United States
Environmental Protection
Agency

Environmental Research
Laboratory
Duluth MN 55804

Research and Development EPA/600/M-85/011 May 1985

ENVIRONMENTAL RESEARCH BRIEF

RECEIVED JUN 19 1985 ENVIRONMENTAL PROTECTION AGENCY LIBRARY, REGION V

Experimental Acidification of a Stream Tributary to Hubbard Brook

Ronald J. Hall and Gene E. Likens*

Abstract

Long- (five months) and short-term (one hour to two days) effects of acidic pH were measured in a poorly buffered mountain stream within the Hubbard Brook Experimental Forest, New Hampshire. Over a five-month period aluminum, calcium, magnesium, and potassium were mobilized into the stream water during experimental acidification, and nitrogen was lost via invertebrates and organic matter. Periphyton biomass increased at low pH and fungal densities increased. Emergence of adult mayflies, stoneflies, and true flies decreased, whereas immature invertebrates in the drift increased. Short-term pulses of acid also changed the stream ecosystem as indicated by significant net fluxes of organic carbon, nitrogen, and phosphorus in biologically bound forms.

Aluminum chloride was added to the stream to simulate increased aluminum concentrations during snowmelt. A significant decrease in pH and dissolved organic carbon (DOC) occurred; there was an increase in foam accumulation at the stream surface. Foam production is thought to be due to decreased surface tension of the water. A 20% reduction of surface tension of stream water was measured in the laboratory. The cause of the reduction is postulated to be the formation of organo-aluminum complexes in the stream. Increases in aluminum concentration were accompanied by changes in both terrestrial and aquatic drift behavior.

Introduction

Acid precipitation has resulted in acidification of freshwater and streams in Scandinavia (e.g., Oden, 1968, 1976; Braekke, 1976), the Canadian Shield near Sudbury, Ontario (e.g., Beamish and Harvey, 1972; Beamish, 1976; Conroy et al., 1976), and the northeastern United States (e.g., Likens et al., 1972; Likens, 1976; Schofield, 1976). Acidification of water bodies is particularly acute in regions in which lakes and streams are underlain by a geologic substrate which is highly resistant to chemical weathering (Gjessing et al., 1976; Likens et al., 1979; Wright and Hendriksen, 1978). Sulfuric and nitric acids, formed from the oxidation and hydrolysis of airborne sulfur and nitrogen oxides, are the dominant acidic materials in precipitation entering these stream ecosystems (Cogbill and Likens, 1974; Galloway et al., 1976).

Aquatic organisms at all major trophic levels are affected by acidification (e.g., Bick and Drews, 1973; Sutcliffe and Carrick, 1973; Almer et al., 1974; Grahn et al., 1974; Hendrey and Wright, 1976; Schofield, 1976; Hendrey et al., 1977; Hall et al., 1980) but damage to fisheries has been the most obvious result (Beamish et al., 1975; Leivestad et al., 1976; Schofield, 1976). Most of these investigations, however, have been either qualitative field surveys or laboratory experiments on the physiological responses of organisms to lowered pH. One study quantitatively approached the effects of acidification on stream invertebrates and their recovery, but only on a short-term basis (Herricks and Cairns, 1974). Much research on water affected by acid-mine drainage exists (e.g., Parsons, 1968; Herricks, 1975; Whitton and Say, 1975; Tomkiewicz and Dunson, 1977), but the effects on biota due to lowered pH are confounded by high concentrations of heavy metals and deposition of iron oxide particulates. Few data, thus, are available on the ecological effects on freshwater ecosystems of increased acidity alone particularly in otherwise undisturbed stream ecosystems. Specifically, little quantitative information is available on the relationship between pH stress and community dynamics, trophic interactions among the biota, and biogeochemistry of a freshwater ecosystem at one location.

*Cornell University, Section of Ecology and Systematics, Ithaca, NY 14853.

U.S. Environmental Protection Agency
Region 5, Library
77 West Jackson Boulevard
Chicago, IL 60604

Experimental Acidification of a Stream Ecosystem

Initial Long-Term Acidification

The purpose of this research was to investigate the effects of increased acidity on a stream ecosystem. Qualitative and quantitative effects of experimental pH manipulation in Norris Brook within the Hubbard Brook Experimental Forest, New Hampshire, were studied. Field experiments were designed to test the hypothesis that lowered pH (increased acidity) has detrimental effects on microorganisms, periphyton, macroinvertebrates, and fish. A summary of the experimental research design in Norris Brook from 1977 through 1980 is presented in Table 1.

In 1977 the pH in Norris Brook (see Figure 1) was experimentally decreased to levels found in incident precipitation (pH 4) by the addition of dilute concentrations of sulfuric acid. This experimental depression lasted for five months (see Hall et al., 1980 for further details). Following are the main results from this study:

1. Aluminum, calcium, magnesium, and potassium were mobilized into the stream water during acidification.
2. Emergence of adult mayflies (Ephemeroptera), some stoneflies (Plecoptera), and some true flies (Diptera) decreased at the lower pH.
3. More immature aquatic invertebrates in collector, scraper, and predator functional groups drifted out of the acidified relative to the control area.
4. Fewer adult insects assigned to collector functional groups were found in emergence samples from the acidified reach.
5. Chironomids, tipulids, certopogonids, and mayflies decreased by 75% in the benthos of the acidified relative to the reference area.
6. Periphyton biomass increased and fungal (hyphomycetes) densities decreased at low pH.
7. A basidiomycete fungus increased in the acidified area relative to the reference section.
8. A loss of nutrients (e.g., N) occurred in the invertebrates and organic matter but not in the water; this loss was significant in terms of the total stream ecosystem.
9. Stream acidification altered biotic structure, metabolism, and biogeochemistry of this poorly buffered mountain stream ecosystem.

Subsequent Short-Term Acidic Episodes

In a significant result from the 1977 field work, the largest amount of invertebrate drift occurred within the first five days after acid addition (Figure 2), the peak occurring within two days. Natural pH depressions in streams during spring snowmelt are often only a few days in duration. For example, episodic input of hydrogen ions during spring thaw caused pH of stream water to drop to near 4.0 in first- to third-order streams and remained at that level for three to seven days in the Adirondack Mountains, New York (Schofield, 1977). A similar phenomenon occurred in southern Norway (Leivestad and Muniz, 1976). The ramifi-

Table 1. Summary of Experiments Conducted in Norris Brook Within the Hubbard Brook Experimental Forest from 1977 Through 1980

Year	Season	Duration	Stress Applied	pH Values: Reference/ Treatment	Stream Order	Chemical Determinations	Biological Determinations
1977	Spring/ Autumn	5 mo	H_2SO_4	6-6.4/4.0	3rd	Ca, Mg, K, Na, Al, DOC, POC, etc., $SO_4^{=}$, NH_4^+, NO_3^-, Cl^-, SiO_2, Pb, Zn, Cd, Cu, Mn, Fe	Invertebrate density in drift, emergence, and benthos. Standing crop of periphyton. Aquatic fungi species. Fish behavior.
1978	Spring/ Autumn	1 day each	NO STRESS followed recovery	6-6.4/6-6.4	3rd	Same as above	Invertebrate drift and emergence.
1979	Spring/ Summer	1-hr to 2-day periods	H_2SO_4	6.4/4.0 6.4/3.0 6.4/5.0 6.4/4.5 6.4/3.5	3rd 3rd 3rd 3rd 3rd	Same as above plus TP and different species of Al	Invertebrate and vertebrate drift.
1980	Spring	1-4 hrs	HCl	6.3/4.0 6.3/4.0 6.0/4.0	3rd 2nd 1st	Same as above	Invertebrate and vertebrate drift.
	Spring	1-4 hrs	$AlCl_3$	6.3/5.0-5.25 6.3/5.0-5.25	3rd 2nd	Same as above	Invertebrate and vertebrate drift.

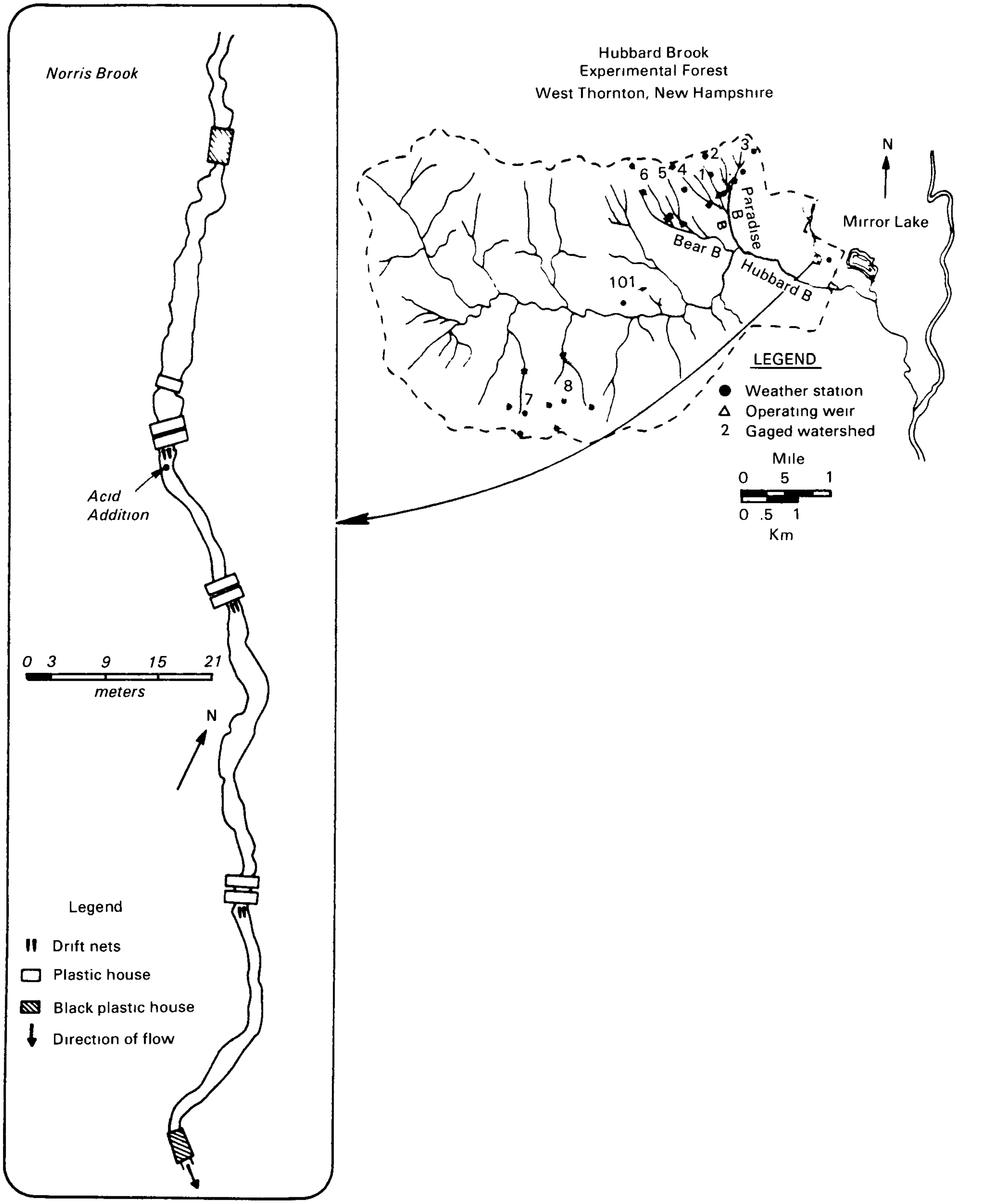

Figure 1. *Norris Brook study area located in the Hubbard Brook Experimental Forest, New Hampshire. Reference area (site A) was located 5 m above the acidification point. Sampling sites in the treatment area were located at 15 m (site B), 50 m (site C), 75 m (site D), and 100 m (site E) below the point of acid addition.*

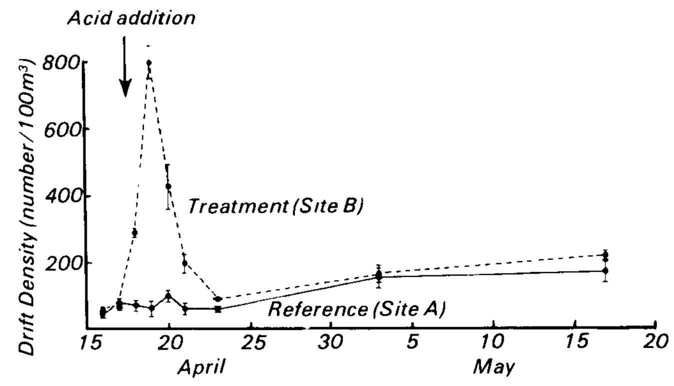

Figure 2. *Drift of invertebrates in relation to experimental acidification of Norris Brook, New Hampshire. Total number of organisms collected in drift nets per 24-h period from 16 April through 17 May 1977. Closed circles represent mean for two drift nets; vertical bars represent range.*

cation of the results of the first five days of our 1977 experimental acidification, then, becomes very clear. The following questions were formulated after analyses of that work:

1. Does episodic input of hydrogen ions during the initial phase of the snowmelt period significantly alter community structure and metabolism of poorly buffered mountain streams?
2. What is the effect of short-term pulses of acidity and aluminum on community structure and metabolism and on nutrient cycling and energy flow in streams?
3. How does the impact of acidity alter nutrient flux during high (spring) and low (summer) discharge, as well as during storm events?

To answer the above questions, additional research was completed. The results are as follows:

1. Hall, R. J. and G. E. Likens. 1980. Ecological effects of experimental acidification on a stream ecosystem. pp. 375-376. In: D. Drabløs and A. Tollan (eds.), Proceedings of the International Conference on Ecological Impact of Acid Precipitation. SNSF Project, Sandefjord, Norway, March 11-14, 1980.

   Experimental acidification to pH 4.0 in a small mountain stream in the Hubbard Brook Experimental Forest, New Hampshire, stressed the biotic and abiotic components of that system. The biotic structure, metabolism, and biogeochemistry of this stream ecosystem underlain by siliceous bedrock were quantitatively altered at pH levels (4.0) commonly found during snowmelt as well as in ambient precipitation.

2. Hall, R. J. and G. E. Likens. 1981. Chemical flux in an acid-stressed stream. Nature, 292:329-331.

   A third-order section of a small mountain stream in the Hubbard Brook Experimental Forest, New Hampshire, was experimentally acidified to pH 4.0 to measure the effects of increased acidity on chemical and biological export in the stream. The most significant inorganic component affected by the experiment was aluminum. A significant net flux of organic carbon and nitrogen occurred in the biologically bound forms but not in the dissolved substances. The net flux of phosphorus was significant only in the biologically bound forms. The increased loss of nutrients in the particulate organic fraction was also important, particularly if scaled to the total stream ecosystem.

3. Pratt, J. M. and R. J. Hall. 1981. Acute effects of stream acidification on the diversity of macroinvertebrate drift. pp. 77-95. In: R. Singer (ed.), Effects of Acidic Precipitation on Benthos. Proceedings of a Symposium on the Effects of Acidic Precipitation on Benthos. NABS, Hamilton, N.Y.

   A third-order reach of Norris Brook, a small stream in the Hubbard Brook Experimental Forest, was experimentally acidified for five months to determine what effects acid precipitation may have on the ecology of a poorly buffered lotic ecosystem. The initial six days of stream acidification simulated a low pH regime that can occur in a small mountain stream receiving meltwater from a rapidly thawing snowpack contaminated with acidic deposition.

   The first two to three days of acid addition constituted a period of acute H^+ stress (pH 4) that elicited a tenfold increase in the daily drift rate of benthic macroinvertebrates. This increased drift leaving the acidified reach was also more diverse overall in terms of major taxa (orders), trophic functional groups, and behavioral groups but less diverse at the generic level than the drift entering. In addition, the macrofauna abandoning the acidified area compared to that entering was particularly more diverse generically in mayflies and midges, collector-gatherers, and clingers and swimmers.

   Ecological implications of the acute changes in drift rate and diversity extrapolated throughout the low-order (1-3) tributaries of a weakly buffered stream are discussed. Recommendations for monitoring the effects of acid-sensitive lotic ecosystems are offered.

4. Hall, R. J., J. M. Pratt, and G. E. Likens. 1982. Effects of experimental acidification on macroinvertebrate drift diversity in a mountain stream. Water, Air, and Soil Pollution, 17:1-15 (1982).

   A small stream (Norris Brook) within the Hubbard Brook Experimental Forest was acidified to determine what effect elevated H^+ stress may have on the ecology of a mountain stream. The experiment was designed to simulate a pH level (4.0) that can occur during initial snowmelt (acute period) and during long-term (chronic period) acidification. Daily macroinvertebrate drift samples were collected from treatment and reference areas of Norris Brook. Drift diversity at the generic level was calculated using Brillouin's formula and partitioned hierarchically following macroinvertebrate classifications based on taxonomy (orders) and feeding strategies (functional groups or guilds).

The rate of movement of individuals and genera was significantly greater for those organisms leaving the acid-stressed area during the first five days than for those entering, whereas no difference between the rate of macroinvertebrates entering or leaving the acid-stressed area was apparent for either numbers or genera over the remaining 25-day study period. For the acute period (first five days), the increased macroinvertebrate drift leaving the acidified area was significantly more diverse at the levels of aquatic insect orders and functional groups but less diverse at the generic level than the drift entering. For the chronic period (25-day period) no significant differences were detected in major taxa, functional group (with the exception of collectors), or generic diversity between the drift entering and leaving the treatment reach. Mayflies and chironomids leaving the acid-stressed area during the acute period were generically more diverse than those drifting into the area. The overall change in the normal pattern of spatial and temporal variation in drift rate and diversity provides quantitative evidence that H^+ stress significantly altered the structure and metabolism of the macrobenthic community.

5. Hall, R. J. and G. E. Likens. 1984. Effect of discharge rate on biotic and abiotic chemical flux in an acidified stream. Can. J. Fish. Aquat. Sci., 41, in press.

Experimental manipulation of hydrogen ion concentration was conducted in a mountain stream ecosystem to estimate the effects on biotic and abiotic chemical flux during high (spring) and low (summer) discharge periods. Dilute concentrations of sulfuric acid were added to Norris Brook, a stream in the Hubbard Brook Experimental Forest. The streamwater was maintained near pH 4.0 from April to September 1977.

During acidification, Al, Ca, Mg, and K were mobilized in the streamwater with the concentrations progressively increasing downstream. Na and NO_3^- were not affected. DOC concentrations decreased downstream during high discharge but did not change during low flow. During storms these elements increased in concentration below acid addition as well as in the reference section.

The net flux of dissolved aluminum in the streamwater was significant during both the high and low discharge periods. The net flux of aluminum in invertebrate biomass was significant only during high flow but was insignificant when compared to the amount in the dissolved state. On the other hand, the net flux of nitrogen was significant only in the biomass of invertebrates at high discharge. This latter amount, however, was totally overshadowed by the transport of dissolved nitrogen during storms.

6. Hall, R. J., C. T. Driscoll, G. E. Likens, and J. M. Pratt. 1984. Physical, chemical, and biological consequences of episodic aluminum additions to a stream ecosystem. Limno. and Oceanogr., in press.

Experimental addition of $AlCl_3$ to a second-order stream was conducted to simulate episodic increases in aluminum concentration during acidic snowmelt. With a stepwise increase in aluminum in the stream water a significant decrease in pH and dissolved organic carbon (DOC) and an increase in foam accumulations at the stream surface were observed. It was hypothesized that foam production was visible evidence of reduced surface tension of the water. Controlled laboratory experiments with stream water corroborated the field results and produced a 20% reduction in surface tension. Electrophoretic mobility studies showed that increased aluminum concentration produced a surface charge reversal on suspended colloidal particles. The mechanism for a change in surface tension, it is postulated, is the binding of aluminum to functional groups (e.g., a carbonyl group) on DOC, thus rendering DOC more hydrophobic and less soluble. Some of these organo-aluminum complexes subsequently accumulate at the air-water interface.

Concomitant with physical-chemical changes in stream water following elevated aluminum levels were alterations in terrestrial and aquatic invertebrate drift behavior in the field. These changes in drift behavior could be attributed to responses either to (1) chemical changes in the stream related to potential aluminum and H^+ toxicity or (2) a physical change in the surface film.

Literature Cited

Almer, B., W. Dickson, C. Ekstrom, E. Hornstrom, and U. Miller. 1974. Effects of acidification on Swedish lakes. Ambio, 3:30-36.

Beamish, R. J. 1976. Acidification of lakes in Canada by acid precipitation and resulting effects on fishes. Water, Air and Soil Pollut., 6:401-514.

Beamish, R. J. and H. H. Harvey. 1972. Acidification of the La Cloche Mountain Lakes, Ontario, and resulting fish mortalities. J. Fish. Res. Board Can., 29:1131-1143.

Beamish, R. J., W. L. Lockhart, J. C. van Loon, and H. H. Harvey. 1975. Long-term acidification of a lake and resulting effects on fishes. Ambio, 4:98-102.

Bick, H. and E. F. Drews. 1973. Self purification and silicate communities in an acid milieu (model experiments). Hydrobiologia, 42:393-402.

Braekke, F. W. 1976. Impact of acid precipitation on forest and freshwater ecosystems in Norway. Res. Rept. 6/76, SNSF Project, Oslo, Norway.

Cogbill, C. V. and G. E. Likens. 1974. Acid precipitation in the northeastern United States. Water Resour. Res., 10:1133-1137.

Conroy, N., K. Hawley, W. Keller, and C. LaFrance. 1976. Influences of the atmosphere on lakes in the Sudbury area. J. Great Lakes Res., 2 (Suppl. 1):146-165.

Galloway, J. N., G. E. Likens, and E. S. Edgerton. 1976. Hydrogen ion speciation in the acid precipitation of the northeastern United States. pp. 383-396. In: L. S. Dochinger and T. A. Seliga (eds.), Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem. Forest Service General Tech. Report NE-23, Northeastern Forest Experimental Station, Upper Darby, Pennsylvania.

Gjessing, E. T., A. Henricksen, M. Johannessen, and R. F. Wright. 1976. Effects of acid precipitation on freshwater chemistry. pp. 64-85. In: F. W. Braekke (ed.), Impact of acid precipitation on forest and freshwater ecosystems in Norway. Res. Rept., 6/76, SNSF Project, Oslo, Norway.

Grahn, O., H. Hultberg, and L. Landner. 1974. Oligotrophication—a self-accelerating process in lakes subjected to excessive supply of acid substances. Ambio, 3(2):93-94.

Hall, R. J., G. E. Likens, S. B. Fiance, and G. R. Hendrey. 1980. Experimental acidification of a stream in the Hubbard Brook Experimental Forest, New Hampshire. Ecology, 61(4):976-989.

Hendrey, G. R. and R. F. Wright. 1976. Acid precipitation in Norway: effects on aquatic fauna. pp. 192-207. In: D. H. Matheson and F. C. Elder (eds.), Proceedings of First Specialty Symposium on Atmospheric Contributions to the Chemistry of Lake Waters. Orillia, Ontario, Canada. J. Great Lakes Res., 2 (Suppl. 1).

Hendrey, G. R., K. Baalsrud, T. Traaen, M. Laake, and G. Raddum. 1977. Acid precipitation: some hydrobiological changes. Ambio, 5:224-227.

Herricks, E. E. 1975. Recovery of streams from chronic pollution stress—acid mine drainage. pp. 43-71. In: J. Cairns, Jr., K. L. Dickson, and E. E. Herricks (eds.), Recovery and Restoration of Damaged Ecosystems. University Press of Virginia, Charlottesville, Virginia.

Herricks, E. E. and J. Cairns, Jr. 1974. The recovery of stream macrobenthos from low pH stress. Revista de Biologia, 10(1-4):1-11.

Leivestad, H. and I. P. Muniz. 1976. Fish kill at low pH in a Norwegian river. Nature, 259:391-392.

Likens, G. E. 1976. Acid precipitation. Chemical and Engineering News, 54:29-44.

Likens, G. E., F. H. Bormann, and N. M. Johnson. 1972. Acid rain. Environment, 14(2):33-40.

Likens, G. E., R. F. Wright, J. N. Galloway, and T. J. Butler. 1979. Acid rain. Sci. Am., 241(4):43-51.

Oden, S. 1968. The acidification of air and precipitation and its consequences on the natural environment. Ecol. Comm. Bull., 1:1-86.

Oden, S. 1976. The acidity problem—an outline of concepts. pp. 1-36. In: L. S. Dochinger and T. A. Seliga (eds.), Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem. Forest Service General Tech. Report NE-23, Northeastern Forest Experimental Station, Upper Darby, Pennsylvania.

Parsons, J. D. 1968. The effects of acid strip-mine effluents on the ecology of a stream. Archiv. fur Hydrobiol., 25:25-50.

Schofield, C. L. 1976. Acid precipitation: effects on fish. Ambio, 5:228-230.

Schofield, C. L. 1977. Acid snow-melt effects on water quality and fish survival in the Adirondack Mountains of New York State. Research Program Technical Comprehensive Report Number A-072-NY, Office of Water Research Technology, U.S.D.I., Washington, D.C.

Sutcliffe, D. W. and T. R. Carrick. 1973. Studies on mountain streams in the English Lake District I. pH, calcium, and the distribution of invertebrates in the River Dudden. Freshwat. Biol., 3:437-462.

Tomkiewicz, S. M., Jr. and W. A. Dunson. 1977. Aquatic insect diversity and biomass in a stream marginally polluted by acid strip mine drainage. Water Res., 11:397-402.

Whitton, B. A. and P. J. Say. 1975. Heavy metals. pp. 286-311. In: B. A. Whitton (ed.), River Ecology, 2. University of California Press, Berkeley, California.

Wright, R. F. and A. Henriksen. 1978. Chemistry of small Norwegian lakes, with special reference to acid precipitation. Limnol. Oceanog., 23(3):487-498.

☆U. S. GOVERNMENT PRINTING OFFICE:1985/559 111/10830