

Nitrate Deposition and Impact on Adirondack Streams

Howard A. Simonin

New York State Department of Environmental Conservation
Rome Field Station
8314 Fish Hatchery Road
Rome, New York 13440

Walter A. Kretser

New York State Department of Environmental Conservation
Adirondack Lakes Survey Corporation
PO Box 296, Route 86
Ray Brook, New York 12977-0296

ABSTRACT

Acidic deposition has a great impact on water chemistry and fish populations in the Adirondack region. Although the Clean Air Act Amendments of 1990 have resulted in some reductions of sulfate deposition, nitrate deposition has not yet been well controlled, and continues to impact aquatic resources. As part of the USEPA funded Episodic Response Project four Adirondack headwater streams were intensively monitored over an 18 month period. Atmospheric deposition was also monitored at a centrally located station. The quantity of nitrate being deposited on the study watersheds was calculated based on monthly net deposition data which ranged from 0.6 kg/ha/month to 3.6 kg/ha/month. These data were then compared to the monthly export of nitrate from the watershed in these streams. Nitrate concentrations were highest in the streamwater during the spring snowmelt period prior to the time when forest vegetation actively utilizes nitrate. On an annual basis the amount of nitrate which left the watershed via stream water exceeded the amount which fell as nitrate deposition. These data are important in documenting the impact of nitrate in the acidification of Adirondack streams during the spring, which coincides with brook trout hatching. Control programs for nitrous oxide emissions are presently aimed at reducing ozone levels during the May-September period. These emissions control programs need to be expanded to also reduce nitrate deposition in the sensitive Adirondack region during the winter and spring periods when nitrate deposition has its greatest impact on aquatic resources.

INTRODUCTION

The Adirondack region of northern New York State is a vast and valuable natural resource consisting of mountains, rivers, lakes, and wilderness areas. The region is visited by thousands of people each year from the relatively nearby metropolitan areas. The region has however been severely impacted by acidic deposition.¹ The bedrock of the Adirondack Mountains is primarily igneous and metamorphic, and the soils are thin, both of which make the region very sensitive to acidification. The region has high deposition rates of both sulfate and nitrate ions, and as a consequence many lakes and streams have been acidified to a level where fish populations have been lost.² Intensive research has been conducted in the region and millions of dollars have been spent to study the problem. Monitoring programs are in place to evaluate the consequences of air emission reductions mandated by the Clean Air Act Amendments of 1990.

In 1988 the U.S. Environmental Protection Agency (EPA) funded the Episodic Response Project (ERP) to evaluate the occurrence and impact of acidic episodes in headwater streams. Acidic episodes were defined as short-term decreases of acid neutralizing capacity or pH that occur during high streamflow associated with rainstorms and snowmelt. Results from the ERP have been reported elsewhere and contributed greatly to our understanding of acidic deposition impacts on streams.³⁻⁷ Significant acidic episodes were observed in the ERP study streams, and these were attributed to multiple factors including high SO_4 , NO_3 or organic acid concentrations or a dilution of base cations. High NO_3 levels were responsible for most of the acidity during spring snowmelt. During acidic episodes the stream water was found to be toxic to fish and other aquatic life. Brook trout fitted with radio transmitters often moved downstream to areas of better water quality in response to acidic episodes.⁶

Intensive continuous monitoring of streams is costly and not frequently done. We decided to further utilize the ERP data to better evaluate the role and importance of NO_3 in stream acidification. Sulfate deposition is declining in the northeastern United States as a result of the Clean Air Act Amendments of 1990, and levels are expected to decline further. Nitrate deposition however, was not reduced to the same extent and although several emissions control programs will lead to reductions in deposition, the overall effect is uncertain.

METHODS

We selected four headwater streams in the southwestern Adirondacks for intensive study as part of the ERP. A monitoring shed was constructed at each of the streams to house the stream gauging and water sampling instruments. Stream stage was measured at 15-min intervals from December 1988 until June 1990 with a pressure transducer connected to a data logger. Conductivity, pH, and temperature were also measured continuously and recorded on the data logger. An ISCO automated water sampler was programmed to collect water samples at specific intervals based on changes in the stream stage. Weekly grab samples were also collected by field staff. Samples were analyzed in the laboratory for: pH, acid neutralizing capacity, specific conductance, Cl, NO_3 , SO_4 , Na, K, Ca, Mg, SiO_2 , dissolved organic carbon, dissolved inorganic carbon, NH_4 , total dissolved aluminum, total monomeric aluminum, and organic monomeric aluminum. Kretser et al.⁸ give a more complete discussion of ERP methods and quality control procedures. In addition to the stream chemistry monitoring, a wet deposition sampling site was established near the study streams. The monthly wet deposition data have been compiled and presented by Barchet.⁹

The depth, water equivalent, and chemical composition of the winter snowpack was measured in the ERP watersheds by collecting snow cores. A 7.6 cm diameter snow tube was used to collect samples on a weekly basis during 1989 and biweekly during 1990.

Our approach for this study was to examine the NO_3 data from a watershed nutrient budget standpoint (Figure 1). Deposition of NO_3 onto the watershed was determined using the monthly wet deposition data. A measure of the amount of NO_3 leaving each stream watershed was obtained by multiplying the mean daily stream discharge times the streamwater NO_3 concentration. This value was then divided by the size of the watershed in hectares. The daily stream data were then summed for each month, resulting in a value for kg NO_3 /ha leaving the watershed in the streamwater each month.

Nitrate is an essential plant nutrient and is actively taken up by forest vegetation during the warmer months of the year. Nitrate is recycled and reused in the watershed as leaves and dead trees decompose. Nitrification and denitrification processes occur in forest soils, and nitrate is either created or changed to other nitrogen compounds. The intensive soils research necessary to measure some of

these nutrient fluxes was beyond the scope of the ERP. While the nitrate budget approach (Figure 1) is somewhat simplified, it is still valuable in evaluating the major nitrate inputs and outputs from undisturbed forested watersheds. Especially during the winter and spring snowmelt period, many of the watershed nutrient fluxes are less important. During this period nitrate inputs to the watershed may directly impact stream and lake water quality.

RESULTS

The monthly wet nitrate deposition data ranged from 0.6 kg/ha in June 1990 to a high of 3.6 kg/ha in November 1989.⁹ The mean monthly deposition rate over the study period was 1.86 kg NO₃/ha and the weighted annual deposition rate was 22.3 kg NO₃/ha.

The amount of precipitation which fell on the ERP watersheds varied throughout the year, ranging up to nearly 2.0 m³/ha (19.8 cm) in September 1989. Monthly stream discharge appeared to be more closely related to snowmelt than to the amount of precipitation received by the watershed (Figure 2). Stream discharge was lowest during the summer of 1989 and highest (up to 10 times baseflow discharge) during the spring snowmelt period. Above freezing weather conditions during several days in January and February 1990 accounted for some thawing, snowmelt, and increased stream discharge during these normally colder months.

Nitrate concentrations in the streams were highest during the spring, with values 3-4 times greater than summertime concentrations. Sulfate concentrations on the other hand, remained relatively constant in the study streams throughout the year, with no clear seasonal trends. Since the amount of NO₃ leaving the ERP watersheds was determined by multiplying concentration times stream discharge, the amounts were considerably higher during the spring snowmelt period (Figure 3). For Bald Mountain Brook 53% of the annual stream discharge left the watershed prior to May 1, and 73% of the annual NO₃ exported from the watershed in the streamwater left prior to May 1. Fly Pond Outlet was our ERP reference stream which did not experience severe acidic episodes, and did not exhibit as large a peak in NO₃ exported from the watershed during spring snowmelt. However, the other three ERP streams exhibited high amounts of NO₃ exported during snowmelt (Figure 3), and also experienced acidic water quality as a result.

As an additional way of viewing NO₃ flux within the ERP watersheds we subtracted the NO₃ exported by each stream from the monthly NO₃ deposition values (Figure 4) This resulted in a monthly NO₃ balance value for each of the streams, and again demonstrated that spring snowmelt in March of 1989 and March 1990 was the time of greatest NO₃ export from all of the ERP streams. On an annual basis Fly Pond Outlet, the reference stream, had a positive NO₃ balance of 3.09 kg/ha, indicating that more NO₃ fell on the Fly Pond Outlet watershed than was exported via the stream. The three ERP streams which experience acidic episodes, however, had negative annual NO₃ balances (Buck Creek - 10.03 kg/ha; Bald Mountain Brook -12.60 kg/ha; Seventh Lake Inlet -9.30 kg/ha). The large amounts of NO₃ leaving these three watersheds during the spring snowmelt appeared to be critical in their overall NO₃ balance.

The snowpack in the Bald Mountain Brook watershed reached a maximum water equivalency of 19.0 cm in March 1989, and decreased rapidly over the following weeks. During the winter of 1990 the snowpack was not as deep and also melted several weeks earlier. Converting the snow chemical measurements to a watershed area basis allowed comparisons with the deposition data. Figure 5 shows the amount of NO₃ present in the snowpack at various times during the winters of 1989 and 1990. NO₃ reached a maximum of 4.9 kg/ha during March 1989 and was generally lower during the winter of 1990.

The maximum amount of SO_4 in the snowpack was 2.4 kg/ha and occurred at the same time as the NO_3 peak.

More recent ongoing monitoring programs have demonstrated relatively little change in water chemistry in Adirondack streams and lakes. Bald Mountain Brook continues to be sampled weekly, with pH ranges between approximately 4.8 and 7.2 (Figure 6). The lowest pH measurements continue to be during spring snowmelt, although acidic episodes do occur occasionally at other times in the year. The highest pH measurements occur during the summer low flow season. A group of 27 Adirondack lakes with thin till soils continue to exhibit nitrate peaks as high as $120 \mu\text{eq/L}$ during the spring snowmelt.¹⁰ These lakes are part of a long-term monitoring effort which will be able to detect changes in lake water chemistry as a result of changes in acidic deposition.

DISCUSSION

The role of sulfate in the acidification of Adirondack waters continues to be important. Numerous studies have documented the high background sulfate concentrations which are present in the lakes and stream water of the Adirondack region. Sulfate concentrations are generally 90-120 $\mu\text{eq/L}$ in Adirondack drainage lakes, and SO_4 is the dominant anion.¹¹ These high SO_4 concentrations are predominantly due to high levels of atmospheric sulfate deposition which peaked in about 1980. Since that time SO_4 deposition rates have declined and continue to drop as emissions are reduced in compliance with the 1990 Clean Air Act Amendments. As a consequence of declining deposition, sulfate concentrations have slowly declined over the past 12 years at a rate of approximately 2% per year.¹¹ However, there has also been an observed decline in the concentrations of base cations over this same period, and the overall effect has been relatively little change in pH.

As shown by our study and others, NO_3 is a major contributor to acidification during spring snowmelt and occasionally episodes at other times in the year.⁴ The timing of high NO_3 concentrations coincides with the most acidic time of the year, resulting in water quality conditions which may be toxic to aquatic life. The toxicity in many cases is due to high monomeric aluminum concentrations, driven by the high acidity levels. Reducing concentrations of NO_3 is therefore critical in our efforts to improve pH levels and improve water quality for the survival of fish and other biota.

Other Adirondack studies have also documented high nitrate concentrations during spring snowmelt. Schofield¹² was one of the first researchers in the United States to report high nitrate concentrations during spring snowmelt concurrent with the most acidic water quality and conditions toxic to brook trout. It is during the spring snowmelt period that young fish are hatching and are most susceptible to acidic impacts. Schaefer et al.¹³ similarly reported that changes in SO_4 concentrations did not significantly contribute to snowmelt acidification, however NO_3 increases were directly associated with the increased acidity of the snowmelt episode.

Studies conducted in New York's Catskill Mountains indicate that streams in this region also experience acidic episodes due to high NO_3 concentrations. Nitric acid in the stream plays an important role in creating toxic conditions for stream biota.¹⁴ In Catskill streams increases in NO_3 concentrations have occurred over several decades, with recent increases in NO_3 levels typical of streams across a broad range of sites.¹⁵ Low-order streams in Maine also experience episodic acidification due to increases in NO_3 during winter and spring.¹⁶

Lakes and watersheds within the Adirondacks are variable in their response to NO_3 deposition. The three ERP streams which experienced acidic episodes are located in watersheds with thin till soils

and exhibited a net annual loss of NO₃ from the watershed. A study conducted in the Arbutus Lake watershed (classified with medium till soils) by Mitchell et al.¹⁷ demonstrated a case where most of the annual NO₃ load was retained in the watershed. The Arbutus Lake situation may be comparable to our Fly Pond Outlet reference watershed.

Our data showed more NO₃ leaving three of the ERP streams than was added through atmospheric deposition of NO₃. Several factors are most likely responsible for this. We did not include any estimates of dry deposition to the watersheds. Since dry deposition of NO₃ can be considerable, this may account for an additional supply of NO₃ to the watersheds, and consequently more being measured in the stream water. Rasher et al.¹⁸ found that mineralization of nitrogen from the forest floor also is an important source of NO₃ during snowmelt. Undoubtedly, mineralization also played a role in nitrogen cycling in the ERP watersheds, and contributed to the high amounts of NO₃ exported during snowmelt.

The Clean Air Act Amendments of 1990 focused on reducing SO₂ emissions to help solve the problem of acidic deposition. The act mandated reductions of SO₂ emissions from power plants by about 10 million tons, to an annual capped level of 8.95 million tons. Emissions allowances are issued to utilities, and these may then be bought, sold, traded, or saved for future use. Thus far SO₂ emissions have been dramatically reduced and should lead to additional reductions in SO₄ concentrations in Adirondack waters.

Emissions of NO_x however were not well controlled as part of the acid rain section, Title IV of the Clean Air Act Amendments. Some reductions will occur as a result of emissions controls on mobile sources and as a result of efforts to reduce urban smog and to meet mandated ozone concentrations. EPA has also finalized a Phase II NO_x rule which will help to reduce emissions from certain utility boilers. However expectations are that NO_x emissions will continue to be a major contributor to our spring snowmelt acidification problem in the Adirondack region.

Stoddard¹⁹ concluded that high nitrate concentrations in streams draining Northeastern forested watersheds are unlikely without high deposition levels of atmospheric nitrogen. Our data and earlier studies show the seasonal nature of NO₃ impacts on aquatic resources and the importance of reducing deposition during the winter and spring. However, efforts to control urban smog are focused on reducing ozone levels during the mid-May to mid-September “ozone season”. Since NO_x is a primary precursor of ozone, expectations are that NO_x emissions (and therefore NO₃ deposition levels) will be reduced during the summer season. Since overall emission rates are generally reported on an annual basis, there is potential for increased emissions during the winter and spring to “balance out” the need for summertime ozone controls.

The primary source of New York State’s NO₃ deposition problem continues to be the upper Midwest states, including Ohio, Kentucky, West Virginia, and Pennsylvania. While New York Phase I utilities reduced NO_x emissions to 16,500 tons in 1994, these upwind states increased their emissions from 1990 to 1994, and Ohio utilities emitted nearly 20 times that of New York.²⁰ Deregulation of the electric utility industry threatens to increase this difference, because many Midwest utilities burn local soft coal and do not have adequate NO_x emissions control systems in place. Prior to deregulation a fair and equitable NO_x emissions control program should be approved. A program which would cap NO_x emissions and permit allowance credit trading within a specific state or region could be an equitable approach if all the sources which impact the Adirondacks are included.

The Clean Air Power Initiative is an example of a program with the potential to achieve a solution to the many concerns of emissions controls. This initiative includes a more holistic approach to emissions controls and deals with multiple pollutants and seasonal concerns. Stakeholders with diverse interests can

work together on the approaches to ensure that no region is allowed to unfairly degrade a neighboring region.

CONCLUSIONS

Acidic deposition continues to impact the Adirondack region of New York State. Data from the Adirondack Episodic Response Project demonstrated that stream water quality during spring snowmelt was acidic due primarily to high NO₃ concentrations. The spring snowmelt event was the most acidic of the year and was toxic to fish and other aquatic life. Monthly totals of NO₃ deposition and NO₃ export from the study watersheds further demonstrated that March was the month of greatest NO₃ impact and export from the watersheds. Efforts to reduce the deposition of NO₃ on sensitive regions like the Adirondacks need to consider the seasonal nature of NO₃ impacts. Current efforts are focused on reducing NO_x emissions during the summer in order to reach ozone standards and control urban smog. However, additional seasonal NO_x reductions during the winter and spring are needed to help reduce acidification of Adirondack streams and lakes during the critical snowmelt period.

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REFERENCES

1. Driscoll, C. T., Newton, R. M., Gubala, C. P., et al.; Adirondack Mountains; D. F. Charles, Ed.; Acidic Deposition and Aquatic Ecosystems, Regional Case Studies; Springer-Verlag, New York, 1991; pp. 132-202.
2. Baker, J. P., Warren-Hicks, W. J., Gallagher, J., et al.; Fish population losses from Adirondack lakes: the role of surface water acidity and acidification; *Water Resour. Res.* **1993** 29, 861-874.
3. Wigington, P. J., Baker, J. P., DeWalle, D. R., et al.; Episodic acidification of small streams in the northeastern United States: Episodic Response Project; *Ecol. Applications* **1996** 6, 374-388.
4. Wigington, P. J., DeWalle, D. R., Murdoch, P. S., et al.; Episodic acidification of small streams in the northeastern United States: Ionic Controls of Episodes; *Ecol. Applications* **1996** 6, 389-407.
5. Van Sickle, J., Baker, J. P., Simonin, H. A., et al.; Episodic acidification of small streams in the northeastern United States: Fish mortality in field bioassays.; *Ecol. Applications* **1996** 6, 408-421 .
6. Baker, J. P., Van Sickle, J., Gagen, C. J., et al.; Episodic acidification of small streams in the northeastern United States: Effects on fish populations; *Ecol. Applications* **1996** 6, 422-437.

7. Simonin, H. A., Kretser, W. A., Bath, D. W., et al.; In situ bioassays of brook trout (*Salvelinus fontinalis*) and blacknose dace (*Rhinichthys atratulus*) in Adirondack streams affected by episodic acidification; *Can. J. Fish Aquat. Sci.* **1993** 50, 902-912
8. Kretser, W. A., Simonin, H. A., Bath, D. W., et al.; Episodic acidification and associated fish and benthic invertebrate responses of four Adirondack headwater streams: an interim report of the Episodic Response Project. EPA/600/3-91/036. 1991, USEPA, Corvallis, OR.
9. Barchet, W. R.; Episodic Response Project: Wet deposition at watersheds in three regions of the eastern United States; PNL-7876; 1991, Battelle Pacific Northwest Laboratory, Richland, WA.
10. Kretser, W. A.; Long-term Monitoring Project (unpublished data), 1997.
11. Driscoll, C. T., Postek, K. M., Kretser, W., et al.; Long-term trends in the chemistry of precipitation and lake water in the Adirondack region of New York, USA; *Water, Air, Soil Pollut.* **1995** 85, 583-588.
12. Schofield, C. L.; Acid snow-melt effects on water quality and fish survival in the Adirondack Mountains of New York State, Project No. A-072-NY Completion Rpt. 1977, Office of Water Research and Technology, U. S. Dept. of Interior, Washington, D.C.
13. Schaeffer, D. A., Driscoll, C. T., VanDreason, R., et al.; The episodic acidification of Adirondack lakes during snowmelt; *Water Resour. Res.* **1990** 26, 1639-1647.
14. Murdoch, P. S., Stoddard, J. L.; The role of nitrate in the acidification of streams in the Catskill Mountains of New York; *Water Resour. Res.* **1992** 28, 2707-2720.
15. Murdoch, P. S., Stoddard, J. L.; Chemical characteristics and temporal trends in eight streams of the Catskill Mountains, New York; *Water, Air, Soil Pollut.* **1993** 67, 367-395.
16. Kahl, J. S., Norton, S. A., Haines, T. A., et al.; Mechanisms of episodic acidification in low-order streams in Maine, USA; *Environ. Pollut.* **1992** 78, 37-44.
17. Mitchell, M. J., Raynal, D. J., Driscoll, C. T.; Biogeochemistry of a forested watershed in the central Adirondack Mountains: temporal changes and mass balances; *Water, Air, Soil Pollut.* **1996** 88, 355-369.
18. Rasher, C. M., Driscoll, C. T., Peters, N. E.; Concentration and flux of solutes from snow and forest floor during snowmelt in the west-central Adirondack region of New York; *Biogeochemistry* **1987** 3, 209-224.
19. Stoddard, J. L.; Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences; L. A. Baker, Ed.; Environmental Chemistry of Lakes and Reservoirs, Advances in Chemistry series No. 237; American Chemical Society, Washington, DC, 1994; pp. 223-284.
20. U. S. Environmental Protection Agency; Acid Rain Program Emissions Scorecard 1994, SO₂, NO_x, Heat input, and CO₂ emission trends in the electric utility industry; 1995, USEPA, Acid Rain Division, Washington, D. C.

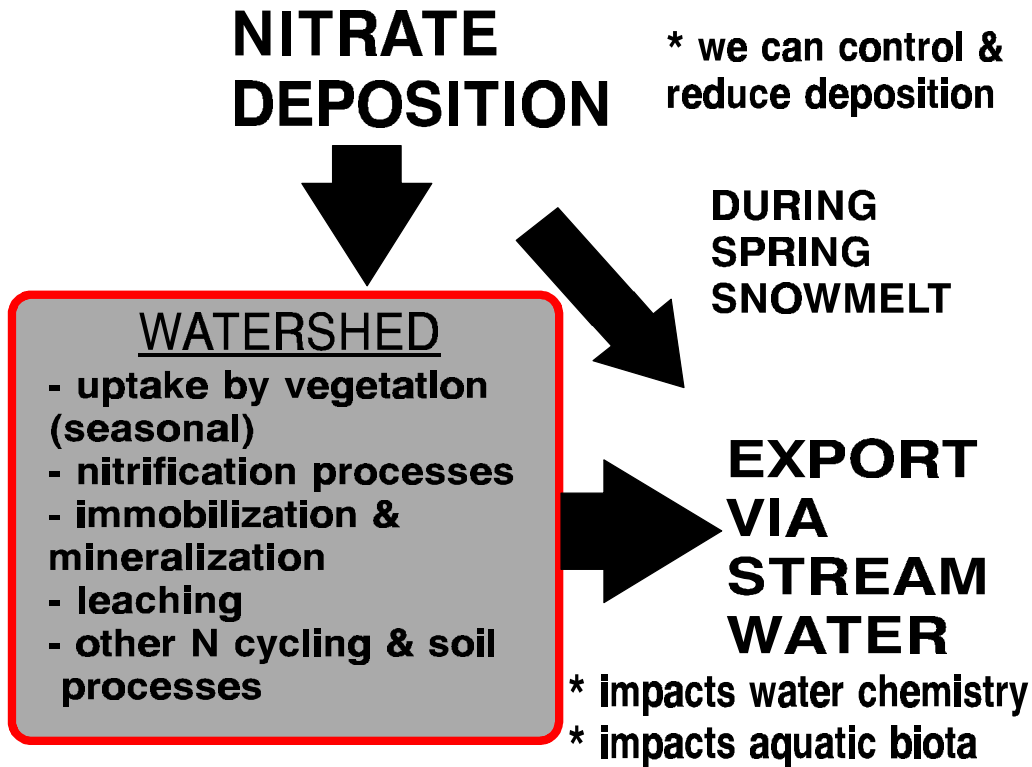


Figure 1. Simplified diagram of nitrate flow through an Adirondack watershed.

Monthly Precipitation and Discharge

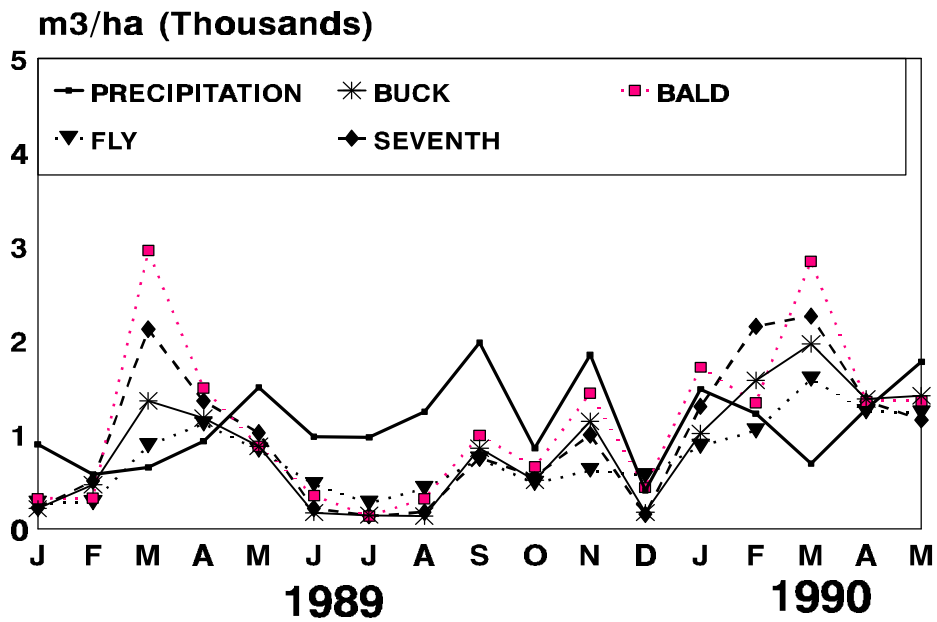


Figure 2. Monthly precipitation and stream discharge for the Adirondack Episodic Response Project streams (Buck Cr., Bald Mt. Brook, Fly Pond and Seventh Lake Inlet). Outlet,

Monthly NO₃ Deposition and Export

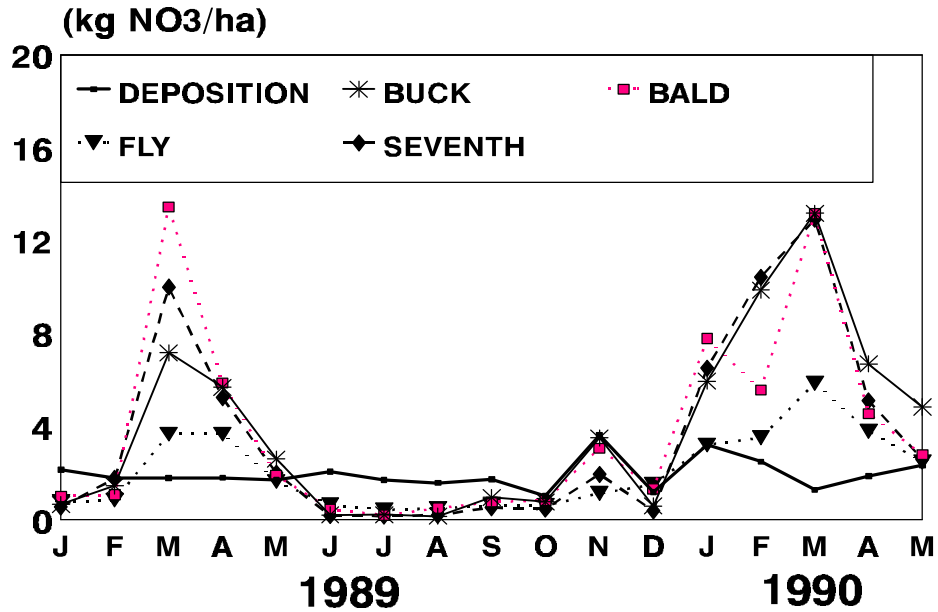


Figure 3. Monthly nitrate deposition and amount of nitrate exported from Buck Cr., Bald Mt. Brook, Fly Pond Outlet, and Seventh Lake Inlet watersheds.

Monthly NO₃ Balance

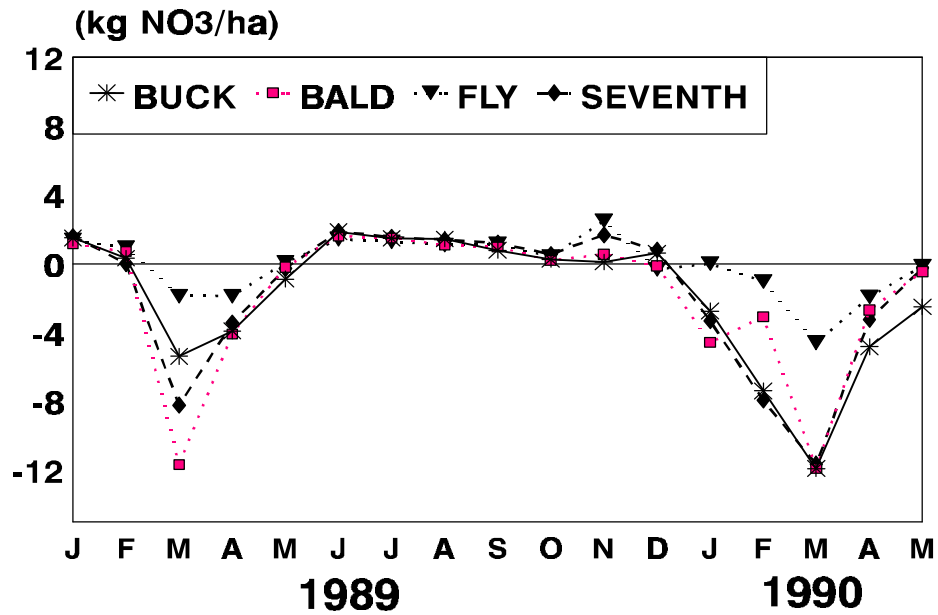


Figure 4. Monthly nitrate balance (monthly deposition-NO₃ exported from the watershed) for Buck Cr., Bald Mt. Brook, Fly Pond Outlet, and Seventh Lake Inlet.

NO₃ in the Bald Mt. Brook Snowpack

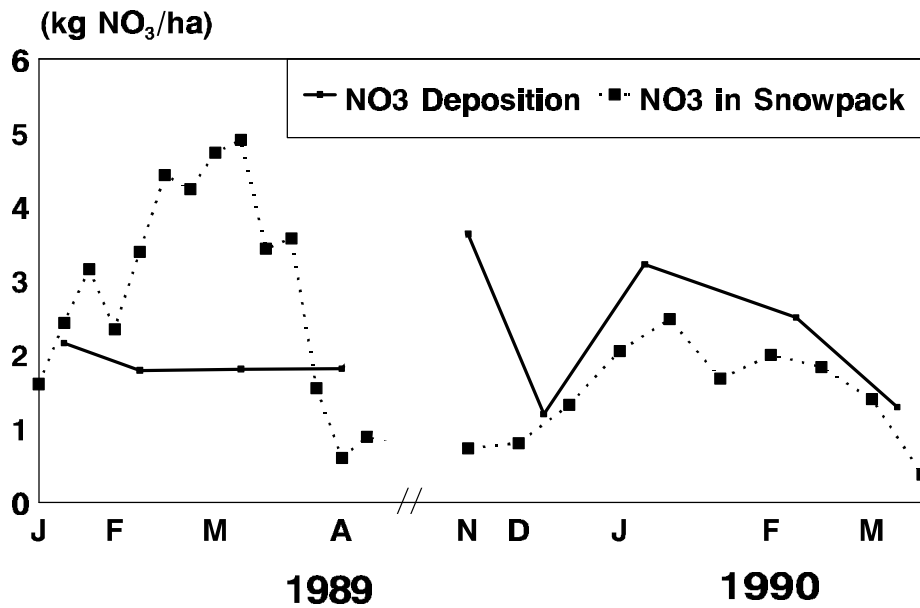


Figure 5. Monthly NO₃ deposition and NO₃ present in the Bald Mt. Brook snowpack. Snow measurements were made weekly during 1989 and biweekly during the winter of 89-90.

Weekly Stream pH Monitoring

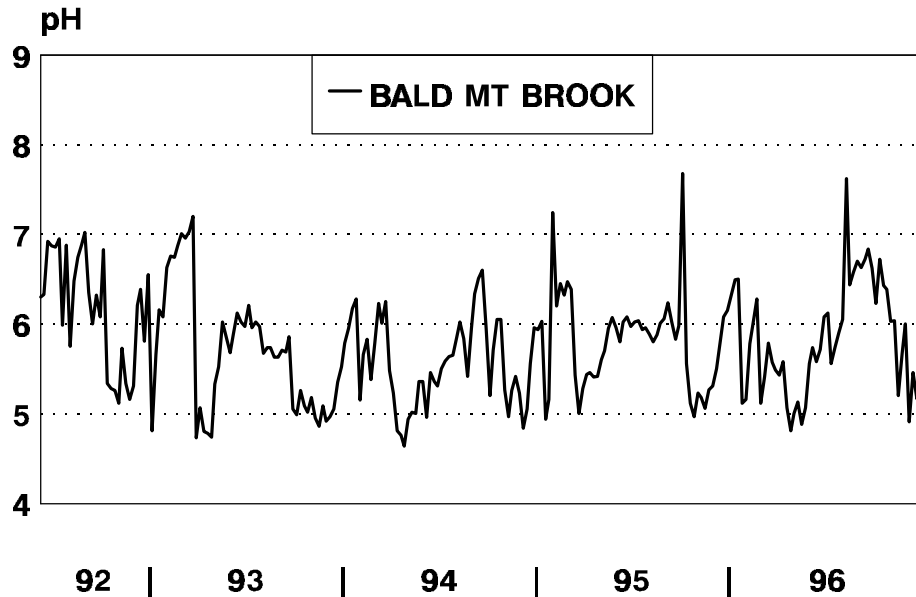


Figure 6. Weekly pH data for Bald Mt. Brook from June 1992 through 1996. Data were collected as part of the Adirondack Long-term Monitoring Project¹⁰.

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