears now to be leaching into surface waters in Europe and North America (Dise and Wright, 1995; Aber et al., 2003). Forests typically require more nitrogen for growth than is available in the soil. However, several recent studies suggest that in some areas, nitrogen levels are above what forests can use and retain. This condition is referred to as “nitrogen saturation” (Aber et al., 1989; Aber et al., 1998). Note that the levels at which atmospheric nitrogen deposition can result in elevated leaching losses of nitrate from forest watersheds appear to be higher in Europe (9–25 kg N ha⁻¹ year⁻¹) than eastern North America (7–8 kg N ha⁻¹ year⁻¹). The reason for this difference is not evident, but may be due to a greater fraction of atmospheric nitrogen deposition occurring as ammonium in Europe; ammonium inputs are more readily retained in watersheds than nitrate. Alternatively, this difference may be due to highly managed forests in Europe and greater nitrogen retention compared to eastern North America.

**Acidic Deposition Stress to Trees**

Although it is difficult to separate the effects of air pollution from other stresses, recent research shows that acidic deposition appears to have contributed to the decline of red spruce trees throughout the eastern North America and sugar maple trees in central and western Pennsylvania in the United States. Symptoms of tree decline include poor crown condition, reduced tree growth, and unusually high levels of tree mortality.

Red spruce and sugar maple are the tree species that have been most intensively researched, and therefore, they provide instructive case studies of the effects of acidic deposition on trees. Red spruce and sugar maple research has shown that acidic deposition has both direct and indirect effects on trees. In acid-impacted forests, acidic deposition harms trees directly by leaching calcium from the leaves and needles (i.e. foliage) of trees, rendering them more susceptible to winter injury. Acidic deposition can also affect trees indirectly by changing the underlying soil chemistry. In acid-sensitive soils, acidic deposition depletes available nutrient cations, such as calcium and magnesium, which are important plant nutrients that are necessary to maintain the health and vigor of trees. The depletion of nutrient cations also leads to soil acidification that increases the availability of aluminum to the trees’ roots, thereby impairing the ability of trees to obtain necessary nutrients from the soil.

**Red Spruce**

Acidic deposition appears to be the major cause of red spruce decline at high elevations in North America. Since the 1960s, more than half of large canopy trees in the Adirondack Mountains of New York and the Green Mountains of Vermont and approximately one-quarter of large canopy trees in the White Mountains of New Hampshire have died. Significant growth declines and winter injury to red spruce have been observed throughout its range, suggesting that damage from acidic deposition is likely widespread (DeHayes et al., 1999).

Recent research indicates that the decline of red spruce is linked to the leaching of calcium from cell membranes in spruce needles by acidic deposition (DeHayes et al., 1999). The loss of calcium renders the needles more susceptible to freezing damage, thereby reducing the tolerance of trees to low temperatures and increasing the occurrence of winter injury and subsequent tree damage or death. In addition, elevated aluminum concentrations in the soil, resulting from soil acidification, limits the ability of red spruce to take up water and nutrients through its roots. This limitation can lead to nutrient deficiencies that can lower a tree’s tolerance to environmental stress and cause decline.

**Sugar Maple**

The decline of sugar maples has been studied in the eastern United States since the 1950s and there is growing evidence that sugar maple decline is linked to acidic deposition. Extensive mortality among sugar maples in Pennsylvania appears to result from deficiencies of base cations, coupled with other stresses such as insect defoliation or drought. Sugar maples are most prone to die on sites where base cation concentrations in soil or foliage are lowest (Horsley et al., 2000). Data from many acid-sensitive regions link the loss of soil calcium and magnesium with the leaching of these base cations by acidic deposition. Low levels of base cations can cause a nutrient imbalance and reduce a tree’s stress tolerance. As such, acidic deposition is a predisposing factor in sugar maple decline. Under these conditions, the likelihood increases that stresses such as insect infestation and drought will cause the dieback of a tree’s crown or kill a tree.

Finally, there may be adverse effects on other tree species. For example, one might speculate that hardwood species such as white ash and basswood, which prefer rich sites high in nutrient cations, may experience problems in areas where nutrient cations have been depleted by acidic deposition. However, additional research is needed.
Acid-neutralizing capacity, or ANC, is the ability of water from a lake or stream to neutralize strong acid (Stumm and Morgan, 1996). ANC is an important measure of the impacts of acidic deposition as well as an indicator of chemical recovery from acidic deposition. Surface waters with ANC values below 0 µeq L⁻¹ during base flow conditions are considered chronically acidic. Waters with ANC values ranging from 0 to 50 µeq L⁻¹ are susceptible to episodic acidification. Waters with ANC values greater than 50 µeq L⁻¹ are less sensitive to acidic deposition. The capacity of a watershed to prevent decreases in ANC and resist the effects of acidic deposition depends on many factors, including climate, soil conditions, surficial and bedrock geology, and land-use history.

**Box 3** What is ANC?

Acid-neutralizing capacity, or ANC, is the ability of water from a lake or stream to neutralize strong acid (Stumm and Morgan, 1996). ANC is an important measure of the impacts of acidic deposition as well as an indicator of chemical recovery from acidic deposition. Surface waters with ANC values below 0 µeq L⁻¹ during base flow conditions are considered chronically acidic. Waters with ANC values ranging from 0 to 50 µeq L⁻¹ are susceptible to episodic acidification. Waters with ANC values greater than 50 µeq L⁻¹ are less sensitive to acidic deposition. The capacity of a watershed to prevent decreases in ANC and resist the effects of acidic deposition depends on many factors, including climate, soil conditions, surficial and bedrock geology, and land-use history.

Effects of Acidic Deposition on Aquatic Ecosystems

Acidic deposition degrades water quality by lowering pH levels (i.e. increasing acidity), decreasing acid-neutralizing capacity (ANC; see Box 3), and increasing dissolved inorganic aluminum concentrations. While sulfate concentrations in lakes and streams have decreased over the last 20 years, they remain high compared to background conditions (<20 µeq L⁻¹; Sullivan, 1991).

An important characteristic influencing the acid–base status of surface waters is the supply of naturally occurring organic solutes. These materials include naturally occurring organic acids that decrease the ANC of waters and mobilize aluminum from soil through complexation reactions. Watersheds with an abundance of wetlands typically have high concentrations of dissolved organic carbon, and associated surface waters can be naturally acidic due to organic acids. However, in contrast to watersheds that are acidified by acidic deposition, waters that are acidic due to organic acids have high concentrations of aluminum which is largely complexed with organic solutes and therefore less toxic to aquatic biota (Driscoll et al., 1980, 1988).

Acidification of surface waters due to elevated inputs of acidic deposition have been reported in many acid-sensitive areas receiving elevated inputs of acidic deposition, including Great Britain, Nordic countries, northern, central, and eastern Europe (Evans et al., 2001), southwestern China (Seip et al., 1995), southeastern Canada (Jeffries, 1991), the northeastern United States (Driscoll, 1991) the upper Midwest (Cook and Jager, 1991), and the Appalachian mountain region of the United States (Elwood, 1991). Large portions of the high-elevation western United States are also potentially sensitive to acidic deposition (Fenn et al., 2003); however, atmospheric deposition to this region is relatively low. Concern over effects of acidic deposition in the mountain regions of western United States may be overshadowed by potential effects of elevated nitrogen deposition, including eutrophication of naturally nitrogen-limited lakes.

One of the most highly impacted areas in North America is the Adirondack region of New York. A comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area was conducted between 1984 and 1987 to obtain detailed information on the acid–base status of waters in this region (Kretser et al., 1989). Of the 1469 lakes surveyed, 24% had summer pH values below 5.0. Also, 27% of the lakes surveyed were chronically acidic (i.e. ANC < 0 µeq L⁻¹) and an additional 21% were susceptible to episodic acidification (i.e. ANC between 0 and 50 µeq L⁻¹; see Box 4). Note that 54% of these acid-sensitive lakes (733 lakes) are characterized by relatively low concentrations of dissolved organic carbon (i.e. <6 mg CL⁻¹). The chemical composition of these lakes suggests that their acidity was largely derived from inputs of sulfate associated with acidic deposition (Driscoll et al., 2003). In contrast, 46% of the lakes are characterized by high concentrations of dissolved organic carbon (i.e. >6 mg CL⁻¹) and naturally occurring organic acids. These lakes are probably naturally acidic. While the contribution of naturally occurring acidity is greater in these lakes, sulfate was the dominant anion; the acidity of these lakes has been clearly enhanced by acidic deposition.

Decreases in pH and elevated concentrations of dissolved inorganic aluminum have reduced the species diversity and
abundance of aquatic life in many streams and lakes in acid-sensitive areas (Table 2). Fish have received the most attention to date, but entire food webs are often adversely affected (Baker et al., 1990).

Decreases in pH and increases in dissolved inorganic aluminum concentrations have diminished the species diversity and abundance of plankton, invertebrates, and fish in acid-impacted surface waters. For example, in the Adirondacks, a significant positive relationship exists between the pH and ANC levels in lakes and the number of fish species present in those lakes (see Figure 8). The Adirondack Lakes Survey showed that 24% of lakes (i.e. 346) in this region do not support fish. These lakes had consistently lower pH and ANC and higher concentrations of dissolved inorganic aluminum than lakes that contained one or more species of fish. Experimental studies and field observations demonstrate that even acid-tolerant fish species such as brook trout have been eliminated from some waters.

Although chronically high acid levels stress aquatic life, acid episodes are particularly harmful because abrupt, large changes in water chemistry allow fish few areas of refuge (see Box 4). High concentrations of dissolved inorganic aluminum are directly toxic to fish and pulses of dissolved inorganic aluminum during acid episodes are a primary cause of fish mortality (Baker et al., 1996; Van Sickle et al., 1996). High acidity and dissolved inorganic aluminum levels disrupt the salt and water balance in a fish’s blood, causing red blood cells to rupture and blood viscosity to increase (MacAvoy and Bulger, 1995). Studies show that the viscous blood strains the fish’s heart, resulting in a lethal heart attack.

**ECOSYSTEM RECOVERY**

Recovery from acidic deposition involves decreases in emissions resulting from regulatory controls that in turn lead to reductions in acidic deposition and allow chemical recovery. The chemical recovery process is characterized by decreases in concentrations of sulfate, nitrate, and dissolved inorganic aluminum in soils and surface waters. If sufficient, these reductions will eventually lead to increased pH and ANC, as well as higher concentrations of base cations in water and on the soil exchange complex. As
chemical conditions improve, the potential for the second phase of ecosystem recovery, biological recovery, is greatly enhanced.

An analysis of the scientific literature suggests that the following five thresholds can serve as indicators of chemical recovery. If chemical conditions in an ecosystem are above these thresholds, it is unlikely that the ecosystem has been substantially impaired by acidic deposition. Conversely, if chemical conditions are below these thresholds, there is a high likelihood that the ecosystem is vulnerable to acidic deposition (see Table 3).

The time required for chemical recovery varies widely among ecosystems, and is primarily a function of:

- the historic loading rate of sulfur and nitrogen oxides;
- the rate and magnitude of decreases in acidic deposition;
- the extent to which available base cations such as calcium have been depleted from soil;
- the extent to which sulfur and nitrogen have accumulated in the soil and the rate at which they are released as deposition declines;
- the weathering rate of the soil and underlying rock and the associated supply of base cations to the ecosystem; and
- the rate of atmospheric deposition of base cations.

As chemical conditions in soils and surface waters improve, biological recovery is enhanced. Biological recovery is likely to occur in stages, since not all organisms can recover at the same rate and may vary in their sensitivity to acidic deposition. The current understanding of the response of biological species to improvements in chemical conditions is incomplete, but research suggests that stream macroinvertebrates may recover relatively rapidly (i.e. within 3 years), while lake zooplankton may need a decade or more to fully reestablish. Fish populations in streams and lakes should recover in 5–10 years following the recovery of the macroinvertebrates and zooplankton that serve as food sources (Gunn and Mills, 1998). It is possible that, with improved chemical conditions and the return of other members of the aquatic food web, the stocking of streams and lakes could help accelerate the recovery of fish.

Terrestrial recovery is even more difficult to project than aquatic recovery. Given the life span of trees and the delay 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. Overall, the timing and extent of chemical and biological recovery depend on how soon and how significantly emissions that cause acidic deposition are reduced. Moreover, human influences (i.e. land disturbance, introduction of exotic or invasive species) in addition to acidic deposition, can delay biological recovery after chemical recovery has occurred.

Long-term stream data from Hubbard Brook reveal a number of long-term trends that are consistent with trends in lakes and streams across Europe and eastern North America (Stoddard et al., 1999; Evans et al., 2001; Stoddard et al., 2003; see Figure 9). Specifically, the concentration of sulfate in streams at Hubbard Brook declined 32% between 1963 and 2000. The pH of streams subsequently increased from 4.8 to 5.0. Although this represents an important improvement in water quality, streams at Hubbard Brook remain acidic compared to background conditions, when stream pH was estimated to be approximately 6.0. Moreover, the ANC at Hubbard Brook – a biologically important measure of a lake or stream’s susceptibility to acid inputs – has remained acidic (ANC < 0 µeq L⁻¹).

Trends in surface water chemistry in Europe (Evans et al., 2001) and eastern North America (Stoddard et al., 1999) indicate that recovery of aquatic ecosystems impacted by acidic deposition is occurring over a large geographic scale since the early 1980s. Some regions are showing rather marked recovery, while others exhibit low or nonexistent increases in ANC. On the basis of long-term monitoring, virtually all surface waters impacted by acidic deposition in Europe and eastern North America exhibit decreases in sulfate concentrations. This pattern is consistent with decreases in emissions of sulfur dioxide and atmospheric sulfate deposition. The exception to
Figure 9  Annual volume-weighted stream water sulfate, nitrate, calcium concentrations, pH, and concentrations of total (Alm) and organic dissolved aluminum (Alo) at the reference watershed of the Hubbard Brook Experimental Forest from 1963 to 2000. Note that dissolved inorganic aluminum is the difference between total and organic dissolved aluminum.

this pattern is streams in unglaciated Virginia. Watersheds in this region exhibit strong adsorption of atmospheric sulfate deposition by highly weathered soils. In Europe, the most marked decreases in surface water sulfate have occurred in the Czech Republic and Slovakia, regions that have experienced historically very high rates of atmospheric sulfate deposition. Almost more than half of the surface waters monitored in Europe show an increase in ANC (Evans et al., 2001). The rate of ANC increase in Europe is relatively high. This pattern is in part due to the relatively high rates of sulfate decreases, but also that decreases in base cations only account for about half of the decreases in sulfate plus nitrate, allowing for relatively large rates of ANC increases. In contrast, in the United States only three regions show statistically significant increases in ANC-lakes in the Adirondacks and upper Midwest and streams in the Northern Appalachian Plateau (Stoddard et al., 2003). In the United States, decreases in the sum of base cations closely correspond to decreases in sulfate plus nitrate, limiting rates of ANC increase.

Three factors have limited the recovery in chemical water quality at Hubbard Brook and other watersheds in acid-sensitive regions that have received elevated inputs of acidic deposition. First, levels of acid-neutralizing base cations in surface waters have decreased markedly because of the depletion of available base cations from the soil.
and, to a lesser extent, a reduction in atmospheric inputs of base cations. Second, as forest ecosystems mature, their requirement for nitrogen decreases (Aber et al., 1989; Aber et al., 1998). As a result, forested watersheds with limited disturbance that extracts nitrogen (e.g., tree harvesting, fire, agriculture) are expected to exhibit increasing losses of nitrate as forests develop. Finally, sulfur has accumulated in the soil under previous conditions of high atmospheric sulfur deposition and is now being released to surface water as sulfate, even though sulfate deposition has decreased.

While there is considerable information about the response of surface waters to decreases in acidic deposition under chronic conditions, much less is known about how episodic acidification responds to these changes. Laudon and Hemond (2002) reported decreases in episodic acidification following decreases in atmospheric sulfur deposition in northern Sweden. Unfortunately, comparable data sets have not been developed for other regions.

An alternative to recovery from controls on emissions of acidic or acid-forming substances is mitigation. Mitigation (or base addition or liming) involves the application of basic materials directly to surface waters or watersheds to neutralize strong acid inputs (Olem et al., 1991). The most common material for mitigation is calcium carbonate (or limestone), although other materials have been effectively used. Mitigation has been practiced in Europe and North America to treat the effects of acidic deposition with some success. Direct application to lakes has been shown to neutralize acidity and allow for the survival of fish and other sensitive aquatic biota. This approach is less successful in lakes with short hydraulic residence times and to recover a reproducing fish population (Driscoll et al., 1996). Alternatively, watershed treatment has been shown to be successful over the longer term by improving the base status of soil and allowing for a reproducing fish population. Note, mitigation is not an attractive alternative to source control. It might be implemented in areas that exhibit severe depletion of exchangeable nutrient cations and/or have biological species that are endangered because of acidic deposition. Acidic deposition impacts ecosystems in remote and wilderness areas that are difficult or inappropriate to treat by base addition. While no negative short-term effects of base treatment have been noted, long-term studies of the ecological response to base treatment have not been conducted.

**Box 5  Acidification models**

Scientists have developed computer models that depict the physical, chemical, and biological processes within forest watersheds. Watershed acidification models can be used as research and management tools to investigate factors responsible for the historical acidification of soil and water, as well as the ecosystem response to anticipated future changes in acidic deposition. In order to effectively predict the pH, ANC, and aluminum concentrations in streams, all major chemicals must be accurately simulated (e.g., sulfate, nitrate, calcium, magnesium). The acidification model PnET-BGC was used for this assessment because it has been rigorously tested at Hubbard Brook and other sites in the northeastern United States, and it allows the user of the model to consider the ecosystem response to multiple chemicals simultaneously. Other frequently used acidification models include Model of Acidification of Groundwater in Catchment (MAGIC) (Cosby et al., 2001), and the nutrient cycling model NuCM (Lui et al., 1992).

RECOVERY OF ACID-SENSITIVE ECOSYSTEMS WITH FUTURE DECREASES IN EMISSIONS

To date, emissions targets set in the United States and Europe have been met or exceeded. There are widespread decreases in surface water concentrations of sulfate and some waters are showing increases in ANC. Nevertheless, data suggest that these targets may not be sufficient to achieve the full recovery of sensitive ecosystems. In order to evaluate the extent to which historic and future emissions reductions will facilitate ecosystem recovery from acidic deposition, it is necessary to use acidification models to project the future relationship between emissions, deposition, and chemical recovery of acid-sensitive forest watersheds (see Box 5).

We used the model PnET-BGC (Gbondo-Tugbawa et al., 2001) to compare current emissions reductions required by the 1990 CAAA with an additional 55% and 75% cut in emissions of sulfur dioxide and 20% and 30% decreases in nitrogen oxides by 2010 (Figure 10). These scenarios are based on the electric utility emission reductions embodied in bills recently introduced to the US Congress. PnET-BGC considered changes in sulfur dioxide and nitrogen oxide emissions. It was assumed that base cation and ammonium deposition and climate would remain unchanged.

According to the results of the computer model, the 1990 CAAA will have a positive effect on stream concentrations of sulfate at Hubbard Brook, but will not facilitate appreciable progress toward chemical recovery of key indicators of acidification stress, such as pH or ANC. With moderate reductions in emissions (i.e., sulfur dioxide 55%, nitrogen oxides 20%) beyond the requirements of the 1990 CAAA, measurable chemical improvements occur. However, none of the five indicators reach the threshold needed to support complete biological recovery at Hubbard Brook by 2050 (see Table 3). More aggressive reductions in emissions (i.e., sulfur dioxide 75%, nitrogen oxides 30%) beyond the 1990 CAAA hastens and promotes more significant improvements in chemical conditions. For example, under this scenario streams in watersheds similar to Hubbard Brook would change from acidic to nonacidic in roughly
Figure 10  Time series of predictions with the acidification model PnET-BGC of changes in stream chemistry at Hubbard Brook to changes in past and potential future emissions of sulfur dioxide and nitrogen oxides, including the 1990 Amendments of the Clean Air Act and moderate and aggressive emission control scenarios. Shown are model-predicted stream concentrations of sulfate, nitrate, acid-neutralizing capacity, pH and dissolved inorganic aluminum, and soil percent base saturation. Measured values are indicated for comparison. A color version of this image is available at http://www.mrw.interscience.wiley.com/ehs

20 to 25 years. By 2050, the concentration of aluminum and the base cation content of the soil in these watersheds would begin to approach recovery thresholds or preindustrial levels.

The model results suggest that full implementation of the 1990 CAAA will not bring about substantial improvements in chemical recovery at Hubbard Brook. The results further demonstrate that the process of recovery will be slow, particularly for sensitive systems such as Hubbard Brook. Similar analyses have been conducted at regional scales using PnET-BGC for the Adirondack region of New York (Chen and Driscoll, 2005) and northern New England (Chen and Driscoll in press), with similar results obtained. Other analyses have been conducted to evaluate the response of watersheds in Canada and Europe to future emission reductions (Wright, 2003).
In sum, acidic deposition is a pervasive problem that has had a greater impact on soils, terrestrial vegetation, surface waters, and aquatic biota than previously projected. Although abatement strategies in Europe and North America have had positive effects, emissions remain high compared to background conditions. Given the accumulation of acids and loss of buffering capacity in the soil, many areas are now more sensitive to acidic deposition and have developed an inertia that will delay recovery. Nevertheless, calculations from computer models show that deeper emission cuts will lead to greater and faster recovery from acidic deposition.

Acknowledgment

This article was developed as part of the Hubbard Brook Research Foundation Science-Links program, funded by Jessie B. Cox Charitable Trust, Davis Conservation Foundation, Geraldine R. Dodge Foundation, McCabe Environmental Fund, Merck Family Fund, John Merck Fund, Harold Whitworth Pierce Charitable Trust, the Sudbury Foundation, and the Switzer Environmental Leadership Fund of the New Hampshire Charitable Foundation. Support was also provided by the W. M. Keck Foundation and the National Science Foundation. We are indebted to Gene Likens for the use of long-term precipitation and steam chemistry data at Hubbard Brook. This is a contribution of the Hubbard Brook Ecosystem Study.

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