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Long-Term Changes in Watershed Retention of Nitrogen

Its Causes and Aquatic Consequences

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Nitrogen saturation occurs when the supply of nitrogenous compounds from the atmosphere exceeds the demand for these compounds on the part of watershed plants and soil microbes. Several factors predispose forested watersheds to N saturation, including chronically high rates of N deposition, advanced stand age, and large pools of soil N. Many watersheds in the eastern United States exhibit symptoms of N saturation. A sequence of recognizable stages produces characteristic long-term and seasonal patterns of lake-water and stream-water NO_3^- concentrations that reflect the changes in rates and relative importance of N transformations as these watersheds become more N sufficient. The early stages of N saturation are marked by increases in the severity and frequency of NO_3^- episodes. The later stages of N saturation are marked by elevated baseflow concentrations of NO_3^- from groundwater. The most advanced symptoms of N saturation usually occur in regions with the most elevated rates of N deposition. Long-term increases in surface-water NO_3^- have important implications for surface-water acidification, but probably will not lead to freshwater eutrophication.

HISTORICALLY, NITROGEN DEPOSITION has not been considered a serious threat to the integrity of aquatic systems. Most terrestrial systems have been assumed to retain N strongly. In such cases there is a small probability that deposited N would make its way to the surface waters that drain these terrestrial systems. Nitrogen within aquatic ecosystems can arise from a

variety of sources, including point-source and non-point-source pollution, biological fixation of gaseous N, and deposition of nitrogen oxides and ammonium. When N was known to be affecting aquatic systems, some source other than deposition was assumed to be responsible. The amounts of N supplied to aquatic systems by these other sources often outweigh by a large margin the amount of N potentially supplied by atmospheric deposition. During the past decade, however, our understanding of the transformations that N undergoes within watersheds has increased greatly. In areas of the United States where nonatmospheric sources of N are small, we can begin to infer cases in which N deposition is having an impact on aquatic systems.

This chapter will establish how watersheds and surface waters are likely to change as the impacts of N deposition become more severe. Aber et al. (1) described the changes that the terrestrial components of undisturbed watersheds undergo as the effects of N deposition increase. I will present the aquatic equivalents of the stages described by Aber et al. (1) and outline the key characteristics of these stages as they influence seasonal and long-term aquatic N dynamics. The second purpose of this chapter is to present accumulated evidence, primarily from the eastern United States, that otherwise-undisturbed watersheds show impacts from elevated N deposition and that the severity of these impacts corresponds to the historical levels of N deposition that the various sites have experienced. The focus on watersheds that are undisturbed, other than by elevated rates of deposition, is important. Other disturbances (especially tree harvesting) can have significant and long-lived effects on N cycling. Elimination of other potential sources of disruption to the N cycle allows us to narrow the field of stresses that might be contributing to the effects we observe.

Estimation of the effects of N deposition on aquatic systems is made difficult by the large variety of forms of N found in air, deposition, watersheds, and surface waters, as well as by the myriad pathways through which N can be cycled in terrestrial and aquatic ecosystems. These complexities separate N deposition from its effects and reduce our ability to attribute known aquatic effects to known rates of N deposition. The organization of this chapter reflects this complexity. Because an understanding of the ways that N is cycled through watersheds is critical to our understanding of N effects, I begin with a brief description of the N cycle and of the transformations of N that may occur in watersheds. I then discuss the two most likely effects of N deposition (acidification and eutrophication).

Nitrogen Inputs

Watersheds are generally several orders of magnitude larger than the surface waters that drain them. Thus most of the atmospheric deposition that may potentially enter aquatic systems falls first on some portion of the watershed. Nitrogen may be deposited to the watershed or directly to water surfaces

in a variety of forms, including NO_3^- , NH_4^+ , and organic N in wet and dry deposition. In addition, plants may absorb gaseous N (as NO, NO_2 , or nitric acid vapor) (2, 3). N thus absorbed may subsequently enter the watershed N budget as litterfall through the death of plant biomass (4, 5).

Concentrations of NO_3^- and NH_4^+ in precipitation vary widely throughout North America: they depend largely on the proximity of sampling sites to sources of emissions. Galloway et al. (6) report mean concentrations of 2.4 $\mu\text{equiv/L}$ for NO_3^- and 2.8 $\mu\text{equiv/L}$ for NH_4^+ for a site in central Alaska sampled in 1980–1981. In the Sierra Nevada Mountains of California, mean concentrations of NO_3^- and NH_4^+ for the period 1985–1987 were 5.0 and 5.4 $\mu\text{equiv/L}$, respectively (7). In a comparison of N deposition at lake and watershed monitoring sites in northern United States and southern Canada, Linsey et al. (8) found NO_3^- concentrations ranging from 15 to 40 $\mu\text{equiv/L}$ and NH_4^+ concentrations from 10 to 50 $\mu\text{equiv/L}$ for 1970–1982 in an area that was considered remote but may be influenced by prairie dust and long-range acidic deposition; neither ion dominated over the other. In some areas closer to anthropogenic N sources (e.g., in the northeastern United States and southeastern Canada) volume-weighted mean NO_3^- concentrations range from 30 $\mu\text{equiv/L}$ (e.g., in the Adirondack and Catskill mountains of New York) to 50 $\mu\text{equiv/L}$ (e.g., in the eastern Great Lakes region). Mean NH_4^+ concentrations range from 10 to 20 $\mu\text{equiv/L}$ in the same areas (9). Ammonium concentrations are highest (~40 $\mu\text{equiv/L}$) in the agricultural areas of midwestern United States.

Some uncertainty exists in all estimates of NH_4^+ deposition derived from measurements made in the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) because of the method of sample collection used by cooperators in this program. Samples are collected weekly from buckets that are covered at all times except during active precipitation. Precipitation that falls early in the week may sit for several days before being collected and filtered for analysis. A high probability exists that some NH_4^+ collected in NADP collectors will be biologically assimilated (transformed into organic forms of N) before samples are filtered. It is not currently known what the magnitude of this problem may be.

Deposition of N depends on its concentration in precipitation, the volume of water falling as precipitation, and the amount of N in dry deposition (2). The last of these values (dry deposition) is difficult to measure and is often estimated as a fraction (e.g., 30–40%) of wet deposition (10). Sisterson et al. (11) discussed direct measurements of dry deposition at regionally representative sites. They concluded that deposition of N species ranges from 40–50% of wet deposition in the northeast to ~80% of wet deposition in the southeastern United States. Given the range of concentrations previously mentioned and the volumes of precipitation falling in different regions of North America, estimates of N deposition rates range from less than 12 equiv/ha per year in Alaska to more than 800 equiv/ha per year in northeastern United States (Table 1).

Table I. Rates of Nitrogen Deposition in Several Areas of North America

Area	NO_3^-	NH_4^+	Total	Source
Alaska ^a (Poker Flat)	6.9	4.8	11.7	6
Sierra Nevada, CA ^b (Emerald Lake)	79	85	164	7
Ontario, Canada ^c (Experimental Lakes Area)	125	140	265	8
British Columbia, Canada ^c	260	130	390	14
Upper Midwest ^d	300	210	510	155
Southeastern U.S. ^e (Walker Branch, TN)	540	180	720	2
New Hampshire ^c	464	200	664	154
Catskills ^g	580	292	874	79
Adirondacks ^d	590	190	780	155

NOTE: All deposition values are in microequivalents per liter.

^aDry deposition was estimated as 35% of total deposition.

^bDry deposition was sampled as part of snowpack; no correction was made for dry deposition.

^cBulk precipitation measurements; no correction was made for dry deposition.

^dValues were corrected for dry deposition based on ratios of Hicks (201).

^eIncludes estimates for dry deposition and gaseous uptake of N.

Generally, NO_3^- dominates over NH_4^+ at sites close to emission sources (8, 12). Dissolved organic nitrogen (DON) concentrations are highly variable in precipitation but often amount to 25–50% of inorganic N deposition (8, 12–14). In some areas, DON can occur in greater concentrations than the inorganic species (15).

In addition to wet and dry deposition, many high-elevation sites may receive substantial inputs of N from clouds or fog (15–17). Few quantitative estimates of cloud deposition are available, but results from one site on Whiteface Mountain in the Adirondacks indicate that clouds and fog can contribute up to 40% of total deposition (18). Rates of wet and dry deposition at Whiteface Mountain were comparable to the Adirondack values given in Table I (~740 equiv/ha), but total deposition rates (including cloud and fog deposition) averaged 1170 equiv/ha.

The Nitrogen Cycle

Atmospheric N can enter aquatic systems either as direct deposition to water surfaces or as N deposition to the terrestrial portions of a watershed. Nitrogen deposited to the watershed is routed and transformed by watershed processes. It may eventually reach aquatic systems in forms only indirectly related to the original deposition. The transformations that N undergoes within the watershed (e.g., in soils, by microbial action, and in plants) play a major role in determining what forms and amounts of N eventually reach surface waters. Much of the challenge of determining when N deposition is

affecting aquatic systems depends on our ability to identify which N transformations are occurring and which are not. A large part of the following discussion is therefore focused on terrestrial processes that alter the forms and rates of N supply. Most of these processes also occur within lakes and streams, and their strengths can determine whether the effects of N deposition will be felt immediately (e.g., through the eutrophication of headwater lakes) or downstream (e.g., in estuaries and coastal waters). In a very real sense N cycling within the terrestrial ecosystems controls whether N deposition will reach aquatic systems (and in what concentrations), whereas N cycling within lakes and streams controls whether the N will have any measurable effect. Nitrogen assimilation, mineralization, nitrification, denitrification, and nitrogen fixation are important processes that affect the fate of N from atmospheric deposition.

Nitrogen Assimilation. Nitrogen assimilation is the uptake and metabolic use of N by plants and soil microbes (Figure 1). Assimilation by the terrestrial ecosystem controls the form of N eventually released into surface waters, as well as affecting the acid–base status of soil and surface waters.

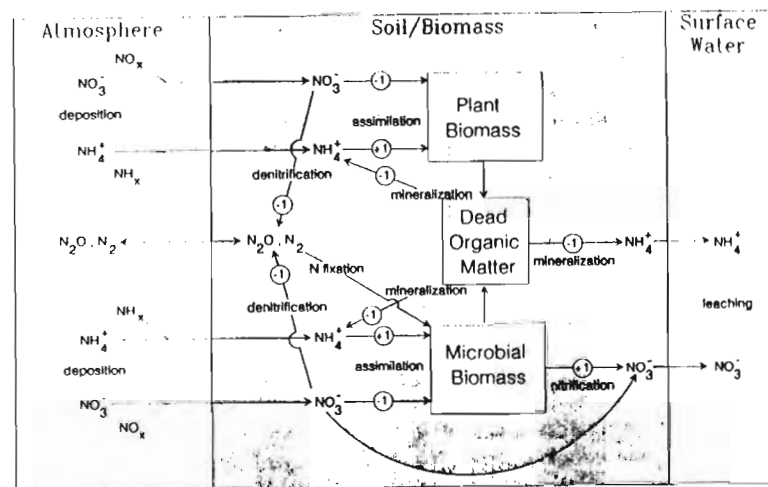
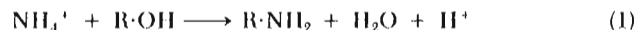


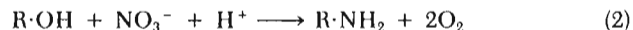
Figure 1. A simplified watershed nitrogen cycle, with major pathways (arrows) and their effects on the watershed hydrogen budget (numbers in circles) shown. Circled numbers represent the number of hydrogen ions transferred to the soil solution or surface water (+1) or from the soil solution or surface water (-1) for every molecule of NO_3^- or NH_4^+ that follows a given pathway. For example, nitrification follows the pathway for NH_4^+ assimilation into microbial biomass (+1) and is leached out as NO_3^- (+1), for a total hydrogen ion production of +2 for every molecule of NO_3^- produced.

Terrestrial assimilation is a major form of N removal in watersheds and may be sufficient to prevent all atmospherically derived N from reaching surface waters (19).

Nitrogen is the most commonly limiting nutrient in North American forest ecosystems (20, 21). The form of N used by terrestrial ecosystems strongly affects the acidifying potential of N deposition (Figure 1). Ammonium uptake is an acidifying process (i.e., uptake of NH_4^+ releases 1 mole of H per mole of N assimilated).



The biological uptake of NO_3^- , on the other hand, is an alkalinizing process (i.e., uptake of NO_3^- consumes 1 mole of H per mole of N assimilated).



Most forested watersheds undergo a dormant period, or at least a period of much reduced growth, during the winter months. Because assimilation of N is also reduced during this season, watersheds have a much lower ability to retain N during the winter and early spring. This seasonality is responsible for the commonly observed pattern of higher surface-water NO_3^- concentrations in winter and spring than in summer and fall (discussed under Stage 0 N loss). If spring snowmelt occurs before substantial forest growth begins in the spring, snowmelt NO_3^- concentrations can be substantial, even in areas of moderate N deposition. Concentrations of NH_4^+ in surface waters, on the other hand, are rarely elevated at any season because soil cation exchange; low mobility; and competition among vegetation, mycorrhizal roots, and nitrifiers all contribute to watershed NH_4^+ retention.

Muller and Bormann (22) proposed that spring ephemeral plants in the understories of forested watersheds may act as "vernal dams" controlling the loss of N from watersheds during the spring. Spring ephemeral plants may exploit the light, water, and nutrients available before forest growth and canopy closure make conditions less optimal in later spring and summer. Zak et al. (23) used radioactive N tracers to corroborate that spring ephemeral communities are associated with N retention during spring. However, they found that most of the retention was attributable to assimilation by soil microbes, not plants. There has been a tendency to think of N assimilation as primarily a plant-mediated process, but assimilation by microbes may be a very important mechanism minimizing N losses from watersheds throughout the growing season. Most forest soils are characterized by a very large, relatively inert, pool of organic N (24), which suggests that microbial uptake and immobilization of N are the dominant processes in most watersheds. Before watershed N demand (from both forest and soils) can be met or

exceeded, uptake requirements of both vegetation and soil microbial communities must be met. If one accepts the common wisdom that forest vegetation is a superior long-term competitor for N (24, 25), then the evolution of a N-sufficient watershed can be seen to consist of two stages: fulfillment of vegetation N demand, followed by fulfillment of soil microbial demand.

Assimilation by aquatic plants, a key process in the potential eutrophication of surface waters by N, may also play a role in their acid-base status. Uptake of NO_3^- in lakes is an alkalinizing process (Figure 1) that may be stoichiometrically important in some lakes (26). Aquatic plants generally favor the uptake of NH_4^+ over the uptake of NO_3^- ; NH_4^+ uptake is energetically favorable because NO_3^- must first be reduced before it is physiologically available to algae (27). McCarthy (28) summarized several studies that consistently show that potential (saturated) NH_4^+ uptake rates are greatly enhanced in N-deficient cells. This relationship is now used, along with various other indices, as a basis for identifying the degree of N limitation in phytoplankton (29, 30).

A crucial difference between aquatic and terrestrial ecosystems is that N additions do not commonly stimulate growth in aquatic systems, as seems to be the case in many terrestrial systems. N limitation may be the exception in aquatic systems rather than the rule. The question of whether N limitation is a common occurrence in surface waters will play a large role in determining whether N deposition affects the trophic state of aquatic ecosystems.

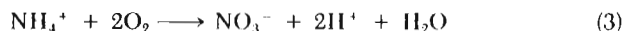
The effects of N supply on uptake and growth rates in phytoplankton and periphyton are the subject of volumes of literature, a summary of which is beyond the scope of this chapter. However, certain aspects of the limitation of algal growth by the supply of N and other nutrients will be discussed later in the section on eutrophication by N deposition. Other details on algal nutrition can be found in reviews by Goldman and Glibert (31), Button (32), Killham and Hecky (33), and Hecky and Killham (34).

Mineralization. Mineralization is the bacterial decomposition of organic matter; it releases NH_4^+ that can subsequently be nitrified to NO_3^- . Mineralization is an important process in watersheds, as it recycles N that would otherwise be tied up in soil organic matter following the death of plants, or as leaf litter (Figure 1). In a comparative study of mineralization in soils, Nadelhoffer et al. (35) found N mineralization rates ranging from 6000 to 9600 equiv/ha per year under deciduous tree species and from 2800 to 5800 equiv/ha per year under coniferous species. These rates should be compared to N deposition rates of 600–900 equiv/ha per year for high-deposition areas of the northeast (Table 1). Nadelhoffer et al. (35) also reported estimated rates of N uptake that were 5–20% higher than rates of mineralization. These rates suggest that internal cycling sources of N far outweigh external sources such as deposition under most conditions.

The effect of mineralization on the acid-base status of draining waters depends on the form of N produced. The conversion of organic N (e.g., from leaf litter) to NH_4^+ consumes 1 mole of H per mole of N produced (Figure 1); it can be thought of as the reverse of the reaction in eq 1. Organic N that is mineralized and subsequently oxidized (nitrified) to NO_3^- (eq 3) produces a net of 1 mole of H per mole of NO_3^- produced. Because the production of organic N (i.e., assimilation) can either produce or consume hydrogen (depending on whether NO_3^- or NH_4^+ is assimilated), the net (ecosystem) effect of mineralization depends on both the species entering the watershed and the species leaving the watershed (Figure 1).

Mineralization often has the initial effect (e.g., immediately after leaf fall) of immobilizing N (36). In ecosystems where plant growth is limited by the availability of N, mineralization is also limited by N in the sense that addition of N to the leaf litter speeds decay and increases the rate at which N is immobilized by decomposers (37, 38). This initial immobilization period is marked by a net increase in the N content of leaf litter. Nitrogen limitation of decomposition follows in part from the low N content typical of litter, which arises from the translocation of N out of leaves during senescence. The immobilization phase of mineralization is followed by a period of slow release of inorganic N from the soil microbial pool (36).

Nitrification. Nitrification, the oxidation of NH_4^+ to NO_3^- , is mediated by bacteria and fungi in both the terrestrial and aquatic portions of watersheds. It is an important process in controlling the form of N released to surface waters by watersheds, as well as in controlling the acid-base status of surface waters (Figure 1). Nitrification is a strongly acidifying process, producing 2 moles of H for each mole of N (NH_4^+) nitrified.



Because nitrification in forest soils transforms NH_4^+ into NO_3^- , the acidifying potential of deposition (attributable to N) is often defined as the sum of NH_4^+ and NO_3^- on the assumption that all N will leave the watershed as NO_3^- (39). Unless NO_3^- leaving the watershed is accompanied by base cations (e.g., Ca^{2+}), it will acidify lakes and streams by lowering their acid-neutralizing capacity (ANC).

Nitrification is limited in most soils by the supply rate of NH_4^+ (40, 41). Competition exists between nitrifiers and vegetation, which may both be limited by the availability of NH_4^+ . This microbial demand for NH_4^+ , coupled with the high cation-exchange capacity of most temperate forest soils, leads to surface-water NH_4^+ concentrations that are usually undetectable. Nitrification rates may also be limited by inadequate microbial populations, lack of water, allelopathic effects (toxic effects produced by inhibitors manufactured by vegetation), or by low soil pH.

Among these potential limiting factors, soil pH plays an obviously vital role in any discussion of the acidification of surface waters by N deposition. Nitrification has traditionally been thought of as an acid-sensitive process (1, 42), but high rates of nitrification have been reported recently from very acid soils (i.e., $\text{pH} < 4.0$) in the northeastern United States (41, 43, 44) and in Europe (45, 46). In the southeastern United States, Montagnini et al. (47) were unable to find any pH effect on nitrification or to stimulate nitrification by buffering acid soils. In a survey of sites across the northeastern United States, McNulty et al. (48) found no correlation between nitrification rates and soil pH, but a strong association ($r^2 = 0.77$) with rates of N deposition. The weight of evidence suggests that nitrification will occur at low soil pH values as long as the supply of NH_4^+ is sufficient and that any inhibition of nitrification by low soil pH can be overcome by excess N availability.

Rates of nitrification in lakes and streams may also be limited by low concentrations of NH_4^+ . Supply rates of NH_4^+ from watersheds are often low (except in cases of point-source pollution), and nitrifying organisms have little substrate with which to work. Two exceptions to this generality are cases in which NH_4^+ deposition is extremely high (such as near agricultural areas) and in which NH_4^+ is produced within the aquatic system. Experiments on whole lakes and in mesocosms have confirmed the acidifying potential of ammonium additions from deposition to surface waters (49, 50). Ammonium deposition is especially deceptive because in the atmosphere it can combine as a neutral salt with SO_4^{2-} to produce precipitation with near-neutral pH values, as seen in the Netherlands (51). Once deposited, however, the ammonium can be assimilated (leaving an equivalent amount of hydrogen) or nitrified (leaving twice the amount of hydrogen). Canadian whole-lake experiments generated conflicting evidence that nitrification in lakes is an acid-sensitive process. Rudd et al. (52) presented data indicating that nitrification was blocked at pH values less than 5.4 in an experimentally acidified lake and that this situation led to a progressive accumulation of NH_4^+ in the water column. Schindler et al. (49) reported nitrification in an experimentally fertilized lake at pH 4.6. Rudd et al. (52) hypothesized that nitrification will occur in low-pH lakes only when winter pH values are sufficiently high ($\text{pH} > 5.4$) to allow nitrifiers to become well established before the low pH values resulting from nitrification develop. This situation existed in the experimental lake described by Schindler et al. (49).

High NH_4^+ concentrations may also result through decomposition in lakes whose deeper waters become anoxic during periods of stratification (usually late winter or late summer). Nitrification of this NH_4^+ occurs when lakes mix during spring or fall. The mixing process supplies the oxygen necessary for nitrifying organisms to survive and metabolize (53). In this case, the main influence of nitrification is to recycle N within the system and to supply NO_3^- either to denitrifiers or to N-deficient algae.

Denitrification. Denitrification is the biological reduction of NO_3^- to produce gaseous forms of reduced nitrogen (N_2 , NO , or N_2O) (54). It is an anaerobic process (i.e., it occurs only in environments where oxygen is absent) whose end product is lost to the atmosphere (Figure 1). In terrestrial ecosystems, denitrification occurs in anaerobic soils, especially boggy, poorly drained soils, or in anaerobic microsites. It has traditionally been considered a relatively unimportant process outside of wetlands (55). However, denitrification could be an episodic process occurring after such events as spring snowmelt and heavy rainstorms, when soil oxygen tension is reduced (56). No single equation can describe the denitrification reaction because several end products are possible. However, denitrification is always an alkalizing process that consumes 1 mole of H for every mole of N denitrified (Figure 1).

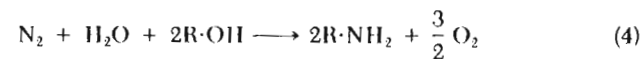
Denitrification can be involved in the production or consumption of N_2O , a product that may have considerable significance as a greenhouse gas (57, 58). In a review of the effects of acidic deposition on denitrification in forest soils, Klemetsson and Svensson (59) concluded that denitrification rates are often limited by the availability of oxygen and may therefore be relatively insensitive to increases in N deposition. Acidification of soils has an uncertain effect on overall rates of denitrification, but it strongly affects the end product of denitrification and favors the production of N_2O over N_2 (56, 60). Even under extreme conditions, denitrification is unlikely to be a significant sink for watershed N. Nonetheless, it may be significant in the global atmospheric budget of N_2O (60, 61).

Denitrification plays a much larger role in N dynamics in aquatic ecosystems than it does in terrestrial ones. In streams, rivers, and lakes, bottom sediments are the main sites for denitrification (62), although open-water denitrification has also been reported (63). In lake and stream sediments NO_3^- is potentially available from the water column, but it is produced mainly when organic matter is broken down within the sediments and the resulting NH_4^+ is subsequently oxidized (62). Denitrification is an especially important process in large rivers, for which Seitzinger (62) reported denitrification rates that were 7–35% of total N inputs. Denitrification in aquatic ecosystems is an alkalizing process, consuming 1 mole of H for every mole of NO_3^- denitrified.

Estimates of denitrification rates range from 54 to 345 $\mu\text{mol}/\text{m}^2$ per hour in streams with high rates of organic matter deposition, 12 to 56 $\mu\text{mol}/\text{m}^2$ per hour in nutrient-poor oligotrophic lakes, and 42 to 171 $\mu\text{mol}/\text{m}^2$ per hour in eutrophic lakes (62). Rudd et al. (64) reported an increase in the rate of denitrification from less than 0.1 to over 20 $\mu\text{mol}/\text{m}^2$ per hour in an oligotrophic lake when nitric acid was added in a whole-lake experimental acidification. This result suggests that freshwater denitrification may be limited by NO_3^- availability. In deep muds of slow-flowing streams, the process can effectively reduce NO_3^- concentrations in

the water column by as much as 200 $\mu\text{equiv}/\text{L}$ over a 2-km length of stream (65, 66). This depletion amounts to 75% of the daily NO_3^- input during a growing season. Thus denitrification can be considered as a method for NO_3^- removal in the management of some slow-moving streams with a deep organic substrate (67).

Nitrogen Fixation. Gaseous atmospheric nitrogen (N_2) can be fixed to produce NH_4^+ by a wide range of single-celled organisms, including blue-green algae (*Cyanobacteria*), and various aerobic and anaerobic bacteria. Symbiotic nitrogen-fixing nodules are present on the roots of some early successional forest species (68). In headwater streams, nodules on rooting structures of riparian vegetation (e.g., *Alnus* sp.) can also be important N fixers (69). Ordinarily, N fixation has no direct effect on the acid-base status of soil or surface waters.



Nitrogen fixation in excess of biological demand, however, can lead to nitrification or mineralization of organic N and ultimately to acidification of soil or surface waters (70, 71).

Nitrogen fixation counteracts denitrification losses of N from surface waters and is fundamental to replenishing fixed forms of N in all aquatic ecosystems. It is thought to be the main process responsible for maintaining surplus inorganic N in lakes and streams. It is therefore basic to the concept that primary production in most lakes and streams is limited by phosphorus (72).

Rates of N fixation are generally related to trophic status in fresh water. Howarth et al. (73) showed that fixation in low-, medium- and high-nutrient lakes is generally <0.02, 0.9–6.7, and 14.3–656.9 mmol/m^2 of N per year, respectively. Fixation is also closely correlated with the abundance of blue-green algae (53). This relationship suggests that the algae, rather than bacteria, dominate N fixation in lakes. Although N fixation does occur in sediments, that source is of minor importance compared to N fixation in the water column. Only in very nutrient-poor lakes, where N loading from all other sources is small, is N fixation in sediments of overall significance (e.g., 32 and 6% of total inputs in Lake Tahoe and Mirror Lake, respectively) (73).

Nitrogen Saturation

Much of the debate over whether aquatic systems are being affected by N deposition centers on the concept of nitrogen saturation of forested watersheds. Nitrogen saturation can be defined as a situation in which the

supply of nitrogenous compounds from the atmosphere exceeds the demand for these compounds on the part of watershed plants and microbes (1, 74). Under conditions of N saturation, forested watersheds that previously retained nearly all of N inputs due to a high demand for N by plants and microbes begin to have higher loss rates of N. These losses may be in the form of leaching to surface waters or to the atmosphere through denitrification. These two potential loss pathways have profoundly different impacts on the acid-base status of watersheds and surface waters (see following discussion). Their relative importance in advanced stages of N saturation will be a decisive characteristic determining the severity of the impact of N saturation.

Progressive Stages. Aber et al. (1) proposed a hypothetical time course for a watershed response to chronic N additions (Figure 2), describing both the changes in N cycling that are proposed to occur and the plant responses to changing levels of N availability. Aber et al. include in their hypothetical time course a trajectory for the loss of N to surface-water runoff, which suggests a simple response (N leaching) in the later stages of N saturation. This chapter seeks to establish whether stages equivalent to those shown in Figure 2 can be described for surface waters and to determine whether the response of surface waters to advanced stages of N saturation is as simple as is suggested in Figure 2.

Stage 0 of the Aber et al. (1) conceptual model is the pretreatment condition; inputs of N from deposition are at background levels and watershed losses of N are negligible (Figure 2). Increased deposition occurs in Stage 1, but effects on the terrestrial ecosystem are not evident. For a limiting nutrient such as N, a fertilization effect might result in increased ecosystem production and tree vigor at Stage 1. Retention of N is very efficient and little or no N would be lost annually to surface waters that drain Stage 1 watersheds. Many forested watersheds in the United States would be considered to exist at this stage.

Negative effects occur in Stage 2 of the Aber et al. (1) hypothetical time course. However, these effects are subtle, nonvisual, and require long time scales for detection. Only in Stage 3 do the effects on the forests become visible and result in major environmental impacts. Aber et al. (1) emphasize that different species and environmental conditions could alter the timing of the effects illustrated in Figure 2.

A number of factors may contribute to a watershed's progression through the stages of N loss, including elevated N deposition, stand age, and high soil-N pools. High rates of N deposition play a clear role, as the ability of forest biomass to accumulate N must be finite. At very high long-term rates of N deposition, the ability of forests and soils to accumulate N will be exceeded. The only remaining pathway for loss of N (other than runoff) is denitrification. Although high rates of N deposition may favor increased rates

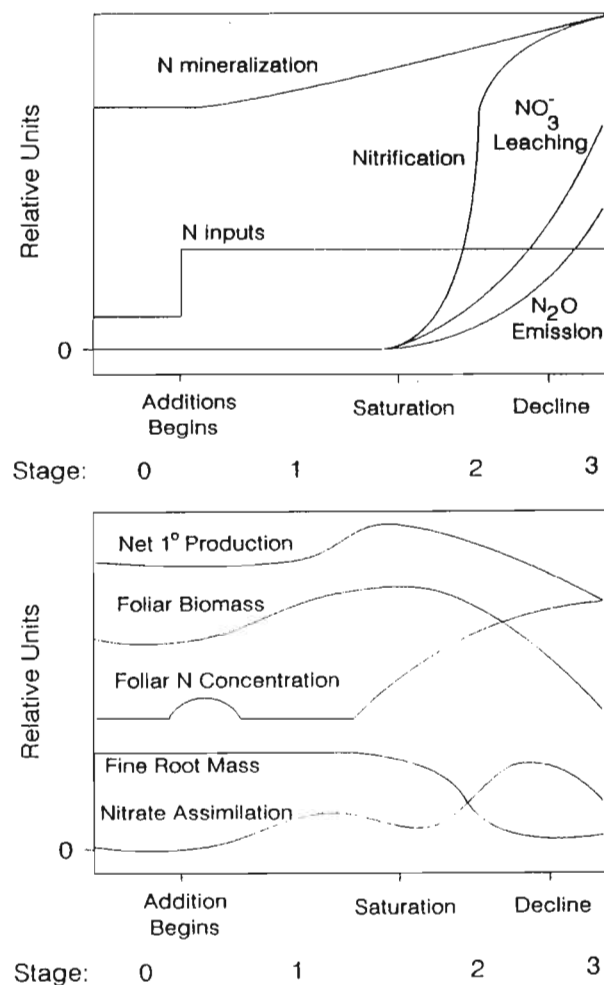


Figure 2. Hypothetical time course of forest ecosystem response to chronic nitrogen additions. Top: relative changes in rates of nitrogen cycling and nitrogen loss. Bottom: relative changes in plant condition (e.g., foliar biomass and nitrogen content, fine root biomass) and function (e.g., net primary productivity and nitrate assimilation) in response to changing levels of nitrogen availability. (Redrawn with permission from reference 1. Copyright 1989 American Institute of Biological Sciences.)

of denitrification, many watersheds lack the conditions necessary for substantial denitrification (e.g., low oxygen tension, high soil moisture, and temperature). Another important factor in N loss from watersheds is the age of the forest stands. A loss in the ability to retain N is a natural outcome of forest maturation, as demand for N on the part of more slowly growing tree species may plateau in later stages of forest development or decline as forests achieve a "shifting-mosaic steady state" (75). Uptake rates of N into vegetation are generally maximal around the time of canopy closure for conifers and somewhat later (at higher rates) in deciduous forests because of the annual replacement of canopy foliage in these ecosystems (76).

Finally, soil-N status may also affect N loss rates. Where large soil-N pools exist, they imply that soil microbial processes that are ordinarily limited by the availability of N are instead limited by some other factor (e.g., availability of labile organic carbon) and contribute to the likelihood that watersheds will leach NO_3^- (24, 77). N saturation occurs in a sequence beginning with the fulfillment of vegetation N demand, which is followed by the fulfillment of soil microbial N demand. The existence of large soil-N pools suggests that the second of these requirements may be easily met. The possible importance of all three factors (deposition, stand age, and soil N) in shifting watersheds from one stage of N loss to another will be discussed later in the context of surface water evidence of watershed N saturation.

Watershed Nitrogen Saturation. The loss of N from watersheds occurs in stages that correspond to the stages of terrestrial N saturation described by Aber et al. (1). The most obvious characteristics of these stages of N loss are changes in the seasonal and long-term patterns of surface-water NO_3^- concentrations, which reflect the changes in N cycling that are occurring in the watershed. The N cycle at Stage 0 is dominated by forest and microbial uptake, and the demand for N has a strong influence on the seasonal NO_3^- pattern of receiving waters (Figure 3). The normal seasonal NO_3^- pattern in a stream draining a watershed at Stage 0 would include very low, or immeasurable, concentrations during most of the year and measurable concentrations only during snowmelt (in areas where snowpacks accumulate over the winter months) or during spring rainstorms. The small loss of NO_3^- during the dormant season is a transient phenomenon. It results because snowmelt and spring rains commonly occur in these environments before substantial forest and microbial growth begin in the spring. (Winter mineralization of soil organic N may be an exception to this inactivity; see ref. 78.) Thus some of the N stored in soils and snowpack may pass through the watershed during extreme hydrological events and generate a pulse of elevated NO_3^- concentration (Figure 3b). The key surface-water characteristics of Stage 0 watersheds are very low NO_3^- concentrations during most of the year and maximum spring NO_3^- concentrations that are smaller than the concentrations typical of deposition.

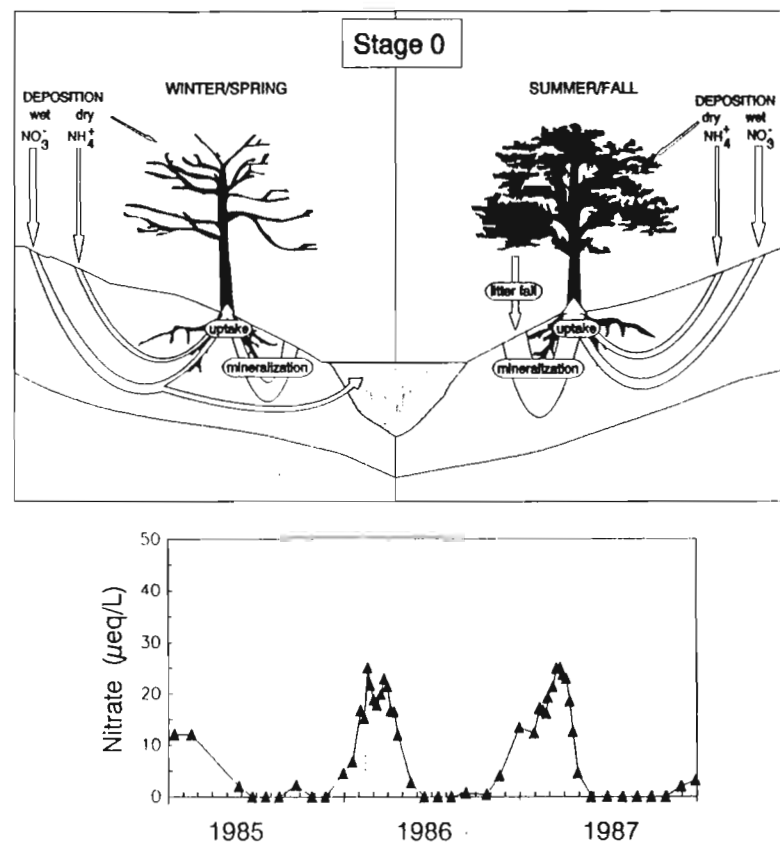


Figure 3. Top panel: Schematic representation of nitrogen cycle in watershed at Stage 0 of watershed nitrogen loss. Sizes of arrows indicate the magnitude of process or transformation. Differences between winter-spring and summer-fall seasons are shown on opposite sides. At Stage 0, nitrogen transformations are dominated by plant and microbial assimilation (uptake), with little or no NO_3^- leakage from the watershed during the growing season. Bottom panel: Small amounts of NO_3^- may run off during snowmelt, producing the typical Stage 0 seasonal NO_3^- pattern. Data in lower panel are from Black Pond, Adirondack Mountains. (Data are taken from reference 157.)

At Stage 1 the seasonal pattern typical of Stage 0 watersheds is amplified. This amplification of the seasonal NO_3^- signal may be the first sign that watersheds are proceeding toward the chronic stages (i.e., Stages 2 and 3 in Figure 2) of N saturation (42, 79). This suggestion is consistent with the changes in N cycling that are thought to occur at Stage 1. A conceptual

understanding of these changes derives from the most common definition of nutrient limitation. Implicit in the definition of nutrient limitation is the idea that "the current supply rate [of a nutrient] prevents the vegetation from achieving maximum growth rates *attainable within other environmental constraints*" (ref. 80; emphasis added). During the cold season these environmental constraints can be severe, and maximum attainable growth rates are clearly much lower than in the warm months. Although much of this discussion is couched in terms of forest trees, the same arguments apply to soil microbial communities (e.g., decomposers, nitrifiers) that may be as important as vegetation in controlling N loss from watersheds (80).

Overall limitation of forest growth in the early stages of N saturation is characterized by a seasonal cycle of limitation by physical factors (e.g., cold and diminished light) during late fall and winter and by nutrients (primarily N) during the growing season. The effect of increasing the N supply (e.g., from deposition) is to postpone the seasonal switch from physical to nutrient limitation during the breaking of dormancy in the spring (Figure 4) and to prolong the seasonal N saturation that is characteristic of watersheds at this stage. At Stage 1, this switch is delayed enough that substantial NO_3^- may leave the watershed during extreme hydrological events in the spring. Watershed loss of N at Stage 1 is still a seasonal phenomenon, and the annual N cycle is still dominated by uptake (Figure 5), but NO_3^- leaching is less transient than at Stage 0. The key characteristics of Stage 1 watersheds are episodes of surface-water NO_3^- that exceed concentrations typical of deposition (Figure 5b). Elevated NO_3^- during these episodes may result from preferential elution of anions from melting snow (81, 82) or from the contribution of N mineralization to the soil pool of NO_3^- that may be flushed during high-flow periods (43, 83).

In Stage 2 of watershed N loss the seasonal onset of N limitation is even further delayed. As a consequence, biological demand exerts no control over winter and spring N concentrations, and the period of N limitation during the growing season is much reduced (Figure 6). The annual N cycle, which was dominated by uptake at Stages 0 and 1, is instead dominated by N loss through leaching and denitrification at Stage 2; sources of N (deposition and mineralization) outweigh N sinks (uptake). The same mechanisms that produce episodes of high NO_3^- during extreme hydrological events at Stage 1 also operate at Stage 2. But more importantly, NO_3^- leaching can also occur at Stage 2 during periods when the hydrological cycle is characterized by deeper percolation (Figure 6). If biological demand is sufficiently depressed during the growing season, N begins to percolate below the rooting zone and elevated groundwater NO_3^- concentrations result. Nitrification becomes an important process at Stage 2 (Figure 2; also see ref. 1). Lowered biological demand leads to a buildup of NH_4^+ in soils and nitrification may be stimulated. This change is pivotal in the N cycle because nitrification is such a

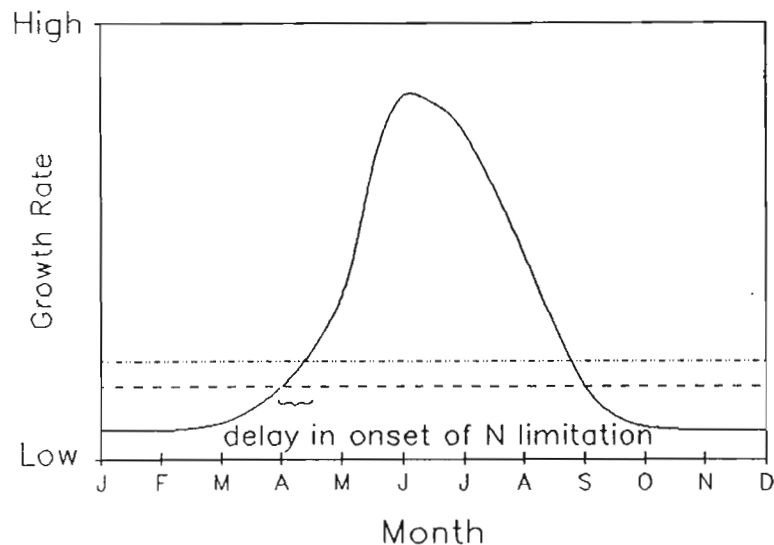


Figure 4. Conceptual model of mechanism responsible for increased incidence and severity of NO_3^- episodes in watersheds in early stage of nitrogen saturation (Stage 1). Solid line is potential growth rate of forest if all nutrients are sufficient and only environmental variables (e.g., temperature, light, and water) limit growth. Dashed line is potential growth rate if environmental variables are optimal, but N is in short supply. Points where dashed and solid lines cross are transitions from N-unlimited to N-limited growth and vice versa. Dotted line is potential growth rate if environmental variables are optimal and N supply is moderate. Shift in onset of N limitation in spring will result from increase in nitrogen supply and is likely to coincide with timing of snowmelt in northern forested watersheds.

strongly acidifying process (Figure 1). The key characteristics of Stage 2 watersheds are elevated baseflow concentrations of NO_3^- , which result from high groundwater concentrations (Figure 6b). Episodic NO_3^- concentrations are as high as Stage 1, but the seasonal pattern at Stage 2 is damped by an increase in baseflow concentrations to levels as high as those found in deposition.

In Stage 3 the watershed becomes a net source of N rather than a sink (Figure 7). Nitrogen-retention mechanisms (e.g., uptake by vegetation and microbes) are much reduced. Mineralization of stored N may add substantially to N leaving the watershed through leaching or in gaseous forms. As in Stage 2, nitrification rates are substantial. The combined inputs of N from deposition, mineralization, and nitrification can produce concentrations of NO_3^- in surface waters that exceed inputs from deposition alone. The key

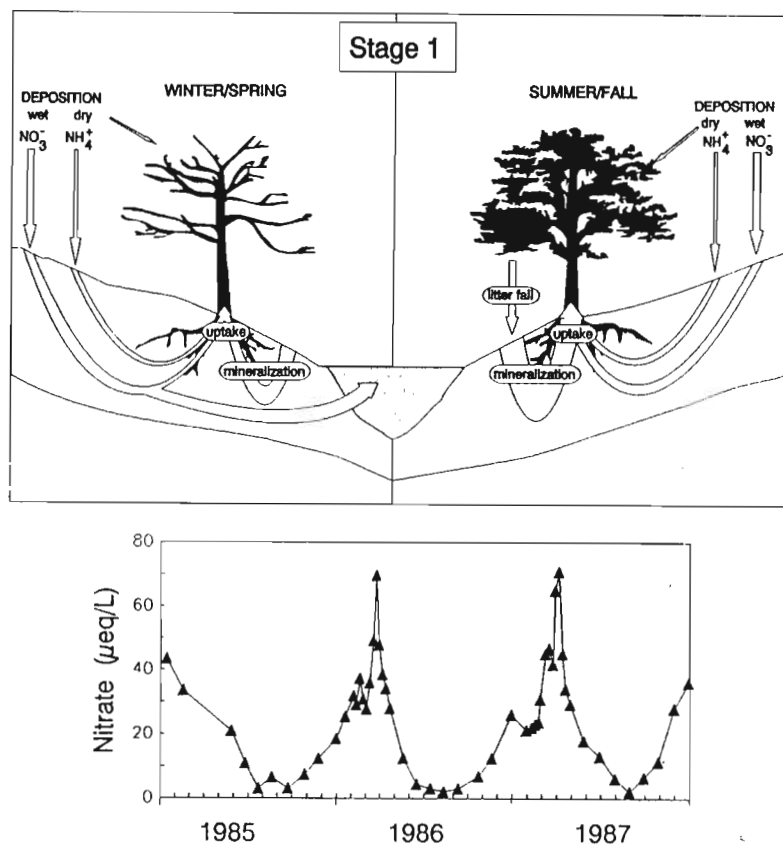


Figure 5. Top panel: Schematic representation of nitrogen cycle in watershed at Stage 1 of watershed nitrogen loss. Size of arrows indicates the magnitude of process or transformation. Differences between winter–spring and summer–fall seasons are shown on opposite sides. As in Stage 0, uptake dominates the nitrogen cycle during the growing season at Stage 1 and little or no NO_3^- leaks from the watershed during the summer and fall. The primary difference between Stage 0 and Stage 1 is the delay in the onset of N limitation during the spring season (see text and Figure 4). Bottom panel: Large runoff events (e.g., snowmelt or rainstorms) during the dormant season can produce episodic pulses of high NO_3^- concentrations, as shown in the typical Stage 1 seasonal NO_3^- cycle. Data in bottom panel are from Constable Pond in the Adirondack Mountains. (Data are taken from reference 157.)

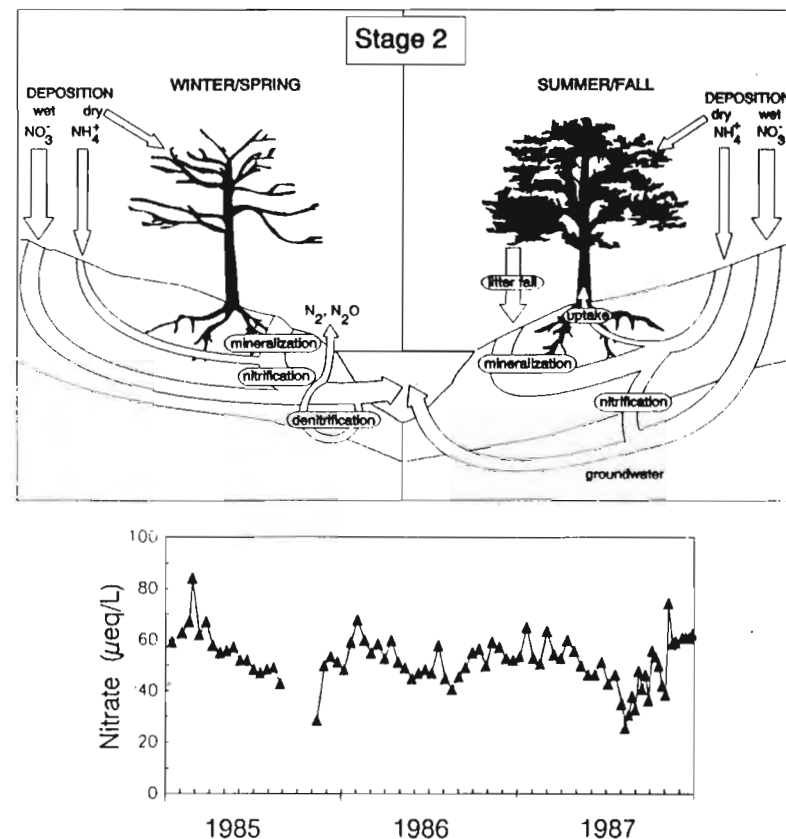


Figure 6. Top panel: Schematic representation of nitrogen cycle in watershed at Stage 2 of watershed nitrogen loss. Size of arrows indicates the magnitude of process or transformation. Differences between winter–spring and summer–fall seasons are shown on opposite sides. Uptake of nitrogen by forest plants and microbes is much reduced at Stage 2, resulting in loss of NO_3^- to streams during winter and spring and to groundwater during the growing season. Loss of gaseous forms of nitrogen through denitrification may also be elevated at Stage 2 if conditions necessary for denitrification are present (see text). Although episodes of higher NO_3^- concentrations continue to occur during high-flow events such as spring snowmelt, the primary difference between Stage 1 and Stage 2 is the presence of elevated NO_3^- concentrations in groundwater. Bottom panel: The typical seasonal NO_3^- pattern at Stage 2 includes both high episodic concentrations and high base-flow concentrations. Data in bottom panel are from Fernow Experimental Forest, Control Watershed No. 4, West Virginia.

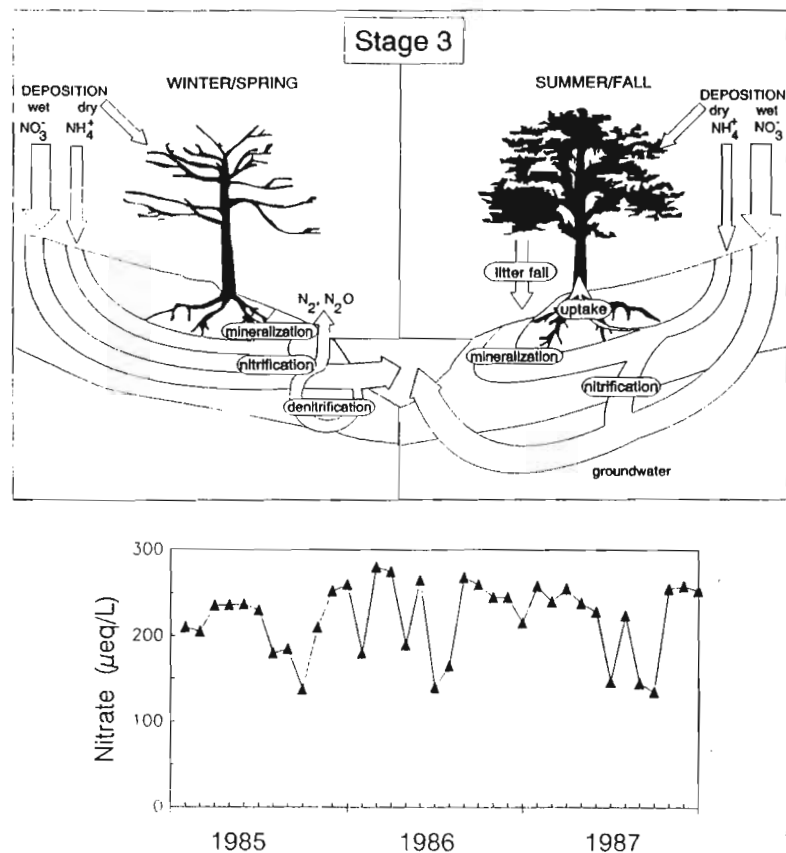


Figure 7. Top panel: Schematic representation of nitrogen cycle in watershed at Stage 3 of watershed nitrogen loss. Size of arrows indicates the magnitude of process or transformation. Differences between winter–spring and summer–fall seasons are shown on opposite sides. At Stage 3 no sinks for nitrogen exist in the watershed and all inputs, as well as mineralized nitrogen, are lost from the system either through denitrification or in runoff water. Because mineralization supplies nitrogen in excess of deposition, concentrations of NO_3^- in runoff may exceed those in deposition. Bottom panel: Typical seasonal NO_3^- pattern at Stage 3 includes concentrations at all seasons in excess of concentrations attributable to deposition and evapotranspiration, as at Dicke Bramke in Germany; data are from reference 190.

characteristics of Stage 3 watersheds are these extremely high NO_3^- concentrations and the lack of any coherent seasonal pattern in NO_3^- concentrations (Figure 7b).

Conceptually, the stages of watershed N loss can be thought of as occurring sequentially, as a single watershed progresses from being strongly N deficient to strongly N sufficient. This sequence is consistent with the conceptual model presented by Aber et al. (1; also Figure 2) and can be supported by two lines of evidence that are presented in the following sections of this chapter. The first line of evidence comes from space-for-time substitutions (84), where the occurrence of various stages across a gradient of current N deposition is used as a surrogate for the temporal sequence that a single site might undergo if it were exposed to chronically elevated levels of N deposition. This technique is commonly applied to current environmental problems for which a good historical record is not available (85). The second line of evidence comes from long-term temporal trends at single sites, where increases in N efflux from watersheds (observable as increasing trends in NO_3^- concentration) and changes in the seasonal pattern of NO_3^- concentration can be directly attributed to the combined effects of chronic N deposition and other factors (e.g., forest maturation). The few cases in which individual sites have progressed from Stage 0 to Stage 1 or Stage 2 of watershed N loss are especially useful in establishing that N saturation occurs as a temporal sequence in areas of high N deposition. These lines of evidence are discussed in the following sections.

The Consequences of Nitrogen Loss from Watersheds

Two possible consequences of watershed N loss are surface-water acidification and eutrophication. The acidification processes in lakes and streams are conventionally separated into chronic (long-term) and episodic (event-based) effects. Surface waters are generally considered acidic if their acid-neutralizing capacity (ANC) is less than zero. The ANC of a lake or stream is a measure of the water's capacity to buffer acidic inputs. It results from the presence of carbonate or bicarbonate (i.e., alkalinity), aluminum, and organic acids in the water (86). In the past decade a great deal of emphasis was placed on chronic acidification in general, and on chronic acidification by SO_4^{2-} in particular (87, 88). This emphasis on SO_4^{2-} has resulted largely because sulfur deposition rates are often higher than those for N (S deposition rates are approximately twice the N deposition rates in the Northeast; ref. 9) and because NO_3^- appears to be of negligible importance in surface waters sampled during summer and fall index periods (89). As mentioned previously, summer and fall are seasons when watershed demand for N is normally very high. This timing creates a low probability that N, in any form, will be leached into soil and surface waters unless the watersheds are in stages 2 and 3 of N loss. Under the usual conditions (i.e., in Stages 0 and 1), N

leaking from terrestrial ecosystems is more likely to be a transient (or seasonal) phenomenon than a chronic one.

Eutrophy generally refers to a state of nutrient enrichment (53), but the term is commonly used to refer to conditions of increased algal biomass and productivity, the presence of nuisance algal populations, and a decrease in oxygen availability for heterotrophic organisms. Eutrophication is the process whereby lakes, estuaries, and marine systems progress toward a state of eutrophy. In lakes, eutrophication is often considered a natural process, progressing gradually over their long-term evolution. The process can be significantly accelerated by the additional input of nutrients from anthropogenic sources. The subject of eutrophication was extensively reviewed by Hutchinson (90), the National Academy of Sciences (91), and Likens (92).

Chronic Acidification. The most comprehensive assessment of chronic acidification of lakes and streams in the United States comes from the National Surface Water Survey (NSWS). It was conducted as part of the National Acid Precipitation Assessment Program (NAPAP). The NSWS surveyed the acid-base chemistry of both lakes and streams by using an index period concept. The goal of the index period concept was to identify a single season of the year that exhibited low temporal and spatial variability and that, when sampled, would allow the general condition of surface waters to be assessed (89). For lakes, the index period selected was autumn overturn, the period when most lakes are mixed uniformly from top to bottom. For streams the chosen index period was spring baseflow, the period after spring snowmelt and before leafout (93). Because of the strong seasonality of the N cycle in forested watersheds (described earlier), the choice of index period plays a very large role in the assessment of whether N is an important component of chronic acidification.

The Eastern Lake Survey (89) was based on a probability sampling of lakes during fall overturn, and the National Stream Survey (NSS; ref. 94) was based on a probability sampling of streams during a spring baseflow period. The results suggest that N compounds make only a small contribution to chronic acidification in North America. Henriksen (95) proposed that the ratio of $\text{NO}_3^-:(\text{NO}_3^- + \text{SO}_4^{2-})$ in surface waters be used as an index of the influence of NO_3^- on chronic acidification status. This index assesses the importance of NO_3^- relative to the importance of SO_4^{2-} , which is usually considered more important in chronic acidification. A value greater than 0.5 indicates that NO_3^- has a greater influence on the chronic acid-base status of surface waters than does SO_4^{2-} .

Median values of $\text{NO}_3^-:(\text{NO}_3^- + \text{SO}_4^{2-})$ ratios for acid-sensitive regions of the United States sampled in the NSWS are shown in Table II. Data are taken mainly from refs. 89 and 96, with data from additional regional surveys included in Table II for comparison (97-99). In all regions the median values of $\text{NO}_3^-:(\text{NO}_3^- + \text{SO}_4^{2-})$ are all less than 0.5, and most are less than 0.2.

Table II. Concentrations and Ratio of NO_3^- to $(\text{NO}_3^- + \text{SO}_4^{2-})$ in Lakes and Streams of Acid-Sensitive Regions of the United States

Region ^a	Year	pH	NO_3^- ^b	SO_4^{2-} ^b	$\text{NO}_3^-:(\text{NO}_3^- + \text{SO}_4^{2-})$
Eastern Lake Survey ^c					
Southern Blue Ridge	1985	6.98	3.1	31.8	0.09
Florida	1985	6.36	1.0	93.7	0.01
Upper Midwest	1985	7.09	0.7	57.1	0.01
Maine	1985	6.91	0.2	74.6	0.00
Southern New England	1985	6.81	0.8	141.1	0.01
Central New England	1985	6.77	0.3	101.2	0.00
Adirondack Mountains	1985	6.71	0.6	118.7	0.01
Catskill-Pocoms	1985	7.02	0.7	159.3	0.00
National Stream Survey ^d					
Pocoms-Catskills	1986	6.96	6	169	0.03
Northern Appalachians	1986	6.60	30	171	0.14
Valley and Ridge	1986	7.05	10	154	0.09
Mid-Atlantic Coastal Plain ^e	1986	5.98	—	—	—
Southern Blue Ridge	1986	6.99	8	17	0.28
Piedmont	1986	6.80	2	48	0.03
Southern Appalachians	1986	7.33	16	58	0.32
Ozarks-Ouachitas	1986	6.62	1	59	0.02
Florida	1986	5.48	5	22	0.19
Catskill Regional Survey ^f	1984-86	6.60	29	138	0.17
Great Smoky Mountains Stream Survey ^g	1984-86	5.58	61.1	76.1	0.44
Virginia Trout Stream Survey ^h	1987	6.70	0	72	0.00

^aValues are weighted medians for each region.

^bValues are given in microequivalents per liter. Data are from reference 89.

^cValues for pH are for entire region (94); medians for NO_3^- , SO_4^{2-} and the $\text{NO}_3^-:(\text{NO}_3^- + \text{SO}_4^{2-})$ ratio exclude sites with potential agricultural or other land-use impacts (96).

^dThe influence of agricultural and land-use practices could not be ruled out for any of the sites in the mid-Atlantic coastal plain (96).

^eMedian value for repeated measurements at 51 streams (data are from reference 79).

^fMean value for repeated measurements at five streams (data are from reference 99).

^gMedian value of 341 streams (data are from reference 98).

These values suggest that NO_3^- does not contribute significantly to chronic acidification in most regions of the United States. Several southeastern regions exhibit ratios in the 0.2–0.4 range, primarily because their current SO_4^{2-} concentrations are relatively low. The Southern Blue Ridge, in particular, has the lowest SO_4^{2-} concentrations found in the NSS, and the relatively high $\text{NO}_3^-:(\text{NO}_3^- + \text{SO}_4^{2-})$ ratios in this region could be considered misleading. Taken in total, regional survey data suggest that the Catskills, Northern Appalachians, Valley and Ridge Province, and Southern Appalachians all show some potential for chronic acidification attributable to NO_3^- . However, in all of the regions shown in Table II chronic acidification is more closely tied to SO_4^{2-} than to NO_3^- .

The highest $\text{NO}_3^-:(\text{NO}_3^- + \text{SO}_4^{2-})$ ratios and the highest mean NO_3^- concentrations were recorded in streams of the Great Smoky Mountains, where baseflow NO_3^- concentrations were as high as, or in some cases higher than, baseflow SO_4^{2-} concentrations (99). Cook et al. (99) stressed that this study included a small number of streams, that the region is known for geological sources of SO_4^{2-} (the Anakeesta geological formation), and that high SO_4^{2-} and NO_3^- concentrations tend to occur simultaneously. The results are entirely consistent, however, with soil lysimeter studies carried out in the Great Smoky Mountains. According to these studies, NO_3^- concentrations in deep soil lysimeters are higher than input concentrations from deposition and throughfall (172). Because deep soil-water concentrations can be assumed to approximate groundwater and baseflow stream-water concentrations, these streams and watersheds in the Great Smoky Mountains are the only known examples in the United States of watersheds at Stage 3 of watershed N loss, as described earlier.

Chronic acidification resulting from N deposition is much more common in Europe than in North America (39). Many European sites show chronic increases in N export from their watersheds (101, 102), and at sites with the highest stream-water NO_3^- concentrations (i.e., Lange Bramke and Dicke Bramke in West Germany) NO_3^- concentrations no longer show the seasonality that is expected from normal watershed processes (39). Henriksen and Brakke (101) reported regional chronic increases in surface-water NO_3^- in Scandinavia in the past decade. These increases in NO_3^- concentration are associated with increasing concentrations of aluminum, which is toxic to many fish species (103, 104). Some evidence (105) suggests that NO_3^- has a greater ability to mobilize toxic aluminum from soils than does SO_4^{2-} . Chronic acidification attributable to ammonium deposition has also been demonstrated in the Netherlands (51, 106). As described earlier, ammonium in deposition can be nitrified to produce both NO_3^- and hydrogen ions, which are subsequently leaked into surface waters. Rates of NO_3^- and NH_4^+ deposition are much higher in Europe (in some places deposition is >2000 equiv/ha per year; ref. 107) than in the United States (Table I). Chronic N acidification may be more evident in Europe than in North America because N saturation is further developed in Europe.

Episodic Acidification. Except in extreme cases, N loss from watersheds is more likely to be an episodic or seasonal process than a chronic one. Therefore, data used to assess the contribution of NO_3^- to acidification must be collected on an intensive schedule so short-term effects of NO_3^- increases can be characterized. This situation places severe limitations on the type of data that can be used in this assessment. Data from regional surveys, although they provide excellent spatial coverage, are hampered by the need to collect samples during a stable index period. In most areas the spring period when NO_3^- effects are most likely to be observable would not meet the requirements described earlier for a stable index period. As a result the regional importance and severity of episodic acidification have not been quantified; that is, the regional information on chronic acidification that was gained from the NSWS has no parallel in episodic acidification, and all conclusions must be based on site-specific data. Even within a given area, such as the Adirondack Mountains, major differences can be evident in the occurrence, nature, location (lakes or streams), and timing of episodes at different sites.

It has been estimated that 1.4–7.4 times as many streams in the eastern United States undergo episodic acidification than are chronically acidic (108). Similarly, the number of episodically acidic Adirondack lakes is estimated to be 3 times higher than the number of chronically acidic lakes (108). Wigington et al. (109) reported that acidic episodes occur in a wide range of geographic locations in the northeastern, southeastern, and western United States, as well as in Scandinavia, Europe, and Canada.

A number of processes contribute to the timing and severity of acidic episodes (42). During high-discharge periods the most important of these processes are

- dilution of base cations (110);
- increases in organic acid concentrations (111);
- increases in SO_4^{2-} concentrations (112); and
- increases in NO_3^- concentrations (110, 113, 114).

In addition to these factors, which produce the chemical conditions characteristic of episodic events, the likelihood of an acidic episode is also influenced by the chemical conditions prevailing before the episode begins. Episodes are more likely to be acidic, for example, if the baseflow ANC of the stream or lake is low. In this way, acidic anions, especially SO_4^{2-} , can contribute to the severity of an acidic episode by lowering the baseflow ANC of the stream or lake, even though they do not increase during the event (97).

In many cases all of these processes will contribute to episodes in a single aquatic system. Dilution, for example, probably plays a role in all episodic decreases in ANC and pH in all regions of the United States (109).

Dilution results from the increased rate of runoff and the channeling of runoff through shallower soil layers that occurs during storms or snowmelt. The shorter contact time produces runoff with a chemical composition closer to that of atmospheric deposition than is typical of baseflow conditions (115–117). Because precipitation is usually more dilute than stream or lake water, storm runoff produces surface waters that are more dilute than during nonrunoff periods. In a sense, dilution sets the baseline condition to which is added the effects of organic acids and atmospherically derived SO_4^{2-} and NO_3^- .

Little information exists about the effects of changes in organic acids during episodes. Driscoll et al. (118) and Eshleman and Hemond (119) concluded that organic acids did not contribute to snowmelt episodes in the Adirondacks or in Massachusetts, respectively. At Harp Lake in Canada, organic acidity is believed to remain constant (120) or decrease (121) during snowmelt episodes. Haines (122) and McAvoy (123) documented increases in organic acidity during rain-caused episodes in coastal Maine and in Massachusetts.

Storage of SO_4^{2-} in watersheds and its subsequent release during episodic events are well documented in many parts of Europe (109), but the process has not been found commonly in the United States. Sulfate episodes have been described for the Leading Ridge area of Pennsylvania (124) and at Filsen Creek in Minnesota (125), but they are not widespread. Sulfate does contribute to episodic acidity, however, in the sense that concentrations may remain high during events and contribute to a lower baseline ANC. The effects of other factors, such as increased NO_3^- , are supplemental to any constant effect of SO_4^{2-} in lowering the baseline ANC (97).

In the discussion of the contribution of NO_3^- to chronic acidification, the importance of NO_3^- was related to the importance of SO_4^{2-} , the primary acidic anion in anthropogenically acidified lakes and streams. For episodic acidification, the importance of short-term increases in NO_3^- concentration must be assessed in relation to the other processes that contribute to acidic episodes. In the Adirondacks, for example, strong NO_3^- pulses in both lakes (110, 113) and streams (118) are apparently the primary factor contributing to depressed ANC and pH during snowmelt. Schaefer et al. (126) examined intensive monitoring data from 11 Adirondack lakes and concluded that the magnitude of the episodes experienced by lakes depends strongly on their base-cation concentration. They concluded that lakes with high base-cation concentrations (and therefore high ANC values) undergo episodes that are largely the result of dilution by snowmelt. Low-ANC lakes, on the other hand, undergo episodes that result largely from increases in NO_3^- concentrations. At intermediate ANC levels, lakes are affected by both base-cation dilution and NO_3^- increases. Therefore these lakes may undergo the greatest increases in acidity during snowmelt episodes (Figure 8). Murdoch and Stoddard (127) reported similar results for streams in the Catskill Mountains.

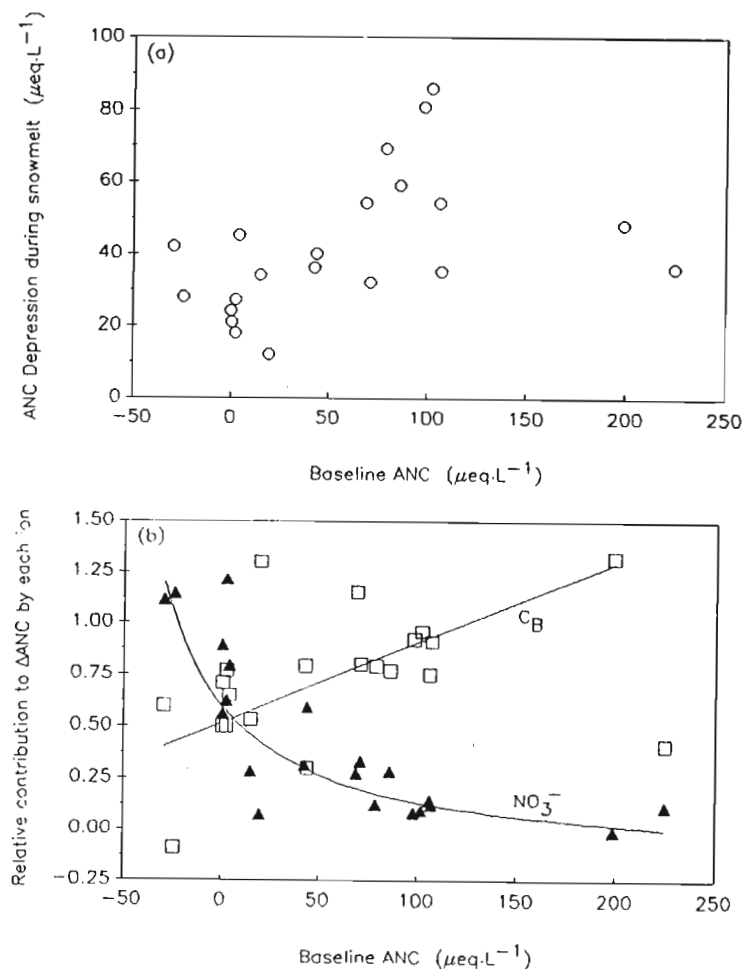


Figure 8. Effect of baseline acid-neutralizing capacity (ANC) and episodic conditions in Adirondack lakes. a. Relationship between baseline ANC and the springtime depression in ANC (baseline ANC—minimum ANC) for 11 lakes sampled in 1986 and 1987. b. The relative contributions of base cations (C_B) and nitrate (NO_3^-) to the springtime ANC depressions in Adirondack lakes. Lakes at intermediate ANC values undergo the largest springtime depressions in ANC. Lakes with lower baseline ANC are affected more by NO_3^- pulses, and lakes with higher baseline ANC are affected more by base-cation dilution. Solid lines represent best-fit relationships. (Redrawn with permission from reference 126. Copyright 1990 American Geophysical Union.)

where NO_3^- increases were the primary determinant of acidic episodes in low- to moderate-ANC streams during the spring. Both base-cation dilution and organic acidity contributed significantly to episodes in the fall.

Eutrophication. Thus far N has been discussed in terms of its prominence as an acidic anion (i.e., as NO_3^-). As in terrestrial ecosystems, inorganic forms of N also act as nutrients in aquatic systems, and a possible consequence of chronic N loss from watersheds is the fertilization of lakes and streams. Establishing a link between N deposition and the eutrophication of aquatic systems depends on a determination that the productivity of the system is limited by N availability and that N deposition is a major source of N to the system. In many cases the supply of N from deposition is minor when compared to other anthropogenic sources, such as pollution from either point or nonpoint sources.

The productivity of fresh waters is generally limited by the availability of phosphorus, rather than N (reviewed in ref. 34). Although conditions of N limitation occur in freshwater systems, they are often either transitory or the result of high inputs of P from anthropogenic sources such as sewage. N limitation is often a short-lived phenomenon because N-deficient conditions favor the growth of blue-green algae (128), many of which are capable of N fixation. In lakes N fixation may be considered a natural mechanism that has contributed to the long-term evolution and ubiquity of P limitation by ensuring an adequate supply of N (72).

Nitrogen limitation can occur naturally (i.e., in the absence of anthropogenic P inputs) in lakes with very low concentrations of both N and P; such low-nutrient lakes are common in the West and Northeast (30). Suttle and Harrison (30) and Stockner and Shortreed (129) suggested that P concentrations in these systems are too low to allow blue-green algae to thrive; blue-green algae are poor competitors for P at very low concentrations (128, 130). In these systems the two nutrients are often closely coupled, and constant shifts between N and P deficiency may occur without obvious changes in community structure. Additional loading of N from atmospheric deposition is likely to have only a small effect on primary productivity because the system quickly becomes P-limited. In a literature survey of 62 separate nutrient-limitation studies in lakes, Elser et al. (131) found that simultaneous additions of N and P produced the largest growth response in 82% of the experiments. These results underline the likelihood that a lake limited by one nutrient may quickly become limited by another if the lake becomes enriched with the original limiting nutrient.

Estimations of nutrient limitation in lake ecosystems follow three major lines of reasoning:

1. evidence from ambient nutrient concentrations and the nutritional needs of algae,

2. evidence from bioassay experiments at various scales, and
3. evidence from nutrient dynamics and input-output studies (34, 132).

Bioassay experiments provide the most direct evidence of nutrient limitation because they involve the experimental addition of selected nutrients (singly or in combination) to assemblages of algae under controlled conditions. Analyses of ambient nutrient conditions are less direct indicators of limitation because the biotic response (i.e., biostimulation) is not measured, but is instead inferred from geochemical principles. In this sense the nutrient ratio approach measures potential nutrient limitation rather than actual limitation, but it often shows results consistent with bioassay results. The ambient nutrient ratio approach has been criticized widely because it ignores several factors known to be important to algal growth. The use of only inorganic nutrient species in the ratios, for example, has been criticized because many algal species are known to make use of organic forms, especially of P (132). Algal growth may also be more dependent on the supply rates of nutrients than on their ambient concentrations (31, 133). Many species of algae may therefore not be limited by nutrients whose ambient concentrations are so low as to be undetectable.

Much of the acceptance of the idea that freshwater lakes are primarily P-limited stems from the close correlations between P concentrations and lake productivity or algal biomass (usually measured as chlorophyll concentration) that have been observed in a large number of lake studies (reviewed in refs. 27 and 134). More recently, researchers have begun to question the ubiquity of the phosphorus:chlorophyll relationship and to identify some of the factors that lead to the large variability observed in this relationship in nature (128, 135-138). Recent reexaminations of the data suggest that the phosphorus:chlorophyll relationship is best described as sigmoidal (139) and that the slope of the relationship is significantly affected by N concentrations, particularly at high concentrations of P ($>1 \mu\text{mol/L}$) that are likely to be caused by anthropogenic inputs: McCauley et al. (139) found that N had little effect on the phosphorus:chlorophyll relationship at low concentrations of P. This effect is expected in nutrient-poor lakes where the primary effect of N additions would be to push lakes into a phosphorus-deficient condition.

Ambient Nutrient Ratios. Arguments based on ambient nutrient concentrations stem from the early work of Redfield (140), who examined particulate concentrations of nutrients from samples of nutrient-sufficient algae taken from marine systems worldwide and found surprisingly consistent results for the ratios of C:N:P concentrations (106:16:1). Deviations from these ratios are considered evidence that one nutrient or another is limiting to algal growth (e.g., N:P ratio values below 16:1 suggest N limitation; values above 16:1 suggest P limitation). Because the relative supply rates

of P and N determine whether one or the other nutrient is in short supply, various researchers have extended the interpretation of the Redfield ratio to include ambient nutrient concentrations in water (Redfield's original work was with intracellular concentrations) and applied the nutrient ratio criteria to lakes to predict their likely limiting conditions (135, 138, 141). This method has the potential to illustrate regional patterns and has gained some support from the results of bioassay experiments. This idea has been refined to exclude from the ratio those forms of N and P that are not biologically available, especially organic forms of N. As a result, good predictions of nutrient limitation can now be made from ratios of total dissolved inorganic nitrogen (DIN) to total phosphorus (TP) (142).

Morris and Lewis (142) conducted nutrient-addition bioassays on natural assemblages of phytoplankton from many lakes and compared their results to DIN:TP values measured in the lakes at the same time as the experiments were conducted. They found that lakes with DIN:TP values less than 9 (using molar concentrations) could be limited by either N or P; often additions of both nutrients were required to stimulate growth. Lakes with DIN:TP values less than 2 were always limited by N. The discrepancy between the 16:1 Redfield ratio and the 2:1 ratio suggested by Morris and Lewis (142) results from a number of differences between the Redfield measurements and the method used here. First and foremost, the DIN:TP ratio compares dissolved concentrations of inorganic N to total concentrations of P in ambient water; the Redfield ratio is based on cellular or particulate organic concentrations. A large amount of variability also results from the range of threshold N:P ratios for individual algal species. Suttle and Harrison (30), for example, reported N limitation at ratios ranging from 7:1 to 45:1 for single species. Such a wide range for single species suggests that critical ratios may also be quite variable in nature. Finally, the 2:1 ratio is a conservative estimate of the nutrient-limitation threshold, in the sense that it marks the boundary beyond which all experimental results indicate N limitation (142).

If a DIN:TP value of 2 is used as the threshold below which lakes are considered to be N-limited and is applied to lake data from the NSWS (89, 143), it is possible to estimate the number of N-limited lakes in most of the mountainous regions of the United States (Table III). The NSWS was designed to survey the acid-base chemistry of lakes by using a probability design. Because the selection of lakes is a stratified random sample of the lakes in each region, results can be extrapolated to the target population of lakes in each region. As an acidification survey, the NSWS excludes many lakes in highly disturbed areas (e.g., urban and agricultural areas). The results in Table III should therefore be interpreted in the context of the target population they represent: nonurban, nonindustrial, nonagricultural lakes above a certain size in each region (size cutoffs were >4 ha in the Eastern Lake Survey and >1 ha in the Western Lake Survey). Lakes with total P concentrations greater than 0.65 $\mu\text{mol/L}$ (20 $\mu\text{g/L}$) have been ex-

Table III. Nitrogen-Limited Lakes in Subregions of the United States Sampled by NSWS

Region	Number of Lakes in Subregion	Estimated Number ^a of N-Limited Lakes	N-Limited Proportion of Population (%)	"Excess P" ^b ($\mu\text{mol/L}$)
Eastern Lake Survey ^c				
Adirondacks (1A)	1290	41	3	0.3
Poconos-Catskills (1B)	1506	177	12	0.6
Central New England (1C)	1494	72	5	0.3
Southern New England (1D)	1325	257	19	0.7
Northern New England (1E)	1542	77	5	0.2
Northeastern Minnesota (2A)	1499	300	20	0.5
Upper Peninsula, Michigan (2B)	1050	322	31	0.5
Northcentral Wisconsin (2C)	1511	209	14	0.7
Upper Great Lakes Area (2D)	4515	1530	34	0.6
Southern Blue Ridge (3A)	286	10	4	0.3
Florida (3B)	2138	234	11	0.7
Total	18,155	3228	18	0.6
Western Lake Survey ^d				
California (4A)	2406	573	24	0.6
Pacific Northwest (4B)	1706	622	36	0.3
Northern Rockies (4C)	2379	857	36	0.4
Central Rockies (4D)	2299	931	41	0.6
Southern Rockies (4E)	1609	754	47	1.0
Total	10,398	3736	36	0.5

^aEstimates are based on ratios of dissolved inorganic nitrogen concentrations ($\text{NO}_3^- + \text{NH}_4^+$) to total phosphorus concentrations.

^bExcess phosphorus: calculated as the amount of added DIN necessary to increase the DIN:TP ratio to 2.0.

^cData are from Kanciruk et al. (202), excluding lakes with total phosphorus >0.65 $\mu\text{mol/L}$ (20 $\mu\text{g/L}$).

^dData are from reference 203, excluding lakes with total phosphorus >0.65 $\mu\text{mol/L}$ (20 $\mu\text{g/L}$).

cluded from this analysis because many of them may have experienced anthropogenic inputs of P (53, 144). This test is therefore conservative for N limitation, both because the DIN:TP value chosen (<2) is a conservative measure of N limitation (142) and because some lakes with naturally high concentrations of P may be excluded. These lakes are more likely to be N-limited than lakes with low P concentrations.

Nitrogen Limitation by Region. The proportions of lakes that can be considered N-limited vary widely from region to region, with the greatest number being found, as expected, in the West. The highest proportions were found in the Rocky Mountains (40% of lakes in the area exhibited low DIN:TP ratios), but all subregions of the West contained substantial numbers ($>20\%$) of potentially N-limited lakes. The smallest proportions of N-limited lakes were found in the Northeast and Southeast (9 and 10%, respectively, of the lakes in these regions exhibited low DIN:TP ratios). One surprise in this analysis is the number of lakes in the upper Midwest that appear to be N-limited. Taken as a whole, 28% of this region's lakes had DIN:TP ratios less than 2.

A more direct indication of nutrient limitation than is available from nutrient ratios can be gained from bioassay experiments. In this procedure a small volume of natural lake water is enclosed and various known concentrations of potentially limiting nutrients are added (145–147). A growth response (usually measured as an increase in biomass) in treatments containing an added nutrient constitutes evidence of limitation by that nutrient. The results of such experiments are available for only a few selected nutrient-poor lakes, however. They indicate a variety of responses, including strong P limitation (148), limitation by P and iron (147), simultaneous N and P limitation in which the two nutrients are so closely balanced that addition of one alone simply leads to limitation by the other (147), and limitation primarily by N (142, 149). No clear pattern of N or P limitation develops from an examination of these few studies.

The potential for N deposition to contribute to the eutrophication of freshwater lakes is probably quite limited. Eutrophication by atmospheric inputs of N is a concern only in lakes that are chronically N-limited. This condition occurs in some lakes that receive substantial inputs of anthropogenic P and in many lakes where both P and N are found in low concentrations (e.g., Table III). In the former case the primary dysfunction of the lakes is an excess supply of P, and controlling N deposition would be an ineffective method of water-quality improvement. In the latter case the potential for eutrophication by N addition (e.g., from deposition) is limited by low P concentrations; additions of N to these systems would soon lead to N-sufficient, and phosphorus-deficient, conditions. The results of the NSWS shown in Table III, for example, can be used to calculate the increase in N concentration that would be required to push N-limited lakes into P limitation (assuming total P concentrations do not change). An increase of only

$0.5 \mu\text{mol/L}$ in N concentration would be sufficient to induce P limitation in half of the N-limited lakes in the NSWS target population. In the eastern United States the largest N increases ($0.7 \mu\text{mol/L}$) would be required in Florida and Southern New England, where anthropogenic inputs of P are most likely. The largest increases of all ($1 \mu\text{mol/L}$) would be required in the Southern Rocky Mountains, which has the highest P concentrations of any of the western subregions (median = $0.26 \mu\text{mol/L}$). This P concentration probably results from natural sources of P (e.g., volcanic bedrock). Increases in N deposition to some of the regions in Table III would probably lead to measurable increases in algal biomass in those lakes with low DIN:TP ratios and substantial total P concentrations, but the number of lakes that meet these criteria is likely to be quite small.

Regional Analysis of the Stages of Watershed Nitrogen Loss

If elevated rates of N deposition contribute to watershed N loss, then patterns of N loss might be expected to mimic patterns of N deposition. In the following discussion, the distribution of monitoring sites in the eastern United States with NO_3^- patterns suggestive of the varying stages of watershed N loss is presented as occurring across a gradient in N deposition from relatively low to very high. This space-for-time substitution is a useful tool in assessing whether N saturation is progressing in high-deposition areas. Although important exceptions do occur (e.g., see discussion of Pennsylvania streams in the next section), lakes and streams with Stage 0 patterns tend to occur in low- to moderate-deposition areas; sites with NO_3^- patterns typical of later stages of N loss tend to occur in high-deposition areas. Results are presented as a series of maps, and the discussion progresses from relatively low-deposition areas in the northeastern corner of the country (Maine) to higher deposition areas in western New England and New York, and moves south into the very-high-deposition areas of southern Pennsylvania and West Virginia. Additionally, results from the few monitoring sites in the western United States, where deposition rates are uniformly low, are presented separately.

In general, sites are included in this analysis if published data of more than 2 years' duration in the 1980s are available and if at least a seasonal sampling schedule was used to collect the data. Each site has been assigned to one of six classes. In addition to four classes representing the four stages of watershed N loss, many of the Stage 1 and Stage 2 sites have data of long enough duration to determine whether they are experiencing upward trends in NO_3^- concentrations; Stage 1 and Stage 2 sites with upward NO_3^- trends are included as separate classes on the maps for the following sections. As mentioned earlier, temporal trends in NO_3^- provide important verification that the stages of N loss occur as a sequence in sites experiencing chronically elevated rates of N deposition.

The Northeastern United States. For approximately 100 sites in the Northeast, the data are intensive enough to determine their status with respect to watershed N loss (Figure 9). From the standpoint of N, the Northeast is the most data-intensive region of North America. Seasonal data are available from a spatially extensive network of sites, so that geographic patterns in watershed N loss can be inferred. Importantly, these geographic patterns in watershed N loss follow the geographic pattern in N deposition, with the most severe effects observable in the Adirondack and Catskill mountains, where deposition rates are high, and little N loss in Maine, where rates of N deposition are roughly 50% lower (42).



Figure 9. Location of acid-sensitive lakes and streams in the northeastern United States where the importance of NO_3^- to seasonal water chemistry can be determined. Only data from undisturbed watersheds are included. (Data are from references 109, 114, 118, 119, 151b, 154, 156–159, 162, 164, 191–194.)

Data from sites in Maine, Vermont, and the Adirondack and Catskill mountains are available from the U.S. Environmental Protection Agency's (EPA) Long-Term Monitoring (LTM) Project (150). In most cases the records from these sites are sufficiently long (7–10 years) to detect trends where they are present. Most of the other sites in Figure 9 have data of shorter duration, and it is not known whether they exhibit long-term trends.

All of the sites in the state of Maine show some seasonality in NO_3^- concentrations, with peak concentrations of less than $20 \mu\text{equiv/L}$ during spring snowmelt and negligible concentrations during all other seasons; the concentrations suggest typical Stage 0 NO_3^- patterns. Data from five LTM lakes in Maine exhibit no long-term trends in NO_3^- concentrations (151a).

Seasonal data are available from two sites in New Hampshire, where deposition rates are slightly higher than in Maine. Baird et al. (151b) studied episodic acidification during snowmelt at Cone Pond, New Hampshire, and were unable to detect any NO_3^- in inlet water. Researchers at the Hubbard Brook Experimental Forest in New Hampshire have been studying the watershed processes and their effects on stream-water chemistry since 1963 (152). In reference Watershed No. 6, stream-water NO_3^- concentrations undergo strong seasonal cycles with peak concentrations as high as $85 \mu\text{equiv/L}$ during snowmelt, similar to Stage 1 watershed N loss. Both NO_3^- and hydrogen ion concentrations increase during snowmelt at Hubbard Brook, although SO_4^{2-} concentrations decrease slightly (153, 154). No long-term trend in stream-water NO_3^- concentration is detectable for the 23-year period of record at Hubbard Brook (155).

In the state of Vermont, 6 of 24 LTM lakes exhibit strong seasonal NO_3^- cycles, and in these lakes seasonal NO_3^- increases are the most important mechanism contributing to spring ANC minima (156). These six watersheds exhibit the characteristics of Stage 1 of N loss, and the remaining 18 lakes exhibit Stage 0 patterns. None of the sites exhibit trends in NO_3^- concentrations for the period 1981–1989.

Driscoll and Van Dreason (157) reported data from 16 Adirondack LTM lakes collected between 1982 and 1990. The patterns in acid-base chemistry at Constable Pond (Figure 10), one of the Adirondack LTM lakes, can be considered typical of surface waters in the Northeast with episodically elevated concentrations of NO_3^- (e.g., at Stages 1 and 2). Constable Pond becomes acidic only during seasons of high runoff, as a result of base-cation dilution and episodic NO_3^- increases. Sulfate concentrations are relatively invariant. In Constable Pond, as in other Adirondack lakes and streams, short-term changes in NO_3^- were highly correlated, and chemically consistent, with changes in the concentrations of acidic cations (hydrogen and aluminum) (155). As mentioned earlier, although dilution of base cations and increases in NO_3^- appear to be the primary causes of episodic acidification in Constable Pond, these episodes are excursions from an already low base-line ANC, which can be attributed largely to high SO_4^{2-} concentrations.

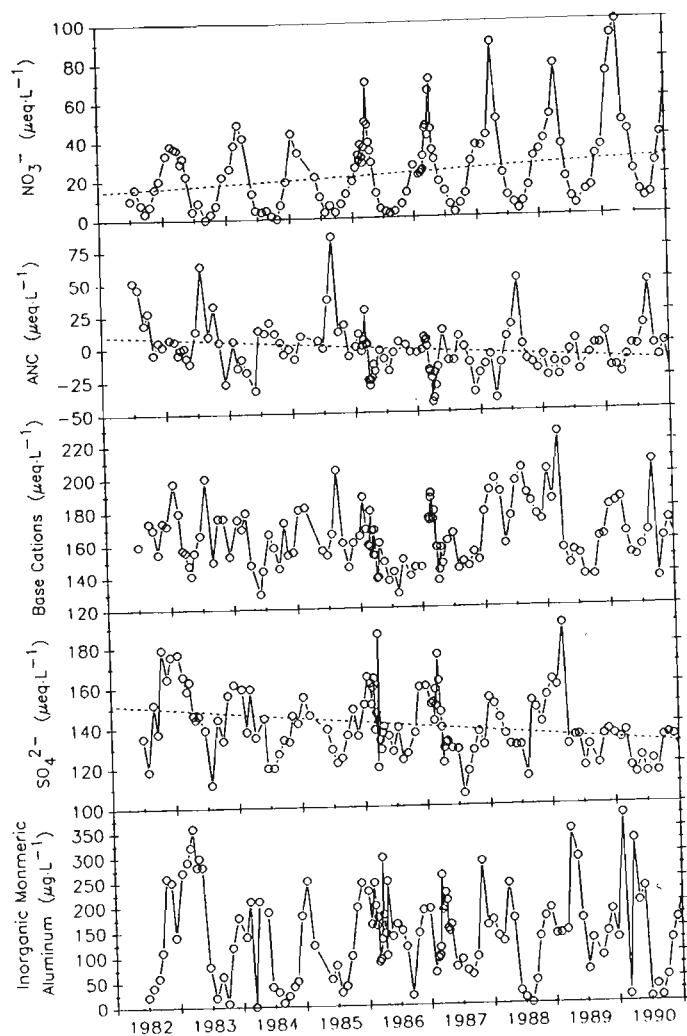


Figure 10. Temporal patterns in lake-water NO_3^- , acid-neutralizing capacity (ANC), base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$), SO_4^{2-} , and inorganic monomeric aluminum (Al) at Constable Pond, a long-term monitoring site in the Adirondack Mountains. Trend lines are shown for variables with significant trends ($p < 0.10$ in seasonal Kendall tau test). Seasonal pattern is typical of Adirondack lakes, with seasonal minima in ANC coincident with seasonal maxima in NO_3^- and Al. Many Adirondack lakes exhibited upward trends in NO_3^- in the 1980s; the primary increase was in episodic NO_3^- concentrations. (Data are from reference 157.)

The period of record is long enough for the Adirondack LTM lakes that long-term trends in NO_3^- concentrations can be estimated (Table IV; ref. 157). Nine out of sixteen Adirondack lakes exhibited significant increases in NO_3^- concentrations, with typical slopes of trends being $+1 \mu\text{equiv/L}$ per year. Data from the seven remaining lakes all suggested upward trends in NO_3^- that were not significant (Table IV). Additionally, plots of temporal NO_3^- patterns indicate that the primary change in these lakes is in their spring values (Figure 10) and that baseflow NO_3^- concentrations are relatively unchanged. This analysis suggests that these lakes are in Stage 1 of watershed N loss and that their condition is worsening.

In low-ANC streams of the Catskills increases in NO_3^- , base-cation dilution, and high-baseline SO_4^{2-} concentrations all contribute to acidic episodes (97). In Biscuit Brook, an intensively studied headwater stream in the Catskills, concentrations of NO_3^- approach or exceed those of SO_4^{2-} during episodes (Figure 11; ref. 127). Values for the ratio of $\text{NO}_3^- : (\text{NO}_3^- + \text{SO}_4^{2-})$, as presented in Table II, illustrate both the general importance of NO_3^- to the acid-base dynamics of this stream and the increase in importance of NO_3^- during high-flow events (Figure 11). Nitrate concen-

Table IV. Trends in NO_3^- Concentrations for Adirondack Long-Term Monitoring Lakes

Lake Name	n ^a	Change in NO_3^- ^b ($\mu\text{equiv/L}$ per year)	p
Arbutus Lake	90	+1.06	<0.01
Big Moose Lake	98	+0.92	0.20
Black Lake	99	+0.00	0.60
Bubb Lake	99	+0.32	0.43
Cascade Lake	98	+0.15	0.65
Clear Pond	97	+0.48	0.02
Constable Pond	99	+1.65	0.03
Dart Lake	99	+0.90	0.08
Heart Lake	98	+0.83	0.01
Lake Rondaxe	99	+0.72	0.09
Little Echo Pond	97	+0.00	0.23
Moss Lake	99	+0.42	0.30
Otter Pond	94	+1.33	0.02
Squash Pond	93	+1.80	0.03
West Pond	99	+0.41	0.07
Windfall Lake	99	+0.46	0.40

NOTE: Slopes are calculated from seasonal Kendall tau test (204, 205). Trends with slopes significantly different from 0 ($p < 0.10$) are shown in bold print.

^aNumber of individual observations; the period of record for most sites is from June 1982 to December 1990.

^bSlopes are medians of the differences between all possible pairs of sequential observations within the same month (204).

SOURCE: Data are taken from reference 157.

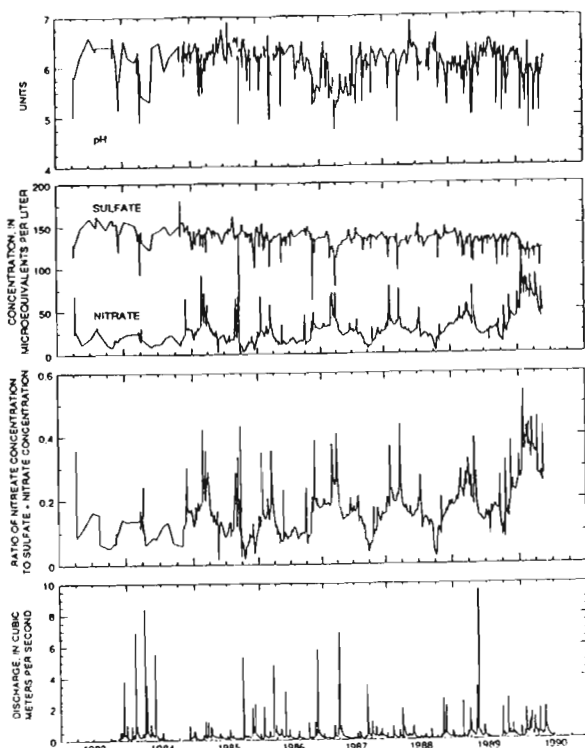


Figure 11. Temporal patterns in stream-water pH, SO_4^{2-} , NO_3^- , ratio of $\text{NO}_3^- : (\text{NO}_3^- + \text{SO}_4^{2-})$, and stream discharge at Biscuit Brook in the Catskill Mountains, 1983–1990. All chemical variables undergo strong seasonality, with strong dependence on stream discharge. As in Adirondack lakes, minima in ANC are coincident with maxima in NO_3^- . Values for the ratio of $\text{NO}_3^- : (\text{NO}_3^- + \text{SO}_4^{2-})$ approach or exceed 0.5 during episodes and indicate that NO_3^- can have as important an acidifying influence as SO_4^{2-} during high-flow events. Significant increases ($p < 0.05$ in seasonal Kendall tau trend test) in NO_3^- concentration ($+2 \mu\text{equiv/L}$ per year) and $\text{NO}_3^- : (\text{NO}_3^- + \text{SO}_4^{2-})$ ($+0.014$) were recorded during the 1980s, indicating the increasing importance of NO_3^- both in absolute terms and in comparison to SO_4^{2-} . (Reproduced with permission from reference 127. Copyright 1992 American Geophysical Union.)

trations remain elevated ($>20 \mu\text{equiv/L}$) throughout all seasons, except for a short period during the autumn. This seasonal pattern has two important implications. First, it suggests that the watershed of this headwater stream (as well as those of seven other headwater LTM streams; 158) has reached Stage 2 of watershed N loss, as indicated by elevated groundwater and stream baseflow NO_3^- concentrations. Second, it suggests that the N demand on

the part of the watershed exceeds the N supply only during a short period immediately following leaffall in the autumn, when the major demand for N is on the part of decomposers rather than plants (127).

Historical data are available from 19 large streams (third and fourth order) in the Catskill Mountains, some of which have been monitored since early in this century (79, 97). Trend analyses indicate that NO_3^- concentrations have increased in all of the streams (Table V), with most of the increase occurring in the past 2 decades (97, 127). These increases are not attributable to watershed anthropogenic sources of N (i.e., point and nonpoint sources of pollution) and are similar to trends observed in eight headwater streams monitored in the 1980s as part of the U.S. EPA LTM project (Table V) (97, 127, 158).

However, the seasonal NO_3^- pattern of the large streams differs from that of Biscuit Brook and the LTM streams. In the large streams, the primary change in NO_3^- has been in episodic concentrations. At four historical Catskill sites where stream discharge data are available, for example, the relationships between NO_3^- concentration and discharge were steeper in the 1980s than in the past (Figure 12). Most of the increase in NO_3^- has occurred at high flows. Apparently these streams have progressed from Stage 0 in the early part of the record to Stage 1 in the 1970s and 1980s. Thus far only small increases in baseflow NO_3^- concentrations have occurred. If these increases continue, however, as they apparently have at Biscuit Brook and the Catskill LTM streams, then important documentation of the progression from Stage 0 to Stage 1 to Stage 2 would exist; further monitoring should verify whether such a sequence is taking place. Taken in all, monitoring data from Catskill streams suggest that the region currently contains a mixture of Stage 1 and Stage 2 watersheds, and that N loss from all watersheds is increasing with time.

Additional evidence indicates increasing NO_3^- concentrations in the Northeast. Kramer et al. (159) reported on NO_3^- trends for four northeastern streams in the U.S. Geological Survey (USGS) Bench-Mark Stream network. Excluding data from one stream that drains a disturbed watershed, two of the three streams (Esopus Creek in the Catskill Mountains and Young Woman's Creek in Pennsylvania) exhibit increasing trends of about $+1 \mu\text{equiv/L}$ of NO_3^- per year for the period 1967 to 1985. Smith et al. (160) examined trends in NO_3^- data from 383 stream locations in the United States collected between 1974 and 1981. They reported increases at 167 sites, especially east of the 100th meridian. Many of the increasing trends could be attributed to increased use of fertilizers in agricultural areas, particularly in the Midwest. In addition to agricultural runoff, Smith et al. identified atmospheric deposition as a major source of NO_3^- in surface waters, particularly in forested basins of the East (e.g., New England and the mid-Atlantic) and Upper Midwest. Despite widespread use of fertilizers in most of the regions covered by the Smith et al. study, they found a high degree of

Table V. Changes in NO₃⁻ Concentration in Historical Monitoring Streams and U.S. EPA Long-Term Monitoring Streams in the Catskill Mountains of New York

Site	Before 1945	1945-1970	After 1970
<i>Historical sites</i>			
Batavia Kill ^a	+0.24	+0.21	+0.28
Bear Kill above Grand Gorge ^b	—	—	+0.70
Bear Kill above Hardenbergh Falls	+0.34	—	—
Beaver Kill ^a	+0.05	+0.10	+1.76
Birch Creek above Pine Hill	—	+0.60	+2.68
Birch Creek at Pine Hill	-0.01	+0.68	+0.73
Biscuit Brook			
Bush Kill	+0.11	+0.00	+2.28
Bushnellville Creek ^a	+0.04	+0.25	+1.57
East Branch Neversink, Headwaters			
East Branch Neversink, Midlength			
Esopus Creek above Big Indian	+0.08	—	—
Esopus Creek below Big Indian	-0.16	-0.01	+1.98
Esopus Creek at Coldbrook	+0.24	-0.08	+2.00
High Falls Brook			
Hollow Tree Brook			
Little Beaver Kill ^a	+0.00	+0.01	+0.85
Manor Kill	-0.12	-0.55	+0.97
Neversink River	—	+0.33	+1.28
Rondout Creek	—	+0.00	+1.79
Schoharie Creek at Prattsville	+0.64	-0.13	+1.93
Stony Clove Creek ^a	-0.00	+0.08	+3.77
West Kill	+0.19	—	—
Woodland Creek ^a	+0.02	+0.08	+3.95
<i>Long-term monitoring sites (current)</i>			
		Since 1983	
Beaver Kill		n.s.	
Biscuit Brook		+2.03	
East Branch Neversink, Headwaters		n.s.	
East Branch Neversink, Midlength		+1.28	
High Falls Brook		+1.90	
Hollow Tree Brook		+2.20	
Rondout Creek		+2.93	
Woodland Creek		n.s.	

NOTE: — indicates insufficient data for analysis; n.s. indicates trend is not significant.

^aData for these sites are available only for periods before 1945 and from 1977 to 1979. Trends reported for the periods of missing data are based on regression lines for the entire data set; median values cannot be listed.

^bData are available for fewer than 2 years in one or more time periods at this site. Trends were not calculated during these time periods at this site, but median values and sample sizes are listed.

SOURCE: Reproduced from reference 127. Copyright 1992 American Geophysical Union.

correlation between stream basin yield of NO₃⁻ and rates of N deposition. The significance of this correlation should be strongly questioned, however, given the overwhelming importance of fertilizer use in this study.

A cautionary note in the interpretation of long-term N trends is introduced by examination of long-term data from streams at the Hubbard Brook

Experimental Forest (HBEF). Data from control Watershed No. 6 for 1963-1977 suggested a strongly increasing trend in NO₃⁻ (161). These data have been used to suggest that the HBEF watersheds are undergoing N saturation (25). Examination of the entire 23-year record (1965-1983) from Watershed No. 6, however, shows no long-term trend (154, 155). This result emphasizes the importance of examining N processes in a truly long-term context. Although some of the data reported here for the Catskill Mountains can be considered truly long-term (up to 65 years of record), data for the Adirondack Mountains (157) and other areas of the United States (160) span only 1-2 decades and should be interpreted with caution.

Finally, no significant effect of NO₃⁻ on episodic acidification has been observed in some areas of the Northeast. Morgan and Good (162) reported data on 10 streams in the New Jersey Pine Barrens and found mean annual NO₃⁻ greater than 1 µequiv/L only in residential and agricultural watersheds. Importantly, Swistock et al. (163) and Sharpe et al. (164-166) reported data on episodic acidification of several streams in the Laurel Hill area of southwestern Pennsylvania. They found that NO₃⁻ played only a minor role in stream acidification and fish kills. Rates of N deposition in this region of Pennsylvania are among the highest in the United States, yet these watersheds appear to remain at Stage 0 of watershed N loss. As mentioned earlier, the three characteristics that predispose watersheds to N saturation are elevated N deposition, advanced stand age, and high soil-N pools. Important information could be gained from an examination of the latter two factors at these seemingly anomalous sites in southwestern Pennsylvania.

The Southeastern United States. There are far fewer sites with sufficiently intensive data to determine their watershed N loss status in the Southeast than in the Northeast (Figure 13). The spatial coverage of sites in the Southeast with seasonal data is poor, and few sites have the long-term data needed to detect trends in NO₃⁻ concentrations.

One important exception is Control Watershed No. 4 at the Fernow Experimental Watershed near Parsons, West Virginia. Edwards and Helvey (167) reported data on stream chemistry in Watershed No. 4 for 1971-1987. Their data indicate that there has been a substantial increase in the loss of NO₃⁻ from this watershed over the past 2 decades (Figure 14b) and that mean annual NO₃⁻ concentrations have increased at the rate of approximately +3 µequiv/L per year. The apparent decrease in mean annual NO₃⁻ in the late 1980s is not significant and is primarily driven by hydrological changes. Important analytical changes occurred during the period of record at this site [NO₃⁻ concentrations were measured by the Hach method (168) prior to 1981 and by ion chromatography thereafter (167)], however, and the trend data should be interpreted with caution. Nonetheless, intensive data measured with consistent methods during the 1980s suggest that baseflow NO₃⁻ concentrations are currently as high as or slightly higher than those in deposition and that episodic concentrations are somewhat higher yet (Figure

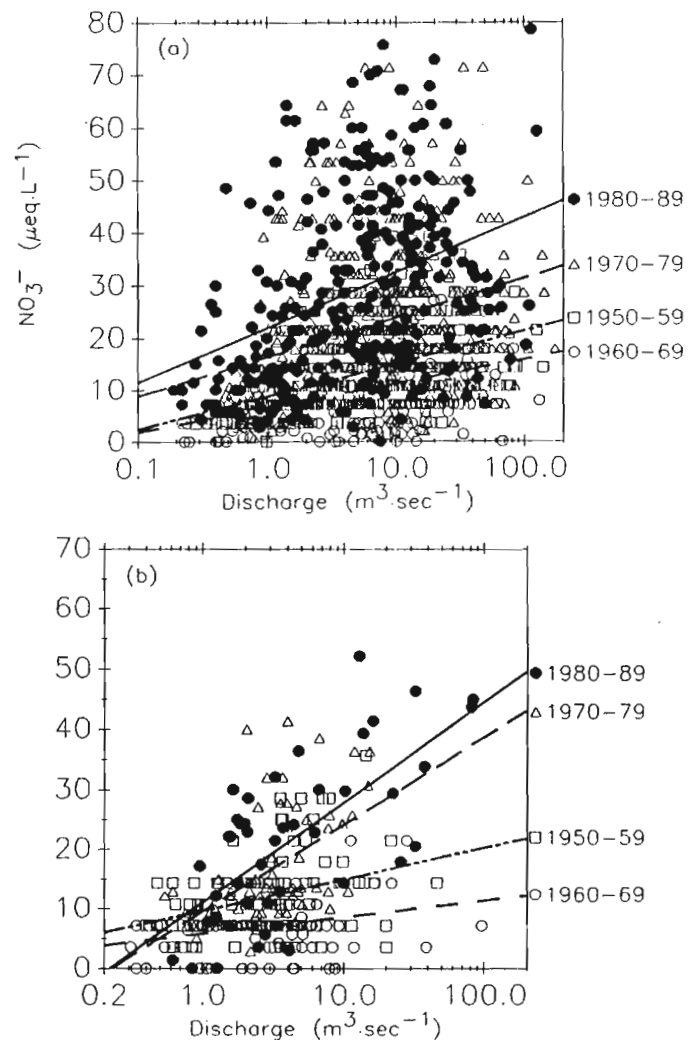


Figure 12. Nitrate concentration as a function of stream discharge in four Catskill streams during 4 decades of data collection, 1950-1989: a, Schoharic Creek at Prattsville; b, Neversink River at Claryville. Regression lines for each decade are from least-squares regression of concentration on the log of stream discharge. All slopes are significantly different from 0 ($p < 0.01$) except for Rondout Creek in the 1960s. All sites indicate that NO_3^- concentrations at high discharges were higher in the 1970s and 1980s than in previous decades. Little change is evident in baseflow NO_3^- concentrations. The stability suggests that these sites are at Stage I of watershed N loss but that episodic conditions are worsening. (Reproduced with permission from reference 127. Copyright 1992 American Geophysical Union.)

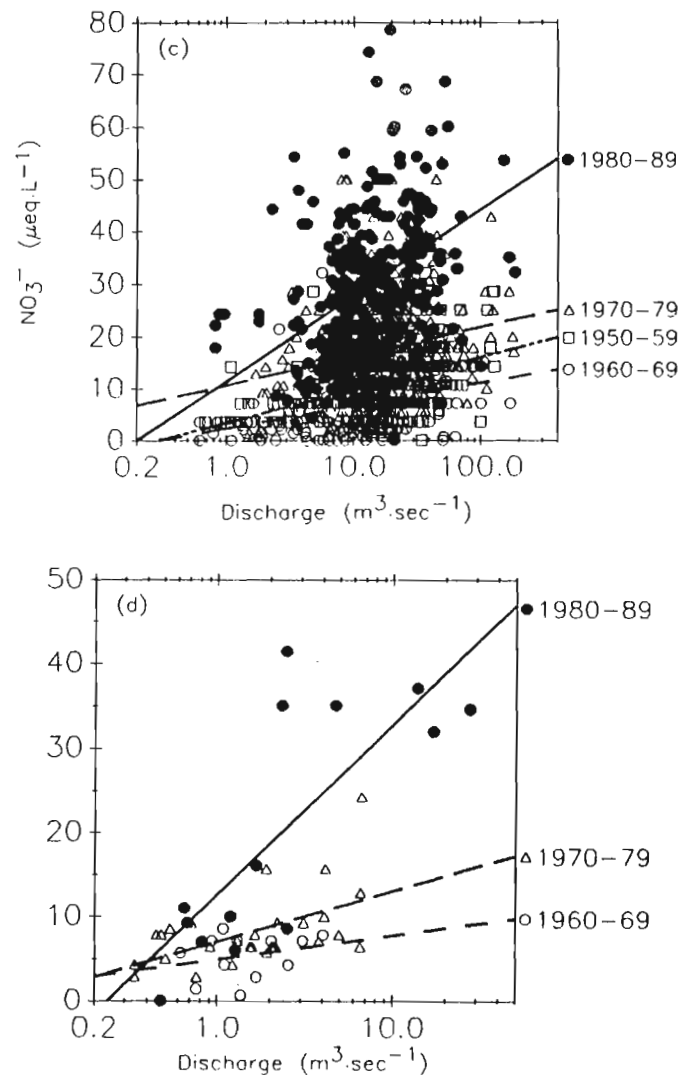


Figure 12. Continued. c, Esopus Creek at Coldbrook; and d, Rondout Creek at Lowes Corners.

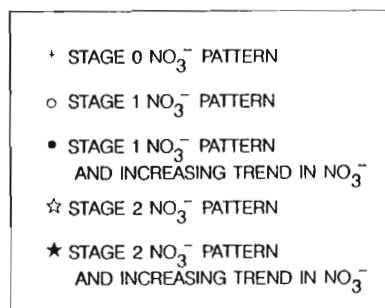
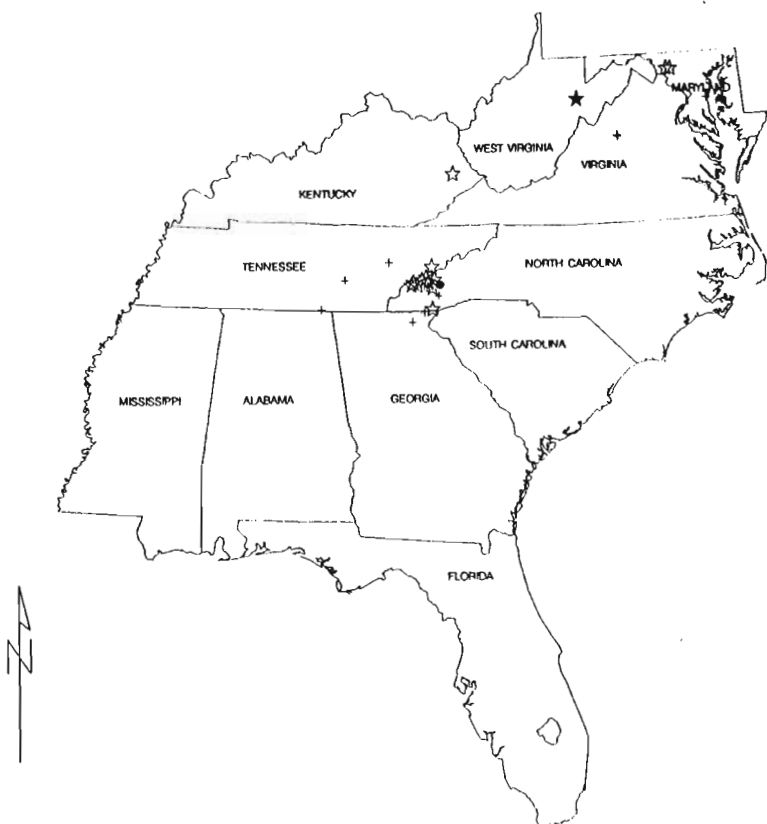


Figure 13. Location of acid-sensitive lakes and streams in the southeastern United States where the importance of NO_3^- to seasonal water chemistry can be determined. Only data from undisturbed watersheds are included. (Data are from references 99, 109, 159, 167, 170–172, 174–176, 195, 196.)

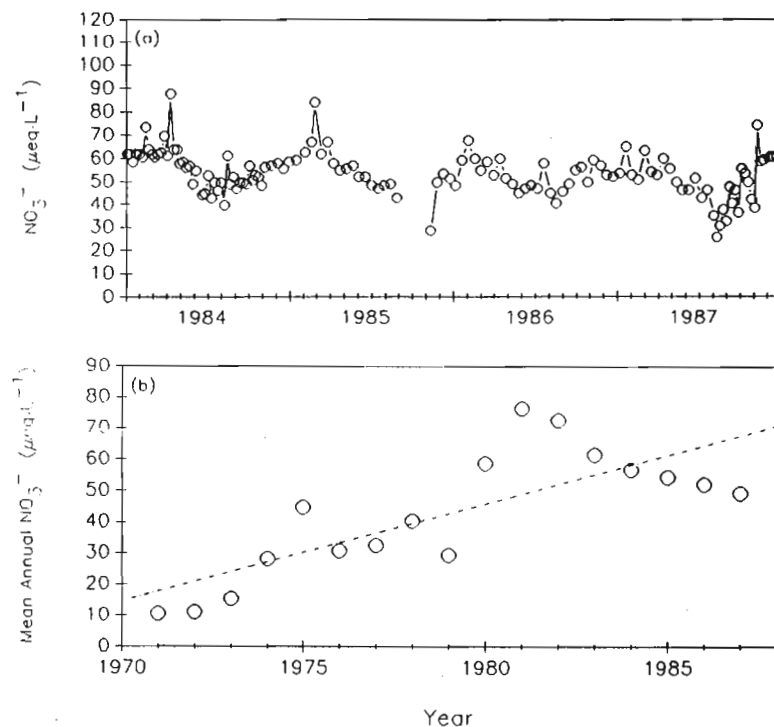


Figure 14. Stream-water chemistry for control watershed No. 4 at the Fernow Experimental Forest in West Virginia. a. Seasonal pattern in NO_3^- indicates both elevated baseflow concentrations and episodic increases during high-flow events in the spring and thus suggests that this watershed has reached Stage 2 of watershed N loss. b. The long-term trend suggests that substantial changes in NO_3^- export have occurred over the past 2 decades. (Data are from reference 167.)

14a). The Fernow site may be the best available example of a watershed at Stage 2 of watershed N loss. This suggestion is strengthened by the results of fertilizer experiments that were carried out in the 1970s at a nearby Fernow watershed. Edwards et al. (169) reported that an application of ammonium nitrate (at 336 kg/ha of N) resulted in large increases in stream-water exports, but that the largest portion of N loss was measured in deep seepage. This experimental result confirms that groundwater N losses can be substantial in Stage 2 watersheds.

The highest recorded NO_3^- concentrations in streams draining undisturbed watersheds in the United States come from the Great Smoky Mountains in Tennessee and North Carolina. Nitrate concentrations in Raven Fork

(170) and several other high-elevation streams (99, 171) range from 50 to 100 $\mu\text{equiv/L}$. In all cases they are comparable to, or higher than, SO_4^{2-} concentrations (*see also* Table II). In a survey of stream chemistry at a large number of sites in the Great Smoky Mountains, Silsbee and Larson (172) reported baseflow NO_3^- concentrations ranging from 0.2 to 90 $\mu\text{equiv/L}$. NO_3^- concentrations were highest at higher elevations and in areas of old-growth spruce-fir forest that have never been logged. In many cases NO_3^- concentrations in streams of the Great Smoky Mountains are higher than N concentrations in deposition. This comparison implies both that rates of biological N uptake are low and that mineralization rates are high (173). This pattern also indicates watersheds that have reached Stage 3 of watershed N loss. At this point watersheds may become sources, rather than sinks, for N. As mentioned earlier, the suggestion that watersheds in this area are at Stage 3 is supported by results from soil lysimeter studies, in which NO_3^- fluxes in deep soil lysimeters were higher than N inputs from deposition and throughfall (100). Unfortunately, few data are available to suggest the original source of the N now being mineralized in this region. The data of Silsbee and Larson (172) suggest strongly that forest maturation is linked to the process of NO_3^- leakage from Great Smoky Mountain watersheds. Mineralization of soil N appears to be high only in old-growth forests (171).

Small increases in NO_3^- concentrations during hydrological events have been recorded at sites in a few other areas of the Southeast, including northeastern Georgia (174), where maximum concentrations were ~ 12 $\mu\text{equiv/L}$. Cosby et al. (175) examined 7 years' worth of data from two streams in Virginia and found no evidence of NO_3^- episodes; NO_3^- concentrations are always less than 15 $\mu\text{equiv/L}$ in these streams. Swank and Waide (176) reported data from seven undisturbed watersheds at the Coweeta Hydrologic Laboratory in North Carolina, where the volume-weighted mean concentrations of NO_3^- were less than 1.5 $\mu\text{equiv/L}$. In all of these cases, undisturbed watersheds exhibit Stage 0 patterns of watershed N loss.

The Western United States. Several studies have reported the existence of NO_3^- episodes in western United States, including the North Cascades (177, 178) and Sierra Nevada Mountains (179) (Figure 15). In general, the maximum NO_3^- concentrations observed in the West are less than 15 $\mu\text{equiv/L}$, substantially lower than in most of the eastern United States. Lakes in the mountainous West, however, tend to be much more dilute and therefore more sensitive to acidic deposition than lakes in the East. Of lakes in the Sierra Nevada Mountains, for example, 39% have ANC values less than 50 $\mu\text{equiv/L}$, as do 26% of the lakes in the Oregon Cascades and 17% of the lakes in the North Cascades (143).

Rates of N deposition are also much lower in the West (Table I), and episodic NO_3^- concentrations of 15 $\mu\text{equiv/L}$ should be placed in the context of mean concentrations of NO_3^- and NH_4^+ in deposition of 5.0 and 5.4

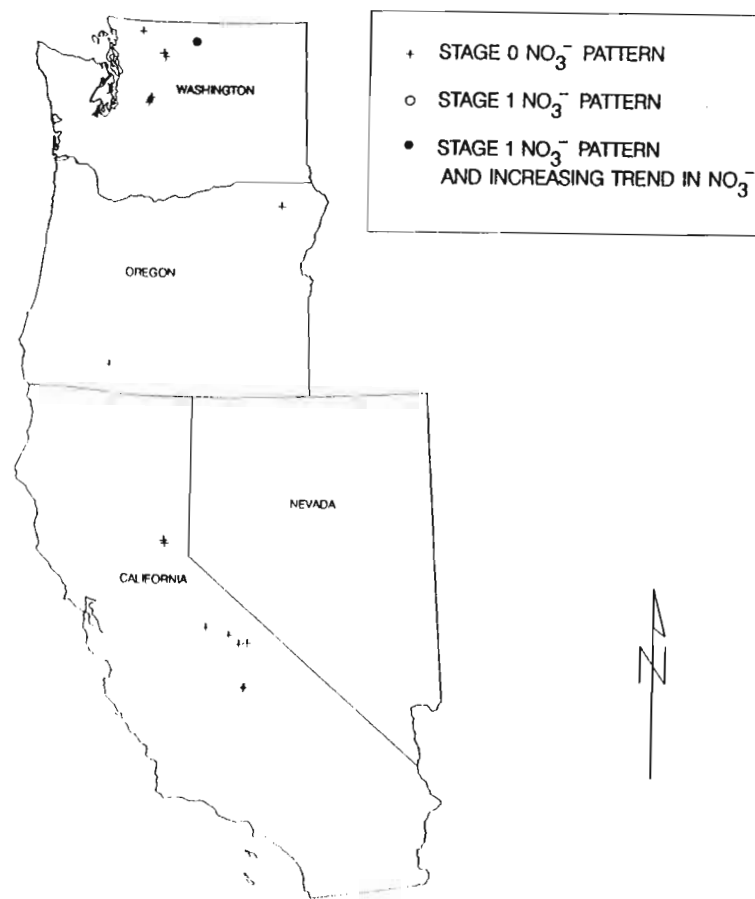


Figure 15. Location of acid-sensitive lakes and streams in the western United States where the importance of NO_3^- to seasonal water chemistry can be determined. Only data from undisturbed watersheds are included. (Data are from references 109, 117, 159, 177, 179, 197-199.)

$\mu\text{equiv/L}$, respectively (7). Combined with base-cation dilution and small concentrations of SO_4^{2-} , the NO_3^- increases observed during episodes at Emerald Lake in the Sierra Nevada Mountains have been sufficient to drive ANC to 0 on two occasions in the past decade (7, 180). Data from the outflow at Emerald Lake in 1986 and 1987 (Figure 16) indicate that minimum ANC values are coincident with maximum concentrations of NO_3^- and diluted base-cation concentrations resulting from high discharge. However, at no

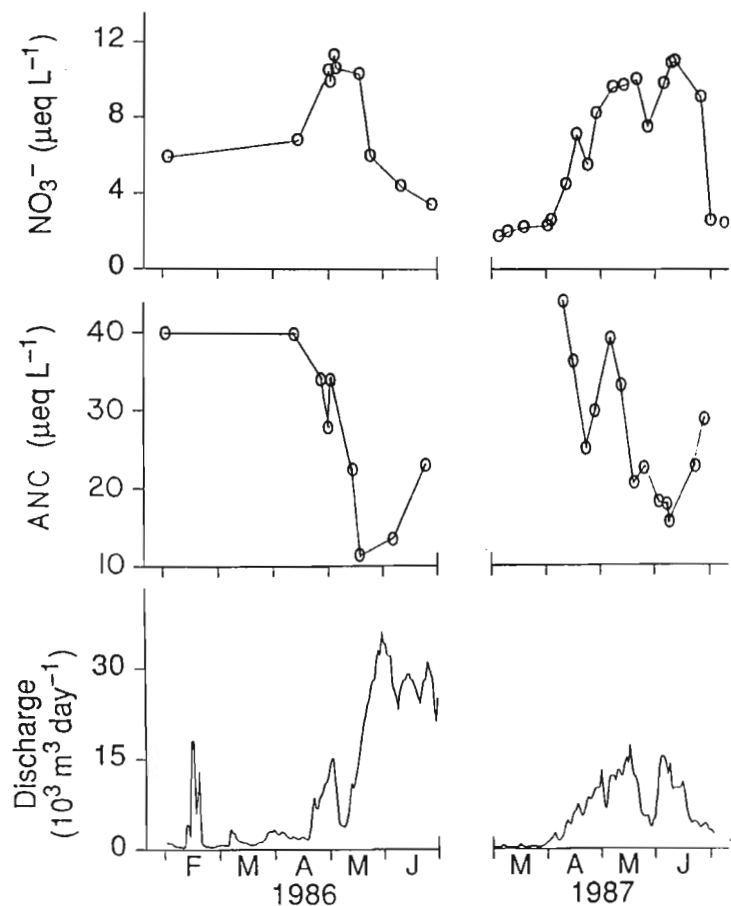


Figure 16. Outflow chemistry from two snowmelt seasons (1986 and 1987) at Emerald Lake, a high-elevation lake in the Sierra Nevada Mountains of California. Maximum NO_3^- concentrations are coincident with ANC minima during the early stages of snowmelt in 1986 and with a rain-on-snow event in 1987. Nitrate episodes are smaller in magnitude than at sites in the eastern United States, but western lakes may be more susceptible to episodic acidification because they have a lower baseline acid-neutralizing capacity than most eastern lakes. (Reproduced with permission from reference 180. Copyright 1991 American Geophysical Union.)

time has the pH of Emerald Lake fallen below 5.5, a level commonly considered the threshold for injury to fish populations. ANC values of 0 can be caused by base-cation dilution alone (a natural process).

The state of episodic acidification in the Sierra Nevada Mountains (and the rest of the West) therefore remains uncertain because few data exist and the data that are available indicate ANC depressions to a value of 0 $\mu\text{equiv/L}$, but not below. For the time being, most western sites would be classified as Stage 0 watersheds. However, in systems as acid-sensitive as those at high elevations in the West, episodic acidification resulting from NO_3^- may be possible in the watersheds that are only seasonally N-saturated.

Links Between Nitrogen Loss and Nitrogen Deposition

The presence of elevated NO_3^- concentrations in streams draining undisturbed forested watersheds does not necessarily implicate N deposition as the source of the N being exported. Currently, little direct evidence links N deposition with either elevated baseflow NO_3^- concentrations or elevated episodic NO_3^- concentrations and acidic episodes. This lack of evidence stems at least partially from a lack of appropriate data to link deposition to stream-water NO_3^- concentrations. High concentrations of NO_3^- during snowmelt, for example, may result when NO_3^- stored in the snowpack during the winter months is released while the forest is still dormant. The reduced biological activity typical of the winter months creates less demand for N, and snowpack NO_3^- may simply run off without entering the N cycle of the forest or watershed. Several mechanisms, however, amplify the signal produced by atmospheric deposition of N to snowpacks. These mechanisms, which will be discussed in more detail, include

- preferential elution of NO_3^- during the early stages of snowmelt;
- nitrification of NH_4^+ to NO_3^- within soils or the snowpack;
- dry deposition of N to the snowpack before melting; and
- mineralization of soil-N pools over the winter.

In areas with large snowpacks (e.g., much of the Northeast and all of the mountainous West), ions have been shown to drain from the pack in the early stages of snowmelt. This process leads to concentrations that are much higher than the average concentration of the snowpack itself (82). Differential elution of acid anions (like NO_3^-) during the initial stages of snowmelt has been shown to be responsible for the elevated NO_3^- concentrations observed in parts of Scandinavia (81), Canada (82), the Adirondack Mountains (181), the Midwest (182), and the Sierra Nevada Mountains (180). Ammonium deposited to the snowpack (either wet or dry deposition) can subsequently

be nitrified to NO_3^- in soils or while still in the snowpack. This reaction would produce NO_3^- concentrations elevated over those calculated from NO_3^- deposition alone (83, 110, 114, 183). Dry deposition of N compounds to the snowpack may also be an important source of NO_3^- in snowmelt water (110, 183). Jeffries (82) presented a review of snowpack storage and release of pollutants during snowmelt.

Some evidence does exist that mechanisms other than atmospheric deposition contribute to NO_3^- episodes, at least on a small scale. Rascher et al. (43), for example, showed that mineralization of organic matter in the soil during the winter months and subsequent nitrification contribute substantially to snowmelt NO_3^- concentrations at one site in the Adirondacks. Schaefer and Driscoll (83) suggested that a similar phenomenon contributes to NO_3^- pulses during snowmelt at 11 Adirondack lakes and that the contribution from mineralization is greater in low-ANC and acidic lakes. Murdoch and Stoddard (127) presented similar results for streams in the Catskill Mountains. Stottlemyer and Toczydlowski (184) also reported that mineralization contributes to snowmelt NO_3^- at a site on the upper peninsula of Michigan. It is not currently known how widespread this phenomenon is.

Some question remains of whether N produced from mineralization is indirectly supplied by atmospheric deposition. Mineralization recycles N from leaf litter, a portion of which undoubtedly originates as atmospheric deposition. Friedland et al. (18) calculated that roughly 30% of the annual N demand of spruce-fir forests in the Adirondack Mountains can be met by deposition alone, setting an upper limit to the proportion of mineralized N that may come indirectly from deposition on an annual basis. In addition, chronic N deposition may also influence the loss of mineralized N by altering the timing of N cycle and providing an opportunity for N to leave the watershed during snowmelt (see discussion of Stage 1), by contributing to the pool of organic N (through fertilization) available for mineralization, or by increasing the rate of mineralization through fertilization (the so-called "priming effect"; 185).

Many of these data suggest that NO_3^- episodes are more severe now than they were in the past, and in some cases that baseflow NO_3^- concentrations have increased. These surface-water N increases have occurred at a time when N deposition has been relatively unchanged in the eastern United States (186-188). If we accept the idea that increases in lake and stream-water NO_3^- concentrations are evidence that N saturation of watersheds is progressing, then current data suggest that present levels of N deposition (350-700 equiv/ha per year) are sufficient to drive this progression in the Adirondack Mountains, the Catskill Mountains, the mountains of West Virginia, and the Great Smoky Mountains. Data from the National Stream Survey (96) suggest a strong correlation between concentrations of stream-water N ($\text{NO}_3^- + \text{NH}_4^+$) at spring baseflow and levels of wet N deposition ($\text{NO}_3^- + \text{NH}_4^+$) in each of the NSS regions (Figure 17a). The only exception

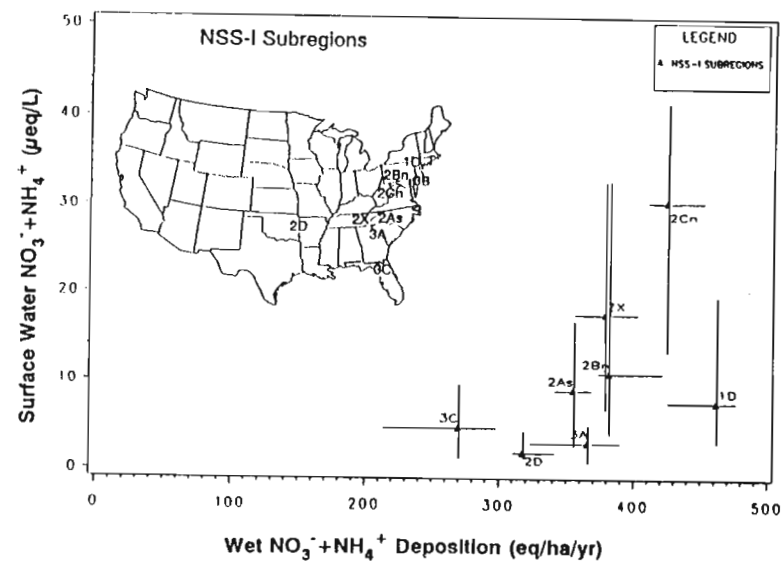


Figure 17a. Relationship between median wet deposition of N ($\text{NO}_3^- + \text{NH}_4^+$) and median surface-water N ($\text{NO}_3^- + \text{NH}_4^+$) concentrations for physiographical districts within the National Stream Survey that have minimal agricultural activity. [Subregions are Poconos-Catskills (1D), Southern Blue Ridge Province (2Bn), Valley and Ridge Province (2As), Northern Appalachians (2Cn), Ozarks-Ouachitas (2D), Southern Appalachians (2X), Piedmont (3A), mid-Atlantic Coastal Plain (3B), and Florida (3C)]. (Panel a is reproduced with permission from reference 96. Copyright 1991 American Geophysical Union.)

to this relationship is the Pocono-Catskill region, where N deposition is highest (450 equiv/ha per year) but where stream-water N concentrations fall below what is expected on the basis of results from the other regions. The median stream-water NO_3^- value for the Catskills alone (Table II) is 29 $\mu\text{equiv/L}$ (79). This value fits the usual relationship much more closely, suggesting that watersheds in the southern portion of this region (the Poconos) are retaining N more strongly than the northern portion. This interpretation is also consistent with the low loss rates of N from watersheds in southwestern Pennsylvania that were discussed earlier.

Driscoll et al. (155) summarized the relationship between N export and N deposition that is indicated by input-output budget data from a large number of watersheds in the United States and Canada; these data are augmented in Figure 17b with results from recently published reports. Driscoll et al. (155) stressed that the data illustrated in Figure 17b were collected by using widely differing methods and various time scales (from 1 year to

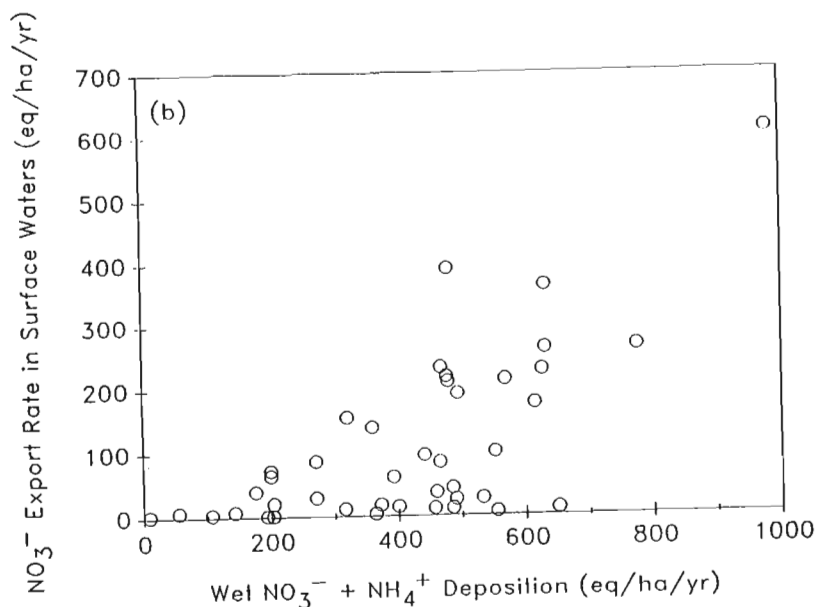


Figure 17b. Relationship between wet deposition of N ($\text{NO}_3^- + \text{NH}_4^+$) and rate of N export for watershed studies throughout North America. Sites with significant internal sources of N (e.g., from alder trees) have been excluded. (Original data in panel b are from reference 155; additional data are from references 117, 119, 127, 164, 167, 171, 174, 175, 179, 192, 193, 195.)

several decades). However, both relationships illustrated in Figure 17 indicate that watersheds in many regions of North America are retaining less than 75% of the N that enters them and that the amount of N being leaked from these watersheds is higher in areas where N deposition is highest. This pattern is consistent with what we would expect if large areas of the eastern United States were experiencing the early stages of N saturation, but is not proof of this situation. Both analyses suggest a threshold value of wet deposition of N (~ 300 equiv/ha per year), above which substantial watershed losses of N might begin to occur. Because dry deposition is not included in these analyses, we can only speculate that threshold values for total deposition (wet + dry) would be substantially higher.

Conclusions

Considerable evidence indicates that high rates of N deposition are contributing to the degradation of water quality in several regions of the United States. The primary effect of deposition appears to be the episodic acidifi-

cation of surface waters. There is no hard evidence of chronic acidification by NO_3^- in the United States (streams in the Great Smoky Mountains may be an exception, but few high-quality data have been published for this area), and no conceptual mechanism exists for deposition to contribute to the long-term eutrophication of lakes.

When seasonal data on stream and lake chemistry are available, it is possible to place sites into a progressive scheme of watershed N loss according to the stages of N saturation described for terrestrial ecosystems by Aber et al. (1). Sites that would be classified at later stages of watershed N loss tend to occur in areas of high N deposition, but substantial variability exists. Apparently high rates of N deposition are necessary, but not sufficient, conditions leading to high rates of watershed N loss. Stand age may also contribute to long-term changes in the ability of watersheds to retain N; watersheds with old-growth forests leak more NO_3^- in both the Northeast (19) and Southeast (171). Another possible source is high levels of soil N (but few data are available).

Sites from three subregions discussed in detail in this chapter bear further examination with respect to stand age and soil N status. Many lakes in the Adirondack Mountains exhibit Stage 1 patterns of watershed N loss (i.e., Figures 5 and 10); forests in the same area were last harvested in the early 1900s (189). Streams in the Catskill region exhibit both Stage 1 and Stage 2 patterns (Figures 11 and 12); forests in the Catskill Mountains were also last harvested in the early 1900s. Control watershed No. 4 at Fernow, West Virginia, exhibits the dramatically elevated baselow NO_3^- concentrations typical of Stage 2 watersheds (Figure 14); forests at Fernow were selectively logged at the turn of the century (167). The forests in the watersheds of all these sites were last harvested at more or less the same time, roughly 90 years ago. Yet the streams and lakes that drain them exhibit different stages of watershed N loss.

The dominant spatial trend evident in this analysis is for sites further south, and sites with higher deposition rates, to exhibit more advanced stages of watershed N loss. The Fernow site may be closer to forest maturation because it experiences a longer growing season than sites to the north; it also is in the region of the country that receives the highest rates of N deposition. Forests at the Adirondack sites might be expected to take longer to reach maturation because of their shorter growing seasons, and they also receive lower rates of N deposition (Table I). Detailed examination of these three sites suggests that both N deposition and stand age play roles in determining what stage of watershed N loss a site has reached. This analysis, however, ignores information from sites in southwestern Pennsylvania where forests are roughly the same age as in these three subregions, but where streams exhibit Stage 0 patterns of seasonal NO_3^- concentrations despite very high rates of N deposition. Further examination of these apparently anomalous sites, especially with regard to their soil-N status, might yield

important information about the long-term ability of forested watersheds to retain atmospheric N.

Finally, the most convincing evidence for United States watersheds showing signs of N saturation comes from sites where long-term trends and changes in the seasonal patterns of NO_3^- concentrations can be identified. Data from numerous site-specific studies in the Adirondack, Catskill, and mid-Appalachian mountains show both that long-term increases in N loss from forested watersheds have occurred (primarily in the past 2 decades) and that sites progress through stages like those described here. Early signs of watershed N loss are episodic increases in NO_3^- , especially during the snowmelt season. Later stages of watershed N loss are characterized by increases in groundwater NO_3^- concentrations, which create elevated concentrations in streams at baseflow and damped seasonal fluctuations in NO_3^- .

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Mass Fluxes and Recycling of Phosphorus in Lake Michigan

Role of Major Particle Phases in Regulating the Annual Cycle

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Biogeochemical cycling of phosphorus in a water column in southern Lake Michigan was examined, and the significance of major particle phases to the annual mass flux and recycling of phosphorus was assessed. Comparison of 1982-1983 total P and total filtrable P concentrations with data from 1990-1991 and other published data showed little change. The measured annual primary flux of P to the sediment surface reflected rapid sedimentation of both allochthonous particles and spring diatom production. Diatoms were the dominant vector of P to the sediment surface. Terrigenous phases and autochthonous calcite were also significant. More than half of the mixed-period diatom P demand was provided by colloidal and particulate P, nearly 60% of diatom-associated P was recycled within the water column, and 55-58% of total primary P flux was recycled at the sediment surface. Ultimately 2.2% of C and 2.7% of P became incorporated into recent sediments. The amount of P supplied by resuspension was relatively small compared with water-column standing pools and major flux vectors. With its relatively long residence, the response time for P changes with respect to loading should be on the order of 5-15 years.

THE PHOSPHORUS STATUS OF THE GREAT LAKES is a continuing concern because of the linkages between P, primary production, and water quality