**11.10 Acid Rain – Acidification and Recovery**

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This article is a revision of the previous edition article by S.A. Norton, J. Veselý, volume 9, pp. 367–406, © 2003, Elsevier Ltd.

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11.10.1 Introduction

Air pollution by acids has been known as a problem for centuries (Brimblecombe, 1992; Camuffo, 1992; Ducros, 1845; Smith, 1872). Nevertheless, only in the mid-1900s did it become clear that it was a problem for more than just industrially developed areas and that precipitation quality could affect aquatic resources (Gorham, 1955). The last three decades of the twentieth century saw tremendous progress in the documentation of the chemistry of the atmosphere, precipitation, and the systems impacted by atmospheric deposition. Acidification in ecosystems results in chemical changes to soil, soil solutions, and surface and groundwater, which progressively increase from episodic through seasonal to chronic stages. The most fundamental changes during chronic acidification are an increase in exchangeable H⁺ (hydrogen ion) or Al³⁺ (aluminum) in soils, an increase in H⁺ activity (concentration) and Al³⁺ in water in contact with that soil, and a decrease in alkalinity (ALK) in waters draining from the watershed. As terrestrial systems and runoff acidify, terrestrial and aquatic biota change.

Acidic surface waters occur in many parts of the world as a consequence of natural processes and also from atmospheric deposition of strong acids (e.g., Canada, Jeffries et al., 1986; the United Kingdom, Evans and Monteith, 2001; Sweden, Swedish Environmental Protection Board, 1986; Finland, Forsius et al., 1990; Norway, Henriksen et al., 1988a; and the United States, Brakke et al., 1988). The concern over acidification in the temperate regions of the northern hemisphere has been driven by the potential for acceleration of natural acidification by pollution of the atmosphere with acidic or acidifying compounds. Atmospheric pollution (Figure 1) has resulted in an increased flux of acid to and through ecosystems. Depending on the ability of an ecosystem to neutralize the increased flux of acidity, acidification can increase imperceptibly or accelerate at rates that endanger ecosystem services and function.

Concerns about acid (or acidic) rain in its modern sense were publicized by Svante Odén (a Swedish soil scientist) in

![Figure 1](Continued)
Figure 1  (a) Concentration of SO$_4$ in the United States for 1985 and 2009 (National Atmospheric Deposition Program) and (b) deposition of SO$_4$ in Europe for 1985 and 2008 (European Monitoring and Evaluation Programme (EMEP) with help from M. B. Posch).
11.10.2 What Is Acidification?

Acidity of waters is typically expressed by the pH (\(=-\log[H^+]\)) as an intensity factor and by acid-neutralizing capacity (ANC), or ALK, as a capacity factor. The latter is commonly expressed in microequivalents (i.e., micromoles of charge) per liter (\(\mu\text{eq} l^{-1}\)). Acidic water has a pH below 7.0. Acidic water is commonly defined as having a pH below that of (distilled) water in equilibrium with atmospheric carbon dioxide (CO\(_2\)), 5.65. Whichever definition is adopted, the process of water acidification involves a decrease in pH and ANC, with accompanying secondary chemical changes.

Early definitions of ALK took the following form (in equivalents):

\[
\text{Carbonate alkalinity} = (\text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^-) - (H^+) \quad [1]
\]

This carbonate ALK was determined by titration with acid to a known pH end point. As the understanding of water chemistry grew, it became clear that other ions played a role in ALK and a more comprehensive definition of ALK was advanced:

\[
\text{Alkalinity} = (\text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- + A^{x^-} + \text{other weak acid anions}) - (H^+ + [M^{3+}(\text{OH}^-)_n]^{3-n}) \quad [2]
\]

where \(A^{x^-}\) = organic anions from dissociation of dissolved organic acids and \([M^{3+}(\text{OH}^-)_n]^{3-n}\) represents variously charged (hydroxylated) species of metals, particularly Al\(^{3+}\) and Fe\(^{3+}\) or S\(^{2-}\), in solution. The ANC of a solution can be defined as charge balance ANC (Hemond, 1990; Reuss and Johnson, 1986). In equivalents,

\[
\sum (+) = \sum (-) \quad [3]
\]

\[
(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + K^+ + [M^{3+}(\text{OH}^-)_n]^{3-n})
+ \text{NH}_4^+ + H^+ = (\text{OH}^- + F^- + \text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-}
+ \text{CO}_2^{2-} + \text{HCO}_3^- + A^{x^-} + \text{other weak acid anions}) \quad [4]
\]

Rearranging we get,

\[
(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + K^+ + \text{NH}_4^+)
- (\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + F^-) = (\text{OH}^- + \text{CO}_3^{2-}
+ \text{HCO}_3^- + A^{x^-} + \text{other weak acid anions})
- (H^+ + [M^{3+}(\text{OH}^-)_n]^{3-n}) \quad [5]
\]

The right-hand side of eqn [5] is the expanded definition of ALK. Therefore,

\[
\sum (\text{Strong base cations}) - \sum (\text{Strong acid anions}) = \text{alkalinity = acid neutralizing capacity} = \sum (\text{Weak acid anions}) - \sum (\text{Weak base cations}) \quad [6]
\]

or

\[
\text{ANC} = \text{ALK} = (\text{SBC}) - (\text{SAA}) = (\text{WAC}) \quad [7]
\]

Thus, in equivalents,

\[
\text{ANC} = (\text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- + A^{x^-})
- (H^+ + [M^{3+}(\text{OH}^-)_n]^{3-n}) \quad [8a]
\]

or

\[
\text{ANC} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + K^+ + \text{NH}_4^+)
- (\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + F^-) \quad [8b]
\]

Two ecosystem-level premises follow:

1. All elemental inorganic and biotic cycles are linked and work together toward an equilibrium; if we independently change some part of this system (e.g., \(H^+\)), all cycles shift toward a new equilibrium of the whole system.

2. Ion charge balance must prevail.

ANC is a summative term that indicates the state of acidification of the water. A declining ANC, for whatever reason, connotes ongoing acidification. According to eqn [8b], all processes adding strong acid anions (SAA) to the system without adding an equivalent amount of strong base cations (SBC) (e.g., acid rain, nitrification, mineral sulfide oxidation, S-org or S\(^{2-}\) oxidation), or removal of SBC without an equivalent amount of SAA (e.g., biomass growth, SBC depletion from soils by exchange for Al\(^{3+}\) and \(H^+\)), lead to acidification (lower ANC) of the system. In contrast, processes removing SAA without equivalent removal of SBC (denitrification, \(\text{NO}_3^-\) assimilation, \(\text{SO}_4\) reduction), or adding SBC without equivalent addition of SAA (weathering, dust deposition, liming), increase ANC.
The ANC or ALK (eqn [8a]) of solutions is commonly measured by Gran titration. In this process, some $A_x/C_0$ and $(M^{3+}(OH^-)_n)^{3-n}$ are titrated, contributing to the ANC. In this chapter, we equate ALK with the term ANC. Concentrations on the right side of eqn [2] vary with soil partial pressure of CO$_2$ (pCO$_2$), but maintain electroneutrality in combination with other dissolved species. The ANC defined by eqn [8b] is commonly calculated as the residual of individual analyses of water for SBC and SAA. The sum of errors in individual analyses, particularly if concentrations are high, can lead to substantial errors in the calculated ANC. Alternatively, in waters with high concentrations of sea salt or dissolved organic carbon (DOC), the ANC can be calculated from the right side of eqn [2] as (carbonate ALK + the estimated contribution of DOC to anions) – (estimated concentration of ionic M) (Evans et al., 2001a; Köhler et al., 1999). Each mg of DOC 1$^{-1}$ adds 3–6 $\mu$eq 1$^{-1}$ to carbonate ALK. The discrepancy between ANC and carbonate ALK, due to DOC and/or M species for low-ANC waters, may exceed 50 $\mu$eq 1$^{-1}$.

In this chapter, we focus on acidification processes affecting surface waters that drain soils and bedrock for which chemical weathering is slow. Bedrock lithologies and soils that contain free carbonate minerals (e.g., calcite, CaCO$_3$) and/or abundant ferromagnesian silicate minerals (e.g., pyroxene, (Ca,Mg)SiO$_3$) release base cations at much higher rates (Sverdrup, 1990; White and Brantley, 1995), rapidly consuming H$^+$ in the process, and thus they are much less susceptible to acidification, requiring considerably more time or stronger acid to deplete base cations from the soil and bedrock.

### 11.10.3 Long-Term Acidification

#### 11.10.3.1 Has Long-Term Acidification Occurred?

Prior to 1960, freshwater pH was infrequently measured and colorimetric methods for pH measurements were commonly inaccurate (Haines et al., 1983), particularly in waters with low ionic strength. Thus, reconstruction of pH for lakes and streams from the literature for even the mid-1950s is problematic. However, dated lake sediment cores have been analyzed for fossil diatom and chrysophyte assemblages. Statistical interpretation of the fossil assemblages enables inferences about longer term trends in past lake environmental conditions, especially pH (Battarbee et al., 1990; Charles and Smol, 1988; Dixit et al., 1992), and also DOC, ALK, and dissolved Al (Davis, 1987). Decreases in atmospheric deposition of acidic compounds since 1990 have coincided with increases in measured lake water ANC and pH, as well as pH inferred from fossil remains. The latter changes have been observed directly, which affirms that the reconstructions of earlier natural acidification were valid.

Reconstruction of the pH history of several northern hemisphere lakes using fossil assemblages showed that the lakes were alkaline shortly after deglaciation but had acidified markedly by the early Holocene (the last 10000 years of earth history) (Norton et al., 2011; Pražáková et al., 2006; Renberg, 1990; Ryan and Kahler, 1987; Whitehead et al., 1986). Neutral to alkaline pH in soil and surface water shortly after deglaciation was caused by weathering of an abundance of finely divided ‘rock flour’ and highly soluble minerals such as calcite (Engstrom et al., 2000) and apatite (Ca$_5$(PO$_4$)$_3$(OH,F,Cl)) (Boyle, 2007; Kopáček et al., 2007; Norton et al., 2011) to produce positive ANC in watersheds. In Sweden, for example, the initial decrease in diatom-inferred pH from as high as 8 to as low as 6 after deglaciation was followed by a long-term decrease from ~6 to 5, caused by the development of vegetation and soils, terrestrial production of DOC, and release of organic acids to some lakes (Renberg, 1990). The inferences about organic acids are borne out by speciation studies of Al in sediment cores (Kopáček et al., 2007; Norton et al., 2011). These natural soil-forming processes acidified soil and surface water over thousands of years in glaciated terrain before the onset of modern acidic precipitation (‘acid rain’) (Figure 2).

Through time, weathering rates slowed as small particles were weathered rapidly, soluble minerals were dissolved and depleted in upper soil horizons, and incongruent weathering reactions became diffusion controlled on larger grains. As a result of declining weathering rate, natural acid inputs were

![Figure 2](image-url) Timescale of processes leading to surface water acidification.
incompletely neutralized, and the pH of solutions draining from the upper soil layers to surface waters declined. Coupled biological and chemical evidence for long-term acidification is rare. Engstrom et al. (2000) studied a chronosequence (substituting space for time at one locality) of postglacial lakes in Alaska, USA, and demonstrated declining pH and ALK with exposure time, with initial lake pHs near 8 and declining pH over several hundred to several thousand years to as low as 5. Similar conclusions were reached for a 16 600 year postglacial record for Sargent Mountain Pond, Maine, USA (Kopáček et al., 2009).

For most streams and lakes in glaciated terrain, the pH was rarely <5 until the post-1800 period. Exceptions include lakes rich in organic acidity (high DOC). Diatom-inferred pH values for soft water lakes in the Sierra Nevada Mountains (California, USA) and the European Alps showed fluctuations that were attributed to climate change during the nineteenth century (Pennner and Schmidt, 1992; Whiting et al., 1989). Cold periods were associated with lower pH values. During warm periods, the pH was higher due to increased evaporation, longer water retention times, stronger lake stratification, and enhanced assimilation of inorganic S and N. These temperature-driven fluctuations of pH were disrupted by the onset of significant acidic deposition shortly before 1900. In acid-sensitive systems, anthropogenic acidification has been much faster than natural acidification, and the pH and ANC has decreased below the natural prehistoric minima for many lakes, as inferred from diatom and chrysophyte species.

**11.10.3.2 What Controls Long-Term Acidification?**

Prior to acid rain, the principal sources of acid input to watersheds were from elevated CO2 in soils (carbonic acid acidity) and DOC from the metabolism of organic matter (eqns [9a] and [9b]).

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^- \quad [9a]
\]

\[
\text{He}(\text{A}) = x\text{H}^+ + \text{He}_{\text{A}}^{=x} \quad [9b]
\]

Organic acidity is produced primarily in the organic-rich layer of forested ecosystems (the ‘forest floor’) or fens and bogs. The pH of soil solutions in organic-rich forest soils may be lower than 4 because of the dissociation of organic acids, caused largely by dissociation of carboxylic groups (–COOH). The concentration of \((\text{A}^{=x})\) can be estimated from chemical analyses of the major base cations, acid anions, and ALK as an ‘anion deficit,’ measured by titration with acid, or calculated from DOC concentrations in conjunction with models for organic acidity (Driscoll et al., 1994; Hruška et al., 2001; Köhler et al., 1999; Oliver et al., 1983). Complexation of Al and Fe by organic ligands enhances the mobilization of these metals, but at the same time reduces the toxicity of dissolved Al. Much of the DOC acidity is lost to aerobic respiration as soil solutions descend through the unsaturated mineral soil, producing substantial amounts of CO2. Carbonic acid acidity is produced throughout the soil column but typically reaches a maximum below the forest floor. Aerobic respiration can increase the soil CO2 pressure \((\text{pCO}_2)\) to as much as two orders of magnitude higher than the atmospheric value to produce pHs as low as 4.5.

Natural acidity is also contributed from emissions of acidic or acidifying compounds from volcanoes (Camuffo, 1992; Pyle et al., 1996), including compounds of S, N, chloride (Cl), and NH3 (ammonia), from the ocean (e.g., methylsulfonate) (Charlson et al., 1987), and from wetlands (e.g., H2S) (Gorham et al., 1987). Ecosystem conditions that have sulfide weathering or mineralization rates sufficient to supply H2SO4 in significant amounts over an extended period of time are rare. Where this occurs, it is most commonly caused by land disturbance associated with construction (e.g., Hindar and Lydersen, 1994), mining or quarrying activities (i.e., acid mine drainage), recent volcanism (Wood et al., 2006), or recent deglaciation (Engstrom and Wright, 1984). Certain changes in the hydrology of soils can mobilize substantial quantities of acidic compounds. For example, runoff from marine sediments in Finland, eustatically uplifted since deglaciation, has high concentrations of SO4 from the oxidation of sulfide minerals (principally pyrite, FeS2) contained within these postglacial marine sediments (Forsius et al., 1990). Runoff from recently drained peatlands can contain high concentrations of SO4 derived from oxidation of sulfide minerals and organically bound S, as well as elevated DOC. Studies of the chemistry of wetlands (Bayley et al., 1988; Gorham et al., 1983) show empirically and experimentally that SO4 from atmospheric sources or added as a treatment is removed from bog water by some combination of precipitation as sulfide minerals, transformation into reduced organic S, or reduction to H2S with emission to the atmosphere. Reduced organic S can be reoxidized during lower groundwater levels and then leached from the system as the water table rises (Dillon et al., 1997). DOC from wetlands can contribute substantial acidity to the runoff, particularly if water tables vary.

Neutralization of soil solution acidity from any source (commonly incorrectly termed ‘acid buffering,’ which refers only to the resistance to change) is typically caused by the leaching of Ca from bedrock and soil. Magnesium is most commonly the second most important cation released during weathering. Rarely, there are watersheds with unusual silicate bedrock (e.g., serpentinite (serpentine, Mg3Si2O5(OH)4)), or unmetamorphosed ultramafic rocks (e.g., dunite (olivine, MgSiO4)) that produce Mg-HCO3 surface waters (Krám et al., 1997) where Mg exceeds Ca in runoff. Acidification is greatest in regions where bedrock and soils are more chemically resistant to weathering, where soils and glacial deposits are thin, rainfall is greater, temperature is higher, and production of organic acids is higher. For example, much of Fennoscandia, Scotland, Wales, the Adirondack Mountains of New York, USA, and the Muskoka Region of Ontario and eastern Nova Scotia, Canada, have recently acidified lake districts as a consequence of atmospheric inputs of SO4 and NO3, in combination with granitic or quartzite/shale bedrock and relatively high concentrations of naturally occurring DOC. Surface waters draining mafic, ultramafic, or calcareous bedrock are relatively unaffected by acidification because of the high base cation weathering rates. Surface waters draining non-calcareous sandstone, granite, and schist are more likely to be impacted by acid rain (Kuylenstierna and Chadwick, 1989). The highly soluble minerals calcite and apatite are commonly
present in small amounts in many rock types. In postglacial time, these two minerals likely controlled pH and Ca in runoff for up to several thousand years before weathering rates became dominated by slower weathering silicates such as amphibole, biotite, and feldspars (Ca, Na, K, Al silicates) (Boyle, 2007).

Although weathering plays an important role in the neutralization of acid, rates at which base cations are released in natural systems are weathering rates are not well known. Weathering rates vary with bedrock and soil composition, concentration of organic ligands, temperature, soil moisture and pH, precipitation amounts and pH, redox (reduction/oxidation) conditions, and vegetation (see, e.g., Klaminder et al., 2011; Sverdrup, 1990; White and Brantley, 1995). Chemical weathering rates of aluminosilicate minerals increase at lower pH in laboratory experiments.

Field-based experiments have yielded a better understanding of the rate at which base cations can be supplied to offset the input of strong mineral acids (Bain and Langan, 1995; Swoboda-Colberg and Drever, 1993). For many elements, chemical budgets for watersheds have been constructed by the simplistic relationship:

\[
\text{Weathering rate} = \frac{\text{stream solute output}}{\text{atmospheric solute input}}
\]

Equation [10] ignores numerous quantitatively important processes including changes in biomass (living and dead), changes in exchangeable soil pools for cations and anions, contributions from dry deposition, and gaseous losses to the atmosphere (e.g., for S and N). A more comprehensive equation for a watershed element mass balance might be:

\[
\text{Weathering rate} = \left[ \frac{\text{stream output} + \text{gaseous efflux}}{\text{atmospheric input (wet) + atmospheric input (dry)}} \right] + \Delta \text{biomass storage} + \Delta \text{secondary soil pools (e.g., exchangeable, adsorbed)}
\]

Equation [11]

Commonly, the weathering rate is calculated by adding and subtracting many fluxes, each of which is difficult to assess (Paes, 1983; Velbel, 1985; White and Blum, 1995). No long-term calibrated watershed studies measure all these variables well and therefore the weathering rates determined from them are only approximate. For example, Bormann and Likens (1979) calculated that Ca weathering from 1963 to 1974 was approximately 11.5 kg ha\(^{-1}\) year\(^{-1}\) at Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA, assuming that all the excess Ca was from weathering of primary minerals. At HBEF, surface waters have very low ALK and have likely been acidified, and they are susceptible to episodic acidification. On the basis of a more complete analysis, Bailey et al. (2003) were not able to resolve the primary weathering from depletion of exchangeable base cations from the soil. At an ecologically and geologically similar site at Bear Brook Watershed in Maine (BBWM), USA, Ca weathering rates were calculated on a similar basis. Assuming steady state for many of the unknown variables, the estimated rates ranged from 11 to 15 kg ha\(^{-1}\) year\(^{-1}\) for 1988–1992 and 1.5 kg ha\(^{-1}\) year\(^{-1}\) for 1988–2000 in the reference watershed, respectively (Norton et al., 1999; Watmough et al., 2005).

Numerous studies suggest that proportions of Ca derived from the watershed compared to the Ca derived from atmospheric inputs can be inferred by using Sr (strontium) isotope data. The Sr isotope ratios \(^{87}\text{Sr}/^{86}\text{Sr}\) for the bedrock, atmospheric input, and output are combined in a linear mixing model to infer the ultimate sources of Ca (bedrock/soil complex vs. atmosphere). The explicit assumption of this technique is that Ca and Sr behave similarly during all biogeochemical processes. This assumption has been challenged (Bullen et al., 2002).

Several studies have suggested that acid deposition accelerates weathering (e.g., Miller et al., 1993). However, Norton et al. (1999) concluded on the basis of runoff chemistry at BBWM that chemical weathering was not affected during a 20-year experimental acidification of an entire watershed (Navrátil et al., 2010). There, Swoboda-Colberg and Drever (1993) acidified in situ soil columns, after removal of the forest floor (organic horizon). They stripped exchangeable cation pools from the mineral soil with strong acid leaching until a steady-state rate of leaching of cations occurred. This steady-state loss was attributed to primary chemical weathering. The values (kg ha\(^{-1}\) year\(^{-1}\)) were 200–400 times higher than those based on the whole watershed (eqn [11], simplified). Dahlgren et al. (1990) used reconstructed soils from the same watershed and determined that experimental acidification of the columns with H\(_2\)SO\(_4\) was accompanied by increased leaching of base cations from the exchangeable pools and dissolution of Al from a solid phase. Silica release was not enhanced by their acidic treatments. Generally, silica is relatively unchanged in nearly all field-scale acidification experiments with the major exception of the wollastonite (CaSiO\(_3\)) treatment at HBEF (Cho et al., 2010), suggesting no substantial change in congruent weathering rates. In summary, most field experiments and watershed studies suggest that variations in short-term base cation release to runoff are dominated by ion exchange equilibria or ecosystem perturbations (e.g., ice storms, wind damage, fire), not changes in weathering rates. As exchangeable base cation supplies become depleted and pH declines, mobilization of ionic Al becomes increasingly important.

Laboratory experimental rates of weathering (typically expressed as mol m\(^{-2}\) s\(^{-1}\)) are generally 2–3 orders of magnitude higher than field rates. These differences are partly an artifact of differing experimental methods, non-steady-state processes (Holdren and Adams, 1982), differences in hydrological conditions between the field and laboratory, disturbance effects, and effective mineral surface area in contact with reacting water. The chemical weathering in soil can be inhibited or virtually stopped in dry periods (Zilberbrand, 1999). Alternatively, as acidic soil solutions dry, the increasing concentrations of solutes causes pH to decline and ionic strength to increase, which should increase weathering rates in a restricted volume of soil solution. Clearly, extrapolating experimental weathering rates determined in the laboratory to the field and regionalization of the results are problematic. The balance between primary weathering sources of base cations and desorption of base cations in contributing to runoff concentrations is difficult to determine. Thus, the resilience of soils to acidification is still poorly understood. Unfortunately, accurate weathering data are important to realistically calibrate...
some dynamic and static models of soil and water acidification (e.g., PROFILE, Sverdrup and De Vries, 1994; Sverdrup and Warfvinge, 1993).

Several types of evidence from soils have been used to estimate long-term weathering rates. The historical approach uses the reduction in base cation concentrations (Johansson and Tarvainen, 1997) or labile minerals (e.g., biotite and hornblende; Frogner, 1990) in the soil profile with respect to chemically unaltered C-horizon soil as an index of weathering. If the age of the soil is known (e.g., post-Wisconsinan in North America, Weichselian in northern Europe), this method provides long-term average weathering rates that are generally greater than present day rates (Klaminder et al., 2011). Weathering rate decreases with increasing soil age (Engstrom et al., 2000) and may follow a power-law equation (Taylor and Blum, 1995). Modern weathering rates could be <10% of the rate immediately after deglaciation.

The base cation status of surface water is also controlled partly by hydrology. Steeper topography generally has thinner soils, shortening contact time between soil solutions and mineral soil, thereby decreasing the rate of chemical weathering and ALK production. Seepage lakes, containing neither surface inlets nor outlets, can recharge or receive discharge from the local groundwater system. In the former case, the lake water chemistry can be similar to atmospheric deposition, modified by evaporation and in-lake processes. As groundwater flow paths change so that more water flows through a seepage lake, the ANC of the lake typically increases as a consequence of the entering ground water having been in contact with mineral soil. For all lakes, residence time of water is important in determining evaporative changes in water composition (Webster and Brezonik, 1995) and the extent to which the in-lake processes alter the acid–base status of the water inputs (see Section 11.10.5.6).

### 11.10.4 Short-Term and Episodic Acidification

Short-term (days to weeks) and episodic (hours to days) acidification events (Figure 2) are caused by a variety of mechanisms including pulsed inputs of water (high discharge from snowmelt or rain) causing preferential dilution of base cations, release of oxidized S and N from organic or inorganic pools (Dillon et al., 1997), atmospheric input of marine aerosols (the salt effect; Wright et al., 1988), and increased leaching of DOC (Hruška et al., 2001). These mechanisms are controlled by weather and climate change. Many aspects of episodic acidification have been thoroughly reviewed by Wigington et al. (1990).

Watersheds have five major lines of defense against short-term and episodic acidification: (1) cation desorption, (2) anion adsorption, (3) Al dissolution, (4) protonation of weak acid anions, and (5) dehydroxylation of metal species.

1. Chemical weathering of silicate minerals in soils is a relatively slow source of base cations, but the total long-term neutralization capacity of soils is typically large. In contrast, ion exchange reactions (cation and anion exchange) in soil are relatively rapid, and tend to buffer $\text{H}^+$, $\text{SO}_4^{2-}$, base cation, and ANC concentrations. The sum of the exchange sites for cations (expressed in moles of charge per kg soil) is termed the cation exchange capacity (CEC). The percentage of the cation exchange sites occupied by the base cations Ca, Mg, Na, and K is traditionally termed the base saturation (BS). The rest of the cation exchange sites are occupied primarily by Al and H. In concept, if desorption of base cations exceeds the weathering rate release of those base cations, BS of soil decreases, site occupancy by Al and H increases, and soil acidification occurs; subsequently, more of the charge balance in runoff is maintained by the export of $\text{H}^+$ and $\text{Al}^{3+}$. The soil- and surface-water thus become more susceptible to short-term and episodic acidification (Wigington et al., 1996) that can last for hours to months.

2. In soils rich in Fe and Al secondary phases, excess $\text{SO}_4$ from the atmosphere can be reversibly adsorbed or desorbed, thereby retarding acidification or recovery from acidification, respectively (David et al., 1991a,b; Navrátil et al., 2009). Well-drained forest soils, such as in southern Europe or the central and southern United States, that were not glaciated during the Wisconsinan, are commonly rich in sesquihydroxides (Al and Fe hydroxides) that cause high $\text{SO}_4$ adsorption capacity (e.g., Cosby et al., 1986). However, even young postglacial soils have an enhanced ability to adsorb $\text{SO}_4$ (Kahl et al., 1999).

Substantial decreases of atmospheric input of S in Europe and North America in the last two decades (Figure 1) have caused a general decline in surface water $\text{SO}_4$ (Evans et al., 2001b; Stoddard et al., 1998). Many soils have switched from being a sink to a source of S (Driscoll et al., 1998; Prechtl et al., 2001). Fluxes of $\text{SO}_4$ in runoff from watersheds with thin (e.g., alpine) soil and low $\text{SO}_4$ adsorption capacity have decreased rapidly (Kopáček et al., 2001a) in comparison to watersheds with deeply weathered and thick soils (Aleurwell, 2001). Stable isotope ($\delta^{34}\text{S}$) studies and budget calculations suggest that the pool of organic S in forest floor and biological S turnover are important contributors to $\text{SO}_4$ export. Organic cycling of deposited atmospherically derived S plays an equally important role in polluted coniferous forests in the Czech Republic (and probably elsewhere; Houle and Carignan, 1995) where over 80% of the total S content in soils is organically bound (Novák et al., 2003). Sulfur isotope studies indicated that up to 80% of sulfate in stream water in polluted areas of the Czech Republic was organically cycled (Novák et al., 2000).

3. As the $\text{pH}$ of soil water decreases below 5.5–5.0 and soil cation exchange sites become depleted of base cations, desorption of exchangeable Al and dissolution of solid Al secondary phases become important because Al hydrolysis increasingly dominates acid neutralization processes. For example,

$$\text{Al(OH)}_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$$

Commonly, studies of changing water quality do not differentiate whether increased dissolved Al is from desorption of Al from soils, or from dissolution of a solid Al phase. Both processes have been demonstrated at some sites. In very acidic forest soils, dissolution of Fe can also contribute to acid neutralization (Bong, 1986; Matschullat et al., 1992; Norton et al., 2004; Ulrich, 1983). Dissolution of Mn solid secondary phases could be rarely important and occurs...
5. Some dissolved metals, for example, Al, Fe, and Mn, are probably only during early acidification stages when Mn is rapidly mobilized (Puhe and Ulrich, 2001).

4. Weak acid anions are loosely defined as anions from acids whose dissociation constants are in the range of pHs exhibited by surface waters (~4–11). Two important acid groups are included. In the system CO$_2$–H$_2$O, there is an equilibrium among the various C-bearing species as a consequence of CO$_2$ dissolving in water

\[
\text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{CO}_3 \quad K = 10^{-3.5} \quad \text{pK} = 1.5 \quad [13]
\]

\[
\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- \quad K = 10^{-6.5} \quad \text{pK} = 6.5 \quad [14]
\]

\[
\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \quad K = 10^{-10.3} \quad \text{pK} = 10.3 \quad [15]
\]

For eqn [14], H$_2$CO$_3$ and HCO$_3^-$ are present in equal concentrations at pH $\geq$ 6.5. Any process not involving dissolving or evaporation of CO$_2$ that tends to lower the pH will result in production of H$_2$CO$_3$ at the expense of HCO$_3^-$, a process called protonation. Carbonate ALK (eqn [1]) is reduced.

Dissolved organic acid typically consists of a mixture of organic acids whose pKs (the negative log of the equilibrium constant) may range from very small values (strong organic acids) to as high as the bicarbonate–carbonic acid pK (eqn [14]) (weak organic acids). Any weak organic anions are also subject to protonation (Hruška et al., 2003; Oliver et al., 1983), supplying additional acid neutralization capacity to the soil water and surface water (eqn [2]).

5. Some dissolved metals, for example, Al, Fe, and Mn, are speciated with differing amounts of hydroxyl, for example, Al$^{3+}$, Al(OH)$_{2+}$, Al(OH)$_{3+}$, Al(OH)$_{4+}$, and Al(OH)$_{5+}$. The relative abundance of each species is a function of pH, similar to organic acids and the CO$_2$-bearing species. Thus, a process that tends to acidify the water can be partly neutralized by consumption of H$^+$, which can be represented as, for example,

\[
\text{Al(OH)}_{2+} + \text{H}^+ = \text{Al}^{3+} + \text{H}_2\text{O} \quad [16]
\]

11.10.5 Drivers of Short-Term and Episodic Acidification

Susceptibility to episodic acidification is increased because of longer term acidification, driven by excess loading of SO$_4$ and NO$_3$; higher ambient DOC; and aggrading biomass, all of which chronically lower base cations, pH, and ANC.

11.10.5.1 High Discharge from Snowmelt and Rain

During snowmelt, acidic pollutants are preferentially eluted. Consequentially, acidic pulses are released and may enter streams and lakes, particularly early in the snowmelt process, and these solutions may have little contact with soils (Jeffries, 1990; Johannessen and Henriksen, 1978). Base cation concentrations become diluted concurrently with elevated concentrations of SAA. The associated pH and ALK depressions can have severe biological impacts on fish and other biota, particularly during their sensitive early life stages. This meltwater may be close to 0°C and thus typically does not mix downward in lakes with warmer, more dense lake water if the lake is covered with ice. The result is a shallow layer of relatively low pH water directly beneath the ice. Acidic episodes kill fish long before the system is chronically acidic; recovery from acidic episodes is a key to biotic recovery. In circumneutral streams and lakes, dilution of Ca is an important factor for fish mortality (Tranter et al., 1994).

11.10.5.2 Pulsed Release of SO$_4$ and NO$_3$ from Soils

Episodic release of SO$_4$ and/or NO$_3$ from soils, unaccompanied by equivalent base cations, may depress pH and ANC, on a timescale of individual high discharge events, or seasonally. Episodically elevated concentrations of SO$_4$ in runoff may be caused by prolonged drought, lowering of the groundwater table, subsequent oxidation of S stored in organic matter, and then leaching during higher discharge (Dillon et al., 1997). Seasonal release of stored S is most strong from watersheds with a high areal percentage of wetlands (Kerr et al., 2011). Increases in DOC may accompany the elevated SO$_4$, enhancing the depression of pH. Normal fluctuations of hydrology are typically unaccompanied by substantial variation in stream SO$_4$ because of anion exchange equilibria in mineral soils and stream sediment. The flux of NO$_3$ is dominated more by biological processes, being strongly diminished in many streams during the vegetation growing season versus the dormant season. Consequently, many watersheds have a strong seasonal cyclicity for release of NO$_3$ (Navrátil et al., 2010; Stoddard, 1994). Superimposed on this seasonality is a short-term release of NO$_3$ caused by flushing of mineralized N (as NO$_3$) from shallow soils during periods of higher flow. It is common for NO$_3$ to vary more in runoff (on both a percentage and absolute basis) than SO$_4$ (Navrátil et al., 2010), apparently because most soils have a low NO$_3$ exchange capacity.

The elevated SAA fluxes from acidic soils during events are usually associated with elevated terrestrial export of H$^+$ and ionic Al forms, which are potentially toxic for water biota (e.g., Gensemer and Playle, 1999). Inorganic Al and DOC interactions and the proportion of ionic and organically bound (nontoxic) Al forms cause variability in fish mortality, as does duration of exposure in an acidic episode (Baldigo and Murdoch, 1997). Changing flow paths during hydrological events (i.e., proportion of snowmelt or rainwater and soil water in the total water input to lakes) are of overwhelming importance in controlling the chemical character of episodes in streams (Davies et al., 1992). For example, acid-sensitive fish species were absent in streams of the northeastern United States that had median pH $\leq$ 5.0–5.2 and inorganic Al $> 100–200$ µg L$^{-1}$ during high flow (Baker et al., 1996).

11.10.5.3 Marine Aerosols

Deposition of marine salt aerosol causes episodic acidification of runoff near the coast by alteration of cation exchange equilibria within strongly acidic soil. During the 'sea-salt effect,' marine aerosol Na and Mg displace primarily H, Al, and Ca from soil exchange sites. The Na/Cl and Mg/Cl equivalent
ratios in runoff can decline below ocean water values, 0.86 and 0.2, respectively, as Na and Mg cations are adsorbed by the soil. The pH of runoff can decline as much as 2 pH units during these sea-salt episodes. The ANC of runoff is reduced while BS and soil pH are increased very slightly. Wiklander (1975) was one of the first to suggest acidification of leachate by the sea-salt effect. The process has been demonstrated experimentally at the laboratory scale (Skartveit, 1981) and at the watershed scale (Wright et al., 1988). Individual high salt inputs can be reflected in surface water chemistry for months to a few years (Evans et al., 2001c; Godsey et al., 2010; Kirchner et al., 2000; Norton and Kahl, 2000). The maximum effect from sea-salt input occurs in thin acidic soils that have low BS and low CEC. Most soils have relatively low Cl exchange capacity. Thus, Cl behaves conservatively. The sites most responsive to sea-salt inputs are those at an intermediate distance from the coast where occasional major sea-salt inputs can generate large proportional changes in Cl and other marine ions (Harriman et al., 1995). Major regional events with pH depressions sufficient to kill fish have been documented by Hindar et al. (1994). These events can occur in areas even where acidification from strong acids is absent. Salt-driven acidification episodes can be relatively common in acidic bogs although it has not been well documented. Pugh et al. (1996) demonstrated a salt acidification effect in an ombrotrophic/poor fen site. The salt originated from road runoff, but the chemical changes in runoff were otherwise analogous.

11.10.5.4 Organic Acidity

The most acidic stream flows in polluted regions commonly have disproportionately higher concentrations of H\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−} and inorganic Al. In unpolluted regions, as in northern Sweden (Hruska et al., 2001) or in North Shore rivers, Quebec, Canada (Campbell et al., 1992), episodic acidification can be primarily caused by dilution of base cations and increase in organic anions during high discharge. In northern Quebec, for example, ‘inorganic anion deficits’ increased from around 35 to 70–100 meq l\textsuperscript{−1} representing up to 20 mg DOC l\textsuperscript{−1} during high flow at snowmelt, causing pH to decline from near 7 to about 5 (Campbell et al., 1992). The episodic pH depression associated with DOC operates independently of anthropogenic acidity and likely is responsible for substantial episodic acidification. Fortunately, as DOC and H\textsuperscript{+} increase, much of the potentially toxic metals that are mobilized (especially Al) becomes bound (complexed) with the DOC and thus biologically much less reactive. Since about 1980, depending on location, atmospheric deposition of SO\textsubscript{4} has declined as has runoff SO\textsubscript{4}. Concurrently, DOC concentration has increased at most localities, especially in watersheds with significant percentage of wetland (Monteith et al., 2007). The correlation between declining SO\textsubscript{4} and increasing DOC suggests a mechanistic linkage. Decreasing ionic strength and increasing soil water pH have been suggested to cause increasing solubility of DOC. Some of the increase in DOC concentration can be attributable to climatic warming, causing increased mineralization of organic matter. Altered hydrology, such as earlier snowmelt, can also enhance DOC export from watersheds. Elevated atmospheric deposition of N can also stimulate mineralization of organic matter. Acidity from increased DOC partially offsets decreased SO\textsubscript{4}, inhibiting recovery from acid rain (Arvola et al., 2010). An additional effect of increasing DOC is the increased mobilization of Al and Fe (and other metals) from soils, and subsequent impact on phosphorus (P) cycling (see Section 11.10.6.2).

11.10.5.5 Dilution

It is common during periods of snowmelt or high rainfall to have most runoff passing through shallow soils or even overland. As a consequence, soil cation exchange processes can be largely by-passed. This causes dilution of base cations in the runoff; however, SO\textsubscript{4} in runoff is less diluted than elements originating in the watershed because some SO\textsubscript{4} exists in the snow or rain that makes up the runoff. Consequently, SAA decrease less than SBC, causing acidification. Such acidification can also occur seasonally as a result of NO\textsubscript{3} mobilization (Laudon and Norton, 2010).

11.10.5.6 In-Lake Processes Affecting pH and ANC

In circumneutral lakes, the water ANC and pH are primarily affected by CO\textsubscript{2} assimilation (eqn [17]; left to right = production of organic matter) and dissimilation of organic matter (reversed eqn [17]; CO\textsubscript{2} production):

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{O}_2
\]  

Changes in concentrations of dissolved CO\textsubscript{2} affect concentrations of HCO\textsubscript{3}\textsuperscript{−} and H\textsuperscript{+} (eqns [13] and [14]), and lake water pH. The pH maxima occur in the epilimnion near midday due to the highest photosynthetic activity and the largest depletion of CO\textsubscript{2} concentrations. Dissimilation of settling organic matter increases CO\textsubscript{2} concentrations and decreases pH in deeper waters. Consequently, pH is usually higher in the epilimnion than in the hypolimnion of circumneutral lakes. An inverse pH–depth relationship (lower pH values in the surface layer than above the bottom) is typical for strongly acidified lakes, with a depleted carbonate buffering system. The reasons for this difference are low pH and negligible carbonate system buffering in acidic waters. Changes in H\textsuperscript{+} concentrations associated with the CO\textsubscript{2} assimilation and dissimilation are relatively small in acidic waters due to low dissociation of H\textsubscript{2}CO\textsubscript{3} at pH < 5 (eqn [14]). In contrast, the effects of other in-lake processes generating or consuming H\textsuperscript{+} (such as Ionic exchange across the sediment–water interface, biotic reduction of SO\textsubscript{4} and NO\textsubscript{3}, photochemical and bacterial oxidation of organic acids, hydrolysis of (M\textsuperscript{3+}(OH\textsuperscript{−})\textsubscript{n})\textsuperscript{3−}, and dissociation or protonation of organic acids) on water pH are more pronounced (and straightforward) in acidic than in circumneutral lakes because the associated H\textsuperscript{+} fluxes are not buffered by the carbonate buffering system.

Laboratory and in situ experiments have demonstrated that stream and lake sediments in contact with the water column are effective ion exchangers for base cations (e.g., Cook et al., 1986; Oliver and Kelso, 1983), anions (Navrátil et al., 2010; Norton et al., 2000), and Al (Henriksen et al., 1988b; Tipping and Hopwood, 1988). Because of the reversible cation-exchange processes, pH depression can be buffered during episodic acidification, as is recovery of ANC during de-acidification (see Section 11.10.8). Exchange of H\textsuperscript{+} for base cations in sediment is commonly reported as a significant ANC
source during the early stage of stream and lake water acidification (e.g., Psenner, 1988; Schiff and Anderson, 1986).

Sulfate and NO₃ are used as electron acceptors during microbial dissimilation of organic matter in anoxic conditions that are typical for sediments but also may occur in the hypolimnion of a productive lake. The biochemical reductions of SO₄ and NO₃ are important H⁺ consuming (ANC generating) processes:

\[ 2\text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ = \text{H}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad [18] \\
5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ = 2\text{N}_2 + 7\text{H}_2\text{O} + 5\text{CO}_2 \quad [19] \\
\]

The rate of SO₄ and NO₃ reduction in sediments is normally governed by diffusion. Total amount of the reduced SO₄ and NO₃ thus increases with SO₄ and NO₃ concentrations in lake water and water residence time (Kelly et al., 1987). As acidification progresses and terrestrial exports of SO₄ and NO₃ to the lake increase, the contribution of SO₄ and NO₃ biochemical reduction to the total in-lake ANC generation increases, and typically becomes the dominant process (Cook et al., 1986; Rudd et al., 1986; Schindler, 1986). However, net storage of SO₄ (as reduced S) in sediment is typically a small percentage of excess SO₄ in lake water (Norton et al., 1987). Besides denitrification (eqn [19]), NO₃ is assimilated during photosynthesis by phytoplankton, consuming 1 mol of H⁺ per 1 mol of NO₃ consumed (eqn [20]). This process is an important ANC source in productive lakes with either naturally high (e.g., Plešné Lake; Kopáček et al., 2004) or artificially elevated (e.g., Davison et al., 1995) P concentrations.

\[ \text{NO}_3^- + \text{R} + \text{OH} + \text{H}^+ = \text{R} - \text{NH}_2 + 2\text{O}_2 \quad [20] \]

DOC is not conservative in water. It can be metabolized, condensed, photooxidized, or precipitated during acidification. Sunlight can effectively reduce concentrations of allochthonous recalcitrant organic matter, decrease its average molecular weight, and produce numerous biologically available compounds, like acetic, formic, citric, malonic, and oxalic acids (Bertilsson and Tranvik, 2000; Kieber et al., 1989; Steinberg et al., 1998). Organic acid anions to inorganic carbon (mono- and dioxide) (Bertilsson and Tranvik, 2000; Kieber et al., 1989; Steinberg et al., 1998) can be chronically maintained in waters of heavy polluted regions (Vesely et al., 1998b). The dissolution of Al is further enhanced by formation of soluble complexes, especially with fluoride and sulfate (Schecher and Driscoll, 1987). Mixing of these acidic Al-rich waters with higher pH waters commonly causes Al precipitation, also a problem for fish (Reinhardt et al., 2004; Rosseland et al., 1992; Teien et al., 2006; Weatherley et al., 1991). Rare earth elements (REE) and beryllium (Be) behave similarly to Al in streams. They are mobilized by DOC and by declining pH during acidic episodes (REE data from BBWM, Norton, unpublished; Tang and Johannesson, 2003; Veselý et al., 2002b; Wood et al., 2006).

Many pollutants other than S and N occur in modern atmospheric deposition. The history of deposition of these pollutants has been determined by chemical and isotopic analyses of ice cores (e.g., Boutron et al., 1995), lake sediment cores (e.g., Renberg et al., 2000), peat cores (e.g., Shotyk et al., 1996), soils (Bindler et al., 1999), vegetation (Steinnes, 1995), and direct measurements (e.g., NADP–NTN, 2009). Most metals have enhanced mobility as a consequence of acidification. Mercury (Hg) and lead (Pb) are relatively conservative in watersheds, in large part because of fixation by particulate organic matter or sorption to sesquihydroxide secondary phases. Atmospheric deposition of Pb increased in eastern and central North America and northern Europe by as much as 50 times preindustrial values, peaking in the 1970s. It has declined since then to generally <5% of peak values (Figure 4). Biological impact of atmospherically deposited Pb, except in grossly polluted regions, has not been demonstrated to be significant. The deposition of Hg is strongly influenced by dry
deposition of Hg to plant surfaces. Thus, Hg deposition was low when Caribou Bog (Orono, Maine, USA) (Figure 4) was a lake, high during the fen stage as the lake filled in, and then low during the ombrotrophic stage, until the present era of pollution. Similarly, at Sargent Mountain Pond (Maine, USA), Hg deposition increased dramatically slightly before the Younger Dryas and afterward, as a consequence of the development of forest vegetation. Modern deposition of Hg at both sites reached unprecedented values as a consequence of anthropogenic emissions. Mercury has increased in atmospheric deposition by more than 100% since the mid-1800s, peaking in the 1970s and declining since then (Figure 4). The effect of pH and atmospheric deposition on concentrations of trace elements in acidified freshwaters: A statistical approach. Water, Air, and Soil Pollution 88: 227–246; Veselý J and Majer V (1998) Hydrogeochemical mapping of Czech freshwaters. Bulletin of the Czech Geological Survey 73: 183–192). The decline of Be, Cd, Mn, and Zn at very low pH is likely caused by acidification-related depletion of exchangeable trace metals from the watershed soils.

**Figure 3** Relationship among median, upper, and lower quartiles of Al, As, Be, Cd, Cu, Mn, Pb, and Zn, and pH in Czech Republic brooks in the late 1980s. Values were calculated after sorting the water samples \((n = 12,988)\) into groups with 0.2 pH unit ranges. Volume-weighted average concentrations in bulk precipitation (○) and throughfall (●) in 1991 samples from the Bohemian Forest are shown (modified from Veselý J and Majer V (1996) The effect of pH and atmospheric deposition on concentrations of trace elements in acidified freshwaters: A statistical approach. Water, Air, and Soil Pollution 88: 227–246; Veselý J and Majer V (1998) Hydrogeochemical mapping of Czech freshwaters. Bulletin of the Czech Geological Survey 73: 183–192). The decline of Be, Cd, Mn, and Zn at very low pH is likely caused by acidification-related depletion of exchangeable trace metals from the watershed soils.

**Figure 4**

<table>
<thead>
<tr>
<th>Element</th>
<th>pH</th>
<th>Concentration (μg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>4</td>
<td>1.2 *</td>
</tr>
<tr>
<td>Al</td>
<td>7</td>
<td>0.5 *</td>
</tr>
<tr>
<td>Be</td>
<td>8</td>
<td>2.0 *</td>
</tr>
<tr>
<td>Mn</td>
<td>6</td>
<td>400 *</td>
</tr>
<tr>
<td>Pb</td>
<td>5</td>
<td>15 *</td>
</tr>
<tr>
<td>Zn</td>
<td>4</td>
<td>60 *</td>
</tr>
</tbody>
</table>

Mercury becomes methylated under reducing conditions, enters the aquatic food chain through phytoplankton, is magnified as much as 10⁶-fold in the food chain, and reaches maximum concentrations in piscivorous fish. The increase of SO₄ in the environment from acid rain could have stimulated methylation of Hg because of enhanced biotic reduction of SO₄ in wetlands, groundwater, and lakes, thus increasing methyl-Hg in fish and the humans who consume the fish (Morel et al., 1998). The trend for the deposition of Cd from the atmosphere is generally parallel to that of Hg for eastern Canada and the United States (Alfaro-De la Torre and Tessier, 2002; Norton et al., 2007). Additional information on trace elements and Hg is included in Chapters 11.3 and 11.4, respectively, of this volume.

### 11.10.6.2 Nutrient Availability

The initial response to acid rain is an increase in the mobilization and export of base cations and, commonly, SO₄ and NO₃ from the watershed. In general, soil acidification and associated leaching of Mg, Ca, and K, and elevated Al mobilization are usually associated with less favorable nutritional status, whereas N deposition tends to increase the fertility of naturally
N-limited terrestrial ecosystems (Puhe and Ulrich, 2001). The elevated N deposition thus may correspond to a period of fertilization of plants in forests and in N-limited surface waters. However, prolonged increased leaching of exchangeable base cations and subsequent decline in exchangeable pools of base cations in soils (Fernandez et al., 2003; Kirchner, 1992; Likens et al., 1996) can have a long-term impact on terrestrial ecosystem health. As the molar ratio (Ca + Mg + K)/Al in soil solution declines during acidification, nutrient uptake by roots can be impaired. Limited Ca or Mg uptake, associated with elevated Al concentrations and low pH in the rooting zone, slows growth and decreases the stress tolerance of trees (Cronan and Grigal, 1995), and adversely affects tree physiology (Šantrůčková et al., 2007). Declining Ca in runoff, which may occur during acidification or recovery, has been implicated in reduced fecundity and survival of Ca-rich Daphnia species (Jezior ski et al., 2008). Similar effects might be expected in other organisms that require higher Ca in water.

Although P is not commonly the subject of acid rain geochemistry research, ecosystem alterations due to acidification inevitably alter P dynamics in watersheds. Reinhardt et al. (2004) demonstrated that the export of P in runoff from the experimentally acidified catchment at BBWM had increased nearly by a factor of 10, along with Al. SanClements et al. (2010) reported that an important source of this P and Al was in the B horizon of these forested Spodosols, a locus of secondary Al and Fe accumulation and thus, significant P adsorption capacity. They suggested that mobilization of Al by the experimental acidification also resulted in P mobilization, and that this effect was evident at both BBWM and a similar experimental watershed acidification study at the Fernow Watershed in West Virginia, USA. Evidence also existed to suggest that for the period of time of accelerated P mobilization, which could be transient, P was more available to biota, with biocycling of this P resulting in redistributions within the ecosystem.

Minimally polluted forest ecosystems export mostly organically bound N and NH₄, instead of inorganic oxidized N (NO₃) (e.g., Hedin et al., 1995; Perakis and Hedin, 2002). Increased atmospheric deposition of N can initially have a...
positive growth effect on N-limited ecosystems. Turnover of mineralized N in the forest floor is generally an order of magnitude higher than atmospheric input of inorganic N, which creates only a small addition to a large N soil pool. Nitrogen demands by biota must be satisfied first, and a certain amount of N can be immobilized in forest organic matter, before N saturation and chronic NO₃ leaching occur (Aber et al., 1989, 1998; Stoddard et al., 2001). Ecosystems vary widely in their capacity to retain N inputs. Excess N is exported mostly as NO₃, increasing the concentration of SAA in water, contributing to acidification. Nitrate leakage is greatest from high-elevation, steep sites, and from mature forests with high soil N stores and low soil C/N ratio (Fenn et al., 1998), and lowest from watersheds containing extensive wetlands. Concentrations and seasonality of NO₃ in stream water are used as indices of N saturation (Stoddard, 1994). Mosello et al. (2000) and Kopaček et al. (2001a) indicated that retention of N in watersheds decreased with time under acidification stress. In contrast, slightly elevated terrestrial N retention may be connected to reduction of acidic deposition during the recovery phase (Lorz et al., 2002; Vesely et al., 1998a, 2002a). Increased concentration of NO₃ in streams increases P demand and the risk of P limitation in stream microbial communities, as demonstrated at BBWM (Simon et al., 2010). This P limitation can be exacerbated by the mobilization of Al from soils and subsequent precipitation of Al(OH)₃ in streams, increasing the capacity for adsorption of dissolved P. Davison et al. (1995) used whole-lake treatment with P to overcome acidification by excess NO₃.

Export of NO₃ in surface waters is linked to soil microbial activity and the soil C/N ratio (Yoh, 2001). Empirical data showed that a C/N ratio of the forest floor <25 and throughfall deposition above 9–10 kg N ha⁻¹ year⁻¹ were thresholds for leaching NO₃ in Europe (Dise and Wright, 1995; Gundersen et al., 1998), with similar findings reported for North America (Aber et al., 2003). In the European data, the slope of the relationship between N input and NO₃ leached was twice for before N saturation and chronic NO₃ leaching occur (Aber et al., 1989, 1998; Stoddard et al., 2001). Ecosystems vary widely in their capacity to retain N inputs. Excess N is exported mostly as NO₃, increasing the concentration of SAA in water, contributing to acidification. Nitrate leakage is greatest from high-elevation, steep sites, and from mature forests with high soil N stores and low soil C/N ratio (Fenn et al., 1998), and lowest from watersheds containing extensive wetlands. Concentrations and seasonality of NO₃ in stream water are used as indices of N saturation (Stoddard, 1994). Mosello et al. (2000) and Kopaček et al. (2001a) indicated that retention of N in watersheds decreased with time under acidification stress. In contrast, slightly elevated terrestrial N retention may be connected to reduction of acidic deposition during the recovery phase (Lorz et al., 2002; Vesely et al., 1998a, 2002a). Increased concentration of NO₃ in streams increases P demand and the risk of P limitation in stream microbial communities, as demonstrated at BBWM (Simon et al., 2010). This P limitation can be exacerbated by the mobilization of Al from soils and subsequent precipitation of Al(OH)₃ in streams, increasing the capacity for adsorption of dissolved P. Davison et al. (1995) used whole-lake treatment with P to overcome acidification by excess NO₃.

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The productivity of temperate freshwater lakes and streams is generally limited by the availability of phosphorus, although light limitation can be of primary importance in already P-poor lakes (Karlsson et al., 2009). Phosphorus occurs in many rocks, primarily in the mineral apatite, which has a relatively high weathering rate. Consequently, older soil profiles are depleted in apatite. Monazite ((REE)PO₄) is common in many rocks but the mineral is very insoluble. Much P is concentrated in organic-rich soils and is strongly recycled or sequestered by adsorption in Al- and Fe-rich illuvial soil layers (SanClements et al., 2009). Lakes predisposed to acidification thus have low concentrations of base cations and P. Acidification of catchments can result in a slightly increased export of dissolved P from soils (Roy et al., 1999). Roy et al. (1999) and Reinhardt et al. (2004) found that two contiguous acidifying streams contained high concentrations of particulate acid-soluble Al and Fe hydroxides and acid-soluble particulate P during acidic episodes. Particulate P was 10–50 times higher than dissolved P and highest in the lower pH stream. Ionic Al species hydrolyze downstream or in lakes at higher pH, as polymeric Al species are formed with large specific surfaces and with strong affinity for PO₄³⁻. The P in acidified streams and lakes (typically with a pH in the 5.5–6.5 range) can be scavenged by these Al- or Fe-rich particles. If the Al hydroxide is deposited as sediment, the flux of P into sediment can be irreversible (Kopaček et al., 2001b), even during periods of hypolimnetic anoxia when pH typically increases, Fe hydroxide dissolves, and adsorbed P would normally be released to the water column (Amirkhahian et al., 2003; Einsele, 1936). Thus, stream acidification can lead to downstream oligotrophication as suggested by Dickson (1978).

As DOC has increased during the decline of SO₄ in runoff, the mobilization of Al to lakes should have increased because Al–DOC complexes, regardless of pH trend. Kopaček et al. (2000, 2005) have demonstrated that precipitation of Al(OH)₃ in the water column of Plešné Lake, Czech Republic, removes P from the lake P-cycle, thereby lowering biologically available P. The source of the Al is partly from inorganic mobilization because of acidification and dominantly from complexation with soil DOC, followed by Al liberation due to photooxidation of the complex in the lake water column. If Al partially controls bioavailability of P, then there is likely a linkage between P and Hg in fish. Higher dissolved P in a lake enhances the food chain, thereby diluting the Hg concentration in algae and the subsequent food chain, including fish. Conversely, if P is lowered in the water column, productivity is reduced and Hg concentration will be higher in the food chain, particularly fish. This concept of biodilution (Chen and Folt, 2005) is not fully understood but is a pressing problem.

11.10.7 Effects of a Changing Physical Climate on Acidification

Global and regional climate models predict spatially variable changes in temperature and precipitation. Consequently, temperature, the timing of runoff maxima, and seasonality can all be expected to change. These changes will alter concentrations and fluxes of solutes and particulates, altering the acid–base status of runoff. Year-to-year changes need to be distinguished...
from biologically driven seasonal cycles that control a number of components in runoff to varying degrees, including NO₃, SO₄, DOC, K, and Mg (see, e.g., Likens et al., 1994; Navrátil et al., 2010). These changes are difficult to distinguish from climate change effects occurring over decades to centuries because of the complexity of potential ecosystems responses. Increases in precipitation may not result in increasing discharge if accompanied by higher temperature (Clair and Ehrman, 1996). As major atmospheric circulation patterns change, the input of marine aerosols can also be substantially altered (Evens et al., 2001c). Empirical evidence has emerged that temperature variability can partially control important abiotic reactions involving AI (Lydersen et al., 1990; Veselý et al., 2003).

Wright et al. (2006, 2010) evaluated the relative sensitivity of several possible climate-induced effects on the recovery of soil and surface water from acidification. The results show that several of the factors are of only minor importance (increase in pCO₂ in soil air and runoff), several are important at only a few sites (sea salts at near-coastal sites), and several are important at nearly all sites (increased concentrations of organic acids in soil solution and runoff). In addition, changes in forest growth and decomposition of soil organic matter are important at forested sites and sites at risk of nitrogen saturation. Increased temperature and adequate moisture would produce at least a transient increase in the mineralization of organic matter, producing an increased release of DOC and nutrients.

11.10.7.1 NO₃

Current mean annual concentrations of NO₃ in stream water generally correlate with the magnitude of N atmospheric deposition and the N saturation status of the terrestrial ecosystem (Aber et al., 1989, 2003; Stoddard et al., 2001; Wright et al., 2001). Nitrate concentrations of many watersheds are commonly highest during the spring snowmelt period and lowest during summer base flow. This pattern implies that nitrification occurs during winter months, with NO₃ accumulating in the soil until flushed by snowmelt, as well as NO₃ stored in the snowpack. However, peak spring and winter NO₃ concentrations vary markedly from year to year. Cyclic interannual variations in these peak NO₃ concentrations have been ascribed to (1) summer drought due to oxidation of organic N in dried out soils (Harriman et al., 2001; Reynolds et al., 1992; Ulrich, 1983); (2) cold dry winters (Mitchell et al., 1996), and also warmer soils during mild winters (Kaste et al., 2008); and (3) variable mean annual temperature (Murdoch et al., 1998). Synchronous variation in NO₃ concentrations among lakes and a strong negative correlation with the winter North Atlantic Oscillation (NAO) Index and mean winter temperature occurred in the United Kingdom. Low NAO winters increased NO₃ in the UK monitored waters (Monteith et al., 2000).

Snow is an insulator against freezing of forest soils (Kaste et al., 2008). Physical disruption during soil freezing can increase fine root mortality and reduce plant N uptake, thereby allowing soil NO₃ levels to increase even with no increase in net mineralization or nitrification (Groffman et al., 2001). The annual mean soil temperature is correlated with mineralization and can shift the C/N ratio of forest floor as much as 0.5 per 1 °C (Yoh, 2001). Thus, climate could become an increasingly important factor governing soil C/N and regulating the NO₃ production due to a metabolic balance between C as a source of energy and N as the commonly most limiting nutrient. Soils with higher C/N ratios typically have lower nitrification and decomposition rates, and almost always demonstrate lower NO₃ leaching losses.

Warming by 3–5 °C increased rates of mineralization of soil organic matter and NO₃ flux in runoff in the climate change experiment (CLIMEX) in Norway (Wright, 1998). The ecosystem switched from being a net sink to a net source of inorganic N, probably due to acceleration of decomposition of soil organic matter induced by higher temperature. In contrast, artificially warmed soils in a coniferous forest in Maine, USA, had lower rates of N cycling, and forest floor N concentration was a better predictor of potential net N mineralization than was total C or the C/N ratio (Fernandez et al., 2000), the results of which were more a function of local factors such as soil moisture availability. A meta-analysis of experimental soil warming studies from around the world showed a strong positive relationship between increased warming and net N mineralization (Rustad et al., 2001), although treatment duration among the 32 research sites was only in the range of 2–9 years, and longer term responses remain unstudied. Generally, the C/N ratio alone is a poor predictor of N leaching or retention.

11.10.7.2 SO₄

In oligotrophic boreal lakes of Ontario, Canada, a drought in the 1980s decreased the water table and lake levels, exposing watershed soils and littoral sediments that contain reduced S. During the drought, the length of the ice-free season, duration of stratification, depth of the photic zone, and light extinction increased while precipitation and then nutrient inputs to the lakes decreased. Sulfur was reoxidized and mobilized to the lakes during subsequent wet periods (Dillon et al., 1997; Jeffries et al., 1995). Drought occurred in Ontario in years following strong El Niño/ENSO events (Dillon et al., 1997), another major circulation feature in addition to the NAO (Jones et al., 2001). When the ENSO Index was strongly negative, the frequency of drought in the following summer was high. If long-term changes in global or regional climate alter the frequency or magnitude of El Niño/ENSO-related droughts (Dai and Wigley, 2000) the recovery of acidified lakes will be longer and more complex.

11.10.7.3 CO₂

Carbon dioxide was the first atmospheric gas shown to be increasing because of human activities and it is often implicated in global warming. Small seasonal variation in atmospheric CO₂ concentrations reflect the net respiration/photosynthesis of the northern hemisphere and possible forcing by El Niño (Bacastow, 1976). The recent increase in atmospheric CO₂ of about 0.5% year⁻¹, documented with direct measurement since 1958 and indirectly by ice core analyses (IPCC, 2007; Schneider, 1989), is largely from the burning of fossil fuels, deforestation, and other alterations of land use. This atmospheric CO₂ increase has little direct impact on freshwater acidification but could be indirectly linked through climate change caused by greenhouse gas effects from the increased atmospheric CO₂. Wright (1998) experimentally
increased ambient air CO₂ by 100% in a miniwatershed in Risdalsheia, southern Norway. This increase, in combination with warming of soil by 3–5 °C, produced an increased concentration of NO₃ in runoff. A more insidious development as a consequence of increased atmospheric CO₂ is acidification of the oceans’ surface waters (Caldeira and Wickett, 2003; Sabine et al., 2004). The increase of atmospheric CO₂ by about 50% over the last 100 years has resulted in a probable titration of the bicarbonate–carbonate pH buffer system, with a lowering of pH by about 0.1 unit. The full consequences of this acidification are not known. An important consequence will be that carbonate-depositing organisms will have to expend more energy during calcite precipitation. Earth has experienced much higher atmospheric CO₂ (and related higher temperature) but the rate of change now is likely greater than at any time in Earth’s history. The warming associated with additional greenhouse gases will likely accelerate some biochemical processes (mineralization of organic matter to produce DOC and CO₂) and provide negative feedback to others (such as the solubility of CO₂ in freshwater).

The increase of atmospheric CO₂ could have imperceptibly decreased the pH of precipitation, but the partial pressure of CO₂ (pCO₂) in soils is far more important to the acid–base status of surface water. Variation in forest soil pCO₂ is influenced by temperature and moisture in soils as well as release of excess soil CO₂ to the atmosphere. Warmer conditions increase microbial and root respiration in the soil thereby increasing soil pCO₂ above the long-term average value and producing short-term increases in runoff ANC, and vice versa. Norton et al. (2001) found that intraseasonal variation in pCO₂ caused by variable snow pack thickness could induce variation in ANC in runoff of 10–15 μeq l⁻¹. Such variability can exceed increases in ANC caused by a 15–20 μeq l⁻¹ decline of SO₄ in runoff. Decline in soil pCO₂, despite increased temperature and possibly increased soil respiration, could result from lower soil moisture content and greater efflux of soil CO₂. Strong seasonality of soil pCO₂, while normal, likely induces variation of 10–20 μeq l⁻¹ in ALK. Variations of water pH would depend on the soil pH.

11.10.7.4 Organic Acids

DOC consists of a complicated mixture of organic acids with differing pK values (the pH at which half of the organic acid is protonated). DOC species with low pKs contain ‘strong’ acid anions, analogous to SO₄ and NO₃. Their contribution to the acidification status can overwhelm that of SO₄ and NO₃ in DOC-rich surface waters. Variable export of DOC from forests is controlled by organic production and decomposition, sorption by soil, and flushing, all connected to local climate (Kalbitz et al., 2000). For example, DOC discharged from sub-watersheds in the Rhode River watershed, Maryland, USA, varied eightfold (Correll et al., 2001). Temperature effects on DOC concentrations were weak and fluxes were not correlated with temperature in a Norway spruce forest in Germany (Michalzik and Matzner, 1999). Drought in western Ontario, Canada caused a decline in DOC export from watersheds, or more removal from lake water columns because of the longer water residence times (Schindler et al., 1996). In a whole watershed acidification, Gjessing (1992) studied the response of Lake Skjervatjern, western Norway, to additions of NH₄NO₃ and H₂SO₄, and cycles of drought. DOC concentrations decreased in the lake as a result of drought-related decreased input of DOC from the watershed, and in-lake processes that consumed DOC. It is not fully clear why DOC concentrations have generally increased over the last two decades in European and North American soft waters (Bouchard, 1997; Evans and Monteith, 2001), but this increase seems to be most likely related to increasing pH and decreasing ionic strength of soil water due to reduced anthropogenic SO₄ and Cl deposition (Monteith et al., 2007). In addition, Anesio and Granelli (2003) showed that DOC is more photoreactive in acidified waters. Thus, with recovery underway as a consequence of reduced SO₄ deposition, photoreactivity may be decreasing, resulting in an increase in DOC. Wright et al. (2010) reported that artificially increased salt loading at Gårdsjön watershed, Sweden, caused a decline in DOC export, supporting the ionic strength hypothesis. Evans et al. (2008a) examined results from 12 European and North American field N addition experiments and found variable response in DOC export related to the chemical form of N addition. They suggested that changes in acidity, such as ANC forcing, might be the more important factors governing DOC export although cause and effect remained undefined. If the quality of the DOC remains constant while the concentration increases, recovery of ANC in a regime of decreasing atmospheric pollution (S and N) will be retarded because of added organic anion acidity. Altered toxicity to fish will depend on whether the increased DOC is saturated with Al.

11.10.7.5 Evaporation/Hydrology

In many upper Midwest lakes of the United States, the widespread decrease in lake SO₄ observed farther east was prevented during a 4 year drought that caused evaporative concentration of the already acidic seepage lakes (Webster and Brezonik, 1995). Lower than normal precipitation reduced seepage lake water levels and groundwater elevations. A decrease and eventual cessation of groundwater inflow, caused by the drought, led to losses of ANC, Ca, and Mg in lakes. Groundwater-dominated (seepage) lakes of Wisconsin, USA, responded to drought, with no relationship between concentrations of solutes in the lake and precipitation (Webster et al., 2000). Landscape position, defined by the spatial position of a lake within a hydrologic flow system, accounted for differences in chemical response to drought (Webster et al., 1996). In the lakes of surface water-dominated Ontario, Canada, chemical response of conservative solutes such as Ca or Cl in low-ANC lakes was negatively related to precipitation amount. In regions with low precipitation and/or high evapotranspiration, such as Finland and central Czech Republic, increased precipitation would cause a decrease of SAA in surface water, and a decline in base cation leaching, which could be more than is caused by dilution because of cation resorption by soils.

11.10.7.6 Marine Aerosols

The sea-salt effect, which has until recently been considered only as an episodic process, may also operate over decadal periods in relation to the NAO Index. The NAO is derived
from the atmospheric pressure difference between the Azore Islands and Iceland. The NAO strongly affects winter temperature and precipitation in regions bordering the North Atlantic (Hurrell, 1995; Jones et al., 2001). High winter NAO Index values are associated with wet and warm, frontally dominated winter weather in northwestern Europe. Such periods are coincident with more marine salt input, increasing Cl (Evans et al., 2001c). Most importantly, the episodic input of the base cations Na\(^+\) and Mg\(^2+\) may cause desorption of H\(^+\) and Al\(^3+\), with potentially significant impact on biota (e.g., Hindar and Kros, 2001; Wright, 1998).

### 11.10.7.7 Biological Feedbacks

Climate variability and atmospheric deposition alter vegetation and microbial activity. Elevated concentrations of atmospheric CO\(_2\) can increase, at least for some period of time, forest growth and nutrient uptake, as does increased N deposition. Warming lengthens the growing season, increases primary production (uptake) and decomposition, thereby accelerating cycling of nutrients. Forested ecosystems can respond to climate warming by increasing inorganic N leaching caused by enhanced mineralization (Mol-Dijkstra and Kros, 2001; Wright, 1998). Changes in vegetative community structure through stand development or human disturbance can produce significant changes in dry deposition of acidic compounds through canopy interception, evapotranspiration, hydrology, and base cation sequestration in biomass. Simulations by the nutrient cycling model (NuCM) at six US sites suggested that increasing temperature caused N release from the forest floor. At N-saturated sites, N leaching increased. At the N-limited sites, increased growth (uptake) occurred (Johnson et al., 2000), limiting any increases in N loss. These examples illustrate the complexity of ecosystem response to multiple stressors, and the challenge of incorporating biological mechanisms into models of acidification and recovery.

### 11.10.8 Acidification Trajectories through Recent Time

Long-term natural acidification trajectories are reflected in freshwater responses to base cation depletion in soils that occurs as a result of pedogenesis in humid environments coupled with an increasing production of DOC. Variations in the acidification trajectory can be induced by variations in the original mineralogy of the soil, hydrology, temperature, biomass accumulation, and the concentrations of weak acids (carbonic and organic). With the onset of accelerated acidification induced from atmospheric deposition of strong acid, the export of base cations (mainly Ca) should increase, either because of their desorption from the soil complex or because of an increase in mineral weathering. Although variations in mineral weathering as a consequence of acidification were studied intensively in the 1980s (see, e.g., Schnoor, 1990; Swoboda-Colberg and Drever, 1993), experimental studies at both the laboratory and watershed scale (e.g., Dahlgren et al., 1990; Fernandez et al., 2003) indicate that increased export of base cations is largely attributable to desorption on decadal timescales or less.

Within a yearly cycle for watersheds that are nearly steady state with respect to acid–base status, Ca and other base cations in runoff commonly vary inversely with discharge (e.g., Feller and Kimmins, 1979). This relationship is caused primarily by dilution of runoff with precipitation (Laudon and Norton, 2010). Although base cation concentrations vary considerably, their ratios commonly remain relatively constant (Figure 5), indicating that short-term variability is controlled by ion exchange equilibria among Al, H, Ca, Mg, K, and Na, with Na and K playing only a minor role. Thus, samples with lower concentration (Figure 5) are from high-flow events. If acid loading is substantially increased to a system (cf. West Bear, Figure 5), the exchangeable base cation soil pool resists acidification by desorbing base cations (and adsorbing H\(^+\)) and the soils adsorb SO\(_4\). The trajectory of changes in the Ca concentration in runoff during acidification related to anthropogenic acidity should follow the path shown in Figure 6(a). A reduction in acid loading reverses these processes. This conceptual model divides the history of anthropogenic acidification and recovery into seven stages:

- **Stage 1** corresponds to a ‘steady state’ where base cation concentrations in runoff are relatively constant, averaged over periods longer than an annual cycle. The rate of export of base cations is equal to the rate of chemical weathering of minerals containing these elements. BS of soils is also relatively constant. The end of Stage 1 represents the onset of a step increase in acid loading to an elevated constant value. Stage 2 corresponds to the period of increasing export of base cations as a consequence of the increased acid loading. Concurrently, the ANC of the stream and BS of the soils decrease. As acidification progresses and soil exchangeable base cations become depleted, base cation concentrations in solution peak, and then decline. **Stage 3** is a period of decreasing stream base cation and ANC concentrations, with increasing H\(^+\) and Al in runoff, and decreasing BS in the soils. **Stage 4** is a new steady state where runoff chemistry approximates Stage 1 steady-state values, and

![Figure 5](image-url) **Figure 5** Weekly concentrations of Ca and Mg in East and West Bear brooks, watersheds, Maine, USA, for 2008–2009, and for 1995 for West Bear Brook (Norton, unpublished) showing strong ion exchange control on the Mg/Ca ratios. The green point is the mean value for 1989 for both watersheds (see Figure 7). Note (1) decrease of Ca and Mg in West Bear from 1995 to 2008–2009, (2) preferential depletion of Mg, and (3) decrease of Ca and Mg in East Bear.
Regrettably, there are not sufficiently strong evidence for such a scenario, including laboratory studies of soils (Dahlgren et al., 1990), ecosystem-level experiments (Fernandez and Norton, 2010), and empirical data (Jenkins et al., 2010). Regrettably, there are not sufficiently long time series to document all stages of this process but studies of watersheds not in steady state can be placed within this evolutionary scheme. In watersheds with low exchangeable base cation reservoirs, anthropogenic acidification can deplete base cations rather quickly. In these watersheds, Al (Neal et al., 1997; Veselý et al., 1998b) or Fe (e.g., Borg, 1986) are typically the dominant cations exported. The conceptual models of Figure 6 are captured in the paired watershed experiment at BBWM, where one watershed (West Bear) was treated with (NH$_4$)$_2$SO$_4$ to accelerate acidification. Acidification of the West Bear watershed has been accelerated from Stage 1 through Stages 2 and 3 in a decade (Fernandez and Norton, 2010), responding at first with increasingly greater leaching of Ca and Mg (Figure 7) for 7 years (equivalent to Stage 2), followed by declining leaching of Ca and Mg as soil BS declined (Stage 3). As base cations became depleted, Al replaced base cations as the principal neutralizer of incoming acid, and Fe started to mobilize as the more easily mobilized forms of soil Al became depleted (Figure 6(b)). Meanwhile, slower acidification of the untreated watershed (East Bear) resulted in a continuous decline over 22 years of observation during declining atmospheric deposition of SO$_4$. Either East Bear has entered Stage 5 (recovery) or is still in the late stages of Stage 3.

11.10.9 Longitudinal Acidification

In general, soil water pH increases with depth below the forest floor in well-drained forest soils because of decreasing soil organic matter sources of DOC, metabolism of acidic DOC, and increasingly weatherable minerals with depth. Consequently, pH in headwater streams generally increases downstream (Driscoll et al., 1988) because (1) soils and flow paths are typically shallow at higher elevation, (2) higher elevations more commonly support coniferous forests whereas deciduous vegetation is typically more common at lower elevation, (3) larger watersheds typically have more heterogeneous geology, with the possibility of higher ANC-producing bedrock/soil,
(4) lower elevation terrain is typically underlain by bedrock with higher ANC-producing chemistry, and (5) mountainous areas typically receive larger quantities of pollutants relative to lowlands due to orographic precipitation effects and interception of cloud droplets with high concentrations of pollutants (Grennfelt and Hultberg, 1986; Lovett, 1992). Thus, there is a general pattern that watersheds are more acid sensitive at upper elevations and acidify from the top down (Hauhs, 1989; Matschullat et al., 1992; Norton, 1989).

Base cations removed from the upper part of a watershed are generally lost from the system, mostly remaining in solution. Some of the base cations are temporarily stored in stream sediment or in wetlands. The concentration of base cations typically increases downstream. Mobilized ionic Al (dominantly) (Roy et al., 1999), Fe, and Mn (Borg, 1986) move downstream where they can be precipitated in higher pH regions of streams (Veselý et al., 1985) or lakes (Kopáček et al., 2001b), scavenging trace metals and P. These Al- and Fe-rich precipitates represent translocated ANC. The acid neutralizing capacity, represented by exchangeable base cations and Al- and Fe-rich precipitates, must be stripped by progressive acidification before an entire stream can become chronically acidic.

Flat topography and a cool, moist climate provide favorable conditions for organic matter accumulation. Bogs and fens along the surface water flow path may substantially alter water chemistry, commonly adding DOC, and removing NO3 and SO4. All other chemical factors being equal, humic waters (those rich in DOC) are more acidic. These waters, commonly naturally acidic, are more common at low elevation on flat terrain with relatively low precipitation, such as in Finland (Kortelainen and Mannio, 1990). Streams that are recharged primarily by springs have relatively stable chemistry (Lange et al., 1995) and low DOC.

11.10.10 Some Areas with Recently or Potentially Acidified Soft Waters

11.10.10.1 Eastern Canada

Much of eastern Canada is underlain by slow weathering rocks with few carbonate minerals. This area includes large parts of Ontario, Quebec, Newfoundland, New Brunswick, Labrador, and Nova Scotia. The regional climate ranges from relatively dry, cool, and continental in western Ontario, the site of the classic Experimental Lakes Area (ELA) (see, e.g., Schindler et al., 1990), to relatively wet cool maritime (see Jeffries, 1997, for an overview). Sudbury, Ontario, once the site of the world’s largest point source of SO2 emissions, has been the focus of chemical and biological studies, first describing the trajectory of acidification and then recovery (Gunn, 1995), after the point source emissions were dramatically reduced. This west-to-east transect also corresponds to a strong gradient of atmospheric deposition of SO2 and NOx, with the highest pollution in eastern Ontario and western Quebec. Consequently, the various lake districts have distinctly different water qualities. The Ontario and Quebec lakes are dominated by relatively low DOC drainage lakes whose modified acid–base chemistry has been dominated by SO4 input. Nova Scotian lakes and streams, on the other hand, are predisposed to impact from atmospheric deposition because of their relatively low Ca and high DOC. The time series of lake chemistries are long, high quality, and commonly of high spatial and temporal resolution so that both the processes of acidification and recovery can be studied, as well as the effects of climate and marine aerosol gradients.

11.10.10.2 Eastern United States

The Adirondack Mountain Region of New York was the first area in the United States to be identified as under stress from acidic deposition. It is close to the region of highest S and N deposition for the United States (Figure 1), receives between 1 and 1.5 m of precipitation, and is underlain by large areas of Ca-poor bedrock and thin soils developed from till. In 1985, the US Environmental Protection Agency conducted a statistically designed national survey to characterize terrane at risk from anthropogenic acidification (Brakke et al., 1988). They identified additional areas outside New York that were receiving significant acid rain and had bedrock and soils that placed them at risk of acidification. Since then, there have been few comprehensive federally sponsored surveys of lake or stream chemistry. Fewer sites have been studied more intensively (e.g., Stoddard et al., 1998). In the last half of the 1990s, SO4 in deposition declined, but recovery of ANC in acidified systems has been slow to nonexistent (Kahl et al., 2004). At some localities, base cations are decreasing faster than SAA (NO3 and SO4) in surface water (Warby et al., 2005, 2009), implying that either acidification from SAA is still continuing or other contemporary processes are occurring (Yanai et al., 1999).

South of the glaciated region in the eastern United States there are few natural lakes, but many streams draining old thin soils developed on Ca-poor bedrock exist. Webb et al. (1989) surveyed 344 trout streams draining the Blue Ridge Mountains in Virginia and found many low-ALK streams with low Ca and Mg. Sulfate concentrations, while the highest of all ions, were maintained at less than one third of values in equilibrium with soil sulfate retention. The soils, dominantly Ultisols, strongly adsorbed SO4 and had not yet equilibrated with the elevated concentrations in deposition, thus delaying acidification. The desorption of SO4 also delays recovery as atmospheric deposition of SO4 declines.

Some of the longest time series of environmental measurements of soils and soil solutions, precipitation quality, and nutrient cycling for the United States come from the Walker Branch Watershed, Tennessee and from the Coweeta Watershed, North Carolina. As for HBEF, much research there was originally designed to evaluate the impact of forest practices on soil fertility. A common characteristic of the older soils is the relatively low concentration of Ca and Mg because of long-term natural acidification. The accumulation of abundant sesquioxide secondary phases in the soils results in adsorption of excess SO4 from the atmosphere, even as base cations are being depleted by acidic deposition (Johnson et al., 1982, 1988).

11.10.10.3 British Isles

The United Kingdom Acid Waters Monitoring Network (UKAWMN) was established in 1988 to assess the effect of emission reduction on selected acid-sensitive sites in the
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United Kingdom (Evans and Monteith, 2001). Widespread declines in nonmarine SO$_4$ concentration did not occur between 1988 and the mid-1990s. Sulfate concentrations have declined substantially since the mid-1990s (Ferrier et al., 2001; Harriman et al., 2001). The most strikingly consistent observation from UKAWMN is the gradual regional increase in DOC, which has slowed recovery. The increase in organic acidity has been of a similar magnitude to the decrease in mineral acidity (Evans and Monteith, 2001). There has also been a general reduction in winter storms connected with the sea-salt effect from the early 1990s with a reduction in Cl and a slight reduction in acidity. Over the past 50 years, patterns of storminess over the United Kingdom, connected with marine salt input, have oscillated on an approximately 10 year cycle (Evans et al., 2001c). Long-term studies at several research sites have enabled detection and understanding of acidification-related processes in addition to acidification from air pollution (e.g., Plynlimon Wales; Neal, 1997).

Aherne et al. (2002) reported, from a stratified pseudo-random survey of 200 lakes in the Republic of Ireland, that variations in lake chemistry were strongly influenced by marine aerosol deposition. The acidity for lakes with pH < 6 was dominated by organic acidity, followed by SO$_4$ (primarily in the east) and NO$_3$.

11.10.10.4 Scandinavia

Acidification of freshwaters has been and remains a major environmental problem for the three Nordic countries (Finland, Norway, and Sweden) where freshwaters have low ionic strength and low concentrations of nutrients. This is mainly due to low bedrock weathering rates and thin soils (Henriksen et al., 1998; Skjelkvaåle et al., 2001b). From western Norway to eastern Finland, there is a gradient from high (~3 m) to low (~0.5 m) precipitation and from mountainous areas with thin and patchy soils to forested areas with relatively thick, commonly organic, soils. Clearwater lakes and streams with low base cation concentrations and low ANC dominate in western Norway and brown, high DOC lakes and streams with higher concentrations of solutes dominate in Finland (Mannio, 2001; Skjelkvåle et al., 2001a). For the northern half of Sweden, changes in water chemistry can be largely attributed to variation in climate (Föhlster and Wilander, 2002). Surveys of 485 lakes in Norway conducted in 1986 and again in 1995 reveal widespread chemical recovery from acidification (Henriksen et al., 1998). At first, most of the decrease in nonmarine SO$_4$ was compensated by a decrease in base cations such that ANC remained unchanged (Stage 4 of the acidification trajectory; see Section 11.10.8). But as SO$_4$ continued to decrease, the concentrations of nonmarine Ca and Mg stabilized and ANC increased (Skjelkvåle et al., 1998). The cessation of further increases of NO$_3$ in the 1990s suggested that N saturation was a long-term process in Nordic countries. Concentrations of DOC or TOC (total organic carbon) have increased significantly in numerous Scandinavian lakes during the last two decades (Monteith et al., 2007).

11.10.10.5 Continental Europe

Geology, weathering rates, and soil composition in much of continental Europe provide better acid neutralizing ability than in most of Scandinavia. Most of central Europe was not glaciated during the Pleistocene. Consequently, soils are richer in secondary Al and Fe phases, enabling them to adsorb more of the excess SO$_4$ from atmospheric deposition. Highly variable bedrock type and thicker soils cause spatial heterogeneity of susceptibility to acidification and chemical recovery of surface water. Acidification of higher elevation watersheds, with less accumulation of weathering products, was rapid and recovery quicker in sensitive areas of central Europe (Evans et al., 2001b; Veselý et al., 2002a), accelerated by large decreases in atmospheric deposition of not only SO$_4$ but also both reduced and oxidized nitrogen compounds. Streams draining watersheds on deeply weathered preglacial soils have no or only a slight decrease in SO$_4$ concentrations and no chemical recovery, even with a substantial decline of acidic deposition (Alewell, 2001; Alewell et al., 2001). Variable soils coupled with regional variation in deposition produced isolated, severely acidified regions at higher elevations of the Czech Republic (Veselý and Majer, 1996, 1998), Slovakia, and Poland (Kopáček et al., 2002b). These sites have undergone regional decline in NO$_3$ concentrations (up to 60%) since the mid-1980s (Veselý et al., 2002a). However, in northwestern Italy, NO$_3$ concentrations increased by about 25% from the 1970s to the 1990s (Mosello et al., 2000). Sites in the central and southern parts of the Netherlands have large NH$_4$/NH$_4$ deposition with high potential for nitrification and acidification (De Vries et al., 1995), although deposition has declined since about 2000.

While impacts of acidification on fish status are the main concern in Scandinavia and North America, damage to planted coniferous forests at high-elevation sites in central Europe was critical. For example, about 100 000 ha of Picea abies died in the Czech Republic in the 1970s and 1980s, and more than 50% of the forest suffered ‘irreversible’ damage (Moldan and Schnoor, 1992). Remarkably, emissions of S and inorganic N were reduced nearly 92 and 60%, respectively, between 1985 and 2008, and the forests are slowly returning to a healthy status (Santrůčková et al., 2007).

11.10.10.6 South America

Much of South America is relatively free of significant air pollution. Nitrate concentrations in remote Chilean and Argentinian streams are low. Dissolved organic nitrogen is responsible for most of the high N losses, 0.2–3.5 kg N ha$^{-1}$ year$^{-1}$, from these forests (Perakis and Hedin, 2002). In Amazonia there is strong internal recycling of N with little export from undisturbed watersheds. The rain is slightly acidic (pH 5.2) with inputs of 3.7–8.7 kg SO$_4$·ha$^{-1}$·year$^{-1}$ and about 0.8 kg NO$_3$·N ha$^{-1}$·year$^{-1}$ (Forti et al., 2001). Abundant DOC depresses the pH of some larger tributary streams of the Amazon (Williams, 1968). The MAGIC acidification model (Modeling the Acidification of Groundwater In Catchments, Cosby et al., 1985) has been used to assess the effects of conversion of a tropical Amazonian rain forest watershed to pasture on water quality (Neal et al., 1992). The modeling demonstrated the sensitivity of tropical rainforest runoff to deforestation, even without climate changes (Forsius et al., 1995).
11.10.10.7 Eastern Asia

In contrast to North America and Europe, emissions of SO$_2$, NO$_x$, NH$_3$, and metals are rising markedly in many developing countries. In East Asia (Japan, Korea, China, Mongolia, and Taiwan), emissions of SO$_2$, NO$_x$, and NH$_3$ are projected to increase by about 46, 95, and 100%, respectively, by 2030 (Klimont et al., 2001). By 2020, Asian emissions of SO$_2$, NO$_x$, and NH$_3$ may equal or exceed the combined emissions of Europe and North America (Galloway, 1995). By 2010, emissions of CO$_2$ by China exceeded those of the United States. Annual mean concentrations of SO$_2$ in air as high as 1300 ppb have occurred in industrial areas of Thailand (Wangwongwatava, 2001). Fujian and Guizhou provinces in south China received significantly acidic rain. Although total S emissions by China as an important user of coal as it rapidly industrialized. At the same time, deposition of these metals in eastern North America and Europe has been rapidly declining.

Total deposition of S compounds over Japan was more than twice the human emissions because of volcanic activity. The emission of SO$_2$ from Japan is <5% of the total emissions in East Asia. As for China, there are few regional long-term datasets to determine environmental impact from S and N emissions.

11.10.11 Experimental Acidification and Deacidification of Low-ANC Systems

Numerous experiments have been conducted to understand the chemical linkages between atmospheric deposition of acidic compounds and acidification of soils, streams, and lakes. Experiments have included additions of acid, exclusion of acids, and the application of limestone (CaCO$_3$) or other acid-neutralizing compounds to add ANC directly to surface water or soils. Many of the studies are discussed in Dise and Wright (1992), Rasmussen et al. (1993), Jenkins et al. (1995), and Van Breemen and Wright (2004). We highlight a few studies here.

11.10.11.1 Experimental Acidification of Lakes

Lake 302S in the ELA was experimentally acidified from an original pH of 6.0–6.7 to pH 4.5. The DOC drastically declined from 7.2 to 1.4–1.6 mg l$^{-1}$, comparable to clear arctic and alpine lakes (Schindler et al., 1996). The increased clarity allowed greater penetration of solar radiation, including UV. The thermal structure of the water column was altered, impacting circulation and nutrient regeneration. Results from both Lake 223 and lakes near Sudbury, Canada, suggest a recovery of lacustrine communities when acidification stress is reversed. Fish reproduction resumed at pHs similar to those at which reproduction ceased when the lake was being acidified.

Dystrophic (humic-rich) Lake Skjervatjern and its watershed, western Norway, were acidified with a combination of H$_2$SO$_4$ and NH$_4$NO$_3$ as part of the humic experiment (HUMEX) (Gjessing, 1992). The research studied the role of humic substances during acidification of surface waters, and the impacts of acidic deposition on chemical and biological properties of humic water (Kortelainen et al., 1992). The watershed and lake were physically divided with a curtain for the treatment. The DOC of Lake Skjervatjern was partly controlled by variable water retention time in the lake basin. DOC decreased with increasing retention time. DOC and water color decreased during acidification, followed by an increase likely caused by fertilization of the watershed with N. Periods with high precipitation and discharge coincided with increased concentration and quality of DOC (Gjessing et al., 1998).

These few experiments illustrate clearly that acidification of surface waters causes a decline in DOC, and fairly quickly, either through altered processes in the watershed or in the lake. The reverse of this change was to be anticipated during the recovery from decreased atmospheric loading of SO$_4$ and has been documented in many lakes in the northern hemisphere (Monteith et al., 2007). The changes in base cation dynamics are slower to respond, being buffered by soil, and thus slower to recover.

11.10.11.2 Experimental Acidification of Wetlands

Bayley et al. (1988) added H$_2$SO$_4$ to a bog in western Ontario, Canada, to evaluate the chemical and biological response of wetlands to atmospheric inputs of SO$_4$. Sulfate was substantially retained in true bogs, or reduced to H$_2$S and reemitted to the atmosphere. The fate of SO$_4$ is unclear because of very strong intraannual variation in concentration due to oscillating oxidation and reduction processes within bogs. The fate of NO$_3$ in true bogs seems quite unequivocal in that bogs always have lower concentrations than are present in precipitation. The N budget (net storage or reemission to the atmosphere) of bogs has not been well studied. Both S and N can be stored in reduced form as organic matter, released to the atmosphere as gaseous compounds, leached to surface water as organically bound S and N, or as the oxidized anion. It seems unlikely that true bogs (with pHs near 4) can be significantly acidified by any reasonable loading of acid from the atmosphere because of the organic acid buffering (Gorham et al., 1987).

11.10.11.3 Experimental Acidification of Terrestrial Ecosystems

At HBEF, New Hampshire, USA, Likens et al. (1977) pioneered the paired watershed approach to biogeochemical experiments,
which included many related to the impact of acidification. For over 35 years, they have examined long- and short-term data for precipitation chemistry, stream chemistry, cation supply from various sources, variable forestry practices, and performed smaller scale experiments with moisture, soil CO₂, salt additions, and Ca amendments to the forest floor. The long-term high-resolution data derived from HBEF have provided important insights into the variability of our chemical climate and have demonstrated the necessity of long-term data to sort out important long-term process from short-term variability (Cho et al., 2010; Driscoll et al., 1989).

BBWM, USA, is a paired watershed (~10 ha each) study with one forested watershed treated with (NH₄)₂SO₄ and the other serving as a reference (Fernandez and Norton, 2010; Norton and Fernandez, 1999). The major changes in stream chemistry for the 1989–2009 manipulation period include decreased pH and ALK, and increased export of base cations, SO₄, NO₃, Al, P, Fe, and Mn. DOC and silica remained essentially constant, suggesting that acidification from ~5.2 to 4.6 was largely controlled by increased nitrification of ammonium plus resident organic N, increased SO₄ flux, desorption of base cations, and dissolution of secondary Al, Fe, and Mn phases from the soil. Fernandez et al. (2003) showed that the excess base cation export in runoff was matched by the loss of exchangeable base cations from soil in the experimentally acidified watershed over the first decade of treatments, in agreement with MAGIC model predictions. Runoff SO₄ has declined in the treated watershed at BBWM as a consequence of increased SO₄ adsorption in the acidifying soils. This process was also observed at HBEF (Nodvin et al., 1986) as a consequence of transient increased nitrification (and soil water acidification) due to tree harvesting. The effect of lower pH on SO₄ adsorption has also been reproduced in laboratory experiments (Navratil et al., 2009).

Watersheds in the Fernow Experimental Forest, West Virginia, USA, have also been artificially acidified with (NH₄)₂SO₄ since 1989 (Adams et al., 2006; Edwards et al., 2002; Fernandez et al., 2010). They reported some parallel results on the trajectory of response to experimental acidification such as the increased export of Ca and especially Mg (Al was not measured), but they had substantial SO₄ retention in the older, unglaciated soils.

Risdalsheia, southern Norway (Wright et al., 1993) is in a region substantially impacted by acidification during the twentieth century. It has been the site for many paired watershed chemical manipulations. At Risdalsheia, a miniwatershed, including the canopy, was covered by a transparent roof to exclude ambient acid precipitation. ‘Clean’ reconstructed rain with natural concentrations of sea salts was applied underneath the roof. Loadings of SO₄, NO₃, and NH₄ were experimentally reduced by about 80%; the remaining 20% occurred as dry deposition of gases and particles. Later, the same miniwatershed was subjected to 3–5 °C warming and elevated CO₂ (to 560 ppmv). The flux of N in runoff increased by about 5–12 mmol m⁻² year⁻¹ (Wright, 1998), probably due to increased mineralization and nitrification rates in the soils because of higher temperature. The pH did not increase substantially because of high concentrations of DOC that buffered pH. Long-term simulations by the SMART2 (Simulation Model for Acidification’s Regional Trends) model (Mol-Dijkstra and Kros, 2001) predicted a long-term increase of N in runoff.

Wright also conducted a series of experiments at Sogndal, western Norway, a pollution-free site with more than one meter of rain. Using the paired watershed design, H₂SO₄ and a combination of H₂SO₄ and HNO₃ were added to the terrestrial part of several watersheds over a long period of time. The acidification trajectory involved increased export of base cations and Al, and decreased ANC and pH (Frogner, 1990). Episodic acidification due to atmospheric deposition of marine aerosols was also demonstrated experimentally at Sogndal. Diluted sea water (~600 mg Cl⁻¹) was added to a miniswatershed, simulating a salty rain event. The runoff response included depressed pH and ALK, and increased export of Al, Ca, and Mg desorbed from the soil (Wright et al., 1988).

Gårdsjøen, Sweden, has been home to the famous roof experiment (Andersson and Olson, 1985; Hultberg and Skeffington, 1998). The watershed complex included terrestrial and aquatic experiments, with acid additions, terrestrial liming, acid exclusion experiments, ¹⁵N additions, and salt additions. Located in southwestern Sweden, the terrestrial and aquatic system had been acidified by anthropogenic acidity from the atmosphere. In a somewhat analogous experiment to that at Risdalsheia, a roof was installed below the canopy of a small watershed to catch all throughfall. The precipitation plus chemicals leached from the canopy were reconstituted to contain only the normal marine salts and then distributed below the roof. This essentially was a step function reduction in acid rain, to assess how ecosystems recover. A subwatershed was part of a European network of manipulations where excess N (as NH₄ or NO₃), labeled with ¹⁵N, was added to systems (see Wright and Rasmussen, 1998; Wright and von Breeman, 1995). This tracer enabled scientists to track the ecosystem processing, sequestration, and release of N. The NITREX (NITrogen saturation EXPERiments) (Disc and Wright, 1992) project involved chemical manipulations with N and N isotopes in Norway, Sweden, Wales, Switzerland, The Netherlands, and Denmark (Moldan and Wright, 2011; Wright and Rasmussen, 1998).

### 11.10.11.4 Experimental Acidification of Streams

Chemical acidification experiments in streams have the advantage of having a chemical and biological reference (upstream of any chemical additions), easy sampling, and repeatability. Understanding the role of sediments during episodic acidification also yields information about the behavior of soils, from which much of the sediment is derived. A classic experiment for stream acidification was conducted by Hall et al. (1980) at HBEF. They demonstrated the ability of stream sediments to yield base cations and Al, thus resisting the depression of pH by addition of HCl. While much of this acid neutralizing ability was exhausted, stream sediment clearly played a role in ameliorating episodic acidification and recovery. Similar experiments have been conducted in the United Kingdom (Tipping and Hopwood, 1988), Norway (Henriksen et al., 1988b), and Maine, USA (Goss and Norton, 2008; Norton et al., 1992, 2000).

In summary, the studies indicate that stream sediments (inorganic and organic) are a pool of reversibly exchangeable
base cations, Al (probably precipitated plus exchangeable), P, and other trace metals including Be, Cd, Fe, and Mn. Stream sediment also has SO$_4$$_2$ adsorption capacity, which contributes to the delay and diminution of episodic acidification, and delays recovery. The effectiveness of the sediment exchange processes is proportional to grain size and organic matter content. Stream water has the ability to buffer excursions of pH if there is sufficient DOC and HCO$_3$ weak acid acidity, as demonstrated by Hruška et al. (1999).

11.10.12 Remediation of Acidity

11.10.12.1 Ca Additions

Treatment with limestone (CaCO$_3$), or something chemically similar that yields ALK during rapid dissolution, has been used as a general antidote for acidification of terrestrial and aquatic systems, first on an experimental basis and then as a long-term management strategy under field conditions. There is no general agreement on the usefulness of liming as a countermeasure to anthropogenic acidification. Nonetheless, all countries with significant acidification problems have studied this method of remediation. Many studies are reviewed in Porcella et al. (1989). Liming generates ANC but not in a way consistent with the natural system and generally not at the same place as natural processes. Thus, while pH may be restored to pre-acidification values in soil or surface waters, the system chemistry may not resemble preacidification conditions and biota may not recover along the trajectory they followed during acidification.

For example, Dillon et al. (1979) followed the response of several lakes in the vicinity of Sudbury, Ontario, Canada. Wright (1985) conducted a three lake study at the Hovvatn site in southern Norway. There, two lake basins were limed in 1981 by several methods, including dispersal on ice and along the shore. A contiguous lake with similar initial chemistry served as a reference lake. A major finding was the rapid loss of ALK generated by the dissolution of CaCO$_3$, due to flushing of the lake with acidic water from the watershed. Similar findings appear in most studies, although detailed response is of the lake with acidic water from the watershed. Similar findings appear in most studies, although detailed response is demonstrated by Hruska et al. (1999).

At HBEE, wollastonite (CaSiO$_3$), a relatively soluble silicate mineral, was applied to an entire watershed (W-1, Peters et al., 2004). The response was for runoff to have elevated Ca, pH, Si, and ANC, and decreased inorganic Al, as the soils increased exchangeable Ca concentrations (Cho et al., 2010). Soil pH increased and exchangeable Al declined. As with application of CaCO$_3$ to watersheds, the effects persisted and can be expected to persist for even longer than lime applications because of the slower dissolution rate of the wollastonite.

11.10.12.2 Nutrient Additions to Eliminate Excess NO$_3$

Forests have a large capacity to retain N and to increase growth even after years of large anthropogenic input of N (Prescott et al., 1995). Similarly, adding P can increase N uptake by trees and significantly reduce NO$_3$ concentrations in soil solution (Stevens et al., 1993). Adding P as an N management strategy would presumably lead to reduced export of NO$_3$ in surface water. Concurrently, it would lead to increased uptake of Ca and Mg, thereby potentially increasing acidification. Adding P to lakes (Davison et al., 1995) and streams (Hessen et al., 1997; Simon et al., 2010) has been shown to reduce NO$_3$ concentrations, increase ANC, and increase the pH of the water (eqn [20]). Modest P addition (<15 µg P L$^{-1}$, still avoiding eutrophication) instead of liming, thus may increase lake water pH and reduce NO$_3$ in a cost-effective way. However, in lakes where Al is precipitating (see Section 11.10.5.2), the addition of P can have a transitory effect because the P is irreversibly scavenged from the water column. Increased leaching of NO$_3$ from watersheds could be producing P limitation in streams and lakes.

11.10.12.3 Land Use

11.10.12.3.1 Deforestation

Understanding rates and processes of immobilization and leaching of N from soil organic matter under different levels of N deposition is crucial for assessment of future acidification.
The tight internal N cycle is broken as summer soil temperature, moisture, stream discharge, and storm-peak discharge increase, and when the vegetation is disturbed by harvesting, forest decline, fire, wind-throw, insect defoliation, and canopy damage by ice storms. Harvesting effects on stream chemistry have been studied extensively in North America, notably at Hubbard Brook (Bormann and Likens, 1979; Lawrence et al., 1987) and the Catskill Mountains (McHale et al., 2007), and in Wales (Reynolds et al., 1995). Deforestation in Wales resulted in a 5–7 year long NO₃ pulse in stream water related to increased mineralization and nitrification in the soil, and to more inorganic N available for leaching due to decreased biogeochemical uptake. The elevated NO₃ export from deforested areas is accompanied by elevated losses of base cations from soils and high leaching of ionic Al (Huber et al., 2004; McHale et al., 2007). Forest disturbances caused by harvesting, wind, or fire over the past several centuries have long-term impacts on forests’ vulnerability to N saturation and their future capacity to store C and N (Goodale and Aber, 2001). Temporarily enhanced production of NO₃ and H⁺ increases adsorption of SO₄ to soil (Gbondo-Tugbawa et al., 2002; Navratil et al., 2009), and H⁺ can exchange for Al and Ca in the soil (Henriksen and Kirkhusmo, 2000). The removal of biomass by harvesting is a removal of base cations, contributing to longer term base cation decreases in streams, thereby increasing the susceptibility of the stream to other acidifying stresses. Decreasing the canopy (by harvesting, defoliation, ice storm damage, or change in species) causes a decrease in the flux of pollutants to the forest floor because of decreased dry deposition (Hultberg and Greenfelt, 1992).

11.10.12.3.2 Afforestation

Aggrading forests contribute to surface water acidification in a number of ways: (1) Water discharge decreases because of enhanced evapotranspiration, causing evaporative concentration of pollutants, (2) hydrological pathways become modified (Waters and Jenkins, 1992), (3) coniferous afforestation commonly results in increasing DOC, (4) dry deposition of acidifying pollutants to a forest canopy increases as the canopy develops and effective leaf area index increases, and (5) inputs of pollutants in fog and rime ice (e.g., Ferrier et al., 1994) are also increased with the development of a canopy. Total deposition of S and other pollutants in throughfall in forests is typically several times higher than in bulk deposition outside the forest (Beier et al., 1993; Hansen et al., 1994; Rustad et al., 1994), with the exception of nutrients like N that can be biologically immobilized in the forest canopy. Episodic acidification caused by marine aerosols probably is enhanced in degree and frequency in forested areas, particularly in polluted areas (Jenkins et al., 1990).

The Plynlimon, Wales, studies of effects of conifer afforestation and deforestation have been carried out since shortly after World War II (Neal, 1997). There, forest plots with varied ages and their surface water discharge and chemistry have been studied for decades to help define the role of forests in acidification processes. Base cations and NH₄ were sequestered in biomass (Nilsson et al., 1982) with a concurrent release of H⁺. The increase of storage of N and base cations in biomass decreases as the forest matures and consequently the acidifying effect of an aggrading forest decreases as standing biomass and dead biomass reach steady state. The time to steady state is species specific (Emmett et al., 1993).

11.10.13 Chemical Modeling of Acidification of Soft Water Systems

11.10.13.1 Steady-State Models

The response of the chemistry of soil, soil solutions, and surface waters to acid deposition has been simulated using steady state and dynamic models since the early 1980s. Models were developed to: (1) interpret the past, (2) guide future research, (3) support policy decisions (Forsius et al., 1997; Henriksen and Posch, 2001), and (4) aid in the explanation of observed ecosystem behavior (Gbondo-Tugbawa et al., 2002). Initial steady-state models used empirical data, in either space or time, to understand and predict regional lake chemistry (e.g., using lake populations; Henriksen, 1980) and stream chemical behavior (e.g., Christophersen and Neal, 1990). Kirchner (1992) developed a watershed-based static model for assessment of acidification vulnerability, based on runoff chemistry. Empirical models remain as powerful tools even as dynamic models have grown in complexity, parallel to computer development.

‘Critical loads’ are a quantitative estimate of the exposure to one or more pollutants below which significant harmful effects on specified sensitive components of the environment do not occur, according to present knowledge (Nilsson and Greenfelt, 1998). The exceedances of critical loads for impacts on soils and surface waters have been the basis for negotiations of emission reductions in Europe. The concept and usefulness of critical loads has spread to Canada and, recently, to the United States. The steady-state model for critical loads implies that only the final results of a certain deposition level are considered. Time to reach the final state is not considered. Critical loads of acidity for surface waters assume that the input of acids to a watershed will not exceed the weathering rate, less a stated amount of ANC (0–50 μeq L⁻¹) in the long term. Early studies of critical loads focused more on S. As S in atmospheric deposition declined, N became a focus. The steady-state water chemistry (SSWC) model (Henriksen et al., 1995) considered only the extant N leaching level. The First-order Acidity Balance (FAB) model (Henriksen and Posch, 2001) for lakes assumed the N immobilization rate to be equal to the long-term annual amount of N that is used for alteration of the C/N ratio in the soil, plus N lost to denitrification and retained within the lake. This is the worst case of NO₃ leaching to surface waters. The FAB model, for example, predicts that more of the Norwegian lakes (46% in comparison to 37% by the SSWC model) could experience exceedances of the critical loads for acidifying deposition in the future (Kaste et al., 2002). Emission reductions negotiated in Gothenburg, Sweden, in 1999 were expected to reduce the area of exceedance of critical load for acidity from 93 million ha in Europe in 1990 to 15 million in 2010 (UN-ECE, 1999). Empirical and modeling studies indicate that recovery is underway (Aber et al., 2008; Evans et al., 2008a,b).

Critical loads for pollutant metals (especially Cd, Hg, and Pb) are being considered in Europe (Skjellvåle and Ulstein, 2002), even as the deposition of these three metals are sharply declining.
11.10.13.2 Dynamic Models

The static models for critical loads for S and N neglect the time component of acidification. Static models exclude long-term processes that can be nonstationary, including acid neutralization by soil adsorption of SO\textsubscript{4} and altered biochemistry of N compounds, desorption of cations, and increasing DOC, all in a constant physical climate. These processes can delay acidification and recovery. The numerical models ILWAS (Integrated Lake Water Acidification Study) (Gherini et al., 1985), MAGIC (Cosby et al., 1985, 2001), SMART (De Vries et al., 1989), SAFE (Soil Acidification in Forest Ecosystems) (Warfvinge et al., 1993), PnET-BGC/CHESS (Kram et al., 1999), AHM (Alpine Hydrochemical Model) (Meixner et al., 2000), PROFILE (Sverdrup and Warfvinge, 1993), and NuCM (Johnson et al., 2000) are based on mathematical formulations of hydrological and biogeochemical processes in soil and waters. The models have been used for both forecasts and hindcasts of water quality in watersheds using data on topography, meteorology, soil chemistry, weathering rates, and acidic deposition. The reliability of model prediction increases with the length of observed data used for calibration. These dynamic models, although varying in detail, are based on similar principles: charge balance of ions in the soil solution and mass balances of the elements considered. Thus they describe the changes of the element pools over time.

The MAGIC and SMART models have been developed and improved for regional scale application. These models have a high degree of process aggregation to minimize data requirements for application at large scales or at multiple sites. The opposite is true for models having relatively complex process formulations, which are developed for application on a site scale, for example, ILWAS. ILWAS is perhaps the most mechanistic and synthetic model, providing detailed description of watershed acidification.

MAGIC is likely the most widely applied model for soil and surface water acidification and recovery studies. It is a process-oriented model, lumping key soil processes at the watershed scale over monthly or yearly time steps (Cosby et al., 1985). MAGIC has a soil–soil solution equilibrium section in which the chemical composition of soil solution is governed by SO\textsubscript{4} adsorption, CO\textsubscript{2} equilibria, cation exchange, and leaching of Al. The mass balance section assumes the flux of major ions is governed by atmospheric inputs, chemical weathering inputs, net uptake in biomass, and loss to runoff. MAGIC version 7 incorporated the major controls on SO\textsubscript{4} fluxes through time (Cosby et al., 2001). Nitrogen leaching to surface waters is modeled as a function of total inorganic N deposition, plant uptake of N, soil uptake or immobilization of N, and nitrification of reduced N. The MAGIC 7 model assumes that the net retention or release of incoming inorganic N in the soil is determined by the C/N ratio of soil organic matter.

Modeling by MAGIC is fairly successful in predicting S and cation dynamics (Figure 8) in freshwater, although stable S isotope research indicates that biological S turnover (not modeled) is an important process (Alewell, 2001; Gbondo-Tugbawa et al., 2002; Novák et al., 2000). Similarly, N cycle modeling is still evolving and further studies are needed to verify N immobilization processes used under varying N and S deposition scenarios. The size, kinetics, and uptake capacity of soil are critical factors determining response to increased N loading, and are influenced by land-use history (Goodale and Aber, 2001; Magill et al., 1997).

The SMART model (De Vries et al., 1989) estimates long-term chemical changes in soil and soil water in response to changes in atmospheric deposition. The model structure is based on the mobile anion concept, incorporating the charge balance principle. SMART2 adds forest growth and biocycling processes, which enable modeling soil N availability and forest growth (Mol-Dijkstra and Kros, 2001). In SMART2, total nutrient uptake is described as a demand function, which consists of maintenance uptake in leaves and net growth uptake in stems. Immobilization of N is dependent on the soil C/N ratio.

The assumption employed in models is that equilibrium chemistry is applicable in all relevant situations. This implies that the reaction of soil pH and other parameters to a change in input is virtually instantaneous and processes such as diffusion are neglected. Long-term, large-scale acidification models are difficult to calibrate and validate because of the paucity of sufficient long-term (>50 years) observations.

11.10.14 Chemical Recovery from Anthropogenic Acidification

The many spatial and temporal lake and stream surveys conducted in many countries, plus experiments, have demonstrated the linkages between emissions of acidic compounds to the atmosphere and terrestrial and aquatic acidification. Mandated and implemented reductions in air pollution in North America and Europe have occurred since the 1970s. The long-term experiment of ecosystem acidification from air pollution is seeing a reduction of the dose in North America and Europe, but not eastern Asia.

Long-term acidification related to soil depletion of soluble ALK-producing minerals is irreversible without soil scarification or substantial soil amendments that, as for liming lakes, must be an ongoing process. Shorter term acidification due to atmospheric deposition is largely reversible if the flux of mobile acidic anions (primarily SO\textsubscript{4} and NO\textsubscript{3}) can be reduced to the point where chemical weathering and atmospheric inputs can provide sufficient base cations to allow soils to recharge their BS (Stages 5 and 6; Figure 6(a)). Recovery from acidification caused by acidic deposition has been demonstrated in whole ecosystem experiments (e.g., in Sweden by Hultberg and Skeffington, 1998, and in Norway by Wright et al., 1993) and probably occurred in some acid-sensitive central European lakes impacted by local smelting in preindustrial times. More generally, partial recovery of ANC has occurred in many areas impacted by acid rain (Evans and Monteith, 2001; Evans et al., 2001b; Wright et al., 2005). The general pattern of recovery involves a reduction of SO\textsubscript{4} (and in some localities, NO\textsubscript{3}) in surface water that exceeds reductions in base cations associated with recovery of soil BS and reduced atmospheric inputs of base cations associated with emission control of particulates (e.g., Hedin et al., 1994). ANC increases because of a decline of SO\textsubscript{4} relative to base cations in runoff. Repeated surveys in the United Kingdom, Scandinavia, the Czech Republic and elsewhere indicate recovery since 1990 in many, but not all, individual lakes and streams (Jenkins et al., 2001; Figure 9). In the
northeastern United States, recovery of ANC has accompanied reduction of atmospheric SO$_4$ while atmospheric NO$_3$ has remained relatively constant (Kahl et al., 2004; Stoddard et al., 1998, 1999, 2001). Considerable recovery in sensitive areas of central Europe includes not only reduction in SO$_4$, but also Al, NO$_3$, and Cl concentrations (Veselý et al., 2002a). The chemical path of lake recovery can follow a hysteresis loop (Kopáček et al., 2002b), also suggested by the artificial acidification and recovery of stream sediments (Figure 10(a) and 10(b)). A simple linear recovery of pH, ANC, and elevated Al from reduced SO$_4$ and NO$_3$ atmospheric deposition is unlikely, due to concurrent variations in climate, including variations in temperature, precipitation, marine aerosol input (Section 11.10.7), and DOC production. For example, an increase in temperature (~1.3 °C) over 17 years accelerated the decrease of inorganic Al during recovery by about 13% in strongly acidified lakes in the Czech Republic; temperature increase was the second most important cause of Al reduction after the SAA decrease (Veselý et al., 2003; Figure 11).

The increased export of P from acidifying watersheds appears to covary with decreasing pH and increasing export of Al. Initially, as soils acidify, retention of P (as PO$_4^{3-}$) would increase as the adsorption capacity of the soil increases (Navrátil et al., 2009). However, with continued decline in

Figure 8 Measured (open circles) and modeled (lines) trends in water chemistry of Čermé Lake, Bohemian Forest, Czech Republic. The model (MAGIC 7; Cosby et al., 2001) was calibrated on long-term data prior to year 2001 (red circles). The best agreement was obtained with a 300% higher SO$_4$ adsorption capacity than determined experimentally, and slightly decreasing N retention during the acidic deposition peak (Majer et al., 2003). The forecast is based on the projected decrease in S and N emission/deposition rate in central Europe according to the Gothenburg Protocol (UN-ECE, 1999). Blue circles represent data measured in 2001–2010, and which are in reasonable agreement with those predicted by the model.
pH, leaching of P from soils can result from desorption of Al-binding sites within the soil, or even dissolution of secondary Al(OH)$_3$. In either case, the loss is largely irreversible because of earlier depletion of the primary source of P, apatite (Ca$_5$(PO$_4$)$_3$), from mineral soil.

The importance of these secondary effects on acid–base status, metal concentration, and toxicity is still being studied. As part of the RECOVER2010 project (Ferrier et al., 2003a), the current state of acidification was simulated by MAGIC7 and projected for many European and eastern Canadian watersheds (see special issue of Hydrology and Earth System Sciences; Ferrier et al., 2003b). Sufficient time has not elapsed since declining acid inputs to assess the accuracy of the model predictions (Majer et al., 2003), yet the general decline of SO$_4$, and
generally increasing pH and ANC are clear (Figure 8). The major uncertainties with the model predictions are linked with the poorly understood biochemistry of N. This collection of studies was followed by a special issue of Hydrology and Earth System Sciences (Dillon and Wright, 2008) where both individual ecosystems and collections of lakes were modeled empirically and with MAGIC7 to predict recovery from acidification in a changing physical climate.

In general, systems that had been acidified most, recovered ANC more quickly. However, many aquatic systems in North America and Europe show little or no recovery, or even continue to acidify as base cations decline faster than the reduction in SO$_4$ plus NO$_3$ (Warby et al., 2005, 2009; Figure 9). The causes of continued acidification during reduced air pollution are likely a complex interaction of many secondary processes including changes in climate-driven hydrology and temperature (Forsius et al., 2010), biomass uptake, net respiration in soils, N processing, regeneration of soil BS, and long-term fluxes of marine aerosols. These secondary effects can mask the recovery of systems from reduced S input for some time. With increasing N saturation in many systems, episodic acidification could become more frequent for systems already damaged by a history of base cation depletion (Kopaček et al., 2009; Figure 12).

**Figure 10** (a) Experimental episodic acidification and recovery of the low ANC East Bear Brook, Maine, USA, showing solute dynamics (reprinted with permission from Goss and Norton, 2008). Acid (HCl) was added to the brook from time = 0 to 1505 min; samples were taken at 16 m below the acid addition at the indicated times. Note reversibility during acidification and recovery as SO$_4$ first adsorbs and then desorbs, while Ca and Mg desorb and then adsorb. (b) Input and output fluxes of S in the watershed of Černé Lake (Bohemian Forest, Czech Republic). The blue points are observed lake water SO$_4$ concentrations, and red points and lines are simulated by MAGIC (Majer et al., 2003). Terrestrial fluxes were calculated from concentration data using average annual runoff (1365 mm), and annual in-lake SO$_4$ removal of 22% (based on a mass budget study in 2000; unpublished data). The relationship exhibits a significant hysteresis in terrestrial SO$_4$ leaching compared to the input–output equilibrium (1:1 line), with significant SO$_4$ retention in the watershed from 1850 to 1990, and leaching substantially higher than atmospheric input since 1990. A new steady state will not probably establish by 2050.

**Figure 11** (a) The linear relationship between Al$^{3+}$ and the sum of strong acid anions (SAA) for Černé Lake, Czech Republic, 1984–2001. (b) The relationship between the residuals of the Al$^{3+}$–SAA relationship (a) and the mean temperature for the 12 months preceding the sample ($T_{12}$) from Černé Lake, Czech Republic, 1984–2001. Modified from Veselý J, Majer V, Kopaček J, and Norton SA (2003) Climate warming accelerates decreased aluminum concentrations in lakes recovering from acidification. *Limnology and Oceanography* 48: 2346–2354.

**Acknowledgments**

We are very appreciative of many thoughtful interactions with colleagues, too numerous to identify, in Europe, North America, and Asia concerning acid rain and its impacts. They have been generous with ideas and presented us opportunities to understand the breadth and depth of research related to anthropogenic acidification. Anthropogenic acidification was perhaps the most important and heavily researched environmental problem in large areas of the northern hemisphere from 1975 to 2005. The attention paid to the terrestrial and aquatic resources at risk has provided the world with an understanding of how they function that is critical to preparing us for assessing the effect of climate change on these same resources. It will also inform emerging nations, such as China and India, of the potential for environmental damage.

The body of research on ecosystem acidification has been built substantially by hundreds of scientists in several dozen countries. Several billion dollars (US equivalent) have been spent achieving significant understanding about where our systems were prior to acid rain, their present status, and their probable future with various scenarios of atmospheric pollution and abatement, and climate change. More than 100 books...


References


and thousands of articles have been published on the topic over the last 35 years. The literature we cite identifies many individuals and organizations responsible for this progress. Not everybody could be recognized, of course. One amazing characteristic of the research effort has been the international cooperation that evolved as a consequence of the people involved and the realization that atmospheric pollution knows no political borders. Its consequences could be understood and remediation implemented only with international political cooperation, driven by excellent science. That cooperation is one of the important secondary results of the effort. We thank the people who, early on, had the vision to identify the ability of human activity to degrade our chemical climate through atmospheric pollution and who stimulated so many people to look, experiment, and understand. These people include, but are not limited to, Svante Odén in Sweden, David Schindler and Peter Dillon in Canada, Ellis Cowling and Gene Likens in the United States, Arne Henriksen and Richard Wright in Norway, and Bernard Ulrich in former West Germany. They were pioneers and still are.

The first version of this chapter was cowritten with the late Josef Veselý of the Czech Geological Survey. His interests and skills ranged from the atomic level to catchments; his timescale of interest ranged from minutes to millennia. His mastery of biogeochemistry was an inspiration to many scientists. We dedicate this revision to him.


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