

Disruption of the Nitrogen Cycle in Acidified Lakes

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Experimental acidification of two small soft-water lakes caused nitrification to cease at pH values of 5.4 to 5.7. The resulting blockage of the nitrogen cycle caused a progressive accumulation of ammonium. When the experimental acidification of one of the lakes was ended and the pH was raised to 5.4, nitrification resumed after a time lag of 1 year.

SEVERAL INVESTIGATORS HAVE HYPOTHESED that acidification of lakes by acidic precipitation would disrupt microbial processes responsible for the cycling of nutrients (1). Many of these hypotheses were based on laboratory studies with bacteria isolated from natural soils and waters or on small-scale field experiments. However, we and others have found that the hypothesized effects often did not occur under field conditions (2, 3). For example, photosynthesis and decomposition of organic material were more resistant to acidification than expected (4), and certain microbial processes such as sulfate reduction, denitrification, and mercury methylation were stimulated in acidified lakes (5). Apparently, certain microbial communities are able to adapt to the rates of acidification experienced in the field, or the microbes in the lake are active in nonacidified microenvironments (6).

Recently we gathered in situ data showing that the nitrogen cycle appears to be more sensitive to acidification than other major nutrient cycles. In two experimentally acidified lakes, nitrifying bacteria, which oxidize ammonia to nitrate, were incapable of adapting to even moderately acidic conditions (pH 5.4 to 5.7). This inhibition of nitrification blocked the nitrogen cycle, causing ammonium to accumulate. When the pH of one of the lakes was allowed to recover above 5.4, nitrification resumed after a 1-year lag.

The data were collected as part of two multiyear whole-lake acidification experiments at the Experimental Lakes Area, northwestern Ontario (7). During the first experiment, the epilimnetic pH of Lake 223

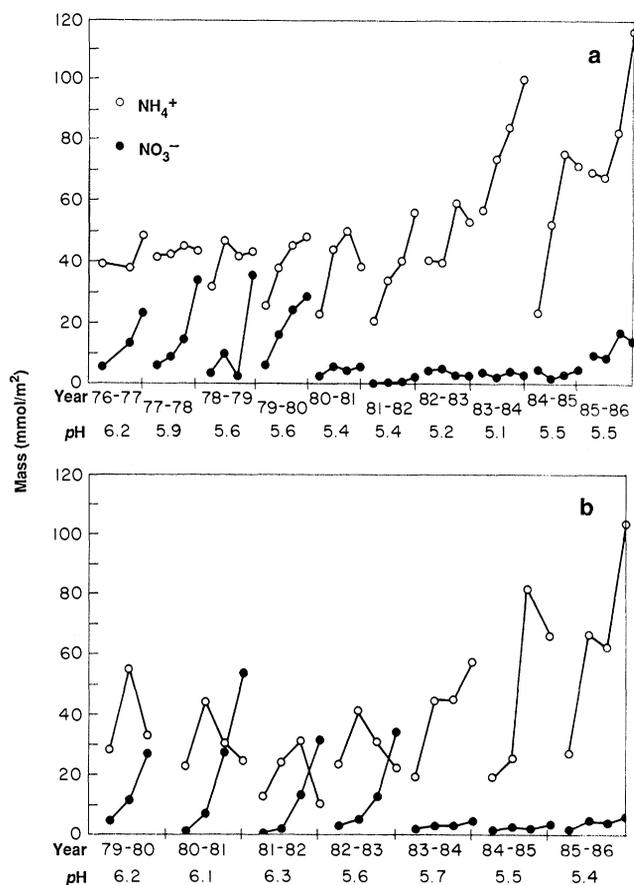
was reduced from 6.6 to 5.1 between 1976 and 1981 by the addition of sulfuric acid (8). After two more years at pH 5.1 to 5.2, the pH was allowed to recover to 5.4 to 5.6. During the second experiment, the epilimnetic pH of Lake 302S was reduced from an original value of 6.7 to 5.4 between 1982 and 1985 by sulfuric acid additions (5, 8). Monthly water chemistry profiles were analyzed for pH, ammonium, and nitrate (8).

Nitrification occurred normally in Lakes 223 and 302S before and during the early years of acidification, with the mass of nitrate per unit area increasing each winter

(1976 to 1980 and 1979 to 1983, respectively, Fig. 1). The timing was similar during all these years, with very low masses of nitrate per unit area present early in the winter, but rapidly increasing amounts as the winter progressed. Ammonium masses per unit area remained low, presumably because nitrification kept pace with ammonium production by decomposition. Calculation of changes in nitrate mass at each sampling depth in the lakes demonstrated that most of the nitrate accumulation during the early winters of acidification occurred at mid-depths where ammonium diffusing upward from anoxic bottom waters came into contact with oxygen-containing water (Fig. 2). Throughout the early years of both experiments, ammonium masses per unit area in late winter were similar from year to year (Fig. 1).

In contrast to the early years of acidification, there was almost no increase in nitrate in Lake 223 during the winter of 1980–81, when the average pH of the lake was 5.4. Instead there was a large increase in ammonium (Fig. 1a). This lack of nitrate accumulation, replaced by increasing ammonium, was repeated in the following two winters as the pH was reduced to 5.1. Changes in depth profiles of nitrate mass showed that the accumulation was low throughout the water column of Lake 223 (Fig. 2a). The

Fig. 1. Under ice mass of ammonium and nitrate in Lake 223 (a) and Lake 302S (b) during multiyear whole-lake acidification experiments. The pH values shown are time- and volume-weighted means for winter only.



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nitrate concentrations at all depths remained near the limit of detection throughout the winter ($<0.07 \mu\text{mol/liter}$). A similar response to acidification was observed in Lake 302S, where nitrification was severely inhibited during the winter of 1983–84 at an average lake pH of 5.7 (Figs. 1b and 2b).

As in Lake 223, inhibition of nitrification in Lake 302S caused year-to-year increases in winter quantities of ammonium (Fig. 1). Mean summer epilimnetic ammonium concentrations also increased from <1 to about $6 \mu\text{mol/liter}$ during the years of lowest pH.

Experimental additions of sulfuric acid to Lake 223 were reduced during the summer of 1984, and the average pH recovered to 5.5 during the winter of 1984–85. There was no nitrification that winter, but the following winter (1985–86) there was a small accumulation of nitrate at an average pH of 5.4. It therefore appears that populations of nitrifiers recover only after a considerable time lag.

When the nitrogen cycle functions normally during winter, nitrate is produced by nitrification and consumed by denitrification. Thus the nitrate concentration in a lake is the net difference between these two processes, and the amount of nitrate produced (ammonium oxidized) exceeds the amount of nitrate that accumulates. Thus, when nitrification is disrupted in acidified lakes, the increase in ammonium accumulation should be greater than the decrease in nitrate accumulation. This is the case (Fig. 1).

A consequence of the inhibition of nitrification is that rates of denitrification, which are dependent on nitrate concentration (5, 6, 9), must also be inhibited because less nitrate is produced. This inhibition of denitrification blocks the reduction of nitrate to nitrogen gas and thus blocks atmospheric loss of fixed nitrogen from the lakes.

Laboratory experiments lead us to hypothesize that the inhibition of nitrification was caused by the difficulty, at low pH, of ammonium uptake by nitrifying bacteria (10). A key factor seems to be the pH at the beginning of winter, which must exceed 5.4 to 5.7 for significant nitrification to occur. Once begun, nitrification can continue at pH levels below 5.4 (11).

The specific effect that disruption of the nitrogen cycle will have on the long-term health of a lake ecosystem is unknown, but continuous cycling of nitrogen is crucial to the stability of ecosystems (12). One possible destabilizing effect of under ice accumulation of ammonium could be the rapid uptake of large quantities of ammonium by algae during early spring. Ammonium uptake results in equimolar H^+ accumulation, and this would occur at the same time as the low pH stress from spring snowmelt.

The nitrification process has not been studied in atmospherically acidified lakes. Inhibition of nitrification in these lakes may not be obvious from examination of surface-water chemistry during the open water season, when plant uptake of ammonium would tend to mask trends in water column

chemistry. This effect is most evident during winter when plant uptake of ammonium is negligible.

The inhibition of nitrification represents an ecosystem-scale blockage of an element cycle by the acidification of lakes. Existing chemical models of acidified lakes should be modified because they assume that reactions involving ammonium are unaffected by low pH (13).

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3. P. J. Dillon, N. D. Yan, W. A. Scheider, N. Conroy, *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 13, 317 (1979); P. J. Dillon, N. D. Yan, H. H. Harvey, *Crit. Rev. Environ. Control* 13, 167 (1984); C. A. Kelly, J. W. M. Rudd, A. Furutani, D. W. Schindler, *Limnol. Oceanogr.* 29, 687 (1984); G. Persson and O. Broberg [*Ecol. Bull. (Stockholm)* 37, 158 (1985)] found that phosphorus inputs to acidified Lake Gardsjon were reduced by reactions in the terrestrial watershed rather than in the lake.
4. In a whole-lake acidification experiment, decomposition of newly sedimented organic carbon was not affected until pH 5.25 to 5.0. Decomposition of organic material from earlier years was unaffected at pH 4.0 (3).
5. D. W. Schindler and M. A. Turner, *Water Air Soil Pollut.* 18, 259 (1982); C. A. Kelly and J. W. M. Rudd, *Biogeochemistry* 1, 63 (1984); L. Xun, N. E. R. Campbell, J. W. M. Rudd, *Can. J. Fish. Aquat. Sci.* 44, 750 (1987); C. A. Kelly *et al.*, *Biogeochemistry* 3, 129 (1987). After acidification of Lake 302N by experimental additions of nitric acid, rates of denitrification in the surface sediments increased from undetectable levels to between 200 and 1000 $\mu\text{eq m}^{-2} \text{day}^{-1}$.
6. In most acidified lakes, anoxic microbial activities near the sediment-water interface maintain the porewater pH at near preacidification values [J. W. M. Rudd *et al.*, *Limnol. Oceanogr.* 31, 1267 (1986); A. T. Herlihy and A. L. Mills, *Biogeochemistry* 2, 377 (1986)]. Other microbial processes such as denitrification and mercury methylation appear to adapt to the low pH surface water (5).
7. D. W. Schindler *et al.*, *Can. J. Fish. Aquat. Sci.* 37, 342 (1980); R. B. Cook, C. A. Kelly, D. W. Schindler, M. A. Turner, *Limnol. Oceanogr.* 31, 134 (1986).
8. We added sulfuric acid to the epilimnia of the lakes during the ice-free season by draining it slowly into the propeller wash of a motor boat. The resulting distribution of the acid was uniform, and no acid penetrated the thermocline (2). Water chemistry profiles were analyzed within 3 hours of collection by methods described in M. Stainton, M. J. Capel, and F. A. J. Armstrong [*Can. Fish. Mar. Serv. Misc. Spec. Publ.* 25 (1977)]. During stratification periods, anoxia developed below a depth of 12 m and 8 m in Lakes 223 and 302S, respectively. This was not changed by acidification of the lakes.
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10. I. Suzuki, U. Dular, and S. C. Kwok [*J. Bacteriol.* 120, 556 (1974)] found the autotrophic nitrifiers were inhibited at low pH because they do not have the capability of assimilating ammonium, the prevalent species at low pH (the $\text{p}K_a$, where K_a is the acid constant, of NH_4^+ is 9.25). It is unlikely that heterotrophic nitrifiers were responsible for nitrification before acidification because they remain active below pH 5.0 [R. F. Strayer, C. Lin, M. Alexander, *J. Environ. Qual.* 10, 547 (1981)]. It is

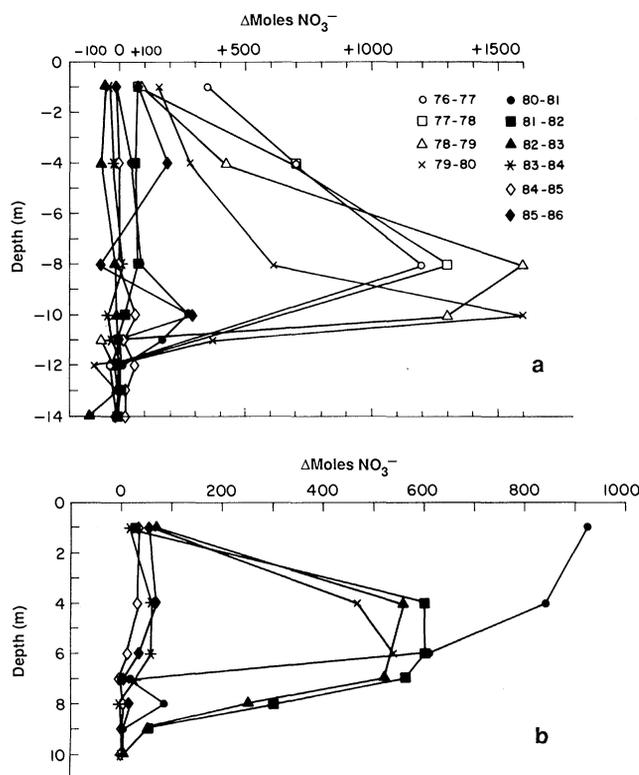


Fig. 2. Changes of nitrate mass with depth in Lake 223 (a) and Lake 302S (b) under ice cover during multi-year whole-lake acidification experiments. Values are the products of the changes in nitrate concentrations (December to March) at sampling depths multiplied by the volume of a 1-m depth interval at each depth. The average pH values of the lake water during these winters are given in Fig. 1.

possible that the autotrophic nitrifiers could also be inhibited by the low concentrations of inorganic carbon of acidified lakes [L. S. Jahnke, C. Lyman, A. B. Hooper, *Arch. Microbiol.* **140**, 291 (1984)].

11. We have identified three categories of lakes with respect to nitrification: case 1, the natural situation ($pH > 5.4$ to 5.7, ammonium $< 7 \mu\text{mol/liter}$), where nitrification converts most of the ammonium to nitrate under ice (Lakes 223 and 302S before acidification); case 2, acidified lakes, where early winter pH values are below 5.4 to 5.7 and inhibition of nitrification results in ammonium accumulation (Lakes 223 and 302S after acidification and Lake 302N, where 1 year after acidification by hydrochloric acid addition nitrification has been inhibited); case 3, lakes where ammonia concentrations are high (70 to $140 \mu\text{mol/liter}$) and early winter pH is above 5.4 to 5.7. Under these circumstances, the population of nitrifiers that develops at the early winter pH is capable of remaining active until nitrification has reduced the pH to 4.0 to 4.5 [Lake 304 [D. W. Schindler, M. A. Turner, R. H. Hesslein, *Biogeochemistry* **1**, 117 (1985); L. d'Orta and R. A. Vollenweider, *Mem. Ist. Ital. Idrobiol. Dott. Marco Marchi* **16**, 21 (1963)]]. This third pattern is also shown in the growth of nitrifying bacteria in the laboratory [M. Gerletti and A. Provini, *Prog. Water Technol.* **10**, 839 (1987)].
12. Alkalinity production by elevated ammonium accumulation is one possible beneficial effect of inhibiting nitrification but the amount of alkalinity produced would be small [S. Schiff and R. Anderson, *Can. J. Fish. Aquat. Sci.* **44** (Suppl.), 173 (1987); (7)].
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North Carolina Climate Changes Reconstructed from Tree Rings: A.D. 372 to 1985

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Millennium-old bald cypress trees (*Taxodium distichum* [(L.) Rich.] have been used to develop a 1614-year reconstruction of the June Palmer drought severity index for North Carolina. This proxy paleoclimatic record indicates that the growing season climate of North Carolina has undergone many changes between significantly different regimes of drought and wetness that persist for approximately 30 years. Alternating wet and dry regimes were particularly well developed during the Medieval Warm Epoch (A.D. 1000 to 1300). The record June droughts in 1985 and 1986 and the preceding three decades of much wetter than average conditions both appear to have been rare climatic events, equaled only five times each since A.D. 372.

LIVING BALD CYPRESS TREES UP TO 1700 years old have been discovered along Black River, a nutrient-poor blackwater tributary of the Cape Fear River in southeastern North Carolina (Fig. 1). Millennium-old trees are rare, and the swamp-grown bald cypress at Black River are the oldest trees in eastern North America. Annual ring width in these trees reflects precipitation and temperature variations during the growing season (1). We have used the Black River cypress to reconstruct the statewide June Palmer drought severity index (PDSI) (2, 3) from A.D. 372 to 1985.

Increment cores were extracted above the bald cypress root buttress, and the cross-dated annual rings were measured to within 0.01 mm (4). A cross-correlation procedure was used to confirm the dating and measurement accuracy of each ring width series (5).

The Black River tree ring chronology was

calculated as a mean-value function of the prewhitened ring width index series available at each year since A.D. 372, after nonclimatic age trend and significant low-order autocorrelation in the ring measurement series were removed (6–8). A long-term variance trend remained in the 1614-year chronology. We removed this undesirable trend by fitting a stiff cubic spline to the absolute departures from the mean, dividing by the spline values, restoring the sign of the departures, and rescaling so that the series had no negative values and mean of 1.0 [the spline reduced 50% of the variance in a sine function with a 200-year wavelength (9)]. The distribution of the original chronology index values was also non-normal (positively skewed), and a square root transformation before variance detrending made the series approximate a normal distribution.

The Palmer index is a soil-water balance model that measures departures from average moisture conditions and is calculated from monthly temperature averages and precipitation totals (2). The PDSI has been

successfully used in many dendroclimatic analyses of trees from a variety of habitats (1, 10), in part because it approximates the response of tree growth and the soil moisture reservoir to current and antecedent climatic conditions. Correlations between the Black River cypress chronology and monthly PDSI values were all positive and significant during the bald cypress growing season (primarily April to July), but the highest correlation was obtained for June, as has been observed for other cypress chronologies from Arkansas (1) and South Carolina.

A split-period regression procedure involving autoregressive (AR) modeling (7, 8) of both the predictor (Black River tree rings) and predictand [North Carolina average June PDSI (3)] was used to calibrate tree growth and climate during the period of meteorological observation. The weak persistence in the observed June PDSI series (first-order serial correlation = 0.176) was modeled as a lag 1 autoregressive process [AR(1) coefficient = 0.188]. Persistence in the 89 tree-ring series composing the Black River chronology was modeled on average as a lag 4 autoregressive process [AR(1) to AR(4) coefficients equal 0.0573, 0.1270, 0.0199, 0.0922, respectively (7, 8)]. The large AR(2) and AR(4) terms are not evi-

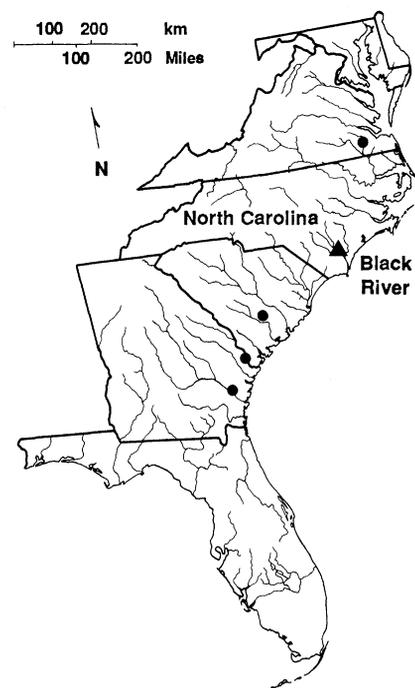


Fig. 1. Tree-ring samples were obtained from old-growth bald cypress trees in an undisturbed swamp forest along Black River, North Carolina (triangle). This swamp covers 100 hectares and contains the largest concentration of millennium-old bald cypress currently known. Four additional 1000-year-long cypress chronologies are under development elsewhere in the Atlantic Coastal Plain (circles).

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